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6.1
Cobalt

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6.1.1 INTRODUCTION

6.1.1.1 Introductory Remarks and General Scope

Since the publication of the first edition of this volume, the field of cobalt coordination chemistry has continued to grow apace. Historically, cobalt has been a popular metal for coordination chemists, driven in part by the generally inert and diamagnetic nature of the trivalent oxidation state that has permitted detailed studies in solution and in the solid state by key physical methods.

Even after all these years subsequent to the first edition of *Comprehensive Coordination Chemistry* (*CCC*, 1987), cobalt has maintained its appeal, as is evident in Figure 1. A survey of the chemical literature (1900–2001) revealed that 60% of the ca. 30,000 articles on Co coordination chemistry have appeared since the early 1980s. Clearly, this level of activity presents a daunting task for reviewers with a brief to cover that particular period, and hence this review necessarily is selective in capturing the present state of Co coordination chemistry and its impact. The nature of information retrieval has also changed significantly since the early 1980s, notably through the availability of on-line computer-based data retrieval, which permits and indeed demands a distillation of the field without exhaustive referencing. Subsequently, partly in a bid to capture the field as widely as possible, we have chosen to make use of secondary references along with primary references. This has been essential, given the space available, and we trust the following presents a representative "taste" of the more recent coordination chemistry literature of Co.

In the period since the mid-1980s, great advances have been made in our understanding of transition metal ions in biological systems, and Co chemistry has been an unexpected beneficiary. At the time of the first volume, little was known about the biological chemistry of Co aside from the cobalamin (Vitamin B_{12}) cofactors. Since then, advances in molecular biology and protein expression coupled with the emergence of even more sophisticated structural and spectroscopic methods have led to the identification of at least eight distinctly different, Co-dependent (non-corrin) proteins. In parallel, the substitution of Co for spectroscopically silent ions (e.g., zinc) in metalloproteins has been an invaluable tool in the determination of active site structure and mechanism. In Section 6.1.3, we discuss the multifarious aspects of biological Co chemistry; most of these are very recent indeed.

The view taken in the analogous chapter in the first edition of this publication[1] was that Co coordination chemistry could be captured under the concepts of *synthesis*, *structure*, and *reactivity*. What has changed since that time is not the correctness of these generalizations, but rather the growth of their sophistication and the rise of a further key concept—*applications*, particularly in the areas of catalysis and (bio)technology. In Section 6.1.4 we hope to alert the reader to the wide range of uses of particular Co compounds that have emerged since the early 1980s. It is noteworthy that a number of these compounds, synthesized at the turn of the twentieth century, were ahead of their time given that the scientific areas in which they ultimately found application, particularly biology, were then still in their infancy.

Cobalt chemistry has become more targeted, with much published work directed towards an application, albeit long-term, or else towards elucidation of an existing problem making use of growing synthetic and instrumental sophistication. The era of synthesis and characterization as an art in itself is passing for Co chemistry; it seems that chemical research itself, not just the electrons

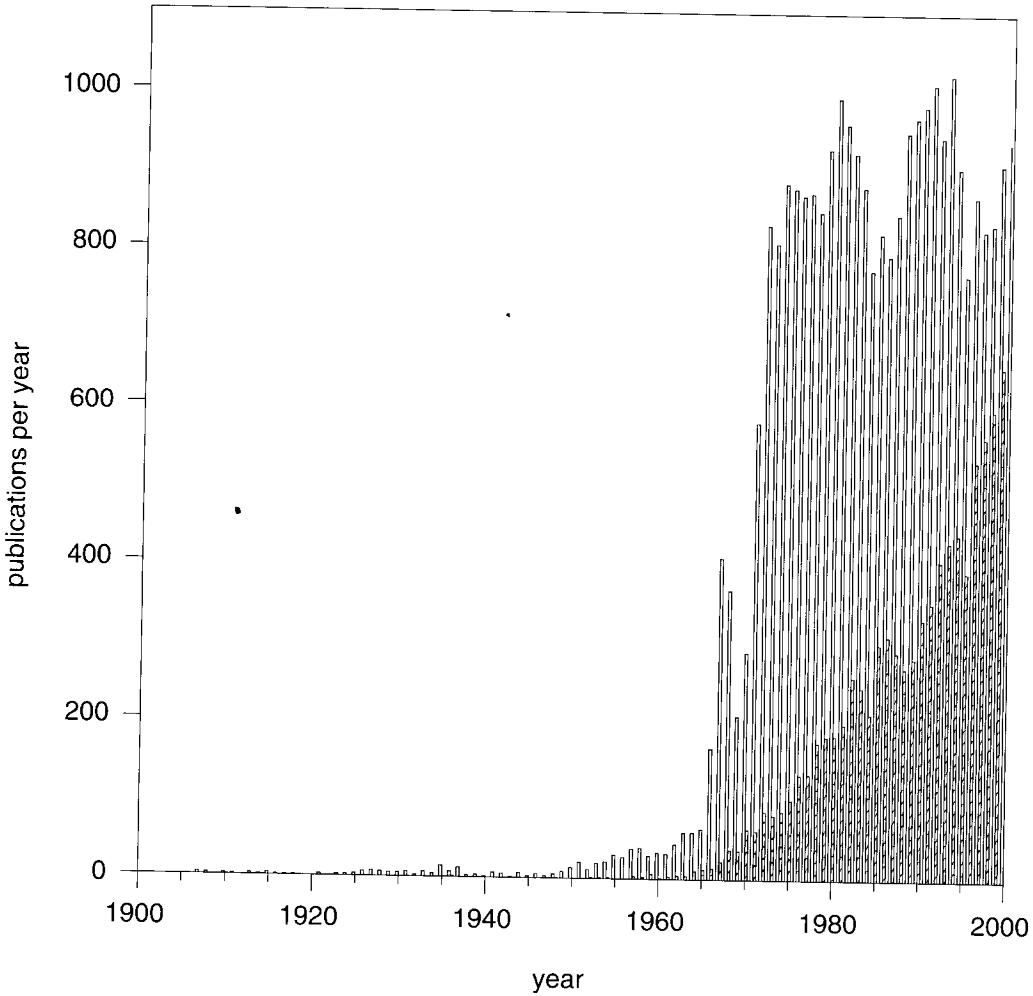


Figure 1 Publications per year featuring cobalt complexes (unshaded bars) and publications reporting at least one crystal structure of a Co-containing complex (shaded bars).

and nuclei that underpin its achievement, must have a "spin". The changing times are reflected in focused reviews of the field. Well over 1,000 reviews and books featuring aspects of Co coordination chemistry have appeared during the past two decades.

It is appropriate to identify our approach to developing the present review in the context of the Co chapter in *CCC*(1987). The first-edition chapter on Co featured a focused discussion and tabulation of synthetic methods, and many of these basic methods are still employed in synthesis today. Consequently, to avoid repetition, there will be diminished description here where prior appropriate methods have been provided, and only newer developments featured. The last two decades feature the development of many mixed-donor and sophisticated multidentate and macrocyclic ligands, which found limited coverage in the previous edition, and these will be discussed in more detail herein. Reaction kinetics and mechanism were also described thoroughly in the previous edition. We shall not reiterate this material, since the core mechanisms of many reactions involving Co compounds are now adequately defined.

Structural aspects were discussed, but not heavily, in the first edition. The complexity of new compounds (and macromolecules) now being investigated has driven many of the technological advances in X-ray crystallographic data collection and structure solution over the last two decades. Small-molecule (m.w. $< 1{,}000\,\mathrm{g\,mol^{-1}}$) structure determinations are now routinely carried out, and Co complexes constitute a significant proportion of these. Indeed, the incorporation of crystal structures in most papers reporting new synthetic coordination chemistry is now a standard feature; much more so than at the time of *CCC*(1987) (Figure 1). Inevitably, most of the new compounds described herein have been the subject of crystal structure determinations, rather

Table 1 Selected reviews and monographs focusing on Co coordination chemistry.

Subject area	*Subsets (and selected references)*
General descriptive/synthetic chemistry	Cobalt–carbon-bonded compounds[10–12]
	coordination compounds[2–9,13–15]
Structural aspects	molecular modeling[16,17]
Kinetics and mechanisms	substitution/isomerization[18–22]
	redox reactions[23]
	coordinated ligand reactions[24]
	organometallic systems[25]
Spectroscopy	optical, NMR, EPR, IR, and Raman[26–30]
Bioinorganic chemistry	dioxygen[31–37]
	DNA/proteins[38]
	porphyrins/corrins[39,40]
	model compounds[41,42]
Applications	organic synthesis[24,43–46]
	inorganic materials[47,48]
	catalysis[49–53]
	polymers and polymerization[54–58]
	magnetism[59]
	photochemistry, solar cells[60–62]

than being identified solely through the use of "sporting" physical methods. Nevertheless, advanced instrumentation, including high-field NMR and electrospray-ionization MS, has augmented the range of physical techniques, so that structural assignment in solution has become more firmly based, as an important complement to solid state structural determination. The very complexity of many new molecules required us to adopt a different approach to reporting compared with *CCC*(1987), with extensive reliance here on line drawings, as distinct from tables, to illustrate effectively the complexes described.

Apart from *CCC*, regular general reviews of Co chemistry have appeared in the period 1984–1998 in *Coordination Chemistry Reviews*.[2–9] These provide distilled supplementary reading covering a large part of the preceding two decades. Organometallic chemistry in particular is further served by an annual survey, which has appeared in the 1980s and 1990s in *Organometallic Chemistry*; several recent examples of these are cited in Table 1 along with a selection of reviews and monographs also featuring Co chemistry.[10–62]

6.1.1.2 Synthesis, Reactivity, and Structure

There are relatively few key synthetic reagents for entry into Co coordination chemistry. Of these, simple compounds are dominant: for low-valent Co chemistry, $Co_2(CO)_8$; for cobalt(II) and cobalt(III) chemistry, the simple CoX_2 ($X =$ halide) salts in hydrated or anhydrous forms. More sophisticated reagents for synthesis have been developed during the last century, but sophistication also frequently involves specificity; the "boutique" precursor, with limited general application. Occasionally, a general concept can be identified as overarching a suite of synthons. For example, an aspect of trivalent Co chemistry that has attracted attention over recent decades is the introduction of labile leaving groups into an inherently inert system. The capacity to have available, in designated coordination sites, ligand molecules that can be readily replaced by other nucleophiles is a sophistication that was not previously so readily achieved. The range of reactivities found for coordinated ligands in Co^{III} chemistry is vast, and the simple hydrolysis rates from the pentaamminecobalt(III) core (Table 2) adequately defines the spectrum from seriously inert to highly labile leaving groups.[63]

One of the earlier employed labile ligands was perchlorato, but the dangers in working with this strongly oxidizing anion are well documented and its use as a ligand in compounds bearing oxidizable (organic) ligands is frowned upon these days, if tolerated at all. Indeed, the establishment of the labile, non-oxidizing trifluoromethanesulfonato ($CF_3SO_3^-$) ligand over the last two decades has obviated the need to employ notorious perchlorato complexes as synthons.[64] More elaborate leaving groups, such as $^-OTeF_5$,[65] have subsequently appeared. Further, the develop-

Table 2 $[Co(NH_3)_5X]^{(3-n)+}$ aquation rate constants for anionic and neutral leaving groups (X^{n-}, $n = 0–3$, at 25 °C); selective lability of coordination sites in complexes of this inherently inert metal offers synthetic opportunities.

X^{n-}	$k_{obs}(s^{-1})$	X	$k_{obs}(s^{-1})$
PO_4^{3-}	1.5×10^{-9}	NH_3	5.8×10^{-12}
NO_2^-	1.2×10^{-8}	$S(CH_3)_2$	1.6×10^{-6}
CH_3COO^-	2.7×10^{-8}	OH_2	5.9×10^{-6}
CF_3COO^-	1.5×10^{-7}	$OH(CH_3)$	5.9×10^{-5}
SO_4^{2-}	8.9×10^{-7}	$OP(OCH_3)_3$	2.5×10^{-4}
Cl^-	1.7×10^{-6}	$NH_2SO_2NH_2$	$\sim 1 \times 10^{-2}$
Br^-	6.5×10^{-6}	NH_2COCH_2F	1.3×10^{-2}
NO_3^-	2.7×10^{-5}	CH_3COOCH_3	$\sim 2 \times 10^{-2}$
$CH_3SO_3^-$	2.0×10^{-4}	$NH_2SO_2C_6H_4NO_2$	3.8×10^{-2}
FSO_3^-	2.2×10^{-2}	$OC(CH_3)_2$	$\sim 4 \times 10^{-2}$
$CF_3SO_3^-$	1.5×10^{-2}	$NH_2SO_2C_6H_4CH_3$	$\sim 1 \times 10^{-1}$
ClO_4^-	$\sim 1 \times 10^{-1}$	N_4O $(N_3^- + NO^+)$	$\gg 10^{-1}$

ment of solvated complexes, where weakly coordinating solvent molecules such as sulfolane or acetone occupy key substitution sites, has expanded the armory of synthons. Chemical treatment of a normally robust ligand to generate a very short-lived intermediate, such as azide with NO^+ forming an N_4O entity that rapidly decomposes to release N_2 and N_2O and leave a "naked" coordination site, provides yet another route which has been established for some decades but not heavily exploited.[63]

Reaction mechanisms in Co chemistry continue to attract interest, and the level of sophistication and depth of understanding of reactions has grown. The elucidation of reaction mechanisms in Co chemistry has benefited from the application of high pressure to provide activation volumes, which in concert with reaction volume information allows a full volume profile analysis.[66] A parallel advance has been the study of electrode reactions at high pressures.[67] Study of self-exchange reactions for a series of $Co^{III/II}$ systems has provided mechanistic insight into heterogeneous electrode redox reactions, including establishing a simple relationship with the homogeneous self-exchange process. Nevertheless, in light of the ample treatment of this area of Co chemistry in *CCC*(1987), mechanistic studies will receive a limited coverage in this chapter, which by no means reflects the contribution of this area to our control of the element's chemistry. It simply reflects the fact that space within this review, unlike the scope and breadth of Co coordination chemistry, is limited.

There are now many on-line and CD-ROM databases of important structural and thermodynamic data of relevance to Co chemistry. The Cambridge Structural Database is the first port of call when seeking complete structural information (molecular dimensions) of any carbon-containing Co complex, and we shall not attempt to duplicate this invaluable resource through the tabulation of structural data. Complex formation constants of relevance to this review (mostly with divalent Co) are to be found in Martell's *Critical Stability Constants*, which is updated regularly and checked rigorously, or in focused reviews. For this reason, no tables of thermodynamic data will be presented. Specific redox potentials (for example $Co^{III/II}$ couples) may be found within a range spanning more than 2 V, and although some examples will be mentioned, no attempt will be made here to assemble a "representative" table of redox potential data. The reader is referred to either compendia such as the *Encyclopedia of Electrochemistry of the Elements* or to the original papers, which often themselves present focused collections of electrochemical potentials.

6.1.2 METAL COMPLEXES

The bulk of this chapter is devoted to the descriptive coordination chemistry of Co with a diversity of ligands, addressed separately for the key Co^{II} and Co^{III} oxidation states as well as for each of low-valent and high-valent cobalt. Throughout the chapter, ligand types are treated separately. Given the omnipresence of mixed-ligand complexes, we have tackled this problem by focusing on a particular class of ligand while other ligands that complete the coordination sphere are viewed as "spectators".

6.1.2.1 Co^{-I}, Co^{0}, and Co^{I}

Of the known low-valent forms of Co, Co^{-I} is rarely met while the coordination chemistries of the more commonly encountered zero- and monovalent Co are dominated by four-coordinate tetrahedral complexes. For Co^{I} (d^8), coordination numbers from three to six are known but with the extremities very rarely found, and four-coordinate tetrahedral (paramagnetic) and five-coordinate trigonal bipyramidal (diamagnetic) most common. Traditionally, the low oxidation state compounds are susceptible to oxidation in air and the tendency toward the formation of cluster compounds is strong. Low-valent Co chemistry remains dominated by carbonyl chemistry, although increasing numbers of examples of low-valent compounds with no carbonyl groups are appearing, as is evident from the following sub-sections.

6.1.2.1.1 Carbon

The chemistry of the low-valent Co—C bond is extensive, and dominantly the regime of organometallic chemistry, which is covered in the companion *Comprehensive Organometallic Chemistry* series; hence the coverage here will be limited. There are few examples of carbon-only compounds of cobalt, a notable exception being the buckminsterfullerene cations $[Co_n(C_{60})_m]^+$ (where n, m range up to 5); these form by a combination of laser vaporization and molecular beam approaches. One example is the $[Co(C_{60})_3]^+$ ion, which appears to adopt a planar structure with the Co surrounded by three C_{60} molecules.[68] In the $[CoC_{60}]^+$ ion, the metal assists gas phase reactions to produce metallated $[CoC_{60}(CH_2)_n]^+$ ($n = 1$–5) species.[69]

(i) Cyanides

Organocyanocobaltate(I) chemistry has been reviewed.[70] Mononuclear and polynuclear forms are known, and CN^- continues to appear regularly as a co-ligand, as it does in other Co oxidation states, and examples of it as co-ligand appear throughout the review.

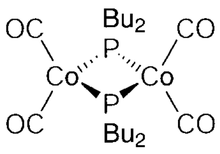
(ii) Carbonyls

The diversity and depth of studies in this field is exceptional, and a detailed exposure cannot be provided here. Aspects of this chemistry appear in detail in the companion series *Comprehensive Organometallic Chemistry*. Here, we will concentrate on compounds that are CO-rich, and attempt to provide an overview of their chemistry.

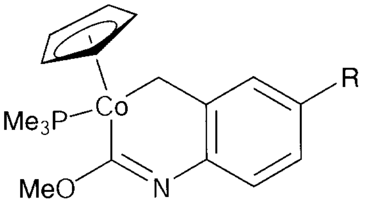
Small Co metal clusters Co_n^- ($n = 2$–8) react with CO, with sequential addition leading to the saturated Co species $[Co_2(CO)_7]^-$, $[Co_3(CO)_{10}]^-$, $[Co_4(CO)_{12}]^-$, $[Co_5(CO)_{13}]^-$ and $[Co_6(CO)_{15}]^-$.[71] This points towards one of the features of low-valent Co carbonyls; a tendency to form stable clusters. Reactivity of Co_n^- with O_2 is higher but leads to cluster fragmentation, whereas N_2 is essentially unreactive. Entry into carbonyl chemistry of low-valent Co is frequently via the well-known dimer $Co_2(CO)_8$. A range of reactions commencing with this compound has been developed, as follows.

(a) Simple substitution reactions. Direct substitution in $Co_2(CO)_8$ produces a range of dinuclear compounds. Reaction with phosphines or arsines readily produces derivatives such as $Co_2(CO)_6L_2$ where the core stereochemistry is retained. Substitution with some rearrangement may also occur; for example, reaction with $(t\text{-}Bu)_2PH$ by heating in toluene yields the phosphido bridged compound (**1**).[72] Whereas $\{Co_2(CO)_6\}$ complexes of alkynes $R\text{–}C{\equiv}C\text{–}R'$ formed from substitution in $Co_2(CO)_8$ have been known for some time and are reasonably stable to attack by nucleophiles and electrophiles, when heated with an alkene they react in a regiospecific $[2 + 2 + 1]$ cycloaddition to form a cyclopentenone.[73]

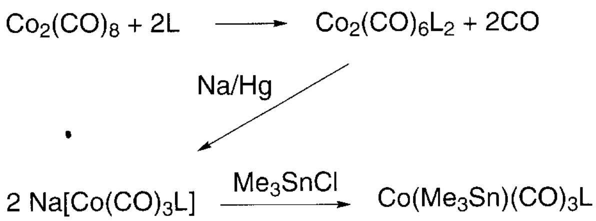
(b) Cleavage reactions. These reactions involve monomer formation through cleavage of the Co—Co bond. Reaction of $Co_2(CO)_8$ in liquid SO_2 in the presence of AsF_5 leads to Co—Co bond cleavage and yields monomeric $[Co(CO)_4(SO_2)]AsF_6$, providing a simple route to cationic Co^{I} sulfur dioxide complexes.[74] Tetra-coordinated monomeric Co^{I} is readily obtained via reductive cleavage of the Co—Co bond in $Co_2(CO)_8$ and also in substituted derivatives such as $Co_2(CO)_6L_2$ ($L =$ a phosphine, phosphite or arsine), under a nitrogen atmosphere. Subsequently, pentacoordinated Co^{I} can be achieved by addition of entities such as trimethyltin (Equation (1)).[75] One example is the trigonal bipyramidal arsine complex $Co(Me_3Sn)(CO)_3(AsPh_3)$, where the carbonyl ligands occupy the equatorial positions.[75,76]



(1)



(2)

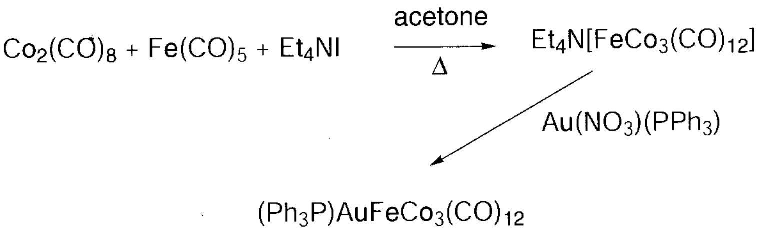


(1)

Mononuclear acyl Co carbonyl complexes $ROC(O)Co(CO)_4$ result from reaction of $Co_2(CO)_8$ with RO^-.[77] These also form via the carbonylation of the alkyl precursor. The $ROC(O)Co(CO)_4$ species undergo a range of reactions, including CO ligand substitution (by phosphines, for example), decarbonylation to the alkyl species, isomerization, and reactions of the coordinated acyl group involving either nucleophilic attack at the C or electrophilic attack at the O atom.

(c) Cluster formation. Clusters with at least three metals are accessible. The dimer $Co_2(CO)_8$ reacts in THF at −15 °C with $B_2H_6{\cdot}THF$ to form $[(CO)_4Co(BH_2)]{\cdot}THF$.[78] This is a useful synthetic reagent, mainly because it is a very active reducing agent which can condense with metal fragments to yield clusters, as illustrated by the formation of the "tailed" cluster $(CO)_9Co_3C(CH_2)_nOH$ ($n = 4$, 5), where the Co atoms form a commonly encountered equilateral triangular arrangement.

Mixed-metal clusters are also accessible from $Co_2(CO)_8$. For example, the following reaction (Equation (2)) leads to a purple–black Au–Fe–Co cluster with a trigonal bipyramidal array of metals, via a long-known mixed Co–Fe red–brown colored cluster intermediate.[79]



(2)

Likewise, reaction of $Co_2(CO)_8$ with $Ru(CO)_5$ yields $[RuCo_3(CO)_{12}]^-$, which can be reacted with HCl to form the hydride-containing cluster $HRuCo_3(CO)_{12}$.[80] A trinuclear mixed-metal cluster featuring a μ_3-S^{2-} ion, $(\mu_3\text{-}S)Co_2Fe(CO)_9$, is formed from reaction of $Co_2(CO)_8$, $Fe(CO)_5$, and C_2H_5SH, where $[Co(CO)_4]^-$ and S^{2-} are intermediate species.[81] Clusters such as this have reactive M—M bonds useful for further synthesis, but do not undergo total fragmentation.

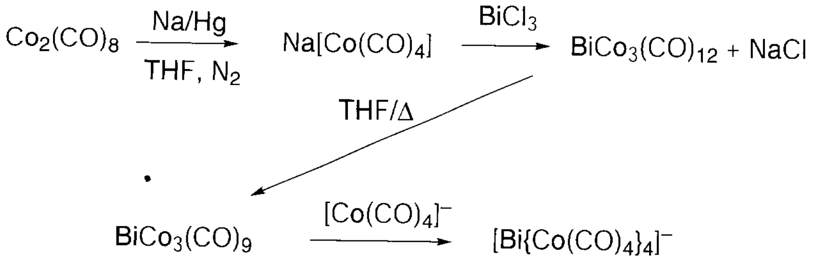
The $(\mu_3\text{-}X)Co_3(CO)_9$ core, which has three tetrahedral $\{Co(CO)_3\}$ units each bonded to a central entity in a trigonal array, is a common cluster geometry, as are analogs with Co substitution. A recent example of such a structure is via the reaction of $Co_2(CO)_8$ with $(C_6F_5)_2S$, which yields $(\mu_3\text{-}S)Co_3(C_6F_5)(CO)_8$.[82]

These types of clusters represent some of the more modest sizes and geometries detected in homo- and hetero-metal carbonyl clusters. From dimetallic up to pentadecametallic clusters have been defined by crystal structures, and assembly of the metal centers in these clusters adopt a number of well-defined arrangements.[83] Redox activity in these polymetallic clusters is anticipated and has been observed. Routes to large carbonyl polymetal clusters have been reviewed.[83,84]

Water-soluble carbonyls are relatively rare. A route to such a species involves reaction at room temperature of the sulfonated phosphine $P(PhSO_3)_3^{3-}$ as its water-soluble Na^+ salt with $Co_2(CO)_8$ in a two-phase water/toluene mixture, whereupon the product forms in the aqueous phase in high yield.[85]

Complex clusters incorporating multiple-bridging groups such as O^{2-}, CCl, and CCO_2 have been known for some time, with clear synthetic routes available.[86] Typical species include $(\mu_3\text{-CCl})Co_3(CO)_9$, $(\mu_3\text{-CCO}_2)Co_3(CO)_9$, and $Co_4(\mu_4\text{-O})[(\mu_3\text{-CCO}_2)Co_3(CO)_9]_6$. Substitution of further carbonyls can lead to chiral clusters.

Main-group cobalt carbonyl clusters are well known, with neutral clusters such as $Sn\{Co(CO)_4\}_4$ and anionic clusters such as $[Bi\{Co(CO)_4\}_4]^-$ reported.[87] Synthesis proceeds for the former as follows (Equation (3)):



(3)

(d) Photochemical reactions. Photoreactivity is exhibited by many carbonyl complexes. Photosubstitution reactions, where a CO ligand is commonly replaced, are assumed to proceed by an associative mechanism. A simple example is given in the reaction below (Equation (4)).[88]

$$Co(CO)_3(NO) + PPh_3 \longrightarrow Co(CO)_2(NO)(PPh_3) + CO \qquad (4)$$

Photooxidation of $Co_2(CO)_8$ is a complex reaction, with major products being the simple monomers $Co(O_2)(CO)_n$ ($n = 1, 2$) with the dioxygen bound side-on (η^2).[89] The same products arise from reaction of Co atoms with CO and O_2 at 10–12 K.

(e) Other reactions. Reduction reactions from a higher oxidation state offer an alternative route to low-valent Co compounds. For example, cobalt(II) chloride serves as a precursor for generation of $[Co(CO)_4]^-$ by treatment with $NaBH_4$ or Na_2S under a CO atmosphere.[90] This, in turn, catalyzes the double carbonylation of aryl halides (RX) to give RCOCOOH in the presence of $Ca(OH)_2$.

Dendrimers incorporating Co carbonyls and other organocobalt species have been the subject of a recent review.[91] This sets the scene for a likely growth of interest in such systems in the future.

(iii) Alkyls and aryls

The field of alkyl and aryl Co complexes in low formal oxidation states has been extensively studied, and is frequently associated with cluster chemistry.[92] Alkyl and aryl ligands, with or without additional functionality, are often co-ligands with π acceptors such as carbonyls and/or phosphines, e.g., $(MeOCOCH_2)Co(CO)_3(PPh_3)$.[93] A simple example of a cluster is $(RC)Co_3(CO)_9$, where the triangular $\{Co(CO)_3\}_3$ moiety is capped by the η^3-alkyl fragment, which occupies the apex of a distorted Co_3C tetrahedron.

Cobalt incorporation in a ring is one less common way in which Co–alkyl bonding is observed. One interesting example is the cobaltadihydroquinoline (**2**).[94] This arises from reaction of $(Cp)Co(PMe_3)(CO)$ (Cp = cyclopentadienyl anion) with an aryl isocyanide (CNR) and CH_2ClI in benzene, which first forms the carbenoid cation $[(Cp)CoCH_2Cl(PMe_3)(CNR)]^+$, then yielding the cobaltadihydroquinoline on addition of KOH to a methanolic solution. A crystal structure defines a slightly distorted octahedral environment for the Co center.

(iv) Other carbon-bonded ligands

Complexation of CO_2 to Co demands a somewhat different approach. C-bound η^1-CO_2 is invariably a co-ligand with multidentate unsaturated N-donor ligands, particularly imines, and discussion of this area is deferred until Section 6.1.2.1.3(v). Close analogs which bind Co are carbonyl sulfide (COS) and carbon disulfide (CS_2).[95] The latter has been characterized in a η^2-C,S coordination mode to cobalt. These undergo reductive cleavage to produce sulfido and thiocarbonyl ligands.

The first transition metal isonitrilate complex reported was the tetrahedral Co^{-I} complex $[Co(C{\equiv}NPh^*)_4]^-$ where $Ph^* = 2,6\text{-}Me_2C_6H_3$,[96] characterized by a crystal structure analysis. Oxidation yields the zerovalent dimer $Co_2(C{\equiv}NPh^*)_8$, which features two bridging isonitrile groups.

6.1.2.1.2 Silicon

Silicon–cobalt bonds are essentially exclusive to low-valent cobalt. The companion series *Comprehensive Organometallic Chemistry* provides a coverage. Although monomers such as $Co(CO)_4(SiEt_3)$ are known, silyls tend to be found more often in clusters; for example, reaction of $Na[Co(CO)_4]$ in THF at −5 °C with $MeSiHCl_2$ yields $MeSiCo_3(CO)_9$.[97] Typically, Si–hydride and Si–halogen bonds can be replaced by Co carbonyl units, such as in the reaction of SiH_4 with $Co_2(CO)_8$ in dry hexane in a sealed tube, which forms $SiCo_4(CO)_{14}$.[98] A recently characterized simple cluster with a silicon-bonded chelate is (μ-$PhSiCH_2CH_2SiPh$) $Co_2(CO)_6$, formed from substitution in $Co_2(CO)_8$.[99]

6.1.2.1.3 Nitrogen

The most commonly encountered N-donor ligands, the amines, are not usually associated with Co in its low oxidation states. However, unsaturation coupled with chelation opens up many opportunities for the stabilization of monovalent Co with N donors such as imines, porphyrins, and pyrazoles.

(i) Amines

The monovalent Co chemistry of amines is sparse. No structurally characterized example of low-valent Co complexed exclusively to amines is known. At low potentials and in non-aqueous solutions, Co^I amines have been identified electrochemically, but usually in the presence of co-ligands that stabilize the reduced complex. At low potential, the putative monovalent $[Co(cyclam)]^+$ (cyclam = 1,4,8,11-tetraazacyclotetradecane) in NaOH solution catalyzes the reduction of both nitrate and nitrite to give mixtures of hydroxylamine and ammonia.[100] Mixed N-donor systems bearing π-acceptor imine ligands in addition to amines are well known, but these examples are discussed separately in Section 6.1.2.1.3.

(ii) Pyridine and oligopyridines

The π-acceptor ability of these unsaturated ligands offers more extensive low-valent Co chemistry than found with amines. Photochemical irradiation of $[Co(py)_6](BPh_4)_2$ (py = pyridine) results in reduction to the Co^I complex with the anion as the electron donor.[101] The same Co^I complex has been found to catalyze the cyclotrimerization of but-2-yne and hex-1-yne at room temperature,[101] and to reduce CO_2 at atmospheric pressure forming a carbonyl complex.[102] The formally monovalent $[Co(bpy)_3]^+$ and $[Co(phen)_3]^+$ complexes (bpy = 2,2′-bipyridine; phen = 1,10-phenanthroline) have been well characterized. The crystal structure of $[Co(bpy)_3]Cl$ is known[103] and the coordination geometry is almost identical to that of the divalent analog $[Co(bpy)_3]Cl_2$, suggesting considerable electron delocalization stabilizing this rare low-valent CoN_6 compound.

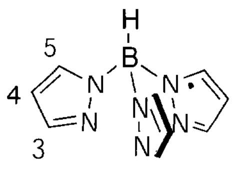
The $[Co(terpy)_2]^+$ ion (terpy = 2,2′;6′,2″-terpyridine) has been found to catalyze the reduction of CO_2 when the divalent precursor is immobilized on electrode surfaces. The vinyl-substituted terpy analog was electropolymerized to give a film that reduced the overpotential for CO_2 reduction in DMF and MeCN by more than 1 V.[104] The activity of this surface-confined species was superior to that of the complexes in solution.[105] Similarly, in water, the $[Co(terpy)_2]^{2+}$ ion immobilized and reduced *in situ* within a Nafion film also catalyzes the reduction of CO_2[106] and H^+ ions.[107]

(iii) Porphyrins

Most recent advances in the area of low-valent Co porphyrin chemistry involve their use as reduction catalysts of organic substrates, and this work appears in Section 6.1.4.3.

(iv) Pyrazole and related ligands

By far the most studied pyrazole-containing ligand is the symmetrical monoanionic tripod hydridotrispyrazolylborate, Tp (**3**). Substituents introduced at each of the 3-, 4- or 5-positions ($3,5\text{-Me}_2\text{Tp}^{108}$, 3-*i*Pr,4-BrTp[109]) have led to a number of sterically encumbered threefold symmetric complexes and some remarkable Co coordination chemistry has ensued. Hydride substitution at the B atom is also possible by organic groups such as *p*-bromophenyl, which enables further functionalization of the ligand.[110]



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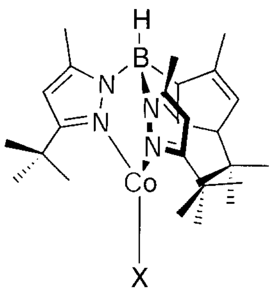


(4a) X= CO
(4b) $X=N_2$
(4c) X=H
(4d) $X=C_2H_4$

The diamagnetic $(3\text{-}t\text{Bu},5\text{-MeTp})\text{Co(CO)}_2$ has been prepared and structurally characterized.[111] In solution it spontaneously loses CO to give the paramagnetic (3-*t*Bu, 5-MeTp)Co(CO) (**4a**). In the presence of CO, the two complexes are in equilibrium. A Mg reduction of (**4a**) yielded the dimer $[[(3\text{-}t\text{Bu},5\text{-MeTp})\text{Co}](\mu\text{-CO})]_2\cdot\text{Mg(THF)}_4$.[112] The crystal structure of this compound shows a linear CO bonding mode. However, in the crystal structures of the di mononuclear neopentyl analogs $[(3\text{-npTp})\text{Co}]_2(\mu\text{-N}_2)$ and (3-npTp)Co(CO) the CO and N_2 ligands are bent away from the pseudo-threefold axis of the complex by about 30°.[112] Hydrogenation of the mononuclear dinitrogen complex (**4b**) produced the hydride (**4c**), whereas reaction with ethylene yields the corresponding olefin complex (**4d**), all of which were structurally characterized (Figure 2).[113]

(v) Imines

Polyimines of low-valent Co are now well represented, particularly with macrocyclic or mixed-donor ligands. The monovalent Co complex (**5**) of the 14-membered macrocyclic hexamethyl diimine (hmd), may be generated electrochemically from its divalent precursor. Furthermore,

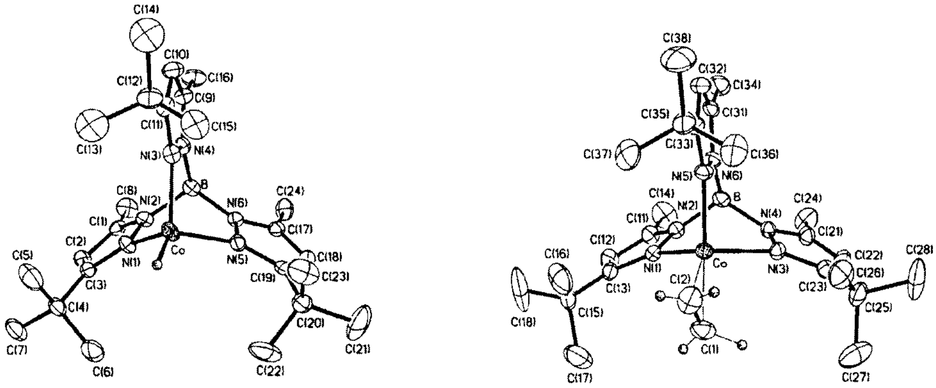
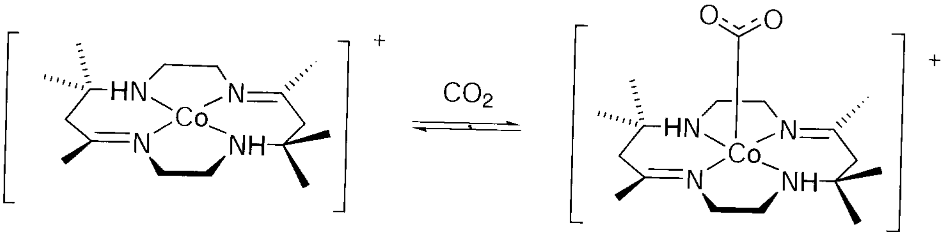


Figure 2 Crystal structures of the monovalent hydrido (**4c**) (left) and ethylene (**4d**) (right) complexes of *i*-Pr-5-MeTp (reproduced with permission of the American Chemical Society from *Organometallics*, **1999**, *18*, 300–305).

cyclic voltammetry of $[Co(hmd)]^{2+}$ in 0.1M Et_4NClO_4-DMSO in the presence of CO_2 showed a pronounced anodic shift in the $Co^{II/I}$ potential, indicating a large CO_2 binding constant for the monovalent complex.[114] Subsequently it was found that **(5)** rapidly forms a purple 1:1 adduct **(6)** with CO_2 in MeCN ($K_a=1.2\times10^4$ M^{-1}).[115] In ultrapure MeCN, **(6)** slowly reacts to give $[Co(hmd)]^{2+}$, CO, and HCO_3^-.



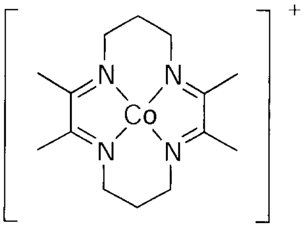
(5) **(6)**

The dinuclear complex $[Co_2(hmd)_2(\mu\text{-}CO_2H)](ClO_4)_3$ and the monomeric carbonyl $[Co(hmd)(CO)](ClO_4)$ were crystallized and structurally characterized. The structure of the dinuclear complex finds both Co ions in a square pyramidal environment, with axial sites occupied by the bridging ligand. A μ-η^1:η^1 coordination mode (Co–C(OH)O–Co) was defined involving a distorted trigonal planar C atom. The thermodynamics and kinetics of complex formation between pulse radiolytically generated **(5)** and the species H^+, CO_2, and CO were also studied in aqueous formate solutions.[116] Subtle stereochemical influences were revealed in parallel investigations of the N-based *meso* and *rac* diastereomers of **(5)** and **(6)**, the *rac* isomer having both amine H atoms *syn* to the coordinated CO_2. Although the *meso* and *rac* isomers have identical $Co^{II/I}$ redox potentials, their CO_2 binding constants in DMSO differ by a factor of 100 (*rac* being more stable) indicating that steric effects are at work.[117] The effects of solvent dielectric constant and electrolyte were also explored. A similar, but independent, CO_2 binding study was published soon after,[118] also incorporating the thermodynamics and kinetics of binding CO and H^+ to the *rac* and *meso* isomers of the same complex. Hydrogen bonding was also found to be a factor in stabilizing **(6)**.[119] The solution structures of the five-coordinate **(6)** and its six-coordinate solvated adduct were examined with XANES and EXAFS together with the related **(5)**, $[Co(hmd)(CO)]^+$, $[Co(hmd)]^{2+}$, and $[Co(hmd)(CO_3)]^+$. The edge position of **(6)** and $[Co(hmd)]^{2+}$ are the same, whereas the edge position for six-coordinate $[(MeCN)Co(hmd)(CO_2)]^+$ shows significant metal-to-CO_2 charge transfer consistent with a Co^{III} C-bound carboxylate.[120] The pressure dependence of this five- to six-coordinate equilibrium was studied,[121] with high pressures favoring the six-coordinate form.

Photoreduction of CO_2 using *p*-terphenyl as a photosensitizer and a tertiary amine as a sacrificial electron donor is efficiently catalyzed by $[Co(hmd)]^{2+}$ using continuous and flash photolysis, and charge separated species (Co^I and terphenyl cation) were identified.[122] Similarly, photoreduction of $[Co(hmd)]^{2+}$ by several bis-bipyridyl Ru^{II} photosensitizers leads to Co^I-mediated reduction of CO_2.[123] The tetramethyl-tetraimine (tmt) relative $[Co(tmt)(NCMe)_2]^{2+}$ also undergoes facile one-electron reduction in MeCN to give the corresponding monovalent species **(7)**, which is a potent Lewis acid toward a variety of monodentate ligands (pyridine; 2,6-lutidine; 1-Me-imidazole; Br^-).

Electrogenerated monovalent Co complexes of the well-known open chain N_2O_2 Schiff base ligands salen **(8)**, salphen **(9)**, and their substituted derivatives undergo oxidative additions with alkyl halides. Reactions of the complex with substrates within the series RBr (R = Pr, Bu, *t*-Bu) proceed at different rates. The reaction occurs by an inner-sphere alkyl-bridged electron transfer, with a $Co^I\cdots R^+\cdots X^-$ transition state, which is sensitive to distortions of the complex in different configurations.[124]

A crystal structure of the CO_2 derivative of **(8)**, $K[Co(salen)(\eta^1\text{-}CO_2)]$, has been reported in which the Co—C bond is 1.99 Å, the C—O bonds are both equivalent at 1.22 Å and the O–C–O angle is 132°.[125] Carboxylation of benzylic and allylic chlorides with CO_2 in THF-HMPA was achieved with **(8)** electrogenerated by controlled-potential electrolysis,[126] in addition to reductive coupling of methyl pyruvate, diethyl ketomalonate and *p*-tolylcarbodiimide via C—C bond formation. Methyl pyruvate is transformed into diastereomeric tartrates concomitant with oxidation to the divalent Co(salen) and a free-radical mechanism is proposed involving the homolytic cleavage of the Co—C bond. However, reaction with diphenylketene (DPK) suggests an alternative pathway for the reductive coupling of CO_2-like compounds.



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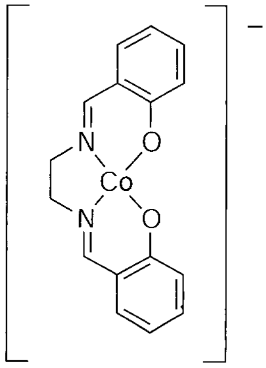

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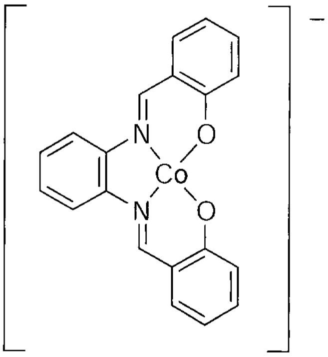
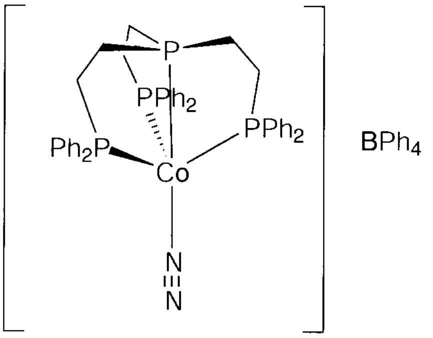


(9)

(vi) Dinitrogen

The dinitrogen coordination chemistry of Co is restricted to low oxidation states and phosphine co-ligands appear to be a requirement. The formally monovalent hydrido complex $CoH(N_2)(PPh_3)_3$ when reacted with Et_2Mg, then BuLi, gives $[Co(N_2)(PPh_3)_3]Li(Et_2O)_3$ or $[Co(N_2)(PPh_3)_3]Li(THF)_3$ depending on the solvent used.[127] The complexes possess threefold symmetry with the N_2 ligand bridging Co and Li with an N—N bond length of ca. 1.18 Å. In contrast to the hydrido precursor, the ligated N_2 in $[Co(N_2)(PPh_3)_3]^-$ is attacked by conc. H_2SO_4 to afford N_2H_4 and NH_3, providing the first examples of this conversion involving N_2 coordinated to Co. Also, $CoH(N_2)(PPh_3)_3$ catalyzes oligomerization and cyclization reactions of alkynes under mild conditions.[128] The Mg reduction of (3-*t*Bu, 5-MeTp)CoX (X = Cl, I) in an N_2 atmosphere yields (3-*t*Bu,5-MeTp)$Co^I(N_2)$ (**4b**) as an intermediate, which upon exposure to O_2 yielded the superoxo Co^{II} analog.[129] Heterogeneous reactions of the monovalent tripodal phosphine complex $[(dppep)Co(N_2)]BPh_4$ (**10**) with gaseous C_2H_2, C_2H_4, CH_2O, CH_3CHO, and CO lead to N_2 displacement and either 1:1 complexes or C—H bond cleavage at cobalt. The latter case ultimately results in either H_2 elimination or hydrogen transfer from metal to the coordinated ligand.[130]



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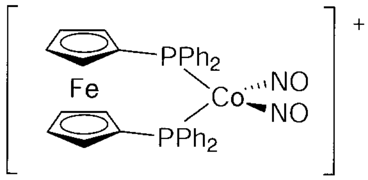


(11)

The symmetrical dimer $[(Me_3P)_3CoH]_2(\mu\text{-}N_2)$ is formed by protonation of the dinitrogen cobaltate precursor and its crystal structure is reported.[131] The complex reversibly binds N_2, forming the monomer $CoH(N_2)(PMe_3)_3$.

(vii) Nitrosyl

Nitrosyl is now well established as a ligand for low-valent cobalt. The distorted tetrahedral $[Co(NO)_2(py)_2]^+$ has been prepared and structurally characterized.[132] In contrast to bis-phosphine analogs, the bis-pyridine complex decomposes rapidly in solution unless stabilized by excess pyridine. This was correlated with structural parameters, most notably the compressed ON–Co–NO coordination angle. Electrochemistry of the four-coordinate $[Co(P(OEt)_3)_2(NO)_2]^+$ in MeCN at Pt or Hg electrodes reveals two consecutive reductions and a single oxidation process. The less negative reductive wave yields a stable neutral species in the absence of oxygen.[133] The novel pseudo-tetrahedral complex (**11**) also bears two P donors and two NO ligands, but a ferrocenyl group bridges the two phosphines.[134] The interaction between the two metallic centers bridged by the two Cp–PPh_2 linkers was studied by ^{57}Fe Mössbauer spectroscopy and cyclic voltammetry.

The doubly bridged nitrosyl complex $[(Cp)Co]_2(\mu\text{-}NO)_2$ has attracted a considerable amount of interest with regard to its electronic ground state. *Ab initio* calculations carried out on this d^9–d^9 species predicted a triplet ground state 280 cm^{-1} lower in energy than the singlet state, and the authors suggested that the magnetic properties of the compound be more closely examined.[135] In response, experimental reinvestigation of the magnetic susceptibility of the complex found that the compound is actually diamagnetic in the solid state (from 5 K to 280 K) and in benzene solution (in the range 303–327 K).[136]

Coordinated nitrosyl can participate in further chemistry, as illustrated in the following example. Methylation of $[(Cp)Co(NO)]^-$ with MeI in THF at −40° gives (Cp)Co(Me)(NO) which in the presence of PPh_3 undergoes NO migratory insertion to give $(Cp)Co(N(O)Me)(PPh_3)$. The ethyl, isopropyl, and *p*-methyl-benzyl analogs behave similarly.[137]

(viii) Nitriles and azides

These are adequate ligands for low-valent Co, but their chemistry is somewhat limited. Dicobalt hexacarbonyl complexes of propargyl acetates and acetylenic acetals couple efficiently with diethylaluminum cyanide to produce the corresponding complexed propargyl nitriles and cyanohydrins.[138] Electron-poor dipolarophiles such as alkynes, alkenes, and nitriles undergo 1,3-dipolar cycloadditions with azido Co complexes to give five-membered heterocycles such as triazoles (from nonterminal alkynes), triazolines (from alkenes), and tetrazoles (from nitriles).[139] Tetracyanoethylene is an effective one-electron oxidant and also is capable of forming sigma-bonded complexes such as (Cp)Co(CO)(TCNE).[140,141]

6.1.2.1.4 Phosphorus

Most work done on the coordination chemistry of phosphorus ligands bonded to Co lies within the realm of organometallic chemistry where the P donor is in the minority of non-C-bonded ligands. Examples such as these where the principal ligands are CO, Cp, and olefins, will not be discussed here. Tertiary phosphines (trialkyl and triaryl) and phosphite esters dominate the examples of phosphorus coordinated to Co, as they are excellent ligands for low-valent Co. Of the monodentate P donors, PMe_3, PEt_3, $P(i\text{-}Pr)_3$, $P(ch)_3$, and PPh_3 are the most commonly encountered examples.

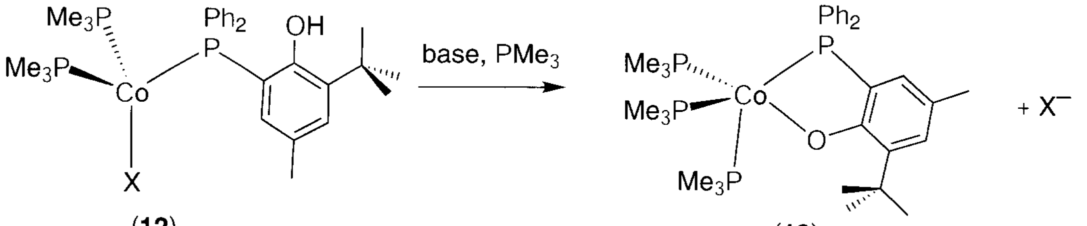
(i) Monodentate phosphines

The simple tetrahedral complex $[Co(PMe_3)_4]PF_6$ reacts with formaldehyde to give the trigonal bipyramidal derivative $[Co(CO)(PMe_3)_4]PF_6$ where the CO ligand is in an equatorial position. Curiously, the BPh_4^- salt reacts to give the axially bound CO isomer in addition to the *cis*-octahedral Co^{III} dihydrido species $[CoH_2(PMe_3)_4]^+$.[142] Reaction of $[Co(PMe_3)_4]^+$ with O_2 in MeCN yields the octahedral divalent phosphine oxide complex *trans*-$[Co(MeCN)_2(OPMe_3)_4]^{2+}$ and its X-ray crystal structure was determined.[143] The dioxygen complex $[Co(PMe_3)_4(O_2)]^+$ (with $\bar{\nu}_{O\text{-}O} = 880\ cm^{-1}$) was identified as an intermediate.

The tetrahedral halide-bridged monovalent compounds $[Co(PPh_3)_2X]_n$ (X = Cl, Br) or $[Co(PPh_3)X]_n$ (X = Cl, I), may be prepared by reduction of CoX_2 with $NaBH_4$ in the presence of PPh_3.[144] The $[Co(PPh_3)_2Br]_n$ analog reacts further with PPh_3 to form paramagnetic tetrahedral monomeric $Co(PPh_3)_3Br$. Although $Co(PPh_3)_3Cl$ is formally a homolog of its illustrious Rh^I analog $Rh(PPh_3)_3Cl$ (Wilkinson's catalyst), their structures and reactivities are in no way similar. Unlike the square planar diamagnetic Rh complex, $Co(PPh_3)_3Cl$ is tetrahedral and paramagnetic.

Nevertheless, the $Co(PPh_3)_nX$ compounds are excellent synthons for a variety of low-valent phosphine complexes, as the Co—P bonds are quite stable, allowing the investigation of ligand addition and substitution reactions at the remaining coordination site(s). For example, the first Co^I siloxide complex $Co(PPh_3)_3(OSiMe_3)$ was synthesized and characterized structurally by reaction of $Co(PPh_3)_3Cl$ with trimethylsilanolate.[145] The paramagnetic tetrahedral $Co(PMe_3)_3Br$ reversibly binds ethylene in a variety of solvents (toluene, acetone, and MeOH) to give the diamagnetic $CoBr(C_2H_4)(PMe_3)_3$ species.[146] By contrast, reaction of $Co(PMe_3)_3Br$ with diphenylacetylene yields different mononuclear diamagnetic Co-alkyne species depending on the solvent; $CoBr(C_2Ph_2)(PMe_3)_3$ forms in toluene, whereas in acetone the salt $[Co(PMe_3)_3(C_2Ph_2)]Br$ is also present. MeCN is also found to be a competitive ligand in these systems.[147] Homologs of the form $[Co(PMe_3)_3(RC{\equiv}CR_1)]^+$ (R = Ph, R_1 = Me, pentyl; R, R_1 = Me) were also prepared from Co $(PMe_3)_3Br$.[148] The alkyne ligand acts as a four-electron donor but is weakly bound. Reaction of $HC{\equiv}CPh$ in excess with $Co(PMe_3)_3Br$ and $NaBPh_4$ in MeOH gave the phosphonium salt $[Me_3P(CH_2CH(OMe)Ph)]BPh_4$, which was characterized in the solid state by X-ray diffraction and in solution by ^1H and ^{31}P NMR.[149] Addition of aryl halides (ArX) to $Co(PPh_3)_3Me$ yield ArAr and ArMe when Ar = 4-toluyl, but exclusively ArMe for 1- and 2-bromonaphthalene and 4-bromobiphenyl.[150]

In the four-coordinate complexes (**12**) (X = Cl, Br) the phenol phosphine is coordinated as a monodentate.[151] In the presence of base, the phenolate O atom deprotonates and coordinates to give (**13**). The five-membered chelate ring in this complex is resistant to protonation, and ring-opening is not observed even in the presence of CO or C_2H_4.



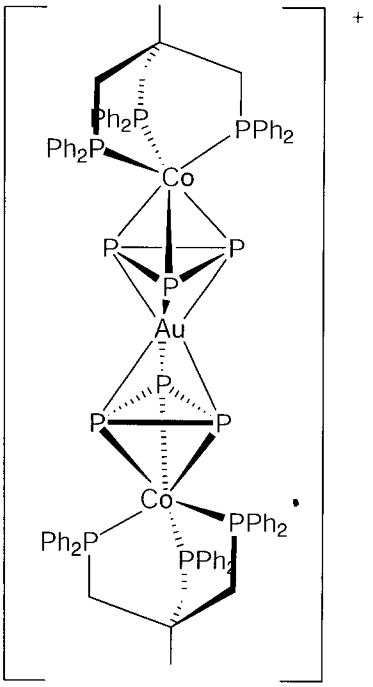
(12) **(13)**

At least partial substitution of other inherently strong ligands by phosphines can be achieved. Trialkylphosphines substitute partially into arylisocyanide complexes $[Co(CNR)_5)]^+$, with monosubstitution and at best disubstitution observed, influenced by the steric bulk of the phosphine.[152]

(ii) Multidentate phosphines

There is a wide range of examples extant, but a selection illustrates recent chemistry sufficiently. There are many Co complexes, both monomers and clusters, of the facially coordinating tridentate phosphine triphos (1,1,1-tris((diphenylphosphino)methyl)ethane) and its dimethylphosphino (mtriphos) or diethylphosphino (etriphos) analogs. The novel mixed P-ligand complex Co(triphos)(P_3) reacts with $AuCl(PR_3)$ (R = Me or Ph) and $Au_2Cl_2(Ph_2PCH_2PPh_2)$ in the presence of $TlPF_6$ to give the P_3-bridged compound (**14**). The Au atom is sandwiched between the two cyclic P_3 units of each Co(triphos)(P_3) moiety.[153] Similarly, treatment of Co(triphos)(P_3) with Cu^I and Ag^I salts affords $[M\{Co(triphos)(P_3)\}_2]^+$ (M = Cu, Ag).[154] The protonated form $[Co(triphos)(P_3H)]CF_3SO_3$, also containing an η^3-coordinated P_3 unit, reacts with $Pt(PPh_3)_2$ to give the trinuclear compound $[((triphos)Co)_2(P_6H_2)PtPPh_3](CF_3SO_3)_2$.[155] In this compound, the P_6 fragment bears a P—P bond between two different P_3 moieties and this novel ligand is stabilized by coordination to three metal–ligand fragments.

The dinucleating hexaphosphine eHTP binds as a bridging bis-tridentate ligand and several dicobalt complexes have been isolated, such as (**15**).[156] The solution conformational behavior of (**15**) was examined with NMR, which identified a number of solvent- and temperature-dependent shifts of the methylene bridge and chelate ring proton resonances.[157] Chemical shift changes for the $P{-}CH_2{-}P$ proton resonances were assigned to CO shielding from different rotational conformers, whereas variations in the chelate ring resonances were attributed to trigonal–bipyramidal/square–pyramidal coordination geometry changes. In the same study, reduction of (**15**) with the naphthalenide anion produced the zerovalent Co—Co-bonded dimer $Co_2(CO)_2(eHTP)$. In dry



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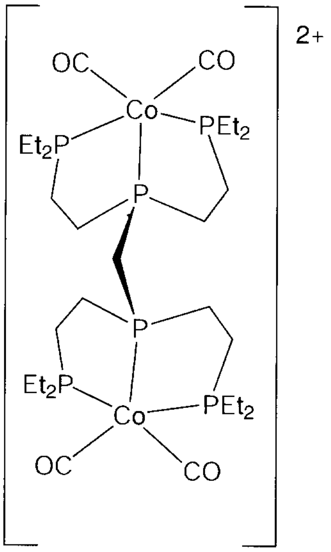

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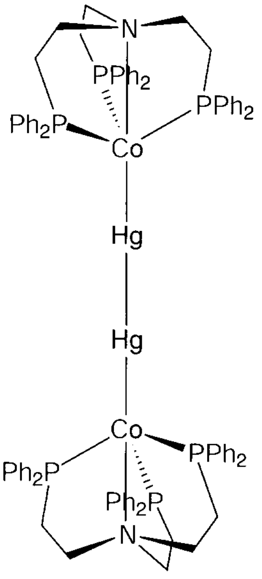
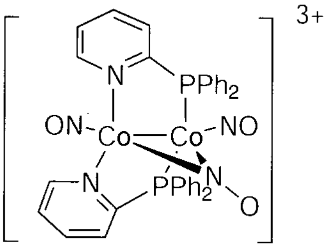


(16)

MeCN, the divalent analog Co_2Cl_4(eHTP) undergoes P oxidation (by dioxygen) at each donor atom to produce the corresponding hexaphosphine oxide.[158]

A rather unusual Co–Hg–Hg–Co moiety was stabilized by the NP_3 tripod tris(2-diphenylphosphinoethyl)amine (tdppea) in (**16**).[159] The complex is converted to the monomer $[Co(tdppea)(CO)]^+$ by reaction with either CO or CO_2 at room temperature and atmospheric pressure. The five-coordinate mixed tri-/dimethylphosphite complex $Co(P(O)(OMe)_2)(P(OMe)_3)_4$ has been reported along with its Rh and Ir analogs.[160] There is a range of other ligands incorporating both P and N donors. One deceptively simple example is 2-(diphenylphosphino)pyridine (dpppy), whose chemistry has been reviewed.[161] The dpppy ligand can chelate in both a simple fashion, as in the tetrahedral monomer $[Co(dpppy)(NO)_2]^+$, and in a bridging mode, as in the dimer (**17**).[162]



(17)

Diphosphinoamines (X_2P–NR–PX_2) are examples of a more unusual potentially chelating diphosphine. The dimer $Co_2(F_2PN(CH_3)PF_2)_3(CO)_2$ has three of these ligands bridging symmetrically between the two tetrahedral Co centers, which also carry a terminal CO group; this molecule can undergo reduction with $LiEt_3BH$ in THF to form a stable mixed valence (d^9–d^{10}) radical anion.[163]

6.1.2.1.5 Arsenic

Low-valent arsine complexes of Co are few and these bear mostly C ligands such as CO (see Section 6.1.2.1.1 for an example).

6.1.2.1.6 Oxygen

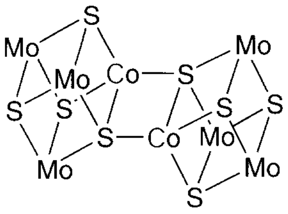
Stable low-valent Co is not often found with simple O-donor ligands such as water, hydroxide, dioxygen, and oxoanions. Carboxylate anions are also not frequently met as ligands in low-valent Co chemistry. One interesting compound, however, is the Co cluster-substituted carboxylic acid μ_3-$[(CO)_9Co_3]CCOOH$, which can perform its function as a carboxylate ligand; for example, it reacts with $Co(OAc)_2$ in THF to yield $Co_2[(CO)_9Co_3CCOO]_4(THF)_2$.[164] This class of compound catalyzes the selective hydrogenation of 2-butenal.

6.1.2.1.7 Sulfur

(i) Sulfides

Sulfide-capped triangular Co clusters are a well-known feature in organometallic systems. A number of examples will serve to illustrate this. The simple monomeric phosphine complex $(Ph_3P)_2CoBr_2$ reacted with Na_2S yields the symmetric cluster $Co_6S_8(PPh_3)_6$, where the six Co atoms form a distorted octahedral core with each octahedral face bridged by a μ^3-S^{2-} atom.[165] Each Co is identically surrounded by four S and one P atom in a distorted square–pyramidal environment. In a quite different approach, reaction of $CoCl_2$, 2-aminobenzenethiol (Habt), $NaOCH_3$, and $P(t\text{-}Bu)_3$ in the absence of air with following addition of Li_2S yields a cluster of this type, $Co_3(\mu_3\text{-}S)(abt)_3(P(t\text{-}Bu)_3)$.[166] The paramagnetic sulfide-capped cluster $Co_3(CO)_9(\mu_3\text{-}S)$ has been developed as a reagent for the synthesis of $Co_3(CO)_7(\mu\text{-}SR)(\mu_3\text{-}S)$ species via reaction with organic compounds possessing S—S or S—H bonds.[167]

The heteronuclear cluster $[Mo_3CoS_4(H_2O)_{10}]^{4+}$ has been reported, where the Co is formally zerovalent.[168] The core structure (**18**) features two edge-linked cubane units with Co—S bridging the two clusters.



(**18**)

(ii) Thioethers

Multidentate thioethers are readily introduced into the coordination sphere of low-valent cobalt. As an example, the tridentate thioethers 1,3,5-trithiacyclohexane and tris(methylthio)methane both replace three facially arranged carbonyl ligands in $Co_3(CO)_9(\mu\text{-}CPh)$, leaving the cluster otherwise intact.[169]

(iii) Thiolates

In organometallic systems in particular, clusters with bridging alkylthiolates are well known, as exemplified by $Co_2(Cp)_2(\mu\text{-}SCH_3)_2$, which undergoes reactions with alkyne-cobalt complexes to yield trinuclear clusters.[170]

(iv) Thiocarbamates

Dithiocarbamates in stable low-valent Co systems are rare and usually restricted to organometallic systems. An example is the heteronuclear metal cluster $WCo_2(\mu_3\text{-}S)(\mu_3\text{-}SCNEt_2)(CO)_4(S_2CNEt_2)$, characterized by a crystal structure, and formed by reaction of $Co_2(CO)_8$ with $W(CO)(PhCCPh)(S_2CNEt_2)_2$ and subsequent rearrangement in solution following carbonyl loss from an intermediate.[171] The three metals are arranged in a triangular array, bicapped by the sulfido and thiocarboxamido anions. Each Co is also bonded to two terminal carbonyl groups, the remaining ligands binding to the tungsten center.

(v) Thioureas

A rare example of thiourea coordination to low-valent Co is of a disubstituted thiourea as bridging ligand, observed in the cluster $Co_3(CO)_7(\mu_3\text{-}S)(\mu\text{-}\eta_2\text{-}PhNC(S)NHCH_2Ph)$ which is formed by reaction of $Co_2(CO)_8$ with the thiourea.[172] The crystal structure of the product defines a tetrahedral Co_3S core with all carbonyls in terminal positions and the deprotonated thiourea bridging two Co centers via the S and an amido N.

6.1.2.1.8 Halogens

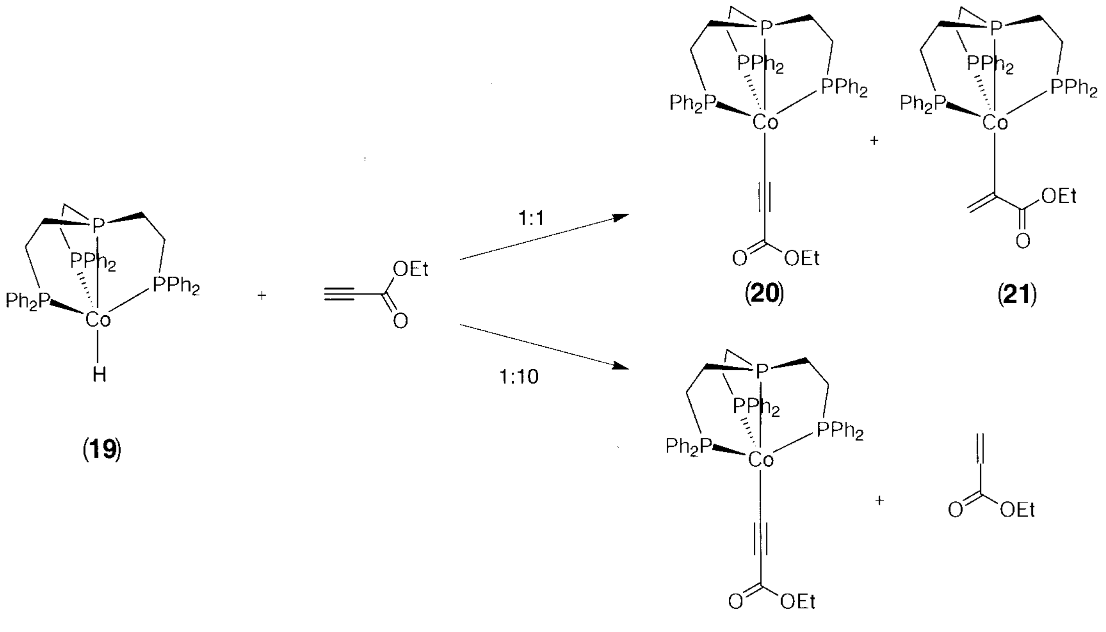
Compounds containing Co and only halogen ligands are extremely rare in low oxidation states. However, halogen is a common companion ligand in low-valent Co chemistry, particularly to phosphorus (see Section 6.1.2.1.4), where they are often the leaving group in substitution reactions. Of course, the effectiveness of a leaving group is determined by its stability in isolation, so it is no surprise that halides play a similar role across all oxidation states of Co coordination chemistry.

6.1.2.1.9 Hydrogen

(i) Hydrides

Cobalt compounds with hydride as the sole ligand are not usually observed, and hydride compounds, at least in isolable form, include other companion ligands. However, using a time-of-flight atom-probe field ion microscope, the interaction between hydrogen and Co atoms in an external electric field led to the Co hydrides CoH, CoH_2, and CoH_3,[173] although these species have no extended stability. Recent advances in the chemistry of hydrides in general have been reported in a monograph.[174]

The effect of stoichiometry, substituent, and temperature were investigated in reactions between the hydride HCo(tdppep) (**19**) and a number of alkynes.[175] The σ-acetylide complex (**20**) and the σ-alkenyl (**21**) are formed from the stoichiometric reaction with ethyl propiolate. However, when a ten-fold excess of ethyl propiolate is used, the acetylide complex is formed quantitatively and one equivalent of alkyne is hydrogenated to alkene. Forcing conditions and a large excess of



(**19**) (**20**) (**21**)

alkyne were required to form the analog (tdppep)Co(C≡CPh). The electrochemical behavior of these Co^I σ-acetylides was also reported.

Unsually short NMR T_1 relaxation values were observed for the metal-bonded H-ligands in $HCo(dppe)_2$, $[Co(H_2)(dppe)]^+$ (dppe = 1,2-bis(diphenylphosphino)ethane), and CoH(CO) $(PPh_3)_3$.[176] A theoretical analysis incorporating proton–metal dipole–dipole interactions was able to reproduce these T_1 values if an $r_{Co\text{-}H}$ distance of 1.5 Å was present, a value consistent with X-ray crystallographic experiments. A detailed structural and thermodynamic study of the complexes $[H_2Co(dppe)_2]^+$, $HCo(dppe)_2$, $[HCo(dppe)_2(MeCN)]^+$, and $[Co(dppe)_2(MeCN)]^{2+}$ has been reported.[177] Equilibrium and electrochemical measurements enabled a thorough thermodynamic description of the system. Disproportionation of divalent $[HCo(dppe)_2]^+$ to $[Co(dppe)_2]^+$ and $[H_2Co(dppe)_2]^+$ was examined as well as the reaction of $[Co(dppe)_2]^+$ with H_2.

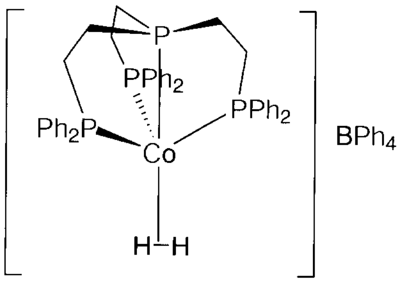
The electrochemical behavior of monovalent phosphite ester Co hydrides of the type $HCo(PR_3)_4$ ($PR_3 = P(OEt)_3$, $PPh(OEt)_2$, $PPh_2(OEt)$) in CH_2Cl_2 and MeCN was examined.[178] Cyclic voltammetry in CH_2Cl_2 identified a reversible single electron oxidation to $[HCo(PR_3)_4]^+$, followed by a second irreversible oxidation, for all the ligands employed. In MeCN, the behavior was similar, but stability of the compounds in this solvent was diminished. Bulk electrolysis gave a new Co^{II} hydride, $[HCo(P(OEt)_3)_4]BPh_4$.

The monovalent hydride $HCo(PPh(OEt)_2)_4$ is a versatile synthon and catalyst. Photoirradiation of $HCo(PPh(OEt)_2)_4$ generates the coordinatively unsaturated complex $HCo(PPh(OEt)_2)_3$ which catalyzes H transfer from secondary alcohols to carbonyl compounds.[179] Intermediate coordination of the carbonyl compound to $HCo(PPh(OEt)_2)_3$ was proposed. The rate-determining step involves hydride transfer to the carbonyl carbon at the stage of transformation of the hydrido aldehyde/ketone complex into its alkoxo derivative. A kinetic analysis showed that aldehydes reacted considerably faster than ketones, attributable to steric repulsion hindering approach by the Co complex to the carbonyl group. Reaction of $HCo(PPh(OEt)_2)_4$ with $p\text{-}MeC_6H_4N_2^+$ affords the paramagnetic $[HCo(PPh(OEt)_2)_4]^+$. When reacted with NO^+, the dinitroso complex $[Co(NO)_2\text{-}(PPh(OEt)_2)_2]^+$ is formed and protonation with $HBF_4{\cdot}Et_2O$ to give the dihydrogen complex $[Co(H_2)(PPh(OEt)_2)_4]^+$ occurs.[180] Reaction of the monovalent HCo(tdppea) (hydrido monomer of (**16**)) with CS_2, SCNPh, or OCNPh affords the corresponding η^2-bonded sulfide, isothiocyanate, or isocyanate.[181]

$HCo(N_2)(PPh_3)_3$ has been shown to promote C—O bond cleavage selectively in allylic and vinylic trimethylsilyl ethers, resulting in $Co(OSiMe_3)(PPh_3)_3$ and free olefin at room temperature.[182] The mechanism of C—O bond cleavage involves insertion of the olefinic double bond into the Co—H bond, followed by β elimination of the Me_3SiO group from the transition metal complex. The same group reported that C—O bonds in aryl and alkyl carboxylates ($R'CO_2R$) are selectively cleaved by the same complex.[183] The reaction products are accounted for by assuming insertion of the ester C=O bond into the Co—H bond, followed by abstraction of the β alkoxo group by Co. Other derivatives prepared include $Co(OCH(CF_3)OEt)(PPh_3)_3$ (from trifluoroacetic acid) and $Co(OPh)(PPh_3)_3$ from (phenyl acetate). Borohydride is well known to form nonclassical η^2-bonded complexes through a pair of bridging H atoms. The diamagnetic monovalent $Co(terpy)(H_2BH_2)$ undergoes rapid exchange between its terminal and bridging H atoms, as shown by NMR.[184]

(ii) Dihydrogen

Dihydrogen is an effective and usually η^2-bonded ligand, as exemplified here. The remarkably stable η^2–H_2 complex $[Co(tdppep)(H_2)]PF_6$ (**22**) was prepared via three routes: protonation of the hydride HCo(tdppep) by a strong acid; displacement of N_2 by H_2 in $[(Co(tdppep)(N_2)]PF_6$; or H_2 addition to the 16-electron fragment $[Co(tdppep)]^+$.[185] X-ray crystallography identified a trigonal–bipyramidal geometry with the H_2 ligand presumably *trans* to the bridgehead P donor, although the actual position of the H_2 ligand was not resolved. The complex catalytically isomerizes dimethyl maleate to dimethyl fumarate. However, an unusual counter-ion dependence was seen for the reaction with H_2 and two salts of the dinitrogen complex (**10**) in the solid state.[186] With BPh_4^- as the counter ion, the classical dihydro distorted octahedral complex $[(tdppep)Co(H)_2)]BPh_4$ (**23**) results (characterized by its X-ray crystal structure), rather than the non-classical $[(tdppep)Co(\eta^2\text{-}H_2)]PF_6$ (**22**).[185] Both reactions are reversible upon treatment with N_2. In solution the complexes are indistinguishable and consistent with a η^2-bonded H_2 ligand.



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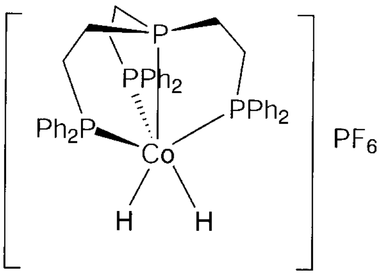


(23)

6.1.2.2 Co^{II}

Cobalt(II) is a key oxidation state, and the range of compounds extant is truly vast. Four-coordinate tetrahedral and six-coordinate octahedral complexes, in particular, abound, with five-coordinate trigonal bipyramidal complexes also common. However, three- to eight-coordinate compounds have been reported, with examples at the extrema sparse, and their formation is usually particularly dependent on ligand topology. Traditionally, the complexes of this d^7 paramagnetic ion are considered to be labile and ligand exchange facile.

6.1.2.2.1 Carbon

(i) Cyanides

Cyanide complexes have a venerable history (see *CCC*(1987)),[1] and find utilization in many industrial processes including as synthetic catalysts e.g., Co cyanides on inorganic supports catalyze alkylene oxide polymerization,[187] molecular magnetic materials, in electroplating, and in mining. Their pharmacology and toxicology is well explored

(f) Mononuclear. Given the long history of cyanide complexes, it is not intended to cover simple complexes to any marked extent. One interesting example is the characterization of the well-known anion $[Co(CN)_5]^{3-}$ formed inside Zeolite Y by treatment of the Co zeolite first with CsCl and then with methanolic NaCN.[188] This encapsulated complex has been shown to reversibly bind dioxygen in the zeolite lattice with high selectivity, whereas the usual reaction is irreversible formation of a dioxygen-bridged dimer. The simple aquapentacyanocobaltate(II) ion is an efficient catalyst for photolytic hydrogen evolution.[189] In aprotic solutions, a synthetic, spectroscopic and X-ray structural study has identified the existence of species with from one to five cyanide ions coordinated to cobalt.[190] The $Li_3[Co(CN)_2]\cdot 3DMF$ species was isolated and structurally defined, and a salt of $[Co(CN)_4]^{2-}$ was also isolated.

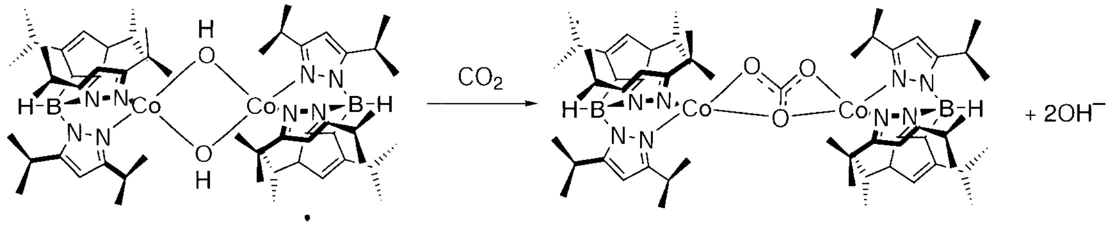
(g) Oligonuclear and polymeric. The Co–Co linked dimer $[Co_2(CN)_{10}]^{6-}$, which is readily prepared in liquid ammonia as solvent, reacts with water to yield a number of products identified by ^{59}Co NMR, including $[HCo(CN)_5]^{3-}$.[191] Monomeric species such as $Li_3[Co(CN)_5]\cdot 3DMF$ can form and may be isolated from aprotic solvents. Cyanide features as a bridging ligand as well as a terminal monodentate in polymetallic species. A recent example of a mixed-metal Co^{II}/Mn^{II} dimer arises from reaction of trans-$Mn(CN)(CO)(dppm)_2$ (dppm = bis(diphenylphosphino)methane) with $CoCl_2$ in THF, which leads to the μ-cyano complex $Cl_2(THF)Co^{II}(\mu\text{-}NC)Mn^{II}(CO)(dppm)_2$, defined by a crystal structure which shows the Co^{II} center is pseudo-tetrahedral.[192]

(ii) Carbonyls

Cobalt(II) carbonyls are rarely met, except as transient redox products from stable lower-valent precursors.

(iii) Carbon dioxide

Carbon dioxide is activated by metal complexes, including Co^{II}, to undergo a range of reactions: oxidative coupling with unsaturated substrates; insertion into M—X bonds; and insertion into M—M′ bonds. The $Co(dmg)_2(H_2O)_2$ complex reacts with CO_2 to form $Co(dmg)_2(H_2O)(CO_2H)$ bearing a Co—C bond.[193] Insertion of CO_2 into the core of the substituted Tp di(μ-hydroxo)dicobalt(II) complex (**24**) leads to the bridged carbonato complex (**25**).[194] Electrochemical reduction of CO_2 is activated by Co^{II}(cyclam) and analogs, promoting the two-electron reduction in aqueous acid to form CO and H_2O.[195] Coordination of CO_2 to the reduced complex as intermediate is implicated.



(24) **(25)**

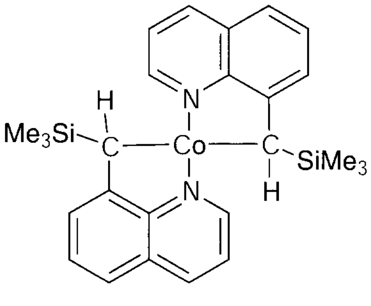
(iv) Alkyls and aryls

No attempt to cover the coordination chemistry of unsaturated cyclic anions such as cyclopentadienyl is made here, due to their coverage in the companion series on *Comprehensive Organometallic Chemistry*. The only example to be mentioned here, because it is the first example of a high-spin Co^{II} organometallic complex, is Co(Cp)(Tp).[196]

Simple alkyl and aryl σ-bonded complexes are conveniently prepared by reaction of an alkylating reagent with a halocobalt(II) precursor. All-alkyl systems are rare, but the pentamethylcobaltate(II) anion is known.[197] More typically, the coordination sphere of the metal contains additional co-ligands, particularly with P, S, or N donors. Some examples that reflect the style of reactions extant appear below.

Reaction of Li(2-($(Me_3Si)_2C$)pyridine) with $CoCl_2$ in ether yields the thermally stable bis cobalt(II) dialkyl complex, which is planar with *trans*-disposed C,N-chelates.[198] The strained four-membered rings are reflected in a C—Co—N angle of 69.6(2)°, while Co—C and Co—N distances are 2.094(6) Å and 1.919(4) Å respectively. Earlier, related chemistry produced the tetrahedral ion with only Co—C bonds, $[Co(CH(SiMe_3)_2)_4]^{2-}$, and an ion $[CoCl(CH(SiMe_3)_2)_2]^-$, , with two Co—C bonds and a rare trigonal planar geometry.[199]

Examples with S- and P-donor companion ligands abound. The thioether-containing complex Ph(ttb)CoCl (ttb = tris((*tert*-butylthio)methyl)borate) can be reacted with either Me_2Mg or MeLi in THF to yield the alkylcobalt(II) compound Ph(ttb)CoMe in high yield.[200] The high-spin divalent tetrahedral complexes Co(pnp)X (pnp = $^-N(SiMe_2CH_2PPh_2)_2$; X = Cl, Br) are conveniently prepared from CoX_2 and Li(pnp),[201] and subsequently react with alkylating reagents to form low-spin square-planar Co(pnp)R (R = alkyl) compounds. Treatment of $CoCl_2$ with organolithium precursor compounds yields low-spin Co^{II} dialkyls which include (**26**).[202]



(26)

Bis(aryl)cobalt(II) compounds have been prepared by reaction of R′MgX (where $R' = C_6H_{6-n}Cl_n$; $n = 2$–4) with $Co(PR_3)_2Cl_2$.[203] They undergo both thermally and oxidatively induced decomposition, with the corresponding biphenyl a product. The reactions of alkyl-cobalt complexes have been reviewed recently, and include thermolysis, photolysis, oxidation, and reduction reactions.[25] Homolysis of the Co—C bond is a feature of reactions.

6.1.2.2.2 Nitrogen

All known types of N-donor ligands are found in complexes with divalent Co, so our treatment of this topic will be selective in an endeavor to provide an overview of this vast area. There is a crossover in stability of divalent Co complexes going from hard amine donors (almost all being oxygen sensitive) to the highly unsaturated polyimines, which are rather difficult to oxidize. Divalent Co forms a variety of N-donor complexes of all electronic ground states (high and low spin) depending on the ligand field strength and symmetry.

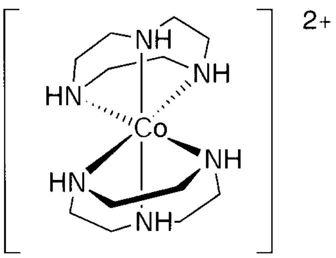
(i) Amines

(h) Monodentate. The simplest classical amine complex is the hexaammine. The $[Co(NH_3)_6]^{3+/2+}$ redox potential is −0.04 V (vs NHE) making the $[Co(NH_3)_6]^{2+}$ ion air sensitive as well as substitution labile. Nevertheless, the divalent hexaammine complex has been thoroughly characterized. The X-ray crystal structure of $[Co(NH_3)_6]Cl_2$ has been reported at both 294 K and 128 K, revealing six crystallographically identical Co—N bonds of 2.170(2) Å in the room-temperature structure and no phase change at lower temperature.[204] By contrast, differential scanning calorimetric study of $[Co(NH_3)_6](ClO_4)_2$ and $[Co(NH_3)_6](BF_4)_2$ found that these complexes were polymorphic between 100 K and 300 K.[205] In solution, the changes in Co—N bond length upon reduction from Co^{III} to Co^{II} have been studied with EXAFS. The bond length changes report on the inner sphere reorganizational energy of the complex, and this allowed the calculation of outer sphere electron transfer cross reaction rates using semi-classical theory that were in excellent agreement with experiment.[206]

(i) Multidentate. The ethane-1,2-diamine (en) complex of Co^{II} represents this category of ligands well. Crystal structures of the air-sensitive $[Co(en)_3]^{2+}$ with simple anions have been known for some time. A hydrothermal reaction of $CoBr_2$ with Na_3SbS_3 and en led to the isolation of $[Co(en)_3]CoSb_4S_8$ comprising $[Co(en)_3]^{2+}$ cations and infinite $[CoSb_4S_8]^{2-}$ layers which form a novel open framework structure.[207] Low-dimensional structures of the type $[Co(en)_3]Sb_2S_4$ and $[Co(en)_3]Sb_4S_7$ have also been reported.[208]

Although somewhat more stable than its hexaammine relative, the air-sensitive $[Co(en)_3]^{2+}$ is still substitutionally labile and racemizes rapidly in solution. Chiral discrimination in its (racemic) solutions has been observed in outer sphere electron transfer reactions with optically active oxidants including $[Co^{III}(EDTA)]^-$,[209,210] $[Cr(ox)_3]^{3-}$,[211,212] Co^{III} oxalate, malonate, and acetylacetonate (acac) complexes.[213]

(j) Macrocyclic. Like most divalent amines of Co, the bis macrocyclic $[Co(tacn)_2]^{2+}$ (tacn = 1,4,7-triazacyclononane) complex (**27**) is a high-spin, air-sensitive complex. Its crystal structure and spectroscopy have been reported.[214] When fewer than six N-donors are present, divalent Co complexes become more stable. Electrochemical oxidation of the putative five-coordinate complex (**28**) $[(H_2O)Co(teta)]^{2+}$ (teta = *meso*-5,5,7,12,12,14-hexamethyl-1,4,8,11-



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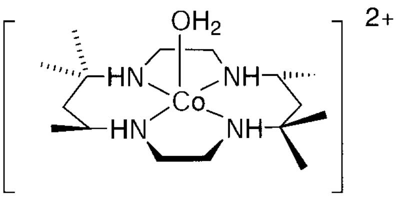
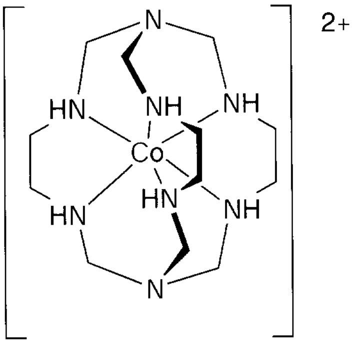


(28)

tetraazacyclotetradecane) has been studied, and the effect of ligands *trans* to the aqua ligand upon oxidation of the complex was examined.[215] The *trans*-Co(teta) $(OSO_2CF_3)_2$ complex has been structurally characterized, providing a rare example of triflate coordinated to divalent Co.[216]

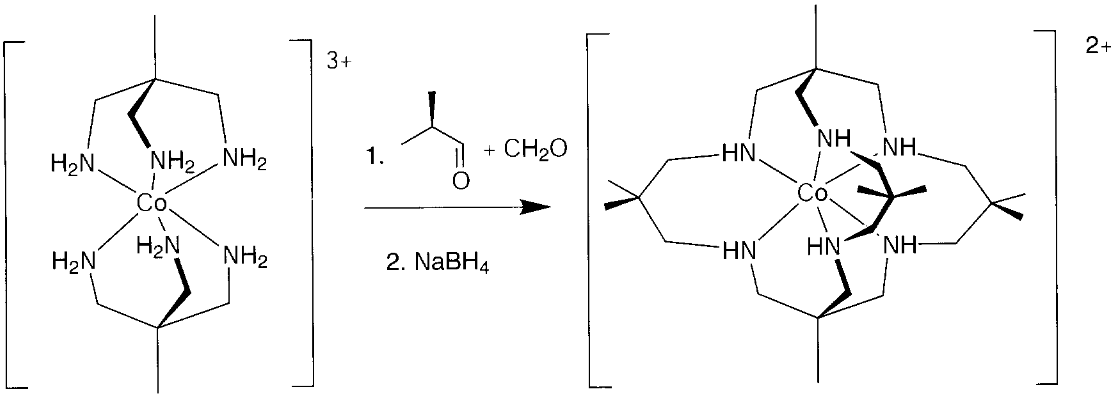
In methanolic MeCN, the resulting photoreduced Co^{II} complex of the unsubstituted (cyclam) analog of (**28**) mediates electron transfer in the reduction of CO_2 to CO and formate with *p*-terphenyl as the photocatalyst and tertiary amines as sacrificial electron donors.[217] Similarly, photoreduction of CO_2 to formate can be achieved by the same complex using phenazine as the photosensitizer, the Co complex as electron mediator, and Et_3N as an electron donor.[122] The multi-step photoreduction of O_2 to H_2O_2 is achieved with $[Co(cyclam)(OH_2)_2]^{2+}$ (and various C-methylated analogs) generated *in situ* by oxidative quenching of photoexcited $[Ru(bpy)_3]^{2+}$.[218]

The remarkable physical properties exhibited by the divalent macrobicyclic cage complex $[Co(sep)]^{2+}$ (**29**) are unparalleled in Co chemistry.[219] The complex, characterized structurally, is inert to ligand substitution in its optically pure form and resists racemization in stark contrast to its $[Co(en)_3]^{2+}$ parent. The encapsulating nature of the sep ligand ensures outer sphere electron transfer in all redox reactions. For example, unlike most divalent Co amines, the aerial oxidation of (**29**) does not involve a peroxo-bound intermediate.



(**29**)

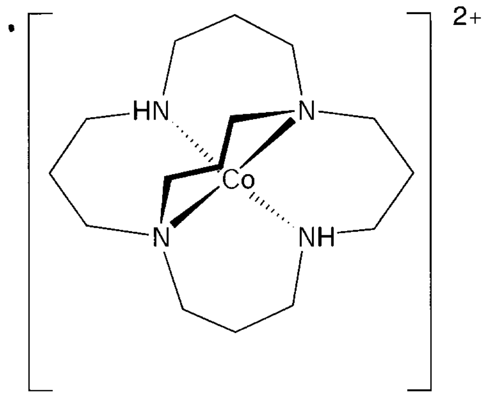
Larger cavity cages have been reported by reaction of $[Co(tame)_2]^{3+}$ (**30**) (tame = 1,1,1-tris (aminomethyl)ethane) with paraformaldehyde and isobutyraldehyde leading to the expanded octamethylated cage (**31**), with distinctly different properties to any other hexaamine.[220] Foremost, the $Co^{III/II}$ redox potential of (**31**) is more than 1 V positive of the couple found in the smaller cavity cage (**29**). In fact, (**31**) is resistant to oxidation by O_2 and H_2O_2; a unique feature in Co hexaamine chemistry. N-Based diastereomers were crystallized and characterized structurally. Controlled potential electrolysis of these isomers led to the observation of two distinctly different Co^{III} complexes; one yellow and the other a most unusual blue in color.



(**30**) (**31**)

Smaller macrobicycles and macrotricycles bearing less that six N-donors are also known. These ligands comprise tertiary or secondary amines and are derived from insertion of one or more straps between pairs of potentially bridgehead N-donors contained within a small ring macrocycle, and in this sense they may be considered analogs of the well-known azacryptands. The inability to offer six N-donors, and the presence of tertiary amines in these ligands leads to the preference for divalent over trivalent Co.

The small bowl-shaped tetraamine 3^5-adamanzane (1,5,9,13-tetraazabicyclo[7.7.3]nonadecane) comprises the 16-membered macrocyclic tetraamine ([16]aneN_4) with one pair of diagonally opposite N atoms linked by a trimethylene bridge. The crystal structure of its $\mathrm{Co^{II}}$ complex (**32**) reveals a distorted tetrahedral $\mathrm{CoN_4}$ array, with the metal ion slightly too large to be bound symmetrically within the confines of the small cavity (Figure 3).[221] Solution behavior is more complicated. The tetrahedral complex exhibits limited stability in aqueous solution, although its electronic spectrum is essentially the same as its pseudotetrahedral [16]aneN_4 parent, with five- and six-coordinate $\mathrm{Co^{II}}$ complexes being formed in the presence of coordinating anions ($\mathrm{Cl^-}$) and solvents. Kinetic analysis showed that $\mathrm{Cl^-}$ ions accelerate extrusion of the $\mathrm{Co^{2+}}$ ion from the small cage.



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(ii) Pyridine and oligopyridines

(k) Monodentate. Pyridine complexes of $\mathrm{Co^{II}}$ may take several forms depending on the method of preparation. Blue tetrahedral $[\mathrm{Co(py)_4}]^{2+}$ is well known in addition to the polymeric halide-bridged six-coordinate $\{\mathrm{Co(py)_2X_2}\}_n$ species in the solid state. Investigations of the solution equilibria between these four- and six-coordinate species are well documented. The tetrahedral $[\mathrm{Co(py)_4}]^{2+}$ ion has been shown to catalyze the aromatization of 1,4-dihydropyridine[222] and also

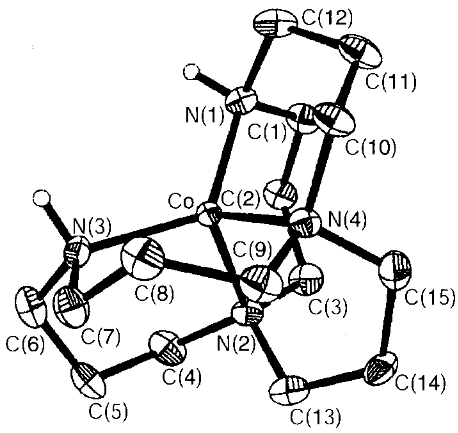
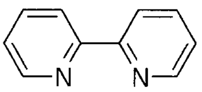


Figure 3 View of complex (**32**) with alkyl H-atoms omitted (reproduced with permission of the American Chemical Society from *Inorg. Chem.*, **2001**, *40*, 2323–2334).

1,3-dipolar cycloadditions.[223] More recently, the crystal structure of a novel square planar form $[Co(py)_4]Cl(PF_6)$ has been reported.[224] The formation and low-energy collision-induced dissociation of $[Co(py)_6]^{2+}$ and derivative complexes has been investigated by electrospray ionization mass spectrometry.[225]

Halopyridinecobalt(II) complexes have been explored in detail, and exhibit either distorted octahedral or tetrahedral geometries, depending on ligands involved. The preparation and characterization of dihalotetrakis(3,5-dimethylpyridine)cobalt(II) complexes with chloro, bromo and iodo ligands have been reported.[226] The crystal structure of the elongated octahedral chloro complex defines the chloride ions in a *trans* disposition with Co—Cl distance of 2.455(2) Å, with Co—Br and Co—I being 2.63 Å and 2.88 Å respectively. The difluoro analog has also been characterized separately, with an equivalent structure and Co—F distance of 2.016(3) Å.[227] IR spectroscopy shows clear differences between the coordinated chloride complex and a pyridinium tetrachlorocobaltate(II) species. In a related study, halocobalt(II) complexes of 2-, 3- and 4-methylpyridine have been examined,[228,229] and molecular mechanics studies supplemented crystal structural studies. A correlation between solid-state structure and thermal properties was defined. In the dibromobis(2-bromopyridine) cobalt(II) complex,[230] a slightly distorted tetrahedral geometry was defined by a crystal structure analysis. A series of four- or six-coordinate 2-, 3- and 4-methylpyridine compounds of formula CoL_2X_2 or CoL_4X_2 ($X = Br$, I) have been prepared and their thermal stability examined.[231] Dibromobis(2,4-dimethylpyridine)cobalt(II) and bromotetrakis(2,4-dimethylpyridine)cobalt(II) have been prepared and characterized by X-ray crystal structures.[232] The former exhibits tetrahedral geometry and the latter the more rarely observed five-coordinate square pyramidal geometry. Thermal decomposition occurs with release of pyridines from the former in one step at 335 °C, whereas three successive steps releasing one (at 130 °C), one (at 193 °C), and two (at 360 °C) pyridines are observed for the latter. Thermal decomposition of a large series of $Co(Rpy)_2X_2$ (Rpy = substituted pyridine, $X = Cl$, Br) has been probed by thermogravimetric analysis,[233] with pyridine loss a primary process prior to halide loss. The temperature and pressure effects on the equilibrium between octahedral $Co(Mepy)_4X_2$ and tetrahedral $Co(Mepy)_2X_2$ (Mepy = 3-methylpyridine; $X = Cl$, Br) has been probed.[234] Higher pressure favors the octahedral species, whereas higher temperature favors the tetrahedral species.

(l) Multidentate. Complexes of the bidentate bpy (**33**) and phen (**34**) ligands share many common features. The $[Co(bpy)_3]^{2+}$ and $[Co(phen)_3]^{2+}$ ions typically possess high-spin ($S = 2$) electronic ground states, but they are close to the high/low-spin crossover, in contrast to their (exclusively) high-spin hexaamine relatives. The crystal structures of $[Co(phen)_3]^{2+}$ with a number of simple and more complex anions have been reported, including perchlorate[235], antimony tartrate,[236] benzene-1,2-dioxyacetate[237] and octa- and nonanedioate.[237] The latter two dicarboxylate salts inhibit the growth of *Candida albicans*.



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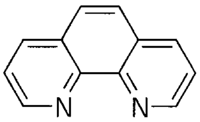

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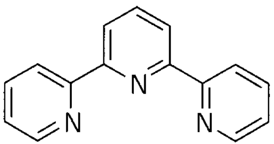


(35)

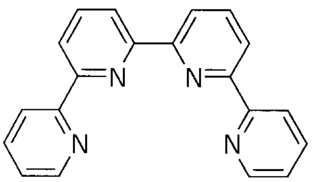
An interesting study of the $[Co(bpy)_3][MCr(ox)_3]$ system (ox = oxalato dianion) found that when $M = Na^+$ the Co^{II} complex is high spin, but when $M = Li^+$, the compound assumes a low-spin electronic ground state due to contraction of the counter ion network surrounding the bpy complex.[238] Optical spectroscopy and magnetic susceptibility studies reveal that $[Co(bpy)_3][LiCr(ox)_3]$ exhibits temperature-dependent spin-crossover behavior. A related system, $[Co(bpy)_3][MCr(ox)_3](ClO_4)$, where M is a divalent transition metal ion, has been investigated. The separate cationic and anionic tris-chelate complexes within this network are necessarily homochiral.[239]

Encapsulation of $[Co(bpy)_3]^{2+}$ within zeolite frameworks has also been shown to have a remarkable influence on the electronic spin state of the complex.[240] Distortions imparted on the tris-chelate complex by the confines of the zeolite "supercage" are found to be responsible for stabilizing the unusual low-spin electronic ground state.[241,242] The $[Co(bpy)_3]^{3+/2+}$ couple has been measured for the encapsulated complex and it has been found that the complexes remain within the zeolite and do not exchange with the bulk solution.[243] Electrochemistry of $[Co(bpy)_3]^{3+/2+}$ immobilized within a sol–gel has also been studied.[244]

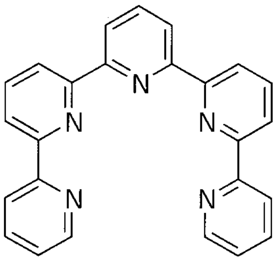
The structural and magnetic properties of divalent Co complexes of the tridentate terpy (**35**) are distinctly different. The high-spin/low-spin equilibrium of $[Co(terpy)_2]^{2+}$ has attracted considerable attention and a marked anion dependence has been identified. In the solid state, $[Co(terpy)_2]I_2$ exhibits a temperature-dependent magnetic moment coupled with temperature-dependent Co—N bond lengths.[245] At 295 K, the intermediate magnetic moment (μ_{eff} 3.2 B.M.) and Co—$N_{central,distal}$ bond lengths (1.942(7) Å and 2.104(5) Å) are consistent with a high/low-spin equilibrium in the solid state. On cooling to 120 K, the bond lengths (1.912(5), 2.083(4) Å) and magnetic moment (μ_{eff} 2.2 B.M.) reflect an exclusively low-spin electronic ground state. By contrast, $[Co(terpy)_2](ClO_4)_2$ exhibits a much higher room-temperature solid state magnetic moment (4.2 B.M.) and longer Co—$N_{central,distal}$ bond lengths (2.03 Å and 2.14 Å).[246] In the nitrate salt the Co—N bond lengths are longer again.[247] Solid state optical and EPR spectroscopy have also been used to study the temperature and anion dependence of this spin equilibrium.[248] The structurally imposed Co—$N_{central}$ bond compression of the terpy ligand directs the Jahn–Teller enforced tetragonal elongation along one of the N_{distal}–Co–N_{distal} axes of the complex to remove the orbital degeneracy of the ^2E (O_h) electronic ground state.

In solution, $[Co(terpy)_2]^{2+}$ is also in a high-spin/low-spin equilibrium. Ultrasonic absorption measurements determined the spin equilibrium relaxation time in both water and MeOH solution to be less than 2 ns.[249] Electron-donating functional groups such as methoxyl appended to the terpy ring result in a shift towards the high-spin form of the complex,[250] as does replacement of one pyridyl ring with a pyrazole.[251]

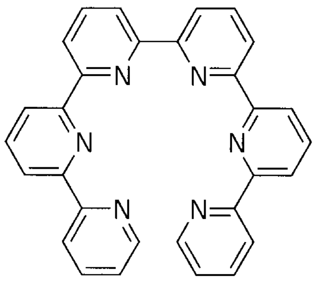
Further extension of the terpy structure generates a novel class of oligopyridines that typically behave quite differently from the mono-, bi-, and terpyridyl analogs. Steric repulsion between the two distal pyridyl rings disfavors planarity of oligopyridines larger than terpy, and enforces a helical conformation. Mononuclear and dinuclear Co^{II} complexes of quaterpyridine (**36**), and its substituted derivatives,[252,253] and quinquepyridine[222,254] (**37**) have been reported where the distinctly non-planar helically disposed ligand occupies the equatorial coordination sites of the six- or seven-coordinate ion. In solution the Co^{II} 4′,4‴-di-(*p*-chlorophenyl)quinquepyridine complex is typically mononuclear but can be crystallized as either a 1:1 (Figure 4) or 2:2 (helical) complex.[255,256] Double helical, homometallic, oligonuclear complexes of Co^{II} predominate when at least six donor atoms can be provided by the ligand i.e., sexipyridine (**38**) and higher oligomers. In these cases, pairs of tridentate (terpy-like) chelates are forced to bind separate Co^{II} centers. The introduction of a second bridging bis-tridentate oligopyridine completes the six-coordinate geometry of the two Co^{II} centers. For example, (**38**) forms a double helical 2:2 ($[Co_2L_2]^{4+}$) complex with each ligand binding in a bridging bis-tridentate manner.[257] A substituted derivative of septipyridine forms a double helical 2:2 complex comprising two $[Co(terpy)_2]^{2+}$ moieties with each strand containing a single non-coordinated pyridyl ring; one central and the other terminal (Figure 4).[258] The nonadentate novipyridine forms a trinuclear double helicate $[Co_3L_2](PF_6)_6$ as shown by mass spectrometry and elemental analysis.[259]



(**36**)



(**37**)



(**38**)

The linear bis-bidentate ligand bis(pyridylpyrazolyl)borate (**39**) ligand reacts with $Co(OAc)_2$ in MeOH to yield a discrete cyclic nanostructure $[Co_8L_{12}(PF_6)]^{3+}$.[260] This complex was characterized intact by ESMS, with the anion apparently trapped in the central cavity, a concept supported by the crystal structure of the perchlorate analog (Figure 5). Other oligopyridine ligands complexed with divalent Co include the tripodal tris(2-pyridylmethyl) amine (**40**),[261] and the novel dinucleating bis(2-pyridylmethyl)amine dimer (**41**).[262]

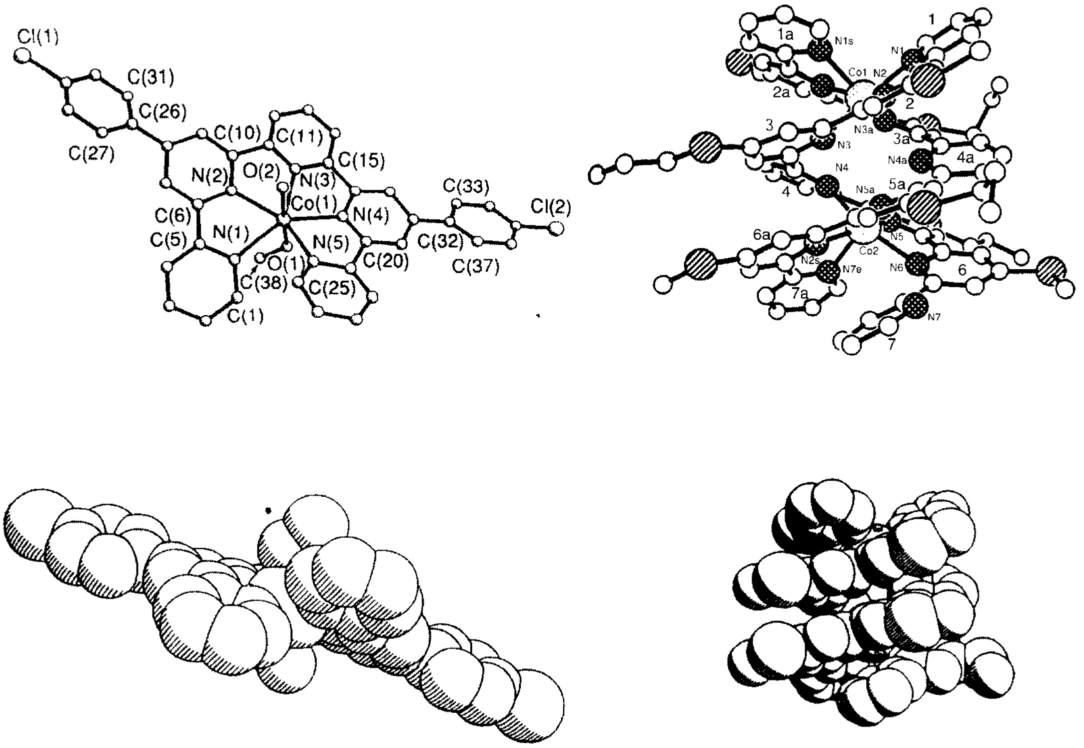


Figure 4 Mononuclear quinquepyridine (4′,4‴-bis(4-chlorophenyl analogue) Co^{II} complex (left, reproduced with permission of the Royal Society of Chemistry from *J. Chem. Soc., Chem. Commun.*, **1992**, 768–771) and dinuclear septipyridine (4′,4′′′′′-bis(4-mercaptomethylphenyl)-4′′′′,4′′′′′-bis(4-mercaptopropylphenyl) derivative) dicobalt(II) complex (right, reproduced with permission of the American Chemical Society from *Inorg. Chem.*, **1993**, *32*, 5477–5484). Space filling representations also shown.

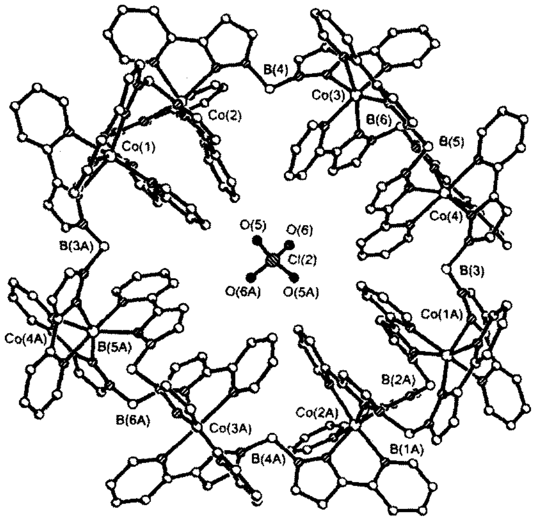
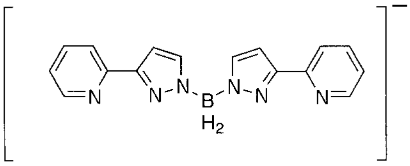
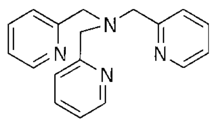


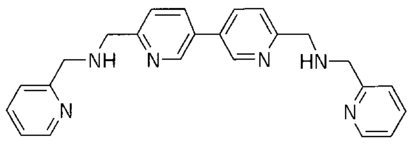
Figure 5 Cyclic octacobalt(II) complex of (**39**) with encapsulated ClO_4^- ion. H-atoms omitted (reproduced with permission from the Royal Society of Chemistry from *J. Chem. Soc., Chem. Commun.*, **1997**, 1361–1362).



(39)



(40)

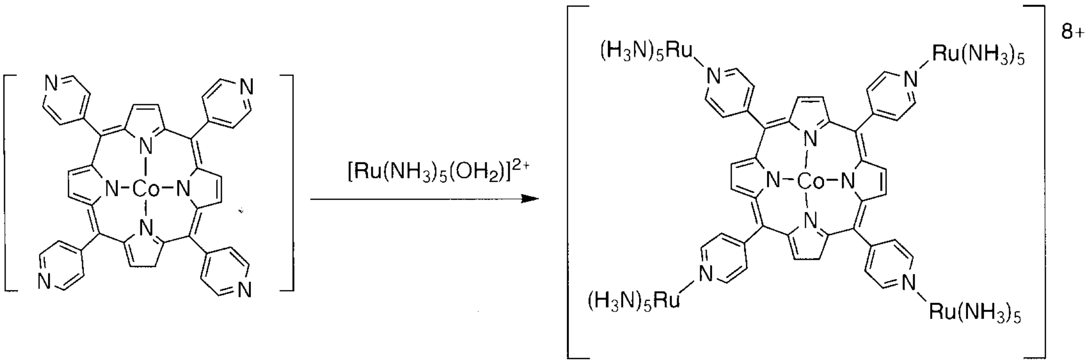


(41)

(iii) Porphyrins

Cobalt complexes of these compounds and their properties have been widely studied for some time. Substituted porphyrin complexes of divalent Co catalyze a wide variety of useful inorganic and organic transformations. The catalytic four-electron reduction of dioxygen to water in aqueous solution close to its thermodynamic potential is of great importance to fuel cell and battery technology. However, the two-electron reduction of O_2 to H_2O_2 is a more common and much less useful side reaction. Anson, Collman, and co-workers have published a series of papers using bridged dicobalt "face-to-face" porphyrins, some of which are efficient catalysts of the four-electron reduction of O_2 to H_2O.[263,264] Participation of both Co ions in O_2 binding (in a sandwich configuration) and in inner sphere electron transfer was implicated. Later, a superoxo-bridged dicobalt co-facial porphyrin complex, an intermediate in the four-electron reduction, was isolated and characterized.[265]

Anson and co-workers have shown that two Co ions were not necessary for four-electron O_2 reduction.[266] The *meso*-substituted complex porphyrin Co(TPyP) (**42**) complex bears four active pyridyl donors which readily react with four equivalents of $[Ru(NH_3)_5(OH_2)]^{2+}$ to produce the tetra-ruthenated derivative. The four Ru centers are sufficiently remote that their $Ru^{III/II}$ potentials coincide. Under steady state conditions $[Co(TPyP)]\{Ru(NH_3)_5\}_4]^{8+}$ (**43**) adsorbed onto a pyrolytic graphite working electrode catalyzes the reduction of dioxygen (Figure 6).



(42) **(43)**

Of the total current passed, 72% results in complete reduction to H_2O, while the remainder generates H_2O_2.[267] Catalytic activity was somewhat lower when the complex was confined to a Nafion polyelectrolyte film coated on a graphite electrode.[268] The roles of the Ru and Co centers in catalysis were elucidated by varying the number of Ru centers and their ancillary ligands. A tri-(pentaammine)ruthenated analog was also an efficient four-electron catalyst,[269] although the di-, mono-, and non-ruthenated analogs could only act as two-electron reductants. It was established[268] that (**43**) is a (homogeneous) two-electron O_2 reduction catalyst in solution, illustrating the importance of a rapid supply of electrons to the complex (adsorbed to an electrode surface) to ensure complete reduction before dissociation of the intermediate peroxo-bound form. This foreshadowed the fact that the four-electron reduction did not involve redox cycling of the four peripheral Ru centers in parallel. Subsequently it was established that Ru^{II}–pyridine π-back bonding (ultimately into the $Co^{II}-O_2$ reaction center) was the key factor in determining two- or four-electron reduction at the Co center of the porphyrin. Attachment of $\{Os(NH_3)_5\}^{3+}$ groups to the pyridyl rings (in a η^2 fashion, not involving the N-donor) instead of $\{Ru(NH_3)_5\}^{3+}$ led to

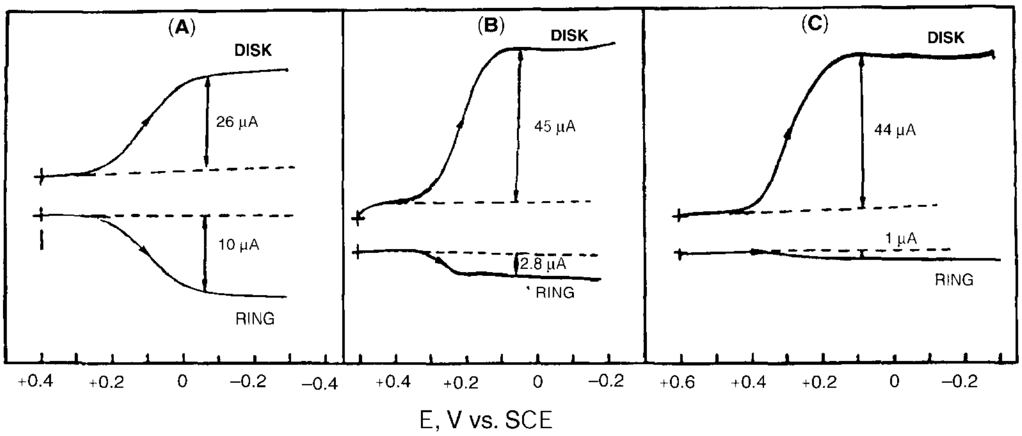
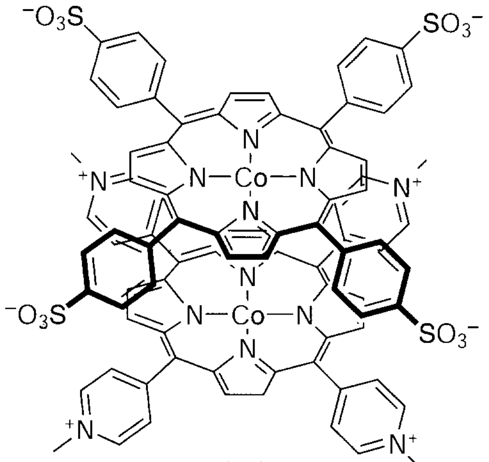


Figure 6 Steady state rotating ring-disk voltammograms of (A) compound (**42**); (B) compound (**43**) and (C) a Ru-bridged polymer of (**43**) each adsorbed to a graphite working electrode. Disk current shows reduction of O_2 while ring current reveals the presence of H_2O_2 simultaneously reoxidised at the ring anode poised at +1.0 V (reproduced with permission of the American Chemical Society from *Acc. Chem. Res.*, **1997**, *30*, 437–444).

significant (30%) four-electron O_2 reduction at a potential more positive than the $Os^{III/II}$ couple, thus ruling out participation of the peripheral subunits in electron transfer.[268]

More recently, even simpler non-covalently linked porphyrin dimers, self-assembling through hydrophobic[268] or electrostatic[270] interactions have been shown to achieve the four-electron reduction of O_2 to H_2O. The Co^{II} complex of the parent porphine ligand and its tetra-methyl derivative Co(TMP) aggregate in aqueous solutions, and in the absence of bulky *meso*-substituents, can form cofacial dimers in solution and on electrode surfaces reminiscent of the covalently linked analogs.[271] The porphyrin ion pair (**44**) comprising $[Co(TMpyP)]^{4+}$ (Mpy = 4-methylpyridinium) and $[Co(TSpP)]^{4-}$ (Sp = 4-sulfonatophenyl) similarly spontaneously dimerizes to form an active four-electron O_2 reduction catalyst.[270] The inter-planar separation (~3.1 Å) is close to that required for O_2 insertion between the Co centers of the cofacial assembly.



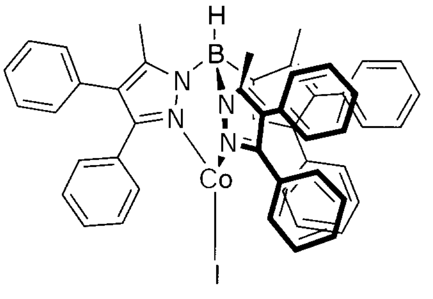
(**44**)

These studies have led to the development of other Co porphyrins with potential applications in a variety of areas with the common theme of catalyzing the efficient reduction of O_2. These systems are explored in Section 6.1.4.

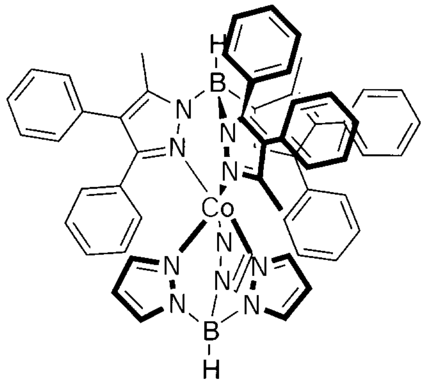
(iv) Imidazole, pyrazole, and related ligands

The fact that imidazole (Him) residues are particularly popular transition metal binding sites within metalloproteins is a major driving force for investigations of this heterocycle. The divalent oxidation state is preferred for the hexakisimidazolecobalt ion, and a number of complexes of this class have been characterized structurally including $[Co(Him)_6]^{2+}$,[272,273] $[Co(Meim)_6]^{2+}$,[274] and $[Co(vinyl\text{-}im)_6]^{2+}$.[275] The structures of simple tetrahedral complexes $Co(Him)_2(OAc)_2$ and its propionate analog were determined, and were found to be very similar to their Zn^{II} analogs. The implications of these results are relevant to Co^{II}-substituted Zn proteinases. Ternary complexes such as $[Co(ATP)(Him)]^{2-}$ were studied by potentiometric pH titration as a simple model for competition between ligating groups of biological relevance. The Him ligand was found to form more stable adducts than NH_3 at physiological pH, as proton competition for Him was negligible at pH 7.4, unlike NH_3.[276] Some examples of multidentate imidazole-containing ligands that have been complexed with Co^{II} include histamine (4-(2′-aminoethyl)imidazole) and its glycyl and sarcosyl derivatives, which, when reacted with Co^{II} in aerated aqueous solution, form mixtures of O_2 adducts that were studied by potentiometry, NMR, and spectrophotometry.[277]

Monomeric, pseudo-tetrahedral complexes of the type Co(Tp′)L and dinuclear centrosymmetric five-coordinate complexes of the form $Tp'Co(L)_2CoTp'$ (Tp′ = 3-*i*Pr,4-BrTp; 3-*t*Bu,5-MeTp; L = NCS^-, NCO^-, and N_3^-) have been synthesized.[278] The ligand-field spectral data for the monomeric complexes indicate a strong, trigonally distorted tetrahedral ligand field. In an elegant study, the tris-trisubstituted 3,4-Ph_2,5-MeTp reacts with CoI_2 to form the pseudotetrahedral (3,4-Ph_2,5-MeTp)CoI (**45**). Steric effects from the 4-Ph group on the 3-Ph group prevent the formation of bis (octahedral) complexes, whereas the isomeric ligand (3,4-Ph_2-5-Mepz)(3-Me-4,5-Ph_2pz)$_2$B does form an octahedral complex (**46**), with (unsubstituted) Tp as the ancillary tridentate ligand.[279]

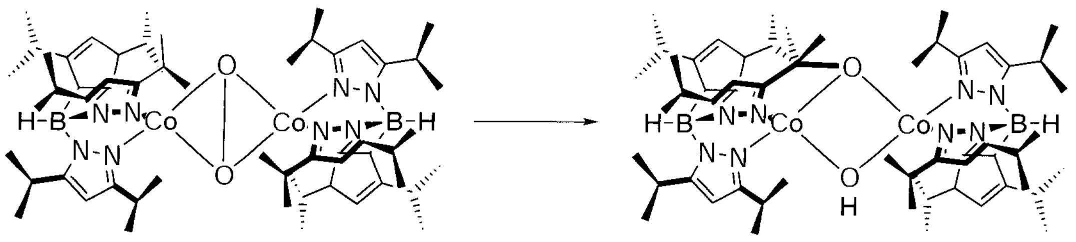


(45)



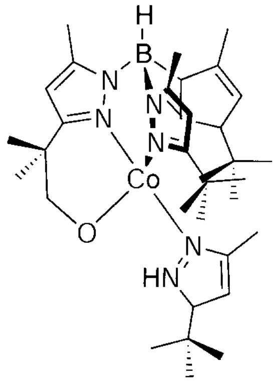
(46)

Compounds of the [Co(3-*t*Bu,5-MeTp)X]$^{n+}$ family have been found to exhibit a number of remarkable properties in the coordination and stabilization of small molecules and ions in the labile fourth coordination site.[280] The iodo derivative (3-*t*Bu,5-MeTp)CoI has been prepared and its X-ray crystal structure reported.[281] Reduction of (3-*t*Bu,5-MeTp)CoX (X = Cl, I) under N_2 generates the monovalent N_2 complex (**4b**) which upon reaction with O_2 yields the novel divalent side-on bound superoxo complex (3-*t*Bu,5-MeTp)Co(O_2) which was structurally and spectroscopically characterized ($r_{O\text{-}O}$=1.262(8) Å, ($\nu_{O\text{-}O}$=961 cm^{-1}).[129] This complex is stable in the solid state, but decomposes in solution to give [(3-*t*Bu,5-MeTp)Co]$_2$(μ-OH)$_2$.[282] The dioxygen-bridged dimer [(3-*t*Bu,5-MeTp)Co]$_2$(μ-O_2) is an intermediate and can be prepared independently by reaction of [(3-*t*Bu,5-MeTp)Co]$_2$(μ-N_2) with oxygen[282] or from reaction of the monovalent carbonyl (**4a**) with oxygen.[283] This later study showed that, at low temperature, the dimer is in equilibrium with its monomer. The crystal structure of [(3-*t*Bu,5-MeTp)Co](μ-O_2) was also determined. An independent study found that reaction of the 3,5-diisoproyl dihydroxo-bridged dimer (**24**) with a stoichiometric amount of H_2O_2 generates the unusual planar, side-on bound peroxo-bridged dinuclear complex [(3,5-*i*Pr_2Tp)Co]$_2$(μ-η^2:η^2-O_2) (**47**) on the basis of two intense absorptions attributable to $O_2^{2-} \rightarrow Co^{II}$ LMCT transitions in the UV-visible spectrum and a low energy $\tilde{\nu}_{O\text{-}O}$ vibration in the resonance Raman spectrum.[284] This group had previously identified a similar μ-η^2:η^2 binding mode in a peroxo-bridged dicopper(II) oxyhemocyanin model complex. Compound (**47**) is highly reactive and decomposes by hydroxylation of one of its isopropyl groups (at the secondary C atom) to give a novel μ-alkoxo-μ-hydroxo dinuclear compound Co_2(μ-OH)(μ-3-OCMe_2-5*i*Prpz)(3,5-*i*Pr_2pz)$_2$BH)(3,5-*i*Pr_2Tp) (**48**) where the deprotonated hydroxyl group and a hydroxo ligand bridge the two Co ions.



(47) **(48)**

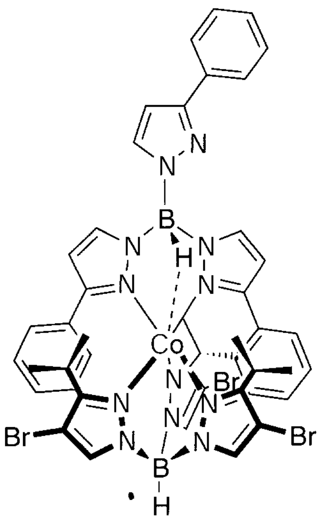
Somewhat similar observations were made separately in a study of the heterogeneous reaction between solid (3-*t*Bu,5-MeTp)CoH (**4c**) and O_2 which led to hydroxylation of one *t*-butyl group and coordination of the resulting deprotonated hydroxymethyl group.[285] The complex was crystallized as the mononuclear (((3-(OCH_2)Me_2C)pz)(3,5-*t*Bu_2pz)$_2$BH)Co(3-*t*Bu,5-MepzH) adduct (**49**) which exhibited a trigonal bipyramidal CoN_4O coordination geometry. In solution, the reaction with O_2 proceeds via a spectroscopically observable hydroperoxide (HOO^-) which decomposes to give (3-*t*Bu,5-MeTp)Co(OH) and (3-*t*Bu,5-MeTp)Co(O_2).



(49)

A number of other homo-substituted (threefold-symmetric) Tp derivatives have been complexed with Co^{II}. The 15-electron four-coordinate alkyl complex (3,5-*i*Pr_2Tp)Co(CH_2CH_3) was prepared and structurally characterized. Despite bearing a ligand with β H-atoms, the complex is resistant to β-hydride elimination.[286] The same group subsequently reported an extended series of these compounds including (3,5-*i*Pr_2Tp)CoR where $R = \eta^3$-allyl, η^1-*p*-methylbenzyl and η^1-1-α-naphthylmethyl.[287] Independently, the paramagnetic analogs (3-*t*Bu,5-MeTp)CoR (R = Me, Et, *n*-Bu) were prepared, and the related (3-*t*BuTp)Co(Me) complex was structurally characterized.[113] Like the di-isopropyl analog, these alkyls are thermally stable and show no tendency to β-eliminate. When the alkyl complexes are reacted with CO, homolytic cleavage of the Co—C bond is found instead of migratory insertion. The crystal structure of the fluorinated Tp complex (3-CF_3,5-MeTp)Co(η^2-NO_3)(MeCN) reveals a distorted octahedral N_4O_2 coordination sphere.[288] This complex catalyzes the oxidation of cyclohexane by cumene hydroperoxide to give a 1:1 mixture of cyclohexanol and cyclohexanone at a rate 50% faster than the nonfluorinated complex.

Octahedral bis-Tp complexes bearing different substituents on the separate Tp ligands have been prepared by sequential ligand substitution. The tetrahedral Co(3-*i*Pr,4-BrTp)Cl reacts with Tp or 3-*i*Pr,4-BrTp to form the corresponding hetero-bis-Tp complex Co(3-*i*Pr,4-BrTp)(Tp) and the symmetrical Co$(Tp)_2$.[109] However, reaction with the bulkier 3-PhTp leads to the coordination of only two pyrazolyl groups in (**50**) featuring an agostic B—H—Co interaction, as shown by X-ray crystallography. A similar agostic B—H—Co interaction was identified in the bis-pyazolyl-dihydroborate analog Co(3-*i*Pr,4-BrTp)((3-Phpz)$_2$$BH_2$). Substitution of both hydrides by phenyl groups leads to Co(3-*i*Pr,4-BrTp)((3-Phpz)$_2$$BPh_2$) (**51**) which is strictly five-coordinate. By comparison, the Co(3-*i*Pr,4-BrTp)((3-Ph-pz)$_4$B) adduct is tetrahedral.



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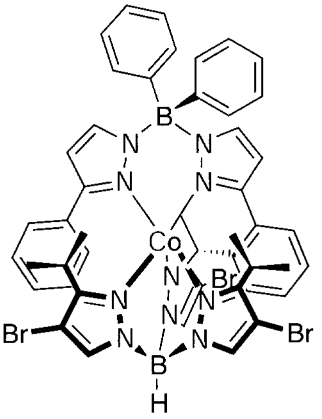


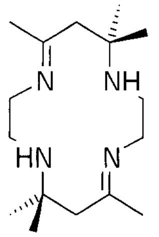
(51)

The synthesis of heterosubstituted Tp ligands (lacking a C_3 symmetry axis) has enabled a systematic investigation of substituent effects on both structure and reactivity of their Co complexes. The homo- (3-PhTp) and hetero- ((3-Phpz)$_2$(3-*t*Bupz)BH) trisubstituted ligands were complexed to Co^{II}. Four- or five-coordinate complexes ensued, depending on the steric demands of the substituents.[289] The {(3-PhTp)Co} moiety is able to coordinate two additional ligands such as NCS^-, pyrazole (Hpz) and MeOH, whereas the more sterically demanding {((3-Phpz)$_2$(3-*t*Bupz)BH)Co} unit forms tetrahedral complexes. Crystal structures of the five-coordinate (3-PhTp)Co(NCS)(Hpz) and four-coordinate ((3-Phpz)$_2$(3-*t*Bupz)BH)Co(NCS) were reported. The structures of the asymmetric hexacoordinate complexes ((3,5-Me$_2$pz)(3,5-Ph$_2$pz)BH)Co(η^2-NO$_3$)(THF) and ((3,5-Ph$_2$pz)BH$_2$)((3,5-Ph$_2$pz)$_2$(3,5-Me$_2$pz)BH)Co were established by X-ray crystallography.[290] An agostic H—Co interaction in the former (2.035 Å) was identified. The symmetrical analog ((3-Ph,5-MeTp)Co(η^2-NO$_3$)(THF) was also investigated for comparison. The symmetrical bis-bidentate coordinated tetrahedral Co((3-Ph$_2$pz)$_2$BH$_2$)$_2$ (CoN$_4$) and octahedral mixed ligand complexes (3-PhTp)Co((3-Ph$_2$pz)$_2$BH$_2$) (CoN$_5$H) have been isolated and characterized structurally.[291] The presence of an adjacent phenyl substituent prevents participation of the nitrile group as a bridging ligand, thus avoiding coordinative polymerization in the tetrahedral CoN$_4$ complex Co((3-Ph,4-CNpz)$_2$BH$_2$)$_2$.[292]

A Co *K*-edge X-ray absorption spectroscopic study of Co(Tp)$_2$, Co(3,5-Me$_2$Tp)$_2$, and Co(3,4,5-Me$_3$Tp)$_2$ was undertaken at 295 K and 77 K to investigate the ground electronic states of the complexes. EXAFS analysis indicates that the three complexes are all structurally similar, with Co—N bond lengths consistent with high-spin ground states, and these are unchanged upon cooling from 295 K to 77 K. However, the complexes are gradually converted from high-spin to low-spin state with increasing pressure, with Co(3,4,5-Me$_3$Tp)$_2$ showing the greatest change in spin state of the three complexes.[293] Heterodinuclear pyrazole-bridged complexes were reported by the reaction of (mes)Ru(pz)$_2$(Hpz), as one example, with CoCl(3-*i*Pr,4-BrTp) to give (mes)Ru(μ-pz)$_2$(μ-Cl)Co(3-*i*Pr,4-BrTp).[294]

(v) Imines and oximes

Imines, either acyclic or macrocyclic but invariably multidentate, have a rich coordination chemistry that has been investigated at length. The π-accepting ability of imine donors results in the stabilization of lower oxidation states relative to their saturated amine analogs, and there exist many air-stable divalent imine complexes of Co, in contrast to amine relatives. The hexamethyl-diene (**52**) has been the most intensively studied ligand of this class, particularly when complexed with Co. In addition, Co complexes of the dimethyl (**53**),[295,296] tetramethyl (**54**),[297] pentamethyl (**55**)[298] and octamethyl (**56**)[299] macrocyclic dienes are also known. In the presence of bidentate chelates such as amino acids[297] or carbonate[300], *cis* configurational isomers are formed, whereas monodentate ligands usually lead to *trans* isomers.[297]



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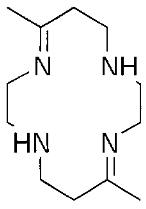

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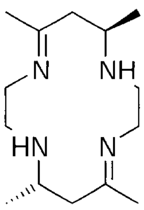

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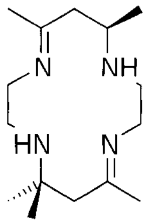

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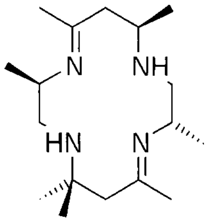
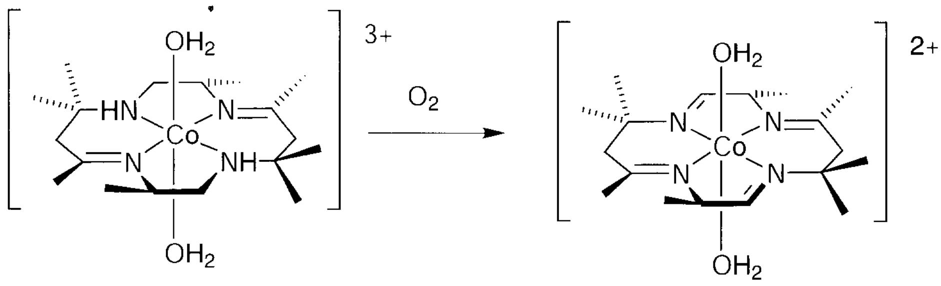


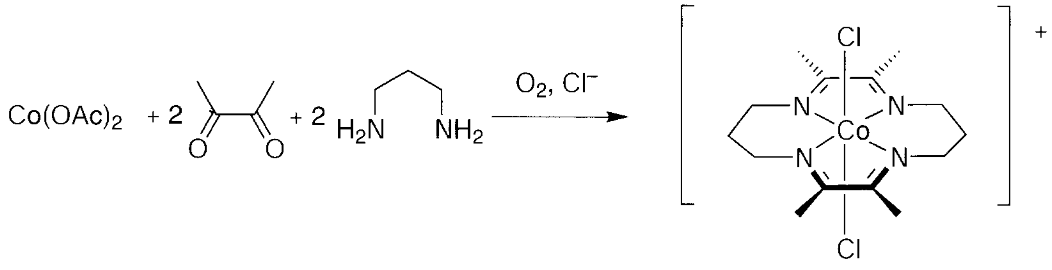
(56)

In an interesting variation, aerial oxidative dehydrogenation of the trivalent octamethyl diene complex (**57**) generates the divalent tetraimine complex (**58**).[301]



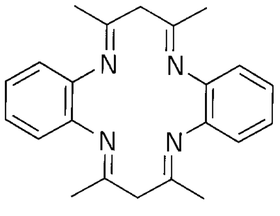
(57) **(58)**

The macrocyclic tetraene 2,3,9,10-Me_4[14]tetraene (tmt) may be synthesized by a metal-directed condensation between trimethylenediamine (tn) and 2,3-butanedione in the presence of $Co(OAc)_2$, ultimately resulting in the *trans*-dichloro Co^{III} complex $[Co(tmt)Cl_2]^+$ (**59**).[302]



(59)

The 14-membered tetraaza-annulenes (such as tmtaa (**60**)) are somewhat similar to porphyrins in that they are highly conjugated, tetradentate dibasic acids. The crystal structure of the *trans*-dipyridyl adduct of (**61**) reveals coordination by the four macrocyclic N donors and the two axial pyridines. The macrocycle exhibits its characteristic non-planar (saddle-shaped) conformation.[303] Complex (**61**) undergoes three reversible one-electron oxidations (0.01, 0.55, and 1.04 V vs. SCE) and one low potential reduction (−1.65 V).[304] Oxidation of the complex by controlled-potential electrolysis resulted in an absorbance shift of the visible band from 595 nm to 543 nm after removal of the first electron, but removal of the second electron produced little change in the spectrum. This two-electron oxidized species exhibited an isotropic EPR spectrum consistent with a ligand-centered radical. Reduction to the monovalent complex resulted in a visible maximum shift to 629 nm. Divalent pyridyl and trivalent superoxo adducts were also examined. The potential uses for Co complexes of tetraaza-annulenes to bind and reduce O_2 was recognized some time ago, and a large class of substituted analogs of (**61**) was patented for this purpose.[267]



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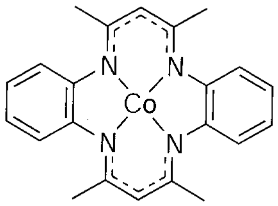
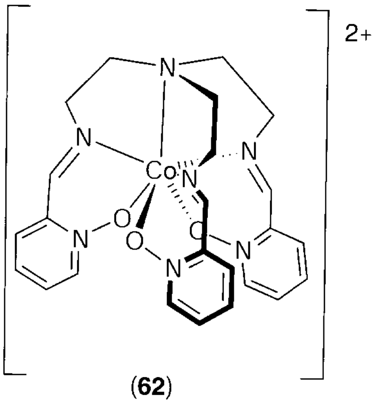


(61)

Divalent Co forms a trigonally symmetric seven-coordinate complex (**62**) with the N_4O_3 pyridine N-oxide trenpyo.[305] The effect of spin state on the electron-transfer properties of the six-coordinate $[Co(pdci)_2]^{2+}$ family (**63**) (R = *t*-Bu, *i*-Pr, *p*-tol, Bz) was studied.[306] The reversible Co$^{III/II}$ and Co$^{II/I}$ potentials were correlated with the solvent dielectric constant and H-bonding acceptor ability. Although no correlation was found between the N-substituent type and either the electron transfer rate constant or half-wave potentials, some correlation did exist between the substituent type and the magnetic moment of the central divalent complex. Much later, the use of Co complexes of this class as propylene oligomerization catalysts in the presence of polymethylaluminoxane was patented.[307] Dinucleating cryptands derived from the 2:3 condensation of tris(2-aminoethyl)amine (tren) and various dialdehydes (1,3-benzenedicarbaldehye, 2,5-furyldialdehyde and 2,6-pyridinedicarbaldehyde (**64**)) have been prepared and Co^{II} complexes have been reported.[308]



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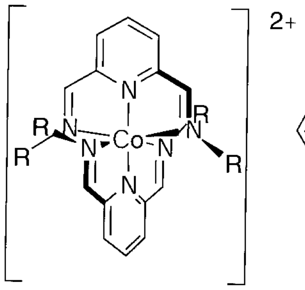

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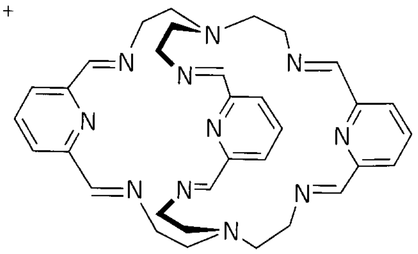
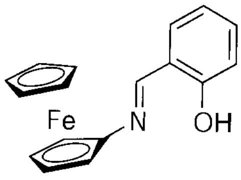


(64)

Salicylaldehyde condenses with primary amines (RNH_2) to form bidentate monobasic ligands of the form *o*-$(HO)C_6H_4CH{=}NR$. In a novel example, a ferrocenylamine adduct Hsalfc (**65**) results in the bis complex $Co(salfc)_2$.[309] The serine derivative (**66**) as its Co^{II} complex $Co(salser)_2$ is an efficient catalyst for conversion of a number of secondary alcohols to their corresponding ketone in the presence of O_2 and 2-methylpropanal[310] or ethyl 2-oxocyclopentanecarboxylate.[311] This versatile catalyst also oxidizes hydrocarbons such as cyclohexane to cyclohexanol and cyclohexanone (1:9).[312] The tyrosine analog (**67**) (as its methyl ester) $Co(saltyr)_2$ oxidizes benzylic substrates to their ketone.[313] The requirement of an aliphatic aldehyde or ketone in these processes is such that an active Co^{III}-superoxo species (identified in EPR experiments) is formed.[314] Electrochemical oxidation of the 1-(3′-aminopropyl)pyrrole analog $Co(salappr)_2$ in MeCN produces a conducting polymeric film at the electrode surface, which is catalytically active in the electroreduction of O_2 and CO_2.[315]



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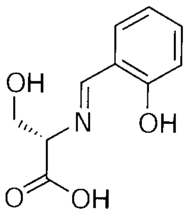

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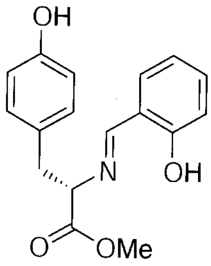

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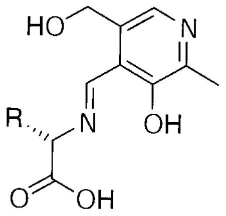
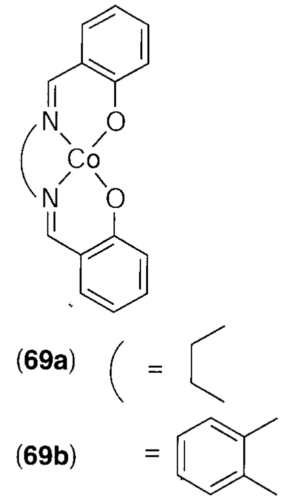
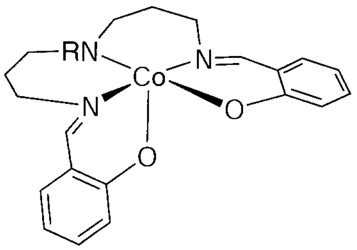


(68)

Pyridoxal is a biologically important aromatic aldehyde also bearing an *ortho* hydroxyl group. A variety of tridentate Schiff base ligands incorporating amino acids have been prepared from this aldehyde (H_2pdxaa) (**68**) and also from salicylaldehyde (H_2salaa), and their Co complexes bind O_2.[316] Coordinating solvents are required to activate the Co(pdxaa) and Co(salaa) complexes for O_2 binding, unless amino acids with coordinating side groups (e.g., aa = histidine) are present. Either 1:1 or 2:1 Co:O_2 adducts are formed dependent on the bulk of the amino acid side groups, which hinder dimerization and enhance reversibility. The reaction of H_2pdxphe with Co^{II} in the presence of H_2O_2 generates $[Co(pdxphe)_2]^-$ which is converted to the novel asymmetric complex where one phenyl alanine α-C atom has been hydroxylated, while the other bears a hydroperoxo group.[317] Schiff base complexes derived from sulfanilamide, homosulfanilamide, and *p*-aminoethyl-benzenesulfonamide coupled with heterocyclic and aromatic aldehydes were investigated for their ability to inhibit three isozymes of carbonic anhydrase (CA, one bovine and two human enzymes). Unusually, several of the free ligands were more active against the membrane-bound bovine CA than the human isozymes, which contrasts with other known CA inhibitors. However, metal complexes of these Schiff bases (including Co^{II}) showed a reverse activity.[318]

The divalent Co(salen) complex (**69a**) is one of the most versatile and well-studied Co coordination compounds. It has a long and well-documented history and we shall not restate this here. Recent applications of (**69a**) as both a synthetic oxygen carrier and as a catalyst for organic transformations are described in Sections 6.1.3.1.2 and 6.1.4.1 respectively. Isotropic shifts in the ^1H NMR spectrum of low-spin Co(salphn) (**69b**) were investigated in deuterated chloroform, DMF, DMSO, and pyridine.[319] Solvent-dependent isotropic shifts indicate that the single unpaired electron, delocalized over the tetradentate π-electron system in $CHCl_3$, is an intrinsic property of the planar four-coordinate complex. The high-spin/low-spin equilibrium of the 3-carboxy derivative of Co(salen) was studied by variable-temperature magnetic susceptibility measurements and EPR spectroscopy in a number of substituted pyridine solutions.[320] In the five-coordinate 2-methylpyridine adduct, a quartet ground state was found, whereas the 4-methylpyridine adduct is low-spin (doublet).

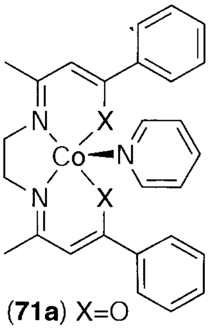




(**70a**) R=H
(**70b**) R=Me

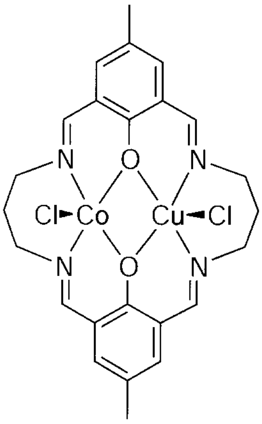
Divalent cobalt complexes of the pentadentate Schiff base H_2saldtn bearing a bis(trimethylene) triamine linker and its N-methyl derivative H_2salMedtn have also been intensively investigated. A study of the structures, electrochemical behavior, and O_2 reactivity of the complexes Co(saldtn) (**70a**), Co(salMedtn) (**70b**) and aromatic-substituted analogs has been reported.[321] A linear correlation was found between the $Co^{III/II}$ redox potential and $\log K_{O2}$ values. Electronic and steric factors of the Co—O_2 complexes with aromatic and N-substituted derivatives of (**70a**) were examined with regard to their ability to catalyze phenol oxidation.[322] The conversion of 2′-hydroxychalcones to flavanones occurs in MeOH in the presence of O_2.[323] Compound (**70b**) catalyzes the oxidation of 1-hexene by O_2 to give a mixture of 2-hexanone and 2-hexanol.[324] The more commonly encountered auto-oxidation, Wacker-type (peracids) and peroxylmetallocycle mechanisms do not apply in this case.[325] Rather, reaction of (**70b**) with H_2O_2 (generated *in situ* by oxidation of the primary alcohol solvent, or as a reagent) results in a hydroperoxy radical Co complex as the active species, which attacks the olefin double bond. Ultimately the alkyl hydroperoxide decomposes to give the ketone and secondary alcohol products. By contrast with the en-based system, the dien-linked analog Co(saldien) adopts a trigonal bipyramidal structure, with *trans* imine groups.[326]

An EPR study of the monomeric O_2 adducts of the Schiff base complexes of Co(bzacen)(py) (**71a**) and the thiobenzoyl analog Co(Sbzacen)(py) (**71b**) characterized the five-coordinate mono (pyridine) precursors and the six-coordinate O_2 adducts.[327] Increased covalency in the Co—S bonds was seen in the EPR parameters, indicative of π-backbonding. Substituent effects on the aromatic rings had no effect on the EPR spectra, but these were reflected in the observed redox potentials. Furthermore, the S-donors stabilize the Co ion in lower oxidation states, which was consistent with destabilization of the O_2 adducts.

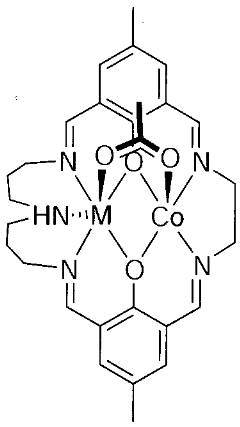


(**71a**) X=O
(**71b**) X=S

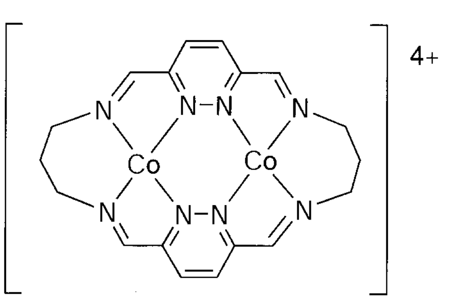
Ditopic macrocyclic imines may be formed by condensation of 2,6-diformyl-4-methylphenol with tn. Heterodinuclear complexes such as (**72**) have been made, with both metal ions in square pyramidal coordination geometries.[328] Variable-temperature magnetic susceptibility data (4.2–385 K) were complicated and fit to an expression derived from a Hamiltonian that included axial and rhombic single-ion zero-field effects, spin–orbit coupling for the Co ion, and an isotropic exchange interaction. The two metal binding sites may be tailored for different metal ions if individual diamine linkers are used. For example, a heterobinucleating ligand comprising salen and saldtn units has been made and the isomorphous series of compounds (**73**) ($M^{II} = Mn$, Fe, Co) has been characterized.[329] The thiocyanate derivatives are similar except the SCN^- ligand forms part of a one-dimensional zigzag coordination polymer (N-bound to M^{II}, S-bound to Co). Interestingly, magnetic susceptibility experiments reveal that the Co^{II} ions (in the N_2O_2 site) in the acetate structures are high spin, whereas in the thiocyanate structure they are low spin. The M^{II} ions in the six-coordinate site are all high spin. Replacement of 2,6-diformyl-4-methylphenol with 3,6-diformylpyridazine leads to a dinucleating macrocycle, with two independent, but closely spaced, N_4 donor sets and the structure of its dicobalt(II) complex (**74**) was reported.[330] Single-electron reduction generates a mixed valent complex exhibiting a NIR intervalence transition.



(**72**)

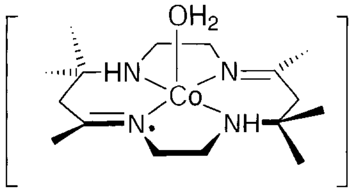


(**73**)

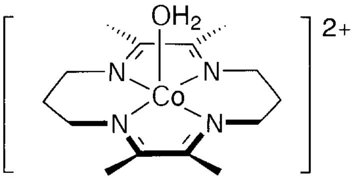


(**74**)

Low-spin square pyramidal divalent complexes of the form $[Co(hmd)(X)]^{n+}$ ($X = OH_2$ (**75**) and $OClO_3^-$) have been structurally characterized.[331] The rate of outer-sphere ($[Co(OH_2)_6]^{3+}$) and potentially inner-sphere ($[Co(OH_2)_5Cl]^{2+}$) oxidation of $[Co(hmd)]^{2+}$ has been investigated and variations in reactivity by more than four orders of magnitude were found.[332] Other oxidants studied included $[Ru(bpy)_3]^{3+}$[333] and the novel hydroperoxopentaaquachromium(III) ion.[334] Oxygenation of (**75**) gives the trivalent peroxo-bridged dimer $[\{(H_2O)(hmd)Co\}_2(\mu\text{-}O_2)]^{4+}$, which may be deoxygenated in acidic solution.[335] In an electrochemical study, the O_2 and O_2^- coordination chemistry of the $[Co(hmd)]^{2+}$ system in DMSO was investigated.[336] The divalent complex forms an adduct with O_2 (K_a=54 M^{-1}), which is reduced at potentials more positive than the formal potential of the O_2/O_2^- couple owing to the high affinity of the divalent complex for superoxide. The reduction and oxidation kinetics of $[(hmd)Co(OOH)]^{2+}$ by a variety of inner and outer sphere electron transfer agents has been reported.[337] The unusual S-bonded sulfite complex $[(H_2O)Co(hmd)(SO_3)]^+$ has been characterized structurally and found to undergo photoisomerization to its O-bound linkage isomer. A mechanism involving Co^{II} and the SO_3^{2-} was proposed.[338]



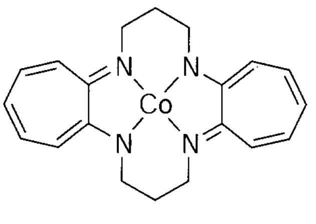
(**75**)



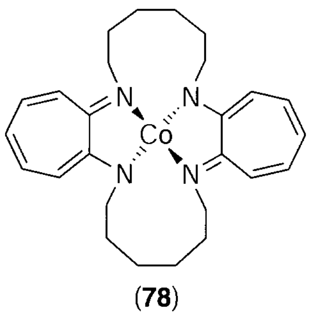
(**76**)

The tmt complex (**76**) reacts slowly with O_2 but this reaction may be catalyzed by Fe_{aq}^{2+} in acidic aqueous solution. A kinetic study revealed first-order dependence on complex, O_2, and Fe_{aq}^{2+} which leads to the trivalent Co complex and H_2O as products,[339] bypassing hydrogen peroxide as an intermediate. Formation of the intermediates $[(tmt)CoOOFe]^{4+}$ then $[(tmt)Co(OOH)]^{2+}$ was proposed to account for these observations. However, adsorption of (**76**) on graphite electrodes makes the complex an active catalyst for the reduction of O_2 to H_2O_2 in a single voltammetric step.[340] By comparison, (**75**) exhibits two separate voltammetric steps in the reduction of O_2 at more negative potentials. In a study somewhat related to these oxygenation reactions, the catalytic auto-oxidation of azide by (**76**) in the presence of dioxygen was observed.[341]

Air-sensitive divalent Co complexes of the tropocoronand ligand TC^{2-} in addition to larger ring relatives were prepared in an extensive investigation. The square-planar 14-membered Co(TC) (low-spin) complex (**77**) changes to tetrahedral (high spin) for the 20-membered analog (**78**).[342] The dihedral angle between the two five-membered aminotroponiminate chelate rings increases from 9° (pseudo-planar) to 85°, which was attributed to torsional strain within the polymethylene linker chains of the macrocycle.

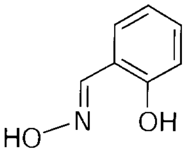


(**77**)



(**78**)

In contrast with the Schiff base salen, salicylaldehyde oxime (**79**) (salox) complexes of Co have received comparatively little attention, but a series of bis-bidentate divalent complexes of the form *trans*-$Co(salox)_2(DMSO)_2$ have been reported.[343] The heterocyclic bidentate oxime violurate (1H,3H-pyrimidine-2,4,5,6-tetrone 5-oximate, Hvi) (**80**) and its *N*-methyl (mvi) and *N,N'*-dimethyl (dmvi) derivatives form high-spin divalent $[Co(vi)]^+$ and $Co(vi)_2$ complexes, whereas $[Co(vi)_3]^-$ is low spin.[344] The mixed-ligand $Co(dmvi)_2(phen)$ complex is also low spin. The crystal structure of *cis*-$Co(pxo)_2Br_2$ (pxo = 2-acetylpyridine-1-oxide oxime) is isostructural with the Ni^{II} relative.[345] The dichloro complex also adopts a *cis* configuration. The tridentate dioximes 2,6-diformyl-4-methylphenol dioxime and 2,6-diacetyl-4-methylphenol dioxime (Hdampo) form binuclear complexes of the type (**81a**) and (**81b**) respectively.[346] Cobalt oxide nanoparticles were prepared by pyrolysis of $Co(pao)_2$ (Hpao = pyruvic acid oxime, Me(HOOC)C=NOH). Electron microscopy showed the products were nanocrystalline with various morphologies (rod-like or quantum dot).[347]



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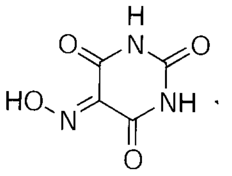

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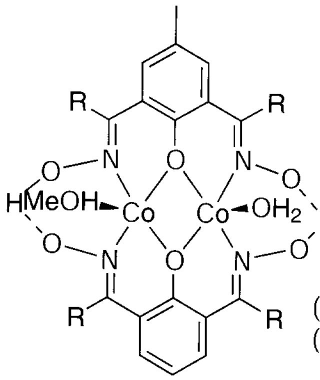
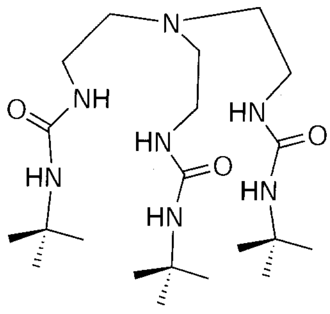


(81a) R=H
(81b) R=Me

(vi) Amides

N-Containing heterocycles bearing carbonyl functional groups adjacent to the ring heteroatom(s) are ubiquitous in nature. As N-deprotonation accompanies coordination, they may be considered formally as amide ligands. A number of divalent Co complexes of purines and pyrimidines showing a variety of coordinating modes have been studied, such as 5-chlorouracil (monodentate, tetrahedral $[Co(ur)(OH_2)_3]^+$)[348] and cytosine (bis-bidentate, $Co(cyt)_2Cl_2$).[349] A range of divalent 4-oxopteridine Co complexes with substituents at the 2-, 6- and 7-positions of the bicyclic ring system have been prepared. Electronic and IR spectral data on the series of complexes indicate that all are coordinated to Co via the O atom in the 4-position and the pyrazine ring N in the 5-position.[350]

The tren derivative (**82**) was used to synthesize monomeric complexes with terminal hydroxo ligands. Trigonal bipyramidal complexes of the trianionic ligand with both divalent and trivalent hydroxocobalt were reported; the latter is a rare example of a trigonal bipyramidal, paramagnetic Co^{III}.[351] A feature of their structures is the presence of intramolecular H bonds from the urea cavity of the ligand to the coordinated hydroxo O atom, which results in an unusually long Co—O bond (Figure 7). The tripodal tetradentate triamide (**83**) is structurally similar to tren, and the ligand enforces an unusual trigonal pyramidal coordination geometry on divalent metal ions, including Co (Figure 7).[352]



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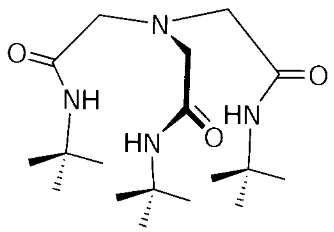


(83)

(vii) Nitrosyl

The structures of the oxime complex $Co(NO)(dmg)_2$ (**84**) and its diphenylglyoxime analog exhibit strongly bent Co—NO groups, which are easily oxidized to the corresponding nitro compound.[353] A mechanistic study of NO transfer from $Co(NO)(dmg)_2$ to hemoglobin established that the reaction involves NO association with the protein subsequent to dissociation of NO from the Co complex.[354] This mechanism is also consistent with the observation of nitrato complexes in reactions

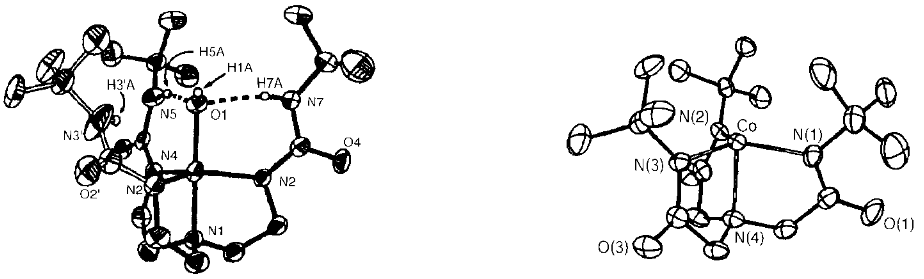
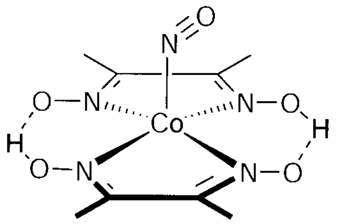


Figure 7 Tripodal triamide complexes of (left) (**82**) with hydroxocobalt(III) (divalent complex is similar) (reproduced with permission of the American Chemical Society from *Inorg. Chem.*, **2001**, *40*, 4733–4741) and (right) (**83**) with Co^{II} (reproduced with permission of the American Chemical Society from *Inorg. Chem.*, **1998**, *37*, 1527–1532).

of these metal nitrosyls with O_2. This process is also relevant to the oxidation of oxymyoglobin (MbO_2, Fe^{II}) to metmyoglobin (Mb^+, Fe^{III}) by $Co(NO)(dmg)_2$, where the free NO released from the Co complex oxidizes the heme.[355] Nitrate formation accompanying the production of Mb^+ is proposed to arise from isomerization of the initially formed peroxynitrite ion. Furthermore, the $Co(dmg)_2$ product is an effective trap for the O_2 released from MbO_2. The 8-quinolinolate (qn) complexes $Co(qn)_2$ and $Co(NO)(qn)_2$ react with NO forming $Co(NO_3)(qn)_2L$ (L = py, DMF), releasing N_2O.[356]



(84)

(viii) Nitriles, azide, cyanates, and thiocyanates

These rod-shaped ligands share a sterically efficient terminal N-donor and their divalent Co chemistry is well established. They will be discussed here only with selected examples. $[Co(NCMe)_6](TFPB)_2$ ($TFPB^-$ = tetrakis(3,5-bis(trifluoromethyl)phenyl)borate)) has been synthesized and characterized in the solid state along with a number of other divalent transition metal analogs.[357] As a result of the extremely poor coordinating ability of the anion and facile loss of MeCN ligands from the cation, the salt is an excellent source of "naked" Co^{2+} ions. Thermolysis up to 100 °C leads to the loss of one MeCN and formation of a η^2-bound nitrile, whereas above 130 °C decomposition occurs with loss of MeCN and abstraction of fluoride from the anion to form CoF_2.

Reactions of nitriles may be promoted by the presence of divalent Co. The conversion of sterically unhindered nitriles RCN (R = Me, Et, *n*-Pr, *n*-Bu) into the corresponding amidines $RC(NH_2){=}NH$ occurs in the presence of $Co(NO_3)_2.6H_2O$ and the ketoxime $Me_2C{=}NOH$. The metal free amidinium ions were crystallized as their nitrate salts.[358]

The well-known tetrahedral $[Co(NCS)_4]^{2-}$ ion has continued to attract attention from analytical chemists, physical chemists, and spectroscopists. The inelastic electron tunneling (IET) spectrum of $(Me_4N)_2[Co(NCS)_4]$ was compared with IR and Raman spectra of the same complex.[359] The vibrational bands due to the Me_4N^+ were prominent in all three spectra, but Co-ligand stretches were absent from the IET spectra. The lowest $^4A_2 \rightarrow {}^4T_2$ electronic transition was strong in the IET spectrum but absent from the IR spectrum. The electric dipole allowed $^4A_2 \rightarrow {}^4T_1$ electronic transition was observed in both the IET and IR spectra and no fine structure was observed. Complex formation equilibria between Co^{II} and SCN^- were studied calorimetrically in both aqueous solution and in micellar solution of the surfactant Triton X-100. The formation of $[Co(NCS)_3]^-$ is virtually negligible in any of the solutions examined, whereas $[Co(NCS)]^+$ is formed only in the aqueous phase and $[Co(NCS)_4]^{2-}$is formed mainly in micelles as ion pairs.[360] The $[Co(NCS)]^+$ ion was also identified as a major species in an independent study involving conductivity and visible absorption spectroscopy of DMSO–water solutions of $Co(NCS)_2$.[361]

The intense blue color of $[Co(NCS)_4]^{2-}$ has been exploited as a spectroscopic signal for a number of analytical methods for determining Co^{II} in solution. A method for the determination of trace concentrations (1–15 μg) of Co^{II} as its NCS^- complex was reported by fixing the complex on a coagulated material composed of anion and cation exchange resins, followed by colorimetry (using a densitometer).[362] Methods for simultaneously determining Fe^{II} and Co^{II} have been reported that are applicable to a disparate range of samples (e.g., blood and steel) involving complexation of Co with NCS^- and chelation of Fe with *N*-phenylcinnamohydroxamic acid (HPCHA) to form their respective blue $[Co(NCS)_4]^{2-}$ and red $[Fe(NCS)_2(PCHA)_2]^-$ complexes, which extract quantitatively into EtOAc from dilute HCl solution.[363] Spectrophotometric detection of tamoxifen citrate,[364] lignocaine,[365] mefloquine,[366] mebeverine,[367] the surfactant Pluronic F-68,[368] trazodone.HCl and amitriptyline.HCl[369] have also been reported through their association with divalent $Co-NCS^-$ adducts.

Octahedral coordination of N-bonded thiocyanate was achieved in $[Co(NCS)_6]^{4-}$ accidentally as a polyammonium salt while trying to coordinate a tetraamine.[370] Thiocyanate is frequently met as a co-ligand in Co chemistry. A recent example where both monodentate and bridging thiocyanate occur is the trinuclear Co^{II} complex $[Co_3(amt)_6(SCN)_6]\cdot 2H_2O$ (amt = 4-amino-3,5-dimethyl-1,2,4-triazole), where bridging between pairs of antiferromagntically coupled Co centers involves both an SCN^- and two amt ligands.[371] The complex forms simply from reaction of $Co(NCS)_2\cdot 6H_2O$ in water with the amt ligand. A general method for synthesis of anionic thiocyanate Co complexes (such as $[Co(NCS)_4]^{2-}$), as well as neutral mixed-ligand species, by oxidation of a sacrificial Co anode has appeared.[372]

Azide appears as both an effective monodentate and bridging ligand. As an example, the one-dimensional 1,3-azido bridged coordination polymer is defined by the structure of $[Co(py)_4(N_3)]PF_6$.[373] A μ-1,1 bridging mode has been observed for N-bound cyanate in conjunction with di-2-pyridyl ketone in an unusual tetranuclear dicubane-Co^{II} complex where two vertices are missing from the core. Ferromagnetic coupling between the Co centers was found.[374]

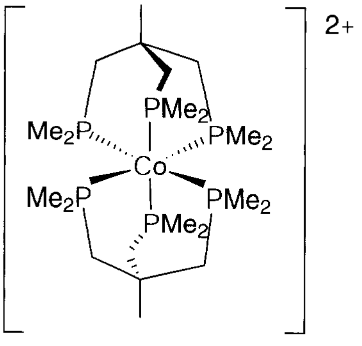
6.1.2.2.3 Phosphorus

(i) Monodentate phosphines

Examples of monodentate phosphines appear as companion ligands in other parts of the review, and only limited additional examples will be presented here. The reactivity of $Co(NO_2)_2$ toward a variety of monodentate phosphines such as PMe_3, PEt_3, PMe_2Ph, $PMePh_2$, and PPh_3 has been investigated.[375] For PMe_3 and PMe_2Ph, five-coordinate square–pyramidal $Co(NO_2)_2(PR_3)_3$ complexes were isolated, but for PEt_3 only the pseudo-octahedral, formally trivalent $Co(NO)(NO_2)_2(PEt_3)_2$ was obtained. The analogs $Co(NO)(NO_2)_2(PMe_3)_2$ and $Co(NO)(NO_2)_2(PMe_2Ph)_2$ were prepared indirectly from the dinitro precursor by reaction with NO gas. The resultant Co^{III} species contain both O-bonded and N-bonded NO_2. Reactions of R_3PI_2 (R = Et, Pr, Bu, $PhMe_2$, Ph_2Me, Ph_2Pr, Ph, *m*-MeC_6H_4), with unactivated Co metal in dry ether produce $[PR_3I][Co(PR_3)I_3]$ in quantitative yield,[376] and the X-ray crystal structure of $[PPh_3I][Co(PPh_3)I_3]$ is reported. However, the reaction with $PPhMe_2$ is more complicated and generates the Co^{III} compound $Co(PPhMe_2)_2I_3$ as an additional product. The simple tetrahedral complex $CoCl_2(PPh_3)_2$ bound to a polymer support catalyzes the oxidation of alcohols to aldehydes (e.g., benzyl alcohol to benzaldehyde, 86% yield) and the preparation of anhydrides from reaction of acid chlorides with carboxylic acids.[377]

(ii) Multidentate phosphines

Chelating phosphines are effective ligands for Co^{II}. The $[Co(mtriphos)_2]^{2+}$ cation (**85**) was formed by controlled potential electrolysis of its trivalent relative and characterized by EPR and spectrophotometry.[378] This divalent CoP_6 species has a low-spin electronic ground state with a large Jahn-Teller distortion. The $Co^{III/II}$ electron self-exchange reaction is very fast ($\sim 10^4 M^{-1} s^{-1}$), which is consistent with other low-spin/low-spin $Co^{III/II}$ couples. The nephelauxetic effect of the P donors is responsible for stabilizing the low-spin state in Co^{II}.



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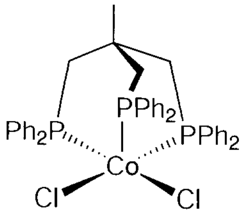

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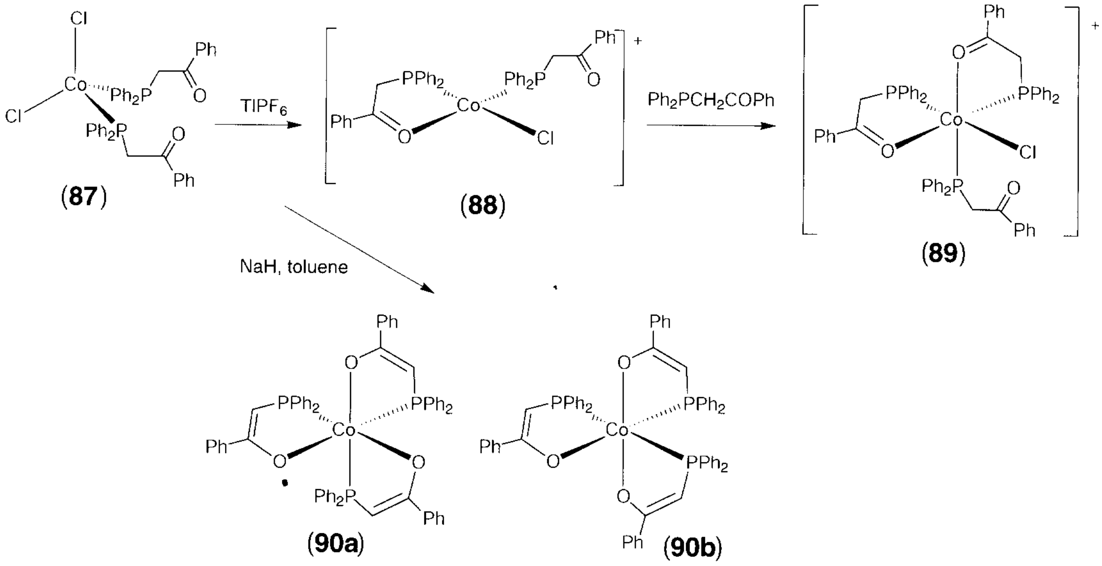
The bi- and tridentate phosphines dppp (1,3-bis(diphenylphosphino)propane) and dppep (bis(2-diphenylphosphinoethyl)phenylphosphine) have been complexed with Co and their divalent four- and five-coordinated thiophenolate complexes $Co(dppp)(SPh)_2$ and $Co(dppep)(SPh)_2$ have been isolated and structurally characterized.[379] Somewhat related to dppp is the bidentate silane $Ph_2PCH_2SiMe_2CH_2PPh_2$, which forms high-spin, pseudo-tetrahedral dihalocobalt(II) complexes.[380]

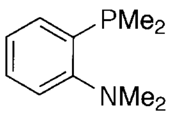
The five-coordinate triphos complex (**86**) undergoes selective substitution of its Cl groups on activation with KPF_6 in the first substitution step and by $TlPF_6$ in the second. This enabled the synthesis of mixed-ligand complexes of the type $[Co(triphos)(L)(L')]^{2+}$, e.g., the divalent hydride $[Co(triphos)H(PEt_3)]^{+}$.[381] Homo-disubstituted compounds $Co(triphos)L_2$ are directly accessible from $Co_{aq}{}^{2+}$ as the starting material.[382] Depending on the reaction conditions, a variety of products including $[(triphos)Co(S_2CPEt_3)]^{2+}$, $[(triphos)Co(S_2C(H)PEt_3)]^{2+}$, and $[(triphos)Co(\mu\text{-}CS_2)Co(triphos)]^{2+}$ are obtained from the reaction of the $[Et_3P][CS_2]$ adduct with $Co_{aq}{}^{2+}$ and triphos. Triphos may also be substituted by its diethylphosphino analog (etriphos).[383] Reaction of the template $\{(triphos)Co\}^{2+}$ with potentially bridging ligands (L) generates dinuclear $[(triphos)Co(L)Co(triphos)]^{n+}$ species. When L is oxalate, a biscobalt(II) complex is formed, whereas when L is the dianion derived from 2,5-dihydroxy-1,4-benzoquinone, two-electron transfer within the dimetallic unit occurs and a biscobalt(III) complex results.[384] Single-electron reduction of the dinuclear $[(triphos)Co(L)Co(triphos)]^{2+}$ complexes (L = dianion of tetrahydroxybenzene or tetrahydroxyanthracene) by cobaltocene gave the corresponding mixed-valence monocation $[(triphos)Co(L)Co(triphos)]^{+}$.[385] The tetrahydroxybenzene bridged system exhibits a strong metal–metal interaction leading to delocalized class-III behavior while the extended tetrahydroxyanthracence bridging ligand leads to only partial electron localization. Reaction of the pseudo-tetrahedral complex (η^2-triphos)$CoCl_2$ with O_2 yields the mixed phosphine/phosphine oxide ligands triphos-O and triphos-O_2, the latter being formed in quantitative yield using catalytic amounts of the Co precursor.[386] Complexes of triphos-O and triphos-O_2, proposed as intermediates in the oxygenation reaction, were isolated and fully characterized structurally.

The coordination chemistry and catalytic applications of chelating P,O-donor ligands (phosphine esters, ketophosphines and phosphinocarboxylates) has been reviewed.[387] A variety of divalent complexes of keto-phosphine ligands of the form $CoX_2(Ph_2PCH_2C(O)Ph)_2$ (X = Cl, Br, I) have been investigated.[388] These complexes exhibit tetrahedral–octahedral equilibria in MeOH, but this does not involve coordination of the keto O atom, but instead by the solvent. The crystal structure of the pseudotetrahedral complex (**87**) was reported with the ligand binding as a monodentate P-donor. When reacted with $TlPF_6$, the square planar Co^{II} complex (**88**) is formed initially and then is transformed in solution to the six-coordinate (**89**). Reaction of (**87**) with bases (NaH, NaOMe, $K[OSiMe_3]$) in toluene or THF at 0 °C gives deprotonated tris-P,O-chelated octahedral cobalt(III) enolates of the form $Co(Ph_2PCHC(O)Ph)_3$ where *fac* (**90a**) and *mer* (**90b**) isomers are observed.[388] The potentially tridentate ligand benzylbis(2-ethoxyethyl)phosphine (L) reacts with $CoCl_2$ to give the monodentate P-coordinated tetrahedral $CoCl_2L_2$ complex, but when reacted with $CoCl_2.6H_2O$ and $AgCF_3SO_3$ the *trans*-(P,O)-$CoL_2(O_3SCF_3)_2$ complex is the result.[389]



(87) (88) (89) (90a) (90b)

The P-N chelate (**91**) (dapdmp) exhibits a variety of coordination geometries in complexes with divalent Co. Pseudotetrahedral Co(dapdmp)X_2 (X = Cl, Br, I, NCS), low-spin five-coordinate $[Co(dapdmp)_2X]^+$ (X = Cl, Br, I), planar $[Co(dapdmp)_2]^{2+}$ and pseudo-octahedral Co(dapdmp)$(NO_3)_2$ were all identified.[390] The tetradentate P_2N_2 Schiff base complex (**92**) is formed by reacting the free ligand with CoI_2. The iodo complex is low spin and square pyramidal.[391]



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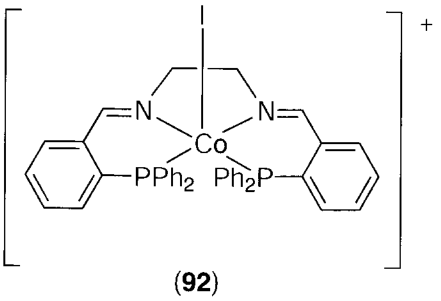

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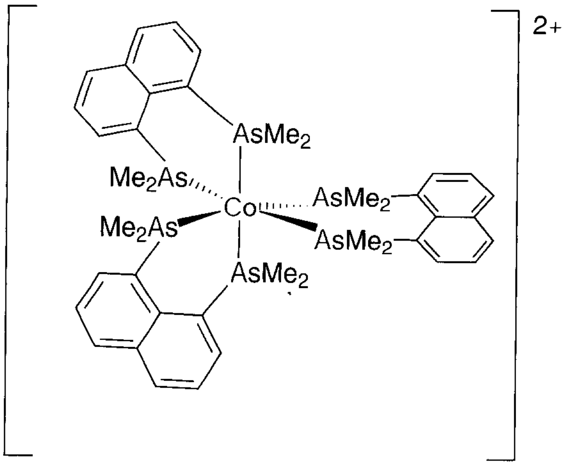
Tetrahedral, high-spin halo(amidodiphosphine)cobalt(II) complexes Co(L)X where X = Cl, Br, I and tridentate $L = {}^-N(SiMe_2CH_2PPh_2)_2$ have been described.[392] Amongst a range of reactions with organic halides studied, they undergo a one-electron oxidation reaction with $PhCH_2X$ to yield five-coordinate cobalt(III) complexes Co(L)X_2.[201]

6.1.2.2.4 Arsenic

(i) Monodentate and multidentate arsines

Arsenic is an obvious replacement for phosphorus particularly in multidentate ligands, and some limited examples will suffice to define this fact. The rigid aromatic diarsine nas (1,8-naphthylenebis(dimethylarsine)) forms a divalent tris bidentate complex $[Co(nas)_3]^{2+}$ (**93**) upon reaction with Co_{aq}^{2+} (Cl^-, Br^- and ClO_4^- salts), but similar treatment of $CoI_2{\cdot}6H_2O$ gave the five-coordinate $[Co(nas)_2I]I$.[393] Mixed donor As-chelate complexes of Co^{II} have been reported. The ligand o-$C_6H_4(AsMe_2)(PMe_2)$ forms only 2:1 ligand:Co complexes such as $[CoL_2X]^+$ (X = Cl, Br, I), which are low spin and five-coordinate in solution.[390] By comparison, o-$C_6H_4(AsR_2)(CO_2H)$ (R = Et, cyclohexyl and *p*-tolyl) reacts with $Co(OAc)_2$ to give the neutral bis complex of the ligand monoanion CoL_2.[394] Electronic spectra and magnetic susceptibility measurements are consistent with a pseudo-tetrahedral geometry.



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6.1.2.2.5 Oxygen

Oxygen-donor ligands represent, along with nitrogen, the most likely to be met in Co^{II} chemistry. The variety of ligands reported is extensive.

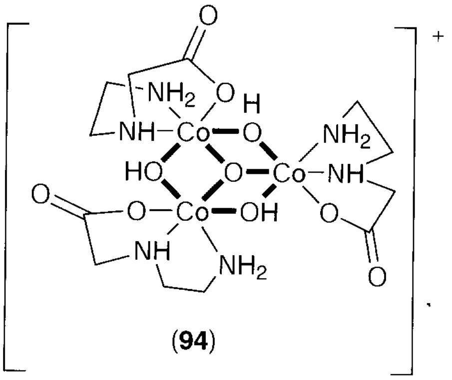
(i) Aqua, hydroxo, and oxo

Water and its successively deprotonated forms hydroxide and oxide are classical ligands for Co in both its di- and trivalent oxidation states. Whereas H_2O is typically found as a monodentate ligand, hydroxide may be monodentate or else bridge two metals (μ_2), and oxide can be any of monodentate, dibridging (μ_2) or tribridging (μ_3), with tetrabridging (μ_4) rare but known. Acidity of any ligand is enhanced by the influence of additional coordinated metal ions. Indeed, the fully deprotonated oxo ligand is only encountered in divalent Co chemistry as a bridging ligand; terminal oxo complexes do not feature.

The chemistry of the aqua ions has been extensively covered in a monograph with that title.[395] The hexaaquacobalt(II) ion undergoes exchange rapidly[396] and often serves as an entry point into the chemistry of both Co^{II} and Co^{III}. Although commonly found as a monodentate, several examples of water as a bridging ligand between two Co^{II} centers have appeared. An example is $Co_2(\mu\text{-}OH_2)(\mu\text{-}OOCCCl_3)_2(OOCCCl_3)_2(tmen)_2$ (where tmen = *N,N,N′,N′*-tetramethylethane-1,2-diamine).[397] This dimeric structure with a bridging aqua ligand is stabilized by intramolecular hydrogen bonding.

Apart from water, hydroxide and oxide are well-established ligands for Co^{II}. This includes the latter ions adopting bridging modes. An example of a complex featuring both the (μ_2-OH) and (μ_3-O) ligands is the cluster (**94**).[398] The dicobalt complex (**95**) bears both bridging hydroxide and acetate ligand and is stabilized by the trimethylated 1,4,7-triazacyclononane ligand.[399] The substituted Tp dimer (**24**) reacts with one equivalent of H_2O_2 to give the reactive trivalent μ-oxo dimer (**96**), which was isolated and characterized structurally.[400] The polymeric trimethylacetate complex $[Co(OH)_n(OOCCMe_3)_{2-n}]_m$ is transformed upon recrystallization from non-polar aromatic solvents into discrete clusters such as $Co_6(\mu_3\text{-}OH)_2(\mu\text{-}OOCCMe_3)_{10}(HOOCCMe_3)_4$, where each hydroxide ions bridge three Co centers.[401] A cluster featuring μ_4-oxo groups is also reported.

Perhaps the highest nuclearity complex containing divalent Co ever structurally characterized is the cluster $Co_{24}(\mu_3\text{-}OH)_{14}(\mu\text{-}OH)_4(\mu_3\text{-}OMe)_2(\mu_3\text{-}Cl)_2Cl_4(mph)_{22}$ (Hmph = 2-methyl-6-hydroxypyridine), which has a high-spin ground state and indications of superparamagnetic behavior.[402] It self-assembles from reaction of the sodium salt of Hmph with $CoCl_2$ in methanol. Polyiron oxo chemistry offers another class of readily prepared clusters in which Co^{II} plays a cameo role as a core metal, as in the cluster $Fe_{16}CoO_{10}(OH)_{10}(OBz)_{20}$, where Co occupies a center of symmetry of the compact $Fe_{16}CoO_{10}(OH)_{10}$ core, surrounded by the twenty coordinated benzoates.[403] Large



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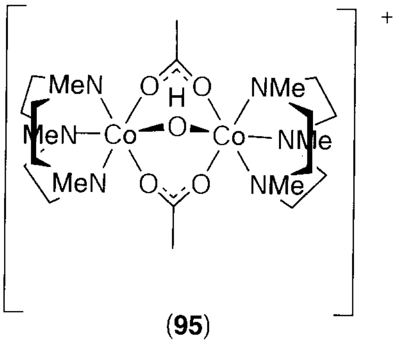

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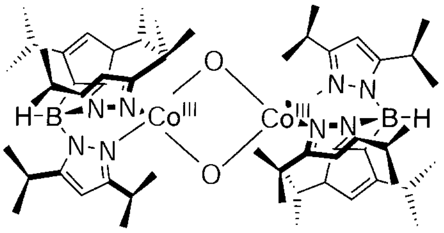

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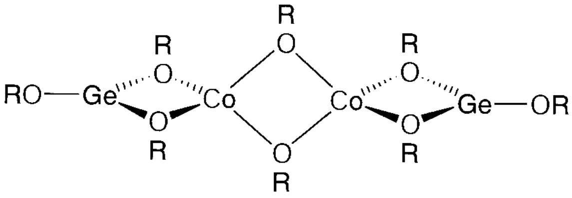

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clusters are accessible via thermal "dimerization" of smaller clusters, as exhibited by heating $Co_4(\mu_3\text{-}OH)_2(OOCCMe_3)_6(EtOH)_6$ in decalin, which forms an octanuclear oxo-bridged cluster with ethanol loss.[404] An unusual cluster where oxo groups play a key structural role forms when $Co(OAc)_2$ is heated with $Me_3SiNPEt_3$ at 180 °C and recrystallized from diethyl ether.[405] The blue crystals obtained are of $[Co_7(\mu_4\text{-}O)_2(OOCCH_3)_8(NCO)_2(HNPEt_3)_4]\cdot 2OEt_2$, where the Co centers are arranged in a $\{Co(Co)_6\}$ octahedron with two μ_4-oxo ions and four bridging acetates linking the octahedral central Co to the six peripheral Co centers, four of which have a distorted trigonal bipyramidal geometry while the other two adopt tetrahedral coordination.

Definitive structural characterization of Co in a solid state oxide lattice has been achieved for a single crystal of partially Co^{II}-exchanged zeolite A.[406] Dehydration at high temperature and low pressure for two days afforded the characteristic color change from light pink to deep blue. Exposure to H_2S gas gave a black crystal whose X-ray structure was determined. Four Co^{II} ions were found recessed into the large cavity of the zeolite at six-oxygen ring sites, each coordinated to three framework oxygens (Co—O 2.24(1) Å) and to one H_2S sulfur (Co—S 2.60(2) Å)

A pH-controlled interconversion from a dicobalt(II) complex where each Co carries a single monodentate hydroxo group to a compound with a shared μ-hydroxo group has been reported; a pendant arm dinucleating polyimine macrocycle completes the coordination sphere of the two Co ions.[407] The process features interchangeable coordination geometries, as the yellow–green μ-hydroxo compound is octahedral and the purple dihydroxo compound trigonal prismatic.

(ii) Dioxygen

Dioxygen can bind reversibly to several classes of Co^{II} complexes including porphyrins, peptides, Schiff bases, and macrocyclic polyamines. Diverse physical studies of dioxygen binding have been reported. Thermodynamics and kinetics of dioxygen binding to Co^{II} have been well studied, as exemplified by a recent study involving macrocyclic tetraamines.[408] Binding to Co^{II} complexes of tetraimine "lacunar" macrocycles is typically fast and differences in dissociation rates define dioxygen affinity (see Section 6.1.3.1.3). Dioxygen complexes of particularly μ-phenoxo and μ-alkoxo bridged dimetal complexes of compartmental ligands has appeared recently.[409] Dioxygen binding to Co^{II} porphyrins has also been observed and the catalytic reduction of dioxygen to water has been a motivating force driving their study (see Section 6.1.2.2.2).

(iii) Neutral oxygen donors

Apart from water as the ubiquitous neutral solvent donor for cobalt(II) chemistry, other neutral O donors are known, including alcohols, ketones, amides, and sulfoxides. The complex $[Co(DMSO)_6]$ $[CoCl_4]$ has been characterized by an X-ray structure, which confirmed monodentate O coordination around the octahedral Co center.[410] Formally neutral molecules such as amine N-oxides and nitrosoalkanes are effective ligands. A ligand such as nitrosomethane (MeNO) can be considered to benefit from resonance forms such as $H_3C—N^+—O^-$, where its capacity as an O-donor ligand would be clearly enhanced. This ligand has been characterized in $[Co(MeNO)_4]^{2+}$, whereas pyridine-*N*-oxide (pyo) exists in the octahedral complex $[Co(pyo)_6]^{2+}$. The same ligand forms a range of ionic complexes with cobalt(II) halides, including the tetrahedral anion $[Co(pyo)I_3]^-$.[411] The triarsine oxide tetrahedral complex ion $[Co(OAsR_3)_4]^{2+}$ was prepared by light-catalyzed decomposition of tetrakis(alkylisocyanide)-bis (triarsine)cobalt(II) in dichloromethane.[412]

(iv) Alkoxides and aryloxides

Cobalt(II) alkoxides are known and monomeric forms are part of a wider review.[413] The interest in these compounds pertains to a potential role in catalysis. For example, a discrete cobalt(II) alkoxide is believed to form *in situ* from a chloro precursor during reaction and performs the catalytic role in the decomposition of dialkyl pyrocarbonates to dialkyl carbonates and carbon dioxide.[414] A number of mononuclear alkoxide complexes of cobalt(II) have been characterized by crystal structures, as exemplified by $[CoCl(OC(t\text{-}Bu)_3)_2{\cdot}Li(THF)]$.[415] The Co ion in this structure and close relatives has a rare distorted trigonal–planar coordination geometry due to the extreme steric crowding around the metal.

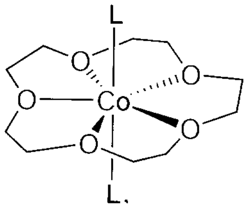
Polymeric forms have also been reported. One example, which also includes germanium heteroatoms terminating the chain, is the oligomer $(RO)Ge(RO)_2Co(RO)_2Co(RO)_2Ge(OR)$, **(97)** where each Co center is surrounded by four bridging *tert*-butoxide ions.[416] These form via a photochemically induced labile solvent complex, or else through thermally induced substitution into carbonyl compounds.

(v) Ethers

(m) Acyclic. Ether oxygens are not considered strong donors for cobalt. Nevertheless, simple ethers can be the sole occupant of the Co^{II} coordination sphere, as exhibited in the crystal structure of the $[Co(THF)_6]^{2+}$ ion.[417] Ethers are met as a component donor group in mixed-donor polydentates; an example is the N,O,N-donor bis(pyrazolylethyl)ether,[418] which binds meridionally to Co^{II}. The weak character of the ether bond is illustrated in the reaction of benzylbis(2-ethoxyethyl)phosphine (bbp) with $CoCl_2$.[389] Reacted alone, the tetrahedral $Co(bbp)_2Cl_2$ forms with the ligand a P-bound monodentate; however, when $Ag(O_3SCF_3)$ was included, the octahedral *trans*(P),*trans*(O),*trans*(O)-$Co(bbp)_2(O_3SCF_3)_2$ forms where the ligand is P,O-chelated and in addition the weak ligand triflate is also bound. However, ^{31}P NMR suggests the solution structure is different, with a dimer believed to form.

(n) Macrocyclic. Crown ethers also do not form strong complexes with Co^{II}, and crown ethers with pendant groups carrying strong donors tend to coordinate Co ion via the pendant donors rather than involve the ether oxygens. A measure of the poor capacity of the ether oxygen as a donor is exemplified in the structure of $[Co(ONO_2)(OH_2)_5](NO_3){\cdot}H_2O{\cdot}$(18-crown-6), the product of an attempted crown ether complexation, where the ether oxygens are only linked by hydrogen bonding to coordinated water molecules.[419] However, syntheses leading to ether coordination have appeared, usually in non-aqueous media. Reaction of 15-crown-5 with anhydrous $CoCl_2$ in acetonitrile yields the blue cation $[Co(15\text{-crown-}5)(MeCN)_2]^{2+}$, with the ether surrounding the Co as part of a rare pentagonal bipyramidal structure with apical acetonitrile donors.[420] Hydration leads to replacement of the acetonitrile groups by water, while retaining the intact ether coordination. An ethanol analog is also known, as well as 18-crown-6 complexes. Complexes of $Co(ClO_4)_2$ with 16-crown-5 and a lariat ether derivative 15-(2,5-dioxahexyl)-15-methyl-[16-crown-5] have been prepared and the latter structurally characterized.[421] The Co ion is again heptacoordinated with five crown ether O atoms in the equatorial plane (average Co—O 2.20(2) Å), with a pendant-arm oxygen and a water molecule in apical sites. One novel approach involves reaction of

$Co_2(CO)_8$ with HCl gas in the presence of 15-crown-5 and water in toluene. This led to a complex species which included seven-coordinate pentagonal bipyramidal Co^{II} centers (**98**) which included the metal ion in the macrocyclic polyether.[422]



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(vi) Ketones and esters

Monoketones are poor ligands. Di-2-pyridylketone ($(py)_2C{=}O$) accommodates this deficiency in an unusual way when it reacts with $Co(OAc)_2$ to form clusters, including $[Co_4(HQ)_4(OAc)_4]\cdot H_2O$, where the monodeprotonated hydrated gem-diol form of the ketone (HQ^-) (Equation (5)) binds as an ionic ligand.[423] This cluster adopts a tetranuclear cubane shape with four deprotonated O atoms of the diol occupying the alternating vertices to the Co ions.

$$(py)_2C{=}O + H_2O \rightleftharpoons (py)_2C(OH)_2 \rightleftharpoons (py)_2C(O^-)(OH) + H^+ \tag{5}$$

The well-established chemistry of β-diketones has been widely reported previously. These monoanionic enolate chelates readily form complexes with cobalt. A more elaborate recent example is a pyridine with t-Bu–CO–CH_2–CO arms attached in the 2- and 6-positions, which acts as a pentadentate tritopic chelator when reacted with Co^{2+} to form the octanuclear cluster $Co_8O_2L_6$.[424] Polyvinyl ketone forms coordination polymers with Co^{II} and other divalent ions which exhibit 1:2 metal:ketone stoichiometry, suggesting the coordination is β-diketone-like.[425] Alkylation of β-diketones at the central C atom has been achieved through reaction of their Co^{II} or Co^{III} complexes with alkyl halides; for example, the adamantyl group has been introduced into pentane-2,4-dione (Hacac) by this route.[426]

The β-ketoesters $[RC(O^-){=}CHC(O)OR]^-$ are close analogs which also chelate effectively. A useful general method for synthesis of Co^{II} compounds of these molecules has been reported, which uses the lithium, caesium, or trimethylsilyl enolate of the β-ketoester reacting with a Co^{II} salt in tetrahydrofuran.[427]

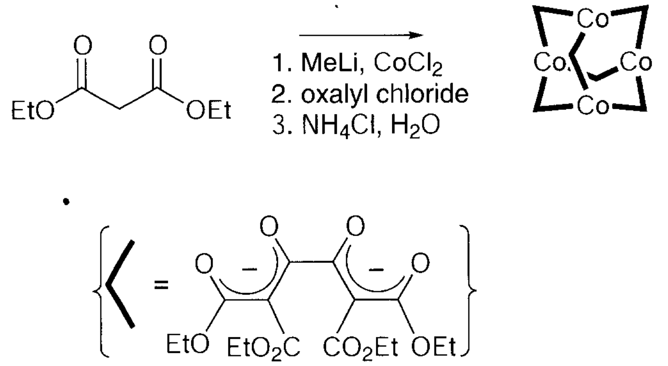
(vii) Amides

Divalent Co complexes of N-bound amides are discussed in Section 6.1.2.2.2. Examples of simple O-bound amides consist of acetamides (H_2NCOCR_3), N-alkylacetamides ($R'_3CNHCOCR_3$), N,N-diakylacetamides ($(R'_3C)_2NCOCR_3$), dimethylformamide (Me_2NCHO) and N-alkylpyrrolidones. As an example, acetamide forms an octahedral complex *trans*-$[Co(acetamide)_4(OH_2)_2]^{2+}$, where the Co—O(amide) distance lies in the range 2.10–2.13 Å.[428]

(viii) Carbonates, carbamates, and carboxylates

Carbonate is a well-established ligand, but its coordination diversity continues to surprise. Elaborate bridging modes have been reported for carbonate; for example, a μ_4-carbonato-bridged Co^{II} compound $[Co_2(2,2'\text{-bipyrimidine})(OH_2)_2(\mu\text{-}CO_3)(\mu\text{-}OH)]^+$ has been characterized.[429]

Acetate remains the classical carboxylate ligand, with the capacity to bind in monodentate (μ_1), bidentate chelate (μ_2), or bridging ($\mu_1{:}\mu_1$) modes. Whereas early chemistry featured simple μ_1 coordination, more frequent examples of bridging coordination are now appearing. A typical example is the dinuclear complex with three acetate bridges, $Co_2L_2(OOCCH_3)_3$ (L = bis[(2-dimethylaminoethyl)iminomethyl]benzene,[430] (**99**) where the geometry around each Co is a trigonal bipyramid. Elaborate oligomeric complexes based on heptanuclear Co^{II} fragments supported by carboxylates have been reported, and three heptanuclear cages characterized structurally, including $Co_7(OH)_2(OOCCMe_3)_4(chp)_8(H_2O)_{0.25}$ (chp = 6-chloro-2-pyridonate).[431] The alternate use of phthalate leads to a tridecanuclear cage. Complex (**100**) features both bridging and terminal carboxylates, and reflects the differing reactivities of the two coordination modes, since it undergoes carboxylate exchange reactions with other simple monocarboxylates featuring selective terminal carboxylate substitution by bulky carboxylates.[432] A tetracobalt(II) cluster featuring only oxygen donor anionic ligands can be formed in a relatively straightforward self-assembly reaction (Equation (6)).[433]



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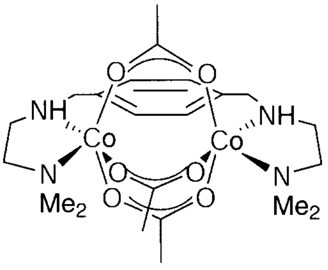
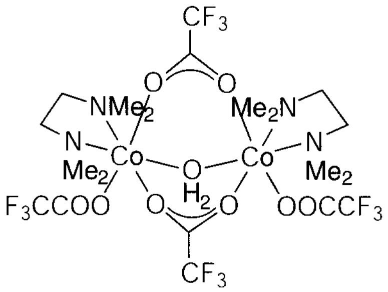


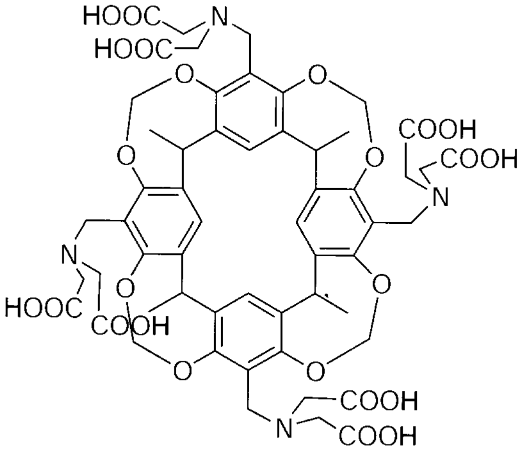


(**99**) (**100**)

Simple polycarboxylates are well known ligands, and but a few examples appear here. Succinate features in an example of a three-dimensional ferrimagnetic Co^{II} carboxylate, $Co_5(OH)_2(C_4H_4O_4)_4$ which has a three-dimensional array of layers of edge-sharing Co octahedral pillared by succinate ions, the Co octahedra forming 12-membered rings within the layers.[434] This was prepared, in a typical example of hydrothermal reactions for this class of compound, by reacting $CoCl_2$, succinic acid, KOH and water in a 2:3:8:120 ratio in a sealed vessel at 180° for 72 h. Citrate, a member of a class of carboxylic acids found in biological fluids, has a key role in several biochemical processes in lifeforms ranging from bacteria to humans. Previously, its interaction with Co has not been well elucidated, but the synthesis from aqueous solution of a 1:2 Co:citrate mixture at pH 8, and subsequent spectroscopic and structural characterization of octahedral $[Co(citrate)_2]^-$ has now appeared.[435] It may offer a source of bioavailable cobalt.

Pyromellitate, the tetracarboxylate of benzene, forms red crystals of formula $[Co_2(C_6H_2(COO)_4)_4]\cdot 18H_2O$ from aqueous silica gel, and feature infinite chain-like polyanions with $[Co(OH_2)_4[C_6H_2(COO)_4)]_2]_n^{2n-}$ stoichiometry where Co is in an octahedral environment of four waters and two *trans*-disposed carboxylates.[436]

An example of a cage molecule based on resorcinarene and carrying polycarboxylate pendants is shown in (**101**). When the ligand was treated in dilute aqueous acid with $CoCl_2$ and the pH raised to ~6 with carbonate ion, $[Co_4L_2]^{8-}$ was formed and characterized by a crystal structure.[437] The two resorcinarene molecules are linked by four octahedral Co^{II} ions each bound to an iminodiactetate unit from separate resorcinarenes, creating an oblate spherical cavity big enough to encapsulate small molecules.



(101)

Organic carbamates (RNHCOO$^-$) commonly display monodentate coordination, as exemplified in the structurally characterized tetrahedral Co(bmc)$_2$Cl$_2$,[438] (bmc = *N*-(benzimidazoyl-2-yl)-O-methylcarbamate). An unusual route to a carbamato complex involves the reaction of Co$_2$(CO)$_8$ in the presence of a fourfold excess of the stable radical species tmpo, which yields the blue Co$_4$O(OOCNC$_9$H$_{18}$)$_6$ cluster, presumably via a Co(CO)$_2$(tmpo) intermediate, with the nitroxyl radical serving as oxidant.[439]

(ix) Oxoanions of N, S, P, and the halogens

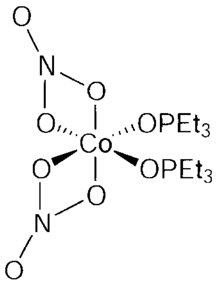
The oxoanions of these elements represent an extensive set of potential ligands, characterized by a dominant, but not exclusive, tendency towards O bonding. Practically every known oxoanion has been introduced into the Co coordination sphere during the last century.

(o) Nitrogen oxoanions. Nitrate and nitrite both bind to Co^{II}, as monodentate or bidentate ligands. Nitrate is found as a monodenate co-ligand in a wide range of structures, as exemplified by octahedral *trans*-Co(cb-im)$_4$(NO$_3$)$_2$ (cb-im = 4′-cyanobenzyl-1-imidazole)[440] It is also met in mononuclear complexes as a bidentate chelate, as in the distorted octahedral [Co(bpa)$_2$(NO$_3$)](NO$_3$) (bpa = bis(2-pyridyl)amine).[441] An example featuring both monodenate and bidentate nitrate in the same complex ion is Co(ddae)(NO$_3$)$_2$ (ddae = bis(2-(3,5-dimethyl-1-pyrazolyl)ethyl)ethylamine);[442] the Co—O (monodenate) distance is 2.060(8) Å whereas the Co—O (chelate) distances are longer at 2.172(8) Å and 2.216(8) Å, reflecting strain in the four-membered ring.

Syntheses of many nitrato complexes are straightforward, such as by reaction of hydrated cobalt(II) nitrate with stoichiometric amounts of ligand in alcohol, although whether nitrate is incorporated into the coordination sphere or simply acts as a counterion is hard to predict. Perhaps some of the more interesting compounds appearing including coordinated nitrate are the so-called "molecular ladders"; a simple example is $[\mathrm{Co(NO_3)_2(4,4'\text{-}bpy)_{1.5}}]_\infty$ as MeCN or CHCl$_3$ solvates.[443] This polymeric structure comprises 4,4′-bpy ligands bridging Co centers forming both the rungs and side rails of the ladder, with chelated nitrates completing the Co coordination sphere. The solvent molecules are enclathrated in the large square hydrophobic cavities of the structure.

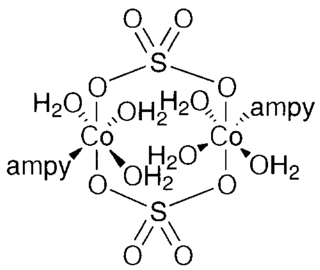
Although the bulk of work with NO$_2^-$ as a ligand features Co^{III}, nitrite can also be O- or N-bonded to Co^{II}, and both modes have been observed in complexes formed by the reaction of several PR$_3$ compounds with Co(NO$_3$)$_2$, as well as in mixed nitro/nitroso complexes.[375] The product Co(NO)(NO$_2$)(PEt$_3$)$_2$ reacts with dioxygen to form Co(NO$_3$)$_2$ (OPEt$_3$)$_2$, a distorted octahedral structure with bidentate nitrate and *cis* phosphine oxides (**102**).

(p) Sulfur oxoanions. The various oxoanions of sulfur are known to bind effectively to Co^{II}, and a few examples will suffice to define the chemistry. Sulfate is reported to bind as either a monodentate or bidentate chelate to divalent Co. Sulfate in a bridging role to Co^{II} has also been observed, as the 2-aminopyrimidine (ampy) complex (**103**), where two bridging sulfates and the two Co^{II} centers form an eight-membered ring.[444] A μ_3-coordination mode for sulfate has been observed in the product of the reaction of Co(CF$_3$COO)$_2$ with SOCl$_2$ in dimethoxyethane (dme)



(102)

under a nitrogen atmosphere, the cluster $Co_3Cl(CF_3COO)_3(SO_4)(dme)_3$.[445] The Co ions occupy corners of an equilateral triangle, each in a distorted octahedral environment which includes a sulfate ion acting as a tripod ligand bridging to each Co center (**104**). Sulfite is formed as a chelate bound through two O donors when SO_2 is reacted with $[\{(triphos)Co\}_2(\mu\text{-}Cl)_2]^{2+}$; likewise, CO_2 and CS_2 form CO_3^{2-} and CS_2O^{2-} chelates in metal-assisted oxidations.[446]



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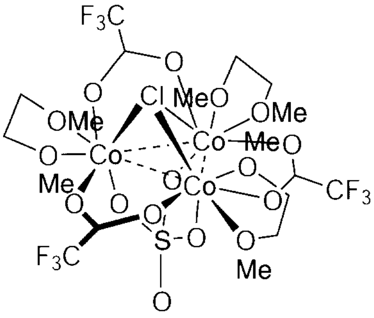


(104)

(q) Phosphorus oxoanions. Phosphate and its protonated forms, as well as polyphosphates, have been well characterized in complexes with divalent cobalt, being involved in monodentate, chelate, and bridging coordination modes. It is usually met with other companion ligands; even simple compounds such as $Na_2Co(H_2PO_4)_4{\cdot}2H_2O$ finds Co in an octahedral environment comprising four dihydrogen phosphates and two aqua ligands.[447] Anhydrous compounds featuring only phosphate ligands such as $Na_4Co_3(PO_4)_2(P_2O_7)$ have appeared, albeit as structurally complex polymeric solids.[448]

Apart from inorganic phosphates, analogs with C—P bonds, the phophonates (RPO_3^{2-}) and phosphinates ($R_2PO_2^-$), are known ligands for Co^{II}. They may be present as the sole ligand; for example, diphenylphosphinate forms the polymeric $[Co(R_2PO_2^-)_2]_\infty$ where the metal is tetrahedrally bound with double phosphinate bridges.[449]

Recently, highly branched macromolecular polyamidoamine dendrimers have been prepared with Co^{II} bound where the metal ions have additional exchangeable coordination sites.[450] These macromolecules show a capacity for catalyzing the hydrolysis of phosphate esters, presumably via intermediate bound phosphoester species.

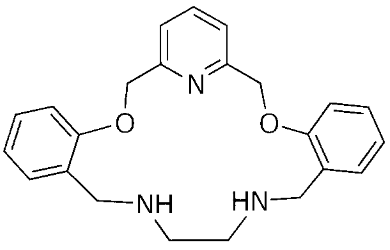
(r) Halogen oxoanions. The suite of oxoacids HXO (hypohalous), HXO_2 (halous), HXO_3 (halic), and HXO_4 (perhalic) in principle all form anions capable of coordination to cobalt. Of all possibilities, perchlorate is the best known of the halogen oxoanions, although it is a weak ligand and met more often as a counter ion. As mentioned in Section 6.1.1.2, ClO_4^- complexes are potentially hazardous due to their inherent thermal instability particularly in coexistance with organic ligands. Nevertheless, there are many examples of it found as a ligand for Co^{II}, for example in tetrakis(2,6-diethylphenylisocyanide)bis(perchlorato)cobalt(II).[451] Also, a Co^{II} corrinate derived from Vitamin B_{12} has been isolated and structurally characterized with a coordinated axial perchlorato ligand bound to the face opposite the one used for nucleotide binding in cobalamin.[452]

(s) Other oxoanions. Transition metal oxoanions can also act as ligands. As an example, the trans-$Co(py)_4(HCrO_4)_2$ complex of Co^{II} with hydrogenchromate(VI) and pyridine has been characterized by an X-ray structure.[453] The complex efficiently oxidizes benzyl halides to aldehydes.

(x) Mixed O, N Donors

Mixed O, N donor molecules are truly extensive and structurally diverse, and only a few selected examples will be presented. In line with other 2-substituted pyridine analogs reported in this chapter, it is worthwhile noting the chemistry of 2-pyridone (or 2-hydroxypyridine, Hopy), which can form O-bonded monodentate complexes such as $Co(Hopy)_4(NO_3)_2$, but as the monoanion is an effective chelate ligand, forming $Co(opy)_2$ and $Co(bpy)(opy)_2$ compounds.[454] An unusual solid state melt reaction with $Co(OAc)_2$ yields the dodecanuclear cluster $Co_{12}(OH)_6(OAc)_6(opy^-)_{12}$.[455]

Polydentate ligands resulting from the Schiff base condensation of primary amines and aldehydic phenols have a venerable history; the products are, when deprotonated, strong ligands for Co^{II} (see Section 6.1.2.2.2). While this chemistry is sufficiently well established to need little discussion, one recent example illustrates the sometimes unexpected outcomes of supposedly straightforward syntheses. Reaction of $Co(OAc)_2$ with $salpnH_2$ (the propane-1,2-diamine analog of salen) yields a Co^{II} trimer where the two end Co ions are tetracoordinated by the salpn ligands but the phenolic oxygens all bridge to the central Co ion and each terminal Co is also linked to the central Co by a bridging acetate.[456] Macrocyclic polyether–polyamine ligands are an extensive family, which have been widely exposed in the literature. One example is the mixed donor macrocycle (**105**), which forms a $[Co(L)(NO_3)](NO_3)$ complex with all five macrocycle donors coordinated in addition to a chelated nitrate, giving a rare example of seven-coordinate Co^{II}.[457]



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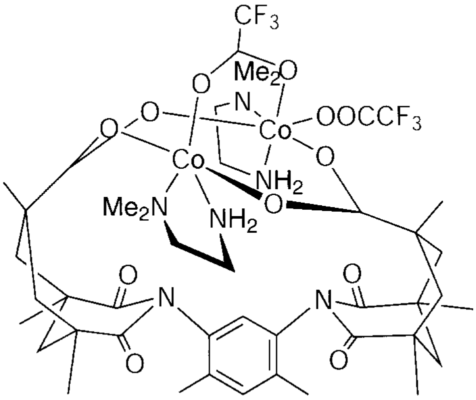


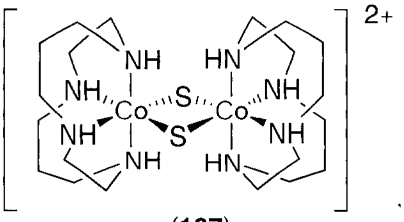
(**106**)

Mixed-donor ligands featuring carboxylate groups appear throughout this chapter. One example of a polycarboxylate-derived ligand is the convergent dicarboxylate ligand formed from Kemp's triacid and xylenediamine, shown as a dinuclear complex in (**106**) with diamine and trifluoroacetate co-ligands. The cobalt(II) complex of this with 2,9-dimethyl-1,10-phenanthroline as co-ligand adopts a highly distorted trigonal bipyramidal geometry. However, in the presence of alkali metal ions the structure adopts an unusual distorted trigonal pyramidal form.[458] Since binding of the alkali metal also leads to significant changes in the visible spectrum, this complex functions as a metallochromoionophore. The participation of this ligand and other carboxylates in dinuclear cobalt(II) binding had been demonstrated earlier,[459] when seeking models of non-heme dinuclear proteins.

6.1.2.2.6 *Sulfur*

(i) Sulfides

Sulfide is a well-established ligand for Co. In addition to S^{2-}, the protonated form SH^- is known as a ligand, with a linear polymer of $[Co(cyclam)(SH)]^+$ cations, where the SH^- acts as a bridging group, forming from reaction of $Co(ClO_4)_2 \cdot 6MeCN$ with SH^- in the presence of the cyclam macrocycle.[460] Further, the bridged dinuclear complex $[\{(cyclam)Co\}_2(\mu\text{-}SH)_2]^{2+}$ forms on varying the Co:S ratio, and $[\{(cyclam)Co\}_2(\mu\text{-}S)_2]^{2+}$ (**107**) results if disulfide S_2^{2-} is used instead of SH^-, with all products defined by X-ray crystallography. Not only bridging sulfide, but selenide and telluride also, are found in $\{(Me_3P)_3Co\}_2(\mu\text{-}X)_2$ (X = S, Se, Te), featuring a planar Co_2X_2 metallocycle (**108**).[461] These form in a number of ways, including oxidation of $Co(Me_3P)_3Cl$ with Te, Se, or S.



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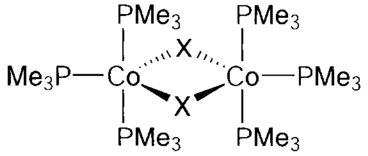
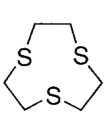


(108)

(ii) Thioethers

Thioethers lack the capacity to neutralize positive charge and display weak σ-donor properties. Consequently, they do not readily displace strong donor solvents (water) or strongly bonding anions (such as halides) from the coordination sphere. As a consequence, many thioether complex syntheses employ aprotic or alcoholic solvents and precursor complexes with weakly bound solvents (such as DMSO or acetone) or anions (such as $CF_3SO_3^-$). Despite the synthetic challenges, a wide range of complexes has been reported, particularly with the cyclic polythioethers, where the macrocyclic effect overcomes many of the above difficulties.

A range of polythioether macrocycles is known, along with mixed thioether–ether and thioether–amine analogs. Macromonocyclic ligands and their Co complexes have been known for some time, with the three most frequently encountered ligands being $[9]aneS_3$ (**109**), $[14]aneS_4$ (**110**) and $[18]aneS_6$ (**111**). Crown thioether chemistry has been reviewed.[462] The most intensively studied cyclic thioether is (**109**), which forms bis-ligand complexes of both Co^{II} and Co^{III}, both six-coordinate, the former Jahn–Teller distorted low-spin.[463] The Co^{II}—S distances range from 2.240(7) Å to 2.356(6) Å. The purple Co^{II} complex may be oxidized reversibly to Co^{III} (+0.68 V) and reduced reversibly to the green Co^{I} (−0.29 V), stabilized by π delocalization. The S_6 crown thioether (**111**) forms a low-spin octahedral complex by reaction with cobalt(II) picrate in refluxing acetone/acetonitrile for a short period, and is one of the few examples of a structurally characterized divalent CoS_6 complex.[464] A $Co^{II}S_6$ Jahn–Teller distorted octahedral complex with Co—S distances in the range 2.251(1)–2.479(1) Å was found.[465] The $Co^{III/II}$ couple (+0.84 V) shifts to a slightly more positive potential (+0.89 V) if the ring size is increased to 24 atoms with additional methylene groups. A much more rapid $Co^{III/II}$ self-exchange electron transfer in the CoS_6 systems compared with CoN_6 analogs (~10^5-fold faster) has been assigned for the S ligands to both extensive delocalization of metal electron density over the ligands and a small reorganization of the coordination sphere with oxidation state change due to comparable Co—S distances in the di- and trivalent oxidation states.



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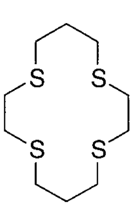

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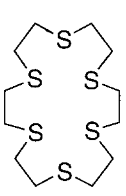

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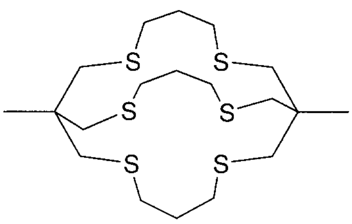

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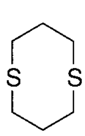

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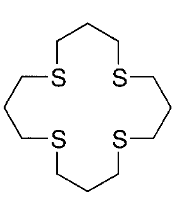


(114)

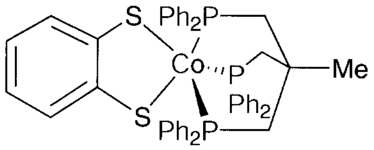
The S_6 macrobicyclic cage (**112**), when complexed to divalent Co, also exhibits four short and two long Co—S bonds in a distorted octahedral environment.[466] Smaller cyclic thioethers such as (**113**) and $[16]aneS_4$ (**114**) react with $Co(BF_4)_2$ in acetonitrile in the absence of air to form square–pyramidal CoS_4N complexes, with the solvent completing the coordination sphere.[467] A wide range of mixed-donor ligands incorporating thioethers have appeared as ligands for Co^{II}, but their coordination chemistry is generally not unusual. One example of a mixed S,O-macrocycle characterized by a crystal structure is $[Co([20]aneS_4O_2)]^{2+}$.[468]

(iii) Thiolates

Thiolates (RS^-) represent an extensive family of ligands, and include chelating forms. Thiolates are known to act as monodentate donors, but often act in a bridging role. There is a clear biological interest, through participation of thiolates (cysteine residues) as donors in many metalloproteins both as terminal S donors and bridging ligands in, for example, Fe–S clusters.

Cobalt(II) alkylthiolates of the types $[Co(SR)_4]^{2-}$, $[Co_2(SR)_6]^{2-}$, and $[Co_4(SR)_{10}]^{2-}$ have been reported and structurally characterized.[469] Tetrahedral, dark green $[Co(SR)_4]^{2-}$ ions are fairly well known and studied. The PhS^- complex can be formed by reaction of $Co(S_2COC_2H_5)_3$ with K(PhS) and isolated as the Ph_4P^+ salt.[470] Reaction of $CoCl_2$ with sodium 2-aminobenzenethiolate and Et_4NCl in MeOH yields the tetrahedral $(Et_4N)_2$ $[Co(SC_6H_4NH_2)_4]$, where coordination is through the S (Co—S 2.295(2) Å) and not the N atom.[471] The electronic spectrum implies an equilibrium in solution between the tetrahedral form characterized in the solid state and an octahedral form. A new mixed halide–thiolate cluster complex of cobalt(II) arises from reaction of NaSPh and Et_4NCl with $CoCl_2$ in methanol.[472] The $[Co_4(SPh)_6Cl_4]^{2-}$ cluster ion crystal structure shows the four Cl ions bind to different Co centers and define a tetrahedron, whereas the S-donors are arranged in an irregular octahedron. Each Co center exhibits distorted tetrahedral symmetry, while the core itself consists of a distorted Co_4 tetrahedron.

More complex coordination modes can arise if other potential donors are in appropriate positions. For example, reaction of anhydrous $CoCl_2$ with tris(*t*-butoxy)silanethiol (tbstH) in acetonitrile in the presence of Et_3N as base yields $Co(tbst)_2(MeCN)$, where the $tbst^-$ chelates through the S and one of the O atoms to form a trigonal bipyramidal structure.[473] Chelated dithiolates also form complexes with Co^{II}; the classical chelator $o\text{-}C_6H_4S_2{}^{2-}$ binds in a complex with a $Co^{II}S_2P_3$ donor set, with a tripodal phosphine occupying the other sites (**115**).[474] The 2,3-disulfanylmaleonitrile chelate binds in a square–planar $Co^{II}S_4$ arrangement with stacking in the crystal allowing for S atoms to interact axially with another Co center.[475]



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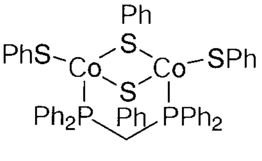
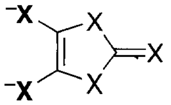


(116)

Thiolates often bind in concert with other strong donors. An unusual example is the dimeric $Co_2(dppm)(\mu\text{-}SPh)_2(SPh)_2$, which displays terminal and bridging modes for the thiolate, as well as bridging by the diphosphine ligand in (**116**).[476] Clusters $[Co_3(\mu\text{-}SR)_6(PEt_3)_3]^+$ involving thiols and phosphines form readily from the reaction of an alkylthiolate with cobalt(II) acetate in the presence of excess PEt_3.[477] The three cobalts form a triangle, with six symmetrically bridging thiolates and a terminal phosphine on each cobalt. The cluster can be oxidized or reduced in one-electron steps.

Thiolates coupled with other donors are effective chelators. Pyridine-2-thiolate (pyt) forms four-membered chelate rings to Co^{II} in $Co(pyt)_2$ compounds which are conveniently formed by anodic oxidation at a Co electrode in an acetonitrile solution of the ligand.[478] These are able to be oxidized further to tris(pyt)cobalt(III) compounds. The ligand 2-methyl-1-[methyl-(2-pyridin-2-ylethyl)amino]propane-2-thiolate (pyat) forms distorted tetrahedral cobalt(II) complexes Co(pyat)X- (X = Br, SCN), where pyat acts as an N_2S-tridentate, the first examples of this type defined by crystal structures.[479] Four-coordination appears to persist in solution regardless of solvent, and only one diastereomer is detected and predicted by molecular mechanics due to a favorable conformation of the ligand. It is suggested the complexes are structural mimics of metalloproteins such as peptide deformylase, which possess a His_2Cys site. Cobalt(II) binding to thiolates in biological molecules has been probed. Interaction of a 34-amino acid peptide derived from α-fetoprotein with cobalt(II) and zinc(II) has been examined by UV–visible and CD spectroscopy, and coordination by two thiolate (from cysteine) and two imine (from histidine) donors with similar protein conformations is implied.[480] The Co ion acts in the opposite way to the zinc in the sense that the former catalyzes the loss of the anti-growth form of the peptide whereas with the latter there is stabilization.

1,1-Dithiolates ($R_2C{=}CS_2^{2-}$) and analogs dithiocarbimates ($RN{=}CS_2^{2-}$), trithiocarbonates ($^{-}S{-}CS_2^{2-}$), and dithiocarbonates ($^{-}O{-}CS_2^{2-}$) were introduced in *CCC*(1987) (Section 47.8.10),[1] and will not be exhaustively reviewed here. The dithiolates and their selenium analogs have continued to attract attention because of potential applications of their complexes as superconducting materials; the first molecular superconductor was a nickel dithiolate complex. One extensively studied family of ligands is 1,3-dithiole-2-thione-4,5-dithiolate (dmit) and its isologs (**117**).[481,482] Although work has concentrated on Ni and Pd chemistry, complexes such as $[Co(dmit)_2]^{2-}$ have been reported, along with mixed-ligand species such as $[Co(Cp)(dmit)]^{-}$.



(**117**) [X = S, Se]

(iv) Dithioacids and thiosemicarbazones

The dithioacid family of ligands includes dithiocarbamates ($R_2N{-}CS_2^{-}$), xanthates ($RO{-}CS_2^{-}$), thioxanthates ($RS{-}CS_2^{-}$) and dithiocarboxylates ($R{-}CS_2^{-}$), which have been described in *CCC*(1987, Section 47.8.10).[1] The ligands are prepared by addition of a suitable nucleophile to the carbon center in CS_2, usually in the presence of a base. It has been established for some decades that they bind to Co almost exclusively as bidentate chelates, including S-donors acting as bridging ligands in dinuclear systems.

Chelating thiosemicarbazone ($RNH{-}CS{-}NH{-}N{=}CR'R''$, Htsc) complexes of Co^{II} were briefly mentioned in *CCC* (1987, Section 47.8.6), with tetrahedral, trigonal bipyramidal, and octahedral forms known for compounds of empirical formula $Co(Htsc)_2X_2$ ($X = Cl^{-}$, Br, I^{-}), the geometry influenced by R groups present. Chelation as an *S,N*-bidentate is dominant, but not exclusive, with *N,N*-bidentate known. Since the last edition, driven by potential medical applications as fungicides and antimicrobials, more extensive examples of thiosemicarbazone cobalt(II) complexes have appeared, with 1, 2, 3, or 4 donors coordinated, almost invariably including the S and usually a N atom as donors. The ligands commonly bind in an N-deprotonated (thiolene) form, although neutral coordination (as a thione) can occur.[483] Reported complexes are typically mononuclear, although coordination polymers have been proposed. Octahedral coordination has been proposed in most cases, though tetrahedral and trigonal bipyramidal geometries have been suggested. For example, octahedral $Co(mftsc)_2X_2$ and tetrahedral $Co(mftsc)X_2$ (with mftsc = 5-methyl-2-furaldehyde thosemicarbazone) have been reported, with coordination through both the S and azomethine N atoms supported.[484]

Ligands of higher denticity have appeared. Tridentate coordination as an S,N,O-donor is reported for the cobalt(II) complex of salicylaldehyde N(4)-cyclohexylthiosemicarbazone, with four- or five-coordinate complexes proposed where additional sites are occupied by heterocyclic bases.[485] A mixed ligand complex $Co(stsc)(amN)_3$ where stsc = salicylaldehyde thiosemicarbazone and amN is an aromatic amine has been reported, with the stsc bound as an S,N,O-tridentate dianion.[486] Methyl 2-pyridyl ketone thiosemicarbazone forms a bis(tridentate)cobalt(II) complex with N_4S_2-coordination, from spectroscopic evidence and by analogy to the crystal structure of the copper(II) analog.[487] Tridentate S_2N-binding is proposed in octahedral cobalt(II) complexes of 2-acetyl thiophene thiosemicarbazone, involving the azomethine N, cyclic thioether S and thiol S.[488] The complexes proved effective as fungicides against several species. Vanillin thiosemicarbazone (vtsc), as the $[Co(vtsc)_2(H_2O)_2]^{2+}$ complex, also displays fungicidal activity.[489] Tetradentate (N_2S_2-donor) examples bound to cobalt(II) of the form benzil-bis(4-alkylthiosemicarbazone) have been proposed, where the dianion forms apparently octahedral $Co(dtc)(OH_2)_2$.[490]

Introduction of an organometallic moiety has been achieved by coupling ferrocenecarbaldehyde with thiosemicarbazide, with the resulting thiosemicarbazone (fctsc) forming the presumably octahedral cobalt(II) complex $Co(fctsc)_2Cl_2$,[491] which showed antibacterial activity. Acetylferrocene thiosemicarbazone complexes of Co were reported earlier,[492] including a species of the same form as that given above.

The cobalt(II) complexes may be readily oxidized to cobalt(III) species. For example, use of different cobalt(II) salts in syntheses have been reported to direct the formation of either tetrahedral cobalt(II) species or oxidized octahedral cobalt(III) species.[493] Also, μ-peroxodicobalt(III) complexes of 2,6-diacetylpyridine-bis(N(4)-azacyclic thiosemicarbazones) form by rapid reaction of the cobalt(II) complex in organic solvents with oxygen; the kinetics have been probed in detail.[494]

Fungicidal activity of cobalt(II) and other divalent metals of tsc compounds have been observed, and is usually greater than for the free ligand.[495] Broad antimicrobial activity has been reported for the cobalt(II) complex of acetophenone-4-(2′-carboxy-5′-sulfophenyl)-3-thiosemicarbazone.[496]

(v) Thioureas

Thiourea ($H_2NC(S)NH_2$, tu), as typically an S-bound monodentate ligand, has been commonly observed. The simple S-bound tetrahedral tetrakis(thiourea)cobalt(II) ion has been defined by an X-ray crystal structure.[497] The S-coordination of thiourea has also been defined in high-spin, octahedral cobalt(II) complex $Co(phen)(tu)(H_2O)Cl_2$.[498] A similar coordination mode is observed in aqua(thiourea)(semicarbazidediacetato)cobalt(II).[499] Cobalt(II)-coordinated thiourea has also been defined in a crystal structure of Co(tsd)(tu) (tsd = thiosemicarbazide diacetate).[500] Digestion of $[Co_2(CNCHMe_2)_{10}]^{4+\bullet}$ in ethanol with an excess of thiourea produces octahedral monomers *trans*-$[Co(CNCHMe_2)_4(tu)_2]^{2+}$,[501] rather than the presumed initial cleavage and addition product $[Co(CNCHMe_2)_5(tu)]^{2+}$, assigned to a preference for a structure with two strongly σ-bonding ligands in *trans* dispositions. Lability of the thiourea cobalt(II) systems has been probed in a study of ^{60}Co exchange in $Co(SCN)_2(tu)_2$.[502]

Substituted thioureas have been extensively studied over the decades. Reaction of CoX_2 (X = Cl, Br) with substituted phenylthioureas yield a range of complexes involving halide and thiourea as ligands, characterized by spectroscopy and thermogravimetric analysis.[503] Both $[Co(Rtu)_4(OH_2)_2]^{2+}$ (Rtu = thiourea, phenylthiourea, allylthiourea) and $[Co(Rtu)_2(OH_2)_4]^{2+}$ (Rtu = diphenylthiourea) have been prepared and characterized as low-spin octahedral species.[504] The octahedral bis(phenylthiourea)bis(dithiolate)cobalt(II) complex, one of a number of complexes of phenylthiourea, chlorophenylthiourea and bis(diphenylphospinothioyl)methane prepared and characterized,[505] proved the most biologically active of those tested.

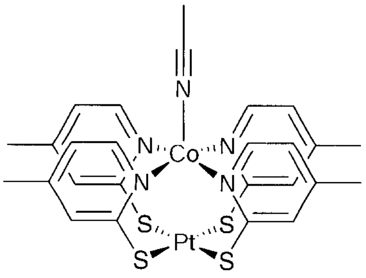
Chelated species are less common. The substituted thiourea *N*-ethoxycarbonyl-*N*-[3-(*p*-anisyl) pyrazol-5-yl]thiourea (eatu) acts as a monoanionic O,S-chelate to cobalt(II), forming $Co(eatu)_2$.[506] Whereas ethylenethiourea (etu) has been observed to act as a S-donor monodentate in $Co(etu)_2X_2(H_2O)_2$ (X = Cl, Br), it binds as an S,N-chelate in $Co(etu)_2(OOCCH_3)_2$.[507] Both violet octahedral and blue tetrahedral cobalt(II) compounds $Co(pptu)_2Cl_2$ and $Cp(pptu)Cl_2$ respectively were prepared with bidentate *N*-2-(5-picolyl)-*N*′-phenylthiourea (pptu) chelated.[508] Refluxing Co powder with thiourea in 4-methylpyridine provides a route to isothiocyanates, which form by decomposition of thiourea to ammonium thiocyanate[509] with one product, $Co(pic)_4(NCS)_2$, characterized by a crystal structure.

(vi) Mixed S, N and S, O ligands

Ligands with S donors in addition to N and or O donors bound to Co^{II} are reasonably large in number. For example, the 4-amino-3-alkyl-1,2,4-triazole-5-thione can bind Co^{II} as a chelate employing the primary amine and thione substituents on the five-membered ring,[510] whereas the trifluoromethyl ligand (afmt) forms $[Co(afmt)_2(H_2O)_2](NO_3)_2$, defined as the all-*trans* isomer by a crystal structure.

The simple ligand 4-methylpyridine-2-thiolate (pyt) participates in a lantern-type heteronuclear complex $(MeCN)Co(pyt)_4Pt$ where the four thiolate groups bind Pt^{II} in its preferred square–planar arrangement while the four pyridine groups and the acetonitrile bind the Co^{II} center in a square–pyramidal geometry (**118**).[511] The complex forms readily by reaction of $[Pt(pt)_4]Cl_2$ with $CoCl_2$ in basic solution, and the complex characterized was obtained following recrystallization from acetonitrile. The complex has a close Co—Pt distance of 2.573(2) Å, enforced by the short donor separation in the bridging ligands.

An unusual *S,N*-chelate is the anion $R'NH{-}PR_2{-}S^-$, which has no carbon atoms amongst the four-membered chelate ring atoms, and forms a tetrahedral bis Co^{II} "spirocyclic" complex.[512] Higher denticity ligands also feature in the literature. A dipyrazoyl-dithioether ((**119**), bddh) forms a simple octahedral *cis*-α-$Co(bddh)(NCS)_2$ complex.[513] The ketal coronand (**120**) forms a complex with Co^{II} which leads to a change in orientation of the bipyridyl unit from *anti* in the free ligand to *syn* in the complex.[514] One example of a simple S,O chelate reported is the dianion of 2-mercaptophenol (spo). This forms strong complexes of the type $[Co(spo)_2]^{2-}$, clearly defined in a crystal structure determination.[515]



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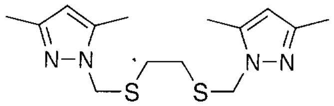

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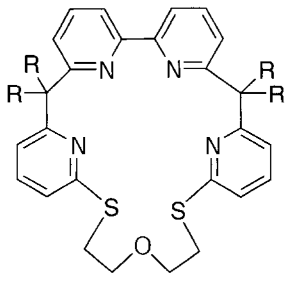

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6.1.2.2.7 Halogens

(i) Halides

Halides are common coligands, partly because Co^{II} halides feature as a common entry point into Co chemistry. As such, examples are scattered throughout the chapter.

(I) Mononuclear. Cobalt(II) with halide ligands alone occurs in the well-known tetrahedral $[CoX_4]^{2-}$. Electrochemical oxidation of Co in a HX/acetonitrile solution containing a neutral tertiary phosphine provides a route to crystalline $[CoX_4]^{2-}$ as the phosphonium salts.[516] The same complex anion has also been reported with rhenocene cations, as $[Cp_2Re]_2[CoBr_4]$, characterized by a crystal structure.[517] The 1,5-pentanediammonium form of $[CoCl_4]^{2-}$ has also appeared.[518] Apart from $[CoCl_4]^{2-}$, the ions $[Co_2Cl_6]^{2-}$ and $[CoCl_3(MeCN)]^-$ have been structurally characterized as counterions to a Co^{II} crown ether complex cation.[420]

Speciation of halocobalt(II) compounds in solution has been examined. Absorption spectra of $CoCl_2$ and $CoBr_2$ in aqueous halide solutions (up to 5 M) were measured over the temperature range 25–90 °C and used to probe speciation in solution.[519] At low temperatures and halide concentrations, octahedral aquahalo complexes dominate, with a transformation to tetrahedral $[CoX_4]^{2-}$ complexes occurring as temperature and halide ion concentration rises. Thermodynamic data for all complexation reactions were determined, and geological implications discussed. Octahedral/tetrahedral transformations have also been probed in the molten state, with addition of halide ion (Cl, Br) to cobalt(II) in ammonium/calcium nitrate melts leading to apparently tetrahedral species with at least two halide ions coordinated to the Co ion.[520] From spectroscopic studies, extraction of cobalt(II) halides from aqueous solution with quaternary ammonium chloride and bromide salts is thought to involve formation of dinuclear anionic complexes.[521] The kinetics of complex formation reactions for cobalt(II) with halide ions (Cl, Br, I) have been studied,[522] and an associative interchange mechanism proposed.

The simple tetrahedral $[CoX_4]^{2-}$ ions can undergo substitution, with neutral species such as $Co(L^+)Cl_3$ reported [$L^+ =$ (1H-benzimidazol-2-ylmethyl)-(ethyl)ammonium-N-3)],[523] as well as the long-established CoL_2Cl_2 species with neutral ligands such as monoimines.

Mixed ligand halocompounds abound, and only a few illustrative examples of simple complexes appear here. Octahedral dihalotetra(imine)cobalt(II) complexes of the simple monoimines butyraldoxime and acetaldoxime with the halogens chloride or bromide were prepared and characterized by X-ray structures, which revealed stabilization arising from intra- and in one case inter-molecular hydrogen bonding.[524] Decomposition occurs, however, in a moist atmosphere. Cobalt(II) chloride and bromide reacted with aminopyridines yielded complexes that were characterized by a range of physical methods, with the propeller-shaped octahedral complex $Co(3\text{-aminopyridine})_4Cl_2$ characterized by a single crystal X-ray structure.[525]

Surface complexation to form a tetrahedral $Co(L)X_2$ species is proposed to account for the adsorption of cobalt(II) chloride and bromide from acetone and ethanol solution onto silica gel modified with 3-amino-1,2,4,-triazole,[526] supported by electronic and ESR spectroscopy.

(u) Oligonuclear and polymeric. Halides are well established as bridging ions in a wide range of coordination polymers, and feature in this role as one of several ligands in often complicated structures. The facile formation of triangulo–trihalocobalt(II) moieties, similar to Ti, V, Fe, and Ni homologs, and their structural characterization represents an interesting sub-class, featuring compounds such as $[Co_3Cl_5(tmen)_3]^+$.[527] One apical halide is readily replaced by hydroxide.

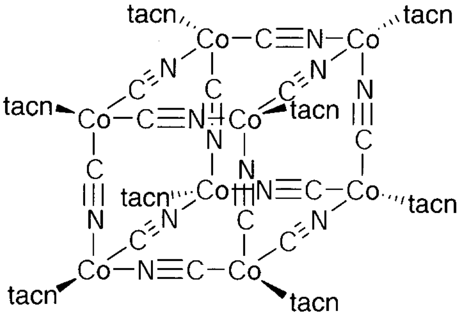
6.1.2.3 Co^{III}

Trivalent Co is one of the most thoroughly investigated ions in transition metal chemistry. The overwhelmingly inert and mostly diamagnetic complexes encountered offer ease of handling and facile spectroscopic characterization, which have assisted to drive the field. Six-coordinate octahedral geometry is particularly dominant in this oxidation state, with nitrogen donors particularly favored. Nevertheless, a range of other coordination numbers (from four to seven) and geometries has been observed. Despite a century of exploration, cobalt(III) chemistry continues to reward and surprise the investigator.

6.1.2.3.1 Carbon

(i) Cyanides

Cyanide has an extended history as a ligand for Co^{III}, and only some aspects will be mentioned here. The $[Co(CN)_6]^{3-}$ ion is well known, and mononuclear Co^{III} complexes with a mixture of cyanide and other ligands abound in the literature; some examples appear elsewhere in this chapter. The pentacyanocobalt(II) ion reacts in solution with air to form peroxo-bridged (and, on oxidation, superoxo-bridged) Co^{III} dimers $[\{(CN)_5Co\}_2(\mu\text{-}O_2)]^{5-/6-}$. With Co^{III}-cyanide complexes usually C-bound, one important paper reports the isolation of the elusive isocyano complex $[Co(NH_3)_5(NC)]^{2+}$, formed through a selenium-abstraction reaction involving N-bound selenocyanate.[528] One other interesting recent example is the $[Co(dbsq)(CN)_4]^{2-}$ octahedral ion, which includes the chelated radical anion of 3,5-di(*tert*-butyl)-1,2-semiquinone (dbsq).[529] The complex was characterized by a crystal structure and by ESR spectroscopy, and was formed by reaction of the Co^{II} tetramer $[Co(dbsq)_2]_4$ with $Bu_4N(CN)$ in THF via a cyanide-induced redox reaction. The coordinated cyanides display the usual essentially linear Co—CN bonds with average Co—C distances of 1.89(2) Å. An interesting example of bridging cyanide occurs in the trivalent Co cluster $[Co_8(tacn)_8(CN)_{12}](OTs)_{12}$ (**121**), which forms from boiling equimolar mixtures of $[Co(tacn)(OH_2)_3](OTs)_3$ and $Co(tacn)(CN)_3$ in water.[530] The tridentate tacn ligands cap the "external" coordination sites of each Co ion situated at a vertex of the cube.



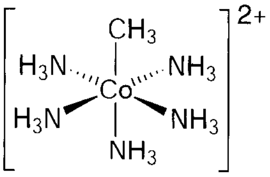
(**121**)

(ii) Carbonyls

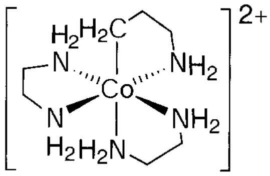
High-valent Co complexes incorporating carbonyl ligands are rare, and those extant are outside the scope of this review. The companion series *Comprehensive Organometallic Chemistry* covers this area.

(iii) Alkyls and aryls

The Co^{III}–alkyl bond was established some time ago with the characterization of simple complexes with Co—CH_3 or other Co—R groups. Incorporation of R^- as an axial ligand in Co^{III} porphyrins, Schiff base and bis(dimethylgloximato) compounds were early types defined, and examples continue to appear. This is a key feature of cobalamin (B_{12}) model complexes and a review of this area appears in Section 6.1.3.1.1. The deceptively simple isoelectronic alkyl homologs of $[Co(NH_3)_6]^{3+}$ and $[Co(en)_3]^{3+}$, (**122**)[531] and (**123**), have appeared since the first edition of *CCC*.[532,533]



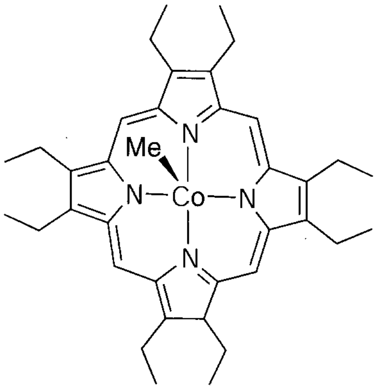
(**122**)



(**123**)

Introduction of several CH_3^- ligands into the Co^{III} coordination sphere is facilitated with phosphine ligands in other sites. For example, the octahedral $[Co(CH_3)_2(PMe_3)_4]^+$ is known, and the Co—C bonds are sufficiently stable to be unaffected by phosphine exchange in THF with the chelate dmpep ($Me_2PCH_2CH_2PMe_2$), which results in $[Co(CH_3)_2(PMe_3)_2(dmpep)]^+$.[534]

Trivalent five-coordinate methyl (**124**) and six-coordinate (*trans*) methyl pyridyl complexes of the octaethylporphyrin dianion (OEP) have been reported.[535] In (**124**) the square–pyramidal geometry results in an axial Co—C distance of 1.973 Å and the Co is displaced 0.10 Å out of the porphyrin plane towards the methyl group. The latter complex, with a pyridine *trans* to the methyl ligand, finds the Co ion centered in the plane of the porphyrin and with a Co—C distance of 2.018 Å; the elongation reflecting a strong mutual *trans* effect of the Me and py axial ligands. This is relevant to the methyl transfer ability of these complexes as B_{12} mimics (Section 6.1.3.1.1), as base coordination in the site *trans* to the Me ligand accelerates Co—C homolysis in the natural systems. The ethyl analog of (**124**) has also been characterized.[536]



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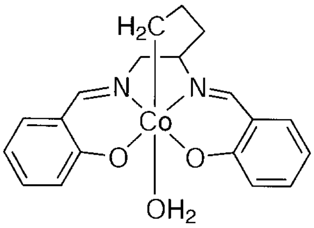
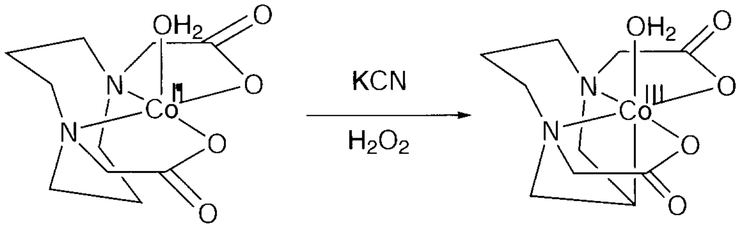


(**125**)

Introduction of a pendant coordinated alkyl chain to Co(salen) has been achieved through condensation of salicylaldehyde with the branched ethylenediamines $H_2NCH((CH_2)_nCl)CH_2NH_2$ ($n = 2$–5). Complexation to Co^{II}, reduction to Co^I, and subsequent intramolecular alkylation results in the novel complex (**125**).[537] Oxidative addition of several alkyl halides to the Co^I compound generated on reduction of divalent $[Co(pabo)(Hpabo)]^{2+}$ (Hpabo = 2-(2′-pyridylethyl) amino-3-butanone oxime) led to the alkylcobalt(III) compounds $[RCo(pabo)(Hpabo)]^+$.[538] A pseudo-octahedral geometry was defined by several crystal structures, with Hpabo and pabo acting as bi- and tridentates respectively, and the alkyl group occupying the remaining site.

A series of trivalent organocobalt complexes of the form $[RCo(cyclam)(OH_2)]^+$ have been reported, where R = Me, Et, Pr, CH_2Cl, CH_2Br, CH_2OMe, and CH_2Ph.[539] These compounds are photosensitive, decomposing to Co^{II} and carbon-centered radicals when irradiated with visible light. These carbon-centered radicals abstract hydrogen atoms from thiols (C_2H_5SH, cysteine, or glutathione), generating thiyl radicals.[540] In the absence of light, the alkyl complexes are air-stable in acidic aqueous solutions whereas the benzyl complex undergoes rapid homolysis of the Co—C bond. Visible light photolysis of the methylcobalt(III) complex causes nicking of supercoiled DNA; the complex is inactive in the absence of light, implying a photo-initiated radical mechanism.[541]

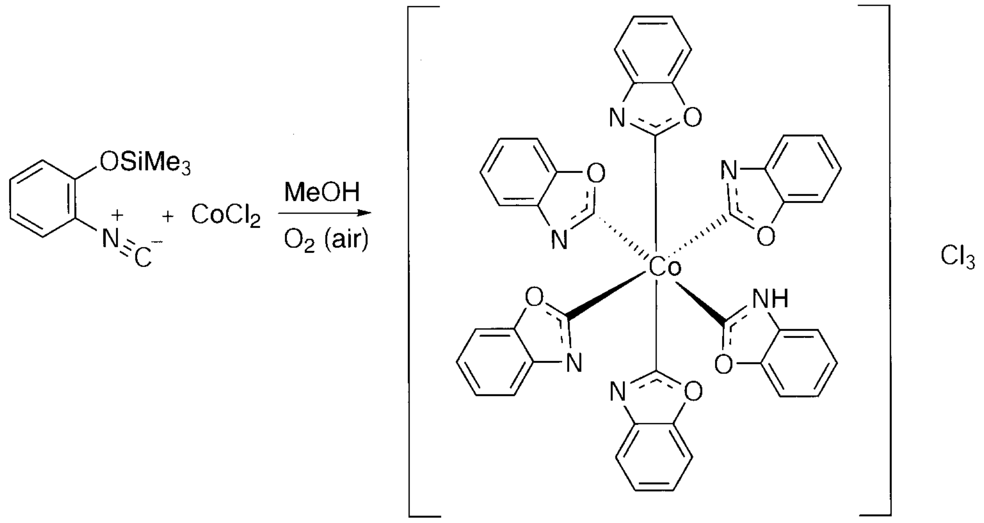
Reaction of the 1,5-diazacyclooctane-*N*,*N*′-diacetate complex (**126**) with H_2O_2 in the presence of KCN forms an octahedral complex (**127**) containing the now pentadentate ligand coordinated through a deprotonated carbon atom in addition to the N_2O_2 donors. A particularly short Co—C distance (1.941(4) Å) was found.[542] The cyclic thioether 1,4-diaza-7-thiacyclodecane was prepared recently, and, in addition to the anticipated N_2S-bonded Co^{III} complex, a C-bonded form involving the anion 1,4-diamino-7-thiacyclodecan-8-ide was described.[543]



(**126**) (**127**)

Carboranes also offer the capacity for Co^{III}—C bond formation. Perhaps the best-known example of a mixed cyclopentadienyl–metallocarborane sandwich complex is the cobalt(III) compound (Cp)Co(1,2-$C_2B_9H_{11}$), which serves as a precursor for other species.[544]

Ylide compounds of cobalt(III) have been reported, but are usually traditional organometallic compounds. For example, the cobalt(III) ylide complex $[(Cp)Co(CH_2PMe_3)(PMe_3)Br]^+$ made from a labile Co^I precursor has been described.[545] Reaction of *o*-C_6H_4 ($OSiMe_3$)(NC) with $CoCl_2$ in methanol in the presence of air affords an octahedral Co^{III} complex ion (**128**) with a monocarbene ligand producing a $Co^{III}C_6$ environment.[546] This is similar to the analogous oxazolidin-2-ylidene chemistry.[547] The monoanionic tricarbene ligand hydrotris(3-ethyl-imidazoline-2-yliden-1-yl)borate (triset) forms the Co^{III} complex $[Co(triset)_2](BF_4)$.[548] From its crystal structure, the hexacarbene complex does not display M—C multiple bonding, which might have been expected with an electron-rich stabilized carbene and a high-valent metal.



(**128**)

6.1.2.3.2 Silicon and tin

There appear to be no well-characterized Co^{III}—Si bonded compounds. Interactions with silicates, particularly on surfaces, are through oxygen atoms. The use of the complex $[Co(en)_2(LL)]Cl_3$ (where $LL = (MeO)_3SiCH_2CH_2CH_2NHCH_2CH_2NH_2$) permits bonding of the substitution-inert CoN_6 species to a silica surface.[549]

There are few well-established examples of Co^{III}—Sn bonds. Stannanes R_3SnH react with OEP complexes (**124**) or the divalent Co(OEP) to form $Co(OEP)SnR_3$.[550] This is also accessible from R_3SnCl and $[Co^I(OEP)]^-$. The structure shows a square-pyramidal Co displaced 0.777 Å out of the porphyrin plane and towards the Sn, which is 2.510(2) Å distant from the Co^{III} center.

6.1.2.3.3 Nitrogen

(i) Amines

The trivalent Co coordination chemistry of amines is simply immense. Amines, both mono- and multidentate, are typically thermally and air stable, often commercially available, easily derivatized, and are well matched to the electronic needs of trivalent Co. Space does not permit a discussion of all categories of amines that have been investigated since *CCC*(1987) nor their limitless permutations when bound to mostly six-coordinate Co. Much of the synthetic and mechanistic work that underpins Co amine chemistry has long been known and will not be restated here. The emphasis here will be on novelty rather than breadth. That is, recent innovative aspects of the structure, reactivity, and applications of selected, but representative, collections of these simple but ever-present compounds will be our focus.

(v) Monodentate. The hexaamminecobalt(III) ion is the simplest closed-shell octahedral coordination compound of the first transition series. With only 84 electrons and effectively no conformational isomers, the $[Co(NH_3)_6]^{3+}$ ion has been an ideal subject for computational chemists. Quantum mechanical calculations have dealt with vibrational[551–553] and electron transfer[554–559] properties of this ion. Ligand field[560] and molecular mechanics[561–563] calculations have also been reported.

The $[Co(NH_3)_6]^{3+}$ ion is inert to substitution reactions, like most Co^{III} compounds, and it possesses a high positive charge and 18 strong hydrogen bond donors. These features result in the complex ion having a strong tendency for ion pairing, and a number of investigations of the association between the complex and inorganic anions have been reported.[564–571] Liquid crystalline phases containing the $[Co(NH_3)_6]^{3+}$ ion have also been studied.[572,573] Second sphere coordination of $[Co(NH_3)_6]^{3+}$ through NH···O bonding to ionophores such as crown ethers are also well known.[574,575] The affinity of $[Co(NH_3)_6]^{3+}$ for DNA and RNA has been the subject of a considerable amount of attention but discussion of this topic is deferred until Section 6.1.3.1.4.

However, there are a number of other miscellaneous biological roles played by this complex. The $[Co(NH_3)_6]^{3+}$ ion has been shown to inhibit the hammerhead ribozyme by displacing a Mn^{2+} ion from the active site.[576] However, $[Co(NH_3)_6]^{3+}$ does not inhibit ribonuclease H (RNase),[577] topoisomerase I,[578] or hairpin ribozyme,[579] which require activation by Mg^{2+} ions. The conclusions from these studies were that an outer sphere complex formation between the enzyme and $Mg_{aq}{}^{2+}$ is occuring rather than specific coordination of the divalent ion to the protein. These results are in contrast to DNase I inhibition by the same hexaammine complex. Inhibition of glucose-induced insulin secretion from pancreatic cells by $[Co(NH_3)_6]^{3+}$ has been found.[580] Intracellular injection of $[Co(NH_3)_6]^{3+}$ into a neurone has been found to cause characteristic changes to the structure of its mitochondria, and this offers a simple technique to label neuronal profiles for examination of their ultrastructures.[581]

The solid state chemistry of various $[Co(NH_3)_6]^{3+}$ salts has been investigated. Phase transitions[582] and conformational changes[583] have been studied by variable temperature crystallography. The thermal decomposition of a number of $[Co(NH_3)_6]^{3+}$ salts has been reported.[584–587]

Outer-sphere electron transfer reactions involving the $[Co(NH_3)_6]^{3+/2+}$ couple have been thoroughly studied. A corrected $[Co(NH_3)_6]^{3+/2+}$ self-exchange electron transfer rate ($8 \times 10^{-6}\,M^{-1}\,s^{-1}$ for the triflate salt) has also been reported,[588] which is considerably faster than an earlier report. A variety of $[Co(NH_3)_6]^{3+/2+}$ electron transfer cross reactions with simple coordination compounds,[589] organic radicals,[590,591] metalloproteins,[592] and positronium particles (electron/positron pairs)[593] as redox partners have been reported.

The simplest member of the hexakis-alkyamines, $[Co(MeNH_2)_6]^{3+}$, possesses a prominent UV ligand-to-metal charge transfer transition.[594] The hexaamine and a number of $[Co(MeNH_2)_5X]^{2+}$ (X = halide) analogs exhibit photoactivity, with ligand substitution, i.e., release of $MeNH_2$, occurring upon either excitation into the N → Co or X → Co LMCT bands. Incorporation of these complexes into thin films of the copolymer of glycidyl methacrylate and ethyl acrylate gave a photosensitive material that underwent base-initiated crosslinking upon exposure to 254 nm radiation.[594,595] This property may be utilized for pattern delineation at the 1–2 μm level. Higher hexakis-alkylamines of Co are yet to be synthesized.

(w) Multidentate. The $[Co(en)_3]^{3+}$ ion is one of the most commonly encountered coordination compounds in undergraduate teaching laboratories as both a precursor [596,597] and as a product.[598] The chirality of the $[Co(en)_3]^{3+}$ complex ion is central to many studies of its chemistry, and it has been the subject of many fundamental investigations that have dealt with the influence of a chiral molecule on its environment and its spectroscopy. There are numerous X-ray crystal structures of both racemic[599–609] and resolved[610–614] $[Co(en)_3]^{3+}$ salts of both simple and complex anions. A novel isotopic crystallographic study[615] found that deuteration of $([Co(en)_3](C_2O_4)I)_2{\cdot}3H_2O$ led to crystallization of $([Co(d_4\text{-}en)_3]I_2{\cdot}D_2O)_2(C_2O_4)$ as a racemate in a centrosymmetric space group whereas the nondeuterated analog crystallized in an acentric space group. The isotope effect on the strength of intermolecular H bonding was held responsible for this unusual phase transformation.

It is usually found that the conformation of the three chelate rings in $[Co(en)_3]^{3+}$ is such that each C–C vector lies approximately parallel (*lel*) with respect to the molecular C_3 axis. This has been examined with a number of experimental and theoretical methods including NMR and IR,[616] vibrational circular dichroism[617] spectroscopy as well as molecular mechanics calculations.[618]

Ion-pairing constants of $[Co(en)_3]^{3+}$ with simple inorganic anions have been reported[571,619] and the rotational correlation times of ion-paired complexes with lanthanoid complex anions have been studied.[620] More specifically, and fundamental to the resolution of racemic $[Co(en)_3]^{3+}$ mixtures, are diastereoselective ion pairing investigations with chiral anions such as tartrate. This has continued to be a major focus of investigation with a variety of theoretical,[621] chromatographic[622–625] and spectroscopic techniques including circular dichroism[626] and NMR.[627]

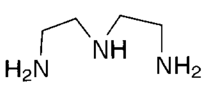
The adsorption[628] and ion exchange[629–631] reactions of chiral $[Co(en)_3]^{3+}$ with clays have been studied. When the $[Co(en)_3]^{3+}$ ion exchanges with lamellar clays such as fluorhectorites, it increases the interplanar separation of the lamellae and influences the selectivity for intercalation of small molecules and atoms (H_2, D_2, Ne, and O_2) within the clay over larger ones such as isobutane and neopentane.[631]

The $[Co(en)_3]^{3+}$ ion has been shown to be a useful template for the synthesis of unusual cobalt, aluminum, gallium, and magnesium phosphates exhibiting framework,[632–637] layered[638–641] and chain[642] structures, as well as for the hydrothermal synthesis of novel zeolites[643,644] and other framework structures such as molybdenum phosphates.[645]

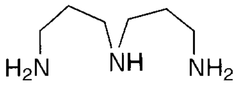
A number of electrochemical studies of the $[Co(en)_3]^{3+/2+}$ couple have been reported, investigating the effects of pressure[646,647] and solvation[648,649] on the redox potential and electron transfer rate. The self-exchange $[Co(en)_3]^{3+/2+}$ electron transfer rate has been determined, and its pressure dependence investigated.[650] Outer sphere electron transfer cross reactions of the $[Co(en)_3]^{3+}$ ion with a variety of cationic,[651] neutral,[652] and anionic[653,654] coordination compounds in addition to reduced viologens,[590,655] flavins, and polymer-immobilized reductants[656,657] have been studied, with the rates of electron transfer usually conforming to predictions from Marcus theory. Ion pairing with potential redox partners may lead to ion pair charge transfer (IPCT) transitions. Excitation into the IPCT transition leads to photoinduced electron transfer between the paired ions. Examples of this include $[Co(en)_3]^{3+}$ paired with tetraphenylborate[658] and a number of cyanometallate anions.[659] As a result of its high isotopic abundance, the technique of ^{59}Co NMR has been used as a sensitive probe for the chemical environment of the metal ion. Studies of $[Co(en)_3]^{3+}$ within micelles[660] and surfactants[661] are known.

There are many variations on the simple tris(bidentate) structure of $[Co(en)_3]^{3+}$, such as expansion of the chelate ring size to six and seven (propane-1,3- and butane-1,4-diamine) or the introduction of alkyl groups and fused rings for chirality and rigidity (propane-1,2-diamine and *meso* and *rac*-cyclohexane-1,2-diamine). These analogs, although yielding interesting chemistry, will not be explored here.

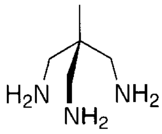
Tridentate amines come in a variety of forms. Diethylenetriamine (dien) (**129**) and its bis-trimethylene homolog ditn (**130**) may adopt either facial or meridional coordination modes. Furthermore, the *fac*-$[Co(dien)_2]^{3+}$ complex may exist as either the centrosymmetric *meso* or dissymmetric *rac* isomer where the secondary amines are *trans* or *cis* respectively.[662] However, there are some triamines that coordinate exclusively in a facial configuration due to stereochemical requirements of the ligand. Some examples include the symmetrical tripods tame[663] (**131**), *cis,cis*-cyclohexane-1,3,5-triamine (tach)[664] (**132a**) (including its 2,4,6-trihydroxy analog, taci[665] (**132b**)) and triazatrishomobenzene (**133**).[666]



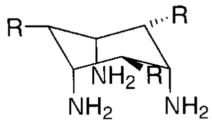
(**129**)



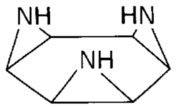
(**130**)



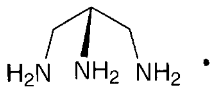
(**131**)



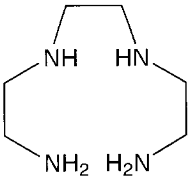
(**132a**) R=H
(**132b**) R=OH



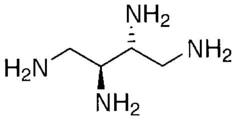
(**133**)



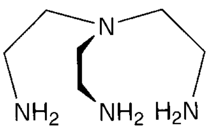
(**134**)



(**135**)



(**136**)

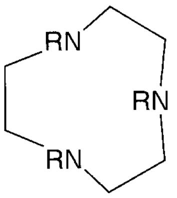


(**137**)

The less symmetrical and more rigid propane-1,2,3-triamine (trap) (**134**) has also been complexed with Co^{III}.[667] Even more isomers arise with linear tetraamines such as triethylenetetraamine (trien)[668] (**135**) or its branched homolog *rac*-butane-1,2,3,4-tetraamine[669] (**136**) when bound to Co^{III}, and this number proliferates when the amine is asymmetric. The tripodal tris(2-aminoethyl)amine (tren) (**137**) may bind as tri- or tetradentate to Co in various oxidation states;[670,671] the latter binding mode resulting in a single stereoisomer. There are simply too many combinations of these amines and their co-ligands to do justice to their chemistry in this review. A review of trivalent Co amine chemistry is available, which covers this area in greater detail than space permits herein.[672]

(x) Macrocyclic. There are many potential rewards for synthetic efforts devoted to the closure of open chain multidentate amines to afford their macrocyclic analogs. Enhanced complex stability (particularly upon conversion to the divalent state) and greater stereochemical control are the two most obvious benefits. Additionally, the ring may provide a scaffold onto which extra functional groups may be attached to give so-called pendent arm macrocycles. General reviews concerned with complexation and structural aspects of N-functionalized polyazamacrocycles (of various sizes, in complexes with a range of metal ions) have appeared.[673,674]

The smallest macrocyclic amine is the facially coordinating tridentate 1,4,7-triazacyclononane (tacn or [9]aneN_3) (**138a**). The $[Co(tacn)_2]^{3+}$ ion exhibits physical properties typical of other hexaamines, and the complex has been thoroughly characterized.[463,675] Like other macrocyclic amines, the outer sphere electron transfer reactions involving the $[Co(tacn)_2]^{3+/2+}$ couple with proteins[676] and simple coordination compounds[677] as well as its electrochemistry[678] have been well studied.

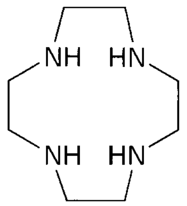


(**138a**) R=H
(**138b**) R=Me
(**138c**) R=*i*-Pr
(**138d**) R=*i*-Bu
(**138e**) R=$CH_2CH_2NH_2$
(**138f**) R=$CH_2CH_2CH_2NH_2$
(**138g**) R=CH_2-2-pyridyl
(**138h**) R=CH_2COO^-
(**138i**) R=(*R*)$CH(CH_3)COO^-$
(**138j**) R=(*S*)$CH(CH_3)OH$
(**138k**) R=2-CH_2(Me-imidazole)
(**138l**) R=CH_2-pyrazole

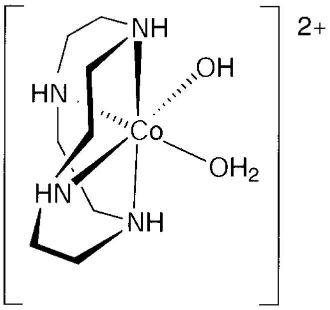
In contrast to its secondary amine parent, the *N*-trimethylated derivative (**138b**) (tmtacn) has a distinct preference for 1:1[679] or 2:2[399] metal:ligand stoichiometries as a consequence of steric effects of its methyl groups. Face-sharing octahedral, bridged dinuclear complexes of the type $[\{(\text{tmtacn})\text{Co}\}_2(\mu\text{-X})_3]^{n+}$ (where $X = OH^-$, Cl^-, Br^-, AcO^-) are known where the metals can be in either their di- or trivalent states (or mixed valence).[399,680] The sterically encumbered tris-isopropyl (**138c**) and isobutyl (**138d**) analogs of tacn have been reported and complexed with Co.[681] Mononuclear complex formation is favored in these cases.

A vast array of hexadentate, threefold symmetric tris-*N*-substituted derivatives of tacn have been reported incorporating a variety of pendent groups such as those seen in (**138e**),[682] (**138f**),[683] (**138g**),[684] (**138h**),[685,686] (**138i**),[652] (**138j**),[687,688] (**138k**)[689] and (**138l**),[690] each of which has been complexed with Co^{III} and characterized. Wieghardt and co-workers have identified many interesting trisubstituted tacn derivatives featuring phenolate or thiophenolate ligating groups that, when complexed with Co^{III}, are capable of stabilizing ligand-centered radicals. Examples include homo- and heterotrisubstituted tacn ligands such as tris(3,5-di-*tert*-butyl-2-hydroxybenzyl), tris(3-*tert*-butyl-5-methoxy-2-hydroxybenzyl), diacetate-(3,5-di-*tert*-butyl-2-hydroxybenzyl), diacetate-(2-mercaptobenzyl), diacetate-(3,5-di-*tert*-butyl-2-mercaptobenzyl), dimethyl-(3-*tert*-butyl-5-methoxy-2-hydroxybenzyl), and di-isopropyl-(3,5-di-*tert*-butyl-2-hydroxybenzyl) where Co^{III}-phenoxyl or Co^{III}-phenylthiyl radicals are formed upon oxidation of the complex.[691–693] Pendent arms bearing donors capable of bridging two metal centers (alkoxides, phenolates, and thiophenolates) have been reported and the degree of magnetic coupling mediated by the bridging ligand has been studied.[694,695] Mono-*N*-substituted derivatives of tacn in complexes with Co^{III} include 2-aminoethyl[696] and the versatile ethylene-bridged bis-macrocycle 1,2-bis(1,4,7-triaza-1-cyclononyl)ethane (dtne),[697] which is capable of both mononuclear and dinculear complex formation.

The Co^{III} coordination chemistry of the 12-membered macrocyclic tetraamine 1,4,7,11-tetraazacyclododecane (**139**) (cyclen or $[12]aneN_4$) has been extensively studied. A feature of this macrocycle, like tacn, is that its small ring size restricts its mode of coordination. All known Co^{III} cyclen complexes exhibit *cis*-N_4X_2 coordination geometries, where the macrocycle folds to leave a pair of *cis* coordination sites available for other ligands, although *N*-based isomers are known. There has been a particular focus on the reactivity of the $[\text{Co}(\text{cyclen})(\text{OH}_2)(\text{OH})]^{2+}$ ion (**140**) towards polyphosphate and phosphate ester hydrolysis, and its relevance to biomimetic chemistry (see Section 6.1.3.1.3). Attachment of active substituents to the cyclen N donors may be achieved with standard alkylation procedures. A number of Co complexes of tetra-*N*-substituted cyclen derivatives bearing both coordinating (2-carbamoylethyl[698]) and non-coordinating (2-cyanoethyl[699]) pendent arms have been reported. The incorporation of C substituents on the ring instills chirality in the ligand and its complexes. Examples of this approach include a homochiral C-tetraethyl cyclen Co complex which forms diastereomeric pairs of complexes with bidentate coordinated amino acids such as methionine[700] and methyltyrosine.[701]



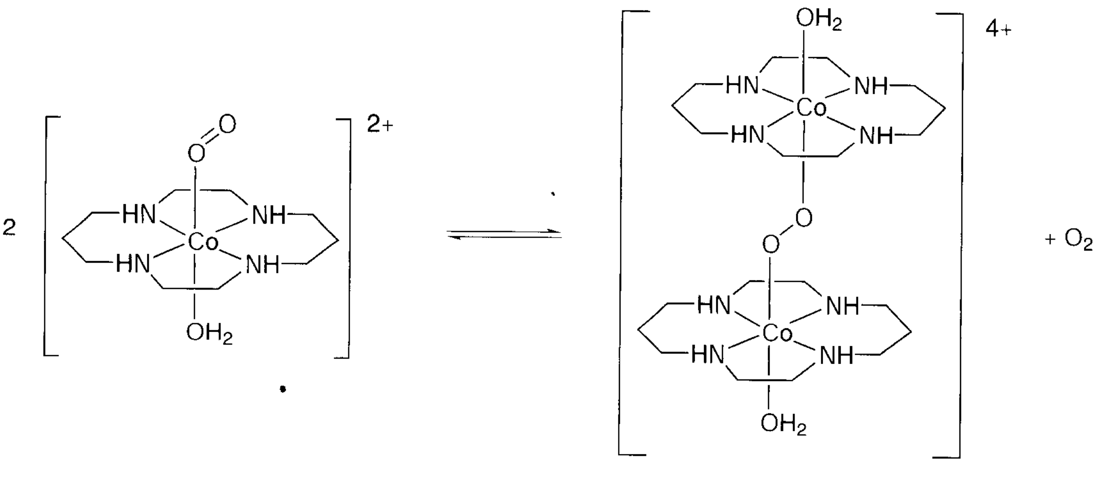
(139)



(140)

The 14-membered macrocycle 1,4,8,11-tetraazacyclotetradecane (cyclam or $[14]aneN_4$), unlike cyclen, is capable of encircling most transition metal ions and in the case of Co^{III} the *trans* configuration is much preferred by comparison with the folded *cis* isomer. Electrochemical reduction of *cis*-$[\text{Co}(\text{cyclam})(\text{OH})_2]^+$ in 3M NaOH leads to rapid isomerization to the *trans* form, and the relative stabilities of the *trans* and *cis* isomers of the di- and trivalent complexes were determined from a thermodynamic cycle.[702] This preference for *trans* orientation of the non-macrocyclic donors has enabled the isolation and investigation of many Co complexes without the complications of isomerization. Some novel examples include *trans*-$[\text{Co}(\text{cyclam})(\text{O}_2^{-\cdot})(\text{OH}_2)]^{2+}$

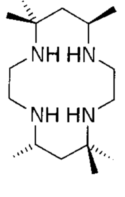
(**141**), which exists in equilibrium with its peroxo-bridged dinuclear analog (**142**).[703] The mononuclear hydroperoxo analog was found to accelerate the rate of I^- oxidation (to I_3^-) by three orders of magnitude relative to H_2O_2.[704]



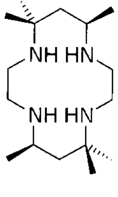
(**141**) (**142**)

Due to their ease of synthesis (from the cation-templated condensation reaction of ethylenediamine and acetone), C-methylated analogs of cyclam such as *meso* and *rac* 5,5,7,12,1214-hexamethylcyclam (tet*a* (**143a**) and tet*b* (**143b**) respectively) have been extensively studied, where the stereogenic C-atoms in the 7- and 14-positions of the ring lead to distinctly different coordination chemistries. The racemic ligand (**143b**) has been resolved and its resulting chiral Co^{III} complexes have been investigated.[705] A number of crystallographic[706,707] and spectroscopic[100,708] studies of these ligands in complexes with Co^{III} have been reported. The steric effects of the C-methyl groups influence the reactivity and stereochemistry of their resulting Co complexes significantly relative to the unsubstituted cyclam parent. The unusual hydroperoxocobalt complex [Co(tet*a*)(MeCN)(OOH)]$(ClO_4)_2$ has been isolated and structurally characterized.[709] The O—O stretch in the IR spectrum appears at 815 cm^{-1} and photolysis of an acidic aqueous solution of the complex results in homolytic splitting of the Co—O bond, yielding the diaqua complex as a product. The reaction of aminomethylmalonate with *cis*-[Co(tet*b*)$Cl_2]^+$ in DMSO in the presence of Et_3N yielded a novel 2-iminocarboxylato complex via oxidative decarboxylation of the malonate ligand. The reaction is specific for Co^{III} complexes containing C–Me-substituted cyclic tetraamines.[710]

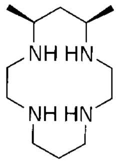
A remarkable variety of methylated analogs are known and their Co^{III} complexes have all been synthesized and characterized. Examples include 5,7-dimethylcyclam (*meso* isomer) (**144**),[711,712] 5,12-dimethylcyclam (*meso* (**145**) and *rac* isomers),[713,714] 5,5,7-trimethylcyclam (**146**),[711] 5,7,12,14-tetramethylcyclam (**147**),[715] 1,5,8,12-tetramethylcyclam (**148**)[716] and 3,10-C-*meso*-3,5,7,7,10,12,14,14-octamethylcyclam (**149**).[717]



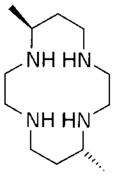
(**143a**)



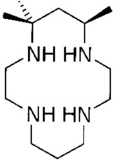
(**143b**)



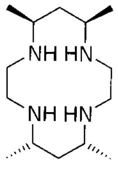
(**144**)



(**145**)



(**146**)



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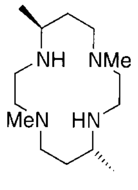
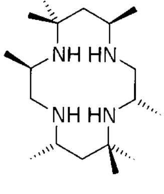


(**148**)

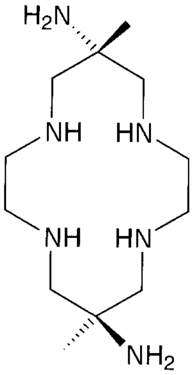


(**149**)

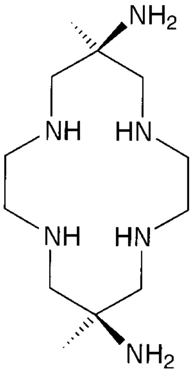
Ligating pendent arms have been attached to the cyclam ring to give penta- and hexadentate coordinated cyclams coordinated to Co. *N*-functionalization of the macrocycle is synthetically more straightforward, although the resulting (tertiary) amine donors are less effective ligands due to the increased steric effects of the pendent group. An example of this that has been complexed to Co^{III} is the hexadentate 5,12-dimethyl-7,14-diphenyl-4,11-diacetatocyclam.[718]

Actually, C-substituted cyclams are more common in the coordination chemistry of Co, with ligating pendent groups typically attached to the trimethylene ring C atoms. The synthetic strategies are many and varied. An unusual example concerns conversion of *trans*-[Co(tet*a*)Cl$_2$]$^+$ to its 5-hydroxymethyl analog by aerial oxidation of the precursor in refluxing MeOH containing Et$_3$N.[719] 5-Aminomethyl-2,5,10,12-tetramethylcyclam was prepared by nucleophilic addition of MeNO$_2$ to the imine precursor, followed by reduction of the pendent nitromethyl group.[720] The chlorocobalt(III) complex of this pentaamine ligand was characterized structurally and rapid base hydrolysis of the chloro ligand was reported.

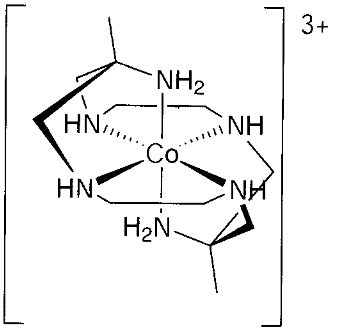
The *trans*[721] (**150**) and *cis*[722,723] (**151**) isomers of the hexadentate ligand 6,13-diamino-6,13-dimethylcyclam (also known as diammac) have been complexed with Co^{III} and characterized structurally, spectroscopically, and electrochemically. The ligands are synthesized by a metal-directed condensation reaction between [Cu(en)$_2$]$^{2+}$, EtNO$_2$, and formaldehyde, followed by reduction of the nitro groups. Each isomer may coordinate in but one hexadentate configuration, thus the isomers [Co(*trans*-diammac)]$^{3+}$ (**152**) and [Co(*cis*-diammac)]$^{3+}$ (**153**) provide a unique example of *trans*/*cis* isomerism at a metal center predetermined by ligand stereochemistry. In [Co(*trans*-diammac)]$^{3+}$, the Co—N bond lengths are amongst the shortest reported for a Co^{III} hexaamine, and this leads to unusually high-energy electronic maxima and a particularly negative Co$^{III/II}$ redox potential.[721] By contrast, the structural,[723] spectroscopic, and electrochemical[722] properties of [Co(*cis*-diammac)]$^{3+}$ are typical of other hexaamines such as [Co(en)$_3$]$^{3+}$. A rapid Co$^{III/II}$ self-exchange electron transfer rate was determined[721] for [Co(*trans*-diammac)]$^{3+}$ and, coupled with its particularly negative Co$^{III/II}$ redox potential, it was found to efficiently catalyze the reduction of H$^+$ when adsorbed in its divalent form to a Hg working electrode.[724]



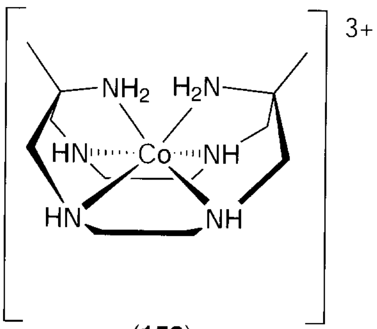
(**150**)



(**151**)

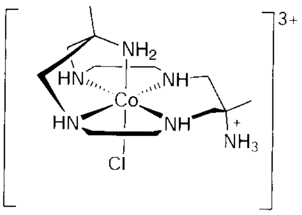


(**152**)



(**153**)

Other coordination modes of *trans*-diammac have been identified where one (**154**) or both (**155**) primary amines are free from the metal.[721,725] An extension of this concept involves attachment of active functional groups such as crown ethers selectively at one primary amine to generate ditopic ligands capable of electrochemically sensing alkali metal ions through their inductive effect on the Co$^{III/II}$ redox potential. One example is provided by (**156**); further, the 15-crown-5 and 18-crown-6 analogs were also prepared.[726]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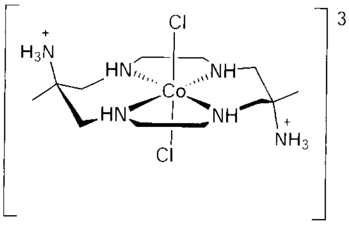
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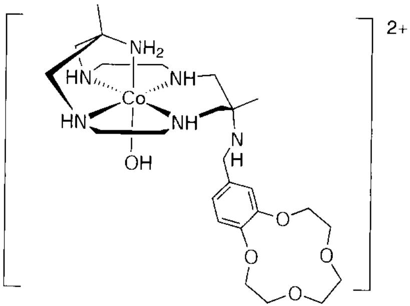
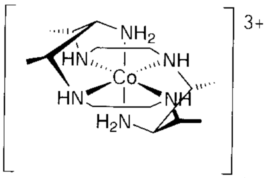

(156)

Some diammac analogs complexed with Co^{III} include 6,13-diamino-6,13-diethylcyclam (*trans* and *cis* isomers),[727] and the isomeric *meso*-5,7,12,14-tetramethyl-6,13-diaminocyclam (**157**) (*trans* isomer). The 6-amino-6-methyl analog (ammac) may only occupy five coordination sites and its greater degree of flexibility leads to *trans* (**158**)[728,729] and *cis* (**159**)[730] coordination modes when bound to Co^{III}. The ability to isolate non-interconverting isomeric forms of these pentaamine Co^{III} complexes has enabled the investigation of steric and electronic effects on the rates of reactions at the sixth coordination site such as base hydrolysis of coordinated Cl^{-}[728,730,731] and nitrito to nitro linkage isomerism.[732] The introduction of ferrocyanide as a ligand (N bound to Co) into the sixth coordination site of these Co complexes results in a novel class of dinuclear mixed valent compounds (**160**) exhibiting a prominent Fe$^{II}\rightarrow$Co^{III} metal-to-metal charge transfer transition in the visible region of the spectrum.[733,734] A number of other examples of mono-C-substituted cyclam ligands coordinated to Co^{III} include 5-(4′-imidazolyl)cyclam,[735] and 6-amino-6-(4′-aminobenzyl)cyclam.[736–738]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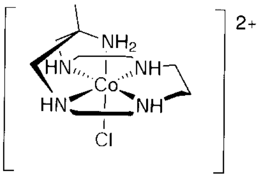
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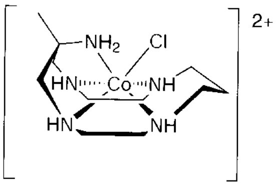
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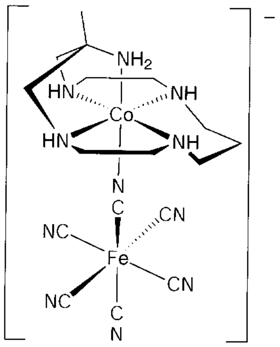
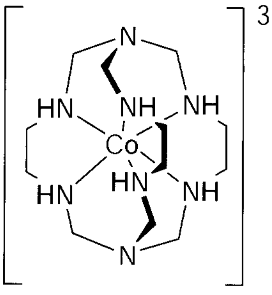

(160)

Sargeson and co-workers pioneered the metal template syntheses of a class of ligands that effectively encapsulate the metal ion within a macrobicyclic N$_6$ array or secondary amines. Most of this work focused on [Co(en)$_3$]$^{3+}$ as a template onto which two "caps" were attached using Mannich reactions involving formaldehyde and a potentially tribasic nucleophile such as NH$_3$ or MeNO$_2$, leading to the sepulchrate (sep) (**161**)[739] and substituted sarcophagine (sar) (**162a**)[740] Co^{III} cage complexes, respectively (Equation (7)). The initial reports of this chemistry focused on (**161**) and its Co^{II} analog. Remarkable physical properties of this system were reported,[219] including an unusually inert divalent complex. The [Co(sep)]$^{3+/2+}$ self-exchange rate constant was found to be several orders of magnitude greater than that of the [Co(en)$_3$]$^{3+/2+}$ parent. Moreover, the cage redox couple is reversible.

The C-capped [Co(sar)]$^{3+}$ (**162a**) (and its various homo- and hetero-disubstituted derivatives) exhibit very similar structural[741] and physical properties, although the sar class of ligands has the advantage of being isolable as the metal-free base,[742] in contrast to sep which is unstable in the absence of Co. A number of electrochemical investigations of [Co(sep)]$^{3+}$ and [Co(sar)]$^{3+}$ (and its substituted analogs) have appeared.[743,744] The facile and reversible one-electron redox chemistry of these complexes has led to their employment as electron relays in the photoinduced oxidation of coordination compounds such as [Ru(bpy)$_3$]$^{2+}$[745–747] and organic photosensitizers such as



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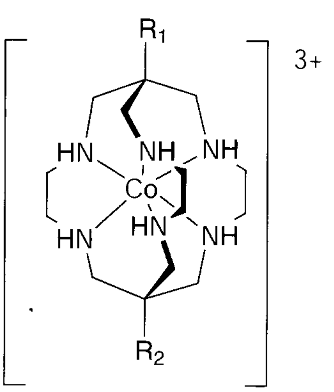


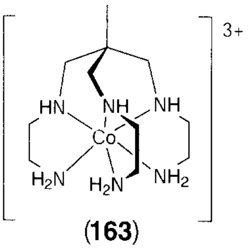
(162a) $R_1=R_2=H$
(162b) $R_1=R_2=NO_2$
(162c) $R_1=R_2=NH_2$
(162d) $R_1=R_2=Cl$
(162e) $R_1=CH_3R_2=H$
(162f) $R_1=CH_3R_2=NO_2$
(162g) $R_1=CH_3R_2=NH_2$
(162h) $R_1=CH_3R_2=4\text{-py}$

$$[\mathrm{Co(en)_3}]^{3+} + 6\mathrm{CH_2O} + 2\mathrm{NH_3} \xrightarrow{\text{base}} (\mathbf{161})$$

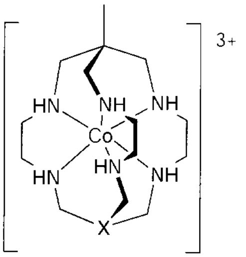
$$[\mathrm{Co(en)_3}]^{3+} + 6\mathrm{CH_2O} + 2\mathrm{MeNO_2} \xrightarrow{\text{base}} (\mathbf{162b}) \xrightarrow{\text{Zn/HCl}} (\mathbf{162c}) \xrightarrow{\mathrm{HNO_3/Cl^-}} (\mathbf{162d}) \xrightarrow{\text{Ni(Al)}} (\mathbf{162a}) \tag{7}$$

anthracene.[748,749] Outer sphere electron transfer between divalent Co cages and metalloproteins such as plastocyanin[750] and cytochrome *c*[751] has been demonstrated. The amino substituents of $[\mathrm{Co(NH_2)_2sar}]^{3+}$ have been used to attach a variety of functional groups through either reductive alkylation[752,753] or amide coupling.[754]

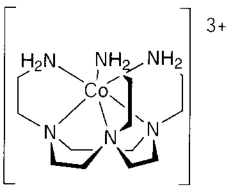
Other "capping" reagents and templates have been employed to create Co cages with different substituents, donor atoms, and chelate ring sizes. The acyclic hexaamine complex $[\mathrm{Co(sen)}]^{3+}$ (**163**) offers one set of facially coordinated primary amines when bound to $\mathrm{Co^{III}}$ and this template has been used to synthesize a number of similar cages bearing an inert methyl group at one cap. By analogy with the chemistry employed in the synthesis of $[\mathrm{Co(sep)}]^{3+}$, the group 15 hydrides $\mathrm{NH_3}$,[219] $\mathrm{PH_3}$,[755] and $\mathrm{AsH_3}$[756],with $\mathrm{CH_2O}$ have been used as capping reagents for $[\mathrm{Co(sen)}]^{3+}$ to form their respective cages (**164a–c**). Synthesis of the P- and As-capped cages required anhydrous conditions (and paraformaldehyde), and the P-oxide analog of (**164b**) was also isolated from the synthesis of its phosphine cage precursor.[755] The longer As—C bonds in (**164c**) induce a conformational change (*lel*$_3$ to *ob*$_3$) in the ethylenediamine chelate rings of the cage relative to their precursor conformers.[756] The $\mathrm{Co^{III}}$ complex of the hexadentate ligand *N*,*N*′,*N*″′-tris(2′-aminoethyl)-1,4,7-triazacyclononane (**165**) also offers three facially coordinated primary amines, and this complex reacts with formaldehyde and either $\mathrm{NH_3}$ or $\mathrm{MeNO_2}$ to give the corresponding tricyclic cages (**166a–c**).[682]



(163)



(164a) X=N
(164b) X=P
(164c) X=As



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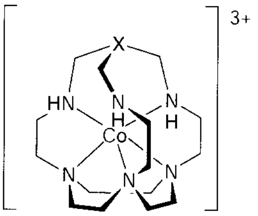
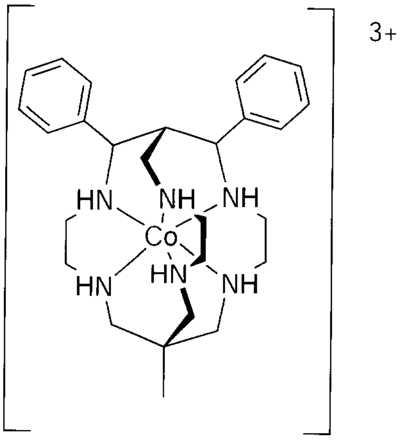


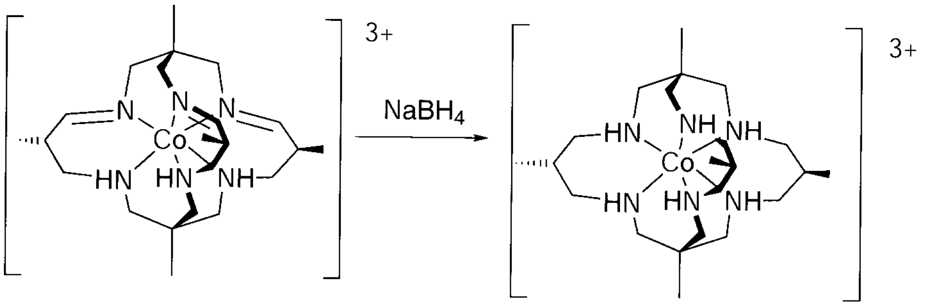
(166a) X=N
(166b) $X=C\text{-}NO_2$
(166c) $X=C\text{-}NH_2$

The use of formaldehyde with carbon acids including higher aldehydes, ketones, and esters has seen the expansion of this chemistry to incorporate many other substituents into the cap of the cage. *N*-benzylation of 4-methylpyridine enhances the acidity of the methyl group sufficiently to enable its employment as a carbon acid. The pyridyl-capped cage (**162h**) results.[757] Condensation of the diketone dibenzoylmethane with $[Co(sen)]^{3+}$ and formaldehyde leads to a diphenyl-substituted diimine cage, which may be reduced to the corresponding amine (**167**), with stereogenicity induced at the reduced imine C atoms.[758] Methyl aryl ketones ($ArCOCH_3$) are also sufficiently acidic to enable their use as capping reagents for $[Co(sen)]^{3+}$ in combination with paraformaldehyde, which leads to the corresponding aroyl-substituted cage (Ar = phenyl, naphthyl, phenanthryl, anthracenyl, anthroquinonyl).[759] These compounds have been proposed as candidates for DNA intercalation[760] and also as photosensitizers.



(167)

Variations on the basic bicyclo-eicosane (20-membered) $[Co(sar)]^{3+}$ cage structure were a later development. Instead of capping the $[Co(en)_3]^{3+}$ or $[Co(sen)]^{3+}$ templates, "strapping" reactions involving the threefold cross linking of $[Co(tame)_2]^{3+}$ (**30**) with combinations of aldehydes have been achieved, albeit in poorer yields. The first example of this approach involved the synthesis of the pentamethyl expanded bicyclo-tricosane (23-membered) triimine cage (**168**) with formaldehyde and propionaldehyde as the strapping reagents, followed by imine reduction to the hexamine (**169**). The hexamine exhibits contrasting physical properties with its smaller-cavity $[Co(sar)]^{3+}$ relatives (**162**) such as an anodically shifted $Co^{III/II}$ redox potential, elongated Co—N bond lengths and red-shifted electronic maxima.[761] Substitution of priopionaldehyde with isobutyraldehyde in this synthesis leads to further stabilization of divalent Co. The ensuing octamethylated hexamine analog of (**169**) (with *gem*-dimethyl groups on each strap), is as stable in the divalent oxidation state as compound (**31**), and the trivalent complex is only accessible through using controlled potential electrolysis.[220]



(168) **(169)**

(ii) Pyridine and oligopyridines

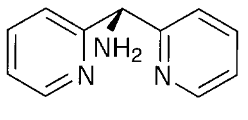
(y) Monodentate. No trivalent Co complexes bearing six pyridine ligands are known. The *trans*-$[Co(py)_4(OH_2)_2]^{3+}$ and $[Co(py)_4(OH)_2]^+$ complexes are known, but they are highly reactive in acidic chloride solution to ligand substitution and ultimately to reduction to the divalent state.[762]

(z) Multidentate. There are many parallels between the coordination chemistries of the bidentate ligands 2,2′-bipyridine (bpy) and 1,10-phenanthroline (phen). Both ligands form five-membered chelate rings comprising a pair of pyridyl N-donors, and they stabilize the trivalent forms of their Co complexes relative to the unknown $[Co(py)_6]^{3+}$ analog. This can be attributed to the chelate effect but also to the elimination of H ··· H repulsion in the pyridyl complex through the formation of covalent C—C bonds in their place. Both $[Co(bpy)_3]^{3+}$ and $[Co(phen)_3]^{3+}$ are well-characterized, stable low-spin complexes. The crystal structures of both $[Co(phen)_3](ClO_4)_3$ and $[Co(bpy)_3](ClO_4)_3$ have been reported.[763] The $[Co(bpy)_3]^{3+}$ ion has been crystallized with a number of paramagnetic complex anions and the magnetic and spectroscopic properties of these systems have been studied.[764,765] Furthermore, it is found that the inert chiral Co^{III} complex induces the crystallization of chiral, anionic three-dimensional coordination polymers of oxalate-bridged metal complexes of the form $[M^{II}_2(ox)_3]_n^{2n-}$ or $[M^IM^{III}(ox)_3]_n^{2n-}$.[764]

Outer sphere electron transfer reactions involving these complexes have been extensively investigated. The high Co$^{III/II}$ redox potentials of the bpy and phen complexes make them ideal one-electron oxidants. The pressure-dependence of their redox potentials have been examined, with substantial (ca. 200 mV) negative shifts being found at high pressure (10 kbar).[766] Outer sphere reactions of $[Co(bpy)_3]^{3+}$ and $[Co(phen)_3]^{3+}$ with simple coordination compounds have revealed a number of interesting features. Reaction with $Cr_{aq}{}^{2+}$ led to a variety of products including $[Cr_2(bpy)(OH)_2(OH_2)_6]^{4+}$, $Co_{aq}{}^{2+}$, $[Co(bpy)(OH_2)_4]^{3+}$, in addition to uncomplexed (intact) bpy and reduced bpy.[767] The kinetics of oxidation of a series of $[Ru(NH_3)_5X]^{2+}$ complexes (X = substituted pyridine) by $[Co(bpy)_3]^{3+}$ have been studied,[768] with the electron transfer rates being correlated with Hammett sigma parameters of the pyridyl substituents. Oxidation of the $[Cr(bpy)_3]^{2+}$ and $[Cr(phen)_3]^{2+}$ ions by their Co^{III} analogs were found to be significantly non-adiabatic,[651] a result confirmed in other outer sphere reactions involving these oxidants where a large driving force is operant.[769] A number of other studies of electron transfer with Co^{II}[589,770] and ferrocene[771] have appeared. Outer sphere electron transfer reactions between proteins and polypyridylcobalt complexes are discussed in Section 6.1.3.1.5.

Chiral recognition of Δ-$[Co(phen)_3]^{3+}$ has been observed in a modified β-cyclodextrin.[772] Chiral discrimination has also been seen in photoinduced energy transfer from luminescent chiral lanthanoid complexes[773] to $[Co(phen)_3]^{3+}$ and between photoexcited $[Ru(bpy)_3]^{2+}$ and $[Co(phen)_3]^{3+}$ co-adsorbed on smectite clays.[774] The $[Co(bpy)_3]^{3+}$ ion has been incorporated into clays to generate ordered assemblies and also functional catalysts. When adsorbed onto hectorite, $[Co(bpy)_3]^{3+}$ catalyzes the reduction of nitrobenzene to aniline.[775] The ability of $[Co(phen)_3]^{3+}$ to bind to DNA has been intensively studied, and discussion of this feature is deferred until Section 6.1.3.1.4.

The structures of Co complexes of the tridentate terpy invariably exhibit a compression of the Co—N$_{central}$ coordinate bonds relative to the Co—N$_{distal}$ bond lengths, as a consequence of restraints imposed by the meridionally disposed pair of five-membered chelate rings. This is clearly seen in the $[Co(terpy)_2]Cl_3$ crystal structure[776] where the Co—N$_{central,distal}$ bond lengths are 1.86 Å and 1.93 Å respectively. Like their amine analogs, there are countless examples of more complicated mixed-donor pyridyl-based ligands complexed with Co and these examples cannot be covered in a review of this breadth. Some miscellaneous examples of mixed-donor polypyridyl-amine complexes of Co^{III} include di(2-pyridyl)methanamine (**170**),[777] and *N,N,N′,N′*-tetrakis (2-pyridylmethyl)ethylenediamine (**171**).[778]



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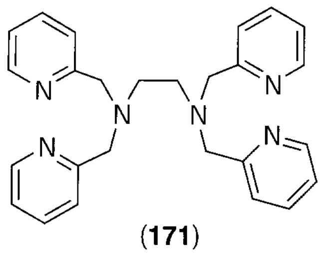
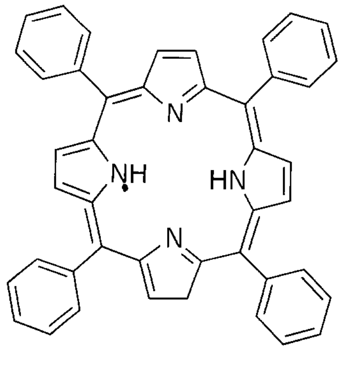


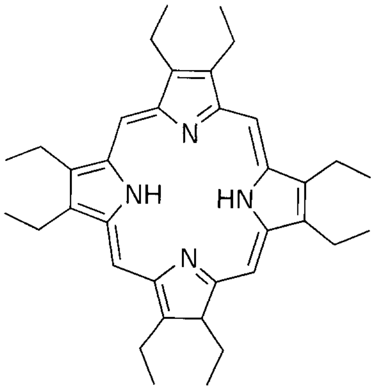
(171)

(iii) Porphyrins, corrinoids, and polypyrroles

Trivalent complexes of porphyrins (like their divalent analogs) have found many uses in sensor technology and catalysis. *Meso*-tetraphenylporphyrin (H_2TPP) (**172**), the most common of all synthetic porphyrins, has been used extensively in this regard. The $\{Co^{III}(TPP)\}$ moiety has been incorporated into a chemically modified, heat-treated glassy carbon electrode to produce an amperometric sensor for hydrazine operating at 0.5 V vs. Ag/AgCl, incorporated into a flow injection analysis system.[779] A substituted analog Co(TmapP) (Tmap = 4-trimethylammoniumphenyl) also exhibited catalytic electro-oxidation of hydrazine in solution.[780]



(**172**)

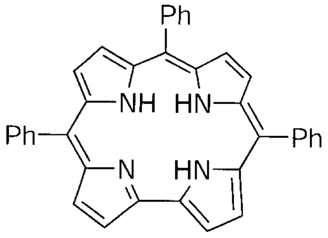


(**173**)

It has been shown that Co^{III} porphyrins are effective oxygenation catalysts. Alkyl- and aryl-substituted Co complexes of the dianions of H_2TPP and H_2OEP (**173**) undergo dioxygen insertion reactions to form alkyl(aryl) peroxy intermediates, which have been isolated and characterized.[781] The alkylperoxy complexes ultimately break down to release the corresponding alcohol. Peroxidation of fatty acids and esters (linoleic acid, methyl linoleate, and linolenic acid) has been achieved with Co(TPP)Cl as a precursor, which initiates an auto-oxidative radical-chain reaction in oxygen-saturated MeCN solution. Another transformation catalyzed by a Co porphyrin is the oxidation of $CH_2{=}CHCH{=}CHCO_2Et$ to $MeCH_2COCH{=}CHCO_2Et$ catalyzed by $Co(T\ (2,6\text{-}Cl_2Ph)P)$.[782]

A detailed chemical and electrochemical investigation of the oxidation and coupled chemical reactions of alkyl substituted trivalent Co(TPP)R (R = Bu, Et, Me, Ph) found that one- or two-electron oxidation of the Co^{III} σ-bonded complexes led to R group migration to give the *N*-aryl or *N*-alkyl Co^{II} porphyrins.[783] The rates of migration (from Co to N) in the series varied by six orders of magnitude. Determination of the Co—C bond dissociation enthalpies and entropies revealed that the Co^{IV}—C bond in the singly oxidized species is significantly weaker than the Co^{III}—C bond of the precursor. A high-valent $Co^{IV}{=}O$ intermediate was postulated as the active species in the catalytic hydroxylation of alkanes by an electron-deficient Co^{III} porphyrin in the presence of *m*-chloroperbenzoic acid with high regioselectivity.[784] $Co(TPP)(NO_2)(py)$ is capable of oxo-transfer catalysis, involving a pentacoordinate $Co(TPP)(NO_2)$ intermediate which can stoichiometrically oxidize allyl bromide.[785] Both radical and nonradical oxo-transfer steps are involved in the mechanism, suggesting a peroxynitro intermediate in the reaction of reduced Co(TPP)(NO) with dioxygen. Kinetics of the reaction of the porphyrin complex Co(TTP)Cl with a range of substituted imidazoles (R-im) has shown that Co(TTP)(R-im)Cl is formed rapidly, then undergoes slower interconversion by rate-determining chloride ionization to the cationic complex [Co(TTP)(R-im)]Cl, a process sensitive to hydrogen-bonding interactions.[786]

The ring-contracted analogs of the porphyrin family (corroles) and their hexahydro derivatives (corrins) have attracted a considerable amount of attention because of their biological relevance (the Co–corrin moiety is found in co-enzyme B_{12}, see Section 6.1.3.1.1) and also due to their potential use in optoelectronics and catalysis. By analogy with their porphyrin relatives, substituents on the corrole ring may be found at the *beta* (pyrrole) or *meso* (methine) positions. An important distinction between these ligands is that the smaller ring corrole is a tribasic acid, in contrast to its dibasic porphyrin analogs. The 5,10,15-triphenylcorrole (H_3TPC) (**174**) may be synthesized in one pot by reaction of benzaldehyde with an excess of pyrrole (the same reagents used in the synthesis of H_2TPP).[787] The crystal structure of $Co(TPC)(PPh_3)$ was also reported.



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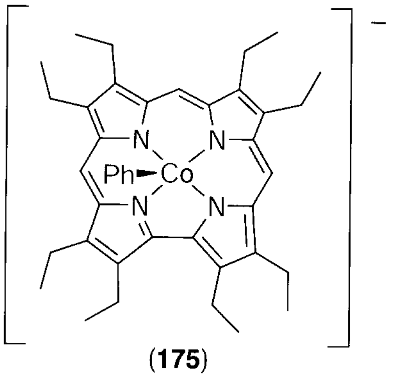
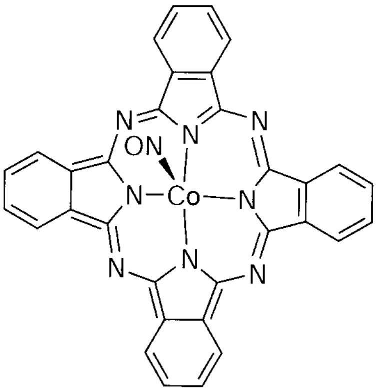


(175)

In the tris-pentafluorophenyl analog (TFPC), in contrast to other Co corroles, aromatic amines can substitute PPh_3 to form six-coordinate trivalent bis(amine) complexes.[788] Bis-chlorosulfonation of TFPC occurs regioselectively to give the 2,17-(pyrrole)-bis-chlorosulfonated derivative fully characterized as its triphenylphosphinecobalt(III) complex.[789] The amphiphilic bis-sulfonic acid was also obtained.

Electrochemical oxidation of the Co^{III} complex of the octamethylcorrole trianion (OMC) identified two reversible, ligand-centered responses, and two metal-centered reductions, depending on solvent.[790] Similarly, the octaethyl analog $[PhCo(OEC)]^-$ (**175**) undergoes sequential facile ligand-centered oxidations and the crystal structures of the one and two-electron oxidised complexes PhCo(OEC) and $[PhCo(OEC)]ClO_4$ have been determined.[791] A number of *meso*-phenyl substituted derivatives of OMC were reported and spectroscopic measurements indicated the maintenance of ligand planarity despite the insertion of the bulky aromatic groups.[792] The structures of a number of alkylcobalamin complexes have been investigated by molecular mechanics calculations, and it was concluded that the structure of the ground state is influenced by the same factors that control the strength of the Co—C bond in these compounds.[793] A density functional theory analysis of these complexes has been reported and the results from this study are consistent with experimentally observed structural and magnetic data for the ground state electronic configurations of these compounds.[794] Dimeric corrole complexes of Co have been investigated bearing bridges such as anthracene.[795] This and other "face-to-face" Co–corrole dimers are capable of catalyzing the four-electron reduction of O_2 to water.[796]

Co–corrins are also efficient catalysts of a number of (bio)organic transformations including the oxidation of quinols,[797] raising the possibility of their use as catalytic generators of oxygen-based radicals for targets such as DNA. The nitrosyl phthalocyanine complex Co(Pc)(NO) (**176**) reacts with pyridine in air at high pressure to give the nitro complex $Co(Pc)(py)(NO_2)$ which is an oxidant for the stoichiometric and catalytic oxidation PPh_3 to Ph_3PO (in an inert atmosphere) regenerating the nitrosyl complex.[798]



(176)

(iv) Imidazole, pyrazole, and related ligands

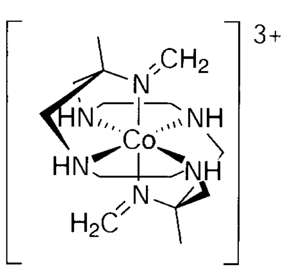
These heterocyclic unsaturated ligands share similar coordination chemistry with trivalent Co. The isomers imidazole (Him) and pyrazole (Hpz) are monodentate ligands in their neutral state. Upon deprotonation, they gain the ability to act as bridging ligands. Oxidation of $[Co(Him)_6]^{2+}$ with H_2O_2 generates the trivalent octahedral complex.[799] The first three pK_a values of the $[Co(Him)_6]^{3+}$ ion were determined to be 8.65, 9.88, and 10.63. The pK_a values of coordinated imidazole itself (or as part of a histidyl residue) have been determined for $[Co(NH_3)_5(Him)]^{3+}$,[800] $[Co(en)_2(Him)(OH_2)]^{3+}$[801] and in the peptide histidylglycylglycine complex $Co(hisglygly)(NH_3)_2$.[802] In these cases, the imidazole pK_a is in excess of 10. The Co^{III} complex of the peptide N-(2-(4-imidazolyl)ethyl)pyridine-2-carboxamide (PyepH), a molecule resembling part of the metal-chelating portion of the antitumor drug bleomycin, has been prepared.[803] Electrochemical reduction of the compound in DMF or MeOH gives rise to an unstable Co^{II} species. The photoactive Co complex showed high capacity for DNA cleavage under UV illumination.[804] The imidazole group was found to be capable of bridging two Co centers in both trinuclear and tetranuclear analogs of this system.[805] The imidazole-bridged binuclear and trinuclear ammine complexes $[\{(H_3N)_5Co\}_2(im)]^{5+}$ and *cis*-$[(H_3N)_4Co\{(im)Co(NH_3)_5\}_2]^{7+}$ have been synthesized, and the crystal structure of the latter complex reported.[806]

Studies of the reactivity of imidazole coordinated to Co^{III} have identified some interesting chemistry. The imidazole ligand in *cis*-$[Co(en)_2Cl(Him)]^{2+}$ may be nitrated (at the 4-position) under mild conditions with a $HNO_3-H_2SO_4$ nitrating mixture, whereas the pyridine analog cannot be nitrated without complex decomposition.[807] Nucleophilic displacement of the nitro group of the coordinated ligand by Cl^- was also found. Treatment of $[Co(NH_3)_5(Him)]^{3+}$ with $Br_{2(aq)}$ in acetate or phosphate buffer between pH 4 and 6 results in exclusive formation of the oxidized $[Co(NH_3)_5(2,4,5\text{-oxo-im})]^{2+}$ complex (2,4,5-oxo-im = conjugate base of imidazolidine-2,4,5-trione, or parabanic acid). A mechanism involving a tetrabrominated imidazole intermediate was proposed.[808] Chlorination results in the same product. An unusual linkage isomerization of $[Co(NH_3)_5(4\text{-Meim})]^{3+}$ (from adjacent to remote methyl group isomer) was observed and a mechanism involving a largely dissociative transition state was proposed.[809]

There are relatively few reports of trivalent Tp complexes by comparison with mono- and divalent systems. One interesting example involved transmetallation (from Sn to Co) in the reaction of $TpSnCl_3$ with $[Co(CO)_4]^-$ to give a mixture of products from which $[Co(Tp)_2]$[*trans*-$[(CO)_4Co(Cl_2Sn)_2Co(CO)_3]$ was isolated and characterized by X-ray crystallography.[810]

(v) Imines

Cobalt(III)-directed reactions, where the metal either directs the stereochemistry or activates the coordinated precursor, have played an important role in the development of imine coordination chemistry. Mixed donor imines coordinated to Co^{III} have been produced by metal-templated reactions. Anation of $[Co(NH_3)_5(OH_2)]^{3+}$ by 5-bromo-2-oxopentanoate at pH 5 gives two major products, the 2-oxo-2-cyclopropylethanoato complex and the 5-hydroxy-2-oxopentanoato complex, both which were converted to tetraammine-iminocarboxylato chelates by attack of an adjacent deprotonated ammine ligand.[811] The tridentate monoimine analog of dien (dienim) is formed directly by condensation of acetaldehyde with ethylenediamine in the presence of $CoCl_2$ and H_2O_2, and isolated as the *mer*-$[Co(dienim)(en)Cl]ZnCl_4$ complex.[812] A series of α-amino acid complexes $[Co(en)_2(H_2NCH(R)CO_2)]^{2+}$ (R = CH_2OH, CH_2SMe, CMe_2SMe, $CH(Me)OH$) react with $SOCl_2$ in DMF, undergoing β-elimination to give the related imine complex or else reacting further to give chelated isothiazole-3-carboxylato complexes.[813] Intramolecular condensation between *N*-bound aminoacetaldehyde and the terminal primary amine of coordinated trien (**135**) leads to the imine, $[Co(tetraenim)Cl]^{2+}$; the (hydrated) carbinolamine intermediate was also identified. The carbinolamine results from condensation of the aldehyde with the most acidic coordinated amine *trans* to Cl^- and this species is unable to dehydrate until after ligand rearrangement that permits formation of a planar imine *N*-donor.[814] Methylene imines coordinated to Co ((**177**)[815] and (**178**)[756]) have been isolated from reactions of hexaaminecobalt(III) precursors with formaldehyde in anhydrous solvent. These imines are highly reactive towards nucleophiles and are rapidly hydrolysed in neutral aqueous solution, but are stable in strong acid. The trigonally symmetric potentially heptadentate triacid trensal forms charge neutral complexes with most trivalent metal ions, including Co^{III} (**179**), although the apical tertiary amine does not coordinate in this case.[816]



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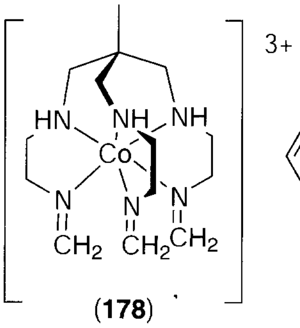

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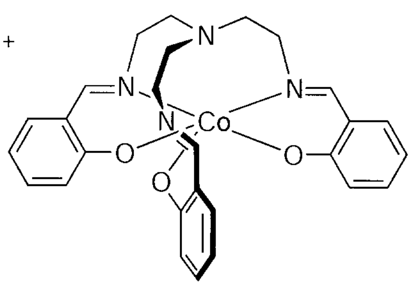

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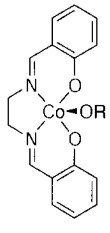
Complexes of imine ligands formed from salicylaldehyde have been widely investigated. Oxygenation of Co(salen) (**69a**) in alcoholic (ROH) solution involves a rate-determining proton transfer from ROH to the coordinated O_2 ligand, ultimately affording the corresponding alkoxycobalt(III) complex (**180**), which may be hydrolyzed to the hydroxocobalt(III) derivative in water.[817] The rate of oxidation of Co(salen) in MeOH solution is increased rapidly in the presence of Bu_3SnCl, leading to $[Co(salen)Cl][BuSn(OMe)Cl_2]$ where the trivalent Co moiety may be considered a ligand for the Sn complex.[818] The coordinatively saturated Co(saldtn)(OH) complex (**181**) catalyzes the selective aldol condensation between dibenzoylmethanes and formaldehyde in methanol to give 1,1,3,3-tetrabenzoylpropanes, which undergo a retro-Claisen reaction to give 1,3-dibenzoylpropanes in CH_2Cl_2.[819] The complex of the substrate anion is the reactive species.



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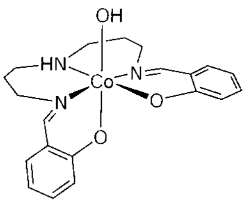

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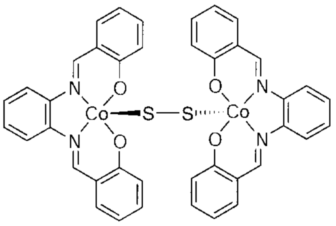

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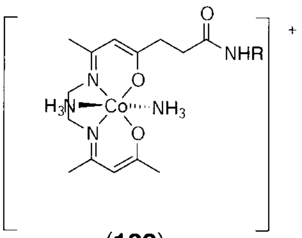

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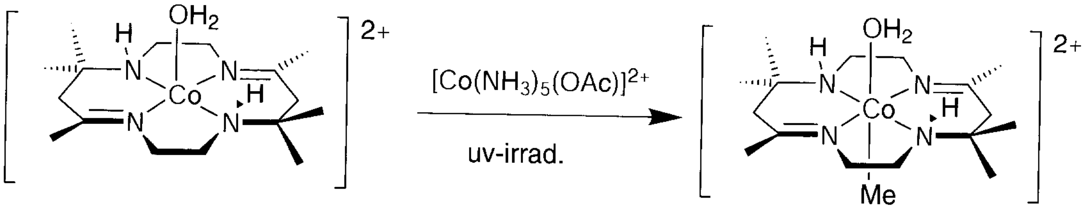
Spectroelectrochemistry of the trivalent peroxo-bridged dimer $\{(DMSO)(salen)Co\}_2(\mu\text{-}O_2)$ in DMSO has been investigated.[820] Two-electron, controlled-potential oxidation liberates O_2 leaving the solvated complex $[Co(salen)(DMSO)_2]^+$, while reduction produces the divalent compound. By analogy with the dioxygen/peroxide chemistry of these systems, treatment of Co(salphn) (**69b**) with elemental S in THF or pyridine gives the tetrasulfide complexes $\{(L(salphn)Co\}_2(S_4)$ (L = THF, py), whereas in the presence of Na^+ in THF the trivalent μ-persulfido complex (**182**) $[(salphn)Co(\mu\text{-}S_2)Co(salphn)Na(THF)_2]BPh_4$ results. A S—S distance 1.962(9) Å was determined from its crystal structure.[821] Removal of the Na^+ ion (not shown here), which bonds with the O donors and the bridging persulfide, leads to decomposition of the complex.[822]

Complexes based on (**183**) ($[Co(acacen)(NH_3)_2]^+$ with a peptide spacer attached to one of the methyl groups) have been patented as potential agents that bind to surface histidine residues on proteins.[823,824] The potential uses for this are as bactericides, antimicrobial or antiviral agents, as reducing agents, or for protein labeling. Inhibition of proteins such as carbonic anhydrase, thermolysin,[825] α-thrombin[826] and a zinc finger-containing transcription factor[827] was demonstrated by this class of compound. The activity of these compounds was found to be dependent on the amino acid residues in the linker. The structure and spectroscopy of the 3-chloro derivative of the parent complex *trans*-$[Co(acacen)(NH_3)_2]^+$ were reported separately.[828]

The kinetics of electron transfer (both heterogeneous and homogeneous) involving trivalent Co complexes of hmd[590,829] and tmt[830,831] have been well studied. $[Co(hmd)(OH_2)_2]^{3+}$ undergoes photoreduction in an aqueous acidic solution using $[Ru(bpy)_3]^{2+}$ as photosensitizer and phenol as the sacrificial electron donor.[832] Ligand substitution reactions of *trans*-$[Co(hmd)X_2]^{n+}$ at the labile (X) sites have been thoroughly investigated. Examples of leaving groups (X) include halide[833–835] and aqua.[836]

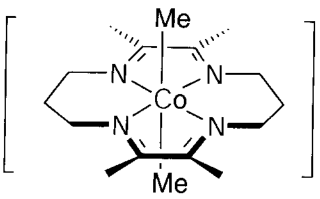
The UV irradiation of a mixture of $[Co(NH_3)_5(OAc)](ClO_4)_2$ with the divalent precursor (**184**) in 0.1 M $HClO_4$ yields the methyl complex *rac*-$[MeCo(hmd)(OH_2)]^{2+}$ (**185**). The complex was crystallized and its structure has been determined.[837] The alkyl homologs $[RCo(hmd)(OH_2)]^{2+}$

(R = Et, Pr), prepared independently, undergo unimolecular homolysis (effectively the reverse process) and the activation enthalpy for these processes were determined.[838]



(**184**) (**185**)

Methylation of $[Co(tmt)]^{2+}$ with MeI leads to the potent methyl carbanion donor *trans*-$[Co(tmt)Me_2]^+$ (**186**). Reaction of this complex with variety of methyl–lead(IV) compounds in MeCN is rapid, leading to the same monomethylcobalt(III) product, but resulting in different methylated Pb derivatives depending on the reaction stoichiometry and Pb compound.[839] The same complex rapidly transfers Me groups to Zn^{2+} and Cd^{2+} in MeCN,[840] or Pb^{2+} and Sn^{2+} in water.[302,841] The kinetics of Co—C bond formation in the reactions with primary alkyl and substituted primary alkyl radicals has been found to be influenced more by the structure of the macrocycle than by the nature of the radicals.[842]



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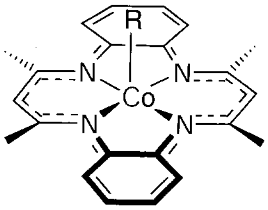
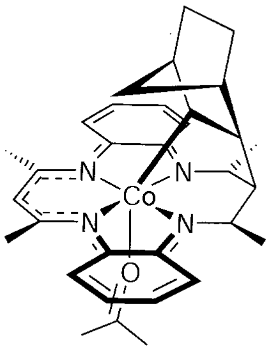
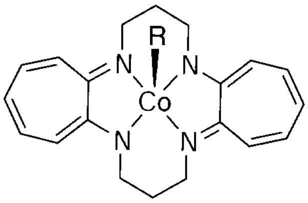


(**187**)

The alkyl complexes RCo(tmtaa) (**187**) (R = Me, Et, or Ph), were synthesized and studied by cyclic voltammetry.[843] Two anodic waves, assigned to single-electron, ligand-centered, oxidative processes were observed that were only moderately influenced by the R group. Two cathodic waves were found. Growth of thin films by electropolymerization on a Pt electrode was achieved during which the Co—C bond remained intact. An interesting example of an axially bound alkyl group is provided by the norbornyl complex (**188**), prepared by reacting Co(tmtaa) with norbornene in the presence of dioxygen. The crystal structure of this novel pendent arm macrocyclic complex was reported.[844,845] In contrast to the saddle-shaped tmtaa complexes, the 6,13-dimethyl analog adopts a planar conformation when bound to Co^{II}, stabilizing the Co^I oxidation state by 250 mV and destabilizing the trivalent state by 160 mV relative to the tmtaa complex.[846]



(**188**)



(**189**)

Cobalt complexes of the fused 7-membered ring unsaturated analogs of the dibenzo-[14] tetraazaannulenes, the tropocoronands (H_2TC), have also been reported. The crystal structure of five-coordinate ClCo(TC) has been determined ((**189**) where R = Cl).[847] The alkyl derivatives RCo(TC) (R = Et, Pr) were prepared, but were diamagnetic in contrast to the chloro precursor. The alkyl complexes homolyze in solution either on exposure to light or at elevated temperatures in the dark, to afford the corresponding divalent tropocoronand complex and an alkyl radical.[848] Five-coordinate thiolate and nitrosyl derivatives have also been prepared.[849]

(vi) Oximes

Although oxime complexes of Co share many of the physical properties of their imine relatives, the presense of an ionizable OH group attached to the coordinated N=C group leads to these ligands binding in their anionic forms. For this reason, the trivalent oxidation state is preferred in the Co coordination chemistry of oximes.

The hexadentate so-called clathrochelates are formally derived from $Co(dmg)_3$ with borate "caps" at either end; the archetypal example being the trivalent (**190**). Like the hexaamine analog $[Co(sep)]^{3+}$ cage, the encapsulated metal ion is insulated from its surrounding solvent. Furthermore, the low charge of the complex decreases outer sphere (solvent, ion pairing) contributions to electron transfer and a number of structural and electron transfer investigations have been reported for these systems.[850–852] Increasing the bulk of the oxime substituents (diphenglyoxime, cyclohexanonedioxime) decreases further the outer sphere contributions to electron transfer leading to an enhancement of the $Co^{III/II}$ self-exchange rate.[853] Further, Co complexes bearing a variety of different caps including ferrocenylborate,[854] butylborate,[855] phenylborate,[856] and trichlorostannate(IV)[857] have been reported.

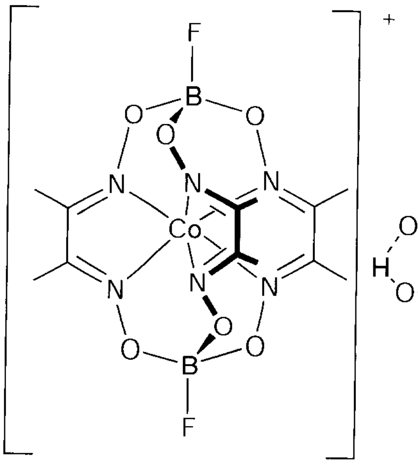
A variety of 4-substituted-1,2-benzoquinone-2-oximes (Me, Cl, Br) (analogs of the green pigment ferroverdin) form tris bidentate Co^{III} complexes, that are mixtures of *fac* and *mer* isomers.[858] Another ferroverdin analog, 1-phenyl-2-(hydroximino)-1,3-butanedionate, forms a tris-bidentate Co^{III} complex which has been synthesized and characterized structurally.[859] A trigonally symmetric (*fac*) isomer was observed. The hexadentate tripodal trioxime $MeC(CH_2NHCMe_2C(Me){=}NOH)_3$ (H_3tox) was synthesized from the triamine tame (**131**) and 2-chloro-2-methyl-3-nitrosobutane.[860] The complex with Co^{III} was crystallized in both its tripositive (fully protonated) and singly deprotonated dipositive forms. Attempts to cap $[Co(H_3tox)]^{3+}$ with aqueous borate and phenyl boronate were unsuccessful, resulting instead in partial ligand hydrolysis. Oxamide oxime forms a trigonally symmetric tris-bidentate Co^{III} complex $[Co\ (H_2oxao)_3]I_3$ and its structure was determined by single crystal X-ray diffraction.[861] The bis-bidentate (N,O) complexes *trans*-$Co(HQ)Q(L)_2$ (H_2Q = 2-oximinopropionic or 2-oximino-3-phenylpropionic acids; L = monodentate aromatic N-donor) were reported.[862] Extension of this ligand by addition of a glycyl residue produces the tridentate ligand N-(2-oximinopropionyl) glycinate and its bis Co^{III} complex (*mer* isomer) was also characterized.[863]

One of the most commonly encountered oxime ligand systems involves the cooperative coordination of two bidentate dmg anions. When coordinated in a *trans* configuration internal hydrogen bonding between *cis*-disposed protonated and deprotonated oxime groups (N–O–H$\cdots$O–N) leads to a 14-membered pseudo-macrocyclic CoN_4 array, as seen in the structures of *trans*-$[Co(dmg)_2X_2]^+$ ((**191**) X = H_2O[864] and py[865]). There has been a substantial effort devoted to the biomimetic chemistry of cobalamins (B_{12}) using polyoxime ligands, and a discussion of this area is to be found in Section 6.1.3.1.1.

Alkyl Co oxime complexes have been used as chain transfer catalysts in free radical polymerizations.[866,867] Regioselective hydronitrosation of styrene (with NO in DMF) to PhCMe=NOH is catalyzed by $Co(dmg)_2(py)Cl$ in 83% yield.[868,869] Catalytic amounts of the trivalent $Co(dmg_2tn)I_2$ (**192**) (X = I) generate alkyl radicals from their corresponding bromides under mild reaction conditions, allowing the selective preparation of either saturated or unsaturated radical cyclization products.[870]

(vii) Amides

Amides offer both O and N-donors for Co coordination. N-bound amides are accessible through hydrolysis of their corresponding coordinated nitrile or by linkage isomerization of the *O*-bound form. The preparation of an extensive series of pentaamminecobalt(III) complexes of (monodentate-coordinated) amides of the form $RCONH_2$ (R = H, Me, CF_3, CH_2Cl, CH_2F, $CH{=}CH_2$, Ph,



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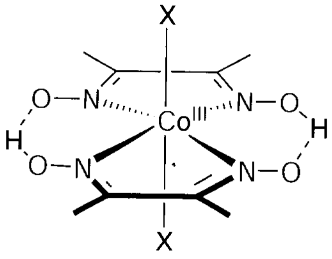

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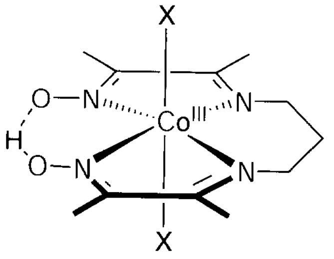

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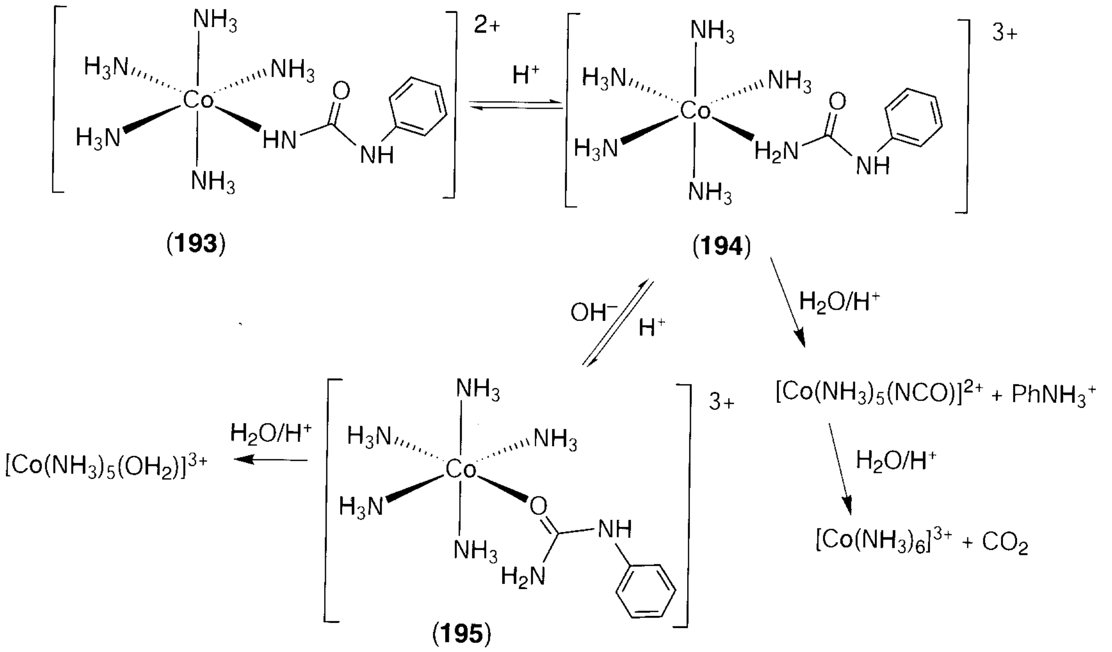
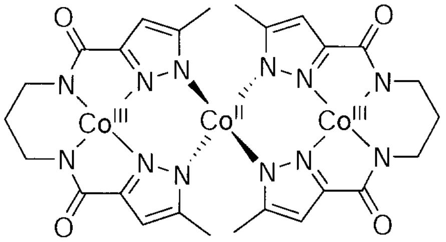
p-C_6H_4F, o-$C_6H_4NO_2$) has appeared.[871] N-Bound amides are quite acidic (p$K_a < 4$) and are able to be isolated in both their neutral (enol) $[(H_3N)_5CoNH{=}C(OH)R]^{3+}$ and monoanionic (amidate) $[(H_3N)_5CoNHCOR]^{2+}$ forms. For example, the N-bound amidate form of the phenylurea complex (**193**) is stable, whereas the protonated form (**194**) spontaneously undergoes linkage isomerization to the *O*-bound isomer (**195**). This reaction is in competition with ligand hydrolysis via $[Co(NH_3)_5(NCO)]^{2+}$ to give $[Co(NH_3)_6]^{3+}$.[872] Interestingly, (**195**) does not undergo hydrolysis but instead ligand substitution (aquation) occurs to give $[Co\ (NH_3)_5(OH_2)]^{3+}$ and unbound urea.



Addition of $[Co(en)_2(gly)]^{2+}$ to a solution of $SOCl_2$ in DMF followed by hydrolysis resulted in oxidation and formylation of the glycinato ligand. The *N*-formyloxamato complex and elemental S were identified as products.[873] Multidentate amides met as peptides, for example, invariably bind through at least one deprotonated peptide N atom. A number of mixed ligand Co^{III} complexes of the dipeptide gly–gly have been prepared. The peptide coordinates in a meridional configuration, and the crystal structure of *mer*-Co(gly–gly)(en)(NCS) was reported.[874] The corresponding nitro complex undergoes a condensation reaction at the N terminus with CH_2O to give an unusual 1,3-oxazine, which is coordinated through carboxylato O, peptide N, and imine N atoms.[875] The dipeptides (H_2dipep = L-met-gly, gly-L-met, L-met-L-ala and L-ala-L-met) have been complexed with Co. A number of compounds of the form $[Co(dipep)_2]^-$,

$[Co(dipep)(en)]^+$ and *cis*-$[Co(dipep)(NH_3)_2]^+$ were prepared and characterized by NMR and CD spectroscopy.[876] The dipeptides coordinate through the terminal and peptide N atoms, the carboxylate and the S atom of the side chain. The complexes $Co(dipep)(NO_2)_3$ (H_2dipep = gly-gly, gly-L-ala, gly-L-val, gly-L-nva, gly-L-leu, β-ala-gly) were prepared and interproton NMR coupling over five bonds of the peptide was identified.[877] The crystal structure and CD absorption spectum of the tripeptide complex $Co(NH_3)_2$(L-ala-gly-gly) has been reported. The sole methyl side chain on the tetradentate ligand (at the N terminal end) is in an equatorial position.[878] Proline residues attached to either end of dien result in the pentadentate ligand H_2prodien, which was characterized structurally, as well as with CD spectroscopy, as its complex $[Co(prodien)(OH_2)]^+$.[879] The ^{15}N NMR spectra of a number of dipeptide, tripeptide, and tetrapeptide complexes of Co^{III} were measured. Coordination of oligopeptides resulted in large upfield shifts for both amine and deprotonated amide nitrogens, and specific *trans* effects were also identified.[880]

The novel tetrabasic ligand 1,3-bis(5-methylpyrazole-3-carboxamido)propane forms a trinuclear Co^{III}–Co^{II}–Co^{III} complex (**196**). The tetradentate diamide-pyrazolyl chelates encircle the terminal trivalent metal ions while the central divalent Co is in a distorted tetrahedral environment provided by the four bridging pyrazolyl rings.[881]



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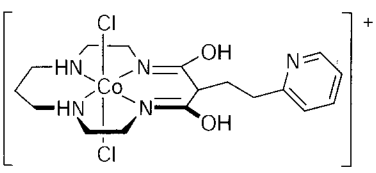
The Co^{III} complexes of the macrocycle 5,7-dioxocyclam and a pendent pyridylethyl derivative (**197**) have been structurally characterized.[882] The ligands bind in their enol tautomeric forms in the complexes when isolated from acidic solution, as shown by X-ray crystallography and IR spectroscopy. The tripodal triamides (**198**) and (**199**) have been synthesized and their Co complexes exhibit a pronounced cathodic shift of their $Co^{III/II}$ redox couples relative to the hexaamine analog $[Co(sen)]^{3+}$ (**163**).[883] The crystal structure of (**198**) was reported. Amide analogs of the macrobicyclic $[Co(sar)]^{3+}$ cages (**200**), using ester groups as capping fragments, have been synthesized.[884,885] Alternatively, homologous cages derived from tris(cyclohexane-1,2-diamine)cobalt(III) undergo oxidative dehydrogenation to give diamide complexes where one of the cyclohexyl rings has undergone aromatization.[886]



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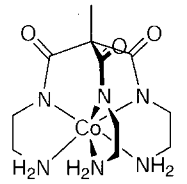

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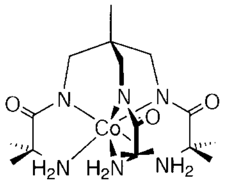

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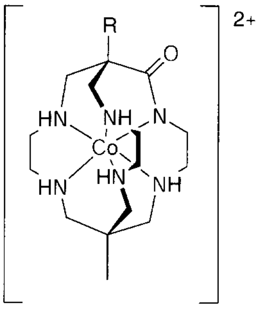

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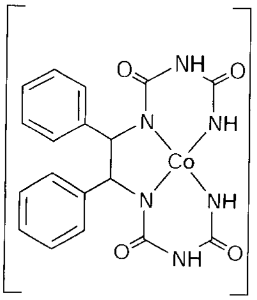
Examples of paramagnetic ($S = 1$) trivalent Co complexes are unusual, but multidentate amide ligands provide a significant proportion of known examples. The square planar tetraamide amide complex (**201**) bears a ligand formally derived from a pair of biuret molecules bridged by a 1,2-diphenylethyl moiety.[887] The crystal structure reveals that the Co—N bonds are on average shorter than those found in diamagnetic (octahedral) Co^{III} amide complexes. Similarly, (**202**) is square planar, as shown by an X-ray crystal structure.[888] A spin triplet ground state was also identified in the solid state. An octahedral diamagnetic complex is formed upon addition of two equivalents of pyridine to an aqueous solution, but no adduct forms in aprotic solvents.



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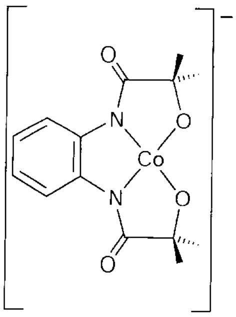

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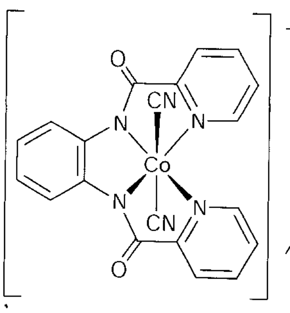

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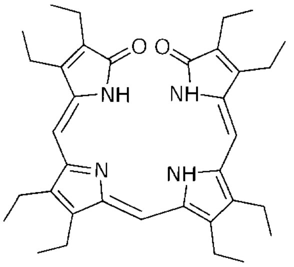
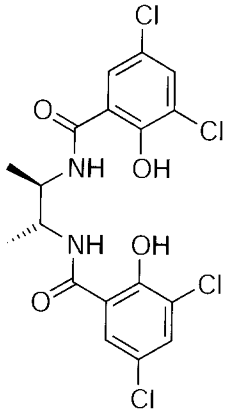


(204)

The dianionic tetradentate ligand 1,2-bis(pyridine-2-carboxamido)-benzenate (bpc) is non-innocent. The anion (**203**) can be oxidized to Co(bpc$_{ox}$)(CN)$_2$ which has a $S=1/2$ ground state, and the crystal structure of the complex has been determined.[889] The open chain tetradentate octaethylbilindione (**204**) (H$_3$OEB) bears a tetrapyrrole unit found in biliverdin, an intermediate in heme catabolism and a commonly found pigment. Carbonyl groups at opposite ends of the open chain porphyrin relative forbid the adoption of planar conformations by this ligand in contrast to porphyrins themselves.[890] Instead, the tetrapyrrole ligand adopts a helical conformation; the monomeric Co(OEB) complex has been characterized by X-ray crystallography and spectroscopic techniques. The compound exhibits a rich electrochemistry, with four electrochemically reversible redox states [Co(OEB)]^n ($n=-2$, -1, 0, and $+1$).[891] The monopositive complex has also been characterized structurally, and spectroscopic evidence indicates that it is a divalent complex of the 2-electron oxidized ligand, i.e., [Co^{II}(OEB$_{ox}$)]$^+$. A ligand-centered radical has been observed upon reaction of this compound with pyridine to give the [Co^{III}(OEB$^{-\cdot}$)(py)$_2$]$^-$ species.[892]

Epoxidation of norbornene with t-BuOOH or PhI as terminal oxidant catalyzed by the Co^{III} complex of (**205**) was explored.[893] Co catalysis is associated with the Co^{III}- to Co^{II}-driven formation of t-BuOO radicals. By contrast, there is no evidence for radical intermediates in Co catalysis with PhIO and an oxo-cobalt(IV) species was postulated instead in this case. The chiral square planar complex of 2,4-bis((*R*)-2-methylbutyramido)-2,4-dimethylpentan-3-one and other close relatives were prepared and characterized by NMR and X-ray crystallography.[894] Asymmetric epoxidation of styrenes with these complexes and PhIO were achieved in varying yields with modest enantiomeric excess. The pyridyl-substituted pentadentate ligand, N,N′-bis(2-(2′-pyridyl)ethyl)-2,6-pyridinedicarboxamide (H$_2$py$_3$p), when complexed with Co^{III}, catalyzes the selective oxygenation of phenols to the corresponding p- or o-quinones.[895] Crystal structures of the [Co(py$_3$p)X]$^{n+}$ (X$=$H$_2$O, $n=1$; X$=$OH$^-$, t-BuOO$^-$, $n=0$) complexes have been reported.[896] The t-butylperoxo complex oxidizes alkanes such as cyclohexane via homolytic scission of the O—O bond. The t-BuO$^\cdot$ radicals liberated abstract an H atom from cyclohexane and the cyclohexyl radical reacts with O$_2$ to give a mixture of cyclohexanol and cyclohexanone. The bis(pyr-



(205)

azolylethyl) analog H_2pypz_2p has also been synthesized and its analogous pentadentate coordinated Co^{III} complexes have been reported.[897] By contrast, the pentadentate coordinated complex $[Co(pypz_2p)(OH_2)]^+$ is converted quantitatively to the bis-bidentate $[Co(pypz_2p)_2]^-$ in solution. The influence of the strong field amide N-donors is the driving force for this transformation.

(viii) Nitrosyl

Bound nitrosyl can display either a linear or bent geometry. The ^{15}NO NMR shifts for five-coordinate Co^{III} complexes with Schiff base or dithiocarbamato basal ligands and bent apical nitrosyl ligands have been reported.[898,899] As in C-nitroso groups, bent ^{15}NO ligand resonances are strongly deshielded (by 500–800 ppm) relative to comparable linear nitrosyls, and both ^{59}Co and ^{15}NO shielding was found to decrease with the Co—N—O angle.

Nitrosyl complexes of Co porphyrins have attracted considerable attention. As an example, Co(TPP)(NO), and some methoxy and nitroaromatic homologs, were prepared and the Co—NO bonding interaction was probed using cyclic voltammetry and reflectance IR spectroelectrochemistry. These experiments revealed $\bar{\nu}_{N=O}$ vibrations for the one- and two-electron oxidized complex; the latter being consistent with an effectively σ-bonded nitrosyl.[900] An extended series of Co(TPP)(NO) analogs bearing an even greater variety of aromatic substituents was reported by reaction of the precursor Co porphyrin with NO or with $NOBF_4$, then reduction with cobaltocene. The complexes are diamagnetic, display $\bar{\nu}_{N=O}$ bands around 1,690 cm^{-1} and possess a bent nitrosyl ligand (Co—N—O ~120°).[901] Spectroelectrochemical IR experiments showed that the complexes undergo a reversible one-electron oxidation of their porphyrin ring and a one-electron reduction of the Co center.[902] An accurate crystal structure of Co(OEP)(NO) was determined in order to probe apparent structural distortions found in the Fe analog.[903] The Co—N vector was within 2° of perpendicular to the porphyrin plane, whereas the Fe—N vector was tilted by more than 6°. Equatorial M—N(porphyrin) bond length asymmetry was seen in both structures, which was correlated with the axial M—N(O) tilt angle. Subsequent theoretical studies confirmed this structural correlation.[904]

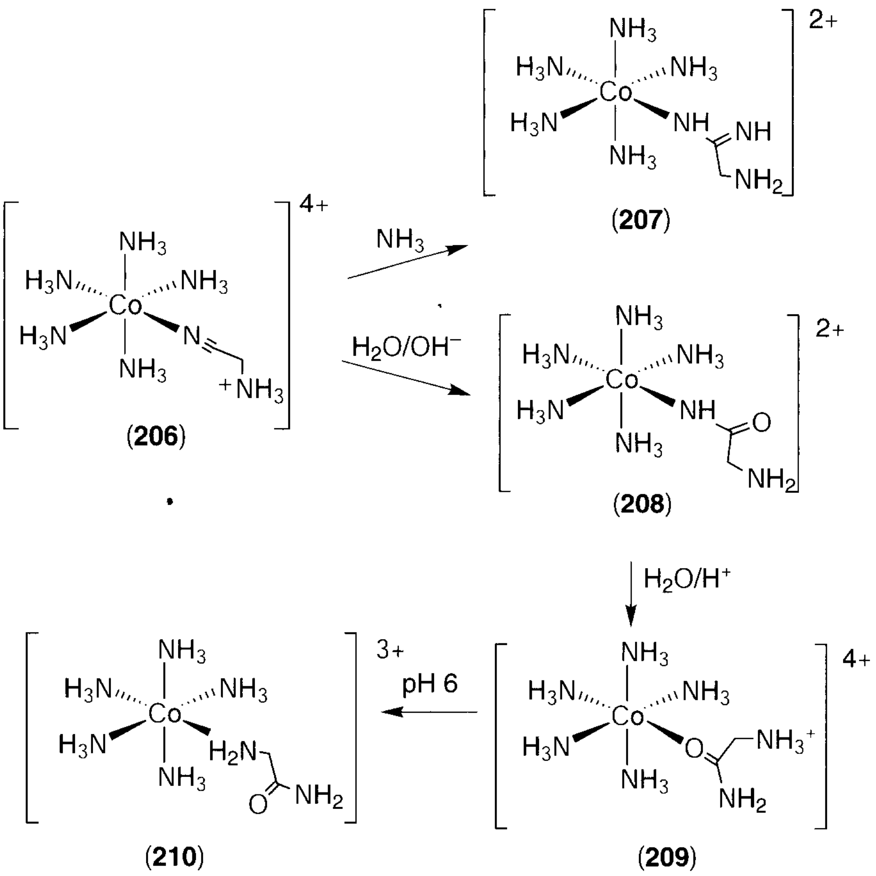
Coordination of NO to the divalent tetrasulfonated phthalocyanine complex $[Co(TSPc)]^{4-}$ results in a complex formally represented as $[(NO^-)Co^{III}(TSPc)]^{4-}$ ($k_f = 142\,M^{-1}s^{-1}$, $K_a = 3.0 \times 10^5\,M^{-1}$). When adsorbed to a glassy carbon electrode, $[Co(TSPc)]^{4-}$ catalyzes the oxidation and reduction of NO with catalytic currents detectable even at nanomolar concentrations. Electrochemistry of the same complex in surfactant films has also been studied.[905] Bent nitrosyl complexes of the paramagnetic trivalent tropocoronand complex Co(NO)(TC) ((**189**), R = NO) have also been reported.[849]

(ix) Nitriles, azides, isocyanides, cyanates, and thiocyanates

Nitrile coordination chemistry of Co has attracted attention as the influence of the trivalent metal ion greatly enhances the reactivity of the C≡N bond toward nucleophilic attack, especially hydrolysis. Amine complexes of Co^{III} have been popular scaffolds upon which to perform these reactions. Following syntheses of the pentaamminecobalt(III) complexes of 2- and 4-nitrobenzonitrile, base hydrolysis of the coordinated nitrile to the corresponding carboxamides was investigated. Rate constants for nitrile hydrolysis for these and a number of other substituted aromatic nitrile analogs were correlated with the Hammett substituent parameters.[906] The N-bonded nitrile complexes $[Co(tetren)(NCR)]^{3+}$ (R = Me, Ph, p-$MeOC_6H_4$; tetren = linear tetraethylenepentaamine) were prepared and the kinetics of base hydrolysis were studied. The reactions involved displacement of the nitrile to give the hydroxopentaamine as opposed to nucleophilic attack at the nitrile carbon, i.e., the corresponding carboxamido complex is not formed.[907]

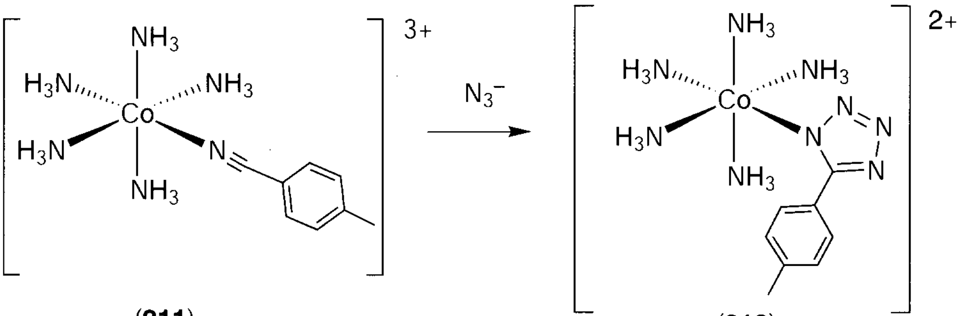
The ammonioacetonitrile complex (**206**) reacts with NH_3 to produce the amidine-bonded aminoacetamidine (**207**) complex, whereas in aqueous base it hydrolyzes to the amido-*N*-bonded glycinamide complex (**208**).[908] Acid-catalyzed linkage isomerization to first the *O*-bound form (**209**) precedes formation ultimately of the amino-bonded isomer (**210**) as the stable product upon deprotonation of the free amine above pH 6.

The 1,3-dipolar cycloadditions of N_3^- with coordinated nitriles (**211**) may result in formation of 5-substituted tetrazole complexes (**212**). Some examples include $[Co(NH_3)_5(N_4R)]^{2+}$-(R = *p*-methylphenyl, *p*-chlorophenyl, *p*-nitrophenyl (N1 bound), *m*-formylphenyl (*N*2 bound)).



(206) **(207)** **(208)** **(209)** **(210)**

The kinetics of the reaction is first order in both nitrile complex and azide.[909] NaN_3 reacts with $[Co(tetren)(NCMe)]^{3+}$ at pH 5.7 to give the 5-methyltetrazolato complex $[Co(tetren)(N_4CMe)]^{2+}$. The reaction is biphasic, involving the initial rapid formation of the *N*1-bonded tetrazole followed by the slow linkage isomerization to the N2-bonded complex.[907]



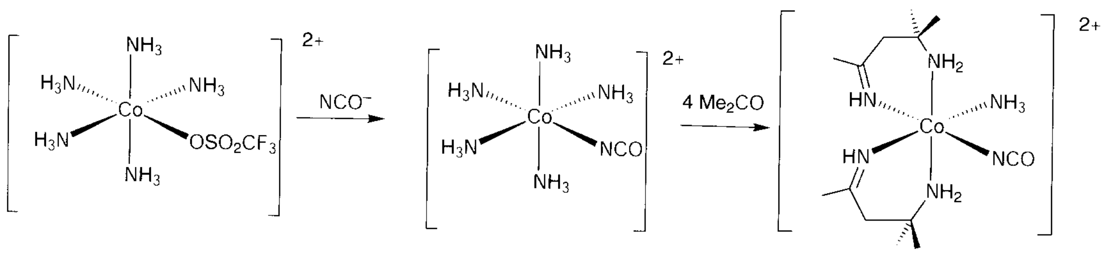
(211) **(212)**

The ambidentate isomers 3-cyanopyridine and 4-cyanopyridine have been complexed to the pentaamminecobalt(III) moiety and their corresponding linkage isomers $[(H_3N)_5Co(NCpy)]^{3+}$ and $[(H_3N)_5Co(pyCN)]^{3+}$ have been prepared.[910] Their electron transfer cross reactions with $[Fe(CN)_5(OH_2)]^{3-}$ were investigated and were found to proceed in two stages. In the first stage, pyCN-bridged Fe^{II}–Co^{III} dinuclear complexes are formed as intermediates, but their fate depends on the linkage isomer present that undergoes rapid inner-sphere electron transfer. The binuclear $(H_3N)_5Co^{III}(NCpy)Fe^{II}(CN)_5$ complex undergoes inner-sphere electron transfer followed by complex dissociation, whereas the $(H_3N)_5Co^{III}(pyCN)Fe^{II}(CN)_5$ isomer simply dissociates to its reactants without electron transfer taking place. For the latter systems, outer-sphere electron transfer is more competitive. The Cr^{II} reduction of the nitrile-bonded pentaamminecobalt(III) complexes of 3- and 4-cyanobenzoic acid has also been studied.[911] The reaction between Cr^{II} and $[(H_3N)_5Co(NCCH_2I)]^{3+}$ gave the unusual dinuclear complex $[(H_3N)_5Co(NCCH_2)Cr(OH_2)_5]^{5+}$ as the only product.[912] The Hg^{II} analog was also prepared.

The potentially bridging 2-cyano-acetylacetonato anion has been complexed with Co in its N-bound form to give $[Co(NH_3)_5(NCC(C(O)Me)_2)]^{2+}$. The bridged dicobalt(III) complex $[(H_3N)_5Co(\mu\text{-}NCC(C(O)Me)_2)Co(tn)_2]^{5+}$ was also prepared.[913] Inner-sphere electron transfer between $[Co(NH_3)_5(NCC(C(O)Me)_2)]^{2+}$ and Cr^{II} was verified by blocking the acac coordination site with a non-reducing metal ion, which inhibited reaction with divalent Cr. The cyanoborane complexes $[Co(NH_3)_5(NCBH_2R)]^{3+}$ ($R = Et_3N$, py, PPh_3) were prepared from the triflatopentaammine precursor in acetone; further, the syntheses of some alkane nitrile analogs were described as well as the kinetics of their base-catalyzed hydration reactions.[914]

Coordinated azide complexes have been widely reported. The azido complex $[Co(NH_3)_5(N_3)]^{2+}$ has been well explored. Amongst its applications, it is an efficient photoinitiator of polymerization of 2-hydroxyethyl methacrylate (HEMA).[915] The interaction of Me_3SiN_3 with *mer*-$CoMe_3(PMe_3)_3$ gives the octahedral $CoMe_2(N_3)(PMe_3)_3$ complex. This azido complex and its trigonal bipyramidal carbonyl derivative $Co(N_3)(CO)_2(PMe_3)_2$ were characterized structurally.[916]

The complex $[Co(NH_3)_5(OSO_2CF_3)]^{2+}$ undergoes triflate substitution by cyanate and condensation with acetone to form the unusual bis-bidentate imine complex (**213**)[917] in a reaction reminiscent of the classic Curtis condensation of acetone with ethylenediamine. Apart from the novelty of the synthesis, the reported crystal structure was only the second of a CoN_6 complex bearing a cyanate ligand.



(213)

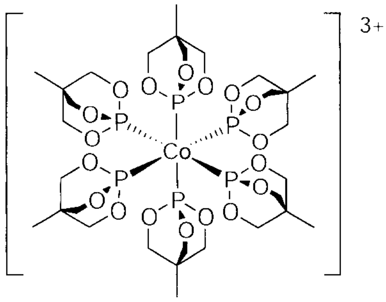
The coordination chemistry of the ambidentate SCN^- and its linkage isomerism when bound to Co^{III} has been reviewed.[19] With Co^{III}, the *N*-bound isomer is thermodynamically stable and commonly observed, and the Co–NCS unit (typical Co—N 1.90 Å) is usually linear, although some deviations from strict linearity are sometimes found in practice. A more unusual monomeric complex is *mer*-$Co(NCS)_3(PMe_3)_3$, formed via reaction of $Co(NCS)_2(PMe_3)_2$ with NO, where a disproportionation leads to the CoN_3P_3 species as well as $[Co(NO)_2(PMe_3)_2]\,[Co(SCN)_4]$.[918]

6.1.2.3.4 Phosphorus

Phosphorus ligands bound to cobalt are met more broadly in the parallel *Comprehensive Organometallic Chemistry* series, but some representative examples not also including Co—C bonded species are presented here.

(i) Mono- and bidentate phosphines

The bicyclic phosphite ester $P(OCH_2)_3CMe$ and the bidentate bis-diphosphite $((MeO)_2PCH_2CH_2P(OMe)_2)$ form trivalent CoP_6 complexes of the form (**214**) and (**215**). A photophysical study observed emission from the $^3T_{1g}$ electronic state in both complexes.[919] Photolysis of (**215**) in aqueous solution at 300 K results in photoaquation. An NMR investigation reported the longitudinal relaxation times (T_1) of ^{59}Co and ^{31}P nuclei across a series of $CoP_6{}^{3+}$ complexes (where P was $P(OMe)_3$ or a mono or bicyclic phosphite ester).[920] The magnitude of T_1 decreased as the symmetry of the ligands was lowered and the $^{59}Co-^{31}P$ coupling constants decreased as the exocyclic group in the monocyclic phosphite ligand was enlarged.



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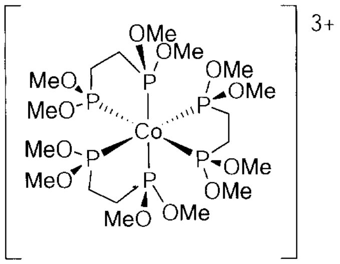

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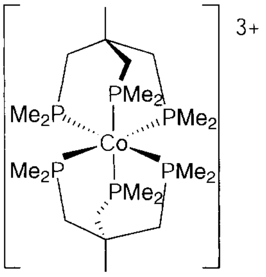


(216)

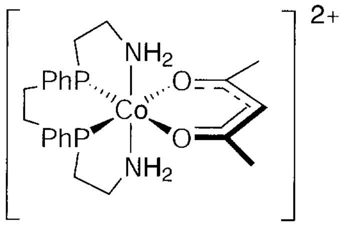
The reaction of *trans*-$[Co(acac)_2(PPh_3)_2]PF_6$ with PR_3 (R = Me or Et) in MeOH yields *trans*-$[Co(acac)_2(PR_3)_2]PF_6$. These *trans* complexes are stable in dry solvents, but are rapidly hydrolyzed in wet MeOH to give *trans*-$[Co(acac)_2(PR_3)(H_2O)]^+$ and isomerize to *cis*-$[Co(acac)_2(PR_3)_2]^+$ in the presence of a catalytic amount of activated charcoal.[921] The *cis* isomers did not undergo aquation under similar conditions. X-ray crystal structure analyses showed that the Co—P bonds in the *trans* isomers were longer by approximately 0.07 Å than those of the corresponding *cis* isomers. The Co—O bonds *trans* to the phosphine ligands were also longer than those of the mutually *trans* Co—O bonds, owing to the strong *trans* influence of phosphine ligands. In a comprehensive systematic study a larger number of monodentate phosphine bis (acac)cobalt(III) complexes were prepared. The observed ratios of the *cis* and *trans* isomers of $[Co(acac)_2(P(R_nPh_{3-n})_2]^+$ depend upon the bulkiness (R = Me or Et) and basicity of the phosphine.[922] The *trans* isomers exhibit a strong absorption band in the expected *d–d* transition region, which was assigned to a charge transfer transition between the Co^{III} ion and a phosphine ligand, whereas the *cis* isomers exhibit the first *d–d* band split into two components by the lower symmetry ligand field. Other systems studied included *trans*-$[Co(acac)_2(H_2O)(P(R_nPh_{3-n})]^+$, *trans*-$[Co(acac)_2(amine)(PMe_2Ph)]^+$, and *trans*-(P,P)-$Co(acac)(CN)_2(P(R_nPh_{3-n}))_2$. The crystal structures of a number of these complexes were subsequently reported.[923]

Five-coordinate complexes of the form $Co(PR_3)_2X_3$ (X = Cl, Br; $PR_3 = PMe_3$, PEt_3, PMe_2Ph, PEt_2Ph, $PEtPh_2$) were prepared by oxidation of their divalent $Co(PR_3)_2X_2$ precursors at low temperature.[924] The intensely colored, paramagnetic ($\mu_{eff} = 2.9–3.3$ B.M) Co^{III} complexes were formulated as trigonal-bipyramidal species on the basis of vibrational and UV-visible spectroscopic data. Coordinate bond lengths for $Co(PEt_3)_2X_3$ and $Co(PEt_2Ph)_2X_3$ were obtained by Co and Br K-edge EXAFS spectroscopy and average values of Co—P 2.30, Co—Cl 2.20, and Co—Br 2.36 Å were obtained.

The bidentate phosphine dppe (1,2-bis(diphenylphosphino)ethane) and the aminophosphine eddp (2-aminoethyl-diphenylphosphine) form mixed ligand (N, P, O) complexes such as Co(acac) $(edpp)_2$ and Co(acac)(en)(dppe). A preference for *trans* N–Co–P and P–Co–P configurations over N–Co–N was found for the bis(edpp) complexes.[925]

(ii) Multidentate phosphines

The tripodal phosphine mtriphos (1,1,1-tris(dimethylphosphinomethyl)ethane) forms a stable trivalent complex (**216**) that has been characterized by X-ray diffraction.[119] The Co—P bond distances (2.291(9)–2.357(7) Å) are longer than those normally found in Co^{III}–phosphine complexes. A number of trivalent CoP_4X_2 and CoP_3X_3 ($X = Cl^-$ and Br^- but not I^-) complexes have been prepared incorporating chelating phosphines such as the bidentate o-$C_6H_4(PPh_2)_2$, the tridentate $PhP(CH_2CH_2PPh_2)_2$, and the tripodal $P(CH_2CH_2PPh_2)_3$ and linear $Ph_2PCH_2CH_2PPhCH_2CH_2P(Ph)CH_2CH_2PPh_2$ tetraphosphines.[926] Mixed donor P,N,O-ligands such as o-$C_6H_4(CH{=}NCH_2CH_2PPh_2)(OH)$ have been prepared by standard Schiff base condensation reactions.[927] On deprotonation these ligands coordinate as tridentates to give trivalent bis complexes of the form $[CoL_2]^+$. The distortions in the free ligand predispose it for coordination in a *fac* geometry to Co with *cis*-PPh_2 groups, as shown by X-ray crystallography. Another example is the linear P_2N_2 tetradentate which forms *cis*-α- (**217**) and *cis*-β-$[Co^{III}(L)(aa)]^{n+}$ (aa = oxalate or acetylacetonate) complexes.[928]



(217)

6.1.2.3.5 Arsenic

(i) Monoarsines and multidentate arsines

The Co coordination chemistry of As donors is less developed than that of phosphorus, although there are obvious parallels between the two. Treatment of Me_3AsI_2 with Co metal powder gives both trivalent ($[CoI_3(AsMe_3)_2]$) and divalent ($[AsMe_3I][CoI_3(AsMe_3)]$) complexes as products.[929]

$CoAs_6$ complexes bearing chelating tertiary arsines are well known. Preparation of the homoleptic $CoAs_6$ and $CoAs_3P_3$ complexes $[Co(o\text{-}C_6H_4(AsMe_2)_2)_3]^{3+}$ and $[Co(o\text{-}C_6H_4\ (PMe_2)(AsMe_2))_3]^{3+}$ have been described,[930] and the X-ray structure of $[Co(o\text{-}C_6H_4\ (AsMe_2)_2)_3](BF_4)_3$ reveals a Co ion coordinated (Co—As 2.365(2)–2.395(2) Å) within an approximately D_3 symmetrical ligand field. The Co^{III} complexes of a variety of the bi-($o\text{-}C_6H_4(AsMe_2)_2$) tri-(MeAs $(o\text{-}C_6H_4AsMe_2)_2$, $MeC(CH_2AsMe_2)_3$) and tetradentate ($(As(CH_2CH_2CH_2AsMe_2)_3)$) arsines have appeared and their ^{59}Co NMR spectra studied.[931] The characteristic chemical shift range for $CoAs_6$ complexes was identified as about −350 ppm to +200 ppm relative to $[Co(CN)_6]^{3-}$. Solvent effects were identified in the $CoAs_6$ chromophores, but these were diminished in $CoAs_3I_3$ and $CoAs_4I_2$ complexes.

The CD spectra of a series of *cis*-$[CoX_2(o\text{-}C_6H_4(AsMe_2)_2)_2]^+$ complexes ($X^- = Cl$, OH, NO_3, NO_2) were reported,[932] and the absolute configurations of the resolved enantiomers were inferred. In a related study the chiral and diastereomeric octahedral Λ-*cis*-α and Δ-*cis*-β Co complexes of the linear tetraarsine $Me_2As(CH_2)_3As(Ph)(CH_2)_2As(Ph)(CH_2)_3AsMe_2$ gave complex CD spectral patterns for their *d–d* electronic transitions, and the conclusions of this study were that CD of complexes of such soft donor atoms are not useful for establishing absolute configuration.[933] A number of bidentate chelate complexes of the saturated diarsines dmae (1,2-bis(dimethylarsino)ethane) and dmap (1,3-bis(dimethylarsino)propane) have been reported including *trans*-$[CoX_2(dmap(e))_2]^+$ ($X^- = Cl$, Br, I), *cis*-$[CoX_2(dmap)_2]^+$ ($X^- = Cl$, Br), $[Co(CO_3)(dmap(e))_2]^+$, and $[Co(acac)_{3\ n}(dmap)_n]^{n+}$ ($n = 0, 1, 2$).[934] Isomerization of *cis*-$[CoCl_2(dmap)_2]^+$ to the *trans* isomer in MeOH is one hundred times faster than that reported for *cis*-$[CoCl_2(o\text{-}C_6H_4(AsMe_2)_2)_2]^+$ at the same temperature. The crystal structure of *trans*-$[CoCl_2(dmap)_2]ClO_4$ was subsequently reported.[935]

Trivalent Co complexes of the mixed donor amino arsine emda (2-aminoethyl)dimethylarsine) have been synthesized.[936] Examples include *trans*(X,X), *cis*(As,As)-$[CoX_2(edma)_2]^+$ ($X^- = Cl$, Br, and I), *trans*(As,As)- and *trans*(As,N)-$[Co(acac)(edma)_2]^{2+}$, *trans*(As,N)-$[Co(CO_3)(edma)_2]^+$, $[Co(acac)_2(edma)]^+$, and *fac*-$[Co(edma)_3]^{3+}$. The *fac*-$[Co(edma)_3]^{3+}$ complex was resolved and the absolute configuration of the $(+)_{490}$ CD isomer was assigned as Λ on the basis of the CD spectrum. Racemization of this complex was first order in both complex and hydroxide ions. The crystal structure of $[Co(acac)_2(emda)]ClO_4$ has been reported.[937]

Uncomplexed chirotopic tertiary As atoms are known to undergo slow inversion and so chiral polyarsines may be resolved into their enantiomeric and diastereomeric forms. The mixed donor tetradentate ligand (R^*,S^*)-1-[(2-dimethylarsinophenyl)methylarsino]-2-[(2-aminophenyl)methylphosphino]benzene was prepared stereoselectively and the crystal structure of its dichlorocobalt (III) complex was reported.[938,939] The same group reported the syntheses of the chiral tetraarsine 1-(chloromethyl)-1,1-bis(((2-dimethylarsinophenyl)methylarsino)methyl)ethane and the hexaarsine 1,1,1-tris(((2-dimethylarsinophenyl)methylarsino)methyl) ethane;[940] the latter providing the first example of a chiral hexaarsine.[940] The three diastereomers of the tetraarsine bind to Co^{III} stereoselectively.

6.1.2.3.6 Oxygen

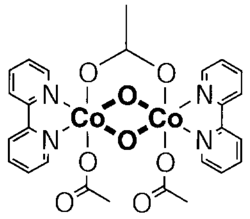
(i) Aqua, hydroxo, and oxo

H_2O, HO^- and O^{2-} are all accessible and well-studied ligands for cobalt(III). The hexaaquacobalt(III) ion is only stable in concentrated acids of non-reducing anions, being a powerful oxidant which oxidizes water. It has been characterized in the solid state as an octahedral ion with Co—O 1.873(5) Å.[941] Due to its instability, it is not a very useful entry point into synthetic cobalt(III) chemistry. Invariably, coordinated water is consequently found in mixed-ligand cobalt(III) complexes. The pK_a of water is reduced substantially on coordination, and the highly polarized aqua ligand is deprotonated around neutral pH to form hydroxo complexes. For trivalent (inert) cobalt, which does not tend to undergo subsequent oligomerization reactions, this is usually a reversible process. Further deprotonation to an isolated oxo ligand is rare, with this ligand found in metal-bridging environments where the presence of several metal ion centers promotes its formation. Of historical significance is the report of the crystal structure of Werner's hexol cation $[Co\{Co(OH)_2(NH_3)_4\}_3]^{6+}$, where the core Co^{III} is surrounded by six bridging hydroxides linked to three distal Co^{III} centers, obtained serendipitously when attempting to grow crystals of carbonatopentamminecobalt(III) nitrate from water.[942] Another compound from the Werner collection characterized structurally recently is the (μ-amido) (μ-hydroxo)(μ-superoxo)hexaamminedicobalt(III) complex.[943] Hydroxo-bridged complexes reported prior to 1988 have been reviewed in detail,[944] and will not be covered here.

Although there is a tendency to associate coordinated water with Werner-type complexes, where it is extensively established, organometallic aqua ions are known.[945] The simple $[(Cp^*)Co(OH_2)_3]^{2+}$ has been established, and is prepared via Equation (8). The lower pK_a is 5.9, similar to values in aminecobalt(III) compounds, and reversible deprotonation and dimerization has been identified as part of the reactions of the aqua ion.[946]

$$[CpCo^{II}Cl]_2 \xrightarrow[(-C_2Cl_4)]{C_2Cl_6} [CpCo^{III}Cl_2]_2 \underset{HCl}{\overset{H_2O}{\rightleftharpoons}} 2\,[CpCo^{III}(OH_2)_3]^{2+} \overset{OH^-}{\rightleftharpoons} [\{CpCo\}_2(\mu\text{-}OH)_3]^+ \tag{8}$$

Multiple bridging involving the oxo and hydroxo anions is well established with Co^{III}. A number of bridging modes can be considered as possible, and examples of most will be exemplified below. Although well established in iron chemistry, the mono-bridged oxygen analog is not well established in Co chemistry. Dihydroxy-bridged systems, however, are well known; an example is $(en)_2Co(\mu\text{-}OH)_2Co(edda)$, which also features different ligand sets around each octahedral Co center.[947] The trihydroxy-bridged systems are less commonly reported, but examples exist; a simple one is the structurally characterized $[\{(tacn)Co\}_2(\mu\text{-}OH)_3]^{3+}$.[948] Two examples of μ_3-oxo in a cobalt(III) complex are in the partial cubane $[Co_3L_3(\mu\text{-}OH)_3(\mu_3\text{-}O)]Cl$ (L = ethylenediamine-*N*-acetate)[949] and in the cubane $Co_4(\mu_3\text{-}O)(\mu\text{-}OAc)_4(py)_4$.[950] Another compound with μ_3-oxo bonding arises from reaction involving salicylaldoxime, leading to a species with a triangular $\{Co_3(\mu_3\text{-}O)(\mu_2\text{-}OPh)\}$ core.[951] A μ_3-O coordination mode is found in $[Co_4O_4(OAc)_2(bpy)_4]^{2+}$,[952] where each Co is in a distorted octahedral environment. The red dicobalt (**218**), green-black partial cubane tricobalt (**219**) and brown cubane tetracobalt (**220**) structures have all been characterized by X-ray crystallography, and their synthesis is straightfor-



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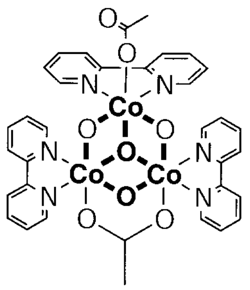

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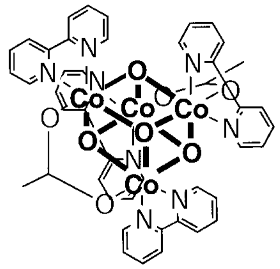


(220)

ward. The first two form via reaction in 3:1 MeOH:H_2O and the latter through "dimerization" in DMSO, as in Equations (9–11).

$$\mathrm{Co(OAc)_2 + bpy\ (1{:}1\ ratio)} \xrightarrow[50^\circ\mathrm{C}]{\mathrm{H_2O_2}} \mathrm{[Co_2(OH)_2(OAc)_3(bpy)_2]^+} \tag{9}$$

$$\mathrm{Co(OAc)_2 + bpy\ (3{:}2\ ratio)} \xrightarrow[50^\circ\mathrm{C}]{\mathrm{H_2O_2}} \mathrm{[Co_3(O)(OH)_3(OAc)_2(bpy)_3]^+} \tag{10}$$

$$\mathrm{[Co_2(OH)_2(OAc)_3(bpy)_2]^+ + 2Li_2O_2} \xrightarrow[70^\circ\mathrm{C}]{\mathrm{DMSO}} \mathrm{[Co_4(O)_4(OAc)_2(bpy)_4]^+} \tag{11}$$

Further, a μ_4-O is reported in the structurally more complex cluster $Co_8O_4(OBz)_{12}(MeCN)_3(H_2O)$, where the $Co^{III}{}_4O_4$ cubane bridges through each of four μ_3-O groups in the core to a Co^{II} five-coordinate site, making the oxo groups μ_4-O by this attachment (Figure 8).[953]

Heteronuclear bridged systems featuring hydroxo and or oxo ligands are also known. An example of this category is the hydroxo-bridged heterotrinuclear complex ion $[Cu\{(HO)_2Co(en)_2\}_2]^{2+}$, where the Cu^{II} is surrounded by four bridging hydroxides linking in pairs from two octahedral Co^{III} centers.[954] Another related example, where in this case the central metal is in an octahedral environment, is the series $[M^{II}\{(HO)_2Co(en)_2\}_3]^{5+}$ (M = Ni, Zn, Mg), prepared by reaction of $[Co(en)_2(OH_2)_2]^{3+}$ with MCl_2 in water at pH ~8.[955] Yet another, where the concept is extended to the central metal ion being an eight-coordinated ion, is the series $[M^{III}[(HO)_2Co^{III}(NH_3)_4]_4]^{7+}$ (M = Ce, Y, La, Pr, Gd).[956]

Oxo ligands find their fullest expression in polyoxometallates, dominantly of high-valent Mo and W. Polyoxometallates have been extensively reviewed.[957–959] An example of a polyoxometallate cluster incorporating cobalt(III) is $[CoW_{12}O_{40}]^{5-}$. This has the Co^{III} in an unusual tetrahedral geometry, as in the Co^{II} analog from which it can be oxidized reversibly.[960] The trivalent complex is a strong oxidizing agent.

(ii) Dioxygen, superoxide, and peroxide

The interaction of dioxygen with Co centers has its roots in the very beginning of Co chemistry. Biorelevance is a theme that retains a sturdy interest in these systems to the present time (see Section 6.1.3.1.3). Dioxygen can bind reversibly to Co complexes where they retain their integrity as monomers. Further, binding which generates a dimer can be reversible, as observed with $[Co(terpy)(bpy)X]^{2+}$ in polar non-aqueous solvents where X is a labile group such as

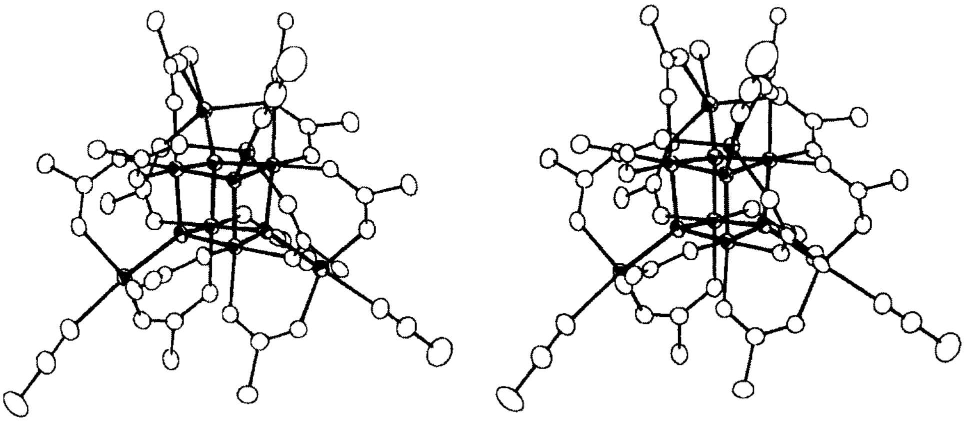
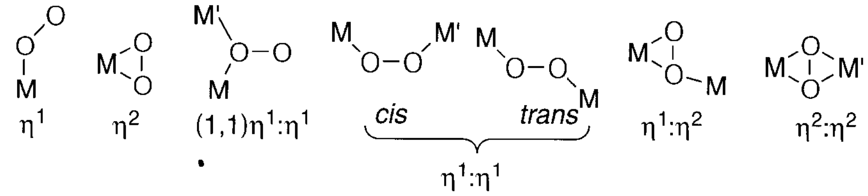


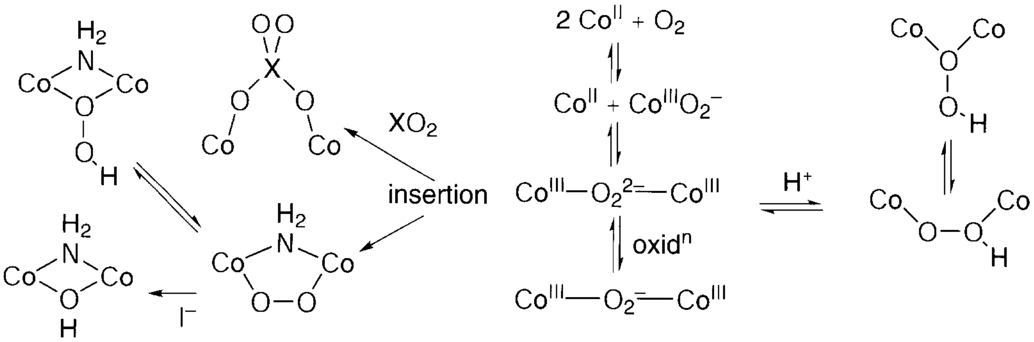
Figure 8 Stereoview of the $[Co_8O_4(OBz)_{12}(MeCN)_3(OH_2)]$ cluster, with phenyl rings and H-atoms omitted (reproduced with permission of the American Chemical Society from *Inorg. Chem.*, **1995**, *34*, 4160–4166).

trifluoromethanesulfonate or 4-chloro-3-nitrobenzenesulfonate.[961] Peroxide (O_2^{2-}) as a bridging ligand between two cobalt(III) centers is an enduring theme in Co chemistry, as is superoxide (O_2^-). The commonly brown μ-peroxo complexes are usually easily oxidized to the typically green μ-superoxo complexes, as defined in the first edition.

Dioxygen and its ions can bind in mononuclear and dinuclear structures in a number of ways,[962] as illustrated in Scheme 1. The typical reaction of dioxygen with Co compounds involves a number of these binding forms, outlined in Scheme 2. Mononuclear Co^{III}–peroxo complexes are relatively rare, but yellow trigonal bipyramidal complexes $[Co(O_2)L_2]^+$ (L = chelating phosphines dppe or dppp) have been characterized structurally where the O_2^{2-} is bonded to the Co in the side-on η^2 form (Co—O 1.858(7)–1.881(4) Å), with O—O stretching frequencies (~870 cm^{-1}) consistent with Co^{III}–peroxo speciation.[963]



Scheme 1



Scheme 2

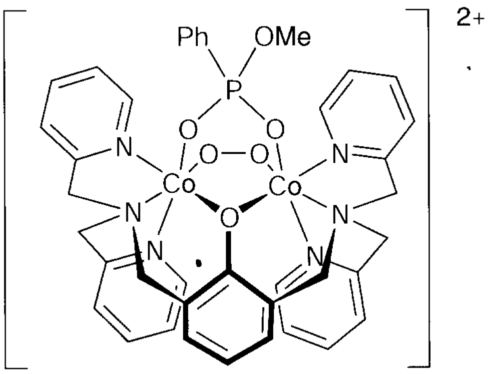
Dioxygen anions (peroxide and superoxide) in a bridging mode are more common. As representative examples, a selection of structurally characterized dicobalt dioxygen complexes is collected in Table 3. It is notable that the type of companion ligands influences the bridged dioxygen moiety. For example, the presence of a polyamine with unusually short Co—N distances has an effect on the superoxide O—O distance, which is shorter than in the simple decaammine analog.[964] Raman spectroscopy provides one method for monitoring behavior in solution for both superoxo and peroxo compounds, with the position of the strong Raman-active O_2 vibration reflecting

Table 3 Some structurally characterized dicobalt dioxygen complexes.

Dioxygen unit	*Other bridging groups*	*Other ligands*	*References*
cis-μ-peroxo	Ph_2PO_2, phenoxo	polyimine/amine	966
cis-bis(μ-superoxo)	hydroxo	polyamine	967
cis-μ-peroxo	acetato, alkoxo	polyimine/amine	968
trans-μ-peroxo		bpy, terpy	961
trans-μ-superoxo		polyamine	964
cis-μ-peroxo	hydroxo	imidazole/thioether	969
cis-μ-peroxo	thiolate	polyamine	970
trans-μ-peroxo		polyamine/imine	971
trans-μ-superoxo		polyamine/imine	971
cis-μ-peroxo	thiosulfato	polyamine	972
trans-μ-peroxo		aminosugar	973

bond strength. Multiple bridging also influences both Raman and structural parameters. A rare example of a $\mu_3(\eta^1,\eta^2)$-peroxo bridge between Co^{III} and Pb^{II} has been reported in a macrocyclic polyimine compartment ligand where phenoxo groups link metals in each compartment.[965]

Examples are tending to be more sophisticated and complex in form. For example, a dinuclear complex featuring a bridging phosphinate and phenolate in addition to peroxide (**221**) has been reported,[966] as a model for phosphodiester systems. Apart from dicobalt(III) systems, a mixed-valence $Co^{II,III}$ di-μ-superoxo complex (**222**) has been prepared.[967] Transition between the three redox states $Co^{II,II}$, $Co^{II,III}$, and $Co^{III,III}$ is electrochemically reversible.



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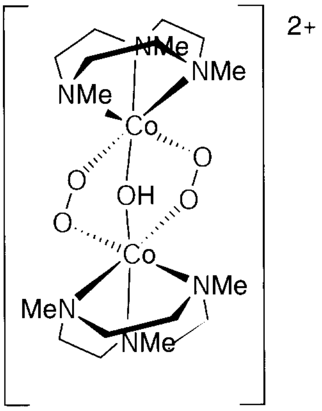


(222)

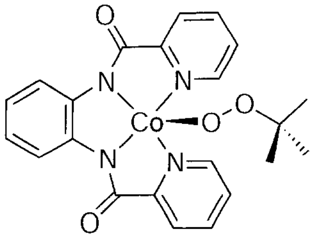
A detailed study of the reaction of the Co^{II} complex of 1,4,7,10,13-pentaazapentadecane ([15]aneN_5) with dioxygen to form Co^{III} complexes has been reported.[974] Formation equilibrium constants for the superoxo ($2.2 \times 10^7\,M^{-1}$) and peroxo ($1.2 \times 10^{20}\,M^{-2}$) were calculated, as well as ligating properties of superoxide and peroxide towards $[Co[15]aneN_5(OH_2)]^{3+}$ ($10^{12}\,M^{-1}$ and $2 \times 10^{37}\,M^{-2}$ respectively), defining the strength of the dioxygen anion complexes. The formation constant with superoxide is similar to a value of $10^8\,M^{-1}$ deduced for the transient superoxo complex of Co^{II}(EDTA).[975] The mechanism of the superoxo monomer $[Co(CN)_5(O_2)]^{3-}$ decomposition in aqueous solution has been examined,[976] and involves partial decomposition to a pentacyanocobaltate intermediate which binds an undissociated dioxygen-bound monomer to form the dimer $[\{(NC)_5Co\}_2(\mu\text{-}O_2)]^{6-}$. This in turn hydrolyzes to form $[Co(CN)_5(OH)]^{3-}$ and $[Co(CN)_5(OOH)]^{3-}$.

(iii) Neutral oxygen donor ligands

In the same way that H_2O is an excellent monodentate ligand for Co^{III}, simple alcohols ROH are known to bind effectively to cobalt(III) as monodentate ligands. They can be conveniently introduced into the coordination sphere where other sites are occupied by amines through simply dissolution of the trifluoromethanesulfonatocobalt(III) precursor in the pure alcohol,[977] or less readily by reaction of the halocobalt(III) complexes with silver ion in the alcohol, and are reasonably inert to substitution. Introduction of polyalcohols is possible through the same paths; for example, the complex $[Co(tacn)(inisotol)]^{2+}$ has been reported, albeit with the hexahydroxycyclohexane (inisotol) monodeprotonated and hence a superior ligand to the neutral alcohol.[978]

(iv) Alkyl peroxides

A number of alkylperoxy Co^{III} complexes including mainly polyimine ligands have been prepared, exemplified by (**223**).[979] Hydroxylation of saturated hydrocarbons, preferentially at the more nucleophilic C—H bonds, yields alcohols, ketones, and *t*-butylperoxo products, whereas olefins form epoxides if they carry no allylic H atoms.



(223)

β-Diketonate cobalt(III) complexes with alkyl peroxo adducts have been prepared recently and characterized structurally, and their value in hydrocarbon oxidation and olefin epoxidation examined.[980] Compounds $Co(acac)_2(L)(OOt\text{-}Bu)$ with L = py, 4-Mepy and 1-Meim, as well as the analog of the first with dibenzoylmethane as the diketone, were prepared. A distorted octahedral geometry with the monodentates *cis* is consistently observed, and the Co—O bond distance for the peroxo ligand lies between 1.860(3) Å and 1.879(2) Å.

(v) Ketones and esters

The monoketone bis(2,2′,*N*,*N*′-bipyridyl)ketone forms a $[Co^{III}L_2]^+$ complex on reaction with $[Co(NH_3)_4(CO_3)]^+$ in water.[981] As reported for a quite different Co^{II} complex, the ketone is hydrated to form the gem diol which binds as a monodeprotonated O-donor along with the two pyridine groups in a tridentate chelate, with very little distortion from octahedral observed in the complex. This appears to represent a facile route for this type of inherently poor donor to achieve coordination. Chelated β-diketonate anions are long-studied examples of O-donor chelates, and continue to be examined. A simple example is the *cis*-$[Co(acac)_2(NH_3)_2]^+$ (acac = 2,4-pentanedionate), structurally characterized and utilized to produce molecular mechanics force field parameters for β-diketones bound to Co^{III}.[982]

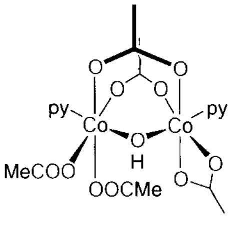
Amino acid esters act as chelates to Co^{III}; for example, the β-alanine isopropyl ester is known as both a chelate and as an *N*-bonded monodentate,[983] and the mechanism of hydrolysis of the ester, which is activated by coordination, to yield chelated β-alanine has been closely examined.

(vi) Carbonates, carbamates, and carboxylates

Carbonate is a well-known ligand for Co^{III}, and can adopt monodentate, chelate, and bridging roles. Recent structurally characterized examples, obtained from prolonged aerial oxidation of a solution of cobalt(II) nitrate and ammonium carbonate in aqueous ammonia, are chelated carbonate in $[Co(NH_3)_4(\eta^2\text{-}CO_3)]^+$ and bridging carbonate in $[(NH_3)_3Co(\mu\text{-}OH)_2(\mu\text{-}CO_3)Co(NH_3)_3]^{2+}$.[984] The four-membered chelate ring is strained, with the internal O—Co—O angle typically near 70°. The protonated form, hydrogen carbonate (HCO_3^-), is usually met as a monodentate; however, chelation has now been reported in the crystal structure of the bicyclic tetraamine complex of (**32**), $[Co(adz)(HCO_3)]^{2+}$, where protonation appears to occur at the non-coordinated O atom.[985]

Carbamates (R_2NCOOR') may be *O* or *N* bonded. Base-promoted isomerization of carbamates from the O- to the deprotonated *N*-bound form in pentaamminecobalt(III) complexes have been defined.[986]

Carboxylates ($RCOO^-$) in simple form or as components of more elaborate polydentate ligands, are commonly met as strong ligands in cobalt(III) chemistry. Monocarboxylate anions can adopt roles as monodentate, bidentate, or bridging anions. Complexes are usually relatively inert to substitution, with hydrolysis of acetato slower than halo ligands. Acetato complexes can be prepared simply by substitution reactions, replacing coordinated solvents and labile anionic groups such as trifluoromethanesulfonate. Acetate in its three possible coordination modes appears in the one dinuclear complex $(py)(\eta^1\text{-}OAc)_2Co(\mu\text{-}OH_2)(\mu\text{-}O,O\text{-}OAc)_2Co(\eta^2\text{-}OAc)(py)$ (**224**).[987] A range of other examples where carboxylates form one of a suite of ligands or one of the donor groups in polydentate ligands is met elsewhere in this chapter. Simple $[Co(NH_3)_5(OOCR)]^{2+}$ ions with long-chain alkyl R groups have been examined for use as catalysts in dishwashing and laundry detergents.



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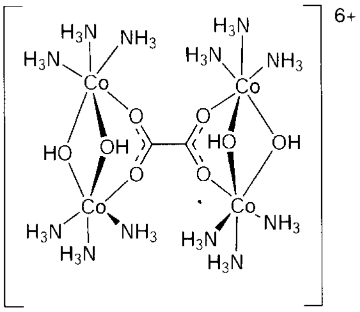

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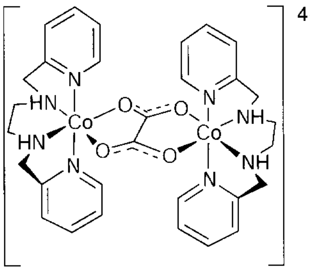


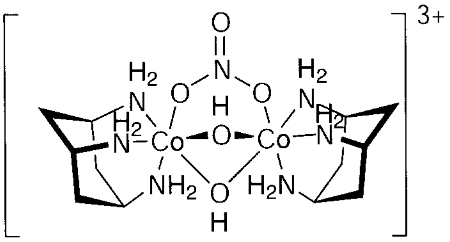
(226)

The classical chelating diacid, oxalic acid, has been studied for many years. It has the potential to bind through any combination ranging from one to four oxygen atoms, including bonding to up to four separate metal ions. The latter arrangement is achieved in the cluster (**225**).[988] More recently, a simple dinuclear μ_4-oxalato complex where the ligand chelates a cobalt(III) on each side has been reported (**226**).[989]

An interesting example of the detailed rearrangement chemistry possible on Co^{III} is the study of pentaamminecobalt(III) complexes of malonamic and phthalamic acids, which can bond through the carboxylate group or else the deprotonated amide nitrogen.[990] The former complexes are readily prepared directly from the amidic acids, whereas the latter form from base hydrolysis of precursors such as (for malonamato-*N*) cyanoacetate-*N*. The *N*-bound compounds undergo in water the usual amide-*N* to amide-*O* rearrangement but, concurrently, an amide-*N* to carboxylate-bonded rearrangement.

(vii) Oxoanions of N, S, P, and the halogens

(aa) Nitrogen oxoanions. The best-known nitrogen oxoanions are nitrate (NO_3^-) and nitrite (NO_2^-). The ambidentate nature of the latter as a monodentate ligand is well known, with *O*-bound (nitrito) and *N*-bound (nitro) isomerism on cobalt(III) well studied, but still producing new insights.[732] Complexes incorporating nitrite are readily formed; for example, reaction of hydrated $Co(ClO_4)_2$ with ethylenediamine and $NaNO_2$ in aqueous solution in air affords the yellow, crystallographically defined *trans*-$[Co(en)_2(NO_2)_2](ClO_4)$.[991] Of course, the anion with nitrite as the sole ligand, $[Co(NO_2)_6]^{3-}$, is well known, and the nitro ligands are readily displaced by, for example, amines and cyanide, as well as rapidly forming a range of mixed aquanitro complexes is aqueous solution, as defined from solution NMR studies.[992] The nitrate and nitrite anions can also act as bidentates and in bidentate bridging modes. Chelated nitrate is exemplified in the complex of the tripodal ligand *N*-(2-aminoethyl)-*N*,*N*-bis(3-aminopropyl)amine (abap), $[Co(abap)(O_2NO)](ClO_4)_2$,[993] where the O—Co—O angle is reduced to 66.1° while the other angles around the plane that includes the nitrate and Co are expanded to as much as 99.9° to compensate. The nitrate ion has been characterized in a bridging mode along with two hydroxide ions (**227**), formed via a tris(alcohol) intermediate.[978] For nitrite, the μ_2-*N*,*O* bridging mode is found in the dimer (**228**).[994]



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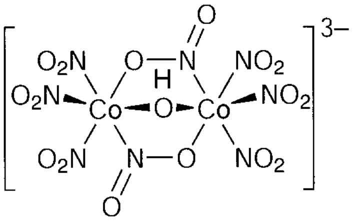
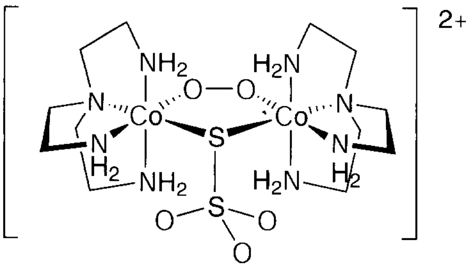


(228)

(bb) Sulfur oxoanions. The sulfur oxoanions all can form complexes with cobalt(III) via simple substitution reactions in solution, and are usually *O*-bound in form. However, S coordination is found in the thiosulfate ion ($S_2O_3^{2-}$), which can act as a *O,S*-chelate in simple complexes such as $[Co(en)_2(S_2O_3)]^+$,[995] and adopt a bridging mode as in the dinuclear complex (**229**).[970] Coordinated *S*-bound thiosulfato in $[Co(NH_3)_5(S_2O_3)]^+$ can be cleanly oxidized by peroxomonosulfate to produce the coordinated $S_2O_5^{2-}$ ion.[996]



(**229**)

Sulfito (SO_3^{2-}) complexes may also be *S*- and *O*-bound; a solution NMR study of sulfite reacting with several simple aquaaminecobalt(III) complexes has identified both monodentate *O*- and *S*-bound linkage isomers.[997] The SO_3^{2-} ion has been characterized in both monodentate[998] and bridging modes.[999] The *S*-bonded coordination of monodentate sulfite was established in a crystal structure of $[Co(hmd)(OH_2)(SO_3)]^+$.[338] The photochemistry is complex, and involves photoisomerization to *O*-bound sulfite as well as photoredox formation of Co^{II}, with secondary photolysis yielding Co^{I}. The reverse *O* to *S* linkage isomerization is usually observed spontaneously in solution, as exemplified by the reaction of $[Co([16]aneN_5)(OSO_2)]^+$ ($[16]aneN_5$ = 1,4,7,10,13-pentaazacyclohexadecane);[1000] the *O*-sulfito complex is also rapidly cleaved to the aqua compound in acidic solution. The trinuclear complex $Ni\{Co(en)_2(SO_3)_2\}_2$ (and other M^{II} analogs) has the sulfite ions *S*-bound to Co^{III} and O bound to the central Ni atom.[1001] Thermolysis in air of several of the mixed-metal compounds above 750 °C yielded spinel oxides. Reaction of $CoCl_2$ with $Na_2S_2O_4$ in aqueous ammonia in air yields similar type of complex, the mixed oxidation state trinuclear complex $[Co^{II}[(O_3S)_3Co^{III}(NH_3)_3]_2]^{4-}$, where the central Co^{II} lies in an octahedral CoO_6 environment provided by six O atoms of bridging sulfito groups.[999] The reactions of sulfur(IV) in solution (as SO_3^{2-}/HSO_3^-) with aquaaminecobalt(III) complexes has been reviewed.[1002]

The sulfate ion, well known as a monodentate and simple bidentate ligand, has been observed also as a bridging ligand, as exemplified in $[(en)_2Co(OS(O_2)O)_2Co(en)_2]^{2+}$.[1003] The *cis*-bis($\mu$-sulfato) bridge undergoes hydrolysis to *cis*-$[Co(en)_2(OSO_3)(OH_2)]^+$ in acidic solution, hydrolyzing further with loss of coordinated sulfate in aqueous base to the dihydroxo complex.

The use of *O*-bound $CF_3SO_3^-$ as a labile leaving group was established with the reported syntheses of complexes with one, two, and three triflato groups, namely $[Co(NH_3)_5(OSO_2CF_3)]^{2+}$, *cis*-$[Co(en)_2(OSO_2CF_3)_2]^+$, and *fac*-$Co(dien)(OSO_2CF_3)_3$.[1004] These are readily formed by reaction of the corresponding chloro complexes with the anhydrous triflic acid eliminating HCl, and this permits introduction of a wide range of neutral and ionic ligands into the coordination sphere in substitution reactions.[64]

(cc) Phosphorus oxoanions. Monophosphate (PO_4^{3-}), diphosphate ($P_2O_7^{4-}$) and triphosphate ($P_3O_{10}^{5-}$) and their various protonated forms have been coordinated to cobalt(III) in a range of complexes. The cis-$[CoL(OH)(OH_2)]^{2+}$ (L = tetraamine) ions are rapidly anated by phosphate to form $CoL(PO_4)$, with a chelating phosphate.[1005] Coordinated polyphosphates are stable to hydrolysis except where a cis-coordinated hydroxy group exists, but hydrolytic cleavage can be catalyzed by addition of two molar equivalents of another hydroxyaquacobalt(III) complex, which form bridging intermediates with a coordinated nucleophile available for attack. Those with 3-aminopropyl(amine), 6-(4-amino-2-azabutyl)-6-methyl-1,4-diazacycloheptane and trien (**135**) "spectator" tetraamine ligands bound in the other sites have proved particularly effective.[1006,1007]

Mono-, di-, and polyesters of phosphates have also been bound as ligands. Acidity of the remaining phosphate acid sites rises as ester groups are introduced, facilitating the ligation of the esters. Interest in the esters of phosphate is high because of their biological relevance (after all, DNA can be considered from a basic chemical viewpoint as simply an oligomeric phosphate diester). Further examples of this chemistry are provided in Section 6.1.3.1.3.

Trimethylphosphate, despite being neutral, is known to form the simple complex $[Co(NH_3)_5(OP(OMe)_3)]^{3+}$; this reacts with nucleophiles $X^{n-} = S_2O_3^{2-}$, I^- and SCN^- in that order of reactivity to produce $[Co(NH_3)_5(O_2P(OMe)_2)]^{3+}$ and MeX up to 150-fold faster than in the absence of coordination.[1008] Both hydroxide and water are ineffective in this reaction, with simple ligand hydrolysis occurring more rapidly than any reaction.

(dd) Halogen oxoanions. The halogen oxoanions are *O*-donor ligands for Co^{III}. Perchlorato complexes are the type most likely to be met, since the weak, labile perchlorato ligand serves as a good leaving group for further chemistry. For example, perchloratocobalt(III) porphyrins bind acetylene reversibly in anhydrous dichloromethane.[1009] Despite this, the hazards of these thermally unstable perchlorato complexes have been well documented and their use is not recommended.

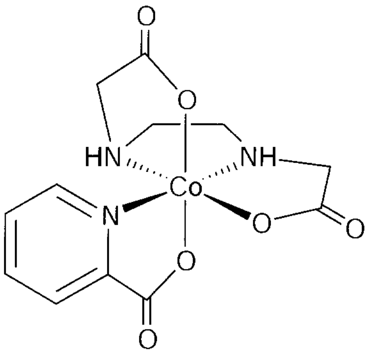
(ee) Other oxoanions. There have been other oxoanions, including metal-centered anions, reported as ligands for Co^{III}. An example is the coordination of molybdate ion in $[Co(NH_3)_5(OMoO_3)]^+$ via reaction of the aquacobalt complex and molybdate.[1010] The rapid hydrolysis kinetics supports Mo—O and not Co—O bond cleavage, unfortunately limiting synthetic usefulness of this compound.

(viii) Mixed O, N ligands

The variety and extent of research devoted to ligands carrying both O- and N-donors is simply immense. The type of cobalt(III) systems extant include amino acids, amino alcohols, amino ethers, amino phosphates, amino phenolates, as well as amide and imine analogs of these. These are met as simple chelates or more elaborate polydentates. Here, we highlight a strictly limited selection of examples to illustrate the type of systems reported; no attempt at exhaustive review has been made.

(ff) Aminoacids. Simple aminoacid complexes have been studied for decades, with strong interest in their stereochemical and chiroptical properties. An example of a well-characterized complex featuring only aminoacids in the coordination sphere is the *mer*-$Co(gly)_2(\beta\text{-ala})$, which has been characterized with glycinato and β-alaninato ligands chelated and in a trans(O5) arrangement, as one of several isomers isolated.[1011] Column chromatography using ionic resins usually features as the best mode of separation of geometric isomers of this type.

The best known of the synthetic polyaminoacids is the tetraanion EDTA, and a wide range of analogs of the N_2O_4 donor set have subsequently appeared.[1012] An example is the propionate analog EDTP. The additional methylene in each carboxylate arm and ensuing twist-boat six-membered chelate rings with Co^{III} [1013] lower the ligand field strength of the chelate as reflected in visible absorption maxima, which shift from bands at 18,630 and 26,040 cm^{-1} for EDTA to 18,000 cm^{-1} and 24,800 cm^{-1} for EDTP. The tetradentate analog EDDA $((^-O_2CCH_2)NHCH_2CH_2NHCH_2CO_2^-)$ has been structurally characterized as *uns-cis-mer*-Co(EDDA)(pic) **(230)**.[1014] Intramolecular reaction of a Co^{III} EDDA complex leading to a macrocyclic aminoacid involves a precursor complex of tetradentate EDDA and a bidentate diamine bearing two 3-chloropropyl groups. This undergoes efficient intramolecular alkylation in basic solution to form the 1,4-bis(carboxymethyl)-1,4,8,11-tetraazacyclotetradecane complex.[1015] The smallest member of the carboxymethylated en family is the N_2O-donor monoacetate EDMA



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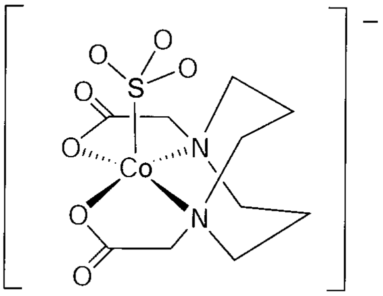
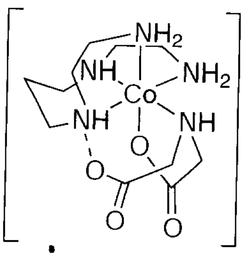


(231)

($(^-O_2CCH_2)NHCH_2CH_2NH_2$), which forms a bis complex *mer*-$[Co(EDMA)_2]^+$.[1016] This undergoes isomerization in aqueous base to a mixture of other forms.

The *N*,*N*′-substituted ligand (**231**) forms an unusual square-based pyramidal Co^{III} complex with SO_3^{2-} in the axial site, presumably stabilized by the strong *trans* influence of the SO_3^{2-} ligand.[998] The enzyme inhibitor α-aminomalonic acid ($^-O_2CCH(NH_2)CO_2^-$, ama), when reacted with $[Co(2,3,2\text{-tet})Cl_2]^+$ (2,3,2-tet = *N*,*N*′-bis(2′-aminoethyl)propane-1,3-diamine) under various conditions, undergoes halide substitution to produce both the simple $[Co(2,3,2\text{-tet})(N,O\text{-ama})]^+$ (**232**) and other species which underwent metal-directed condensations involving the acidic carbon and a nitrogen of the polyamine, such as (**233**).[1017]



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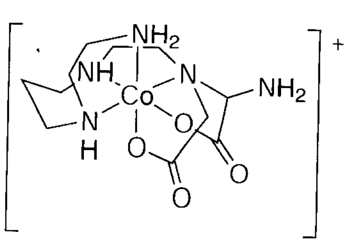

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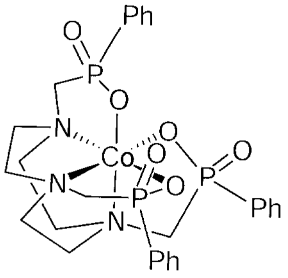
(gg) Aminophosphates. Phosphate and phosphite groups can be attached to amines conveniently through reaction with haloalkylphosphates or analogs. One example features a pendant triazamacrocycle, which acts as a hexadentate ligand to form octahedral complexes (**234**) with both Co^{III} and Co^{II}.[1018]



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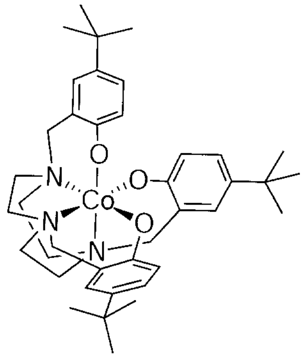

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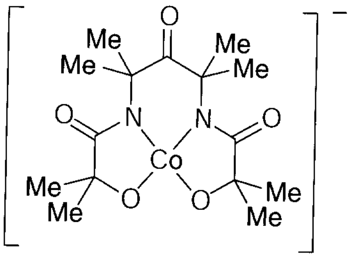

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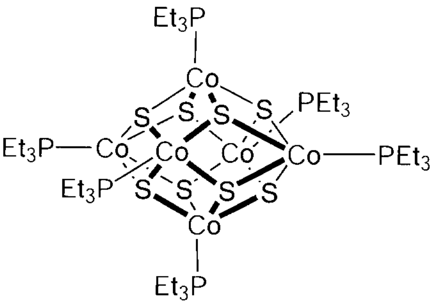
(hh) Aminophenolates. An *N*-pendant phenolate ligand based on tacn (**235**) readily forms a 1:1 complex with Co^{III}.[1019] Further, this reacts with Fe^{2+}_{aq} or Fe^{3+}_{aq} to form mixed trinuclear complexes $(CoL)_2Fe$ where the Fe is sandwiched between two sets of three phenolate oxygens which bridge between the cobalt(III) and iron(II)/(III) centers. Macrocyclic ligands featuring amine and phenolate donor groups, particularly with side-by-side compartments where phenolate ions act as bridging donors to two metal ions, abound.

(ii) Amidoalcoholates. The methylated diamidedialcoholate (**236**) forms another example of the rare square planar cobalt(III) geometry,[1020] with steric congestion presumably blocking facile entry to the axial sites.

6.1.2.3.7 Sulfur and selenium

(i) Sulfides and selenides

Sulfide is a strong ligand, but compounds containing S^{2-} as the only ligand are rare. One example is the compound $M_9Co_2S_7$, formed in a melt with $M_2(CO_3)$ (M = K, Rb, Cs) and S, where both Co^{III} and Co^{II} centers are present in trigonal planar CoS_3 units.[1021] More typically, sulfide is a companion ligand in mixed-ligand systems. These are often clusters, as exemplified by the mixed oxidation state (formally $4Co^{III}$, $2Co^{II}$) diamagnetic cluster $Co_6S_8(PEt_3)_6$ (**237**).[1022] This type of cluster spontaneously self-assembles from reaction of metal salt, chalcogen, and ancillary ligand.



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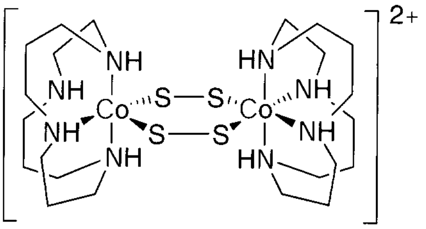

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A Co^{III} compound containing only selenium as a ligand, $[Co_3(Se_4)_6]^{3-}$, has also been reported, prepared by reaction of $CoCl_2{\cdot}6H_2O$ with Li_2Se_6 in DMF at 100 °C.[1023] This trimer includes Se_4^{2-} as a linear chelating fragment, bound in bidentate and bridging arrangements; the average of Co^{III}—Se distances reported was 2.37 Å.

Apart from S^{2-}, the disulfide ion S_2^{2-} is an effective ligand. Reaction of the hexakis(acetonitrile) adducts of CoX_2 ($X = BPh_4^-$ or ClO_4^-) with S_2^{2-} or S_4^{2-}, with a tetraaza macrocycle also present, yields the dimer $[\{([15]aneN_4)Co\}_2(\mu\text{-}S_2)_2]^{2+}$ (**238**) where the two Co^{III} centers are bridged by two disulfido groups, forming a six-membered Co_2S_4 ring.[1024]

(ii) Thioethers and selenoethers

The acyclic and macromonocyclic polythioethers were well illustrated in *CCC* (1987 Section 47.8.3.2).[1] Only a few recent examples will be given of this chemistry here.

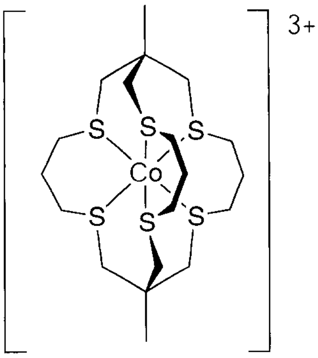
(jj) Acyclic. The simple dimethylsulfide complex ion $[Co(NH_3)_5(SMe_2)]^{3+}$ was prepared from reaction of Me_2S with the trifluoromethanesulfonato precursor complex in sulfolane at 80 °C.[1025] It is hydrolyzed slowly in aqueous acid, but undergoes rapid base-promoted hydrolysis, with Co—S cleavage.

Linear thioethers of the type $MeS(CH_2)_nS(CH_2)_mS(CH_2)_nSMe$ ($n = m = 2$; $n = 2$, $m = 3$) form octahedral dihalo tetrathioether complexes by air oxidation of a solutions of CoX_2 (X = Cl, Br, I) and the ligand in nitromethane.[1026] In addition, $[Co(MeSCH_2CH_2SMe)_2X_2]^+$ and a $Co^{III}S_6$ compound comprising one each of the tetradentate and bidentate ligands were prepared.

Apart from well-established thioether chelates, coordination of selenium analogs has also now appeared. The chelate 2,5-diselenahexane reacts with CoX_2 (X = Cl, Br, or I) in an aprotic solvent in the presence of dry air and $NaBPh_4$ to form the air-stable Co^{III} complex $[Co(CH_3SeCH_2CH_2SeCH_3)_2X_2]BPh_4$, as a mixture of *cis* and *trans* isomers.[1027]

(kk) Macrocyclic. The macromonocyclic polyethers and their Co^{III} complexes have been known for some time, with ttcn ($[9]aneS_3$) (**109**) and $[14]aneS_4$ (**110**) classic examples. The mixed-ligand complex $[Co(tacn)(ttcn)]Br_3$ offers the opportunity to compare the thioether and aza macrocycles within the one compound.[1028] Average Co—S and Co—N distances were 2.247 Å and 1.961 Å respectively, and the complex displayed reversible $Co^{III/II}$ and $Co^{II/I}$ couples near 0.0 V and −1.15 V vs NHE respectively. Larger macrocycles with more thioether donors have been reported; a recent example is the octahedral $Co^{III}S_6$ system with 1,4,7,11,14,17-hexathiacycloeicosane ($[20]aneS_6$) coordinated.[1029] More recently, the synthetically demanding organic chemistry leading to macrobicyclic polythioethers has been developed. The hexathia macrobicyclic tricosane cage complex of Co^{III} has subsequently been reported (**239**).[466] Metal-directed condensations of CH_2O and $MeNO_2$ (or NH_3) with their corresponding acyclic hexadentate Co^{III} complexes lead to their corresponding mixed-donor cage complexes, for example (**240**)[1030] and (**241**).[1031] The asymmetric CoN_4S_2 cage is also known.[1032] The electrochemical and magnetic properties of these mixed-donor complexes are quite distinct from their $Co^{III}N_6$ relatives (**161**) and (**162**). For example, the divalent CoN_3S_3 cage complex is low spin in contrast to its high-spin hexamine relatives. The octadentate ligand tetrakis((2-aminoethyl)thiamethyl)methane, with four identical

aminothioether arms, can similarly be capped to form an N_3S_3 cage with an exocyclic N,S chelate.[1033] The tri- and divalent Co cage complexes have been characterized.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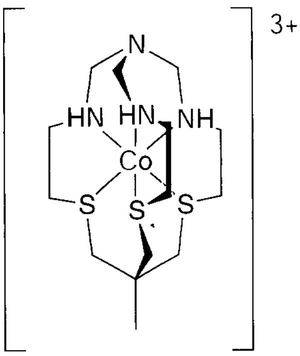
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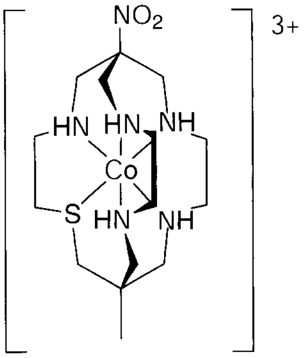
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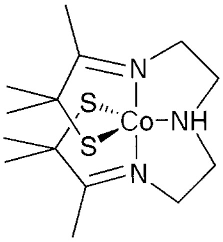
(iii) Thiolates

Thiolates are strong ligands and a rich coordination chemistry with cobalt(III) exists. Normally, thiols are employed directly in synthesis, and this is the usual entry into their coordination chemistry. However, alternative approaches do appear from time to time, and recently the cobalt-mediated direct thiolation of an aromatic ring in bidentate phenyl(2-pyridyl)diazene using dithiocarbamate ion to produce a coordinated tridentate thiolate has been reported.[1034]

A reactive five-coordinate thiolate cobalt(III) complex (**242**) was prepared to model the active site of nitrile hydratase, a cobalt(III) or iron(III) metalloenzyme promoting the conversion of nitriles to amides.[1035] The synthesized complex is facile in its uptake and release of azide and thiocyanate, indicating that ligand displacement in the presence of an appropriate non-leaving group environment is not too slow for catalytic paths in non-redox active Co metalloenzymes. Other model compounds for nitrile hydratase feature new octahedral Co^{III} complexes with carboxamido nitrogen (Co—N 1.91 Å) and thiolate sulfur (Co—S 2.23 Å) donors.[1036] Hydrogen peroxide, or even air and activated charcoal, readily converts the sulfides to sulfinato groups.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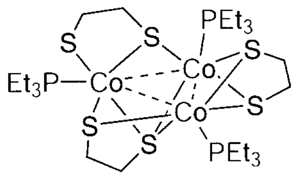
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Chelation of *iso*-maleonitriledithiolate (imdt) has been structurally characterized in the octahedral cobalt(III) complex *trans*-$[Co(imdt)_2(P(n\text{-}Bu)_3)_2]^-$, formed via reaction of cobalt(II) ion with $K_2(imdt)$ in the presence of the phosphine.[1037] Simple chelating thiolates such as $^-SCH_2CH_2S^-$ not only form mononuclear compounds, but participate in bridging in clusters such as $[Co_3(SCH_2CH_2S)_3(PEt_3)_3]^{3+}$ (**243**).[1038]

When electrochemical oxidation of Co metal is carried out in an acetonitrile solution of phosphinothiol ligands, tris(phosphinothiolate)cobalt(III) compounds are formed.[1039] The octahedral P,S-chelated $Co(2\text{-}(Ph_2P)\text{-}6\text{-}(Me_3Si)C_6H_3S)_3$ compound has been characterized structurally.

Thiolates are candidates for oxygenation reaction leading to sulfenates (RSO^-) and sulfinates (RSO_2^-). Oxygenation by H_2O_2-urea of the cobalt(III) complex of the N_2S_2 ligand bis(carboxamido-*N*)dithiolato with *tert*-butyl isocyanide in the axial sites produced the first (carboxamido-*N*) bis(sulfenato-*S*)cobalt(III) complex, in a reaction asserted to model oxygenation of nitrile hydratase thiolate ligands.[1040] Oxidation of thiolates to sulfinates has been achieved in the cobalt(III) complex of *N,N′*-(3-mercapto-3-methyl-butyryl)-*o*-phenylenediamine with axial *t*-butyl isocyanide groups, yielding an octahedral product defined by a crystal structure.[1041] The two oxidized thiolates (now SO_2 groups) lie *trans* to two deprotonated carboxamido N atoms; there is some structural resemblance to Co nitrile hydratases, where thiolate oxidation has been proposed for enzyme activity. Oxidation of thiolates to sulfinates by H_2O_2 has also been described for the mononuclear octahedral CoN_3S_3 complex of the trianion of *N,N′,N*-tris(2-thiobenzyl)-1,1,1-tris(aminomethyl)ethane, whereas a related thiolate-bridged dinuclear dicobalt(III) complex is resistant to oxidation.[1042] The *cis,cis,cis*-$[Co(pyet)_2]^+$ complex (pyet = 2-((2-pyridylmethyl)amino)-ethanethiol) is converted to sulfenato and sulfinato complexes by molecular oxygen alone in the presence of activated charcoal.[1043]

Tri-*tert*-butoxidesilanethiolate forms complexes with both Co^{II} and Co^{III}. Reaction of the thiol with a Co^{II} ammine in water yields a dimer which undergoes oxidation in an ammonia-saturated atmosphere to form octahedral $[Co(SSi(O\text{-}t\text{-}Bu)_3)_2(NH_3)_4]^+$, the first silanethiolate characterized structurally.[1044]

(iv) Thiocarbamates

Thiocarbamate (tc, $RHNCSO^-$) is a monodentate ambidentate ligand, and both oxygen- and sulfur-bonded forms are known for the simple pentaamminecobalt(III) complexes. These undergo redox reactions with chromium(II) ion in water via attack at the remote O or S atom of the S- and O-bound isomers respectively, with a structural *trans* effect suggested to direct the facile electron transfer in the former.[1045] A cobalt-promoted synthesis utilizing the residual nucleophilicity of the coordinated hydroxide in $[Co(NH_3)_5(OH)]^{2+}$ in reaction with MeNCS in $(MeO)_3PO$ solvent leads to the O-bonded monothiocarbamate, which isomerizes by an intramolecular mechanism to the S-bound isomer in water.[1046]

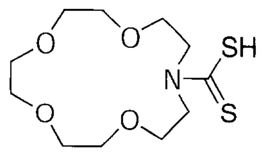
The dithioacid ligands dithiocarbamates ($R_2N\text{–}CS_2^-$), xanthates ($RO\text{–}CS_2^-$), thioxanthates ($RS\text{–}CS_2^-$), and dithiocarboxylates ($R\text{–}CS_2^-$), appeared in *CCC* (1987, Section 47.8.10). Dithiocarbamato (dtc^-) ligands are usually bidentate chelates, although monodentate coordination is known. Their chemistry, and that of the related xanthates and thioxanthates, has been extensively examined in the past, and recent chemistry has been more limited. A long-established, facile route to distorted octahedral $Co(dtc)_3$ is via reaction of $Na^+R_2NCS_2^-$ with $CoCl_2$ in the presence of oxygen. The four-membered planar chelate ring is characterized by a small bite angle, typically below 80°.[1047]

Cobalt(III) complexes of formula *cis*- and *trans*-$[Co(dtc)L_4]^{2+}$ and $[Co(dtc)_2L_2]^+$ where dtc = dimethyl-, diethyl- or piperidino-dithiocarbamate were prepared with phosphites $P(OMe)_3$, $P(OEt)_3$ and 4-ethyl-2,6,7-trioxa-1-phophabicyclo[2.2.2]octane as ligands L.[1048] Whereas Co—P bonding is found, as defined in the crystal structures of each of the two forms of complexes isolated, a linkage isomer in which the phosphite is O bound was detected for the bis(dithiocarbamate) compounds.

The dinuclear dialkyldithiocarbamate precursor $[Co_2(dtc)_5]^+$ reacted with diamine mustards *N,N*- and *N,N′*-bis(2-chloroethyl)ethylenediamine (bce, dce) and their non-chlorinated analogs yield $[Co(dtc)_2(diamine)]^+$.[1049] The bce and dce compounds were prepared and tested as potential hypoxia-selective cytotoxins, but did not prove of value as potential bioreductive anticancer drugs, partly due to their redox instability.

Examples in organometallic systems are known. Reaction of thiuram disulfides, $(R_2NCS_2)_2$, with $Co(Cp)(CO)_2$ produces dithiocarbamato pseudo-octahedral cobalt(III) complexes $Co(Cp)(dtc)_2$ with one chelated and one monodentate dtc, also accessible via Co(Cp)I(dtc).[1050] Fluxional behavior, including monodentate–chelate exchange, was observed for some complexes in temperature-dependent NMR studies. The Co(Cp)I(dtc) complex was defined in a crystal structure.

A mixed cobalt(III)–copper(I) one-dimensional polymer featuring Cu_3Br_3 units linking to tris(dithiocarbamato)cobalt(III) complexes through two of three interligand chelate sites forms readily from reaction of $Co(S_2CNR_2)_3$ with CuBr.[1051] With CuI, a novel and more complex infinite double-stranded polymer featuring CuI_2Cu and Cu_6I_6 linkers results. Dithiocarbamate pendant to a polyether macrocycle (**244**) is an unusual example of a simple chelating ligand. This reacts as the sodium salt with aqueous $CoSO_4$ to form a tris(dtc)cobalt complex.[1052] This complex has the potential to bind appropriate metal ions in the three pendant polyether cavities.



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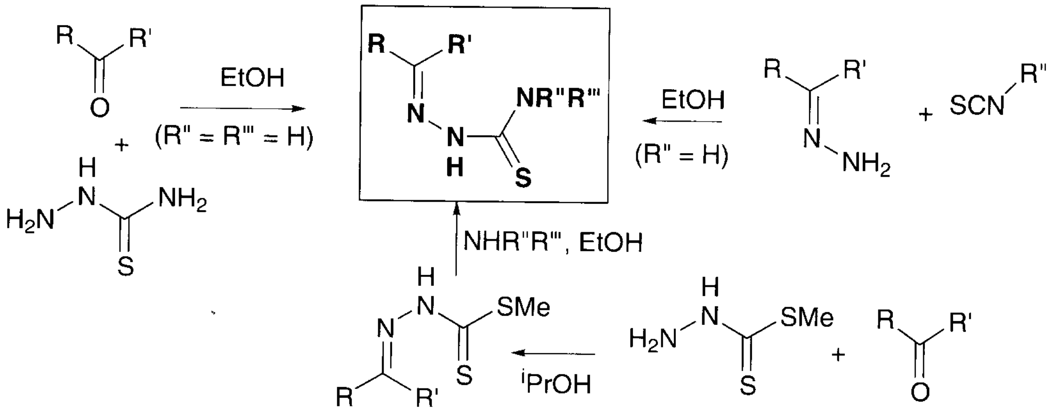
(v) Thiosemicarbazones

Thiosemicarbazone (RNH–CS–NH–N=CR′R″, tsc) complexes of cobalt(III) have been extensively studied since the early 1980s and continue to attract attention, gaining particularly from an interest in their biological activity and potential cytotoxicity. A truly extensive range of tsc compounds has now been reported, although structural definition of their complexes widely relied on basic analytical and spectroscopic techniques up to the late 1980s, when X-ray crystal structural studies of tsc compounds became more common. A review of thiosemicarbazone and *S*-alkyldithiocarbazate complexes has appeared.[1053]

The ligands are synthetically quite accessible through a number of routes (Scheme 3). Co^{II} complexes are formed in an inert atmosphere, with oxidation through to Co^{III} readily achieved in air. The ligands are poorly soluble in water, but their complexes are more soluble, enhancing their value in pharmacological applications. Various complexes have exhibited antitubercular, antileprotic, antiviral, antimalarial, and antitumor activity,[1053] with complexes of tridentate ligands usually exhibiting higher activity.



Scheme 3

Primarily, studies with structural characterization are discussed below. Typically, tsc ligands displaying *N,S*-bidentate, or else tridentate coordination for ligands carrying additional functionality, have been described. The *mer*-bis(tridentate) distorted octahedral geometry occurs as the dominant form of cobalt(III) complexation reported, as evident from the selected examples following. Pyridine-2-carbaldehyde thiosemicarbazone ($pcts^-$) acts as a tridentate ligand, binding through one S and two N atoms in $[Co(pcts)_2](NCS)$, as defined by a crystal structure.[1054] Redox activity and reaction with cell thiols is believed to be involved in the cytotoxicity of metal complexes of this ligand against some melanoma and erythroleukemia cells. Methyl pyruvate and α-ketoglutaric acid thiosemicarbazides form bis(tsc)cobalt(III) complexes, the crystal structure of the latter determined wherein the ligand acts as a tridentate in a distorted octahedral geometry.[1055] The octahedral cobalt(III) ion $[Co(datsc)_2]^+$, where tridentate ligand coordination occurs as defined by a crystal structure, is formed following reaction of dimethyl-2-acetylpyridine-*N*-oxide thiosemicarbazone (datscH) with $CoCl_2$.[1056] The potentially tridentate ligand 2-pyridineformamide N(4)-methylthiosemicarbazone (pntscH) forms following Na reduction of 2-cyanopyridine in dry methanol in the presence of the semicarbazide. The $[Co(pntsc)_2](ClO_4)$ has the thiolato S and both the pyridine and imine N atoms bound.[1057] The neutral octahedral *mer*-

Co(kbtsc)(Hkbtsc) has the 2-ketobutyric acid thiosemicarbazone (H_2kbtsc) bound as both a mono- and di-anion, with small differences between the two forms found in the crystal structure.[1058]

A range of S,N,O-donor ligands bound to Co have appeared. Pyridoxal (3-hydroxy-5-(hydroxymethyl)-2-methylpyridine-4-carbaldehyde) thiosemicarbazone (hhtsc) also forms an octahedral *mer*-$[Co(hhtsc)_2]^+$ ion, where the tridentate binding of the ligand has N-donors *trans* and S and O donors *cis*.[1059] However, for the phenylpyruvic acid thiosemicarbazone (H_2pptsc) dianion bound as an *S,N,O*-tridentate in the octahedral *mer*-$[Co(pptsc)_2]^-$, the S donors are *cis*-disposed and the N- and O-donor pairs each *trans*.[1060] Tridentate S,N,O-chelation of octahedral cobalt(III) by pyruvic acid thiosemicarbazone dianion (patsc) in *mer*-$[Co(patsc)_2]^-$, of 5-formyluracil thiosemicarbazone (ftsc) in $[Co(ftsc)_2]_2(SO_4)$, and of glyoxylic acid thiosemicarbazone (gatsc) in $[Co(OH_2)_6][Co(gatsc)_2]\cdot 3H_2O$ are also defined by crystal structures.[1061–1063] The patsc compound displays an electrochemically reversible $Co^{III/II}$ couple. The $[Co(ftsc)_2]^+$ compound exhibited low activity against human leukemic cell lines.

Both the 2-furfural thiosemicarbazone and semicarbazone Co complexes proved potent in their cytotoxicity against a wide range of cancer cell lines, with suppression associated with DNA nicking and fragmentation rather than base alkylation, intercalation, or crosslinking.[1064] Potent antineoplasticity or cytotoxicity is displayed by a range of heterocyclic thiosemicarbazones and thioureas and their Co complexes.[1065] Cytotoxicity was also established both *in vitro* and in tissue cultures for $[Co(qtsc)_2]X$ (qtsc = *S,N,N*-tridentate quinoxaline-2-carboxaldehyde thiosemicarbazone; X = Cl, Br).[1066] The cobalt(III) complex of 3-acetylisoquinoline thiosemicarbazide displays less antifungal activity than the 2-acetylpyridine analog.[1067]

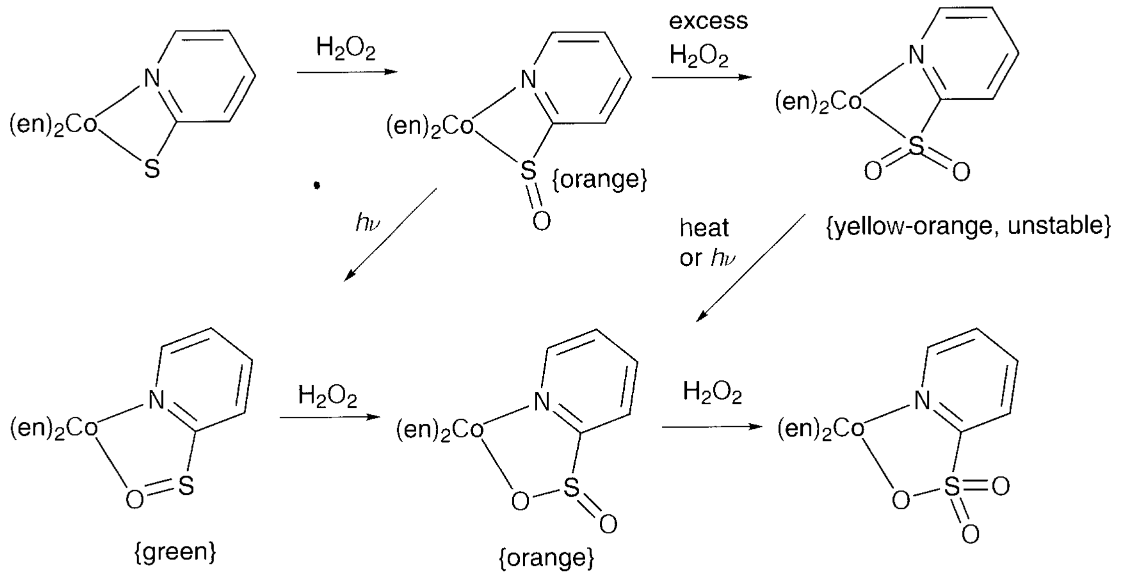
(vi) Thioureas and selenoureas

Thiourea (tu) dominantly forms *S*-bonded complexes with octahedral cobalt(III), with the *trans*-bis(thiourea)cobalt(III) moiety common along with multidentate N- and O-donors in other sites. These are readily prepared; for example, reaction of *trans*-$[Co(dmg)_2(OH_2)_2]^+$ with thiourea at pH 3–4 in hot aqueous solution yields the bis(thiourea) complex on slow cooling.[1068] Alternatively, in a one-pot reaction, heating an alkaline mixture of cobalt(II) and dimethylglyoxime in air to ~80 °C, lowering the pH to 1–2, then treating with thiourea produces the same complex. Further, the selenourea analog forms identically. The *trans* arrangement of the two-coordinated thiourea molecules has been confirmed by a crystal structural characterization of the dimethylglyoxime cobalt(III) complex cation $[Co(dmg)_2(tu)_2]^+$,[1069] and of the methylglyoxime analog $[Co(mg)_2(tu)_2]^+$. The ability of the former compound to stimulate the biosynthetic capacities of micromycetes is also noted. Further, the *trans*-bis(thiourea)bis(α-furylglyoximato)cobalt(III) nitrate has been characterized by a crystal structure analysis, with thiourea S-bonded.[1070] Thiourea is a co-ligand along with 1,2-cyclohexanedione dioxime (cdd) in $[Co(cdd)_2(tu)_2]_2(SiF_6)$, for which a crystal structure defines the octahedral geometry with the thioureas in a *trans* disposition.[1071] A detailed study of the kinetics of substitution by thiourea and other neutral ligands in *trans*-$[Co(salen)(OH_2)_2]^+$ indicates very rapid substitution by the first ligand followed by a slower second substitution.[1072]

Thiourea has the potential to bind through either the S or the amine N atoms, and the existence of linkage isomers may be anticipated. The ambidentate ligands thiourea, NO_2^- and SO_3^{2-}, in interactions with *cis*- and *trans*-$[Co(en)_2(OH_2)_2]^{3+}$ ion, display *N,S*-, *O,N*- and *O,S*- linkage isomerization processes, followed by ^{59}Co NMR studies.[1073] Equivalent reactions have been reported for the bis(2,2′-dipyridyl) and bis(1,10-phenanthroline) analogs.[1074] With *mer*-$Co(dien)Cl_3$ in aqueous solution, *mer*-$[Co(dien)(tu)_3]^{3+}$ forms with both *S*- and *N*-bound thiourea (tu) isomers detected, amongst other analogs.[1075]

(vii) Mixed donor sulfur and selenium ligands

There are growing and diverse numbers of examples of polydentate ligands which feature S-donors in concert with N, O, or P-donors. One simple, but interesting, example is 2-pyridinethiolate (pt). This ligand can bind as a monodentate, a chelate and in bridging modes as a versatile electron-rich ligand, and its coordination chemistry has been reviewed.[1076,1077] The restricted "bite" of the N,S four-membered ring chelate has obvious structural effects. The *mer*-$Co(pt)_3$ complex has been reported, with intraligand S—Co—S angles below 73° and *trans* S—Co—S angles around 166°.[1078] The complex is able to be formed in several ways; via transmetallation from a Zn^{II} cluster of the ligand with Co^{II} in methanol, by base-promoted ligand substitution in tris (acetylacetonate)cobalt(III), or by reaction of the ligand salt with Co(ClO$_4$)$_2$ in acetone in air. Typically, across a range of structures for this ligand and close analogs, Co—S and Co—N distances are ~2.28 Å and ~1.92 Å respectively, with the S—Co—N angle near 73°. Mixed ligand complexes of pt with diamines form by reaction of both diamine and 2,2′-dipyridyldisulfide with Co(ClO$_4$)$_2$ in ethanol.[1079] One of the products, $[Co(en)_2(pt)]^{2+}$, spontaneously resolves upon recrystallization, i.e., as a conglomerate. The ligand, when chelated in $[Co(en)_2(pt)]^{2+}$, also undergoes a series of stepwise oxidation reactions from thiolato to sulfenato, sulfinato, and sulfonato ligands, with some S,O-isomerization reactions also possible.[1080] This is outlined in Scheme 4.

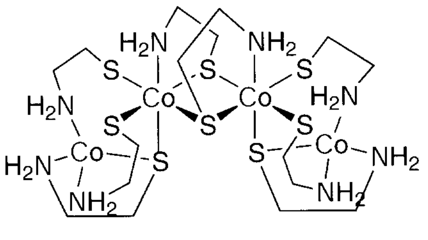


Scheme 4

Chelation of pt to Co^{III} has been observed in the complex $[Co(mpyct)_2(PBu_3)_2]^+$, which has a $CoN_2S_2P_2$ donor set, with the two phosphines in apical sites around an elongated ocatahedron.[1081]

The selenium analog of pt, 2-pyridineselenolate (ps), is known and a series of $[Co(ps)_{3-n}(en)_n]^{n+}$ complexes have been prepared and characterized.[1082] Oxidation by peracetic acid produced seleninato ($^-SeO_2$) and selenonato ($^-SeO_3$) complexes, which were shown by structural studies to undergo change from Se to O coordination, relaxing in the process from a four- to a five-membered chelate ring system.

The *N,S*-chelate 2-aminoethanethiolate (aet$^-$) forms stable cobalt(III) complexes, including clusters where the S can take on a bridging role. Reaction of $[Co(NH_3)_5Cl]^{2+}$ with Ni(aet)$_2$ in water for several hours affords the black tetranuclear compound Co$_4$(aet)$_8$, which features aet$^-$ in simple chelate and bridging roles (**245**).[1083] The simple monomeric complex $[Co(aet)_2(en)]^+$ has been reported;[1084] when heated in water at 50 °C, the trimer Co{Co(aet)$_3$}$_2$ is one product, with the central Co surrounded by six bridging S atoms.



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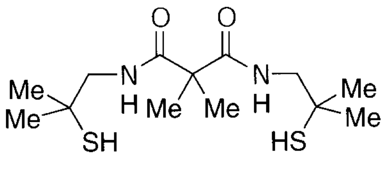

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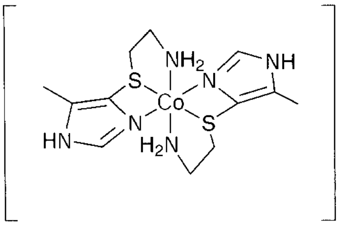
Novel Co^{III} surfactants containing aminothioether ligands have been described.[1085] These involve $[Co(en)_2(NH_2CH_2CH_2SR)]^{3+}$ monomers (R = 6-, 8- or 12-carbon alkyl chain) and $[(en)_2Co(NH_2CH_2CH_2S\text{-}(CH_2)_n\text{-}SCH_2CH_2NH_2)Co(en)_2]^{6+}$ dimers ($n = 8$, 12). The aminothiol chelate in $[Co(en)_2(SCH_2CH_2NH_2)]^{2+}$ is oxidized first to a coordinated sulfenate complex and then, more slowly, to a coordinated sulfinate using oxo diperoxo complexes $MO(O_2)_2$ and $MO(OH)(O_2)_2^-$ (M = W, Mo).[1086] Oxygen atom transfer from peroxide to the coordinated S acceptor is involved. The sulfinate–carboxylate chelate in the cobalt(III) complex *trans*(*t*-N,S)-[Co(tren)-$(S(O)_2CH(CH_3)COO)]^+$ photolyzed with visible light undergoes irradiation-induced desulfurization and yields an organic peroxide complex which was characterized by a crystal structure.[1087]

The di-N-carboxamido dithiolato N_2S_2 ligand (**246**) forms an unusual square–planar Co^{III} complex which mimics the active site of cobalt-containing nitrile hydratases.[1088] Hexacoordination of Co^{III} is only achieved with addition of strong ligands like cyanide and isocyanides in axial sites, which occurs along with an expansion of the Co–donor distances in the equatorial plane, as defined by EXAFS studies.

Reaction of the thiol group in $HSCH_2CH_2NH_2$ with a haloalkane carrying an additional functional group can produce a range of new tridentate ligands. An example is the 5-methylimidazolyl terminated (ati), which readily forms a *fac*-$Co(ati)_2$ complex (**247**) by oxidation of a Co^{II}–ligand mixture, with all equivalent donor types in *trans* arrangements.[1089] This type of chemistry is convenient and straightforward, with the sodium salt of the thiol in dry alcohol very reactive when presented with, particularly, iodo- or bromoalkanes. Reaction of a dithiol usually leads to dithioethers, and elaboration of the chemistry is reasonably straightforward.

Macrocycles featuring multiple N,S donors have been reported. The saturated macrocycle $[18]aneN_2S_4$ readily forms a Co^{II} complex upon reaction with $Co(NO_3)_2 \cdot 6H_2O$ in ethanol, and this is oxidized in air to the Co^{III} complex,[1090] which has all six donors bound in an octahedral form but showing a small tetrahedral distortion of the four S-donors out of the best S_4 plane. Metal-directed $CH_2O/EtNO_2$ cyclization of a diaminodithioether, followed by Zn/HCl reduction leads to an amino-appended N_2S_2 macrocycle which has been complexed as a pentadentate to Co^{III} (**248**).[1091,1092] A somewhat similar ligand, but carrying two carboxylate pendants, binds octahedral Co^{III} with a $N_2S_2O_2$ chromophore (**249**), the two *O*-pendants in *trans* dispositions.[1093]



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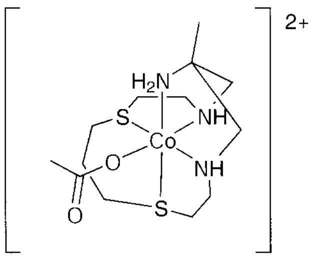

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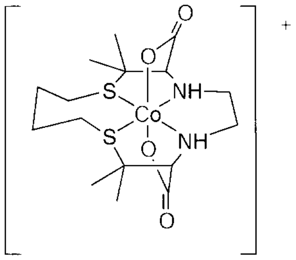


(249)

A suite of S_2P_2-donor ligands $H_3CS(CH_2)_2PPh(CH_2)_nPPh(CH_2)_2SCH_3$ ($n = 2$ or 3) has been coordinated to Co^{III} to give distorted octahedral $[Co(SPPS)Cl_2]^+$ compounds, with a range of geometric isomers identified.[1094] Both Co—S and Co—Cl bond elongation is observed when these are located *trans* to a phosphine. Chelated acetyacetonato ligands were also introduced in place of chloro ligands, forming a mixture of *cis*-α and *cis*-β isomers. A related example, but with the donor locations inverted, is the $Me_2P(CH_2)_2S(CH_2)_3S(CH_2)_2PMe_2$ (mtdmp) ligand, which reacts with *trans*-$[Co(py)_4Cl_2]Cl$ to afford, after addition of $NaPF_6$, the green *trans(Cl,Cl)*-$[Co(mtdmp)Cl_2](PF_6)$.[1095]

6.1.2.3.8 Halogens

(i) Halides

Halides are ubiquitous co-ligands for cobalt(III), and are met throughout this review. Anation of (solvent)cobalt(III) complexes by halide has been examined from time to time. An example is substitution of coordinated acetonitrile in $[Co(L)(MeCN)_2]^{3+}$ (L = tetraaza-macrocycle) by Cl^- and Br^-.[1096] A mechanism involving interchange from within tight ion pairs was proposed. Halo-bridged polymeric complexes are well known with both classical and organometallic complexes.

An example of an unusual cobalt(III) complex is the $[\{(Cp^*)Co\}_2(\mu\text{-}X)_3]^+$ ion (X = Cl, Br, I),[946] with three bridging halide ions present.

6.1.2.3.9 *Hydrogen*

(i) Hydrides

Limited examples of cobalt(III) hydrides are extant, and they tend to be quite reactive species. Equilibration of $[Co(bpy)_3]^+$ with acid produces the trivalent hydrido complex $[HCo(bpy)_2(OH_2)]^{2+}$ and free (protonated) bpy.[1097] A mechanism was proposed in which bpy radical generation (bpyH) via outer-sphere reduction of the protonated bipyridinium monocation by the monovalent Co complex is rate determining. The hydrido complex results from reaction of the Co^{II} complex with the radical bpyH. Reaction of divalent **(75)** (*meso* and *rac* isomers) with pulse radiolytically generated H· generates the trivalent hydride $[HCo(hmd)]^{2+}$;[118] a kinetic and thermodynamic analysis is reported. Mixtures of the porphyrin complex Co(TMeOPP) and alkyl radicals such as $\cdot C(Me)_2CN$ and $\cdot C(Me)(CH(Me)_2)CN$ react with alkenes and alkynes to form alkyl and vinyl complexes and with alkyl halides and epoxides to form alkyl and β-hydroxyalkyl complexes. The intermediate trivalent hydride HCo(TMeOPP) is implicated, which adds to unsaturated substrates or, in its deprotonated from, reacts as a nucleophile $[Co(TMeOPP)]^-$ with alkyl halides and epoxides.[1098] Sequential one-electron electrochemical reduction of the hexaamine $[Co(tacn)_2]^{3+}$ leads to an unstable monovalent complex, which undergoes protonation at a mercury electrode to afford the hydride. The trivalent hydride is believed to decompose via disproportionation to H_2 and a Co^{II} species.[1099]

6.1.2.4 Co^{IV} and Co^{V}

The chemistry of high-valent Co is not extensive. Whereas there are now several examples of Co^{IV}, the higher oxidation state Co^{V} has not been well established. Since Co^{IV} has a d^5 ground state, electron paramagnetic resonance spectroscopy offers an effective way of identification.[1100] Early studies proposed Co^{IV} complexes formed with some dithiocarbamato, Schiff base, and dimethylglyoximato complexes.[1101] $[Co(dtc)_3]^+$ ions form from oxidation of the well-known Co^{III} precursors, and magnetic moments (~2.5 B.M) support the d^5 Co^{IV} assignment. Delocalization of electron density onto the ligands is an issue in nominally Co^{IV} compounds, with the extreme alternative representation being a Co^{III}–ligand radical species. Consequently, the development of a wide range of stable well-characterized Co^{IV} compounds remains unattained, because the metal is likely to oxidize its bound ligand(s) or to oxidize solvents in which the complex is formed. A brief coverage of some more recent examples follows.

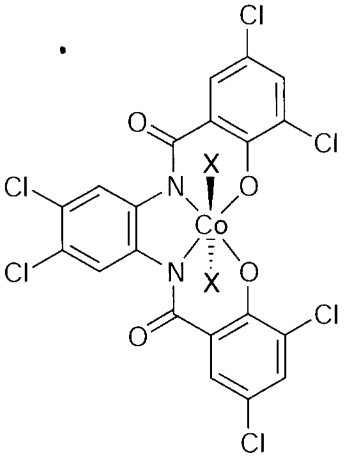
6.1.2.4.1 *Carbon*

The simple methylidyne compound $[HC{\equiv}Co]^+$ has been formulated as a Co^{IV} species.[1102] The norbornyl anion (nor), as the lithium salt, reacts with $CoCl_2$ to produce the brown, paramagnetic tetrahedral $Co(nor)_4$. This can undergo both reduction (to $[Co(nor)_4]^-$) and oxidation (with $AgBF_4$) to what appears to be $[Co(nor)_4]^+$, a diamagnetic tetrahedral compound. This remains one of the very few established examples of Co^{V}.

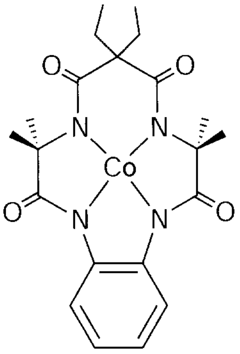
The alkyl complex $[Co(4\text{-}CNpy)(dmg)_2(R)]^+$ has been reported.[1103] The cyclopentadienyl complex $[(Cp)(PPh_3)Co(C_4Ph_4)]^+$ has been detected in frozen haloalkane solvent,[1104] but has no long-term stability.

6.1.2.4.2 *Nitrogen*

N donor ligands for tetravalent Co must be carefully designed in order to prevent disproportionation (ligand dehydrogenation/Co reduction). A key feature is that no H atoms must be present on the C atoms adjacent to the coordinated N-donor. A range of multidentate amide ligands capable of stabilizing high oxidation states of Co have been reported. The Co^{IV} complex **(250)** (X = 4-*t*-Bu-pyridine) of the dioxo-salphn analog was prepared by Ce^{IV} oxidation of the trivalent analog. The presence of four ionizable donor atoms enables the ligand to stabilize this high formal oxidation state and the compound was characterized structurally.[1105] The frozen solution EPR spectrum (10 K) of the complex exhibits an eight-line pattern from hyperfine coupling (16 G) of the single unpaired electron to the Co nucleus ($I = 7/2$), centered at $g = 2.011$. The emergence of three visible maxima in the spectrum of this complex not seen in the precursor was also indicative of metal-centered oxidation. Two sequential reversible electrochemical oxidations of the Co^{III} complex were observed 0.39 V and 0.84 V more positive than the Fc/Fc^+ reference. The square–planar tetravalent complex (**251**) has been reported along with its 4,5-dihalobenzo analogs.[1106] EPR data in toluene at 5.9 K are consistent with a single unpaired electron residing on the metal center. The complex slowly oxidizes H_2O, yielding the trivalent complex. Replacement of the *gem* dimethyl groups of (**251**) with spiro-cyclohexyl moieties and attachment of methoxyl aromatic substituents results in an effective one-electron oxidant in cyclohexane solutions. A number of charge transfer salts of this tetravalent complex with single electron reductants such as ferrocene, *N*,*N*′-tetramethyl-*p*-phenylenediamine and Mg(TPP) were isolated.[1107] Reaction with PhSH gave PhSSPh and with Bu_3SnH gave the tributyltin dimer, while the reduced trivalent monoanionic complex precipitates quantitatively following reaction.



(**250**)



(**251**)

6.1.2.4.3 *Oxygen*

A high-valent oxocobalt porphyrin complex has been suggested as the reactive hydroxylating intermediate for alkane hydroxylation involving an electron-deficient Co^{III} porphyrin and μ-chloroperbenzoic acid.[784] The bis(tridentate) coordinated Co complex (**252**) undergoes electrochemical oxidation to a Co^{IV} species.[1108] EPR spectroscopy identified a single unpaired electron with a characteristic eight-line hyperfine coupling pattern due to the ^{59}Co nucleus ($I = 7/2$).

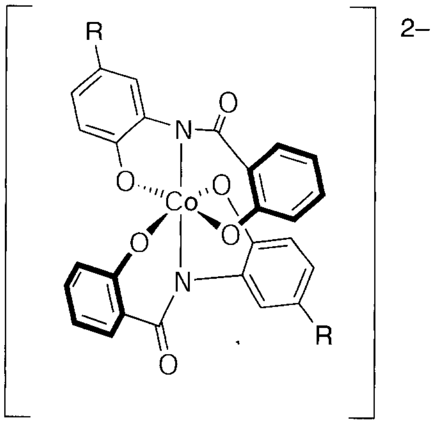
6.1.3 BIOLOGICAL CHEMISTRY OF COBALT

At the time of the first volume of *CCC*(1987), the biological chemistry of cobalt was almost exclusively concerned with the cobalamins. The field has expanded and developed markedly since then. New cobalt-containing proteins have been characterized and applications of traditional cobalt coordination compounds in biology developed. These developments are illustrated below in some detail, as the field was not reviewed in the first edition.

6.1.3.1 Metalloproteins and Cofactors

6.1.3.1.1 *Cobalamins (B_{12})*

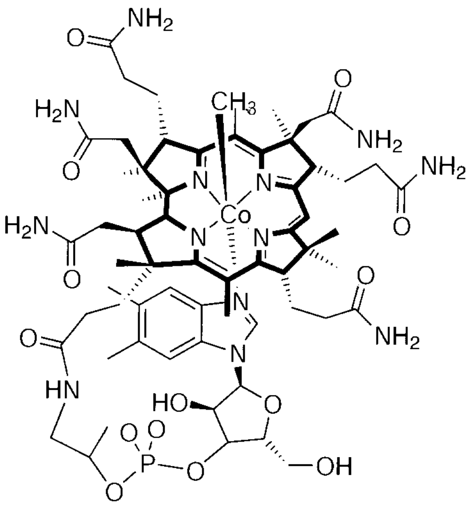
Cobalamin chemistry is the best-established area of cobalt biological chemistry. The 15-membered tetraazamacrocyclic corrin ring (incorporating four pyrrole residues) is the binding site for



(252)

Co within all compounds of the so-called cobalamin (or B_{12}) family. The biological functions of cobalamin cofactors are defined by their axial substituents; either a methyl or an adenosyl group. Both cofactors participate in biosynthesis; the former in methyl transfer reactions while the latter is a free radical initiator, abstracting H atoms from substrates. Decades after their initial characterization, the fascination with the biological chemistry of cobalamins remains.[1109]

In mammals and in the majority of bacteria, cobalamin regulates DNA synthesis indirectly through its effect on a step in folate metabolism, catalyzing the synthesis of methionine from homocysteine and 5-methyltetrahydrofolate via two methyl transfer reactions. This cytoplasmic reaction is catalyzed by methionine synthase (5-methyltetrahydrofolate-homocysteine methyltransferase), which requires methyl cobalamin (MeCbl) (**253**), one of the two known coenzyme forms of the complex, as its cofactor. 5′-Deoxyadenosyl cobalamin (AdoCbl) (**254**), the other coenzyme form of cobalamin, occurs within mitochondria. This compound is a cofactor for the enzyme methylmalonyl-CoA mutase, which is responsible for the conversion of *L*-methylmalonyl CoA to succinyl CoA. This reaction is involved in the metabolism of odd chain fatty acids via propionic acid, as well as amino acids isoleucine, methionine, threonine, and valine.



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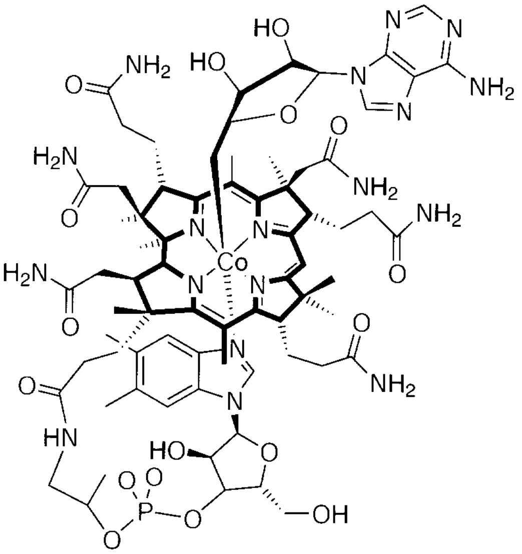

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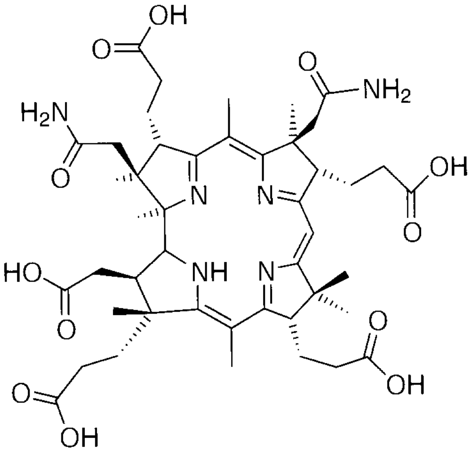
As Co-containing organometallic compounds, cobalamins are unique in nature, and they have a genetic history of more than four billion years. Their biosynthesis, absorption, transport, and metabolism have been well documented in organisms of both marine and terrestrial origin.[1110–1112]

Mammalian intestinal absorption requires the presence of two receptors and two transporters, which is itself a unique feature. Specific transporters such as intrinsic factor, transcobalamin, and haptocorrin have been characterized,[1113] as well as a number of receptors for passage across cell membranes. A number of biochemical studies on cell uptake[1114] and receptors[1115,1116] of cobalamins have been reported. Genetic disorders that impair the synthesis, transport, or transmembrane passage of cobalamins and their consequences have been reviewed.[1117,1118]

The mechanistic and structural chemistry of B_{12} may be separated into (i) investigations of cobalamin cofactors both apart from and in complex with their enzymes, and (ii) biomimetic model complexes, both structural and functional.

(i) B_{12} cofactors

Naturally, the biosynthesis of cobalamins themselves require delivery of Co ions at a particular point in the reaction scheme. Cobaltochelatase catalyzes the ATP-dependent insertion of Co^{II} into the corrin ring during the biosynthesis of coenzyme B_{12} in *Pseudomonas denitrificans*. Cobaltochelatase is a heterodimeric enzyme (140 KDA and 450 KDA subunits each inactive in isolation), and the two components have been isolated and purified to homogeneity.[1119] The reaction product is divalent cobyrinic acid, demonstrating that hydrogenobyrinic acid and its diamide (**255**) are precursors of AdoCbl.



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The structures of cobalamins both in isolation and as cofactors in complex with an enzyme have been probed with a variety of techniques including X-ray crystallography[1120–1124] and EXAFS,[1125,1126] in addition to spectroscopic methods such as NMR[1127] and EPR[1128] and also via molecular mechanics calculations.[793] As one example, an NMR study of some cobalamins and their cobinamide analogs (lacking the axially coordinated dimethylbenzamidazole) has been reported.[1129] Hydrogen bonding interactions involving the aqua ligand in aquacobalamin previously identified crystallographically persist in solution. In the cobinamides, removal of the axial benzimidazole produces characteristic changes in the amide nitrogen and proton chemical shifts of the proximal side chains.

Reduction of aquacobalamin with Zn/AcOH gives the five-coordinate hydrido complex, which reacts with ethylene to give EtCbl.[1130] The same compound may be prepared by using the ethylating agent $[Et_3O]BF_4$ in aqueous solution.[1131] The interactions of MeCbl with the complex anions $[Pt(CN)_4]^{2-}$, $[PtCl_4]^{2-}$, and $[Pt(SCN)_4]^{2-}$ have been investigated by UV–visible and ^1H NMR spectroscopy.[1132] At least three Pt binding sites on MeCbl were identified, one of which is located on the methyl ligand side of the macrocycle, and is implicated in methyl transfer in the presence of a Pt^{IV} complex. The reaction of MeCbl with I_2 in MeOH forms a stable charge transfer complex. In water this species reacts resulting in cleavage of the Co—C bond.[1133] The mechanism involves electron transfer from MeCbl to I_2 to generate a $MeCbl^{+\cdot}$ radical, which undergoes a chloride-induced heterolytic cleavage to yield the Cbl radical and CH_3Cl. The EtCbl analog was also studied. The solution structure of the glutathionyl analog GsCbl, which has been found to be a substrate for MeCbl formation in the presence of *S*-adenosylmethionine and a thiol reductant, was investigated by multinuclear NMR,[1127] establishing *S*-coordination by the ligand. Interactions between cobalamins and NO have been investigated with absorption and EPR spectroscopy.[1134,1135] Marked spectral changes are seen upon reaction of divalent cobalamin with NO, which are consistent with NO-effected oxidation to the trivalent state.[1134] This trivalent Co–NO complex is stable, but transfers its NO ligand to hemoglobin concomitant with reduction to the divalent state. Homolytic cleavage of the trivalent Co–C(Me or Ado) also resulted in the reduction of the Co. Nitrosylcobalamin had diminished ability to serve as a cofactor for methionine synthase, and observation that aquacobalamin could quench NO-mediated inhibition of cell proliferation suggests that interactions between NO and cobalamins may have important biological consequences.

A mechanistic study of dealkylations of a variety of adenosylcobalamins was conducted in acidic solution resulting in competitive homolytic and acid-induced hydrolytic Co—C bond scission pathways.[1136] Two hydrolytic mechanisms were identified; one involving initial depurination followed by elimination from the organometallic intermediate, while the second involved ring-opening protonation at the ribofuranosyl oxygen. These reactions were sensitive to substituents on the adenosyl ligand. The limiting homolytic Co—C bond dissociation rate was found to be insensitive to alkyl ligand substituents.

Sonolytically generated•·OH radicals lead to Co—C bond cleavage in MeCbl in oxygenated aqueous solution.[1137] Under anaerobic conditions, H· scavenging by O_2 is circumvented and reduction to divalent MeCbl occurs instead, which after protonation releases methane. A bioconjugate of cobalamin and the alkylating agent chlorambucil behaves similarly, which suggests that sonorelease of an active alkylating agent from a bioconjugate may be a viable and less toxic alternative method for the selective release of anticancer drugs.[1138] The rate of Co—C bond dissociation in micellar solutions of BzCbl have been studied as a function of detergent concentration and pH.[1139]

5-Methyltetrahydromethanopterin:co-enzyme M methyltransferase (MtrA) is a membrane-associated corrinoid-dependent enzyme that uses a methyl transfer reaction to drive an energy-conserving Na^+ ion pump. The purified enzyme exhibits a rhombic EPR signal indicative of a base-on divalent cobalamin, and was inactive in this form. One-electron reduction with Ti^{III} citrate generates the active monovalent species, and reaction with 5-methyltetrahydromethanopterin leads to methyl group transfer to the Co complex. The reaction is reversible upon reincubation with tetrahydromethanopterin.[1140] The structural properties of the soluble deletion mutant of MtrA (lacking the C-terminal hydrophobic tail) have also been studied.[1141] However, the expressed apoprotein was devoid of its Co prosthetic group and incorrectly folded. Unfolding with guanidinium chloride and successful refolding proceeded with Ti^{III} citrate, suggesting that the monovalent cobalamin is the species that binds to the apoprotein. EPR spectroscopy of the divalent reconstituted protein revealed that the Co is bound in its base-off form and that a His residue is coordinated.

Although the system is catalytically inactive, adeninylethylcobalamin (AdoEtCbl) undergoes Co—C bond cleavage to the enzyme-bound hydroxocobalamin upon interaction with the apoprotein of diol dehydratase.[1142] These results imply that the C—Co bond of AdeEtCbl is activated by the enzyme and undergoes heterolysis in contrast to homolysis of the C—Co bond of AdoCbl in the normal catalytic process. Diol dehydratase undergoes suicide inactivation by the physiological substrate glycerol, which causes irreversible cleavage of the Co—C bond in the cofactor, which remains tightly bound to the enzyme. Recombinant proteins co-purified to homogeneity exist as an A_2B_2 tetramer; a reactivating factor for the glycerol-inactivated holoenzyme that exchanges the enzyme-bound, adenine-lacking cobalamin for free adenosylcobalamin.[1143]

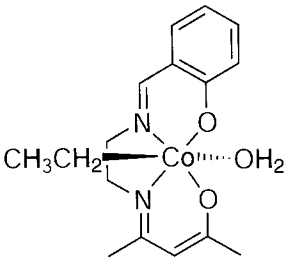
Methionine synthase forms a ternary complex with homocysteine and 5-methyltetrahydrofolate prior to catalyzing a methyl group transfer from the MeCbl cofactor to homocysteine, generating the monovalent cofactor and methionine. The trivalent MeCbl cofactor is restored by methyl transfer from 5-methyltetrahydrofolate to produce tetrahydrofolate prior to release of both products. In cobalamin-dependent methionine synthase, the cofactor may be converted to its EPR-active (but biologically inactive) divalent form. In acid frozen solutions the axial dimethylbenzimidazole substituent is protonated and hence not coordinated.[1128] Reduction of the inactive divalent cofactor to its monovalent form during turnover may be achieved by flavodoxin (from *E. coli*) but not with the corresponding ferrodoxin.[1144] EPR spectroscopy revealed that binding of flavodoxin to divalent cobalamin methionine synthase results in a change in the coordination number of the Co from five to four with loss of the coordinated His residue. Methionine synthase exists in two different conformations that interconvert in the divalent cobalamin oxidation state. In the primary turnover conformation, the enzyme reacts with homocysteine and methyltetrahydrofolate but is unreactive toward adenosylmethionine and flavodoxin. In the reactivation conformation, the enzyme is active toward adenosylmethionine and flavodoxin but unreactive toward methyltetrahydrofolate, and a model has been proposed where these conformational changes control access to the cobalamin cofactor and regulate cobalamin reactivity in methionine synthase.[1145] An additional cobalamin-dependent enzyme that has been characterized is the Fe–S protein CO dehydrogenase.[1146]

Oxidative addition of gaseous or liquid halogenated organic pollutants may be achieved with cobalamins immobilized on solid state supports in the presence of reductants, and this application has been patented.[1147] In DMF solution containing tetrabutylammonium bromide and acetic acid, Vitamin B_{12} itself mediated the reduction of CH_2Cl_2 in the presence of styrene to give cyclopropylbenzene in quantitative yields with high efficiency.[1148] A pathway involving formation and electroreductive cleavage of a chloromethylene–Co^{III} intermediate to liberate a chloromethylene radical, which then attacks styrene, was suggested. The reaction is highly sensitive to solvent and the presence of water as a proton donor leads to 1-chloro-3-phenylpropane as a byproduct.

(ii) B_{12} model complexes

There are many biomimetic model Co complexes of the cobalamins.[1149] The primary criterion for an effective B_{12} model has been that the complex may be reduced to the monovalent state and undergo facile oxidative addition to generate a stable alkylcobalt(III) complex. The two main classes of B_{12} model complexes that have been investigated are Co oximes and Schiff base complexes. The former class shares the planar CoN_4 array of their biological analogs whereas the majority of effective Schiff base B_{12} model complexes comprise equatorial *cis*-N_2O_2 donor sets.

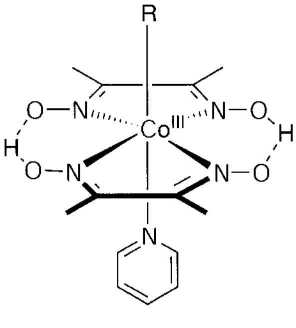
The stabilization of axially coordinated alkyl groups by trivalent Co complexes of the tetradentate Schiff base salen, and analogs, is a feature that has prompted many studies relevant to B_{12} biomimetic chemistry. The mixed aldehyde/ketone Schiff base complex *trans*-EtCo(salacacen)-(OH_2) (**256**) exhibits a number of structural features (elongated Co—OH_2 bond, non-planar CoN_2O_2 moiety) that are desirable in a B_{12} model complex.[1150] A variety of salen complexes bearing secondary alkyls or a bulky diamine in the equatorial position were synthesized and characterized. The complexes RCo(salen)(4-picoline) (R = *n*-Pr, *i*-Bu) are six-coordinate and their coordination geometry is similar to that seen in 5′-deoxyadenosylcobalamin.[1151] By contrast, the bulkier $EtCo(Me_4salen)$ (derived from 2,3-dimethylbutane-2,3-diamine) offers a rare example of a five-coordinate square–pyramidal geometry for this class of compound coupled with a highly reactive Co—C bond. The template syntheses of $[RCo(bzacen)(L)]^+$ (bzacen = benzoylacetone condensed with ethylenediamine, R = Me, Et, L = py_2, en) has been described.[1152] The presence of an alkenyl substituent on the ethylenediamine bridge of Co(salen) leads to an interesting pendent alkyl complex. The overall reaction mechanism involves oxidation of the divalent precursor to give the alkoxycobalt(III) analog followed by attack on the double bond by the metal and ultimately addition to the carbocation by the alcohol.[1153]



(256)

Tridentate Schiff base analogs (bearing a single aromatic residue and a diamine) are capable of stabilizing alkyl ligands. The primary amine of *N*-methylethylenediamine (Me-en) condenses with *o*-hydroxyacetophenone in the presence of Co^{II} to produce the complex Co(MesalMeen)(Me-en), which after reduction to the monovalent state may undergo oxidative addition with MeI to give $[MeCo(salMeen)(Me\text{-}en)]^+$.[1154] The dimethylamino analogs $Co(MesalMe_2en)(N_3)(o\text{-}(MeCO)C_6H_4O)$ and $Co(MesalMe_2en)(SCN)(o\text{-}(MeCO)C_6H_4O)$ have also been reported.[1155]

Like their macrocyclic imine counterparts, Co oximes complexes are capable of stabilizing alkyl groups in their axial coordination sites. Alkyl complexes containing bis-dioxime bidentate and mixed imine–oxime tetradentate ligands of Co have been extensively studied as B_{12} model complexes. The crystal structures of the organocobalt bis-glyoximato (Hglo = HO—N=CHCH=N—OH) complexes, *trans*-$RCo(glo)_2(py)$ (R = Me, Et, *i*-Pr) have been reported.[1156] The coordinate bond lengths in the *trans* (py)–Co–R group both increase with increasing alkylation of R due to both steric bulk (Co—C) and σ-donating strength of the alkyl group (*trans* influence on Co—N). In comparison, the structures of the dimethylglyoxime analogs $RCo(dmg)_2(py)$ (**257**) are less sensitive to alkyl group variations. Dealkylation may be achieved through protonation, and reactions of an extensive homologous series of $RCo(dmg)_2(py)$ complexes (R = Me, CH_2Cl, $CHCl_2$, Et, $CHMe_2$, Bu, $(CH_2)_2CH{=}CH_2$, $CH_2CHMeCH{=}CH_2$) with trifluoroacetic acid (Htfa) were studied by NMR. The reactions are stepwise; the first acid equivalent results in reversible protonation of the complex, the second proton releases the pyridine ligand while irreversible alkyl protonation occurs in excess acid.[1157] The *cis*-$Co(dmg)_2(tfa)_2$ product was structurally characterized. The synthesis and characterization of the diphenylglyoximate series *trans*-$RCo(dpg)_2(L)$ were reported (dpg = diphenylglyoxime, R = Cl, Me, Et, CH_2Cl or *i*-Bu; L = py, 3,5-lutidine, γ-picoline, $P(OMe)_3$).[1158] The crystal structure of $MeCo(dpg)_2(py)$ found that the Co—C bond length was little affected by the methyl-to-phenyl substitution. Mixed oxime complexes such as $(N_3)Co(dmg)(dpg)(py)$ have only recently been described.[1159]



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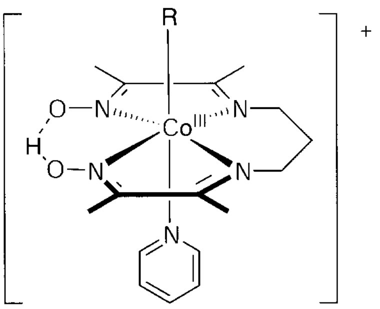

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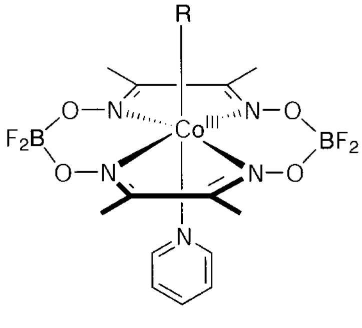


(259)

The *trans* dihalo (Cl^- and Br^-) Co^{III} complexes of the linear tetradentate dmg_2tn react with alkylating agents and $NaBH_4$ and ultimately pyridine to give the so called "Costa-type" B_{12} model complexes $[RCo(dmg_2tn)(py)]^+$ (**258**) in good yields (R = Et, $CHMe_2$, CH_2CMe_3, CH_2CF_3, CH_2CO_2Me, CH_2Ph, CH_2SiMe_3).[1160] The X-ray crystal structures of the R = CH_2CMe_3 analog shows that the dmg_2tn ligand is more distorted from planarity than bis(dmg) cobaloxime relatives, and the Co—N bonds are longer. The carbonyl complex $Co(dmg_2tn)(CO)$ may also be used as precursor to the homologs $[RCo(dmg_2tn)L]^+$ (R = CH_2OMe, CH_2SMe CH_2Cl, CH_2NO_2, CH_2CN, L = monodentate ancillary ligand).[1161] Axial Co—N bond lengthening was observed with increasing electron-donating ability of the R group. Introduction of alkyl substituents onto the trimethylene linker has been studied.[1162] Dimethylation of the central CH_2 group results in a complex with greater rates of py ligand dissociation. This is correlated with the crystallographically determined structure, which shows that the planar py ligand leans away from the more sterically demanding $CH_2CMe_2CH_2$ moiety compared with the dmg_2tn complex. The tetramethylene-bridged analogs $[RCo(dmg_2bn)(OH_2)]^+$ were prepared in an effort to increase ligand-effected distortions that ultimately lead to a weakening of the Co—C bond, as seen in coenzyme B_{12} through folding of the equatorial corrin ring. Although the crystal structure of $[EtCo(dmg_2bn)(OH_2)]^+$ exhibits somewhat elongated Co—C and C—O bonds and an extended Co—C—C bond angle (119.3(5)°) the N_4 array is effectively planar,[1163] in contrast to the Cu^{II} relative. The structure of the $[EtCo(dmg_2bn)(Him)]^+$ analog has also been reported, although two different ligand conformations were identified within the asymmetric unit.[1164] It has been noted that imidazole, once deprotonated, may form μ-imidazolato dimers and such species have been identified by NMR and crystallography.[1165] Near-IR FT-Raman spectroscopy was used to investigate the influence of electronic and steric effects on the Co—Me stretching frequency. It was found that for the series $MeCo(dmg_2tn)L$, the Co—C frequency decreased (from $505\,cm^{-1}$ to $455\,cm^{-1}$) with increasing electron-donating character of L.[1166] The ethylmethyl glyoxime analog

$[(Bz)Co(emg_2tn)(OH_2)]^+$ has been shown to perform an unusual Co-to-C migration of the axial alkyl group upon photolysis, with the benzyl group attacking one of the oxime C atoms.[1167]

1,5,6-Trimethylbenzimidazole (Me_3Bzm) is an appropriate analog for the axial 5,6-dimethylbenzimidazole ligand in cobalamins. The complexes $[RCo(dmg_2tn)(Me_3Bzm)]^+$ (R = Me, Et and CF_3CH_2) have been characterized structurally and the rates of substitution of the axial benzimidazole ligand were determined.[1168] The comparable crystal structures of $[MeCo(dmg_2tn)L]^+$ (L = 1-Meim, 1,2-Me_2im) show the steric influence of the 2-Me group, which extends the axial Co—N bond length from 2.042(2) Å to 2.100(4) Å, while the Co—C bond length is unaffected.[1169] Novel 3-membered metallocycles (Co—C—N) have been formed by attack of a halomethyl axial ligand on the oxime ligand.[1170,1171] An example of this is illustrated in Figure 9.

The tridentate 2-(2-pyridylethyl)amino-3-butanone oxime (Hpeab) is also an effective ligand for the formation of B_{12} model complexes with Co^{III}.[538] Compounds of the general formula $[RCo(peab)(Hpeab)]^+$ (R = Me, Et, CH_2CF_3, *n*-Bu and CH_2Cl) have been synthesized. Crystal structures show that Hpeab binds as a bidentate, while the peab anion coordinates as a tridentate, including the pyridyl group in the coordination sphere. The axial geometry in $[MeCo(peab)(Hpeab)]^+$ is closer to that found in methylcobalamin than has been reported for other B_{12} models.

An electrochemical study of the diaqua bis(dioxime), tetradentate dmg_2tn and macrocyclic $dmg_2(BF_2)_2$ (**259**) Co complexes has been reported.[1172] Both tetradentate ligands stabilize the divalent oxidation state relative to the bis(dmg) analog, with the trimethylene link in dmg_2tn being more effective in this role. The acyclic and macrocyclic diphenylborinic acid adducts $dmg_2(BPh_2)$ and $dmg_2(BPh)_2$ have also been reported.[1173] Cyclic voltammetry and spectroelectrochemistry of the (**256**) series (R = *i*-Pr, neopentyl, *i*-Bu, Et, Bz, Me, $HO(CH_2)_2$, CH_3COOCH_2 and CF_3CH_2) was explored.[1174] A marked influence of axial group bulk on the reactivity of the lower oxidation was found, and this was attributed to their ability to form stable bisalkyl complexes. The series $[LCo(dmg_2tn)Cl]^+$ (L = py, 4-CNpy-, 4-Brpy-, 4-MeOpy, 4-Me_2Npy) and $[Co(dmg_2tn)(py)_2]^+$ were also synthesized. As L becomes more basic, the first $Co^{III/II}$ potential is shifted cathodically, although ligand substitution reactions following reduction complicate the voltammetry.[1175]

The Co complexes of the *o*-phenylenediamine-linked dioxime $Hdmg_2Ph$ bearing a variety of monodentate ligands (halides and pseudo halides) in the axial coordination sites have been synthesized.[1176] B_{12} model complexes $[RCo(dmg_2Ph)(L)]^+$ (R = Me, Et, Me_2CH, Bz, ch; L = py, H-im, or PPh_3) were prepared by the oxidative addition reactions of the alkyl halide to the *in situ*-generated monovalent dibromo complex.

Replacement of the axial pyridine by phosphine has been achieved with the synthesis of the complexes $[MeCo(dmg_2tn)L]^+$ (L = $P(OMe)_2Ph$, $P(OEt)Ph_2$, $PEtPh_2$, $P(OMe)_3$, $P(p\text{-}Me_2NC_6H_4)_3$, $P(CH{=}CH_2)Ph_2$, $P(CHMe_2)Ph_2$, $PCyPh_2$, $P(CH_2CH_2CN)Ph_2$, PPh_3), which were characterized by ^1H NMR spectroscopy and crystallography for the trimethyl phosphite and triphenyl phosphine derivatives. The phosphine/phosphite ligand dissociation rates are twice as fast as bis(dmg) analogs, and vary by four orders of magnitude across the series.

In contrast with the role of cofactor B_{12} in methionine synthase (methyl group transfer to a thiol), functional B_{12} model complexes have provided a formidable challenge. Several oxime alkyl-cobalt (structural) B_{12} models when reacted with arene- and alkanethiolates lead only to

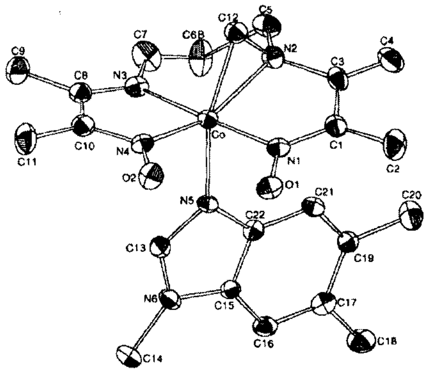


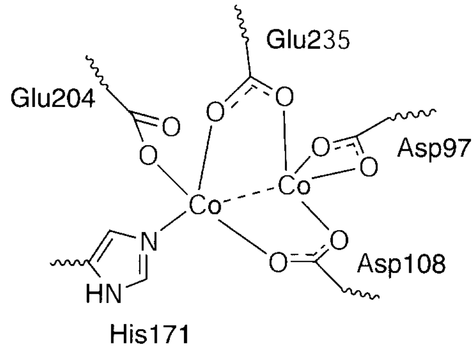
Figure 9 Pendent alkyl complex resulting from intramolecular attack of the chloromethyl axial ligand in $[((ClCH_2)Co(dmg_2tn)(Me_3Bzm)]$ on the coordinated tetradentate dioxime (reproduced with permission of the American Chemical Society from *Inorg. Chem.*, **1997**, *36*, 3854–3860).

thiolate coordination *trans* to the alkyl group.[1177] An example is *trans*-$[(EtS)Co(dmg)_2(Me)]^-$ which exhibits a particularly long Co—S bond consistent with the strong *trans* influence of alkyl ligands.

6.1.3.1.2 Non-corrin proteins

(i) Native cobalt-dependent proteins

Aside from B_{12} cofactors, there are at this time eight known Co-dependent proteins, in addition to so-called chaperone proteins that are involved in Co transport and uptake.[1178] Methionine aminopeptidase (MetAP) represents the first Co-containing (non-corrin) protein to be characterized by X-ray crystallography. The enzyme is present in prokaryotes and eukaryotes and its function is to hydrolyze N-terminal methionine residues from polypeptides. Since the enzyme is isolated as the apoprotein, the identity of the native metal ion has not been established absolutely. However, MetAP from *Salmonella typhimurium* is active upon addition of Co^{2+}, but not divalent Mg, Mn, or Zn. The crystal structure of MetAP from *E. coli* revealed a pair of Co^{II} ions bridged by two carboxylate residues (Glu235 and Asp108). Each metal is in a square-pyramidal coordination environment (**260**) which includes a weak Co—Co bonding interaction.[1179] The vacant *trans* sixth coordination sites may be for substrate binding, or for coordination of a hydroxo ligand that itself is the active nucleophile. More recently, the crystal structure of MetAP from the thermophile *Pyrococcus furiosus* has been reported and a pair of Co ions were again revealed at the active site.[1180] MetAP from other organisms as well as different metalloproteases (leucine (Zn_2) and proline (Mn_2) aminopeptidase) also employ a pair of transition metals at their active sites.



(**260**)

Proline dipeptidase cleaves dipepetides where proline is adjacent to the N-terminal residue. The enzyme is a homodimer, with one Co ion tightly bound in each subunit. However, it has been shown that an additional Co^{II} ion must be added (per subunit) for activity. This second ion is relatively weakly bound and may be substituted by Mn^{II} with somewhat attenuated activity. Curiously, the active site ligands identified in metallohydrolases such as MetAP are conserved in this enzyme despite a generally low sequence similarity.

Nitrile hydratase from various organisms has been well studied and even employed in industrial processes requiring the large-scale hydrolysis of nitriles to amides. The active site structure is believed to comprise two peptide N-donors and three cysteine thiolates bound to Co^{III} on the basis of a high sequence similarity with a structurally characterized Fe^{III} nitrile hydratase. The role of the Co^{III} ion is thought to be that of a Lewis acid that activates a hydroxo ligand for attack on the nearby nitrile. A number of biomimetic systems have recently been studied in an effort to better understand the properties of this enzyme.[1040,1041,1181–1183]

Glucose isomerase catalyzes the conversion of D-glucose to D-fructose and has also been used extensively on an industrial scale.[1184] Some, but not all, enzymes of this family require Co specifically, while others can function with other divalent ions. Environmental and health issues limit the concentrations of Co in culture media during D-fructose production and other metal ions are being sought as substitutes. Although the active site structure remains unknown, EXAFS, optical and EPR spectroscopy has suggest a low-spin divalent Co ion, bound by N and O-donors only (no S-donors).

Other less well-characterized Co-containing proteins include methylmalonyl–CoA carboxytransferase (or transcarboxylase); this is a complex multi-subunit enzyme comprising three different types of subunit, two of which contain Co.[1185] A catalytically important high-spin divalent Co ion has been identified, but only the Co-free (biotin-containing) subunit has been structurally characterized. The Co–porphyrin containing aldehyde decarbonylase acts on fatty aldehyde substrates and is an important energy source in many organisms.[1186] The rearrangement of L-lysine to L-β-lysine is catalyzed by lysine 2,3-aminomutase in the presence of pyridoxal phosphate, an Fe–S cluster and either divalent Co or Zn.[1187] Although there are similarities with B_{12} chemistry (activation by S-adenosylmethionine leading to an adenosyl-bound cofactor) no cobalamins are present nor do they activate the enzyme. Furthermore, the Co ions are not bound within the Fe–S cluster as shown by EPR spectroscopy. Bromoperoxidase specifically requires Co for activity (oxidative C—Br bond formation), but the ion is weakly bound and as yet the essential role of the metal in this enzyme is not well understood.[1188]

(ii) Cobalt-modified proteins

Apart from its natural occurrence, Co may find its way into other proteins either adventitiously or deliberately. A study was undertaken where the blood, serum, and plasma of workers occupationally exposed to Co were analyzed for the element.[1189] When separated by gel electrophoresis under denaturing conditions, the Co fractions in all blood, serum, and plasma samples showed a similar protein pattern. A variety of proteins of differing size were found to bind Co in fractions collected at pH 5, whereas only hemoglobin was found in the pH 7 fractions. The conclusions were that *in vivo* Co is bound to plasma proteins, perhaps albumin and hemoglobin.

(II) Active site structure and spectroscopy. Due to its well-understood coordination chemistry, characteristic spectral properties, lability and compatible ionic radius and charge, divalent Co is a useful active site substituent for spectroscopically silent metal ions such as Zn^{II} and Cu^{I}, and Co substitution has been used as a structural probe of protein active sites. The paramagnetic NMR shifts induced by divalent Co substituted for the native diamagnetic metal ion at the active site is a useful tool in the interpretation of NMR spectra of the protein. The binding of L- and D-phenylalanine and carboxylate inhibitors to Co^{II}-substituted carboxypeptidase A in the presence of pseudohalogens N_3^-, NCO^-, and NCS^- was studied by ^1H NMR.[1190] The proton signals of the bound histidine residues were sensitive to the interactions between the inhibitors and the metal. Enzyme–inhibitor complexes with characteristic NMR features were identified. L–Phe formed a 1:1 complex, whereas D–Phe bound stepwise, first to a non-metal site and then to the Co ion forming a 2:1 complex. The carboxylates CH_3COO^- and $PhCH_2COO^-$ also formed 2:1 adducts stepwise with the enzyme, but 2-phenylpropionate gave a 2:1 complex without any detectable 1:1 intermediate. The pseudohalides N_3^-, NCO^-, and NCS^- generated complexes directly with the Co^{II}:L–Phe adduct but indirectly with the D–Phe and carboxylate inhibitor, 2:1 complexes displacing the inhibitor from the metal. Inhibitor binding constants have also been determined from ^{13}C NMR T_1 and T_2 measurements on the ^{13}C-enriched amino acid inhibitors,[1191] and EPR spectroscopy has been employed as well to gain insight to the active site structure.[1192] Substitution of Cu^{I} by Co^{II} in blue copper proteins has also been achieved for the purpose of NMR investigations. Assignment of the ^1H NMR spectrum of *Pseudomonas aeruginosa* Co-substituted azurin has been made with contact-shifted signals from amino acid residues as distant as 10 Å from the metal being achieved.[1193] Resonances due to the five amino acid residues known to reside at the metal binding site of oxidized (Cu^{II}) azurin (His46, His117, Cys112, Met121 and Gly45) were identified. However, there are metal-dependent differences; most notable being that Met121 appears to be only weakly interacting with the metal ion in the Co protein whereas Gly45 is apparently strongly bound to Co in contrast to the native Cu protein. Overall, a distorted tetrahedral N_2OS geometry for the Co ion was assigned. Metal ion-induced conformational changes in *Serratia* protease (one Zn ion per native protein, replaced by Co) were investigated by small-angle X-ray scattering. The protein is an elongated ellipsoid of approximately 110 × 40 × 40 Å with a large cleft in its central region. Comparisons of the native (Zn) enzyme with the apoenzyme show small but significant differences in their radii of gyration, maximum particle dimensions, and intraparticle pair-distance distributions.[1194]

The Zn^{II} ion of angiotensin-converting enzyme (ACE) has been replaced by Co^{II} to give an active, chromophoric enzyme and inhibitor binding has been identified spectroscopically. Visible and MCD spectroscopy were used to characterize the catalytic metal binding site in the

Co-substituted enzyme and in a number of enzyme-inhibitor complexes.[1195] The visible absorption spectrum of Co ACE exhibits a single weak broad maximum (525 nm) in contrast to the spectra of enzyme-inhibitor complexes, which display red-shifted and more intense maxima (525–637 nm). The presence of S—Co charge-transfer bands in the spectra of the tetrahedral Co ACE-inhibitor complex confirm direct ligation of the thiol group. The optical spectrum of Co-substituted *Aeromonas* aminopeptidase is perturbed by the presence of equimolar concentrations of D-amino acid hydroxamates and acyl hydroxamate inhibitors. D-Valine and D-leucine hydroxamate each produces a splitting of the characteristic 527 nm maximum of the Co enzyme to give three new maxima between 570 nm and 480 nm, whereas hydroxamates of L-valine and L-leucine produce little change in the spectrum.[1196] Conversion of yeast Cu^{I}-thionein to the Co^{II} derivative has been achieved. The optical spectrum of the Co protein is virtually identical to those of Co-substituted metallothioneins originating from vertebrates. Characteristic charge transfer bands and *d–d* transitions led to the proposal of a tetrahedral Co-thiolate coordination with three bridging cysteine S-donors.[1197] Superoxide dismutase has a crucial role in defense against cytotoxic $O_2^{-\cdot}$. It contains both Zn^{II} and Cu^{II} binding sites and these have been replaced by Co^{II} in all three combinations, i.e., $Co^{II}-Co^{II}$; $E-Co^{II}$, and $Co^{II}-E$ where E represents a vacancy at either the Cu or Zn binding site.[1198] The cobalt-protein derivatives have been characterized by optical absorption, CD, and fluorescence spectroscopy. The $Co^{II}-Co^{II}$ protein exhibits an optical spectrum corresponding to the sum of the spectra of the other two derivatives, although the CD spectra were not additive, suggesting that the presence of Co^{II} in one site strongly affects the geometry of the neighboring site. Fluorescence spectra illustrated that Co^{II} ions exert a different quenching effect on tyrosine emission, depending on whether they are located in the Zn^{II} or in the Cu^{II} site.

(mm) Activity and inhibition. There are many Zn-dependent enzymes that retain their catalytic activity or that are equally sensitive to inhibition upon substitution by divalent Co. Although the chelating ligand *N,N*-diethyldithiocarbamate anion is an inhibitor of (Zn-dependent) bovine carbonic anhydrase (CA), no removal of Zn could be detected even at a very high concentrations of anion. At identical pH values a larger inhibitory effect was found for the Co-substituted enzyme, but Co^{II} was removed from the protein by the ligand at pH less than 7. However, Co ion remained bound at pH 10, and a five-coordinate Co^{II} ion was observed spectroscopically.[1199] The kinetics of complex formation between Co^{II}-substituted CA and OCN^-, SCN^-, and CN^- has also been studied.[1200] Formation of a 1:1 complex occurs exceedingly quickly and the explanation for this observation was that the anion enters a vacant coordination site on the metal, effecting a change in coordination number of the Co ion from 4 to 5. Reversible amide inhibition of Co-substituted CA by iodoacetamide, urethane, and oxamate has been reported,[1201] and visible spectroscopy indicated coordination of the inhibitors to the metal with a deprotonated *N*-bound amide being the final product with O-bound linkage isomer intermediates being found in some cases.

Streptomyces griseus aminopeptidase specificity was studied using amino acid 4-nitroanilide substrates. The zinc enzyme hydrolyzes leucine 4-nitroanilide at a ten-fold faster rate than the Co enzyme, the Co enzyme hydrolyzes alanine 4-nitroanilide at a more than 20-fold faster rate than the zinc enzyme.[1202] Activity of the bacterial enzyme *N*-succinyl-L-diaminopimelic acid desuccinylase was completely abolished following dialysis of the enzyme against metal chelators, but restored on addition of Co^{II} or Zn^{II}. The binding constants for both metals were similar and the Co enzyme was about twice as active as the Zn homolog.[1203] The enzyme is highly specific for its natural substrate, and given its essential role in bacterial growth it is an ideal target for the development of inhibitors with antibacterial potential. Divalent Co inhibits the $Ca^{2+}-Mg^{2+}$–ATPase activity of sealed muscle sarcoplasmic reticulum vesicles, of solubilized membranes, and of the purified enzyme. Inhibition by Co^{II} is likely due to free $Co_{aq}{}^{2+}$ binding to the enzyme, which is reversible on addition of Ca^{2+} in millimolar concentrations, indicating that the Ca binding site is the one targeted by Co.[1204] The kinetic and spectral properties of native (Zn) and Co-substituted D-lactate dehydrogenase (a flavin-dependent enzyme) have been compared.[1205] Optical and MCD spectra are consistent with high-spin tetrahedral Co and the metal appears to be involved in substrate binding and reduction. The Zn-containing protein farnesyltransferase catalyzes the addition of a farnesyl isoprenoid to a conserved cysteine in peptide or protein substrates. Substitution of Zn by Co has no effect on catalytic activity, but reveals through optical spectroscopy a thiolate ligand at the active site as part of a pentacoordinate or distorted tetrahedral coordination sphere.[1206] Furthermore, the thiolate charge transfer band intensity is enhanced upon substrate binding, which was indicative of the formation of a second Co–thiolate bond corresponding to the thiolate group of the peptide substrate. Acetylpolyamine amidohydrolase exhibits activity in both its native (Zn) form and upon Co substitutions, although the pH optima are different.[1207]

Co-for-Zn substitution in alcohol dehydrogenase from *Saccharomyces cerevisiae* revealed a 100-fold increase in activity and a higher resistance of the modified protein to the inhibitory action of other divalent transition metals,[1208] making the Co-modified enzyme suitable for biotechnological applications.

The introduction of redox activity through a Co^{II} center in place of redox-inactive Zn^{II} can be revealing. Carboxypeptidase B (another Zn enzyme) and its Co-substituted derivative were oxidized by the active-site-selective *m*-chloroperbenzoic acid.[1209] In the Co-substituted oxidized (Co^{III}) enzyme there was a decrease in both the peptidase and the esterase activities, whereas in the zinc enzyme only the peptidase activity decreased. Oxidation of the native enzyme resulted in modification of a methionine residue instead. These studies indicate that the two metal ions impose different structural and functional properties on the active site, leading to differing reactivities of specific amino acid residues. Replacement of zinc(II) in the methyltransferase enzyme MT2-A by cobalt(II) yields an enzyme with enhanced activity, where spectroscopy also indicates coordination by two thiolates and two histidines, supported by EXAFS analysis of the zinc coordination sphere.[1210]

Divalent Co substitution in copper amine oxidase revealed 19% of the native specific activity (for $MeNH_2$) and 75% of the native reactivity toward phenylhydrazine. The major cause of this was a 68-fold increase in K_m for O_2. These investigations support the idea that electrons flow directly to bound O_2 without the need for a prior metal reduction and that the Cu does not redox cycle but simply provides electrostatic stabilization during reduction of O_2 to $O_2^{-\cdot}$.[1211]

6.1.3.1.3 Biomimetic chemistry

(i) Dioxgen binding

Although the natural O_2 storage and transport proteins hemoglobin and myoglobin bear no Co ions, there have nonetheless been many Co-containing functional models of these proteins reported in the literature. The key to a successful O_2 carrier is reversibility. That is, the metal must not undergo spontaneous auto-oxidation to generate superoxide or peroxide species, nor must the coordinated O_2 ligand be attacked by protons or reductants that may assist this process.

Some 6,13-disubstituted macrocyclic Co(tmtaa) (**60**) complexes were prepared by Busch and co-workers and their O_2 binding affinities were determined.[1212] The complexes slowly undergo oxidation, but the ligand remains intact. This group has made many contributions to the field of O_2 binding through a class of macrobicyclic ligands often referred to as the cyclidenes (or lacunar macrocycles). Examples of 14-, 15-, and 16-membered macrocycles bound to divalent Co have been reported. For example, the planar [14]cyclidene complex has a small cavity which is only capable of partially protecting a bound O_2 from attack by solvent. This is in contrast to the deep saddle-shaped cavities of the 15- and 16-membered homologs. Some Co complexes of the [16]cyclidene family ((**261**) is an example) bind O_2 reversibly at low temperature with an enhanced affinity and lower rate of auto-oxidation compared to the [14]cyclidene analogs, both features attributed to the more exposed O_2 ligand in the smaller macrocycle. Dioxygen affinity decreases monotonically with the length of the polymethylene bridging group from octamethylene to tetramethylene and no binding occurs with a trimethylene bridge.[1213] The X-ray crystal structure of the Co–dioxygen adduct of (**261**) $[Co(MeMeC_6\text{-}[16]cyclidene)(Me\text{-}Im)(O_2)](PF_6)_2$ (Figure 10) reveals that the conformation of the ligand in the six-coordinate complex is crucial in protecting the O_2 ligand. Subsequently, the kinetics of O_2 binding to the vacant coordination site of the divalent complex were found to proceed with a very low activation barrier at rates comparable with the biological oxygen carriers myoglobin and hemoglobin.[1214] An interesting discovery was that ionizable Me groups on the cyclidene ligand enhance the rate of auto-oxidation of the divalent O_2 adduct, which prompted the synthesis of unsubstituted cyclidenes and their Co complexes.[1215] A lower O_2 binding constant was observed to the unsubstituted cyclidene complex, although the rates of dioxygen binding were as fast as those of the Me-substituted analogs, which pointed to differences in the complex dissociation rates as being responsible for the disparate O_2 affinities. Molecular dynamics calculations have been used to examine solution conformations of these complexes.[1216]

The ability of the ubiquitous Co(salen) complex and its tetradentate Schiff base analog complexes to bind O_2 reversibly has been central to most investigations of its coordination chemistry. A density functional computational investigation has been carried out on the O_2 carriers

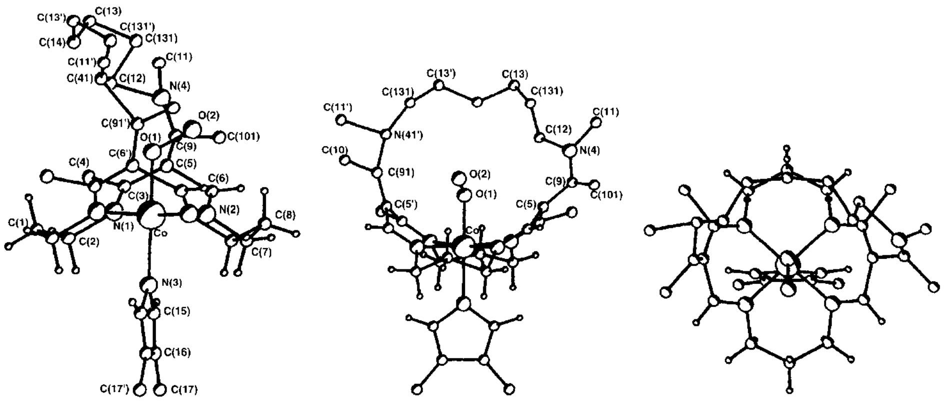
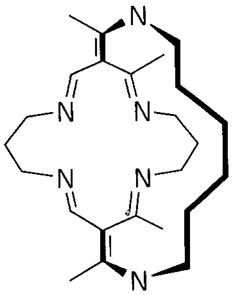
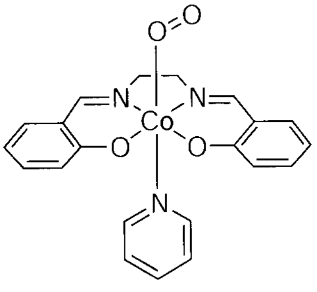


Figure 10 Three views of the Co-O_2 adduct of (**261**), with a disordered N-methylimidazole as the sixth ligand (reproduced with permission of the American Chemical Society from *Inorg. Chem.*, **1994**, *33*, 910–923).

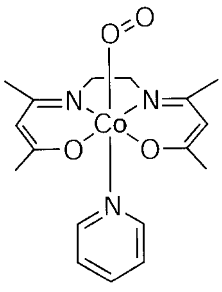
$(O_2)Co(salen)(py)$ (**262**) and $(O_2)Co(acacen)(py)$ (**263**).[1217] The calculated geometries and O_2 binding energies were consistent with experiment. The inclusion of effects due to the basis set superposition error and zero point correction attenuate the calculated binding energy. Magnetic susceptibility measurements showed that 22% of divalent Co(salen) exists as the high-spin $(S = 3/2)$ $Co(salen)(py)_2$ complex in pyridine solution at 295 K and that lower temperatures favor the high-spin species.[1218] In DMF-d^7 temperature-dependent NMR experiments, the formation of antiferromagnetically coupled dimers at low temperature was indicated. The pressure dependence of the high-spin-low–spin spin equilibrium was studied at room temperature for the six-coordinate 3-carboxy derivatives of $Co(salen)L_2$, where L is a coordinating solvent. The high-spin-low–spin crossover was observed with near-edge XANES spectroscopy.[1219] The pressures required to induce a spin transition were less than 1.1 GPa for L = pyridine, 4-tert-butylpyridine and H_2O (which are known to also undergo thermal spin crossover) and 6.5–9.0 GPa for L = 3-methylpyridine, which is normally high-spin at all temperatures.



(**261**)



(**262**)



(**263**)

The single-electron reduction and oxidation of Co(salen) is solvent dependent as a result of the available coordination sites perpendicular to the CoN_2O_2 plane.[1220] Furthermore, substituents on the phenyl rings modulate the observed redox potentials and subsequently the O_2 binding constants. Hammett correlations are obtained.[1221] Potentiometric titrations were performed to determine the O_2 binding constants and species distribution as a function of pH for a variety of Schiff base Co complexes.[1222]

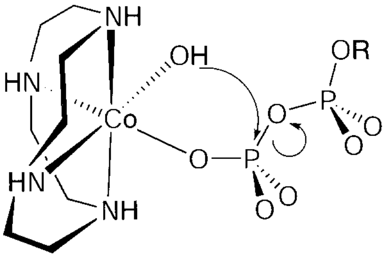
The Co(salen) complex may be prepared *in situ* inside zeolite Y (but not zeolite 5A) by reaction of the free ligand with the Co^{II}-exchanged zeolite (a "ship in a bottle" approach).[1223] When reacted with pyridine, 1:1 O_2 adducts are formed that are too large to exit the interior of the material and although the O_2 complex formation constants are smaller, auto-oxidation is attenuated significantly within the zeolite cavity. Similar experiments were performed to compare the reactivity of Co(salen) within cubic (zeolite Y) and hexagonally symmetric (EMT) cavities.[1224] An analogous approach has been reported using porous organic matrices to encapsulate Co(salen) and its O_2 adduct.[1225] Further, an oxygen-sensitive membrane incorporating Co(salen) has been prepared via sol–gel methods with poly(*N*-vinylpyrrolidone) as the mediation agent.[1226]

Well-dispersed silica and polymer/Co(salen) segments at a molecular level were obtained. Nondestructive immobilization of Co(salen) complexes within silica aero- and xerogels was also achieved with the sol–gel method using silylether-appended salen.[1227]

The mononuclear O_2 adduct $L(salchn)Co(O_2)$ (L = various substituted pyridines) bearing a fused cyclohexyl ring has been investigated by EPR spectroscopy.[1228] The effect of the basicity of the solvent *trans* to the dioxygen ligand on the *g* and *A* values was studied and discussed in terms of the degree of $Co—O_2$ back bonding. 1-Hydroxy-2-naphthaldehyde may be considered as a benzo-salicylaldehyde and Co complexes of its corresponding npthn analogs have been prepared with 2–6 methylene groups connecting the two N donors.[1229] Reversible O_2 binding occurs with the ethylenediamine analog Co(npthn) complexes in DMF, although the reaction is considerably more exothermic than for Co(salen).

(ii) Polyphosphate and phosphate ester hydrolysis

The biomimetic catalysis of polyphosphate hydrolysis by Co^{III} amines has received a great deal of attention. A number of tetraaminecobalt(III) complexes are known to be effective in this role. A stereochemical requirement is a *cis*-octahedral tetraamine complex where a pair of adjacent reactive coordination sites are present; one for a highly polarized hydroxo ligand (the nucleophile) and the other for the polyphosphate (the substrate). ATP,[1230–1232] cAMP (adenosine 3′,5′-cyclic monophosphate),[1233], triphosphate,[1234,1235] and pyrophosphate hydrolysis have been shown to be catalyzed by the macrocyclic complex $[Co(cyclen)(OH_2)(OH)]^{2+}$ (**140**). Monodentate coordination of a terminal phosphate group to produce a species of the type $[Co^{III}(cyclen)(OPO_3PO_2R)(OH)]^{n+}$ (**264**) is followed by rapid intramolecular phosphate hydrolysis involving the *cis*-coordinated hydroxo ligand resulting in the $[Co(cyclen)(OPO_3)(OH)]^-$ ion as a product.



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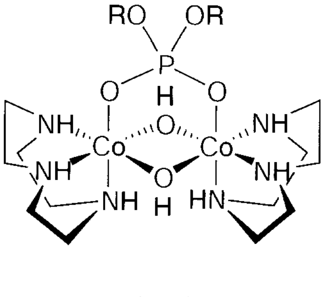
Phosphate monoester, diester,[1236] and triester[1237] hydrolysis is also catalyzed by this versatile ion, and it is known that the amine spectator ligands also influence the observed rates significantly.[1238] Measurable rate increases of up to 10^7-fold have been reported with Co^{III} polyamine catalysts.[1239] The large difference in reactivity of monodentate hydroxyethylphosphate where a *cis*-hydroxy group is also bound, compared with the chelated ester occupying both sites, points to the role of the coordinated nucleophile in hydrolysis of the phosphoester.[1240] With additional aquahydroxycobalt(III) tetraamines present, however, ester hydrolysis is significantly accelerated, pointing to a dinuclear intermediate forming. Indeed, a product of this hydrolysis has been characterized as $[(trpn)Co(OP(O_2)O)Co(trpn)]^{3+}$, supporting this view (trpn = tris(3-aminopropyl)amine).

Understanding the cooperative hydrolysis of phosphoesters by two metal ions, the presumed mechanism in endonucleases, is a current focus of attention, prompting study of dinuclear systems. Diester coordination can involve both terminal O atoms as donors, as exemplified in the bridged dinuclear complexes (**265**).[1241] Ester cleavage is promoted in basic solution via nucleophilic attack by a deprotonated bridging hydroxide. The Co···Co separation (2.9 Å) in the dimer is much shorter than in dinuclear phosphodiesterases.[1242] The diester is hydrolyzed by a mechanism involving double Lewis acid activation and attack from a neighboring bridging oxo ligand, with an exceptional 10^{12}-fold rate acceleration reported. The hydrolysis of methyl aryl phosphate diesters bound to Co^{III} in the dinuclear ion $[\{(tame)Co\}_2(\mu\text{-}OH)_2(\mu\text{-}O_2P(OAr)(OMe))]^{3+}$ is base catalyzed, and sensitive to the basicity of the aryloxy leaving group and to variation of the "spectator" amine ligand.[1243] Further rate enhancements have been observed in carefully designed dinuclear Co^{III} cyclen complexes capable of binding monoester[1244] or diester[1245] substrates within a pocket between the pairs of reactive *cis* aqua/hydroxo ligands on each metal (**266**). A triply bridged dinuclear complex with a bridging phenylphosphonate ester has also been examined as a model of phosphodiester cleavage.[966]



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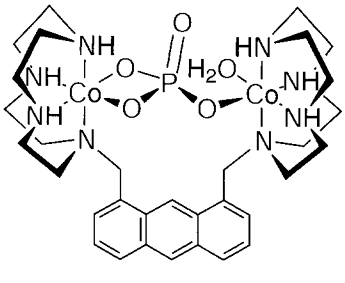

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DNA (phosphodiester) hydrolysis has also been examined with $[Co(cyclen)(OH_2)(OH)]^{2+}$ as the active species.[1239,1246] Significant rate enhancement of linear[1247] and supercoiled[1248] double-stranded polydeoxyribonucleotide hydrolysis is observed by immobilizing the Co complex on a polystyrene support. Wider exploration of reactions with DNA follow.

6.1.3.1.4 DNA binding, intercalation, and scission

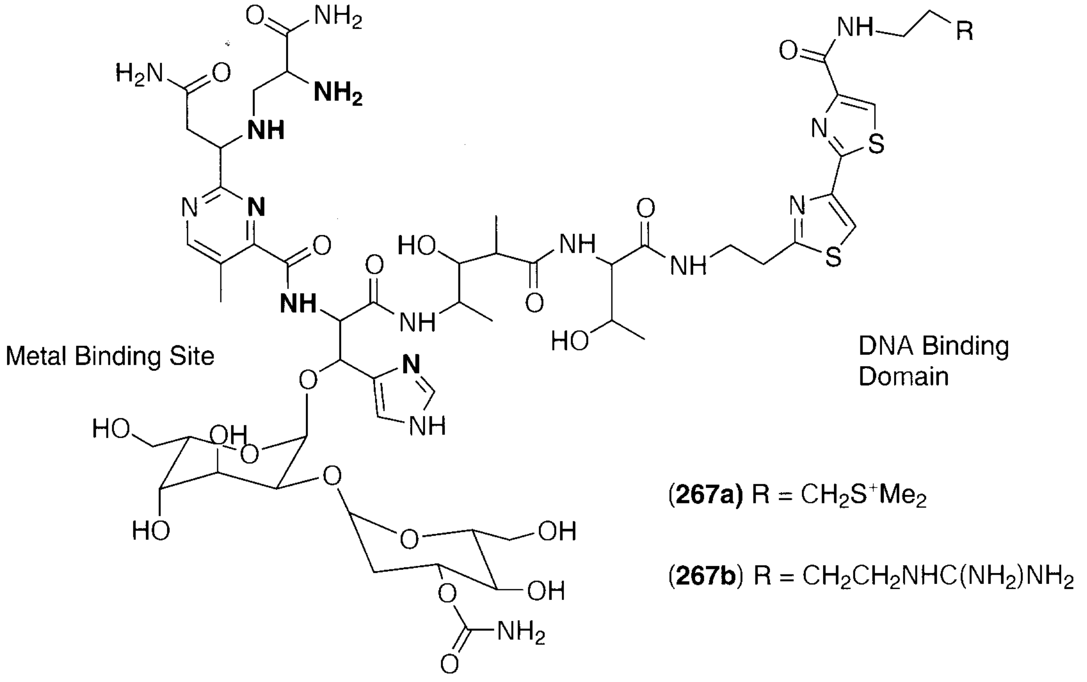
The humble $[Co(NH_3)_6]^{3+}$ ion is an extremely effective hydrogen bond donor, and its high charge density ensures a strong association with oligonucleotide duplexes both large and small. These ion pairing interactions can influence the helical structure of DNA and its relatives considerably.[1249] The oligonucleotide–$[Co(NH_3)_6]^{3+}$ interaction has been studied with a wide variety of physical techniques including crystallography,[1250–1255] electron microscopy,[1256,1257] atomic force microscopy,[1258] circular dichroism,[1259,1260] vibrational spectroscopy,[1261,1262] NMR,[1263–1265] and light scattering.[1266,1267] Condensation of DNA[1268,1269] is affected by the presence of this ion. It has been found that $[Co(NH_3)_6]^{3+}$ effects the conversion of B- (right-handed) to Z-DNA (left-handed) or B- to A-DNA (conformationally distinct right-handed helices) depending on the DNA sequences, and a number of spectroscopic and theoretical[1270] studies have investigated this phenomenon. Marked changes in the helical structure of the oligonucleotide such as bending and photosensitized cleavage of the helix have been observed.[1271,1272]

The interaction of chiral $[Co(en)_3]^{3+}$ with DNA and small oligonucleotides has been extensively studied. A ^1H NMR investigation revealed distinctly different chemical environments of the nucleotide protons of a dodecanucleotide in the presence of the different enantiomers, and concluded that Δ-$[Co(en)_3]^{3+}$ binds with the dodecamer in the major groove, near the center of the duplex and binds more strongly than the corresponding Λ isomer.[1273] This interaction has been investigated with molecular dynamics simulations, and this study identified key H-bonding interactions responsible for the diastereoselectivity.[1274] A ^{59}Co and CD spectroscopic study[1275] of the interaction between the Δ- and Λ-$[Co(en)_3]^{3+}$ with DNA identified a similar sequence selectivity (guanine) to that seen for $[Co(NH_3)_6]^{3+}$, and both enantiomers were found to induce a B-to-A DNA conversion in G-rich regions while leaving other sections of the duplex in the B conformation.[1276] However, Δ-$[Co(en)_3]^{3+}$ binds more strongly to right-handed, guanine-rich DNA than Λ-$[Co(en)_3]^{3+}$. The reverse is true for left-handed DNA. The two enantiomers bind in an indistinguishable manner to AT-rich DNA. These findings were subsequently supported by 2D NMR experiments.[1277] The B–Z DNA transformation in poly (dG-dC)(dG-dC) DNA, known to be assisted by $[Co(NH_3)_6]^{3+}$, has also been achieved with $[Co(en)_3]^{3+}$.[1260] DNA has been shown to co-precipitate rapidly with $[Co(en)_3]^{3+}$ at trace concentrations whereas charge neutral and anionic complexes are left in solution.[1278]

The $[Co(phen)_3]^{3+}$ complex is photoactive and a powerful oxidant in its excited state. The ion has no H-bonding groups and hence is considerably more hydrophobic[1279] than hexaamine relatives. These properties have proven particularly useful. Aryl and alkyl substituted $[Co(phen)_3]^{3+}$ complexes have received a great deal of attention due to their ability to intercalate within the helical structure of DNA through a combination of electrostatic and hydrophobic forces. The chirality of the tris-chelate complex is crucial in determining the degree of association between the complex and

DNA. A key paper by Barton and Raphael[1280] reported that (right-handed) B-DNA associates strongly with Δ-$[Co(4,7\text{-}Ph_2\text{-}phen)_3]^{3+}$ but not with its Λ enantiomer. Upon irradiation DNA nicking was achieved, which was attributed to photooxidation by the Co^{III} complex when closely bound to the helix activating strand scission. The area of DNA intercalation by $[Co(phen)_3]^{3+}$ and other similar complexes has received a great deal of attention subsequently.[1281] The DNA double helix has been shown to be an efficient conduit for intermolecular electron transfer between photoexcited $[Ru(phen)_3]^{2+}$ and $[Co(phen)_3]^{3+}$, where both complexes are intercalated within the double helix.[1282] This concept was extended to the same intermolecular electron transfer reaction on the surface of starburst dendrimers.[1283] Electrochemical methods have been employed to quantify the association constants between the Co complex and various oligonucleotides,[1284–1286] and to gauge the effect of DNA binding on the rate of diffusion of the Co complex.[1287] The concept of association between the DNA double helix and the complementary $[Co(phen)_3]^{3+}$ unit has been extended to DNA-modified electrodes with potential biotechnological applications.[1288–1293] Adsorptive transfer stripping voltammetry at a hanging mercury drop electrode has been used to detect conformational changes of DNA due to binding of DNA intercalators.[1294]

The molecules bleomycin A_2 and B_2, (**267a**) and (**267b**), comprise a potent chemotherapeutic agent for the treatment of cancer. The anti-cancer activity lies in the drug's ability to achieve DNA strand scission in tumor cells through the production of peroxyl species. A single bleomycin molecule is capable of cleaving both strands of DNA in the presence of its required cofactors $Fe_{aq}{}^{2+}$ and O_2 without dissociating from the helix. There are a number of N donors (in bold) that participate in binding the Fe cofactor and produce hydroperoxide as a ligand that initiates strand cleavage. Substitution of Co for Fe enables interactions between the drug and DNA fragments to be investigated by NMR spectroscopy. Conformational properties of the $HO_2\text{-}Co^{III}$-bleomycin A_2 (**267a**) (Form I) and Co^{III}-bleomycin (Form II) complexes bound to DNA oligomers were examined by NMR.[1295] Form I binds in slow exchange to the oligomers $d(GGAAGCTTCC)_2$ and $d(AAACGTTT)_2$, whereas Form II binds with DNA in fast exchange on the NMR time scale. The association constant of Form II with $d(GGAAGCTTCC)_2$ (pH 7.4, 25 °C) is $1.7 \times 10^5\ M^{-1}$. A later 2D NMR study of the complex formed between Co-bleomycin and other oligonucleotides gave a well-defined picture, which found that the bithiazole tail of bleomycin is partially intercalated between T19 and A20 of the duplex and that the metal binding domain is poised for abstraction of the T19 H4′ in the minor groove.[1296] The interaction between the Co^{III} complex of a bleomycin functional model (AMPHIS-NET) and the oligonucleotide $d(CGCAATTGCG)_2$ were examined by 2D NMR methods and molecular dynamics calculations.[1297] The 1:1 cobalt(III) complex of AMPHIS-NET binds in the minor groove of the oligonucleotide at the central AATT site. Cross peaks also indicate that the metal binding moiety of the Co^{III}–AMPHIS-NET complex interacts with the oligonucleotide two base pairs beyond the central AATT site in the minor groove.



(**267a**) R = $CH_2S^+Me_2$

(**267b**) R = $CH_2CH_2NHC(NH_2)NH_2$

6.1.3.1.5 Biological electron transfer

Association of $[Co(NH_3)_6]^{3+}$ with acidic amino acid residues on the surface of proteins has been exploited in the "promotion" of electron transfer reactions of redox active proteins at electrode surfaces.[1298,1299] The $[Co(phen)_3]^{3+}$ and $[Co(bpy)_3]^{3+}$ ions are particularly attractive high-potential, single-electron, outer-sphere oxidants lacking any potential hydrogen bonding sites. The oxidation of blue copper proteins with $[Co(phen)_3]^{3+}$ and $[Co(bpy)_3]^{3+}$ has been studied in a series of papers from Sykes and co-workers,[1300–1305] and other groups.[1306–1309] Reactions of the Co^{III} complexes with ferrocytochromes,[1310–1318] Fe–S clusters,[1319] molybdoenzymes,[1320] and galactose oxidase[1321] have also been reported. Enantioselective oxidation of ferrocytochrome *c* by optically pure $[Co(bpy)_3]^{3+}$ was interpreted as evidence for the closeness of approach of the Co^{III} complex to a hydrophobic, and inherently chiral, pocket of the protein.[1322] Like the bpy and phen homologs, the $[Co(terpy)_2]^{3+}$ ion has been used as a single-electron oxidant of a number of biological targets.[1305,1323] With the $[Co(phen)_3]^{3+/2+}$ couple, the $[Co(terpy)_2]^{3+/2+}$ system has been used as a high potential mediator in redox potentiometry of biological redox centers.[1324]

6.1.3.1.6 Medicinal chemistry

Co porphyrins have been found to play interesting and varied roles in medicine. Co protoporphyrin and *meso*-substituted porphyrins administered subcutaneously to normal adult rats led to decreases in food intake and sustained decreases in body weight, while direct injection of the compound into the brain produced similar changes in food intake and body weight, but requiring about 1–2% of the parenteral dose.[1325] Similar effects were observed with genetically obese rats, chickens, and dogs. These studies demonstrate that porphyrins can act on the central nervous system to regulate appetite and to produce long-sustained diminutions in body weight and content of fat in animals; pharmaceutical compositions for these porphyrins for the treatment of obesity have been patented.[1326]

The high CN^- affinity of trivalent $[Co(TSpP)]^{4-}$ has led to its investigation as a potential cyanide antidote either alone or in various combinations with the cyanide antagonists $NaNO_2$ and $Na_2S_2O_3$.[1327] The study found that administration of $[Co(TSpP)]^{4-}$ alone protects against the lethal effects of cyanide, and that the complex adds to the protection provided by $Na_2S_2O_3$ and/or $NaNO_2$. Co protoporphyrin administered in conjunction with organ transplantation has been found to enhance organ survival. Inhibition of cytotoxicity *in vitro* and prolongation of graft survival in therapy of heart allograft recipients has been demonstrated.[1328] It is known that $CoCl_2$ is a potent inducer of heme oxygenase *in vivo* in animals, so the possibility of the biosynthesis of Co protoporphyrin was examined in human hepatoma cells by incubating them with $CoCl_2$ and protoporphyrin and δ-aminolevulinate, the precursor of protoporphyrin.[1329] Both types of treatment led to a potent induction of heme oxygenase mRNa, with Co protoporphyrin formation demonstrated in cells incubated with the metal and δ-aminolevulinate, which demonstrated that incorporation of Co into the porphyrin is necessary for induction, and indicated that the role of $CoCl_2$ (as its porphyrin complex) was to activate the heme oxygenase gene via a heme-responsive transcription factor.

The therapeutic potential of sarcophagine cage complexes in general has been reviewed.[760] For Co cages, in particular (**162**), the irreversible nature of coordination means that the metal is a spectator in systems examined to date. Most of the uses for this class of Co complex in biology relate to the nature of the substituents introduced at the cap. Long alkyl substituents result in complexes that exhibit surfactant-like properties and these have been found to exhibit antiparasitic activity.[1330–1332] The anthracenyl-substituted (cationic) Co cage (unlike anthracene itself) associates strongly with DNA and irradiation of the intercalated complex at 254 nm leads to single-strand cleavage of DNA.[1333]

6.1.4 INDUSTRIAL AND ANALYTICAL APPLICATIONS OF COBALT COMPLEXES

6.1.4.1 Organic Transformations

The use of transition metal compounds in organic synthesis, where they may be involved in stoichiometric reactions or catalytic reactions, has grown consistently, as recent reports illustrate.[1334–1337]

Catalysts for promoting organic transformations are as diverse as are the reactions they catalyze, and there are a growing number of examples featuring Co extant in the literature. Nevertheless, Co features less commonly than some other metal ions, but may find application in a range of characteristic organic reactions such as alkylation, conjugate addition, oligomerization, acylation, rearrangement, and functional group synthesis. It remains true to say that applications of Co compounds in catalysis are limited relative to other metals such as palladium and ruthenium, and this presents an area for future development of the chemistry of the element. This section does not aim to be exhaustive in its coverage, but to give examples of applications and recent developments in the field; some examples have appeared already for selected complexes throughout the review.

Both heterogenous and homogenous catalysts featuring Co have been reported. The macromolecular heterogenous catalysts are outside the scope of this report, which concentrates on molecular systems. However, it is noted that surfaces can promote reactions in concert with molecular systems. For example, surface reactions between $Co_2(CO)_8$ and an inorganic oxide involves disproportionation and tight ion pair formation, leading to catalytically active $Mg[Co(CO)_4]_2$.[1338] Further, surfaces may be templated with organic molecules capable of binding metal ions strongly, providing modified surfaces for catalytic activity,[1339] or else complex ions may be intercalated in layered inorganic solids such as double hydroxides.[1340] Intercalation of phthalocyanines and porphyrins of cobalt(II), as well as polyoxometallates including cobalt(II), has been established in these anionic clays. Photocatalysis by transition metal complexes has been widely studied also.[1341] Amongst systems identified, cobalt(III) complexes of oxalate and dithiooxalate feature in their use for hydrogen generation from thiols, which also leads to disulfides.

6.1.4.1.1 Oxidations

Cobalt(III)–alkylperoxo complexes find use in the oxidation of hydrocarbons.[1342,1343] Since they release ROO· and RO· radicals upon mild heating in solution, they are effective oxidants under mild conditions, and produce catalytic systems in the presence of excess ROOH. Aliphatic C—H bond oxidation by $Co^{II}OOR$ ($R = Co^{II}$, alkyl, H) complexes including a hydrotris(pyrazolyl) borate ligand have also been reported, with homolysis of the peroxo O—O bond believed to be important in oxygenation of the C—H bond.[1344]

Regioselective hydroperoxygenation of $\alpha,\beta,\gamma,\delta$-unsaturated carbonyl compounds with O_2 and triethylsilane was achieved with a Co^{II} porphyrin complex, to give the corresponding γ-hydroperoxy-α,β-unsaturated carbonyl derivative in good yield.[1345] The same group extended this range of reactions to include other conjugated olefins such as styrene and acrylic esters.[1346] 4-Aryl-substituted derivatives of Co(TPP) catalyze the oxidation[1347] or epoxidation[1348] of organic substrates such as alkenes, allylic or benzylic substrates, alcohols, and hydrocarbons at ambient conditions in the presence of O_2 and 2-methylpropanal.

The 4-methoxy derivative of the Schiff base complex Co(salphn) (**69b**) catalyzes the mild epoxidation of olefins in one atmosphere of O_2 in the presence of a cyclic ketone reductant.[1349] The catalytic dioxygenolysis of 3-methylindole to 2-(*N*-formylamino)acetophenone has been investigated within a series of electronically and sterically designed Co(salen) (**69a**) complexes. The cathodic shifts in the $Co^{III/II}$ redox potential and steric bulk each slow the reaction.[1350] Substituted anilines undergo oxidation by *t*-butyl hydroperoxide in the presence of Co(salen) analogs to give the corresponding nitrobenzene.[1351] A Co(salen)(OO-*t*-Bu) intermediate was implicated in the mechanism. The catalysis of phenol oxidation reactions was investigated using Co(salen) analogs, particularly coniferyl and sinapyl alcohols as substrates. This oxidation of monomeric and dimeric lignin model compounds was also studied with a view to its relevance to practical pulp bleaching conditions.[1352]

Complexes of the Co(salen) family are capable of mediating the electrocatalytic reduction of O_2 to H_2O_2.[1353] The reduction potential is pH dependent, irreversible, and diffusion controlled. The biphenyl-derived dimer of Co(salphn) (joined at the 4-positions of the two *o*-phenylenediamine rings) adsorbs onto a graphite electrode and also catalyzes the reduction of O_2 which is believed to involve axial coordination of O_2.[1354] An electrochemical investigation of the cyclohexane fused analog Co(salchn) identified a reversible $Co^{III/II}$ response in deoxygenated non-aqueous solution in addition to O_2 reduction waves on aeration. An XPS analysis of an anodically formed film of the complex on a platinum electrode identified the Co complex in its trivalent oxidation state. In aerated solution, catalytic oxidation of alkenes such as cyclohexene and 4-methyl-1-cyclohexene was observed.[1355]

Cobalt(II) bis(1,3-diketone) complexes find use for the conversion of olefins into alcohols, ketones, and paraffins, by contacting the olefins with an oxygen-containing gas in the presence of the Co catalysts.[1356] Cobalt catalysts supported on or incorporated into other materials are also recognized as effective heterogeneous catalysts. Co(salen) can be incorporated into the intercrystalline cavities in zeolites, and catalyzes the oxidation of cyclohexene with aqueous peroxide to form cyclohexane-1,2-diol, 2-cyclohexenol and 2-cyclohexenone.[1357] Crosslinked polystyrene is an efficient support for thiosemicarbazone cobalt (II) complexes.[1358] This functionalized polymer, when 10% crosslinked, shows potential as a catalyst for the epoxidation of cyclohexene and styrene. It is also able to catalyze the decomposition of peroxide. Polymer-immobilized EDTA was prepared by redox initiation with sodium EDTA and ceric ion of copolymerization of methacrylic acid and acrylonitrile. The Co complex proved useful for the peroxidation of benzaldehyde, in a selective and high-yielding reaction.[1359] Immobilization of a Co^{III} complex on chemically modified silica has recently been described, and efficiently oxidized alkylaromatics with air and without requiring a solvent.[1360] Immobilized catalysts present the opportunity for more environmentally friendly industrial processes to be developed.

6.1.4.1.2 Carbonylation and formylation

Hydroformylation promoted by metal compounds is sufficiently extensive to attract annual reviews of work in the field.[52,1361,1362] However, Co catalysts form a smaller subset. Of the more established Co catalysts, $Co_2(CO)_8$ continues to be well studied. The equilibrium reaction pertinent to hydroformylation (Equation (12)), has been recently reviewed.[1363]

$$Co_2(CO)_8 + H_2 \rightleftharpoons 2\,HCo(CO)_4 \tag{12}$$

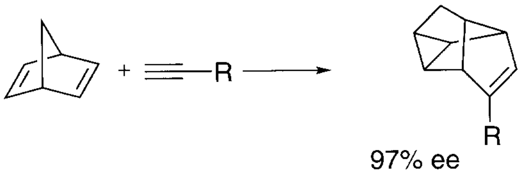
The attainment of regio- and enantioselectivity are continuing challenges, which form the basis of investigations of new catalytic systems. For example, novel mixed-metal catalysts such as $(CO)_2Co(\mu\text{-}CO)(\mu\text{-}HC{\equiv}CBu)Rh(CO)_2$ promote the stereospecific synthesis of *Z*-only $BuC(CHO){=}CHSiMe_2Ph$ from 1-hexyne and $HSiMe_2Ph$.[1364]

A recent example where $Co_2(CO)_8$ serves as a precatalyst is in the preparation of linear and branched aldehydes via propylene hydroformylation in supercritical CO_2 (93–186 bar; 66–108 °C). Cyclohexane carbaldehyde is produced from cyclohexene using $Co_2(CO)_8$ and an acid RCOOH, or else is successful with another established Co catalyst, $Co(OOCR)_2$, assumed to form *in situ* in the former case. Oligomerization of aldehydes such as n-butanal is achieved with $Co_2(CO)_6L_2$ as catalyst ($L = CO, PR_3$).[1364]

High yielding and chemoselective hydrocarbonylation of benzyl chloride and bromide and substituted analogs in a mixed organic/aqueous NaOH two-phase system occurs in the presence of $Co_2(CO)_8$ as catalyst and polyethylene glycol as phase transfer agent.[1365] Proposed intermediates in the catalysis are species such as η^1- and η^3-benzylacetylcobalt carbonyls. Polynuclear $Co_4(CO)_{11}(SMe_2)$ promotes the hydroformylation of alkenes to aldehydes.[1366] Carbonylation of organic halides to form esters with $Co(PPh_3)_mX_n$ compounds as catalyst has been examined,[1367] with yields of up to 80% established in a two-phase benzene aqueous NaOH system with tetrabutylammonium bromide as phase transfer agent. Anhydrous $CoCl_2$ with $[PhEt_2N][BH_3]$ is a useful reagent for hydroboration and carbonylation of alkenes to dialkylketones, after oxidation with H_2O_2/NaOH.[1368] The oxidative carbonylation of aromatic primary amines employs Co(salen) as a catalyst, and produces ureas in high yields, including cyclic ureas.[1369]

6.1.4.1.3 Cycloadditions and asymmetric synthesis

Asymmetric, enantioselective, and regiospecific synthesis is of particular importance for sophisticated syntheses of relevance to the pharmaceutical industry and other industries demanding "boutique" chemicals. The field is attracting continuing effort, and the type of reaction where Co catalysts appear are diverse and activity strong, so it is only possible to give a flavor of the field here. An example is in the Diels–Alder reaction (Equation (13)), which occurs in high yield and with 97% enantiomeric excess where the CoI_2/Zn catalyst incorporating the aminophosphine–phosphinite ligand (**268**) is employed.[1370]



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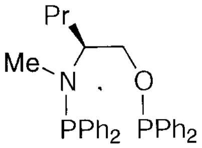

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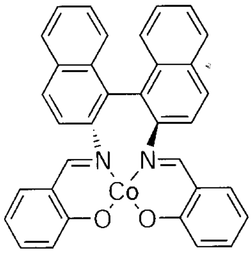
The potential of chiral Co(salen) analogs in asymmetric N, S, and P oxidations has been realized and the preparations of a number of these compounds have been patented.[1371] Chiral Schiff base complexes derived from 2,2′-diamino-1,1′-binaphthalene or 1,2-diaminocyclohexane and various salicylaldehydes have been synthesized and complexed with cobalt (**269**).[1372] The crystal structure of Co(phsaldpen) (derived from 2-hydroxybenzophenone and *rac*-1,2-diphenylethylenediamine) has been determined where the two Ph groups on the chelate ring occupy axial positions and hinder access to the apical coordination sites.[1373] The $Co^{III/II}$ couple is ca. 300 mV anodically shifted relative to Co(salen). The *meso* isomer was also prepared. Chiral tridentate Schiff base complexes have also been exploited as catalysts for stereoselective cycloaddition reactions.[1374] Cyclopropanecarboxylates were obtained with excellent enantioselectivity (>95% ee) from reaction of styrene derivatives and *t*-butyl α-diazoacetate, using the advanced chiral Co^{II}–salen complex (**270**).[1375] Chiral trivalent Co (salen)(OAc) analogs immobilized on the mesoporous siliceous material (MCM-41) achieve hydrolytic kinetic resolution of racemic epoxides (epichlorohydrin, 1,2-epoxyhexane, epoxystyrene and epoxycyclohexane) to their diols.[1376]



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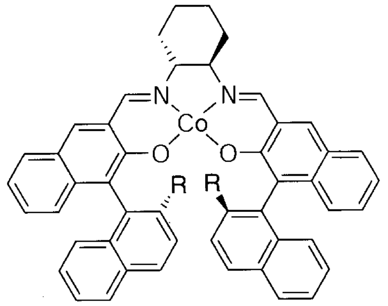

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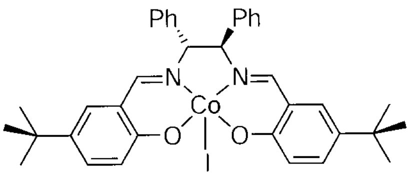
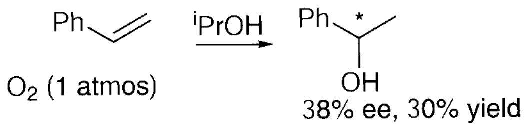


(271)

Catalysts of the Co(salen) family incorporating chiral centers on the ligand backbone are useful in asymmetric synthesis and the field has been reviewed.[1377,1378] In two examples, the hydroxylation reaction (Equation (14)) involving (**269**) proceeds with 38% ee,[1379] whereas the cyclopropanation reaction with (**271**) (Equation (15)) proceeds with 75% ee and with 95:5 *trans:cis*.[1380] A Co(V) salen carbenoid intermediate has been suggested in these reactions.



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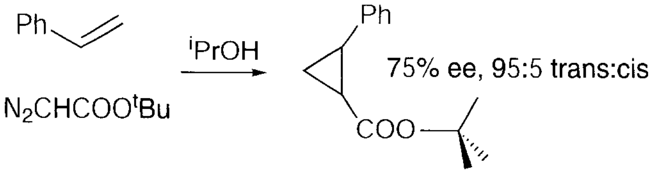

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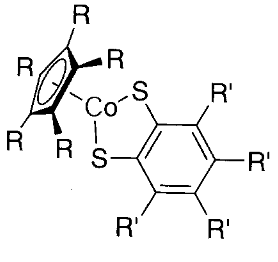
Optically active β-ketoiminato cobalt(III) compounds based on chiral substituted ethylenediamine find use as efficient catalysts for the enatioselective hetero Diels–Alder reaction of both aryl and alkyl aldehydes with 1-methoxy-(3-(*t*-butyldimethylsilyl)oxy)-1,3-butadiene.[1381] Cobalt(II) compounds of the same class of ligands promote enantioselective borohydride reduction of ketones, imines, and α,β-unsaturated carboxylates.[1382]

6.1.4.1.4 Other catalytic reactions

A selected assortment of other organic transformations not discussed above is given here. Catalysis of the condensation reaction between *p*-nitrobenzaldehyde and *p*-aminotoluene by thiourea complexes of cobalt(II) and zinc(II) has been observed, and activation by substrate coordination to the complex in the activated state is implied.[1383] Reductive nitrosation of olefins, α,β-unsaturated and α,β,γ-unsaturated carbonyl compounds have been reported with Me_3CONO and Et_3SiH in the presence of Co^{II} porphyrin catalysts to give the respective acetophenoximes, α-hydroxyimino and γ-hydroxyimino-α,β–unsaturated carbonyl compounds in good yields. The potential role of cyclodextrins functionalized with polyamines as enzymes models and chiral receptors has been reviewed.[1384] Their application as artificial hydrolases is exemplified by the 900-fold enhancement of hydrolysis of *p*-nitrophenyl acetate by a cyclodextrin carrying an appended cyclen macrocycle bound to a cobalt(III) ion, which also carries two *cis*-coordinated water molecules.[1385] These two adjacent sites provide the opportunity for both substrate binding and provision of a coordinated nucleophile for attack of the ester group. The potential of metal complexes, including those of cobalt, as synthetic nucleases has been reviewed.[1386]

Isomerizations are another category of reaction where Co complexes act as catalysts. Mixed S,P donor complexes $Co(SCN)_2(PR_3)_2$ catalyze the isomerization of 1-butene to 2-butene in the presence of $NaBH_4$, with $CoH(SCN)(PR_3)_2$ proposed as the active species.[1366] A cyclopentadienyl complex (**272**) is active in the isomerization of quadricyclene to norbornadiene.



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Rearrangement of trivalent (5-hexenyl)Co(salen) proceeds via a radical chain process leading to the isomeric cyclopentylmethyl complex.[1387] The efficiency with which this rearrangement occurs is dependent on the presence of trace impurities or O_2. The selective reaction of alcohols (ROH) with arylglyoxals (ArCOCHO) to give α-aryl-α-hydroxyacetic esters $ArCH(OH)CO_2R$ is catalyzed by compounds of this family.[1388]

6.1.4.2 Polymerization

Polymerization employing Co complexes as catalysts or else polymers incorporating functionality that includes Co ions represent aspects of polymerization reactions of interest here. Cobalt-mediated free-radical polymerization of acrylic monomers has been reviewed.[55] Co^{II} porphyrins act as traps for dialkylcyanomethyl radicals.[1098] Alkyl complexes of Co(TMesP)

(Mes = mesitylene) have been shown to initiate and control living free radical polymerization of poly methyl acrylates and block copolymers of methyl and butyl acrylate.[58,1389,1390] Oxygen transfer polymerization, using the reversible oxygen carrier Co(TPP)(py), which serves as both oxygen supplier and a fully recoverable initiator, has been reported.[1391] Vinyl monomers are converted under mild conditions to polymeric peroxides. Similarly, Co(TPP) in the presence of O_2 has been found to catalyze the room-temperature free radical polymerization of styrene and methyl methacrylate.[1392] The same group reported the oxidative polymerization of indene with Co(TPyP), leading to the formation of poly(indene peroxide) with narrow polydispersity.[1393] Dual behavior of Co(TPyP) as a dioxygen carrier as well as an initiator was implicated in this study.

Dichloro(2,6-bis(imino)pyridine)cobalt(II) has been characterized by X-ray diffraction.[1394] Upon treatment with methylaluminoxane, a highly active ethylene polymerization catalyst for production of highly linear polyethylene is produced that yields polymer of MW up to 600,000. Poly(salicylaldehyde acrylate) crosslinked with divinylbenzene has been derivatized with thiosemicarbazone, semicarbazone oxime, and ethylenediamine, and their formation of coordination polymers with cobalt(II) probed.[1395] Novel metal halide-complexed polymer films, including that of cobalt(II), were prepared with poly(arylene ether phosphine oxide).[1396] Metal complexation to the polymer was defined by IR and ^{31}P NMR studies. Imprinted polymers have been prepared which use a cobalt(III) imine complex as the template in a surface grafting technique, and their use for reversible dioxygen binding explored.[1397] Polymer materials with immobilized metal complexes of defined structures such as these have potential for application in catalysis, gas storage, and sensor technology.

6.1.4.3 Electrocatalysis and Analytical Sensors

Electrocatalysis employing Co complexes as catalysts may have the complex in solution, adsorbed onto the electrode surface, or covalently bound to the electrode surface. This is exemplified with some selected examples. Cobalt(I) coordinatively unsaturated complexes of 2,2′-dipyridine promote the electrochemical oxidation of organic halides, the apparent rate constant showing a first order dependence on substrate concentration.[1398,1399] Catalytic reduction of dioxygen has been observed on a glassy carbon electrode to which a cobalt(III) macrocycle tetraamine complex has been adsorbed.[1400,1401]

Recent studies on Co porphyrin chemistry have focused on their use as catalysts of reactions involving coupled electron and atom transfer, where the substrate is typically coordinated in a coordination site axial with respect to the CoN_4 plane. Coupled with glucose oxidase, (GO), $[Co(TMpyP)]^{4+}$ adsorbed into a Nafion film was used to monitor O_2 depletion (through glucose oxidation during GO turnover), and the voltammetric current from the porphyrin was used to determine glucose concentrations.[1402] Independently, Kadish and co-workers have investigated the reactions of monovalent $[Co^{I}(TMpyP)]^{3+}$ with O_2 to give a superoxo–Co^{II} complex that is stable in DMF solution. In oxygenated DMF solution, electrogenerated monovalent $[Co(TMpyP)]^{3+}$ catalyzes the epoxidation of cyclohexene.[1403] Although monovalent $[Co(TPP)]^-$ was inactive, the single-electron reduced complex generated chemically, electrochemically, and using pulse radiolysis and assigned as a π-radical, catalytically reduces CO_2 to CO and HCO_2^-.[121] Fluorination of the porphyrin results in an anodic shift of the potential at which catalysis occurs.

The consequences of polychlorination of porphyrins on redox properties of complexes has been investigated.[1404] The highly chlorinated porphyrin β-octachloro-*meso*-tetrakis(3,5-dichloro-2,6-dimethoxyphenyl)porphyrin exhibits a substantial anodic shift for reduction of over 0.5 V and a smaller shift for oxidation versus the unchlorinated precursor. Contrastingly, small potential shifts for the octabromo-substituted 5,10,15,20-tetraphenylporphyrinate arise from the dominance of macrocycle "ruffling" over electronic effects. In the polychloro complex, distortion does not compensate fully for electron-withdrawing effects of the Cl substituents.

Flow-injection spectrophotometric analysis of cobalt(II) has been developed employing pyridoxal 4-phenylthiosemicarbazone as chelating agent in strongly acidic medium, forming an intense yellow-colored 1:2 complex ($\lambda_{max} = 430$ nm, $\varepsilon_{max} = 1.35 \times 10^4$ M^{-1} cm^{-1}), with very few interferences at the low pH used, and detection down to 0.4 µg mL^{-1}.[1405] Direct, simple spectrophotometric analysis of Co down to similar levels has also been reported using 2′-hydroxyaceto--hydroxyacetophenone thiosemicarbazone,[1406] amongst a number of analogous studies. A sophisticated flow-injection method that allows for the simultaneous detection of Co and Ni via complexation with 2-hydroxybenzaldehyde thiosemicarbazone has been described.[1407] This relies on different formation rates of the two complexes. This technique has also been applied to determination of Co and Fe simultaneously.[1408]

A cobalt(II)–ethanolamine complex sorbed onto Dowex-50Wx2 resin serves as a heterogenous catalyst for luminol chemiluminescence, and was developed as a flow-through sensor for hydrogen peroxide and glucose.[1409] Electoactive Co complexes may play a key role in the analytical detection of compounds electrochemically. For example, nitrate in vegetables has been detected accurately in the mg/kg range by forming a complex with thiocyanate and nitric oxide, generated chemically from nitrate ion, and employing polarographic analysis.[1410]

6.1.4.4 Environmental

There is a range of environmental activities employing or dealing with cobalt; this is a growing area, and only a very few selected examples follow to identify the breadth of the field. In their monovalent oxidation state, Co porphyrin complexes are effective dechlorination catalysts of chlorinated hydrocarbons. Electropolymerization of a pyrrole-substituted *meso*-tetraphenylporphyrin (TPP) complex of Co onto a carbon support produces a catalyst that can reductively dechlorinate benzyl chloride[1411] and other organic halides.[1412] Similarly, Co(TPP) adsorbed onto a graphite foil electrode has been used as a sensor for the catalytic dechlorination of organic pollutants when reduced to its monovalent state. The aim of this work was to screen toxic organohalogen pollutants in environmental monitoring situations.[1413] Catalytic electrochemical reduction of *trans*-1,2-dibromocylohexanes is also achieved with Co porphyrins at potentials more than 1 V positive than in the absence of catalyst.[1414] Nitrotoluene reduction is catalyzed by Co hematoporphyrin as a preliminary step to enhance biodegradability of these waste products.[1415]

The treatment of waste water containing sulfide ions by catalytic aerial oxidation in the presence of a Co^{II} tetrasulfophthalocyanine catalyst removed over 95% of sulfide over a period of several hours.[1416] Removal by precipitation of cobalt(II) from waste water in the presence of other complexing agents was achieved by the addition of *N*,*N*-diethyl-*N*′-benzoylthiourea. The use of substituted thioureas can be applied to removal of other heavy metals also.[1417] The very low toxicity of several halo(2,3-dimethylpyrazolone-5-thione)cobalt(II) complexes allowed their use in the development of granulated slow-release fertilizers using collagen hydrolyzate as the organic filler, to deliver Co as a micronutrient.[1418]

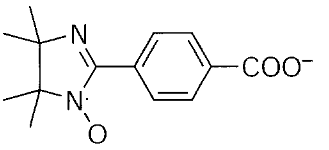
6.1.4.5 Technology

Cobalt complexes find application commercially, or else have been developed for commercial use, in a surprising range of tasks. Even the simplest of complexes may be employed. It has been found that $[Co(NH_3)_6]^{3+}$ salts with oxidizing anions (nitrate, nitrite, and perchlorate) may be used as gas generants for the rapid inflation of automobile airbags.[1419] These compounds are proposed as alternatives to highly toxic sodium azide, which is the most widely used gas generant in this application. Upon detonation, in the presence of co-oxidizers, $[Co(NH_3)_6](NO_3)_3$ liberates gaseous N_2, O_2, and water vapor which inflate the airbag. The same complex cation may be induced to release ammonia on heating at an appropriate stage of electrographic image formation, enhancing image contrast and density markedly.[1420] In testimony to its versatility, $[Co(NH_3)_6]^{3+}$ also finds application in a peroxide-free bleaching mixture in concert with polyoxyethylene lauryl ether and sodium carbonate.[1421] More elaborate complexes have been patented to enhance the bleaching effect of peroxide, as distinct from replacing it, including Co complexes with tripodal ligands and polyamide–polyamine dendrimers. At the other extreme, fabric dyes of dark green Co complexes with glyoxal anil arylhydrazones have appeared.[1422] Potential uses of Co coordination complexes are diverse. A quite different application, making use of cobalt's redox chemistry, uses (pyridine)bis(dialkylglyoximato)cobalt(III) chloride complexes along with acetylene black as cathodes in an effective rechargeable conducting polymer battery where poly(*p*-phenylene sulfide) anodes and $LiClO_4$-propylene carbonate electrolyte also feature.[1423] The complex Co (TMeOPP) (MeOP = 4-methoxylphenyl) has been incorporated into the cathode of an Al–O battery (where Al is the anode) with the goal being the use of this technology as a power source in spacecraft.[1424]

Somewhat unanticipated applications can arise. For example, a process for the production of ultrapure hydrogen peroxide for the electronics industry has been patented recently,[1425] which uses the macrobicyclic hexamine complex (**29**) supported on an inert material for dioxygen reduction. Cobalt(III) EDTA has been patented as a component in polymers to produce flame-retardant plastics,[1426] and simple hexa(alkylamine)cobalt (III) complexes have been examined as new photoinitiators for deep-UV resist materials, via efficient photoredox decomposition which releases free amine to initiate crosslinking.[594] Some other, and by no means exhaustive, examples of developing technological applications are presented below.

Inorganic crystal engineering employing self-assembly processes promises to lead to the future development of planned solids which may have application as molecular-scale devices such as molecular wires. A recent example is $[Co^{II}_2(4,4'\text{-bpy})_3(NO_3)_4]_\infty$ in solids where the pseudo-octahedral metal provides an appropriate junction in "molecular ladder" structures.[1427] Other mixed organic–inorganic composite materials have been developed relying on the differing stereochemistries around two metal centers; for example $Co(bpy)Mo_3O_{10}$ has chains of edge-sharing Mo-based polyhedra where octahedral CoN_2O_4 units link these to form a two-dimensional covalent network.[1428]

Molecular magnets are a rapidly expanding field, where some Co compounds are finding a role.[1429] A series of $Co^{II}_2(OH)_3X$ compounds, where X is an exchangeable organic radical anion produce new metal–radical magnets which feature stacks of Co^{II} hydroxide layers interlayered with organic radicals. The imino-nitroxide radical (**273**) is an example that produces a successful system.



(**273**)

Other molecular magnets have been based on polycyano metal complexes. For example, the Prussian Blue analog $Co^{II}_3[Fe^{III}(CN)_6]_2 \cdot nH_2O$, which is prepared by substitution of hexacyanoferrate(III) into the $Co^{2+}{}_{aq}$ coordination sphere, is a species with a significant photomagnetic effect.[1430] A stable Co^{III}–NC–Fe^{II} pair arises via internal electron transfer. Solids with intermediate stoichiometries can be formed, such as $Rb_{1.8}Co_4[Fe(CN)_6]_{3.3} \cdot 13H_2O$. Further, polynuclear species such as $[Cr^{III}(CN)_3[(CN)Co^{II}L]_3]^{3+}$ where L is a pentaamine ligand, have been prepared and magnetic properties examined. Yet another family of magnetic materials are clusters based on polyoxometallates.[1431] Mixed-metal clusters such as $[Co^{II}_4(H_2O)_2(PW_9O_{34})_2]^{10-}$ and $[WCo^{II}_3(H_2O)(Co^{II}W_9O_{34}]_2]^{12-}$ have been examined, with ferro- and anti-ferromagnetism found in selected examples.

Diagnostic processes in medicine and pharmaceutical applications featuring metal complexes are expanding rapidly.[1432,1433] Of radionuclides of possible value, ^{55}Co complexes have potential for use in positron emission tomography since they undergo β^+ decay with a suitable half-life and energy. To date, however, it has been studied very little. Likewise, cobalt-based drugs are not a high-profile area of development currently, although there are some advances. Cobalt(III) complexes of macrocyclic polyimines have been patented for use as anti-inflammatory agents, due to their superoxide coordination chemistry which is, in effect, antioxidant behavior.[1434]

New solid state materials are a major research target. Most, such as Co nanocrystals, Co nitride films, and zirconia-supported cobalt, do not involve formal coordination compounds, and are outside the scope of this review. One interesting application of a Co compound, however, has appeared recently. Carbon nanoflasks, a new form of fullerene-type carbon, use $Co(CO)_3NO$ as the source of carbon in their synthesis.[1435] Upon decomposition, the $Co(CO)_3NO$ yields fcc Co particles, of from several nanometers to hundreds of nm in size. The cobalt-filled carbon flasks have tube-neck widths of from 50 nm to over 100 nm, whereas the body of the flask ranges from 100 nm to 500 nm, but can reach over 1 mm. Following acid treatment of the sample to remove cobalt, opened and empty carbon flasks are readily obtained. Sol–gel glasses, based on metal oxides/hydroxides that dissolve in ROH partially forming alkoxides[1436] do not feature Co as a metal, partly at least because the Co^{III} aqua ion is a powerful oxidant which oxidizes water, and partly because appropriate oligomerization does not apply. However, a major blue pigment as a colorant is the cubic spinel $CoAl_2O_4$, where the cobalt(II) lies in a CoO_4 tetrahedron. In another example, a transparent glass with Mg–Al spinel nanocrystallites doped with tetrahedrally coordinated Co^{2+} operates as a new saturable absorber Q switch for Er:glass lasers.[1437] A novel route to Co_3O_4 thin films on glass substrates has been established by firing at 500 °C the tributylammonium salt of $[Co(EDTA)]^-$ adhered to the glass.[1438] Pillared clays are an area of growing interest, and Co compounds find application in this field; for example, montmorillonites expanded with small amounts of $[Co^{III}_3(H_2NCH_2CH_2O)_6](ClO_4)_3$ and an aluminum compound (final Si:Co ratio from 38 to 128) and calcinated by firing at 500 °C in air proved to be significantly enhanced in thermal stability.[1439]

6.1.5 CONCLUSION

At the beginning of the twenty-first century, it is still true to say that Co remains a firm favorite for traditional Werner-type coordination chemistry, with perhaps less emphasis on organometallic chemistry than is the case with other transition metals. However, Co coordination compounds are appearing in greater diversity than before and ever more examples of polynuclear systems are appearing. Although the basic synthetic routes established for decades have remained as entry points into Co chemistry, the application of these routes with a wider range of potential ligands and the development of more "boutique" reagents has expanded the possible and encompassed some of the (at least previously considered) impossible. Statements such as "no examples of this type exist" and "it is very unlikely that these can be prepared" simply spur research; it seems that often examples do not exist or are thought unlikely simply because effort has not been spent sufficiently, rather than there being an inherent chemical barrier. After all, that simple polyamine coordination complexes including cobalt(III)–carbon bonds could be easily prepared was not anticipated several decades ago, yet examples continue to expand. Given the growth in chemistry since the early 1980s generally, it is dangerous to predict the paths Co chemistry will travel in the next few decades. However, it takes no great foresight to suggest, broadly, that biologically relevant and advanced materials chemistry of Co will grow more significant in this time. Retrospection and prognostication aside, Co remains today an enticing and rewarding center for coordination chemistry.

6.1.6 REFERENCES

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