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SYNTHESIS AND PROPERTIES OF CO^{II}-COMPLEXES WITH TRIDENTATE DINEGATIVE LIGANDS

door

G.H.L. Nefkens

SYNTHESIS AND PROPERTIES OF Co^{II}-COMPLEXES WITH TRIDENTATE DINEGATIVE LIGANDS

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Aan Lulu, Mireille en Janine

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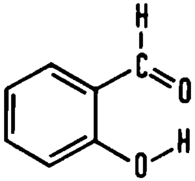
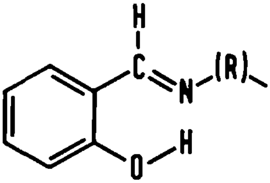
CHAPTER I

INTRODUCTION

Salicylaldehyde (I) has rarely been used as a ligand for the preparation of complexes[1,2]. The corresponding imino derivatives, the Schiff bases (II) however have been used as starting



(I)

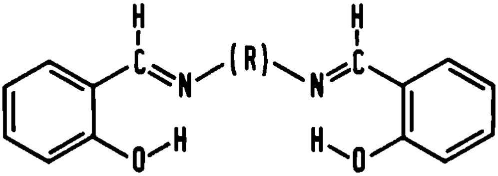


(II)

products for a large number of complexes with transition metals[3]. When (II) is derived from a monoamine, deprotonation of the phenol group yields a bidentate mononegative ligand; in order to obtain a stable complex, two of such groups are required for co-ordination. Such complexes are known with zinc[4], cobalt[4], nickel[5] and copper[6].

A second type of related ligands is obtained when (I) is condensed with an amine containing two primary amino groups, *e.g.* ethylenediamine or phenylenediamine. In this way a dinegative tetradentate ligand (III) is formed. Complexes of (III) are also known with a variety of transition and non transition metals. The Co^{II}-complex of (III) is of particular interest because it binds oxygen in a reversible way[7,8].

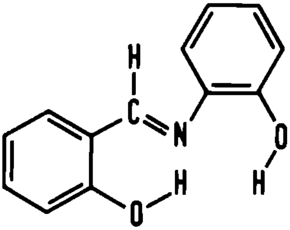
A third group of ligands derived from salicylaldehyde can be obtained by condensation of (I) with an amine containing an-



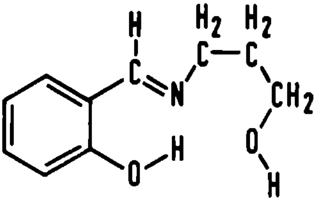
(III)

other ionizable group, *e.g.* *o*-aminophenol or 3-aminopropanol-1. This results in a tridentate divalent ligand, *e.g.* (IV) or (V). Corresponding complexes with a metal to ligand ratio of 1:1 have only been described with copper[9,10].

It was the aim of the present study to investigate if such tridentate ligands could also be co-ordinated with other metals.



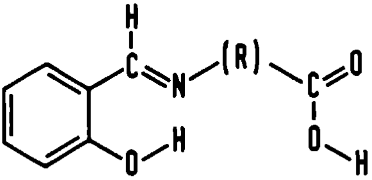
(IV)



(V)

Cobalt^{II} was chosen as the central atom in the hope to obtain compounds, which should be apt to study the interesting phenomenon of oxygenation because no complexes are available at the moment to undertake a systematic study of this problem.

In CHAPTER II the preparation of a large variety of Co^{II}-complexes with tridentate divalent ligands has been described. As ligands we used not only (IV) or (V), but also Schiff bases derived from (I) and α- or β-amino acids (VI), and hydrogenation products of (V) and (VI) as formulated in (VII) and (VIII). Isolated from aqueous solutions these complexes differ in the number of co-ordinating water molecules per Co^{II} atom, dependent on the ligand used. With several ligands more than one complex, differing in the amount of co-ordination water, could be isolated. From most complexes water could be completely eliminated yielding solvent-free complexes.



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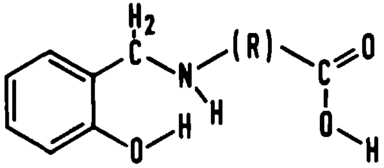

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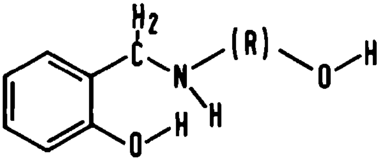

(VIII)

Because the fluctuating composition of this large group of compounds points to differences in their structures we have investigated if some insight into the structure of individual compounds could be obtained without X-ray analysis which could not be used because suitable crystals were lacking. The presence of different co-ordinating groups in ligands (IV) to (VIII) made it possible by the application of I.R. to investigate which of them participate in the co-ordination, and sometimes to what degree they participate.

In order to get an idea about molecular structures such measurements were extended with other physical measurements, *e.g.* magnetic susceptibility, solubility, and U.V. It is clear that the conclusions are not always completely definite, but the tentative structure-models, suggested for most compounds give a rather consistent picture of the way in which variations in the ligand structure are related to variations in the structure of corresponding complexes.

In CHAPTER III a similar study has been described on a large number of amine complexes of Co^{II} and tridentate ligands. They could be obtained from the aquo complexes in an equally rich variety, and appeared to be interesting because most of them, indeed, are sensitive to oxygen.

A selected group of amine complexes has been used for a study of this phenomenon of oxygenation (CHAPTER IV). From previous investigations it is known that oxygenation of Co^{II}-complexes, if possible, is generally accompanied by oxidation of the metal atom. Within relatively small series of strongly related compounds attempts have been made to correlate the ease of oxygenation with parameters related to the electron density on the central metal atom (*e.g.* the number of donating nitrogen-ligands, or the oxidation potential). We thought it possible that also crystal-field parameters (Dq and B) might be used as indices for this electron density, because they are dependent on charge delocalization and charge-transfer.

Our amine complexes seemed to be very useful to study this possibility. They appeared to be stable in the solid state, so that their composition could be determined exactly, and most of them had octahedral co-ordination and were of the high-spin type so that Dq and B-values could be calculated.

Until now stable Co-complexes with bound molecular oxygen have only been obtained in one case[11]. Oxygenation of these complexes is often followed by ligand oxidation, apparent from further uptake of oxygen[12,13]. As far as we know the latter process has never been thoroughly investigated. With two of our complexes the oxidation products were isolated and their compositions were determined.

Finally, a summary of the results has been given.

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CHAPTER II

SYNTHESIS, SPECTRA AND PROPOSED STRUCTURES OF SOME AQUO, DMSO AND SOLVENT-FREE COMPLEXES OF Co^{II} WITH TRIDENTATE LIGANDS

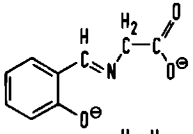
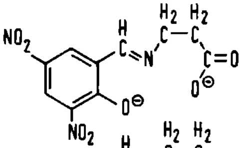
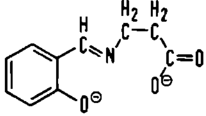
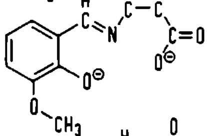
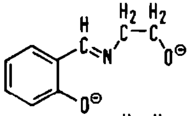
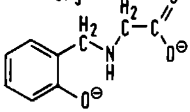
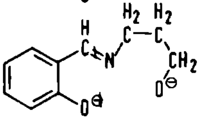
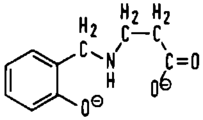
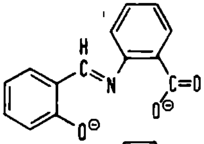
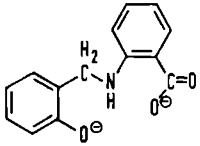
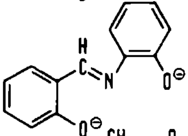
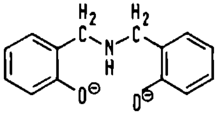
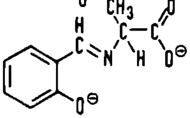
INTRODUCTION

Tridentate ligands have often been used[1-6] to form complexes with Co^{II}. Generally the Co^{II} to ligand ratio appears to be 1:2 in these compounds. As yet 1:1 complexes of Co^{II} with tridentate ligands have only been reported with non-deprotonating species as ligands[7-12]. In this CHAPTER a series of Co^{II}-complexes with anionic tridentate ligands and a 1:1 ratio for Co to ligand are described for the first time. In all of them the ligand is a Schiff's base (Table I). They were prepared from salicylaldehyde or a substituted salicylaldehyde and an amino acid or an amino alcohol. Hydrogenation of a number of these bases gave also suitable ligands (L-10-13). In some cases, ligands 2,5,6,10,11,12 and 13, the products were isolated; often they were used in complex formation without previous isolation.

The high Co to ligand ratio found for these ligands originates from the presence of the phenolic oxygen atom in the compounds. This atom has a lone pair in a π-orbital parallel with the π-orbitals of the aromatic system. It has been shown in many cases that this orbital can participate in co-ordination, giving dimeric or even polymeric products[13].

TABLE I

Anions of the ligands from which 1:1 complexes have been prepared

Ligand	Abbreviation	Ligand	Abbreviation
	L-1		L-8
	L-2		L-9
	L-3		L-10
	L-4		L-11
	L-5		L-12
	L-6		L-13
	L-7		

EXPERIMENTAL

Synthesis of the ligands

N-(2-hydroxybenzylidene)- β- alanine, $C_{10}H_{11}NO_3$, (M=193.20), (abbreviation: H_2L-2). This was obtained by heating 0.1 mole of finely powdered β-alanine and 0.12 moles of salicylaldehyde in methanol until the amino acid had been dissolved. After cooling H_2L-2 was isolated as a yellow crystalline compound.

Calculated: C, 62.0; H, 5.69; N, 7.24%
Found: C, 61.8; H, 5.7 ; N, 7.3 %

N-(2-hydroxybenzylidene)-anthranilic acid, $C_{14}H_{11}NO_3$, (M= 241.24), (abbreviation: H_2L-5). It was prepared by dissolution of anthranilic acid in hot methanol followed by rapid addition of an equimolecular amount of salicylaldehyde. After standing for several hours at 0°, H_2L-5 crystallized in excellent yield. Reported[14] m.p. 196°. Found m.p. 198°.

N-(2-hydroxybenzylidene)-2-aminophenol, $C_{13}H_{11}NO_2$, (M=213.23), (abbreviation: H_2L-6). It was prepared in the same way as H_2L-5, starting from σ-aminophenol.
Reported[15] m.p. 185°. Found m.p. 184°.

Calculated: C, 73.2; H, 5.2; N, 6.57%
Found: C, 73.3; H, 5.3; N, 6.45%

N-(2-hydroxybenzyl)-glycine, $C_9H_{11}NO_3$, (M=181.19), (abbreviation: H_2L-10). 0.1 Mole of glycine and 0.1 mole of NaOH were dissolved in water. After the addition of 0.1 mole of salicylaldehyde the solution was shaken until it became homogeneous. The solution was hydrogenated at 4-5 atm.; 300 mg. of 10% Pd/C were used as catalyst. The hydrogenation ceased after the uptake of 0.1 mole of hydrogen. The catalyst was filtered off and the filtrate acidified with acetic acid. The product cry-

stallized after it had been cooled for several hours at approximately 0°. Recrystallization could be achieved from acetic acid-water (1:1).
The overall yield was 70%; m.p. 215-217°.

Calculated: C, 59.66; H, 6.12; N, 7.73%
Found: C, 59.5 ; H, 6.1 ; N, 7.4 %

<u>N-(2-hydroxybenzyl)- β-alanine</u>, $C_{10}H_{13}NO_3(H_2O)$, (M=213.23), (abbreviation: H_2L-11). This was prepared in the same way as the related compound H_2L-10, but starting with β-alanine. The yield was 60% and the product could be crystallized from water, m.p. 168°. The analysis showed that the product obtained was a hydrate.

Calculated: C, 56.8; H, 7.12; N, 6.63%
Found: C, 56.5; H, 7.1 ; N, 6.65%

<u>N-(2-hydroxybenzyl)anthranilic acid</u>, $C_{14}H_{13}NO_3$, (M=243.26), (abbreviation: H_2L-12). This compound was prepared from ligand H_2L-5 by reduction in methanol; 200 mg. of 10% Pd/C for 0.1 mole of H_2L-5 were used. After filtration of the catalyst the solvent was evaporated *in vacuo* leaving an oily substance which solidified on trituration with petroleum ether (60-80°). The compound was purified by crystallization from toluene, m.p. 176°.

Calculated: C, 69.2; H, 5.35; N, 5.76%
Found: C, 68.9; H, 5.4 ; N, 5.7 %

<u>N-bis(2-hydroxybenzyl)-amine</u>, $C_{14}H_{15}NO_2$, (M=229.27), (abbreviation: H_2L-13). 0.2 Moles of salicylaldehyde were dissolved in 75 ml of methanol. Concentrated ammonia (10 ml) was added giving a yellow precipitate which readily dissolved after vigorous shaking. After the addition of 100 mg. of 10% Pd/C the solution was hydrogenated in a Parr bottle. When the hydrogenation was complete a white precipitate had been formed. The

solution was heated to dissolve the compound. The catalyst was filtered off, and the filtrate partly evaporated and cooled. H_2L-13 was obtained by filtration. The yield was 50%, m.p. 165°.

Calculated: C, 73.4; H, 6.55; N, 6.10%

Found: C, 73.6; H, 6.7 ; N, 6.0 %

Synthesis of the aquo complexes

$\underline{Co(L\text{-}1)(H_2O)_2}$, $Co(C_9H_7NO_3)(H_2O)_2$, (M=272.11).

Method a. 0.1 Mole of glycine and 0.2 moles of NaOH were dissolved in 200 ml. of water and 0.1 mole of salicylaldehyde was added. The solution was slowly added to a boiling solution of 0.1 mole of $Co(NO_3)_2.6H_2O$ in water. During the addition the boiling solution was vigorously stirred. After completion of the addition the solution was kept at 95° for about 15 min. The precipitate formed was filtered off, washed well with water and dried.

Calculated: C, 39.7; H, 4.04; N, 5.15%

Found: C, 39.4; H, 3.8 ; N, 4.9 %

Method b. This method results in a purer product but in lower yield than in the previous procedure. 0.1 Mole of glycine, 0.2 moles of KOH and 0.1 mole of salicylaldehyde were dissolved in 200 ml. of methanol-water (1:1). The solution was quickly added to a solution of 0.1 mole of $CoCl_2.6H_2O$ in 200 ml. of methanol-water (1:1) at room temperature. A homogeneous solution was obtained, which yielded a crystalline product after standing at room temperature for a few hours. It was filtered and washed with methanol-water (1:1). The yield did not exceed 40%.

$\underline{Co(L\text{-}2)(H_2O)}$, $Co(C_{10}H_9NO_3)(H_2O)$, (M=268.13). 0.1 Mole of β-alanine and 0.2 moles of KOH were dissolved in 100 ml. of water. Then 0.1 mole of salicylaldehyde was added at room temperature under vigorous shaking. The homogeneous solution was slowly added to a solution of 0.1 mole of $Co(NO_3)_2$ in water at room temperature. A slightly coloured precipitate was formed. During the stirring of the solution for 0.5 hour it was slowly heated on a water bath at 80-100° for 1 hour. During the heating of the precipitate its colour changed from beige to pink. After cooling the precipitate was filtered off, washed well with water and this was removed by washing with acetone.

Calculated: C, 44.8; H, 4.1; N, 5.21%
Found: C, 44.8; H, 4.1; N, 5.2 %

$\underline{Co(L\text{-}6)H_2O}$, $Co(C_{13}H_9NO_2)(H_2O)$, (M=288.16). The preparation of this was analogous to that of $Co(L\text{-}2)H_2O$ using *o*-aminophenol instead of β-alanine.

Calculated: C, 54.0; H, 3.81; N, 4.81%
Found: C, 53.5; H, 3.7 ; N, 4.6 %

$\underline{Co(L\text{-}13)H_2O}$, $Co(C_{14}H_{13}NO_2)(H_2O)$, (M=304.20). It was obtained in a similar way as $Co(L\text{-}2)(H_2O)$.

Calculated: C, 55.31; H, 4.94; N, 4.61%
Found: C, 55.8 ; H, 5.0 ; N, 4.7 %

$\underline{Co(L\text{-}12)(H_2O)_2}$, $Co(C_{14}H_{11}NO_3)(H_2O)_2$, (M=336.19). This complex was prepared from $H_2L\text{-}12$ and $Co(NO_3)_2.6H_2O$ and isolated by a similar procedure as $Co(L\text{-}2)(H_2O)$.

Calculated: C, 50.00; H, 4.46; N, 4.17%
Found: C, 50.8 ; H, 4.3 ; N, 4.3 %

$\underline{Co(L\text{-}7)(H_2O)_2}$, $Co(C_{10}H_9NO_3)(H_2O)_2$, (M=286.14). This was prepared in excellent yield by way of a procedure as mentioned in <u>method a</u> for the synthesis of $Co(L\text{-}1)(H_2O)_2$.

Calculated: C, 42.00; H, 4.55; N, 4.90%
Found: C, 42.1 ; H, 4.6 ; N, 4.9 %

<u>Attempted synthesis of $Co(L\text{-}5)(H_2O)_x$</u>. 0.1 Mole of $H_2L\text{-}5$ and 0.2

moles of KOH were dissolved in water. The solution was slowly added to a solution of $Co(NO_3)_2.6H_2O$ in water. The solution was kept at room temperature during the addition and stirred for at least 30 min. A yellow precipitate, which was formed, was filtered off and washed well with water. The product however appeared to be very impure. It was purified by the following procedure. The dried precipitate was suspended in an excess of dimethylsulphoxide and the mixture was stirred for several hours at room temperature. A viscous red-brown coloured solution was obtained after filtration through a thick layer of HYFLO supercel. When water was slowly added to the clear filtrate with vigorous stirring, a yellow precipitate crystallized, however in low yield. Analysis showed that the sample was free of nitrogen; its composition appeared to be $Co(C_7H_5O_2)_2(H_2O)_2$ indicating that a salicylaldehyde complex had been formed. (The failure to get an aquo complex with L-5 may be due to hydrolysis of the -C=N- bond with participation of the neighbouring carboxylate residue). The aquo complex could easily be converted into the water-free complex by dissolving the aquo complex in dimethylformamide and heating the solution to the boiling point. A red complex was isolated by filtration $Co(C_7H_5O_2)_2$(M=301.16).

Calculated: C, 55.8; H, 3.33%

Found: C, 55.4; H, 3.45%

<u>$Co(L\text{-}8)(H_2O)_4$</u>, $Co(C_{10}H_7N_3O_7)(H_2O)_4$, (M=412.17). 0.02 Moles of β-alanine, 0.02 moles of 3,5-dinitrosalicylaldehyde[15,16] and 0.04 moles of KOH were dissolved in 100 ml. of water at room temperature. This solution was treated with $Co(NO_3)_2.6H_2O$ in the same way as in the synthesis of $Co(L\text{-}2)(H_2O)$.

The complex could be purified by dissolution in dimethylacetamide and precipitation with ethyl acetate at room temperature.

Calculated: C, 29.10; H, 3.64; N, 10.20%

Found: C, 30.3 ; H, 3.7 ; N, 10.2 %

$\underline{Co(L\text{-}8)H_2O}$, $Co(C_{10}H_7N_3O_7)(H_2O)$, (M=358.12). This was prepared from the previous compound by boiling it in nitrobenzene for a few minutes. After standing overnight the crystalline complex was isolated by filtration.

Calculated: C, 33.54; H, 2.53; N, 11.7%

Found: C, 33.9 ; H, 2.4 ; N, 11.9%

$\underline{Co(L\text{-}9)H_2O}$, $Co(C_{11}H_{11}NO_4)(H_2O)$, (M=298.15). This was prepared from β-alanine and 3-methoxysalicylaldehyde (FLUKA A.G.) according to a procedure (Method a) as used in the synthesis of $Co(L\text{-}1)(H_2O)_2$.

Calculated: C, 44.3; H, 4.36; N, 4.69%

Found: C, 44.7; H, 4.4 ; N, 4.7 %

$\underline{Co(L\text{-}1)(H_2O)_{0.5}}$, $Co(C_9H_7NO_3)(H_2O)_{0.5}$, (M=245.09). $Co(L\text{-}1)(H_2O)_2$ was dissolved in DMF and the solution was heated to the boiling point. After about 15 min. the precipitate formed was filtered off and washed with DMF and ethyl acetate.

Calculated: C, 44.1; H, 3.26; N, 5.70%

Found: C, 44.1; H, 3.2 ; N, 5.7 %

A solvent-free compound, Co(L-1), could be isolated upon prolonged boiling in DMSO.

$\underline{Co(L\text{-}2)(H_2O)_{0.5}}$, $Co(C_{10}H_9NO_3)(H_2O)_{0.5}$, (M=259.12). This was prepared from $Co(L\text{-}2)(H_2O)$ by dissolving the aquo complex in DMSO at room temperature. The solution was filtered. On gentle heating of the filtrate a crystalline compound began to precipitate. It was washed with DMSO and then with ethyl acetate.

Calculated: C, 46.4; H, 3.86; N, 5.4%

Found: C, 46.3; H, 3.8 ; N, 5.3%

Synthesis of DMSO containing complexes

Co(L-4)(DMSO), $Co(C_{10}H_{11}NO_2)(C_2H_6SO)$, (M=314.26). 0.1 Mole of salicylaldehyde and 0.1 mole of 3-aminopropanol-1 (FLUKA A.G.) were dissolved in methanol. Then 0.2 moles of KOH were added. The homogeneous solution was slowly added to a solution of Co^{II} acetate in methanol. The apparently impure precipitate was filtered and washed with a small amount of methanol. The product was air-dried and dissolved in DMSO at room temperature. After filtration the solution was heated to the boiling point. After cooling a crystalline product could be isolated by filtration. The product was well soluble in hot DMSO.

Calculated: C, 45.8; H, 5.40; N, 4.46; S, 10.2%
Found: C, 45.7; H, 5.3 ; N, 4.5 ; S, 9.9%

$Co(L\text{-}6)(DMSO)_{0.5}$, $Co(C_{13}H_9NO_2)(C_2H_6SO)_{0.5}$, (M=309.21). Co(L-6)($H_2O$) was dissolved in DMSO at room temperature and filtered if necessary. Then the solution was heated to its boiling point and after cooling the crystalline compound was isolated.

Calculated: C, 54.4; H, 3.89; N, 4.5; S, 5.18%
Found: C, 54.1; H, 3.7 ; N, 4.3; S, 5.3 %

$Co(L\text{-}13)(DMSO)_{0.5}$, $Co(C_{14}H_{13}NO_2)(C_2H_6SO)_{0.5}$, (M=325.26). This was prepared in the same way as $Co(L\text{-}6)(DMSO)_{0.5}$ starting with Co(L-13)H_2O.

Calculated: C, 55.50; H, 4.94; N, 4.32%
Found: C, 55.5 ; H, 5.0 ; N, 4.3 %

$Co(L\text{-}9)(DMSO)_{0.5}$, $Co(C_{11}H_{11}NO_4)(C_2H_6SO)_{0.5}$, (M=319.20). This was prepared in a similar way as the previous compound.

Calculated: C, 45.10; H, 4.38; N, 4.38%
Found: C, 44.7 ; H, 4.0 ; N, 4.5 %

Co(L-1)(H_2O,DMSO)$_{0.5}$, Co($C_9H_7NO_3$)(H_2O)$_{0.5}$(C_2H_6SO)$_{0.5}$, (M=284.16). Co(L-1)(H_2O)$_2$ was dissolved at room temperature in DMSO. The solution was quickly filtered, and the product crystallized upon standing.

Calculated:	C, 44.2; H, 3.87; N, 4.95%
Found:	C, 43.4; H, 4.0 ; N, 5.2 %

Synthesis of solvent-free complexes

Co(L-5), Co($C_{14}H_9NO_3$), (M=298.16). 0.1 Mole of H_2L-5 was dissolved in 50 ml. of DMF. To this solution 1.2 g of KOH were added. It dissolved when the solution was heated and stirred. The solvent was removed by distillation *in vacuo*. By repeated addition and evaporation of small amounts of DMF water formed during the reaction was completely removed. A similar procedure was used with a solution of Co(NO_3)$_2$(H_2O)$_6$ in DMF. The solution of the ligand was then slowly added to the solution of the cobalt salt. After stirring for about 30 min. the solvent was completely removed *in vacuo*. A brown crystalline compound was obtained in this manner. It was treated with ethyl acetate. The product was filtered and air-dried. The compound was dissolved in DMSO by stirring for at least 1 hour. It was filtered through HYFLO and the filtrate was slowly heated to the boiling point. Soon a crystalline compound began to precipitate. After cooling the compound was filtered and washed with DMSO and ethyl acetate.

Calculated:	C, 56.30; H, 3.02; N, 4.70%
Found:	C, 55.7 ; H, 3.2 ; N, 4.5 %

Co(L-3), Co($C_9H_9NO_2$), (M=222.10). 0.1 Mole of ethanolamine, 0.1 mole of salicylaldehyde and 0.2 moles of KOH were dissolved in water. The solution was slowly added to a solution of 0.1 mole of $Co(NO_3)_2.6H_2O$ in water at room temperature. A yellow-brown precipitate was formed which was isolated by filtration. The impure product was purified by dissolution in DMSO at room temperature, filtration of the solution, and slow heating of the filtrate to its boiling point. The substance precipitated in big needles upon cooling.

Calculated: C, 48.70; H, 4.06; N, 6.30%
Found: C, 49.0 ; H, 4.1 ; N, 6.35%

Co(L-10), $Co(C_9H_9NO_3)$, (M=238.10). This was prepared in the same way as Co(L-3).

Calculated: C, 45.40; H, 3.78; N, 5.89%
Found: C, 45.0 ; H, 3.9 ; N, 5.7 %

Co(L-11), $Co(C_{10}H_{11}NO_3)$, (M=252.13). 0.2 Moles of H_2L-11 and 0.4 moles of KOH were dissolved in ethanol. This solution was slowly added to a solution of Co^{II}-acetate in ethanol. A blue crystalline precipitate was formed which was filtered off. Analysis indicated that it consisted of Co(L-11), two moles of water and half a mole of ethanol. When a solution of the compound in DMSO was heated to the boiling point pure Co(L-11) was obtained upon cooling.

Calculated: C, 47.70; H, 4.37; N, 5.55%
Found: C, 47.0 ; H, 4.4 ; N, 5.45%

Co(L-12), $Co(C_{14}H_{11}NO_3)$, (M=300.17). This was prepared by dissolving Co(L-12)$(H_2O)_2$ in dimethylacetamide. The solution was filtered and heated to the boiling point. The complex crystallized and the solution being hot was filtered as it redissolved when the solution was cooled.

Calculated: C, 56.00; H, 3.68; N, 4.67%
Found: C, 55.1 ; H, 3.85; N, 4.4 %

Some remarks on the presence of co-ordinated solvent molecules in the complexes

Before the complexes were subjected to elemental analysis, they were placed in a vacuum dessiccator at 10 mm. for at least 24 hours. The presence of co-ordinated water or DMSO was tested by I.R. spectroscopy. In a few cases the presence of DMSO was also confirmed by sulphur analysis.

As is apparent from the analytical data given above, the number of water molecules in the complexes described varies considerably with the nature of the organic ligand. The relatively large number of water molecules (4) in one of the aquo complexes of Co(L-8) may be due to the presence of strong polar groups (NO_2) in the ligand. Furthermore, the amount of co-ordinated water seems, however, not only dependent on the structure of the ligand but also on the method of preparation. With several ligands more than one aquo complex can be isolated, but not all of these have been described or used in further investigations.

Magnetic measurements

The magnetic moments of most complexes were measured in the solid state at various field strengths. The results have been shown in TABLE II. It is clear that all compounds belong to the high-spin type. Definite structural assignments cannot be made from these results, although it has been reported[17] that magnetic susceptibility measurements on Co^{II}-complexes were used as an aid in stereochemical diagnosis, *e.g.* to distinguish octahedral from tetrahedral configuration.

In one case, Co(L-2)(H_2O) the temperature dependence of the magnetic susceptibility was measured, see Fig.1.

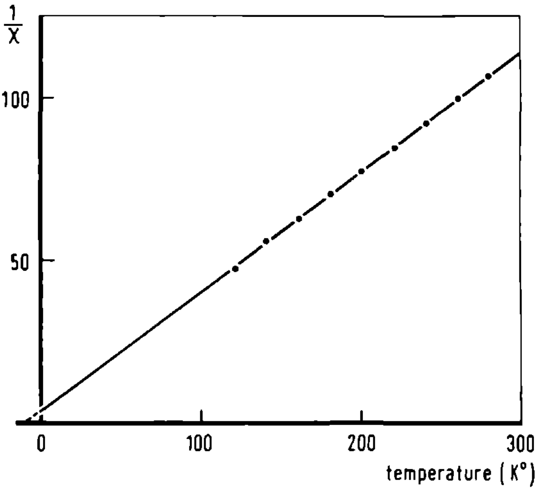


Fig.1. Temperature-dependence of the magnetic susceptibility of Co(L-2)(H_2O). A Θ value of -10^o was found.

TABLE II

Magnetic moment (in B.M.) of some aquo, DMSO and solvent-free complexes.

Compound	$\mu_{eff.}$	Compound	$\mu_{eff.}$
Co(L-1)$(H_2O)_2$	4.62	Co(L-2)(H_2O)	4.61
Co(L-13)(H_2O)	4.70	Co(L-12)$(H_2O)_2$	4.59
Co(L-8)$(H_2O)_4$	4.48	Co(L-8)(H_2O)	4.90
Co(L-4)(DMSO)	4.65	Co(L-6)$(DMSO)_{0.5}$	4.58
Co(L-9)$(DMSO)_{0.5}$	4.56	Co(L-5)	4.49
Co(L-10)	4.62	Co(L-11)	4.82
Co(L-6)(H_2O)	4.58	Co(L-13)$(DMSO)_{0.5}$	4.60
Co(L-7)$(H_2O)_2$	4.66	Co(L-3)	4.77
Co(L-9)(H_2O)	4.57	Co(L-12)	4.84

This was undertaken to see whether the Co-Co distance should be so close that a spin pairing could be observed in the measured temperature range. This appeared not to be the case.

The electronic spectra

The electronic spectra of the compounds synthesized were measured in the solid state using a Beckman DK 2a or a Unicam SP 700 spectrophotometer provided with reflexion units. Several spectra have been reproduced in Figs.2-4. Although the complexes have strongly varying compositions *e.g.* $Co(L)(H_2O)_{0.5}$,$Co(L)(H_2O)_1$,$Co(L)(H_2O)_2$,$Co(L)(H_2O)_4$ etc., their spectra can be rather well subdivided into two distinct groups. Spectra of the first group (Type I) have two (sometimes three) maxima and a small peak or shoulder at a frequency about two times that of the first maximum. The first maximum is found in the infra-red region at 8000-10000 $cm.^{-1}$. The other peak(s) appears in the 18000-20000 $cm.^{-1}$ region. Type I-spectra resemble very close those of regular octahedral Co^{II}-complexes reported in the literature[18]. The other spectra, Type II, exhibit three to five absorption maxima, different from those in Type I spectra. They are quite similar to spectra of compounds, which have been shown to be five co-ordinated Co^{II}-complexes by X-ray analysis.

The octahedral complexes

All typical characteristics of octahedral spectra are observed in the spectral curves of only two aquo complexes, $Co(L\text{-}8)(H_2O)_4$ and $Co(L\text{-}7)(H_2O)_2$. Their spectra do not only show the characteristic absorption maxima at 8000-10000 $cm.^{-1}$ and 18000-20000 $cm.^{-1}$ but also a small absorption peak or shoulder at approxi-

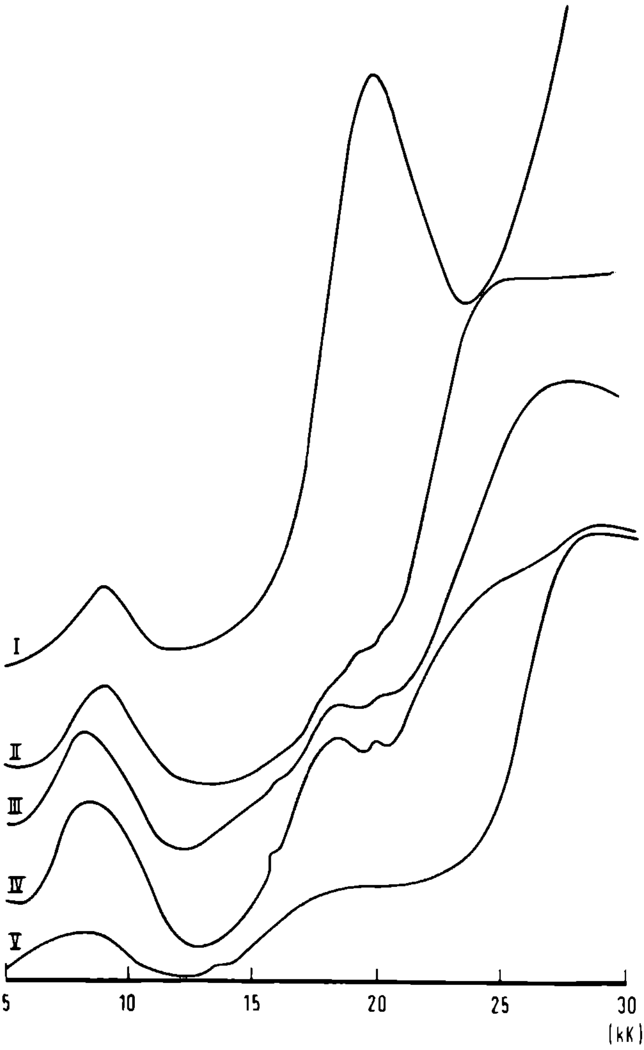


Fig.2. Reflectance spectra of some octahedral Co^{II}-complexes. I, $Co(C_2H_5N)_6.(NO_3)_2$, an authentic six co-ordination; II, $Co(L\text{-}8)(H_2O)_4$; III, $Co(L\text{-}1)(H_2O)_2$; IV, $Co(L\text{-}7)(H_2O)_2$; V, $Co(L\text{-}12)(H_2O)_2$.

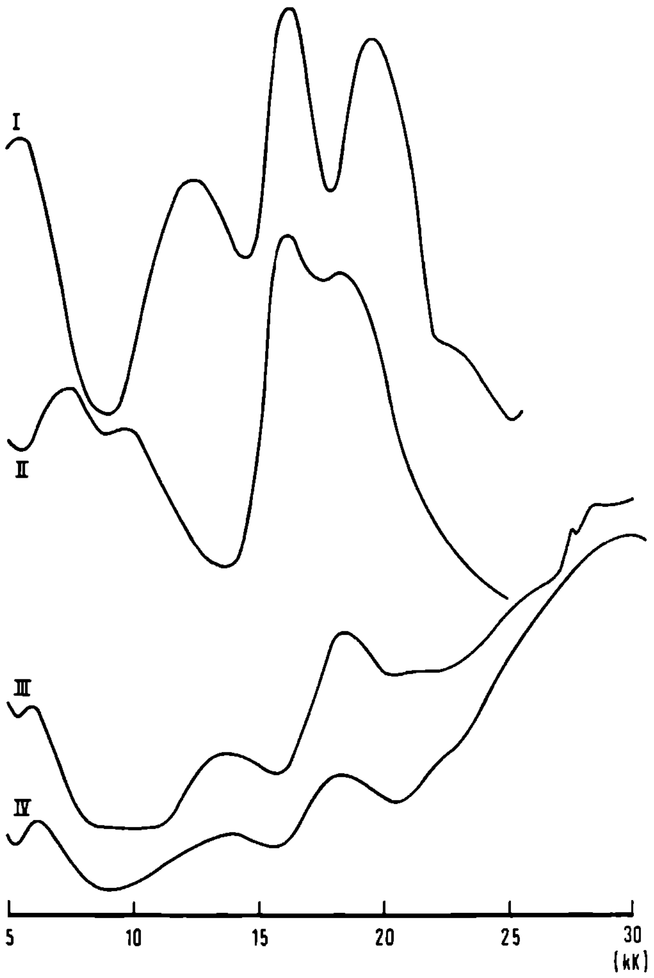


Fig.3. Reflectance spectra of five-co-ordinated complexes with four absorption maxima. I, $\mathrm{Co\{N[-CH_2-CH_2-N(CH_3)_2]_3Br\}Br}$; II, $\mathrm{Co\{O[-CH_2-CH_2-N(CH_3)_2]_2Cl_2\}}$; III, Co(L-13)($H_2O$); IV,Co(L-2)($H_2O$). I and II are authentic spectra of five co-ordinated $\mathrm{Co^{II}}$-complexes.

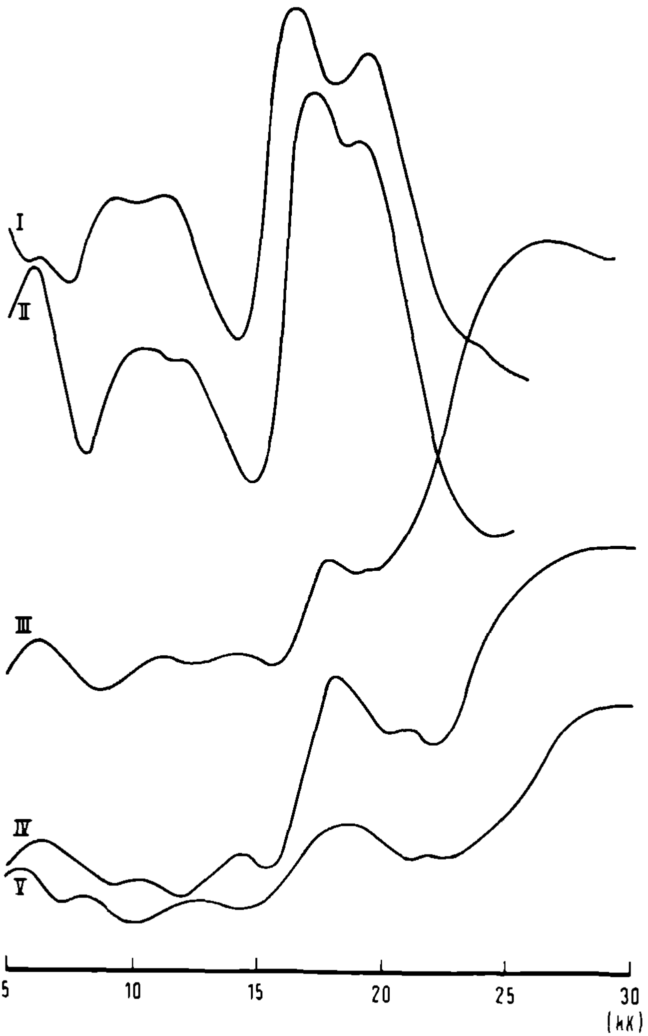


Fig.4. Reflectance spectra of five co-ordinated complexes with five absorption maxima. I, $Co\{CH_3\text{-}N\text{-}[\text{-}CH_2\text{-}CH_2\text{-}N(CH_3)_2]_2Cl_2\}$; II, $Co\{O[\text{-}CH_2\text{-}CH_2\text{-}N(CH_3)_2]_2(CNS)_2\}$; III, Co(L-5); IV,Co(L-12); V, $Co(L\text{-}13)(DMSO)_{0.5}$. I and II are authentic spectra of five co-ordinated Co^{II}-complexes.

mately twice the frequency of the first maximum.
Lever and Ogden[19] reported that for a regular octahedron such a shoulder should not exceed 2.2 times the frequency of the first absorption maximum. The low extinction coefficient of this small peak or shoulder is due to the fact that it belongs to a two electron transition [$^4A_{2g}(F) \leftarrow {}^4T_{1g}(F)$].

The absorption band in the visible region is commonly split into a number of components. The main peak is assigned to a $^4T_{1g}(P) \leftarrow {}^4T_{1g}(F)$ transition. Weakliem[20] and Ferguson *et al.*[21], who investigated the spectra of a number of octahedral Co^{II}-complexes at low temperature, reported that the peaks or shoulders near the main peak in the visible spectrum are due to a quartet-doublet transition. The peak at the high energy side of the main peak was attributed to the $^2T_{1g}(^2P) \leftarrow {}^4T_{1g}(F)$ transition and the peak at the low energy side to the $^2T_{2g}(G) \leftarrow {}^4T_{1g}(F)$ transition. Lever and Ogden[19] who investigated bis (acetato) bis (pyridine) Co^{II}- complexes with D_{4h} symmetry found two absorption maxima owing the splitting of the $^4T_{1g}$ level in $^4A_{2g}$ and ^4E_g components. Ferguson[22] studied the octahedral polymeric form of $Co(pyridine)_2Cl_2$, which has D_{2h} symmetry. Its principal visible absorption band had been split into three components which were assigned to transitions of the $^4T_{1g}(F)$ level to the $^4B_{1g}$, $^4B_{2g}$, and $^4B_{3g}$ levels. These results also show that in our complexes low symmetry splitting or quartet-doublet transitions may be responsible for the presence of more absorption maxima in the visible region. For several other aquo complexes described in this CHAPTER an octahedral structure seems probable, though less certain than for $Co(L\text{-}8)(H_2O)_4$ and $Co(L\text{-}7)(H_2O)_2$, in view of their spectral curves. In TABLE III the absorption maxima and crystal field parameters of these complexes are recorded.

TABLE III

Absorption maxima (in cm.$^{-1}$) and crystal field parameters[x] (in cm.$^{-1}$) of octahedral like complexes

Complex	${}^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$ ν_1	${}^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$ ν_2	${}^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$ ν_3	ν_2/ν_1	10Dq	B	β	$\frac{Dq}{B}$
Co(L-8)$(H_2O)_4$	8850	16100	18700	1.82	9670	763	0.78	1.26
			19700					
Co(L-8)(H_2O)	8700		18400		9500	716	0.73	1.32
Co(L-7)$(H_2O)_2$	8300	15750	18500	1.89	9060	806	0.82	1.12
			20100					
Co(L-1)$(H_2O)_2$	8200		18500		8950	812	0.83	1.10
			20100					
Co(L-12)$(H_2O)_2$	8000	13500	18500	1.68	8740	717	0.73	1.22
			17000					
Co(L-1)$(H_2O)_{0.5}$ $(DMSO)_{0.5}$	8300		18600		9070	777	0.79	1.17

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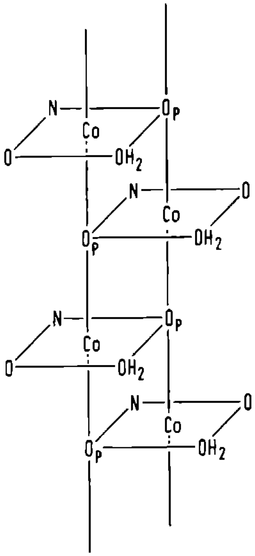
[x] These values were calculated according to the method of Reedijk *et al.* (see CHAPTER III).

The structure of the octahedral complexes

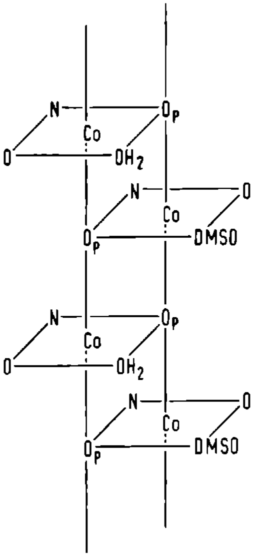
Only the Co(L-8)$(H_2O)_4$ and Co(L-12)$(H_2O)_2$ complexes listed in TABLE III are easily soluble in DMF,DMSO, methanol or acetone. The aquo complexes Co(L-1)$(H_2O)_2$ and Co(L-7)$(H_2O)_2$ do not dissolve in methanol or acetone but are soluble in DMF or DMSO; they lose their co-ordinating water molecules, as shown by elemental analysis, and change into five co-ordination, as appeared from spectroscopic data. The other compounds are completely insoluble in these organic solvents, even at higher temperatures. However, some of them dissolve in co-ordinating bases such as pyridine or piperidine, giving amine complexes (see CHAPTER III). The insolubility of octahedral complexes suggests that their structures are polymeric, whereas the soluble ones have low molecular weights. Owing to the restricted solubility of a part of the complexes and the high tendency to lose solvent molecules of the other ones it was not possible, however, to determine their molecular weights.

All ligands listed in TABLE I have three co-ordinating groups, a phenolic oxygen, a nitrogen atom as part of an imino group or secondary amine and an oxygen atom originating from a carboxylic acid, an alcohol or a phenol. For simplification the co-ordinating atoms will be abbreviated as follows; O_p, denotes the phenolic oxygen which is present in every ligand; N, the central nitrogen atom; O, the other oxygen atom of the ligand.

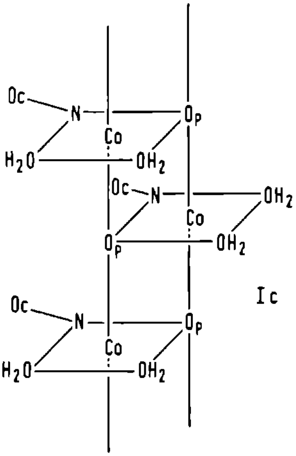
In Fig.5 several possible structures for octahedral aquo complexes of Co^{II} have been represented. Structures Ia-c have polymeric structures in which the cobalt/water ratio 1 and 2 respectively; in Ib half of the water molecules of Ia have been replaced by DMSO, as is found in Co(L-1)$(H_2O)_{0.5}(DMSO)_{0.5}$. Structures IIa,b and c concern low molecular structures with



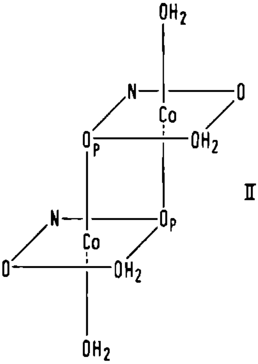
Ia



Ib

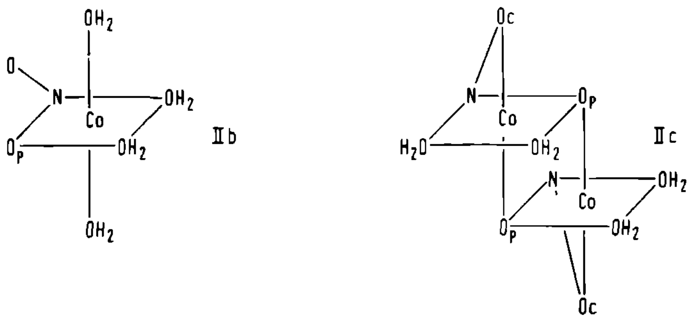


Ic



IIa

Fig.5.Proposed structures for low-and high-molecular octahedral Co^{II}-complexes.



IIb

IIc

Fig.5 (continuation). Proposed structures for low-molecular octahedral Co^{II} complexes.

2 or 4 molecules of water per Co atom.
In a following section, it will be shown that combination of the solubility and U.V. data with I.R. data present possibilities to suggest a probable structure for all octahedral complexes mentioned in TABLE III.

The five co-ordinated complexes

It is interesting that all complexes showing second-type spectra contain, in general, less solvent molecules per atom of Co. Their molecular formulae, Co(L), $Co(L)(B)_{0.5}$ or Co(L)(B) indicate the presence of no, a half or one molecule of solvent (B=water or DMSO), never two or four as found in some octahedral compounds. Their spectra are very similar to known five co-ordinated Co^{II}- complexes. A small number of such compounds have been reported in the literature, *e.g.* the mono 2,2',2''-terpyridine cobalt halide complexes[23], bis (N-methylsalicylaldiminato) Co^{II}, (see ref.24), and triamine Co dihalide complexes[25,26]. The bis (N-methylsalicylaldiminato)Co^{II} is very interesting as it resembles our complexes herein that a related group is present in the organic ligand. The structure of the compound has been established by X-ray analysis. The metal atom exists in a trigonal-bipyramidal structure, and the complex is a dimer in the solid state; phenolic oxygens are bridging atoms between two molecules of the monomeric species. For this reason it is supposed that the phenolic oxygens may also be in bridging positions in the compounds.

The spectra of the five co-ordinated Co^{II}-complexes reported by Ciampolini[27] can be divided into two groups. The first group exhibits four, the second one five absorption maxima. This differentiation has also been found in our spectra.

In Fig.3 a number of spectra have been collected which are closely related to those of five co-ordinated complexes with four absorption maxima. Fig.4 shows a number of spectra with five absorption maxima. The rather good resemblance of our spectra with those of Ciampolini, suggests a five co-ordination for all our second-type compounds. Lower symmetry such as a pseudo tetrahedral configuration having C_{2v} symmetry leads to still more absorption maxima in the visible and infra-red regions as reported by Lever and Nelson[28] and must therefore be rejected. Several possible structures, in accordance with the varying compositions found, have been represented in Fig.7.

Ciampolini, Nardi and Speroni[27] made a crystal field approach of high spin Co^{II} in a trigonal-bipyramidal environment having D_{3h} symmetry. Their results are shown in Fig.6. A tentative assignment of the absorption bands of five-co-ordinated complexes can be made as follows. In accordance with the diagram the four maxima may be assigned to transitions from the ground state to the states $^4E''(F)$, $^4E'(F)$, $^4A_2'(P)$, and $^4E''(P)$ respectively. Ciampolini stated that an additional absorption peak might result from splitting the $^4E'(F)$ level into two components, when

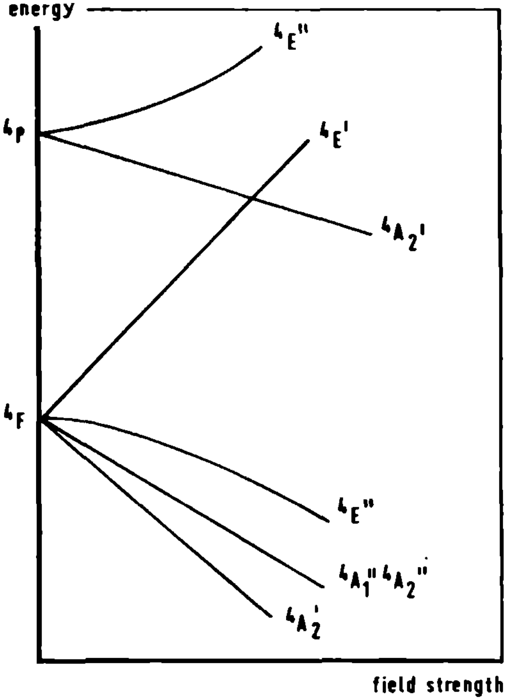
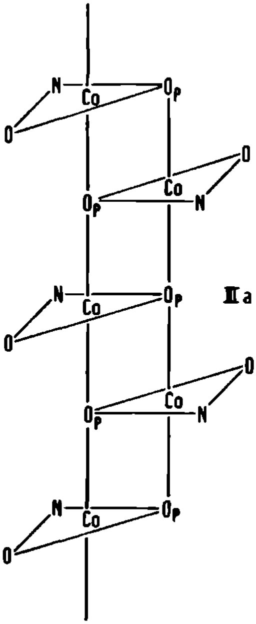
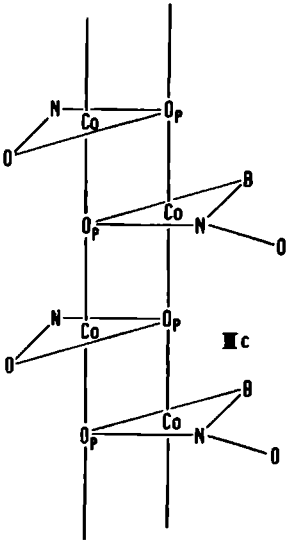


Fig.6. Crystal field approach of high-spin Co^{II} in trigonal-bipyramidal environment, as calculated by Ciampolini *et al.*[27].

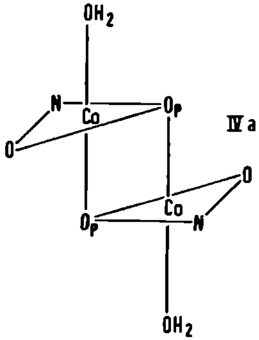
the symmetry of the complex decreases. Ciampolini determined the structure of several compounds by X-ray analysis and found that the presence of an additional absorption maximum is not indicative of a structural change (alteration of co-ordination). We suppose that for our compounds there may be another cause for the presence of an extra absorption maximum. This maximum is situated in the 8000-11000 cm.$^{-1}$ region. The position of the peak coincides with the frequency region for the first absorption maximum of Co^{II} in an octahedral configuration (see Fig.2). Thus it is possible that in some of our compounds octahedral as well as trigonal-bipyramidal units are present.



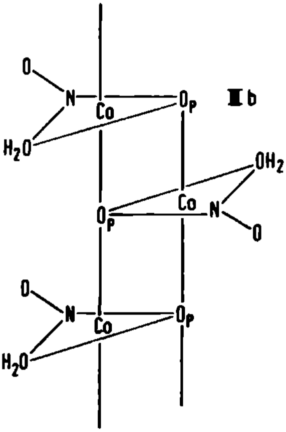
IIa



IIIc



IVa



IIIb

Fig.7. Proposed structures for high- and low-molecular five-coordinated Co^{II}-complexes.

The structures of the five-co-ordinated complexes

Some of the five-co-ordinated compounds are soluble in aprotic polar solvents at room temperature. A few are even soluble in alcohol or in acetone, in particular the compounds containing 1 molecule of solvent per Co *e.g.* Co(L-6)(H_2O),Co(L-4)DMSO, Co(L-13)(H_2O). It is apparent that these complexes are low-molecular compounds; a suggested structure is IVa in Fig.7. The other complexes having no or less than one mole of water or DMSO are practically insoluble in common solvents.

Higher polymeric structures are shown in IIIa,b,c. The structures IIIa,b and c are different in composition because the number of solvent molecules is zero, one or a half, respectively. The solvent molecules (in IIIb and c) have replaced one of the co-ordinating groups (O) of the tridentate ligand in IIIa. As will be shown later on, I.R. data supports this supposition.

The infra-red spectra

I.R.spectra have been measured to investigate which of the functional groups in the organic ligand participate really in co-ordination. First a discussion on the position of relevant I.R. peaks of free and co-ordinated groups will be given.
The I.R. spectra of the complexes were all recorded with a Perkin-Elmer infra-red spectrofotometer Model 257, using KBr discs. Groups investigated are the carboxyl group, the central nitrogen function (amine or imine), and the aliphatic or aromatic oxygen groups. Often the peaks of the -C=N- and C=O (COO^-) stretching vibrations are difficult to assign with certainty because they can be masked by the presence of two rather strong absorption maxima from the -C=C- in plane vibrations of the

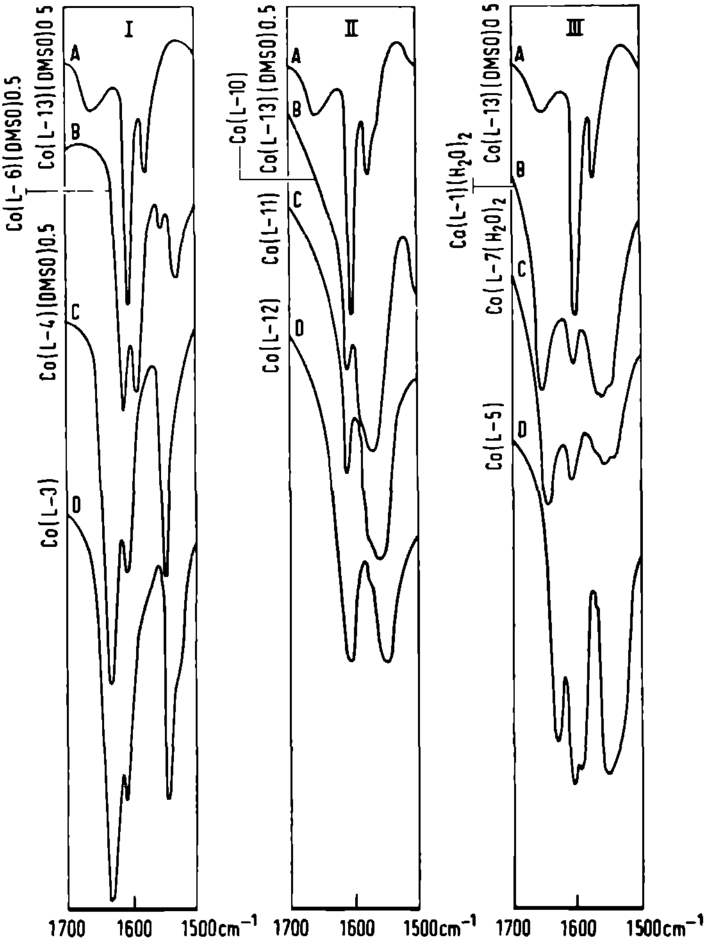


Fig.8. Partial I.R. spectra of complexes with different functional groups. Compound A in all three columns is the same complex. Compounds B,C and D have additional functional group(s). In column I, a -C=N- group; in column II, a carboxyl group; in column III, both a -C=N- and a carboxyl group.

phenyl nucleus, in the 1700-1500 cm.$^{-1}$ region[29,30]. We attempted to localize these peaks by comparing them with a number of complexes lacking the -C=N- group, the carboxyl group, or both. The 1500-1700 cm.$^{-1}$ region of the spectra of relevant compounds have been reproduced in Fig.8. The identical curves on the first row are of the same compound, Co(L-13)(DMSO)$_{0.5}$, in which both -C=N- and C=O are absent. The other spectra in the first column concern complexes which contain a -C=N- group, but no carboxyl group. A strong additional peak is observed on the high-energy side of the sharp -C=C- absorption peak of the phenyl nucleus for the compounds Co(L-4)(DMSO) and Co(L-3). For Co(L-6) (DMSO)$_{0.5}$ the -C=N- absorption appears at a lower frequency. This can be ascribed to the fact that in this complex the -C=N- group is conjugated with two phenyl rings; it has been reported that extension of conjugation shifts the -C=N- vibration to lower frequency[31].

The localization of the -C=N- bond of Schiff base-metal complexes has also been carried out by Dudek and Dudek[32] using N-labelled complexes. They also found the -C=N- absorption at about 1640 cm.$^{-1}$.

Compounds B,C and D of the second column of Fig.8, which contain a carboxyl group but no -C=N- function, exhibit a broad and strong absorption at the low-energy side of the -C=C- peak. This absorption originates clearly from the presence of a carboxyl group in these compounds, and represents the asymmetric carboxyl stretching vibration. Its position will be shifted to higher energy as the metal oxygen bond becomes stronger.

The second absorption peak of the carboxyl group, the symmetrical stretching vibration, was localized in our complexes at about 1400 cm.$^{-1}$, as expected. The influence of co-ordination on the position of this peak is only small; its frequency is somewhat shifted to lower energy as the metal oxygen bond becomes stronger.

Other important groups surrounding the central atom are the phenolic oxygen and the saturated amine groups, Cross[30] reported that the C_{ar}-O stretching vibration of phenols gives a very strong peak at about 1200 cm.$^{-1}$. All compounds investigated gave at least one strong absorption between 1250 and 1300 cm.$^{-1}$. The presence of more than one peak may be ascribed to the fact that these complexes contained more than one C_{ar}-O bond.

The position of the vibration of phenyl-oxygen, participating in co-ordination has been discussed by Sinn[13]. There may be some doubt as to whether the phenyl-oxygen vibration was indeed present in the 1200-1300 cm.$^{-1}$ region, as was noted no change was observed when the oxygen atom was two or three co-ordinated. A large shift to higher energy (at about 1530 cm.$^{-1}$) was reported when a phenolic oxygen was present as the bridging atom. It is assumed that this absorption is related more to a phenyl ring, than to a phenyl oxygen vibration. It is clear that ^{18}O experiments should be carried out to ascertain whether the absorption in the 1530 cm.$^{-1}$ region arises from C_{ar}-O stretching vibration or not.

We did not analyse $-CH_2-N=$ vibrations, because they are of low intensity and their positions are uncertain.

Of course all aquo complexes show up as a strong and broad peak between 3600 and 3300 cm.$^{-1}$, due to water present in the compounds. All I.R. data, which might be relevant in the determination of composition or structure of our complexes, have been collected in TABLE IV.

Because the asymmetric carboxyl vibration shifts to higher energy and the symmetric carboxyl vibration to lower energy as the Co-oxygen bond becomes stronger, the distance Δ between

TABLE IV

I.R. data of some aquo, DMSO and solvent-free Co^{II}-complexes

Complex	Carboxylate vibrations			-C=N-	-O-H	C_{ar}-O	N-H
	Asymmetric	Symmetric	$^{x}\Delta$				
Co(L-1)$(H_2O)_2$	1540	1410	130	1658	3280 3380	1300	-
Co(L-1)$(H_2O,DMSO)_{0.5}$	1630	1410	220	1640	3400	1298	-
Co(L-1)$(H_2O)_{0.5}$	1572 1610	1410	162 200	1645	3410	1290 1285	-
Co(L-2)(H_2O)	1550	1390	160	1644	3300	1300	-
Co(L-8)$(H_2O)_4$	1575	1415	161	1648	3400	1320	-
Co(L-4)(DMSO)	-	-	-	1632	-	1325	-
Co(L-10)	1570	1410	160	-	-	1276	3276
Co(L-11)	1560	1420	140	-	-	1280 1288	3280
Co(L-7)$(H_2O)_2$	1558	1398	160	1645	3300	1304	-
Co(L-5)	1552	1412	140	1630	-	1309	-
Co(L-6)(H_2O)	-	-	-	1612	3490	1300^{xx}	-
Co(L-6)$(DMSO)_{0.5}$	-	-	-	1608	-	1245 1252 1280 1292	-
Co(L-12)	1550	1410	140	-	-	1280	3180
Co(L-13)(H_2O)	-	-	-	-	3602	1264 1274	3280
Co(L-13)$(DMSO)_{0.5}$	-	-	-	-	-	1257 1280 1287 1306	3295
Co(L-9)(H_2O)	1550	1415	135	1630	3380	1250	-
Co(L-8)(H_2O)	1570	-	-	1650	3420	-	-

$^{x}\Delta$, is the difference in cm.$^{-1}$ between the two carboxyl vibrations.

^{xx} This peak was a very broad one.

these peaks may be a measure of the interaction between the carboxylate residue and Co^{II}. Δ-values are tabulated in the fourth column. It is remarkable that high values (strong bonding) are seldom found even in water-free complexes in which co-ordination of the carboxyl group is quite certain. Low Δ-values found for solvent-free complexes may be due to a weak Co-carboxyl oxygen bond caused by a relatively large distance ,*e.g.* in complexes having a ligand with a β-amino group or by a less effective position of the carboxyl group in the ligands with a secondary amine group (L-10,L-11,L-12).

Often the exact localization of the C_{ar}-O vibration is difficult, because in several spectra more than one absorption is found between 1250 and 1300 $cm.^{-1}$. In the complexes with L-6 and L-13 this may be ascribed to the presence of two phenolic residues, which should then have unequal positions in the compound.

As expected the C_{ar}-O peak of $Co(L\text{-}8)(H_2O)_4$ is at relatively high energy (1320 $cm.^{-1}$) owing to the presence of nitro substituents, whereas that of $Co(L\text{-}9)(H_2O)$ is at relatively low energy because the ligand contains a CH_3O- substituent.

For some compounds far infra-red spectra have also been determined. The results appear to be of little value for structural determination. Therefore the data have not been mentioned here.

Tentative assignment of structures to the complexes investigated

In Figs.5 and 7 several structural models, low-molecular and polymeric ones, have been represented, which have octahedral or five-co-ordinated configurations as supposed for the first and second type of compounds respectively. The various models have

TABLE V

Solubility and structure assignment of the complexes

Complex	Solubility in				Assigned structure
	$CHCl_3$	CH_3OH	DMF	DMSO	
Co(L-1)$(H_2O)_2$	insoluble	insoluble	soluble[x]	soluble[x]	Ic
Co(L-1)$(H_2O)_{0.5}$	insoluble	insoluble	insoluble[x]	insoluble	IIIc
Co(L-1)$(H_2O)_{0.5}$ $(DMSO)_{0.5}$	insoluble	insoluble	insoluble	insoluble	Ib
Co(L-2)(H_2O)	insoluble	insoluble	soluble[x]	soluble[x]	IIIb
Co(L-3)	insoluble	insoluble	insoluble	insoluble	IIIa
Co(L-4)(DMSO)	insoluble	slightly soluble	soluble[xx]	soluble[xx]	IVa
Co(L-5)	insoluble	insoluble	insoluble	insoluble	IIIa
Co(L-6)(H_2O)	insoluble	soluble	soluble	soluble	IVa
Co(L-6)$(DMSO)_{0.5}$	insoluble	insoluble	insoluble	insoluble	- [xxx]
Co(L-7)$(H_2O)_2$	insoluble	insoluble	soluble[x]	soluble[x]	Ic
Co(L-8)$(H_2O)_4$	insoluble	soluble	soluble	soluble	IIb
Co(L-8)(H_2O)	insoluble	insoluble	insoluble	insoluble	Ia
Co(L-9)(H_2O)	insoluble	insoluble	soluble[x]	soluble[x]	IIIb
Co(L-10)	insoluble	insoluble	insoluble	insoluble	IIIa
Co(L-11)	insoluble	insoluble	insoluble	insoluble	IIIa
Co(L-12)$(H_2O)_2$	insoluble	soluble	soluble[xxxx]	soluble[xxxx]	IIc
Co(L-12)	insoluble	insoluble	soluble	soluble	IIIa
Co(L-13)(H_2O)	insoluble	soluble	soluble[x]	soluble[x]	IVa
Co(L-13)$(DMSO)_{0.5}$	insoluble	insoluble	insoluble	insoluble	IIIc

[x] The solubility persists for a short time as upon standing a polymeric complex precipitated.

[xx] The solubility depends on the temperature.

[xxx] See text.

[xxxx] Dissolves very slowly at room temperature.

compositions in accordance with the varying compositions, which have been found by elemental analysis in both groups of complexes. Combined solubility, U.V. and I.R. data will now be used to suggest tentative structures for the complexes investigated.

In the polymeric model structures axial bonding *via* the phenolic oxygen has been proposed. This seems the only way to form solvent-free polymeric complexes with our ligands, containing a carboxyl group, because of bridging *via* co-ordination, normal to the carboxyl group, has not been reported[33]. A model with other types of co-ordination *via* the carboxyl group was difficult to be made. In the proposed model the bridging oxygen atom is bound to three metal atoms, an unusual pattern in co-ordination chemistry. A recent example which is somewhat comparable, has been reported[34]. For the aquo complexes and complexes containing a second alifatic or aromatic oxygen atom, bridging might also be achieved *via* the water molecule[35] or *via* the alifatic or aromatic oxygen[36].

Octahedral compounds

The monomeric compound. From those compounds, which were found to be octahedral from U.V. data, only one seems to be monomeric $Co(L-8)(H_2O)_4$. The compound is well soluble in polar solvents, from which it can be crystallized without loss of water. Our conclusion is that all the four water molecules have been co-ordinated. The co-ordination of one group of the tridentate ligand must then be free. The rather low Δ-value suggests, that the COO-residue does not participate in co-ordination; it is also possible that the carboxyl group is hydrogen bonded to a neighbouring water molecule, as reported for aquo compounds of amino acids[37]. The -C=N- absorption is shifted however, from

1700 cm.$^{-1}$ in the free ligand to 1658 cm.$^{-1}$ indicating co-ordination *via* the nitrogen atom. For these reasons structure IIb seems the most probable.

Dimeric compounds. A dimeric octahedral structure (IIa) may be possible for *e.g.* Co(L-1)$(H_2O)_2$, but as shown in TABLE V, this complex is insoluble in several solvents; therefore a more polymeric structure is suggested. The only complex for which a dimeric structure is suggested is Co(L-12)$(H_2O)_2$. The complex is the only one which is soluble in solvents of low polarity *e.g.* acetone, from which it can be crystallized without loss of water. It is probable that the structure of the ligand, which is not flat, prevents the formation of polymers. Thus structure IIc, seems the best choice and holds only for Co(L-12)$(H_2O)_2$.

The polymeric compounds. We have prepared three types of compounds to which a polymeric octahedral structure must be assigned. Their compositions are; Co(L)$(H_2O)_2$, Co(L)(H_2O) and Co(L)$(H_2O)_{0.5}(DMSO)_{0.5}$.

Typical examples of the first type are Co(L-1)$(H_2O)_2$ and Co(L-7)$(H_2O)_2$. These complexes exhibit a low Δ-value, and a polymeric octahedron can only be constructed when the carboxyl residue does not co-ordinate. Structure Ic seems the best choice.

An example of the second type is Co(L-8)(H_2O) which is best represented by structure Ia. The I.R. data for this complex are incomplete as some important peaks are obscured by the presence of the strongly symmetrical nitro vibration peak.

The third type of polymeric octahedron which has been prepared with the ligand L-1, has a constitution which can be derived from structure Ia by replacing a part of the co-ordinating water by a molecule of DMSO. In this way structure Ib is obtained. When this complex was heated in DMSO for a longer time water was replaced further by DMSO and a complex Co(L-1)(DMSO) was obtained. After prolonged heating to the boiling point of DMSO even the solvent-free complex Co(L-1) could be isolated.

The five-co-ordinated complexes

The structure of Co(L-2)(H_2O), is represented best by structure IIIb because of its low Δ-value and low solubility.

A real polymeric structure with a Co to solvent ratio of 2 is presented by structure IIIc, in which the ligand participates sometimes with two and sometimes with three functional

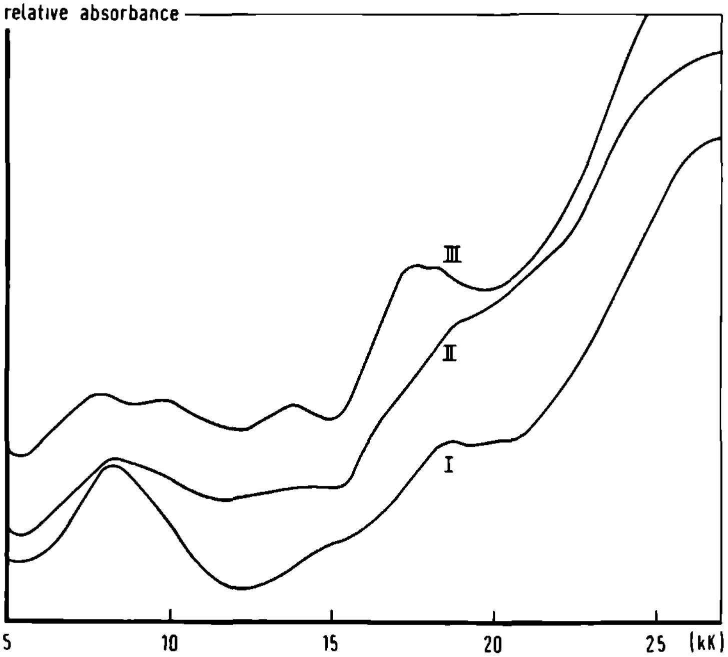


Fig. 9. Reflection spectra of Co(L-1) complexes containing a decreasing amount of solvent. I, Co(L-1)$(H_2O)_2$. II, Co(L-1) $(DMSO,H_2O)_{0.5}$; III, Co(L-1).

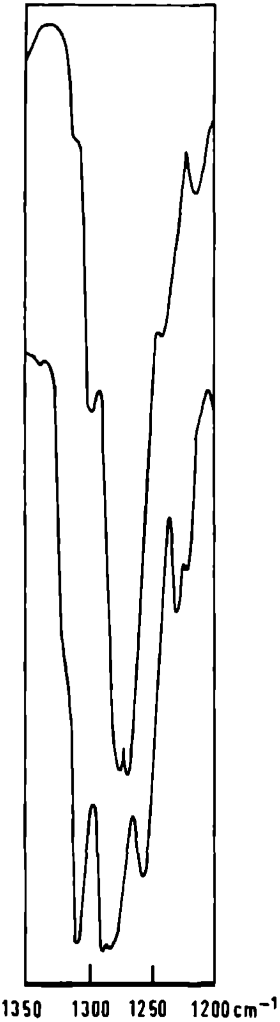


Fig.10 Phenyl-oxygen absorption peaks of: upper curve, Co(L-13)(H_2O);lower curve, Co(L-13)$(DMSO)_{0.5}$.

groups in the co-ordination. An assignment of such a structure to a compound like Co(L-13)$(DMSO)_{0.5}$ could be supported by I.R. spectroscopy in the region of the C_{ar}-O absorptions. In the spectrum of Co(L-13)(H_2O), which will have structure IVa, it is expected that two close, but well separated C_{ar}-O absorptions are found (see Fig. 10, upper curve). Co(L-13)$(DMSO)_{0.5}$ exhibits four peaks in this region (see Fig.10, lower curve) suggesting that not all phenolic groups are in equivalent positions. The number of peaks is consistent with the proposed structure (structure IIIc). A similar observation has been made for the Co(L-6) complexes which behave spectroscopically in the same way. Co(L-6)(H_2O) should have structure IVa. It is difficult to assign structure IIIc to the Co(L-6)$(DMSO)_{0.5}$ complex on stereochemical grounds; in that case an intermolecular co-ordination seems possible *via* a lone pair on the phenolic oxygen. The structure of the polymeric five co-ordinated compounds with formula Co(L) is best represented by structure IIIa.

Although a great number of structures have been constructed, as is shown in Figs.5 and 7, they are all very closely related. Starting with structure IIb practically all other complexes can be derived by omitting one or more functional groups. In some cases the electronic spectra suggest the presence of some traces of mixed complexes as can be seen in Fig.9. $Co(L{-}1)(H_2O)_2$ having structure Ic shows a very regular octahedral spectrum. The related compound $Co(L{-}1)(H_2O,DMSO)_{0.5}$ has a spectrum tending to that of a five co-ordinating character. As can be seen from its structure Ib this might be due to loss of DMSO molecules leaving part of Co in five co-ordination. The complex Co(L-1) with the suggested structure IIIa has only five-co-ordination as is shown by its spectrum.

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CHAPTER III

Co^{II}-COMPLEXES WITH TRIDENTATE LIGANDS AND AMINES

Co^{II}complexes with tridentate ligands can be isolated as aquo complexes as is described in the preceding chapter. With amines as ligands also stable, crystalline products can be formed. Such amine complexes have been obtained with nearly all ligands mentioned in CHAPTER II, TABLE I.

It appears that a wide variety of organic nitrogen bases can be used in the preparation of such compounds, but no complexes can be obtained if the amine function is sterically hindered, as in 2-substituted pyridines, quinoline and tertiary amines.

The number of amine residues in the individual complexes varies with the ligand and amine used, and sometimes with the method of preparation. With a chosen ligand and amine the highest number of amine molecules is co-ordinated, if the synthesis is performed by dissolution of an aquo complex or solvent-free complex in the amine, as the solvent.

Two types of amine complexes, those with Co(L-1) and Co(L-2), have been selected for a more detailed study. They will be discussed in this chapter. Furthermore, a few remarks will be made on some Co(L-8) amine complexes.

This choice has been made on the following grounds: First, the aquo complexes $Co(L\text{-}1)(H_2O)_2$, $Co(L\text{-}2)(H_2O)$ and $Co(L\text{-}8)(H_2O)_4$ can very easily be converted into amine complexes. The reason of this is that they are soluble and react quickly with amines at room temperature, giving rise to crystalline products in good yields. Complexes with other ligands are more difficult to obtain. Secondly, although the ligands L-1 and L-2 are closely related, their cobalt-pyridine complexes behave distinctly; the

(L-1) complex is sensitive towards oxygen, whereas the (L-2) complex is not. This aspect will be discussed in the following chapter.

Amines were chosen over an extended pK range (5.25 for pyridine to 11.27 for pyrrolidine) in order to investigate whether better donating amines could increase the capability of oxygen uptake.

Synthesis of the amine complexes

The amine complexes have been prepared by the following general procedure.

An aquo-complex [$Co(L-1)(H_2O)_2$, $Co(L-2)(H_2O)$ or $Co(L-8)(H_2O)_4$] was dissolved into an appropriate amine in a nitrogen atmosphere with vigorous stirring. Sometimes the mixture was heated or a solvent was used to get a homogeneous mixture. In most cases an amine complex crystallized rapidly from the solution; if not, crystallization was induced by cooling at 0^o or by the addition of an excess of ethyl acetate (with Co(L-1)(3,4-lutidine)). The products were isolated by filtration, washing with the amine or solvent used, and finally with ethyl acetate or petroleum ether (60^o-80^o).

Those complexes, which are sensitive to oxygen, were washed under nitrogen. The nitrogen must be free from carbon dioxide to prevent the formation of insoluble ammonium carbaminates (with the amines), which should contaminate the amine complex.

Experimental and analytical data are shown in TABLE I. Most showed slightly lowered amount of carbon (1-2%), but their nitrogen and hydrogen content were correct. Some of the complexes were prepared *via* an individual procedure, described below. Their analytical data are presented in TABLE I.

TABLE I

Analytical data of obtained amine complexes

			Analysis						
Complex	Formula	Mol.wt.	Calculated			Found			Reaction
			C	H	N	C	H	N	temp.
Co(L-1)(pyridine)$_3$	$Co(C_9H_7NO_3)(C_5H_5N)_3$	473.39	60.80	4.65	11.86	60.9	4.7	12.00	50°
Co(L-1)(pyridine)	$Co(C_9H_7NO_3)(C_5H_5N)$	315.19	53.3	3.81	8.9	52.9	3.9	8.8	-
Co(L-1)(piperidine)$_2$	$Co(C_9H_7NO_3)(C_5H_{11}N)_2$	406.38	56.2	7.16	10.3	55.2	7.4	9.7	50°
Co(L-1)(piperidine)	$Co(C_9H_7NO_3)(C_5H_{11}N)$	321.23	52.3	5.61	8.72	51.2	5.7	8.6	-
Co(L-1)(3,4-lutidine)	$Co(C_9H_7NO_3)(C_7H_9N)$	343.24	55.9	4.66	8.16	55.2	4.6	8.0	-
Co(L-1)(3,5-lutidine)$_3$	$Co(C_9H_7NO_3)(C_7H_9N)_3$	557.55	64.5	6.1	10.04	64.0	6.1	9.9	25°
Co(L-1)(bipyridyl)	$Co(C_9H_7NO_3)(C_{10}H_8N_2)$	392.27	58.0	3.85	10.72	56.5	3.9	10.8	-
Co(L-1)(aniline)	$Co(C_9H_7NO_3)(C_6H_7N)$	329.21	54.7	4.25	8.50	53.7	4.3	8.4	25°
Co(L-1)(pyrrolidine)$_2$	$Co(C_9H_7NO_3)(C_4H_9N)_2$	378.33	53.8	6.62	11.1	53.2	6.9	11.1	25°
Co(L-1)(cyclohexylamine)$_2$	$Co(C_9H_7NO_3)(C_6H_{13}N)_2$	434.44	57.9	7.62	9.6	57.0	7.7	9.3	25°
Co(L-1)(N-methylpiperazine)$_2$(H$_2$O)	$Co(C_9H_7NO_3)C_5H_{12}N_2)_2$ (H_2O)	454.43	50.2	7.27	15.4	50.00	7.4	15.4	25°
Co(L-1)(imidazole)$_2$	$Co(C_9H_7NO_3)(C_3H_4N_2)_2$	372.24	48.4	4.03	18.85	46.5	4.0	18.9	-
Co(L-2)(pyridine)$_2$	$Co(C_{10}H_9NO_3)(C_5H_5N)_2$	408.32	58.80	4.65	10.28	58.6	4.6	10.4	25°
Co(L-2)(bipyridyl)	$Co(C_{10}H_9NO_3)(C_{10}H_8N_2)$	406.30	59.12	4.22	10.01	57.5	4.1	10.0	-

Co(L-2)(4-picoline)$_2$	$Co(C_{10}H_9NO_3)(C_6H_7N)_2$	436.37	60.50	5.25	9.64	59.2	5.1	9.8	25°
Co(L-2)(3-picoline)$_2$	$Co(C_{10}H_9NO_3)(C_6H_7N)_2$	436.37	60.50	5.25	9.64	59.7	5.3	9.5	25°
Co(L-2)(morfoline)$_2$	$Co(C_{10}H_9NO_3)(C_4H_9NO)_2$	424.36	51.00	6.37	9.90	50.8	6.3	9.7	25°
Co(L-2)(4-methylpyrimidine)	$Co(C_{10}H_9NO_3)(C_5H_6N_2)$	344.23	52.3	4.37	12.1	52.0	4.3	11.7	25°
Co(L-2)(cyclohexylamine)$_2$	$Co(C_{10}H_9NO_3)(C_6H_{13}N)_2$	448.47	58.80	7.80	9.38	57.1	7.4	9.7	25°
Co(L-2)(piperidine)$_2$	$Co(C_{10}H_9NO_3)(C_5H_{11}N)_2$	420.41	57.10	7.47	10.00	56.0	7.0	9.8	25°
Co(L-2)(3,4-lutidine)	$Co(C_{10}H_9NO_3)(C_7H_9N)$	357.27	57.20	5.05	7.85	57.4	5.3	8.0	25°
Co(L-2)(3,5-lutidine)$_2$	$Co(C_{10}H_9NO_3)(C_7H_9N)_2$	464.42	62.00	5.8	9.05	60.6	6.1	8.8	25°
Co(L-2)(N-methylpiperazine)$_2$(H_2O)	$Co(C_{10}H_9NO_3)(C_5H_{12}N_2)_2(H_2O)$	468.46	51.3	7.48	14.94	51.2	7.7	15.1	25°
Co(L-2)(imidazole)$_2$	$Co(C_{10}H_9NO_3)(C_3H_4N_2)_2$	386.27	49.7	4.4	18.15	49.4	4.3	18.2	-
Co(L-2)(pyrrolidine)$_2$	$Co(C_{10}H_9NO_3)(C_4H_9N)_2$	392.36	55.00	6.88	10.70	53.9	7.2	10.7	25°
Co(L-8)(pyridine)$_3$	$Co(C_{10}H_7N_3O_7)(C_5H_5N)_3$	577.41	51.90	3.81	14.50	50.7	3.9	14.0	50°
Co(L-8)(pyridine)	$Co(C_{10}H_7N_3O_7)(C_5H_5N)$	419.21	43.00	2.87	13.36	43.6	3.0	13.2	-
Co(L-8)(bipyridyl)	$Co(C_{10}H_7N_3O_7)(C_{10}H_8N_2)$	496.29	48.4	3.03	14.10	48.9	3.1	14.1	-
Co(L-8)(imidazole)$_3$	$Co(C_{10}H_7N_3O_7)(C_3H_4N_2)_3$	544.34	43.8	3.50	23.2	43.1	3.6	23.7	-
Co(L-8)(benzylamine)$_2$	$Co(C_{10}H_7N_3O_7)(C_7N_9N)_2$	554.42	52.0	4.50	12.63	51.8	4.7	12.5	-

Co(L-1)(pyridine). The yellow tris-pyridine complex was dissolved in dimethylformamide with vigorous stirring in a nitrogen atmosphere. The complex dissolved readily and after a few minutes the monopyridine compound crystallized out. It was washed with dimethylformamide and ethyl acetate.

Co(L-1)(3,4-lutidine). Co(L-1)$(H_2O)_2$ was dissolved in a small volume of 3,4-lutidine under nitrogen. After it had stood at room temperature or after it had been cooled to approximately 0° for several days it did not crystallize. After addition of an excess of ethyl acetate, however, a crystalline complex containing one mole of the base was precipitated.

Co(L-8)(pyridine). Co(L-8)$(\text{pyridine})_3$ was dissolved in nitrobenzene and the solution was heated to its boiling point. After standing at room temperature for some days a mono-pyridine complex crystallized out. It was washed with nitrobenzene and ethyl acetate.

Co(L-1)(bipyridyl),Co(L-2)(bipyridyl) and Co(L-8)(bipyridyl). These compounds were prepared by dissolution of the corresponding aquo complexes in dimethylformamide, DMSO or nitrobenzene, respectively. Then an excess of bipyridyl was added to the solution. The solution was heated for several hours at approximately 100° and allowed to cool to room temperature. Only the bipyridyl complex of L-1 has to be prepared under nitrogen as it is sensitive to oxygen. The compounds were washed with the solvent used, then with ethyl acetate.

Co(L-1)$(\text{imidazole})_2$,Co(L-2)$(\text{imidazole})_2$ and Co(L-8)$(\text{imidazole})_3$. These complexes were prepared by a similar procedure as described for the bipyridyl complexes. Dimethylformamide was used as solvent. Except for Co(L-8)$(\text{imidazole})_3$ no excess of imidazole was used. All of these compounds are insensitive to oxygen. They were first washed with dimethylformamide, then with ethyl acetate.

Co(L-1)(piperidine). This was prepared from Co(L-1)(piperidine)$_2$ in a procedure analogous to that given for Co(L-1)(pyridine).

The electronic spectra in the solid state

Most of the amine complexes (see *TABLE I*) with 2 or 3 amine residues per atom of cobalt gave absorption spectra, resembling those of Fig.2 in CHAPTER II. They may be ascribed to an octahedral or nearly octahedral structure. There are only four exceptional complexes: Co(L-1)(imidazole)$_2$,Co(L-2)(morpholine)$_2$, Co(L-2)(cyclohexylamine)$_2$ and Co(L-2)(piperidine)$_2$. Values of the absorption maxima have been collected in TABLE II.

With the exception of the bipyridyl complexes of Co(L-1), Co(L-2) and Co(L-8), the imidazole complexes of Co(L-2) and Co(L-8) and the cyclohexylamine complex of Co(L-1) all octahedral complexes seem to be of low-molecular weight (dimeric or monomeric). The bipyridyl and imidazole complexes are nearly insoluble in polar (DMF,DMSO) as well as in non-polar solvents ($CHCl_3$,CH_2Cl_2).

The spectra of both Co(L-2)(morpholine)$_2$ and Co(L-2)(piperidine)$_2$ (see Fig.7) resemble those reported in Fig.4 of CHAPTER II. The spectra of Co(L-1)(imidazole)$_2$,Co(L-2)(cyclohexylamine)$_2$ and of the complexes with only one amine residue per molecule (*e.g.* Co(L-1)(pyridine),Co(L-1)(3,4-lutidine),Co(L-1)(aniline) and Co(L-8)(pyridine), show similar characteristics as found in Fig. 3 of CHAPTER II (see Fig.5). For these compounds five-co-ordination is probable. Most of them appear to be polymeric because they are insoluble in all solvents investigated. Only Co(L-2)(cyclohexylamine)$_2$ dissolves in polar as well as non-polar solvents, while Co(L-1)(aniline) dissolves well in polar solvents, but only slightly in an apolar solvent like CH_2Cl_2.

The electronic spectra in solution

Generally, the electronic spectra of amine complexes, dissolved in a non-co-ordinating solvent, differ from those measured in the solid state. Of all the compounds investigated not one had a similar spectrum in *e.g.* dichloromethane as found for the pure solid compound.

Although the spectra of various amine complexes of Co(L-2) are not equal in solution, they are very similar. This is illustrated in Fig.1 for five bis-amine complexes of Co(L-2), of

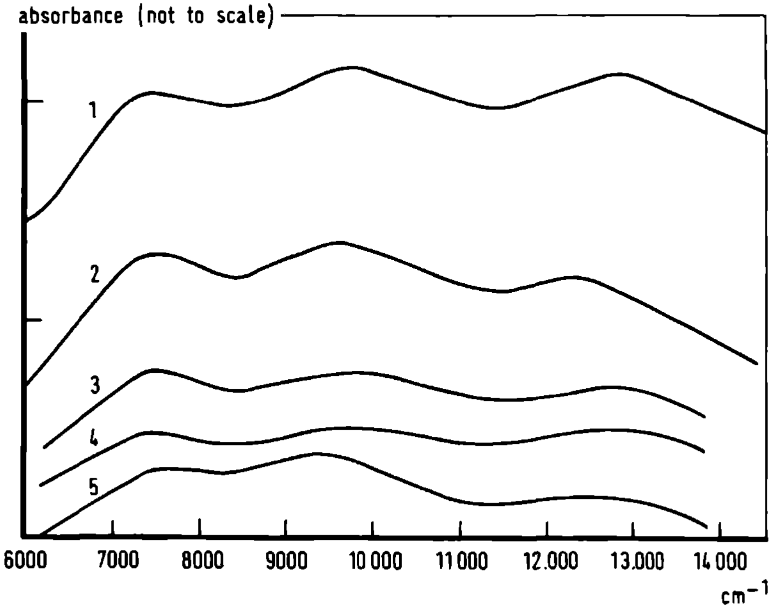

Fig.1. Absorption of bis(amine) complexes of Co(L-2) dissolved in dichloromethane under nitrogen. 1, $Co(L-2)(morpholine)_2$; 2, $Co(L-2)(cyclohexylamine)_2$; 3, $Co(L-2)(N\text{-}methylpiperazine)_2$; 4, $Co(L-2)(piperidine)_2$; 5, $Co(L-2)(pyrrolidine)_2$.

which two are octahedral and three probably five co-ordinated in the solid state. With CH_2Cl_2 and $CHCl_3$ as solvents identical results are obtained.

The results suggest that the amine complexes lose their co-ordinating amine residues in non-polar solvents giving quite similar, probably five co-ordinated compounds of high molecular weight.

This supposition is corroborated by several other observations.

a. After dissolution of a bis-amine complex of Co(L-2) in a non-polar solvent (*e.g.* $CHCl_3$) under nitrogen, a precipitate is formed on standing, heating or concentration. Although these precipitates are crystalline, no good analysis can be obtained for a pure, amine-free complex, but the analytical data indicate that only a small amount of amine can be present.

The I.R. spectra of the products are identical with that of the insoluble $Co(L\text{-}2)(H_2O)_{0.5}$ reported in the preceding chapter.

$Co(L\text{-}1)(pyridine)_3$ and $Co(L\text{-}1)(piperidine)_2$ behave in a different way. By heating these complexes in *e.g.* nitrobenzene or DMF a pure monoamine complex was obtained in both cases.

b. The N-H stretching vibration of free amines is broadened and shifted to lower energy on co-ordination[1].

For the pure morpholine dissolved in nitrobenzene a sharp N-H stretching vibration is found at 3370 $cm.^{-1}$, with an extinction coefficient of 14.5 $l. mole^{-1}.cm.^{-1}$. A solution of Co(L-2) $(morpholine)_2$ in the same solvent exhibits exactly the same spectrum between 4000 and 3300 $cm.^{-1}$ as pure morpholine in the same solvent.

From the transmission values in both cases it could be calculated that both amine residues of $Co(L\text{-}2)(morpholine)_2$ had become free on dissolution of the complex. The measurements could not be made in $CHCl_3$, because the complex forms a precipitate in this solvent at higher concentration. In nitrobenzene a precipitate is only formed after standing for a longer time. Its composition appeared nearly indentical with Co(L-2).

c. Similar observations were made with Co(L-2)(pyridine)$_2$ and Co(L-2)(4-picoline)$_2$. It is known that complexation of pyridine or pyridine derivatives shifts the ring vibration, occuring at 1578 cm.$^{-1}$ (see refs.2,3) by about 10-20 cm.$^{-1}$ to higher energy. Also the out-of-plane vibration, occuring at 405 cm.$^{-1}$ in pure pyridine shifts in Co^{II}-complexes[5] approximately 10 cm.$^{-1}$ to higher energy[4]. In several of our pyridine complexes, measured in the solid state, we found the out-of-plane vibration peak at 420 cm.$^{-1}$. Solution of Co(L-2)(pyridine)$_2$ and Co(L-2)(picoline)$_2$ in $CHCl_3$, however, exhibited the maximum at 405 cm.$^{-1}$.

The phenomenon could not be observed with Co(L-1)(pyridine)$_3$ because on dissolution in $CHCl_3$ a precipitate of the polymeric Co(L-1)(pyridine) is immediately formed. Pricipitates are also formed when solutions of the pyridine and picoline complexes of L-2 in *e.g.* CH_2Cl_2 are heated or allowed to stand. The precipitates have the approximate composition Co(L-2), and their absorption spectra are indicative of five-co-ordination.

d. As reported by Evans[6] the presence of a paramagnetic substance in the solution of an inert compound should lead to shifts in the δ-values of the latter. However, although amine complexes are paramagnetic, a NMR spectrum quite similar to that of piperidine is traced from a dilute solution of Co(L-2)(piperidine)$_2$ in $CDCl_3$.

All these facts illustrate that loss of amine residues by dissolution is a quite general property of the amine complexes.

The process can be formulated by the following equation,

$$n\ \mathrm{Co\,(L)(B)}_m \rightarrow [\mathrm{Co(L)(B)}_q]n + n(m-q)\mathrm{B}. \qquad (n\gg 1).$$

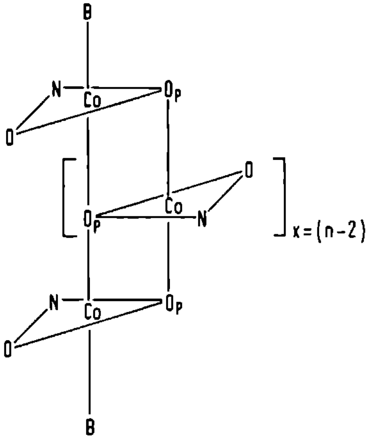

Fig.2. Suggested structure of the product obtained after solution of $\mathrm{Co(L\text{-}2)(B)}_2$ in an apolar solvent.

From two complexes containing L-1 (with m= 3 and m=2, respectively) q appeared to be exactly 1; a polymer Co(L-1)B was isolated in both cases.

The insoluble precipitates obtained from various L-2 complexes had much lower q-values which sometimes depend on experimental conditions during the formation of the precipitates; in precipitates formed at higher temperatures q is generally lower.

Because the precipitates are insoluble in all solvents, and their U.V. spectra are always indicative of five-co-ordination, a probable structure is shown in Fig.2.

The electronic spectra in co-ordinating solvents

All amine complexes exhibit octahedral-type spectra when dissolved in the appropriate amine. The spectra could not be measured in this way with imidazole and bipyridyl complexes because the relevant amines were solids at room temperature.

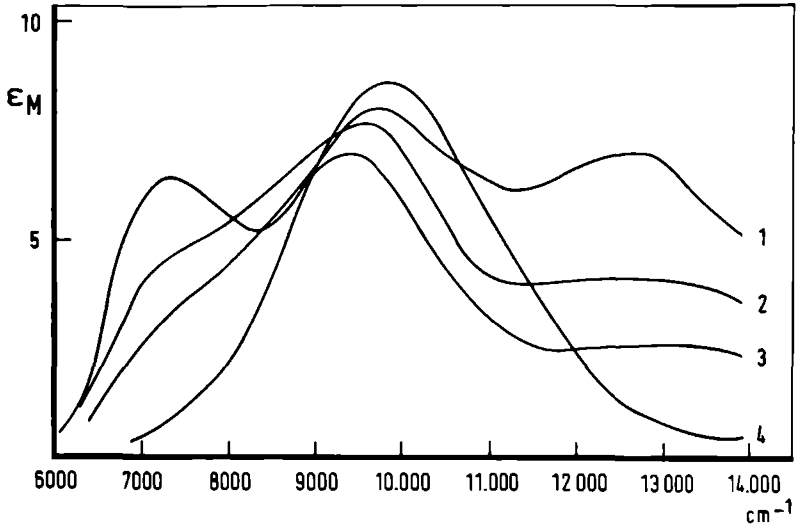

Fig.3. 1, Co(L-2)(morpholine)$_2$ in pure CHCl$_3$; 2, Co(L-2)(morpholine)$_2$ in CHCl$_3$-morpholine (20:1); 3, Co(L-2)(morpholine)$_2$ in CHCl$_3$-morpholine (20:2); 4, Co(L-2)(morpholine)$_2$ in pure morpholine. All measurement were carried out under nitrogen.

Thus, co-ordinating solvents seem to change five co-ordinated amine complexes into octahedral compounds, whereas octahedral amine complexes of Co(L-2) in non co-ordinating solvents are converted into five-co-ordinated polymeric compounds.

The phenonenom was more fully investigated with one of the diamine complexes, Co(L-2)(morpholine)$_2$, which seems to be five-co-ordinated in the solid state. In Fig.3 the U.V. spectra between 6000 and 14000 $cm.^{-1}$ are reproduced for several solutions of the compound in $CHCl_3$, containing increasing amounts of morpholine. The spectra were measured in a nitrogen atmosphere. It appears that addition of the base lowers the maxima at 7350 $cm.^{-1}$ and 12600 $cm.^{-1}$ in respect of that at 9850 $cm.^{-1}$, which becomes more pronounced. In pure morpholine the last maximum, being characteristic for octahedral complexes, has become the only one in this region, and the extinction coefficient (5-8 $l.cm.^{-1}$, $mole^{-1}$) agrees well with that found by Ferguson *et al.*[7],Kiser and Lapp[8] and Lever[9] for octahedral complexes.

The extinction coefficients of the three absorption bands of the initial complex in pure $CHCl_3$ (5-8 $l.cm.^{-1}$, $mole^{-1}$), are much lower than those reported by Dahlhoff[3] (16-190 $l.cm.^{-1}$, $mole^{-1}$), Ciampolini[10] or Sacconi[11] (16-128 $l.cm.^{-1}$, $mole^{-1}$) for well defined five-co-ordinated compounds. Moreover the set of curves do not show an isosbestic point.This may be due to the fact that the polymeric starting compound is not quite homogeneous (see Fig.2 with varying x) whereas the octahedral compound, which arises from it, may be present in a mono as well as in a dimeric form. Finally, there is a real change in polarity of the solvent for the subsequent curves.

I.R. spectra

In view of the stuctural variations, described above, on dissolution, I.R. spectra were only investigated as KBr discs. Under these circumstances oxygen sensitivity of some of the compounds does not influence their I.R.-spectra. In TABLE II the I.R. absorptions which concern ligand groups possibly operative in the co-ordination have been summarized. Data of two aquo com-

TABLE II

I.R.-absorptions of functional groups in amine complexes (cm.$^{-1}$)

Complex	Carboxyl vibrations Asymmetric	Carboxyl vibrations Symmetric	Δ	-C=N-	-N-H	$\succ$-O^{x}
Co(L-1)(cyclohexylamine)$_2$	1590	1380	210	1653	3160 3240 3320	1290
Co(L-1)(3,5-lutidine)$_3$	1636	1360	276	1650		1295
Co(L-1)(pyridine)$_3$	1653	1355	278	1648		1288
Co(L-1)(pyridine)	1605	1410	195	1630		1295
Co(L-1)(piperidine)$_2$	1600	1390	210	1637	3219 3265	1295
Co(L-1)(N-methylpiperazine)$_2$(H$_2$O)	1610	1378	232	1642	3205 3265	1292
Co(L-1)(pyrrolidine)$_2$	1610	1398	212	1641	3210 3355	1290
Co(L-1)(3,4-lutidine)	1605	1410	195	1632		1300
Co(L-1)(bipyridyl)	1635	1360	275	1656		1288
Co(L-1)(aniline)	1635	1390	245	1635	3140 3260	1300
Co(L-1)(H$_2$O)$_2$	1540	1410	130	1658		1300
Co(L-2)(cyclohexylamine)$_2$	1600	1395	205	1622	3160 3275	1310
Co(L-2)(N-methylpiperazine)$_2$(H$_2$O)	1600	1397	203	1640	3260 3150	1316
Co(L-2)(pyridine)$_2$	1600	1383	217	1640		1315
Co(L-2)(3-picoline)$_2$	1635	1372	263	1635		1307
Co(L-2)(3,5-lutidine)$_2$	1605	1390	215	1632		1298
Co(L-2)(bipyridyl)	1550	1404	146	1630		1315
Co(L-2)(piperidine)$_2$	1600	1388	212	1632	3145 3270	1310

Co(L-2)(morfoline)$_2$	1600	1388	212	1638	3140 3270	1310
Co(L-2)(pyrrolidine)$_2$	1600	1398	202	1640	3202 3280	
Co(L-2)(imidazole)$_2$	1575	1392	183	1644		1318
Co(L-2)(H_2O)	1550	1390	160	1644		1300
Co(L-8)(pyridine)$_3$[xx]	1575	1415	160	1658		1318
Co(L-8)(imidazole)$_3$[xx]	1572	1402	170	1654		
Co(L-8)(bipyridyl)[xx]	1585	1402	183	1648		

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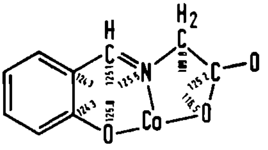
[x] See text.

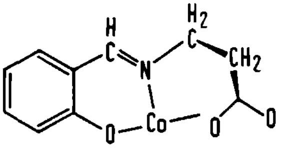
[xx] The assignment of peaks of these complexes is only tentative because they overlap with broad peaks of -C=C- and $-NO_2$ absorptions.

plexes, discussed in the preceding chapter, have been added for comparison.

Before discussing these data a general remark will be made on the consequences of the small difference between the ligands L-1 and L-2 (an additional $-CH_2-$ residue in the side chain) for the structure of their respective Co^{II}-complexes. A reliable, qualitative picture of the structure of these complexes can be derived from available crystallographic data of a large number of Schiff base-metal complexes (with an aromatic part similar to that of L-1 and L-2), of glycine complexes (with an aliphatic part similar to that of L-1), and of Co_2 (salen[12])$_2$ (which might be used to get insight into the spatial relations between the aliphatic and aromatic parts of L-1 and L-2). A useful model of the structure may also be deduced from the reported crystallographic data[13] of a Cu^{II} complex of L-1. The comparable parts of the ligands salen and L-1 exhibit only small differences in the complexes Co_2(salen)$_2$ and Cu(L-1).

This leads to a model for L-1 complexes in which the distance and orientation of the carboxyl group with respect to the Co atom, are more favourable for tetragonal co-ordination than they are in the model for L-2 complexes. In the latter the distance between Co^{II} and carboxyl oxygen is slighty greater, and the relevant Co-carboxyl oxygen bond is not exactly opposite to the co-ordinative bond between Co^{II} and phenolic oxygen. The behaviour of some amine complexes of Co(L-1) and Co(L-2) in non polar solvents is consistent with these differences: octahedral polymeric Co(L)B compounds are found for Co(L-1) and five co-ordinated complexes for Co(L-2).





The carboxyl vibration

Unfortunately there are only three amine, pyrrolidine, N-methylpiperazine and bipyridyl, which, on co-ordination with Co(L-1) and Co(L-2) complexes, yield products with the same co-ordination number (six; octahedral structure) and the same number of co-ordinating amine molecules in both series. These pairs of compounds are most useful to investigate if the structural differences, supposed between octahedral amine complexes containing L-1 and L-2 respectively, are visible in the I.R. region.

The data reveal that the asymmetric carboxyl vibration of the low-molecular pyrrolidine and N-methylpiperazine complexes of L-1 is at higher frequency (1610 $cm.^{-1}$) than that of the compable L-2 complexes (1600 $cm.^{-1}$). Both L-1 complexes also have higher Δ-values than the corresponding L-2 complexes. This indicates better carboxylate co-ordination in the L-1 than in the L-2 complexes, as was expected. A comparison of the polymeric bipyridyl complexes in both series (L-1 and L-2) shows even greater differences between their COO^- asym. and Δ-values. The very low values of Co(L-2)(bipyridyl)($\nu_{as.}$:1550 $cm.^{-1}$, equal to that of Co(L-2)(H_2O) and Δ=146 $cm.^{-1}$) suggest that in this compound the COO^- group does not participate at all in co-ordination with Co^{II}.

The -C=N- vibration

The position of a -C=N- vibration is less affected by co-ordination than that of the asymmetric carboxyl vibration. For the comparable bis(pyrrolidine) and bis(N-methylpiperazine) complexes it appears that the differences in -C=N- values are too small to decide whether there are differences in co-ordination pattern as far as it concerns the -C=N- group. When the changes for the carboxyl and -C=N- vibration are combined it may be concluded that there must be a higher electron density on the metal atom in Co(L-1) than in Co(L-2) complexes, because -C=N- vibrations nearly coincide, but the carboxyl group donates better in the Co(L-1) compounds.

In some amine complexes the position of the -C=N- vibration approaches very closely the value found for the free ligand. (A value of 1650 $cm.^{-1}$ was found for the mono potassium salt of L-2). High -C=N- absorption values of more than 1650 $cm.^{-1}$ were found for the bipyridyl, the tris pyridine, tris lutidine and bis cyclohexylamine complexes of Co(L-1). It is difficult to decide whether these high -C=N- absorption frequencies are caused by a lowering of the positive charge on the metal or by the absence of co-ordination *via* the nitrogen atom of the tridental ligand. Such high -C=N- absorption values have not been observed in the L-2 series, suggesting that for this type of complexes the -C=N- group of the tridentate ligand always participates in the co-ordination.

The N-H stretching vibrations

All complexes containing a primary or secondary amine exhibit two N-H stretching vibrations, and Co(L-1)(cyclohexylamine)$_2$ has three. This is a normal pattern with primary amines: separated peaks for the asymmetrical and symmetrical N-H vibrations; the former at slightly higher energy.

In complexes of secondary amines, the presence of two peaks may be a consequence of unequal positions of amine molecules in the complex. It is known that the N-H absorption frequency is shifted to lower energy upon co-ordination[14]. A similar observation has been reported[15] for a bis morpholine complex. In these cases the peak at higher energy will then arise from those amine residues, which are at a greater distance from Co^{II} and more loosely bound to the metal. The ν_{N-H} value will then be nearer to the value of 3300 cm.$^{-1}$, which is found in free secondary amines.

A comparison between the related Co(L-1) and Co(L-2) complexes with pyrrolidine and N-methylpiperazine, previously discussed, shows that differences in ν_{N-H} values within both pairs are not very great, but in the Co(L-1) complex peaks are always found at slightly higher energy, as should be expected if the electron density on the metal atom is higher. As discussed elsewhere in this chapter B-values point into the same direction.

The C_{ar}-O vibration

The exact localization of this vibration is rather difficult in most amine complexes, and the data given in TABLE III are not always definite. In complexes with pyridine or other heterocyclic bases the intensity is much lower than in aquo complexes. In complexes with primary or secondary amines the exact localization is hindered by the presence of another peak in close vicinity (probably a C-N vibration). Isotopic labelling studies would be necessary to get more definite data.

The Dq and B values of octahedral complexes

Dq and B values of octahedral Co^{II}-complexes are generally calculated by the method of Underhill and Billing[16,17]. However, the procedure, recently reported by Reedijk *et al.*[18] seems to be more attractive for our complexes, because it can also be applied to pseudooctahedral complexes. This is of importance in view of the absence of symmetry in our compounds. A second advantage of the new method is that corrections are made for: (a) the lowering of the ground state energy by spin-orbit coupling, and (b) quartet-doublet interactions.

The observed maxima and the calculated Dq and B-values have been collected in TABLE III. It appears that with pairs of comparable complexes from the L-1 and L-2 series, namely the pyrrolidine and N-methylpiperazine complexes, highest Dq and B-values are found for the Co(L-1) compounds. This result suggests that L-1 is a better donating ligand than L-2, what may possibly be ascribed to a more appropriate orientation of the COO^- group in the former case. For complexes of comparable co-ordination, highest Dq values may be expected when strong donating ligands

TABLE III

Absorption maxima and crystal field parameters in cm.$^{-1}$ of octahedral amine complexes

Complex	Absorption maxima (cm.$^{-1}$)			10Dq	B	$\frac{Dq}{B}$	β
	ν1	ν2	ν3				
Co(L-1)(cyclohexylamine)$_2$	9000	15900	20000	9830	809	1.21	0.83
Co(L-1)(pyrrolidine)$_2$	9000		19800	9750	794	1.22	0.81
Co(L-1)(piperidine)$_2$	8800		18000 19500	9510	733	1.29	0.75
Co(L-1)(N-methylpiperazine)$_2$(H_2O)	9300		19900 20600	10080	806	1.25	0.82
Co(L-1)(3,5-lutidine)$_3$	9600	15500	19500 20500	10480	769	1.36	0.79
Co(L-1)(pyridine)$_3$	9800		19500 20400	10680	751	1.42	0.77
Co(L-1)(bipyridyl)	9300		19600	10060	760	1.32	0.78
Co(L-2)(pyridine)$_2$	9700	15600	19500 20000	10480	736	1.42	0.75
Co(L-2)(pyrrolidine)$_2$	8800		18200 19400	9510	737	1.29	0.75
Co(L-2)(4-methylpyrimidine)	9600		19300 20300	10360	718	1.44	0.73
Co(L-2)(imidazole)$_2$	9400	16600	18900 20500	10190	817	1.24	0.84
Co(L-2)(bipyridyl)	9600		19300 21800	10360	718	1.44	0.73
Co(L-2)(3,5-lutidine)$_2$	9700	15800	19000 20500 22500	10480	743	1.40	0.76
Co(L-2)(N-methylpiperazine)$_2$(H_2O)	9200		18000 19400	9930	703	1.41	0.72

Co(L-8)(benzylamine)$_2$	9800	16400	-----[x]				
Co(L-8)(imidazole)$_3$	9000	17000	-----[x]				
Co(L-8)(bipyridyl)	9200	15500	19000 19900	9950	756	1.31	0.77
Co(L-8)(pyridine)$_3$	8800	16300	18800 19700	9510	737	1.29	0.75

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[x] The third absorption maximum could not be observed owing to the large charge-transfer band of these complexes.

are present.

That donating groups increase the Dq value is substantiated by the results with the amine complexes of Co(L-8), in which the donating properties of the organic ligand are reduced by the presence of the nitro groups. In these compounds a lower Dq value is found.

However, it has been reported that π-interaction may also increase Dq values[19]. In this respect it is a point of interst in our data that pyridine complexes in both series have much greater Dq values, than complexes of saturated amines, although pyridine is a weak donor. The high Dq values are caused by the presence of a donating lone pair in combination with accepting π-orbitals (empty antibonding π-orbitals). This role of pyridine has never been reported, but in the first instance it is comparable with a CN^- ion with a donating lone pair and an empty π-orbital. The great Dq value for Co^{II} with this ion leads to a low-spin compound.

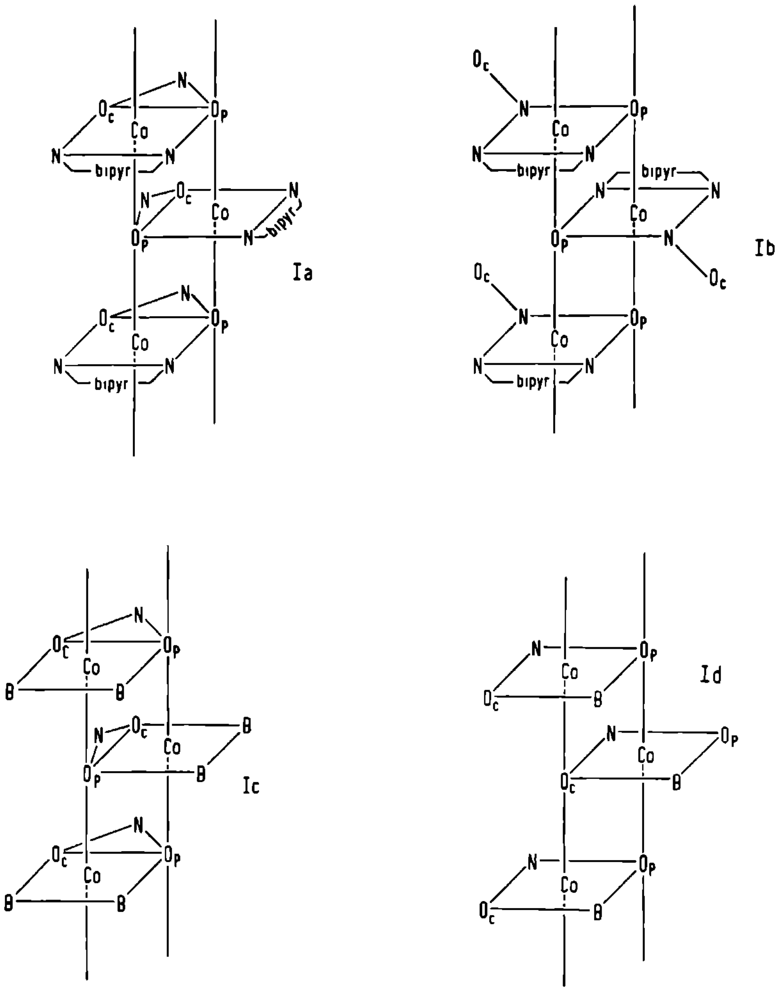
Proposed structures for amine complexes

In the preceding paragraphs the amine complexes have been subdivided according to two criteria: on account of U.V. data in octahedral and five-co-ordinated compounds; and because of the solubility characteristics in compounds with low-molecular weight (mono or dimeric complexes) and polymeric compounds. In this section a more detailed discussion will be presented on the structure of some compounds investigated.

The bipyridyl complexes

The bipyridyl complexes of Co(L-1) and Co(L-2) are both octahedral, and polymeric. However, a great difference is observed in the I.R. data of the carboxyl and -C=N- group. The large Δ-value found for the Co(L-1) complex indicates co-ordination *via* the carboxyl group, while the large value found for the -C=N- vibration (approximately the same as in the free ligand) suggests little or no co-ordination of this function. The inverse is observed for the L-2 complex having a very low Δ-value and a much smaller -C=N- stretching absorption than the L-1 complex. This suggests no co-ordination *via* the carboxyl group, but surely *via* the nitrogen atom. As both complexes are polymeric the structures Ia, for Co(L-1)(bipyridyl), and Ib, for Co(L-2)(bipyridyl), satisfy the experimental data very well.

The proposed structure (Ia) for the L-1 complex is a very unusual one indeed. It is suggested that the complex has a structure in which the central nitrogen atom does not participate in the co-ordination. Such an example has not been found previously in the litterature. As can be seen at model C̲ on p.75 there may be some sterical hindrance when L-1 will remain flat. It was selected from a great number of possibilities because it agreed best with the spectroscopical data (I.R.), in contrast to a more usual model. The positions of the carboxyl vibrations did not



Ia

Ib

Ic

Id

Fig.4. Suggested structures for some high-molecular octahedral amine complexes.

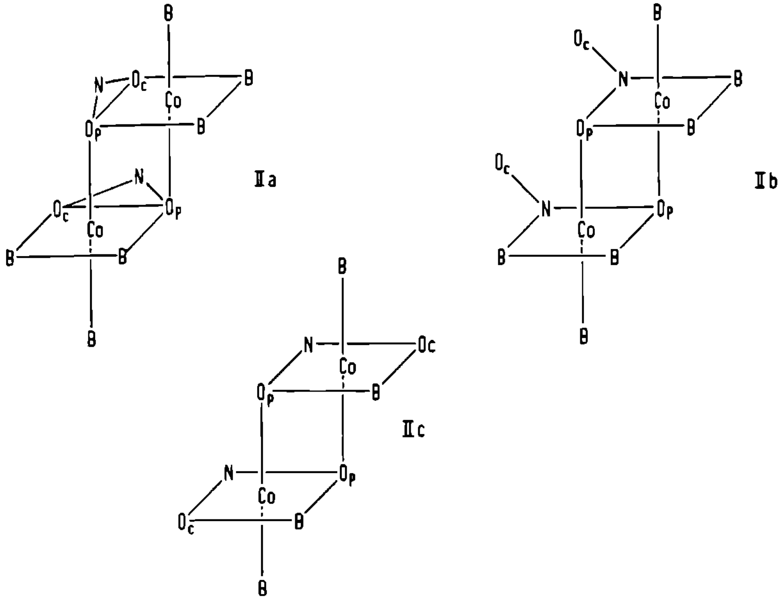


Fig.4. Suggested structures for some low-molecular octahedral amine complexes.

suggest the presence of a structure with a carboxyl group in a bridging position. As far as investigated this type of co-ordination gives relatively low Δ-values (approx. 150 cm.$^{-1}$) and a symmetrical vibration a higher energy (approx. 1450 cm.$^{-1}$) for acetato complexes[20].

We think that the difference in reactivity towards oxygen between the bipyridyl complexes of Co(L-1) and Co(L-2) is related to the remarkable difference in structure (see CHAPTER IV).

Tris(pyridine) complexes. These have only been obtained in the Co(L-1) series (with pyridine and 3,5-lutidine) and Co(L-8) series (with pyridine). All of them are soluble and octahedral. Both Co(L-1) complexes have the -C=N- vibration at high energy (1650 $cm.^{-1}$). This suggests that the nitrogen atom does not participate at all in co-ordination, or that the cobalt-nitrogen bonding is very weak. A monomeric complex in which all the functional groups participate in co-ordination is less likely, because the maximum number of pyridine molecules co-ordinating with Co(L-2) is two, whereas Co(L-1) with a better organic ligand binds three molecules of the base.This consideration leads to a dimeric structure (without co-ordination with the N atom) *i.e.* IIa as the probable one for these compounds. The great spectroscopical resemblence with Co(L-1)(bipyridyl) gives another argument to prefer structure IIa for the tris-pyridine complex of Co(L-1) to a monomeric structure. Co(L-8)$(pyridine)_3$ having the same side chain as Co(L-2) has probably structure IIb. Its low Δ-value fits this supposition. The $\nu_{-C=N-}$ value is very high, but this may be due to the presence of strong electron attracting $-NO_2$ groups. This may also be responsible for an uptake of 3 moles of organic base.

Bis pyridine complexes. This type was only obtained in the L-2 series (with pyridine, 3-and 4-picoline, and 3,5-lutidine). All of them are low molecular, octahedral compounds. Their I.R. data (Δ and -C=N- vibration suggest that all functional groups co-ordinate, resulting in a structure like IIc. The great spectroscopical and chemical differences (*e.g.* solubility) between the bis-pyridine and bipyridyl complexes of Co(L-2) suggested a definitely different structure for these compounds.

Monopyridine complexes. Three monopyridine complexes have been obtained and investigated: Co(L-1)(pyridine), Co(L-1)(3,4-lutidine) and Co(L-8)(pyridine). They are insoluble indicating polymeric structures, and have U.V. spectra indicative of five-co-ordination. The -C=N- absorption values of the Co(L-1) compounds are the lowest in the series (1630 and 1632 cm.$^{-1}$). Therefore co-ordination *via* -C=N- function is rather certain. Participation of the carboxyl residue is less certain ($\nu_{ass.}$ =

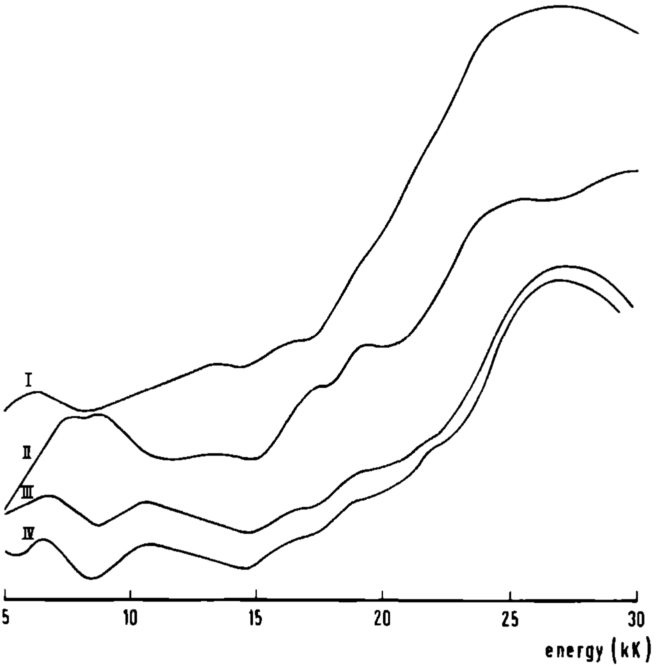


Fig.5. Reflectance spectra of five co-ordinated amine complexes. I, Co(L-2)(cyclohexylamine)$_2$; II, Co(L-8)(pyridine); III, Co(L-1)(pyridine); IV, Co(L-1)(3,4-lutidine).

1605 cm.$^{-1}$ in both compounds). A possible structure is IIIa. A note has to be made on the Δ-values of these compounds. The relative high Δ-value (195) found is apparantly mainly due to the high $\nu_{COO\ asym.}$ and to a less extent to the $\nu_{COO\ sym.}$. Such increases in $\nu_{asym.}$ may be due to an inductive effect of the strong electron donation from N(in -C=N-) to the metal atom. Lever and Ogden[21] found such influences of α-substituents on $\nu_{COO\ asym.}$ in acetato complexes. It is clear that they will be less pronounced in the L-2 series because the N-atoms are there in a β-position.

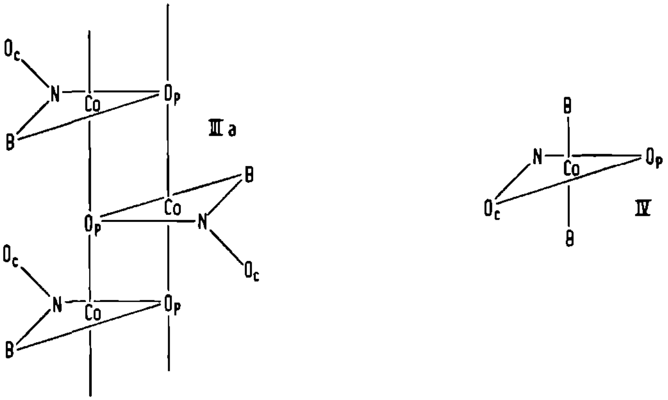


Fig.6. Suggested structures for some five-co-ordinated amine complexes.

A consequence of the supposition that mono pyridine complexes of Co(L-1) have structure IIIa is that its formation from tris-pyridine complexes, supposed to be like IIa, is accompanied by a change from COO$^-$ co-ordination (in a octahedral structure) to -C=N- co-ordination (in a five-co-ordinated structure). This point will be discussed at the end of this chapter. At present it seems to be of interest to denote that the loss of amine bases from tris-pyridine complexes is also accompanied by polymerization, and that the mono compounds are only stable in the solid state. Standing in amine solution they give back tris complexes and even in non-polar solvents like $CHCl_3$ or CH_2Cl_2 they give octahedral compounds.

The cyclohexylamine complexes

The cyclohexylamine complexes of Co(L-1) and Co(L-2) have the same composition, but their properties are very different. The Co(L-1) complex is insoluble in dichloromethane (this is the only saturated amine complex with this property) and exhibits a six co-ordination. Owing to the high -C=N- value, a polymeric structure, without co-ordination of the nitrogen atom, is proposed for the Co(L-1) complex (structure Ic).

The Co(L-2) complex has a five co-ordination (see Fig.5, curve I) and is easily soluble in dichloromethane.

The assignment of a structure to the Co(L-2) complex remains somewhat uncertain owing to overlap of carboxyl and amine vibrations. Its I.R. spectra show an intermediate Δ-value but a very small -C=N- absorption value, suggesting strong interaction *via* the N-atom. As proposed earlier it is possible that the carboxyl group is in hydrogen bond *via* the amine molecule. It is also possible however that this complex is monomeric (structure IV).

Saturated secondary amine complexes

All piperidine, N-methylpiperazine, pyrrolidine and morpholine complexes have the same overall composition ($Co(L)B_2$). The complexes with N-methylpiperazine contain one water molecule but it is assumed that this does not co-ordinate *via* the Co atom, but is hydrogen bonded with the lone pair of the tertiary amine. They are soluble and have octahedral structures based on U.V. data, with the exception of Co(L-2)(morpholine)$_2$ and Co(L-2) (piperidine)$_2$. I.R. data also indicate participation of carboxyl group and nitrogen atom in the co-ordination. This leads to a structure like IIc. The presence of two N-H vibrations are in accordance with such a proposal.

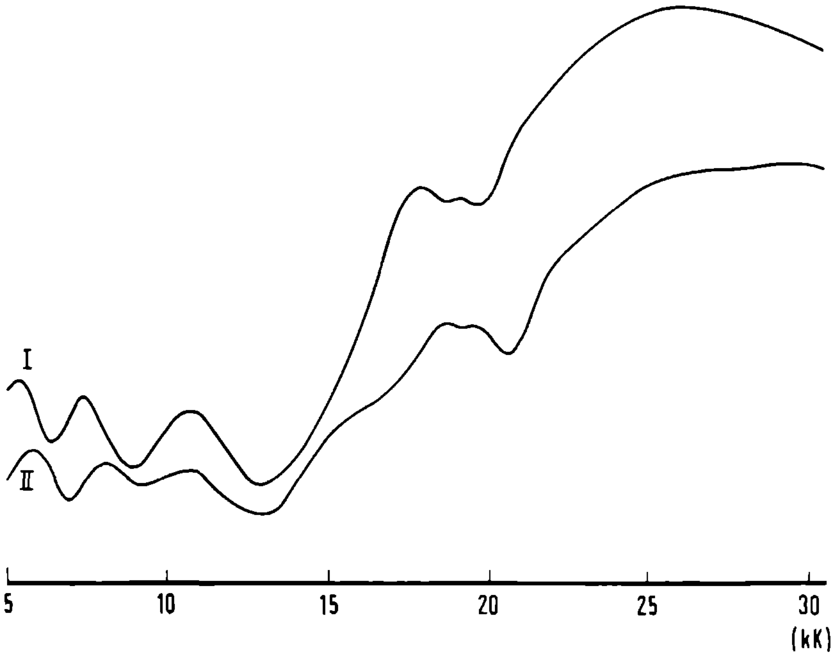


Fig.7. Reflectance spectra of: I, Co(L-2)(piperidine)$_2$; II, Co(L-2)(morpholine)$_2$.

The bis-morpholine and piperidine complexes of Co(L-2) have electronic spectra, which are more like those of five-co-ordinated compounds. It is not clear why these bases lead to structures different from those of the pyrrolidine and N-methylpiperazine derivatives especially as the latter are structurally related to morpholine and piperidine, and have about the same pK value.

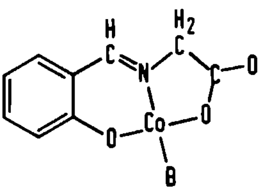
The electronic spectrum of Co(L-2)(morpholine)$_2$ dissolved in morpholine is that of an octahedral compound.

It may be that the compounds have a severely distorted octahedral structure because the presence of two N-H stretching vibrations in the I.R. spectra cannot well be understood in terms of a trigonal structure.

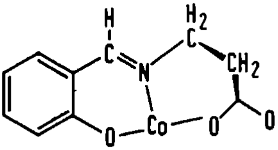
Conclusions

The experimental data clearly show that amine complexes can be easily prepared from the aquo compounds. It has been shown that especially the L-2 complexes easily lose their co-ordinated amine ligands when the free-amine concentration is decreased. On treating an amine complex with water no aquo complex is reformed but a polymer which is nearly solvent-free. This suggests a greater propensity to form a polymeric structure than an aquo complex.

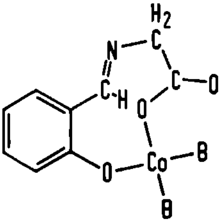
The complexes studied allowed the comparison of the co-ordinating properties of N ligand (-C=N-) with a carboxylate group. In general there is no priority, but with strong donating nitrogen bases *e.g.* bipyridyl and cyclohexylamine a clear difference is observed between the Co(L-1) and Co(L-2) series. In the Co(L-1) complexes the N-atom does not seem to co-ordinate as already indicated; however, in Co(L-2) complexes absence of co-ordination with the carboxyl group seems probable.



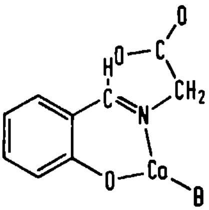
A



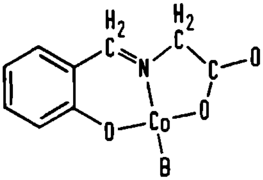
B



C



D



E

The different behaviour shows the great influence of the ligand structure on the co-ordination. The significance of the ligand structure is also seen with the pyridine complexes of Co(L-1) and Co(L-2). The L-1 complex can co-ordinate with 3 moles of pyridine and Co(L-2) with two. By the introduction of a strongly donating base in either Co(L-1) or Co(L-2) the base will co-ordinate opposite to the N-atom. This results in a weakening of the Co-nitrogen (of the -C=N- group) bond. In Co(L-1) (see A) the Co carboxylate will then be displaced as a consequence of the rigid structure of the ligand. In this less-stable situation rearrangement can take place *via* a rotation of the aliphatic part of Co(L-1) giving a structure like C. As a consequence of steric hindrance L-1 will only be partly in plane with Co and the co-ordinating atoms. In Co(L-2) such a process is less probable since a weakening of the Co-nitrogen bond influences the Co-carboxyl oxygen to a less extent owing to the greater flexibility of the aliphatic part of L-2. Based on this hypothesis the different chemical behaviour of the amine derivatives Co(L-1) and Co(L-2) may be clarified.

On dissolution of a complex with structure C *e.g.* the tris pyridine complex, it has been found that the base is easily removed, it is possible that by removal of the amine molecule in trans position, the aliphatic part of C might flip over approximately 180° to give structure D. As reported a compound with structure D is unstable. It is easily converted into structure E in either polar or non polar solvents.

Complexes with structure E convert readily to structures like C.

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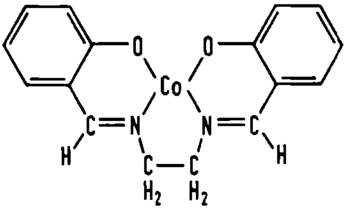
C H A P T E R IV

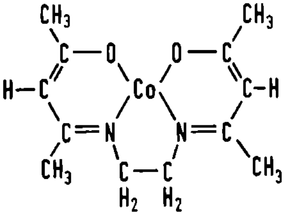
BEHAVIOUR OF AMINE COMPLEXES OF Co^{II} WITH TRIDENTATE LIGANDS TOWARDS OXYGEN

Introduction

Cobalt^{II}-complexes carrying molecular oxygen have been the subject of many investigations. Until recently most adducts studied appeared to be binuclear[1-7] with a Co to oxygen (O_2) ratio of 2:1. Kinetic investigations[5] revealed that such binuclear compounds are formed *via* a mononuclear oxygenated intermediate, which reacts with another molecule of the oxygen-free Co^{II}-complex in a second step.



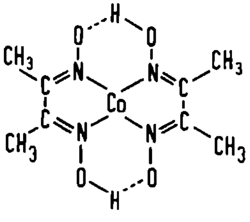
I



II

During the last few years several examples have been found[7-17] in which the second step did not take place at all or took place only slowly. The oxygenated species was a mononuclear compound with a Co to oxygen (O_2) ratio of 1:1. Illustrative examples are the planar Co^{II}-complexes with the N,N'-ethylene bis (salicylidene iminato) dianion (I) or the N,N'-ethylene bis (acetylacetone iminato) dianion (II) as ligand. In the presence of amines they form monomeric octahedral compounds of low-spin type, which can be oxygenated to mononuclear paramagnetic compounds with a Co to oxygen(O_2) ratio of 1:1.

Amine derivatives of the bis(dimethylglyoximato)Co^{II}-complex



III

(III), also of low-spin type but sometimes diamagnetic in consequence of dimerization[13], pick up oxygen in a similar way. E.S.R. spectra of these mononuclear oxygenated species always show eight hyperfine lines (see Fig.5) due to coupling of the unpaired electron with the cobalt nucleus ($I = {}^7/2$). The compounds can be formulated best as superoxo (O_2^-) adducts of Co^{III}-compounds[10,13,16,17]. It appears that in the formation of these compounds oxygenation is closely related to oxidation of the central Co^{II}-ion.

The factors which govern the ability of Co^{II}-complexes to pick up oxygen, are certainly rather complex.

Wilkins[5] demonstrated that in aqueous ammonia solutions of Co^{II}-salts the binuclear oxygenated adduct, $(NH_3)_5\text{-}Co\text{-}O_2\text{-}Co(NH_3)_5^{4+}$ is preferentially formed from the pentamine complex $Co(NH_3)_5H_2O^{2+}$. The rate constant of formation from this species is at least 20 times that of the formation from the hexamine ion $Co(NH_3)_6^{2+}$. The formation of the adduct $(NH_3)_4(H_2O)Co\text{-}O_2\text{-}Co(NH_3)_4(H_2O)^{4+}$ from the pentamine complex is relatively unimportant; the tetramine complex, from which the same adduct might arise, is unable to take up oxygen.

These data suggest that a large number of nitrogen ligands enhance the tendency to pick up oxygen but that complexes with only nitrogen ligands are less reactive or not reactive at all.

Fallab, although he agreed with this general conclusion[18], found oxygenation of complexes containing only three nitrogen ligands[19]. Hoffman[10] showed that N,N'-ethylene-bis(acetylacetone iminato)Co^{II}-complexes(II) take up oxygen when dissolved in pure toluene (*i.e.* without the addition of a nitrogen base). In this case only two nitrogen ligands are present.

The oxygenation of the low-spin complex $Co(CN)_5^{3-}$ is an example[20] of an oxygen-sensitive complex without any nitrogen ligand in the direct co-ordination sphere.

Therefore it is clear that the ability to pick up oxygen is not simple dependent on the ratio between nitrogen and other ligands around the cobalt ion. A better criterium for oxygen sensitivity might be the presence of a relatively large number of well n-donating ligands (*i.e.* N nitrogen ligands), which would maintain a relatively high electron density on the central metal atom.

Evidently to test the usefulness of such a criterium several authors investigated if a correlation could be found between the redox potential of the Co^{III}/Co^{II} system in relevant compounds and their ability to take up oxygen. Bayer and Schretzmann[21] stated indeed that the redox potential has to be sufficiently low to make oxygenation induced by oxygen possible.

Costa[22] made a systematic polarographic study on octahedral Co^{III}-complexes with a planar divalent tetradentate ligand and two amine molecules in axial positions. With a given equatorial ligand the half-wave potential, was reduced by introduction of strong donating molecules in the axial positions. The highest potentials were found with aromatic amines like pyridine and aniline, which have low pK_a values. With constant axial but varying equatorial ligands the redox potential increases with increasing electron delocalization in the equatorial ligand.

So it seems that on the one hand the presence of aliphatic amines, which guarantee better a relatively high charge density on the metal, will lead to compounds sensitive towards oxygenation. On the other hand, complexes with aromatic nitrogen ligands, in which electron-charge can be transfered back from metal to empty π-orbitals are less likely to oxygenate. It is in accordance with this proposition that a large majority of the known oxygen carriers[18,23,25] has aliphatic amines in the ligand sphere. *E.g.* in a series of bis(salicylaldehydato)-bis-amine complexes of Co^{II}, the pyridine and pyridine like complexes are not affected by oxygen, whereas those of aliphatic amines (morpholine, piperidine) are sensitive to oxygen[26].

Results

All Co^{II}-complexes described in the previous chapters have been tested on their ability to bind oxygen. It appeared that all aquo-,DMSO-, and solvent-free complexes are inactive to oxygen. From the amine complexes mentioned in TABLE II of CHAPTER III, all those of Co(L-8) are inactive; those of Co(L-2) are inactive when complexed with pyridine-like bases. All other amine complexes, including the pyridine and bipyridyl complexes of Co(L-1) are sensitive to oxygen. In general our results agree with the introductory comment in this chapter, although the remarkable difference between the bipyridyl complexes of Co(L-1) and Co(L-2) is very surprising as they have similar compositions.

We investigated if crystal-field parameters (Dq and B-values) might provide useful criteria to assess oxygen-sensitivity in series of related compounds. Such an approximation seemed significant because well n-donating ligands enlarge the crystal-field splitting; Reedijk[27] found in a large group of octahedral and pseudo-octahedral Co^{II}-complexes highest Dq-values for compounds with nitrogen ligands. On the other hand, nearly all known low-spin Co^{II}-complexes, which must have large crystal-field splittings, are sensitive to oxygen.

Our compounds seem very well suited for such an investigation because most amine complexes are different from the planar compounds I,II and III, whereas our compounds are of the high-spin type, and are mainly octahedral, so that crystal-field parameters could be readilly calculated (TABLE III, CHAPTER II and TABLE II, CHAPTER III).

Inspection of these data makes it clear that Dq-values of aquo-complexes, insensitive towards oxygen, are generally low in our series (10 Dq is 9500 or lower); amine complexes have always much higher Dq-values (10 Dq always higher than 9500, mostly about 10000). In general complexes with Co(L-8), containing nitro substituents, have lower Dq-values than the corresponding unsubstituted Co(L-2) complexes. On the whole several Co(L-1) complexes have still higher Dq-values than in comparable Co(L-2) complexes. The Co(L-1) as well as the Co(L-2) series highest Dq-values are found in complexes with pyridine-like bases, although exactly these are inactive with oxygen in the latter series.

We suppose that the high Dq-values of the pyridine complexes might originate from π-interaction. However, this interaction leads to charge-transfer from Co^{II} to empty ligand orbitals and should reduce the electron density on the metal. In general several Co(L-1) complexes have still higher Dq-values than in comparable complexes in the Co(L-2) series. Oxygen sensitivity will be found only then when a high Dq-value is found in combination with low metal-ligand charge-transfer. Therefore an attempt was made to investigate charge-transfer in our complexes.

The charge-transfer peaks of the complexes investigated

All complexes exhibit maxima beyond the region for d-d transitions. The spectral data do not reveal if there is charge-transfer from metal to ligand or from ligand to metal. However, investigations of Jörgenson on pyridine complexes of Ir[28], and those of Williams[29] and Byers[30] on a number of first-row transition elements with aromatic ligands show that charge-transfer from metal to ligand is most probable for pyridine complexes.

We found that substitution of bromine in the salicylaldiminato ligand (L-2) resulted in a shift of the charge-transfer maximum (of the solvent-free complex involved) to lower energy (900 cm.^{-1} with the 5-bromo-, 1600 cm.^{-1} with the 3,5-dibromo derivative, both measured in DMF). With nitro substituents the effect could not be measured in consequence of overlap between the absorption band of the ligand and the charge-transfer band. However, the effect found with bromo-substituted ligand is consistent with charge-transfer from the metal to the ligand.

In Fig.1 charge-transfer bands have been reproduced for three compounds with an increasing conjugated system.

Curve 1 concerns a complex in which the ligand (L-10) contains a simple aromatic ring in conjugation with one of the

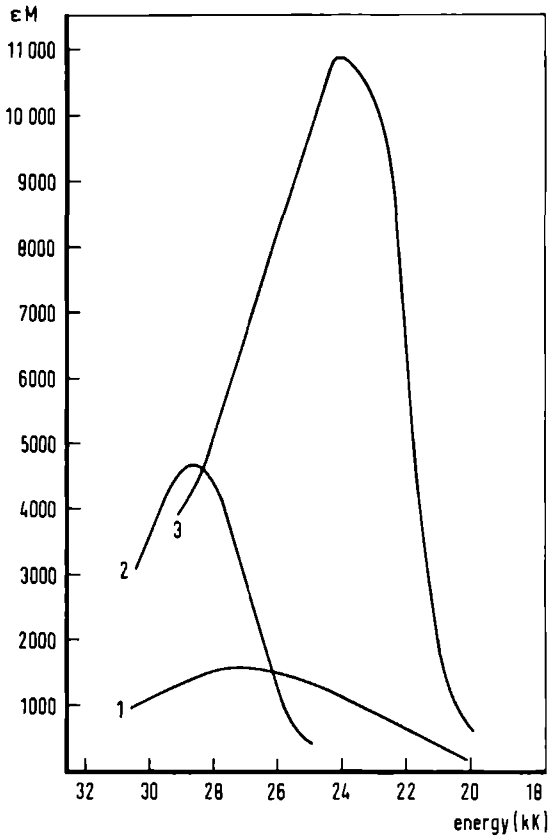


Fig.1. Absorbance (in l mole^{-1} cm.$^{-1}$) of the charge-transfer band of: curve 1, Co(L-10); curve 2, Co(L-2)(H_2O); curve 3, Co(L-6). Methanol was used as solvent.

co-ordinating groups. The oscillator strength is low (12.800). In curve 2 the charge-transfer band is given of a complex in which the conjugated system in the ligand (L-2) is more extended because of the presence of a -C=N- group in conjugation with the aromatic ring. The oscillator strength is raised to about 18.000. The charge-transfer band in curve 3 belongs to

TABLE I

Absorption maxima, extinction coefficients and oscillator strenth of the charge-transfer band of a number of Co(L-1) and Co(L-2) complexes in solution. The complexes were measured in the co-ordinating amine as solvent

Spectrum number	Complex	Solvent	Absorption maximum (cm.$^{-1}$)	Extinction coefficient (1 mole^{-1} cm.$^{-1}$)	Oscillator strength
1	Co(L-1)	piperidine	27200	2480	13800
2	Co(L-1)	pyridine	28000	7200	50500
3	Co(L-2)	piperidine	27200	4700	16000
4	Co(L-1)	N-methylpiperazine	27200	4560	16200
5	Co(L-2)	N-methylpiperazine	27250	4500	16200
6	Co(L-1)	cyclohexylamine	27250	2780	18400
7	Co(L-2)	cyclohexylamine	27250	3500	15000
8	Co(L-2)	morfoline	27000	3640	17500
9	Co(L-1)	morfoline	26950	1800	16500
10	Co(L-2)	pyridine	28600	5800	35000
11	Co(L-2)	4-picoline	28600	5800	28000
12	Co(L-2)	3,4-lutidine	28600	4800	26000
13	Co(L-2)	2-methylpyrazine	28100	1900	8000

a complex in which conjugation in the organic ligand (L-6) is further extended by an additional aromatic ring. Its oscillator strength is very high (130.000).

Apparently the amount of charge-transfered increases with the extension of conjugation in the organic ligand.

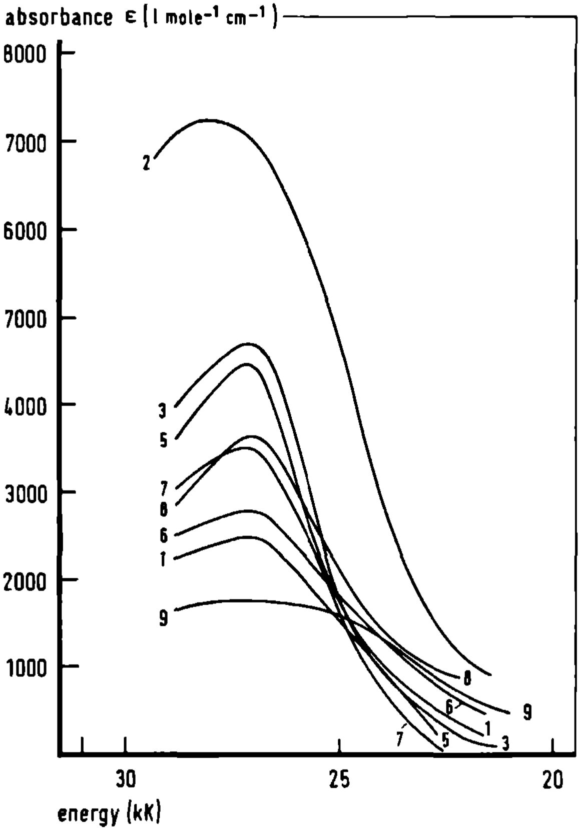


Fig.2. Absorbance (in 1 mole^{-1} cm.$^{-1}$) of a number of Co(L-1) and Co(L-2) complexes in their appropriate amine as solvent. The number refer to the compounds mentioned in TABLE I.

In Fig.2 charge-transfer bands of a number of Co(L-1) and Co(L-2) complexes, dissolved in co-ordinating amines, have been reproduced. In TABLE I maxima, extinction coefficients and oscillator strengths have been collected. Three conclusions may be drawn from these results.

1. Complexes of either Co(L-1) and Co(L-2) with saturated amines exhibit charge-transfer bands with an absorption maximum at approximately the same frequency (27.200 $cm.^{-1}$) and nearly constant oscillator strength (about 16.000).
2. Complexes with pyridine or pyridine-like bases have maxima at slightly higher frequencies (about 28.000 $cm.^{-1}$) and with much higher oscillator strength than those of saturated amines.
3. The oscillator strength of the charge-transfer band of the pyridine complex of Co(L-1) is remarkably high in comparison with that of complexes of Co(L-2) with pyridine-like bases.

Discussion

Several attempts to systematize charge-transfer spectra of metal complexes have been described in the literature[31-34]. Among them the optical electronegativity approach of Jörgensen[31,35,36] has appeared to be rather successful in investigations on inorganic complexes (*e.g.* halides) in which there is charge-transfer from ligand π-orbitals to metal d-orbitals.

Byers[30] used this concept in investigations on complexes of several metals with organic ligands (pyridine-N-oxides), in which there is charge-transfer from metal to ligand. From his data it appeared that the position of the charge-transfer band does not change very much in going from tetra- to hexa-co-ordinated compounds, or on the introduction of substituents in the co-ordinating bases. A similar result has been obtained in our series; the position of the charge-transfer band does not vary much, if the basicity of the co-ordinating base is strongly varied (morpholine pk_b 8.33, piperidine pk_b 11.12), or substituents are introduced into a co-ordinating aromatic base (pyridine, picoline, lutidine). Apparently slight changes in the electronegativities of metal $[\chi(M)]$ and ligands $[\chi(L)]$ involved, do not lead to differences in the difference $[\chi(M)-\chi(L)]$ which, according to the equation

$30.000[\chi_{opt}(M)-\chi_{opt}(L)] = \nu_{ct} - \Delta$ SPE-4 Dq (Δ SPE= change of spin pairing energy) determines the position of the charge-transfer band. It is expected that variations of structure in the complexes have much more influence on the extinction coefficients or oscillator strengths, especially when they concern ligands which participate in charge-transfer.

Replacement of a saturated base by a pyridine-like one causes the appearence of a second charge-transfer band, nearly coinciding with the band, which concerns charge-transfer from metal to organic ligand L-1 or L-2. Summation of two absorptions leads to higher extinction coefficients. In the series of Co(L-2) with pyridine, 4-(or 3-) picoline and 3,4(or 3,5-) lutidine the electron donating methyl substituents reduce the acceptor properties of the pyridine residue and lower the extinction coefficient (and oscillator strength) of the charge-transfer band as can be seen in Fig.3 on p.90.

Strong charge-transfer from metal to ligand reduces the electron density on the metal atom. Evidently this causes complexes, even those with high Dq-values, to become insensitive towards oxygen, as is the case with Co(L-2)$(\text{pyridine})_2$. Lack of time did not allow to prepare an additional amount of active

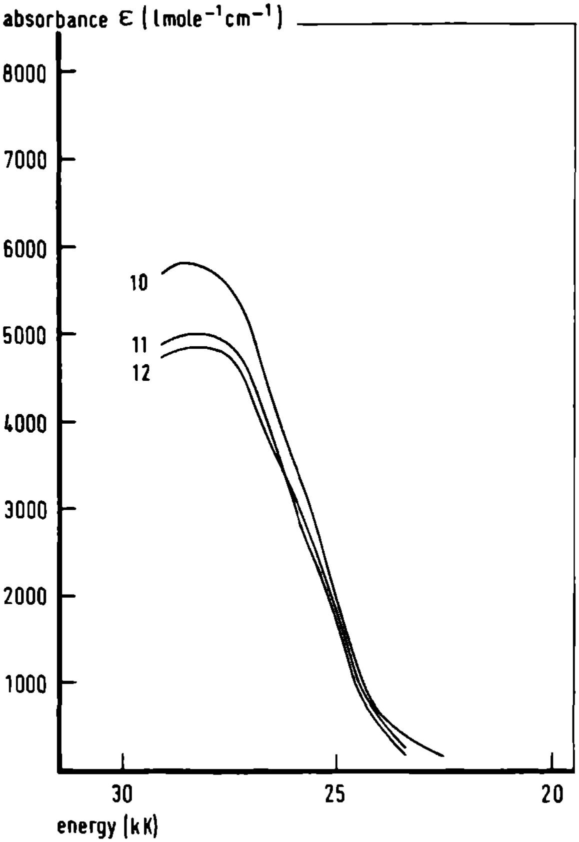


Fig.3. Absorbance of the charge-transfer band of Co(L-2) complexes. The numbers refer to the compounds mentioned in TABLE I. 10, Co(L-2) in pyridine; 11, Co(L-2) in either 3-picoline or 4-picoline; 12, Co(L-12) in either 3,4-lutidine or 3,5-lutidine.

and inactive complexes with di or triamines to test the hypothesis more thoroughly.

Co(L-1) complexes with pyridine-like bases are evident exceptions to this tentative rule. The charge-transfer band of the Co(L-1) complex in pyridine has the highest extinction coefficient and oscillator strength, suggesting strong transfer of charge *via* π-bonding, but it is sensitive towards oxygen.

The difference in reactivity between corresponding Co(L-1) and Co(L-2) complexes must be related to differences in structure. In CHAPTER III it has been supposed that the organic ligand in Co(L-1) complexes with pyridine-like base co-ordinates with the carboxylate residue, but not with the imino nitrogen, whereas in corresponding Co(L-2) complexes the -C=N- groups, but not the carboxylate residue, participates in the co-ordination. This seemed to be even the only structural difference in the bipyridyl complexes. The absence of the -C=N- group in the co-ordination sphere should reduce the transfer of charge to the ligand. It may be that the carboxylate residue, negatively charged, causes σ- and π-bonding by donation with charge-transfer from ligand to metal. Kaden and Fallab have already found that negatively oxygen-ligands in π-systems can increase sensitivity to oxygen[37,38], for some Fe^{II}-complexes. They suggest that this effect may be due to increased charge-density on the metal caused by π-bonding.

In the Co(L-1) complexes with pyridine-like bases such an effect might lead to the surprisingly high extinction coefficient of the charge-transfer band in combination with the proposed structure. This structure would consist of two donating oxygen atoms and two nitrogen atoms in conjugation with the accepting π-system in a trans position to the oxygen atoms.

The oxygen uptake of the Co-complexes

The oxygen sensitivity of the amine complexes can be tested in two ways: (1) by measuring the oxygen uptake, or (2) by recording the E.S.R. spectrum of the Co^{III}-peroxy-anion. The first method does not give certainty that the oxygen is bound to the Co, especially when more than one mole of oxygen is absorbed per Co atom.

We found that the oxygen uptake of the pyrrolidine complexes of Co(L-1) and Co(L-2) does not reach an asymptotic value.

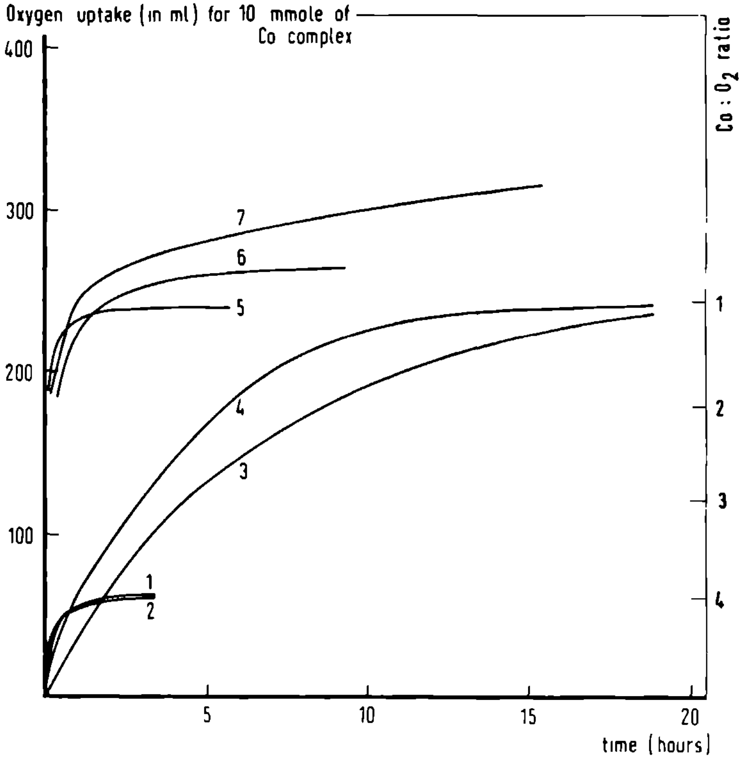


Fig.4. Oxygen uptake for some Co(L-1) and Co(L-2) complexes. 1, Co(L-2) in cyclohexylamine; 2, Co(L-2) in N-methylpiperazine; 3, Co(L-1) in pyridine; 4, Co(L-1) in 4-picoline; 5, Co(L-1) in piperidine; 6, Co(L-1) in cyclohexylamine; 7, Co(L-1) in N-methylpiperazine.

After some time the molar ratio of Co to absorbed oxygen exceeds 1:4. It is probable that in these cases the phenolic part of the ligand has been oxidized as only tar-like products could be isolated. It has been reported that phenolic compounds can be oxidized by Co-complexes[39,40].

In Fig.4 we have reproduced the oxygen uptake curves for a number of Co(L-1) and Co(L-2) amine complexes. The oxygen uptake of the cyclohexylamine and N-methylpiperazine complexes of Co(L-2) is restricted to $\frac{1}{4}$ mole of oxygen by 1 mole of Co. Such a low value is always found when transition metals are oxidized in protic solvents.

It was surprising that no one of the oxygenation products including those which had absorbed 1 mole of O_2 per Co atom showed an E.S.R. spectrum even when isolated in pure state or measured at -100°. However, an E.S.R. spectrum such as reproduced

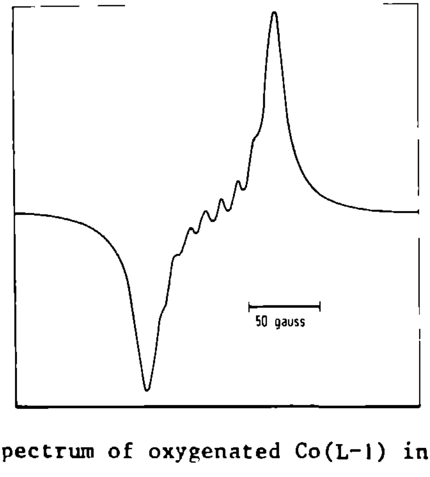


Fig.5. E.S.R. spectrum of oxygenated Co(L-1) in pyridine at -40°.

in Fig.5 for the oxygenation product of Co(L-1)(pyridine)$_3$ was found for most of our complexes, when oxygenation was carried out at approximately -40°. On warming up to room temperature the signal disappeared within a few minutes. The oxygenation is clearly followed by oxidation of the organic ligand. Starting with Co(L-2) in N-methylpiperazine and Co(L-1) in pyridine the resulting products could be obtained in pure form. They were analyzed in order to investigate what kind of process follows the initial oxygenation in complexes with Schiff bases as used in our studies and those of others.

The product resulting from the oxygenation of Co(L-2)(N-methylpiperazine)$_2$(H$_2$O)

The starting compound has the constitution: $Co(C_{10}H_9NO_3)(C_5H_{12}N_2)_2(H_2O)$. The elemental analysis was about $Co_2(C_{29}H_{48}N_6O_6)$ for the products. It is obvious that this formula cannot be built up from the tridentate ligand ($C_{10}H_9NO_3$) and the amine ($C_5H_{12}N_2$).

The I.R. spectrum differed from the starting compound mainly in the 1600 cm.$^{-1}$ region, but low resolution prevented conclusions concerning the structure. It was remarkable that the compound had a magnetic moment (4.8 BM) more or less equal to that of the aquo complexes reported in TABLE II of CHAPTER II. The electronic reflectance spectum shown in Fig.6 revals clearly that the complex is an octahedral Co^{II}-complex. The oxygen uptake, the co-ordination number, the I.R. spectrum and the elemental analysis were unsufficient to formulate a comprehensive molecular structure.

Therefore the product was treated with hydrogen sulphide to eliminate Co. In this way two organic compounds, a polar and a non polar one, were isolated.

Elemental analysis of the non polar compound revealed the

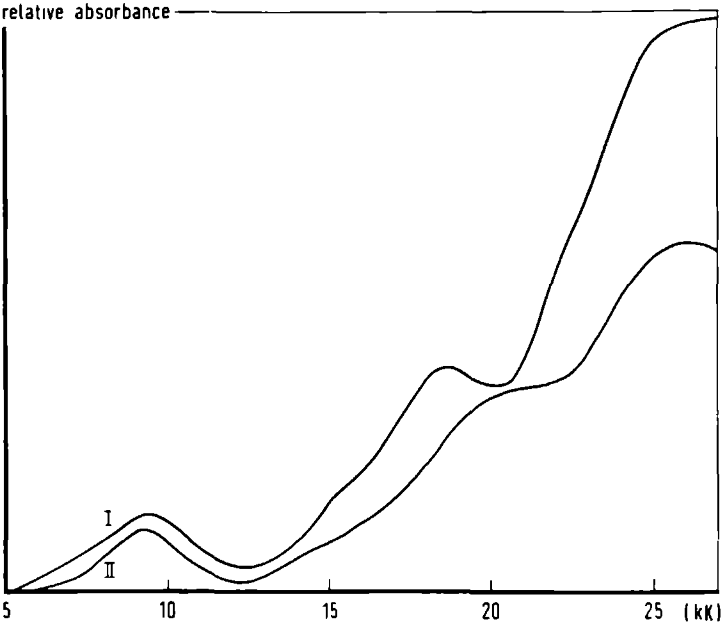
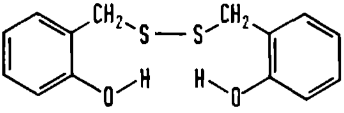


Fig.6. Reflectance spectra of the oxygenation products of: I, Co(L-2) in N-methylpiperazine; II, Co(L-1) in pyridine.

absence of nitrogen. The N.M.R. spectrum showed three kinds of protons: an aromatic group, a singlet (with $\delta \approx 4.1$) and a broad signal (with $\delta = 6.2$) which disappeared after deuteration. Their ratio was 4:2:1. Elemental analysis and the N.M.R. spectrum pointed to 2,2'-dioxydibenzyl disulfide (see formula). Apparently sulphur had been introduced during H_2S treatment.



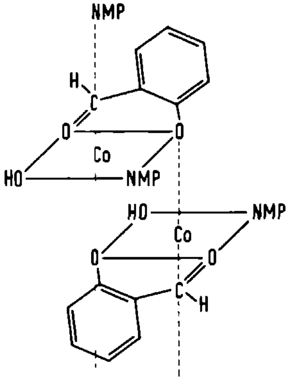
This compound has been prepared by Manchot and Zahn[41] from salicylaldehyde, ammonia and hydrogen sulphide. Therefore it may be that the product investigated contains a salicylaldiminato or salicylaldehyde group.

The polar compound could be converted into a crystalline HBr salt. Elemental analysis of the salt showed that the polar compound was N-methylpiperazine. This was confirmed by comparison of the N.M.R. and mass spectrum with an authentic sample.

Supposed constitution of the product

Even when the H_2S treatment was carried out in water no other compounds were isolated or detected than those mentioned; no residue originating from the β-alanine side chain could be recovered.

The product must (a) fit the elemental analysis, (b) it should be a six co-ordinated Co^{II}-complex, (c) it must be formed *via* an oxygen uptake of 1 mole O_2 per 4 Co, (d) it must contain N-methylpiperazine and a salicylaldiminato or a salicylaldehyde group. Although no conclusive evidence is possible concerning the composition of the product, it is certain that N-methylpiperazine is present and that the original divalent tridentate ligand (L-2) has been oxidized to a monovalent bidentate ligand (salicylaldehyde or a salicylaldimine). Because elemental analysis (Co/C about 1/14) excludes the presence of two molecules of the bidentate ligand. If the metal also coordinates with one or more amine molecules, an anion, other than the phenolic residue, must be present in the co-ordination sphere. This should be then a hydroxide ion. An acceptable structure might then be based on a composition $Co(C_7H_5O_2)(C_5H_{12}N_2)_{1.5}(OH)$ (see experimental part).



NMP=N-methylpiperazine

The product isolated on oxygenation of Co(L-1) in pyridine

Elemental analysis leads to an approximate molecular formula: Co($C_{13}H_{12}N_2O_4$). This formula has one C-atom less than Co(L-1) pyridine. As shown in Fig.6 its electronic spectrum points to an octahedral Co^{II}-compound, although it arises from a peroxo Co^{III} species in view of the E.S.R. data (see Fig.5).

I.R. data are not very clear. OH, NH, and symmetrical carboxylvibration are absent. There is strong absorption at 1630 $cm.^{-1}$ and a peak at 1685 $cm.^{-1}$.

Degradation of the compound with H_2S in water yielded a product which looked crystalline but appeared to be difficult to purify. It contained C and H, had a large O to N ratio, and was free from sulphur.

Pyridine, ammonia and oxalate were found in the degradation mixture, but there was no trace of an amino acid. The presence of the last two compounds may indicate that the aliphatic part of the original tridentate ligand has been destructed. A similar result is reported for the previous complex, the oxidation product of Co(L-2) in N-methylpiperazine.

EXPERIMENTAL

The oxygen uptake

Oxygen absorption was measured in a reaction flask connected with a gas burette. Both were held at constant temperature (25°) in order to detect with certainty the uptake of even small amounts of oxygen. Samples were prepared by dissolving an aquo or solvent-free complex in the appropriate amine under a stream of oxygen-free nitrogen. After complete dissolution (a few amines were rather insoluble) nitrogen was changed by oxygen and after connection to the gas burette and under stirring of the solution the gas uptake was measured.

The oxygenation of Co(L-2) in N-methylpiperazine

Co(L-2)(H_2O) or Co(L-2)(N-methylpiperazine)$_2$(H_2O) was dissolved in N-methylpiperazine. The solution was cooled in ice while a slow stream of oxygen was flushed over the solution under vigorous stirring. The homogeneous solution darkened and the oxygenation continued for two days. After standing for several days a light-brown crystalline product was isolated by filtration. It was washed with N-methylpiperazine and ethyl acetate.

Found	Calculated for: $Co_2(C_{29}H_{48}N_6O_6)$,M=694.38
C 48.7	C 50.0
H 6.9	H 6.9
N 12.1	N 12.1

Oxygenation product of Co(L-1) in pyridine

It was performed in a similar way as described above starting with Co(L-1) or Co(L-1)(pyridine)$_3$ in pyridine. The crystallization of the product happened more slowly.

Found	Calculated for: Co($C_{13}H_{11}N_2O_4$),M=318.18
C 48.0	C 49.0
H 3.5	H 3.46
N 9.1	N 8.8

Degradation of the oxygenation product of Co(L-2) in N-methylpiperazine

The complex was suspended in ethyl acetate and for several days a stream of H_2S was bubbled through the solution under vigorous stirring. The black precipitate (CoS) was filtered off and the solvent was evaporated from the clear solution. The oily residue consisted of two compounds as was found by thin-layer chromatography. It was dissolved in dilute HBr and extracted with ethyl acetate. The ethyl acetate layer was dried and evaporated, leaving a crystalline product which was recrystallized from diisopropylether-petroleum ether. The m.p. was 102°, reported[41] for 2,2'-dioxydibenzyldisulfide: 103.5°.

Found	Calculated for: $C_{14}H_{14}S_2O_2$,(M=278.39)
C 60.7	C 60.5
H 5.3	H 5.04

The aqueous layer was evaporated to dryness and the residue was treated with acetic acid and evaporated. This was repeated several times until a crystalline compound was obtained. The product was treated with a mixture of isopropyl alcohol-ethyl acetate and then filtered. It was recrystallized from DMF-isopropyl alcohol.

Found		Calculated for: $C_5H_{14}N_2Br_2$,(M=261.99)	
C	22.8	C	22.92
H	5.5	H	5.39
N	10.7	N	10.69
Br	61.1	Br	61.00

Degradation of the oxygenation product of Co(L-1) in pyridine

Owing to the low solubility of the complex in organic solvents the degradation could only be achieved in water. After treatment with H_2S for several days the black precipitate was filtered off and the clear filtrate was evaporated. A nearly white residue was left. It was purified by dissolution in water, filtered through activated coal and precipitated by the addition of isopropyl alcohol. The residue was probably a mixture since its composition changed upon repeated crystallization.

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SUMMARY

Various Co^{II}-complexes with mononegative bidentate and with binegative tetradentate ligands have been prepared and investigated. Complexes with this metal with binegative, tridentate ligands have not been described. We found several methods suitable to obtain such complexes in pure state with a great variety of ligands.

The ligands we have used are either Schiff bases, derived from salicylaldehyde and amino components, containing another ionizable group (carboxyl group, alcoholic or phenolic hydroxyl function), or corresponding reduction products, obtained by hydrogenation of the imino function of the Schiff bases.

With these ligands aquo complexes are usually obtained from an aqueous solution. In many cases these aquo complexes could be converted into solvent-free complexes upon treatment with a high-boiling solvent. With dimethylsulfoxide complexes could also be obtained in some cases, which contained this solvent instead of water in the co-ordination sphere.

In general these complexes are thermally very stable. Upon heating only the aquo complexes are usually transformed into corresponding water-free complexes. Magnetic measurements show that all obtained products are high-spin complexes. In only one case this was shown to be so even at -180^{o}.

On basis of their reflection spectra the series of compounds can be divided into two groups: complexes with co-ordination number 6, because the recorded spectra correlate strongly with those of known octahedral Co^{II}-complexes, and complexes with co-ordination number 5, the spectra of which resemble Co^{II}-complexes with trigonal-bipyramidal structure.

By means of I.R. spectroscopy attempts have been made to

examine for all compounds, which of the three functional groups of the organic ligand participates in co-ordination with the metal ion. Moreover by investigating their solubility in several organic solvents an impression was obtained in which compounds, a high-molecular, polymer structure, (undoubtedly in consequence of the co-ordination of certain groups with more metal atoms), had to be accepted, and in which compounds a monomeric or low-molecular structure was probable.

On basis of these data (constitution, U.V., I.R., solubility) a possible structure could be given for all compounds investigated. In some cases however this certainly needs further confirmation.

Upon reaction of the aquo complexes with an excess of an aliphatic, aromatic or heterocyclic N-base, also a great variety of amine complexes was obtained. Of these especially those complexes have been investigated which contained N-(2-hydroxybenzylidene)-glycine (L-1) or N-(2-hydroxybenzylidene)-β-alanine (L-2). This choice has been made, because the relatively small difference in the ligand structure (an additional $-CH_2-$ group in the aliphatic side chain) appeared to give rise to remarkable differences in their properties. All investigated amine complexes of Co(L-1) are sensitive to oxygen; Co(L-2) amine complexes only when an aliphatic amine is present. Co(L-2) amine complexes lose the co-ordinating amine molecules in apolar solvents, and give rise to insoluble polymeric compounds with co-ordination number 5. Under these circumstances and even at a higher temperature Co(L-1) amine complexes hold one amine molecule and give mostly octahedral high-molecular compounds.

Possible structures have been proposed for the amine complexes, in a similar way as for the aquo- and solvent-free complexes. These suggest that for Co(L-2) amine complexes the carboxyl group is more easily released whereas for Co(L-1) complexes a structure is rather formed in which the imino-nitrogen does not co-ordinate. For the bipyridyl complexes of Co(L-1) and Co(L-2), which have the same constitution, the only difference in structure seems to be lack of co-ordination of the -C=N- group in L-1 and the COO^- group with L-2.

In contrast to our aquo and solvent-free complexes many investigated amine complexes seemed sensitive to oxygen. In this case always a Co^{III}-complex with a peroxy-anion (O_2^-) is primarily formed, identifiable by a characteristic E.S.R. signal after reaction with oxygen at low temperature (-40^o). At room temperature this signal is lacking, because oxygenation is followed by oxidation of the organic ligand. In this case Co^{II}-complexes are formed again.

The oxygen sensibility of Co^{II}-complexes has been correlated by several authors with various parameters related to the charge density on the metal atom. We have examined whether in our compounds the crystal field parameters (10Dq) can be used for this purpose. With comparable complexes containing solvent molecules, which give no π-interaction with the Co ion (in contrast to *e.g.* pyridine), this appears to be a useful criterium. Complexes, which are sensitive to oxygen, in general those with aliphatic amines, exhibit greater 10Dq values (9500 $cm.^{-1}$) than aquo complexes, which are insensitive to oxygen.Complexes with pyridine bases (with Co(L-2)) exhibit great 10Dq values but no sensitivity to oxygen. It has been supposed that in consequence of π-interaction charge is transferred from metal to base. Further investigations have been made concerning the occurence of π-interaction by means of the charge-transfer bands of the relevant complexes.

Using this conception the oxygen sensibility of Co(L-1) complexes with pyridine like bases remains quite surprising. We suppose that this is related to the accepted structure lacking co-ordination of the imino group. For *via* the -C=N- group (and not *via* the COO^- group) charge-transfer from metal to ligand is possible, but this possibility is lacking for the Co(L-1) complexes involved.

SAMENVATTING

Diverse complexen van Co^{II} met eenwaardige bidentale en met tweewaardige tetradentale liganden zijn bereid en onderzocht. Complexen van dit metaal met tweewaardige tridentale liganden zijn nog niet beschreven. Wij hebben een aantal methoden gevonden die het mogelijk maken dergelijke complexen met een grote verscheidenheid van liganden in zuivere toestand te verkrijgen.

De door ons gebruikte liganden zijn ofwel Schiff-basen, afgeleid van salicylaldehyde en amine-componenten, die nog een ioniseerbare groep (carbonzuur-groep, alcoholische of fenolische hydroxyl-functie) bevatten, ofwel overeenkomstige reductieproducten, die door hydrering van de imine-functie uit de Schiff-basen verkregen zijn.

Uit een waterige oplossing worden met deze liganden meestal aquo-complexen verkregen. Door behandeling met een hoog-kokend oplosmiddel konden deze aquo-complexen in vele gevallen in solvent-vrije complexen worden omgezet. Met dimethylsulfoxyde konden in enkele gevallen ook complexen verkregen worden, waarin dit oplosmiddel in plaats van water in de coordinatie-sfeer was opgenomen.

In het algemeen zijn deze complexen thermisch zeer stabiel. Bij verhitting gaan alleen de aquo-complexen meestal over in overeenkomstige water-vrije complexen. Uit magnetische metingen blijkt dat alle verkregen producten high-spin complexen zijn. In een enkel geval is aangetoond dat dit ook bij -180° nog het geval is.

Op grond van hun reflectie-spectra valt de reeks verbindingen uiteen in twee groepen: complexen waarin het coordinatie-getal 6 bedraagt, omdat de gemeten spectra sterk overeenstemmen met die van bekende octaëdrische Co^{II}-complexen, en complexen met coordinatie-getal 5, waarvan de spectra gelijken op Co^{II}-complexen met een trigonaal-bipyramidale structuur.

Met behulp van I.R. spectrophotometrie is getracht voor alle verbindingen na te gaan, welk van de drie functionele groepen uit de organische ligand in coordinatie met het metaal-ion participeert. Bovendien is door onderzoek van hun oplosbaarheid in diverse organische oplosmiddelen een indruk verkregen, in welke verbindingen een hoog-moleculaire, polymere structuur (ongetwijfeld ten gevolge van het coordineren van bepaalde groepen met meer metaalatomen) moest worden aangenomen, en in welke verbindingen een monomere, laag-moleculaire structuur waarschijnlijk was.

Op grond van al deze gegevens (samenstelling, U.V., I.R., oplosbaarheid) kon voor alle onderzochte verbindingen een waarschijnlijke structuur worden aangegeven. In een aantal gevallen dient dit echter zeker nog nader bevestigd te worden.

Door de aquo-complexen met een overmaat van een alifatische, aromatische of heterocyclische N-base te laten reageren is ook een grote verscheidenheid aan amine-complexen verkregen. Hiervan zijn vooral die complexen onderzocht, waarin als organische ligand N-(2-hydroxybenzylideen)-glycine (L-1) of N-(2-hydroxybenzylideen)-β-alanine (L-2) voorkomt.Deze keuze is gemaakt, omdat het betrekkelijk kleine verschil in de ligand-structuur (een extra $-CH_2-$ groep in de alifatische zijketen van L-2) tot opmerkelijke verschillen in hun eigenschappen bleek te kunnen leiden. Alle onderzochte Co(L-1) amine-complexen zijn gevoelig voor zuurstof; Co(L-2) amine-complexen alleen als een alifatische amine aanwezig is. Co(L-2) amine-complexen laten in apolair milieu de coordinerende amine moleculen los en geven dan onoplosbare polymere verbindingen met coordinatie-getal 5;

Co(L-1) amine-complexen houden onder deze omstandigheden, zelfs bij hogere temperatuur, een amine molecuul vast en geven meestal octaëdrische hoog-moleculaire verbindingen.

Op dezelfde wijze als voor aquo- en solvent-vrije complexen zijn ook voor de amine-complexen waarschijnlijke structuren vastgesteld. Deze voeren tot de veronderstelling, dat bij de Co(L-2) amine-complexen de carboxylaat-groep gemakkelijker losraakt, terwijl bij de Co(L-1) complexen eerder een structuur ontstaat waarin de imine-stikstof niet coordineert. Bij de bipyridyl-complexen die met Co(L-1) en Co(L-2) dezelfde samenstelling hebben, lijkt het enige verschil in structuur juist daarin te bestaan, dat met L-1 de -C=N- groep en L-2 de COO^- groep niet coordineert.

In tegenstelling tot de aquo- en solvent-vrije complexen bleken vele onderzochte amine-complexen gevoelig voor zuurstof. Hierbij ontstaat altijd primair een Co^{III}-complex met een peroxi-anion (O_2^-), herkenbaar aan een karakteristiek E.S.R. signaal als men zuurstof bij lage temperatuur (-40^o) laat inwerken. Bij kamertemperatuur ontbreekt dit E.S.R. signaal, omdat de oxygenering door oxydatie van de organische ligand wordt gevolgd. Hierbij ontstaan weer Co^{II}-complexen.

Door verschillende auteurs is de zuurstof-gevoeligheid van Co^{II}-complexen in verband gebracht met diverse grootheden, die gerelateerd zijn aan de ladingsdichtheid op het metaalatoom. Wij hebben nagegaan of hiervoor in onze verbindingen de kristalveld-parameter (10Dq) kan worden gebruikt. Bij vergelijkbare complexen, die solvens-moleculen bevatten die geen π-interactie met het Co ion geven (in tegenstelling tot b.v. pyridine), blijkt dit een bruikbaar criterium. Zuurstof-gevoelige complexen (in het algemeen die met alifatische aminen) hebben hogere Dq waarden ($9500\ cm.^{-1}$) dan zuurstof-ongevoelige aquo-complexen. Complexen met pyridine-basen (met Co(L-2)) vertonen hoge 10 Dq-waarden, maar geen zuurstof-gevoeligheid. Verondersteld is, dat ten gevolge van π-interaktie lading van metaal naar base wordt teruggevoerd. Het vóórkomen van π-interaktie is nader onderzocht aan de hand van de charge-transfer banden der betrokken complexen.

Bij deze voorstelling blijft de zuurstof-gevoeligheid van Co(L-1) complexen met pyridine-achtige basen een verrassend gegeven. Wij veronderstellen, dat dit samenhangt met de aangenomen structuur, waarin de imine-groep niet coordineert. *Via* de -C=N- groep(en niet *via* de COO^- groep) is immers ook ladingsoverdracht van metaal naar organische ligand mogelijk, maar deze mogelijkheid ontbreekt bij de bedoelde Co(L-1) complexen.

CURRICULUM VITAE

Na de middelbare school werd door de schrijver van dit proefschrift in 1953 een begin gemaakt met de studie aan de H.T.S. te Eindhoven, richting chemie. In 1956 werd het einddiploma behaald. In augustus van dat jaar trad hij in dienst van de Medische Faculteit te Nijmegen op de toenmalige afdeling Physiologische Chemie. Onder leiding van Professor Nivard werd met Dr.G.I.Tesser onderzoek verricht op het gebied van aminozuren en aminozuur derivaten. Dit resulteerde in een achttal publicaties.

Bij het begin van de studie scheikunde in 1962 werd de schrijver overgeplaatst naar de Faculteit der Wiskunde en Natuurwetenschappen. In 1965 werd het kandidaatsexamen behaald, in 1967 het doctoraal examen.

Het aanvankelijk onderzoek betreffende mononegatieve tridentale liganden vormde het begin van in dit proefschrift beschreven onderzoekingen aan dinegatieve tridentale liganden.

STELLINGEN

I

De geringe racemisatie van N-hydroxypiperidine-esters van N-acyl-aminozuren kan op een meer inzichtelijke wijze verklaard worden dan Young heeft gedaan.

G.T.Young, in Peptides, North-Holland Publishing Co, Amsterdam, 1969. p. 55.

II

De bewering dat $CoCl_2.2SbCl_5.6POCl_3$ een octaëdrische structuur zou hebben, is onvoldoende aangetoond.

W.L. Driessen en W.L. Groeneveld, Rec. Trav. Chim., 87 (1968) 786.

III

Er is onvoldoende rekening gehouden met de mogelijkheid dat 1:1 Co^{II}-complexen met tridentale dinegatieve liganden zouden bestaan.

IV

Ruttenberg heeft bij de semi-synthese van menselijke insuline onvoldoende aangetoond dat zijn eindproduct beter geschikt zou zijn voor klinisch gebruik dan de geïsoleerde dierlijke insuline.

M.A. Ruttenberg, Science, 177 (1972) 623.

V

Zolang een aantal Schiff-base complexen met Fe^{II} nog onvoldoende gekarakteriseerd zijn, moet getwijfeld worden aan de zin van het toepassen van Mossbauer-spectroscopie op deze verbindingen.

R.A. Stukan, V.I. Goldanskii, E.F. Makarov en E.G. Rukadze, Zhurn. Strukt. Khim. 8 (1965) 239.
J.L.K.F. de Vries, J.M. Trooster en E. de Boer, Chem. Communs., (1970) 604.

VI

De bewering van Luh en Stock dat zij de synthese van het kubaan systeem volgens de methode van Eaton en Cole zonder moeilijkheden hebben nagewerkt, moet met grote reserve worden beschouwd.

T.Y. Luh, en L.M. Stock, J. Org. Chem., 37 (1972) 338.
P.E. Eaton en T.W. Cole, Jr., J. Am. Chem. Soc., 86 (1964) 962.

VII

Het is een grove wijze van verspilling in een personen auto met een motorvermogen van meer dan 70 SAE pK te rijden. Omdat veel mensen aan deze verleiding geen weerstand kunnen bieden, is het beter deze motoren niet te produceren, of ze fiscaal zeer zwaar te belasten.

VIII

Het is niet noodzakelijk dat de letterzetter bij het opstellen van een regel rekening houdt met het einde van een woord of een lettergreep, daar de fixatiepauses van het oog tijdens het leesproces zich letterlijk niet aan deze regel houden.

IX

De cultuur van eten en tafelen bevindt zich in Nederland in een primitief stadium; wat dat betreft valt van "la douce France" nog veel te leren.

Nijmegen, 16 maart 1973 G.H.L. NEFKENS