Embracing ligands. A synthetic strategy towards new nitrogen–thioether multidentate ligands and characterization of the cobalt(III) complexes

Clint A. Sharrad, Stefan R. Lüthi† and Lawrence R. Gahan*

*Chemistry Department, The University of Queensland, Brisbane, QLD 4072, Australia.
E-mail: gahan@mailbox.uq.edu.au*

The synthesis of the hexadentate ligand 2,2,9,9-tetra(methyleneamine)-4,7-dithiadecane (EtN_4S_2amp) is reported. The ligand is of a type in which bifurcations of the chain occur at atoms other than donor atoms. The cobalt(III) complex [Co(EtN_4S_2amp)]$^{3+}$ (**1**) was isolated and characterized. The synthetic methodology also results in a number of by-products, notably 2,9,9-tris(methyleneamine)-9-methylenehydroxy-4,7-dithiadecane ($Et(HO)N_3S_2amp$) and an eleven-membered pendant arm macrocyclic ligand 6,10-dimethyl-6,10-bis(methyleneamine)-1,4-dithia-8-azacyclo-undec-7-ene (dmatue). The complexes [Co($Et(HO)N_3S_2amp$)]$^{3+}$ (**2**), in which the alcohol is coordinated to the metal ion, and [Co(dmatue)Cl]$^{2+}$ (**4**) were isolated and characterized. $Et(HO)N_3S_2amp$ also undergoes complexation with cobalt(III) to produce two isomers *endo*-[Co($Et(HO)N_3S_2amp$)Cl]$^{2+}$ (*endo*-**3**) and *exo*-[Co($Et(HO)N_3S_2amp$)Cl]$^{2+}$ (*exo*-**3**), both with an uncoordinated alcohol group. *endo*-**3** has the alcohol positioned *cis*, and *exo*-**3** *trans*, to the sixth metal coordination site. Reaction of **1** with isobutyraldehyde, paraformaldehyde and base in dimethylformamide results in the encapsulated complex [Co(1,5,5,9,13,13-hexamethyl-18,21-dithia-3,7,11,15-tetraazabicyclo[7.7.6]-docosa-3,14-diene)](ClO_4)$_3$·2H_2O ([Co($Me_6docosadieneN_4S_2$)]$^{3+}$ (**5**). All complexes have been characterized by single crystal X-ray study. The low-temperature (11 K) absorption spectrum of **1** has been measured in Nafion films with spin-allowed $^1A_{1g} \rightarrow {}^1T_{1g}$ and $^1A_{1g} \rightarrow {}^1T_{2g}$ and spin forbidden $^1A_{1g} \rightarrow {}^3T_{1g}$ and $^1A_{1g} \rightarrow {}^3T_{2g}$ bands observed. The octahedral ligand-field parameters were determined ($10Dq$ = 22570 cm^{-1}; B = 551 cm^{-1}; C = 3500 cm^{-1}). For **5** $10Dq$ and B were determined (20580 cm^{-1}; 516 cm^{-1}, respectively) and compared with those for similar expanded cavity complexes [Co($Me_8tricosatrieneN_6$)]$^{3+}$ and [Co($Me_5tricosatrieneN_6$)]$^{3+}$.

Introduction

The design and application of hexadentate ligands has been of interest ever since Lions proposed thirty-six different ligand topologies for the hexadentate donor set.[1,2] Numerous examples of the hexadentate ligand type have been reported and in many cases the interest has been their application as precursors for the synthesis of fully encapsulated complexes.[3–14] One ligand topology described by Lions was that in which bifurcations of the chain occur at atoms other than donor atoms.[1,2] Our interest in this particular ligand topology arises from the intrinsic chemistry, and that of the metal complexes formed from them.[15,16] The application of this ligand topology for further synthetic elaboration enabling the synthesis of encapsulating ligands with larger cavities and a larger variety of donor groups is also of interest. The synthesis and characterization of two new examples of this ligand topology, herein called amplector ligands (Latin: *to embrace*) is now reported. Although the synthetic methodology reported allows for variations in the donor type and the chelate ring size, the present work confines itself to the synthesis of a particular mixed nitrogen–thioether ligand 2,2,9,9-tetra(methylene-amine)-4,7-dithiadecane (EtN_4S_2amp) and its cobalt(III) complex. Subsequent elaboration to prepare an encapsulating ligand, as the cobalt(III) complex, is also reported.

The ligands discussed in this work are shown in Chart 1.

EtN₄S₂amp   Et(HO)N₃S₂amp

dmatue   Me₆docosadieneN₄S₂

Chart 1

Results and discussion

Nomenclature

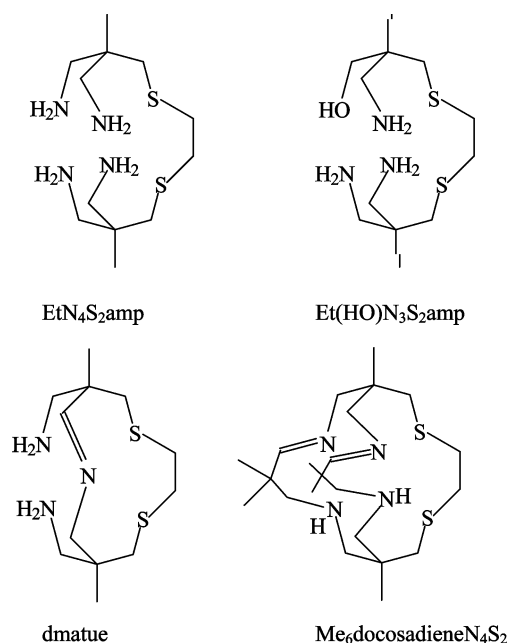The abbreviated nomenclature for the amplector (amp) ligand can be considered in terms of the donor set and a hinge moiety connecting them. Thus, for EtN_4S_2amp (2,2,9,9-tetra(methyl-eneamine)-4,7-dithiadecane) the prefix Et denotes the ethyl hinge and N_4S_2 refers to the tetraamine–dithioether donor set of the ligand. The same nomenclature applies for the major synthetic by-product $Et(OH)N_3S_2amp$ (2,9,9-tris(methylene-amine)-9-methylenehydroxy-4,7-dithiadecane) with a possible chromophore of three primary amines, two thioether donors and an alcohol. In both cases the final two atoms referred to as (S_2) denote the donor atoms of the hinge moiety. The nomenclature employed to describe the encapsulated complex

$Me_6docosadieneN_4S_2$ is similar to that used to describe the expanded hexaaza cage complexes.[17,18]

The abbreviation dmatue employed for the eleven-membered macrocyclic ligand 6,10-dimethyl-6,10-bis(methyleneamine)-1,4-dithia-8-azacycloundec-7-ene is not systematic.

Synthesis of ligands and complexes

The potentially hexadentate ligand EtN_4S_2amp was synthesized by a reaction sequence (Scheme 1) in which 1,3-(dimethylmethylenedioxy)-2-methyl-2-(methylene-*p*-tolylsulfonyl)propane [19] is reacted with the sodium salt of 1,2-ethanedithiol. Removal of the acetal protecting groups, under acidic conditions, resulted in the tetrahydroxy product. Conversion to the corresponding sulfonyl ester and reaction with potassium phthalimide in diglyme at 150 °C resulted in the tetraphthalimide.[20,21] The phthalimide groups were removed as described previously.[20] We have found that multidentate ligands of this type cannot easily be purified; distillation invariably results in pyrolysis and chromatographic methods are relatively inefficient.[9,10,14] The most convenient manner in which to produce a pure sample of the ligand is to prepare and characterize the cobalt(III) complex.[9,10,14]
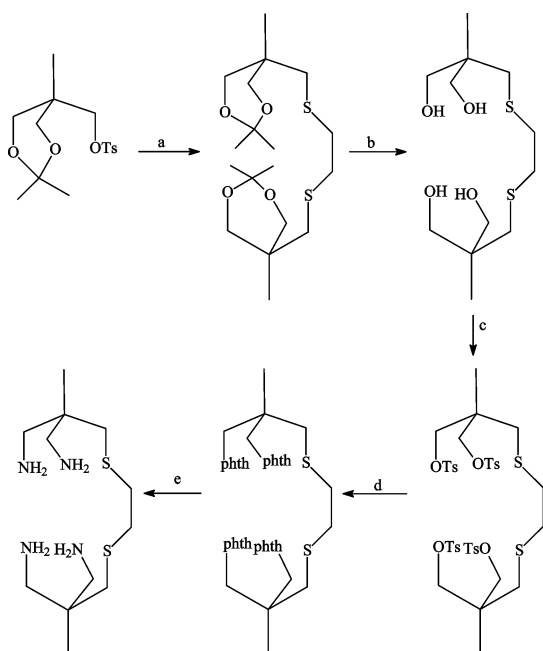
Scheme 1 Synthetic strategy for the formation of EtN_4S_2amp. (a) $HSCH_2CH_2SH$ (0.5 eq.)/Na (1 eq.)/ethanol; (b) H^+, ethanol; (c) toluenesulfonyl chloride (4.4 eq.)/pyridine; (d) potassium phthalimide (4.4 eq.)/diglyme/150 °C; (e) hydrazine hydrate (excess)/ethanol/HCl.

Reaction of EtN_4S_2amp with cobalt(II) and oxygen resulted in the major product $[Co(EtN_4S_2amp)]Cl_3$ ($1 \cdot Cl_3$), isolated as an orange band after chromatographic purification. The chromatography also resulted in the elution of a series of coloured bands preceding the major product. A red–brown band was identified by microanalysis, NMR spectroscopy and X-ray crystallography as $[Co(Et(HO)N_3S_2amp)]Cl(ClO_4)_2$ ($2 \cdot Cl(ClO_4)_2$), a complex with a N_3OS_2 chromophore where the HO is bound to the metal ion. The precursor for the $Et(HO)N_3S_2amp$ ligand is most likely formed in the reaction between 2,2,9,9-tetra-(methylene-*p*-toluenesulfonyl)-4,7-dithiadecane and potassium phthalimide in diglyme. A similar by-product leading to 2,2-bis(aminomethyl)propan-1-ol was isolated in the synthesis of tame (1,1,1-tris(aminomethyl)ethane).[22] A spectrophotometric-pH titration of **2** in water (0.1 M Et_4NClO_4; pH 2–5) showed that the position of λ_{max} shifts to higher wavelengths with increasing pH (476 nm at pH 2; 494 nm at pH 5). Titration with acid (0.1 M Et_4NClO_4; pH 5–2) using the same solution shows

the reversibility of this protonation process. The average fit to the data [23] for the forward and back titrations provides a pK_a of 2.8(1). Similar shifts in the $^1A_{1g} \rightarrow {}^1T_{1g}$ transition are observed on the deprotonation of Co(III) aminoalcohol complexes,[24] and are assigned to the deprotonation of a coordinated alcohol group to a coordinated O^- species.

The ligand $Et(OH)N_3S_2amp$ can function as a pentadentate ligand (N_3S_2 chromophore) which can adopt two major conformations, the *endo* isomer, where the unbound alcohol group is positioned *cis* to the sixth metal coordination site and the other, the *exo*-isomer, where the unbound alcohol group is positioned *trans*. *endo*-$[Co(Et(HO)N_3S_2amp)Cl]^{2+}$ (*endo*-**3**) where the coordination sphere is completed by a bound Cl^- ligand, was found to be the predominant product in the initial fractions eluted from Sephadex cation exchange resin with 0.2 M NaCl. The *exo*-$[Co(Et(HO)N_3S_2amp)Cl]^{2+}$ (*exo*-**3**) complex was isolated in extremely low yield from the tail of the same band. The formation of the *endo*- and *exo*-**3** complexes can be understood in terms of the possible sequence of steps involved in the complexation. In the case of a multidentate ligand with an amine donor at the apex (*e.g.* tren; tris(2-aminoethyl)amine), the nitrogen can readily invert to accommodate the sequence of chelation. For ligands with a carbon apex such ready inversion is not possible once two donors are attached. Chelation of the OH in *endo*-**3** would result in the OH *trans* to the thioether. The observed structure of *endo*-**3** (*vide infra*) suggests that the thioether donor labilises this site leading to replacement of OH by chloride.

The complex $[Co(dmatue)Cl]^{2+}$ (**4**) was isolated in low yield from the first fractions of the eluent from Sephadex cation exchange resin (0.2 M NaCl). The ligand is an eleven-membered pendant arm macrocycle containing an imine in the ring. One proposal as to the origin of this ligand arises from an intramolecular reaction between an aldehyde and a neighbouring amine. Cobalt(II) nitrate has been shown to act as a mild oxidising agent in the low yielding (9%) conversion of cyclodecanol to cyclodecanone.[25] Thus, formation of the aldehyde may arise from $Et(HO)N_3S_2amp$ by reaction with Co^{2+} prior to, or in association with, complexation and subsequent reaction with a neighbouring primary amine.

The metal complex **1** presents opportunities for further synthetic elaboration about the pseudo-C_2 axis, through the four primary amine donors, in a similar manner to the encapsulation reactions of $[Co(tame)_2]^{3+}$.[17,18] These encapsulation reactions are different to those reported for hexaamine complexes, and the mixed thioether/amine analogues where the reaction occurs around the (pseudo) C_3 axis.[9,10,14,26] The imine cage complex $[Co(Me_6docosadieneN_4S_2)]^{3+}$ (**5**) was synthesized from a metal template strategy using **1** with paraformaldehyde in the presence of isobutyraldehyde and base. The imine complex proved difficult to reduce cleanly to the saturated analogue using previously described methodologies.[17,18] Invariably the reactions were low yielding and the products obtained indicative of ligand decomposition under the conditions employed ($NaBH_4$, base).[17,18]

Structures

The structures of **1** and **2** consist of the complex cation (Figs. 1 and 2, respectively), a single chloride anion and two perchlorate anions. For **1** the cobalt atom is coordinated to four primary amine and two thioether donors in an octahedral geometry; the cobalt atom lies on a two-fold axis. In **2** the cobalt is coordinated to three amine, one alcohol and two thioether donors. Attempts to crystallize **2** in its deprotonated form were not successful. The complex cations **1** and **2** have a conformation with the C–C bond of the five-membered dithio-chelate ring parallel (*lel*)[27] to the pseudo-C_3 axis and the remaining six-membered chelate rings all adopt the unsymmetrical skew boat conformation.

Table 1 Crystal data

	$1\cdot Cl(ClO_4)_2$	$2\cdot Cl(ClO_4)_2$	$endo\text{-}3\cdot Cl(PF_6)\cdot\frac{1}{2}H_2O$	$exo\text{-}3\cdot Cl(ClO_4)$	$4\cdot(ClO_4)_2\cdot H_2O$	$5\cdot(ClO_4)_3\cdot 2H_2O$
Empirical formula	$C_{12}H_{30}Cl_3CoN_4O_8S_2$	$C_{12}H_{29}Cl_3CoN_3O_9S_2$	$C_{12}H_{30}Cl_2CoF_6N_3O_{1.5}PS_2$	$C_{12}H_{29}Cl_3CoN_3O_5S_2$	$C_{12}H_{27}Cl_3CoN_3O_9S_2$	$C_{22}H_{46}Cl_3CoN_4O_{14}S_2$
M_r	587.80	588.78	579.31	524.78	586.77	820.03
Crystal system	Orthorhombic	Orthorhombic	Monoclinic	Triclinic	Monoclinic	Monoclinic
Space group	$Pbcn$	$Pna2_1$	$C2/c$	$P\bar{1}$	$P2_1/a$	$P2_1/c$
a/Å	7.6249(5)	17.731(1)	30.357(5)	7.1319(8)	14.079(4)	12.700(1)
b/Å	16.779(3)	16.766(1)	6.908(1)	10.5300(9)	10.515(2)	16.637(1)
c/Å	17.683(1)	7.620(2)	21.547(5)	14.864(2)	15.043(2)	16.102(2)
α/°				74.432(8)		
β/°			102.07(2)	83.163(9)	96.18(2)	94.70(1)
γ/°				82.573(8)		
V/Å³	2262.3(4)	2265.3(6)	4418.6(14)	1062.1(2)	2214.0(8)	3390.8(5)
Z	4	4	8	2	4	4
D_c/g cm⁻³	1.726	1.726	1.742	1.641	1.760	1.606
μ/cm⁻¹	13.44	13.45	13.42	14.10	13.76	9.35
$F(000)$	1216	1216	2376	544	1208	1712
T/K	293(2)	293(2)	293(2)	293(2)	293(2)	293(2)
λ/Å	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073
$R\,(F_o)$	0.0471	0.0462	0.0484	0.0566	0.0384	0.0680
R_w	0.0813	0.0588	0.1575	0.0643	0.0565	0.3422

Table 2 Selected interatomic distances (Å) and angles (°) for $1\cdot Cl(ClO_4)_2$

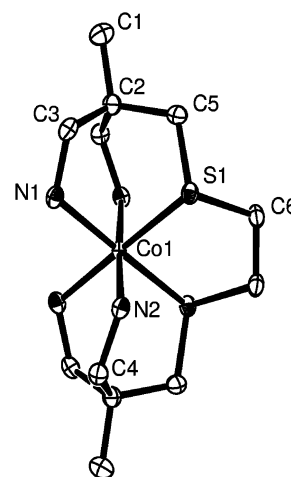|			
Co(1)–N(1)	1.987(4)	Co(1)–N(2)	1.981(4)
Co(1)–S(1)	2.2159(13)		
N(1)–Co(1)–N(1)#1	88.8(2)	N(2)–Co(1)–N(1)#1	89.00(16)
N(1)–Co(1)–S(1)	90.79(12)	N(2)–Co(1)–S(1)#1	90.04(11)
N(1)–Co(1)–S(1)#1	177.13(12)	N(2)#1–Co(1)–N(2)	177.5(2)
N(2)–Co(1)–N(1)	92.80(16)	S(1)–Co(1)–S(1)#1	89.72(7)
N(2)–Co(1)–S(1)	88.17(12)		

Fig. 1 ORTEP plot of the complex cation **1**, with crystallographic numbering. Probability ellipsoids of 30% are shown.
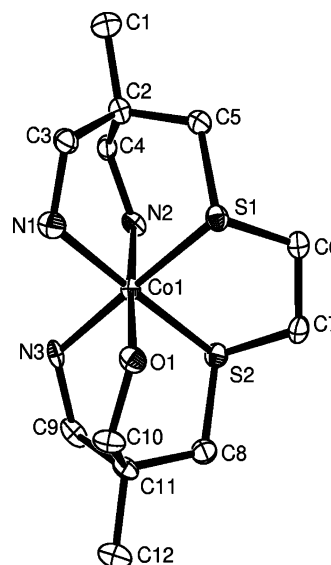

Fig. 2 ORTEP plot of the complex cation **2**, with crystallographic numbering. Probability ellipsoids of 30% are shown.

For **1** (crystal data, Table 1) the Co–N and Co–S bond lengths (1.987(4) and 1.981(4) Å; 2.2159(13) Å, respectively (Table 2)) are similar to those reported for the hexadentate complex $[Co(N_4S_2)]^{3+}$ (N_4S_2 = 5-(4-amino-2-azabutyl)-5-methyl-3,7-dithianonane-1,9-diamine) (Co–N: 1.985(5), 1.975(5), 1.979(5),1.993(5) Å; Co–S: (2.218(2), 2.205(2) Å)[13] and appear typical of the normal range of Co–N and Co–S bond lengths for cobalt(III) complexes of this type (Co–N:1.94–2.01 Å; Co–S: 2.194(5)–2.275(3) Å).[12–14,28]

For **2** the Co–N bond lengths (Table 3) for the bonds *trans* to the sulfur atoms (1.975(7), 1.989(6) Å) are similar to the Co–N bond lengths for **1** but that *trans* to the oxygen atom (1.946(7) Å) is slightly shorter. The Co–O bond length (1.955(7) Å) falls within the range for Co(III) bonds with alcohol groups in multi-dentate ligands (1.898(1)–1.979(8) Å).[29–31] The similar ranges

Table 3 Selected interatomic distances (Å) and angles (°) for 2·Cl(ClO₄)₂

Co(1)–N(1)	1.975(7)	Co(1)–S(1)	2.228(2)
Co(1)–N(2)	1.946(7)	Co(1)–S(2)	2.219(2)
Co(1)–N(3)	1.989(6)	Co(1)–O(1)	1.955(7)
N(1)–Co(1)–N(3)	88.8(2)	N(3)–Co(1)–S(1)	175.4(3)
N(1)–Co(1)–S(1)	90.3(2)	N(3)–Co(1)–S(2)	91.8(2)
N(1)–Co(1)–S(2)	178.2(2)	S(2)–Co(1)–S(1)	89.28(6)
N(2)–Co(1)–N(1)	89.7(3)	O(1)–Co(1)–N(1)	92.1(3)
N(2)–Co(1)–N(3)	94.5(3)	O(1)–Co(1)–N(3)	87.8(3)
N(2)–Co(1)–S(1)	90.0(2)	O(1)–Co(1)–S(1)	87.7(2)
N(2)–Co(1)–S(2)	88.6(2)	O(1)–Co(1)–S(2)	89.60(19)
N(2)–Co(1)–O(1)	177.08(19)		

Table 4 Selected interatomic distances (Å) and angles (°) for endo-3·Cl(PF₆)·½H₂O

Co(1)–N(1)	1.973(5)	Co(1)–S(1)	2.202(2)
Co(1)–N(2)	1.968(6)	Co(1)–S(2)	2.2348(19)
Co(1)–N(3)	1.986(6)	Co(1)–Cl(1)	2.281(2)
N(1)–Co(1)–N(3)	88.7(2)	N(3)–Co(1)–S(2)	95.92(15)
N(1)–Co(1)–S(1)	89.90(18)	S(1)–Co(1)–S(2)	88.10(7)
N(1)–Co(1)–S(2)	175.00(17)	N(1)–Co(1)–Cl(1)	93.03(17)
N(2)–Co(1)–N(1)	87.1(2)	N(2)–Co(1)–Cl(1)	86.96(17)
N(2)–Co(1)–N(3)	173.7(2)	N(3)–Co(1)–Cl(1)	88.65(17)
N(2)–Co(1)–S(1)	94.15(17)	S(1)–Co(1)–Cl(1)	176.92(8)
N(2)–Co(1)–S(2)	88.47(16)	S(2)–Co(1)–Cl(1)	89.06(7)
N(3)–Co(1)–S(1)	90.47(18)		

Table 5 Selected interatomic distances (Å) and angles (°) for exo-3·Cl(ClO₄)

Co(1)–N(1)	1.969(4)	Co(1)–S(1)	2.2012(11)
Co(1)–N(2)	1.973(4)	Co(1)–S(2)	2.2272(12)
Co(1)–N(3)	1.980(4)	Co(1)–Cl(1)	2.2771(11)
N(1)–Co(1)–N(2)	87.72(16)	N(3)–Co(1)–S(2)	95.27(11)
N(1)–Co(1)–N(3)	88.14(16)	S(1)–Co(1)–S(2)	88.39(4)
N(1)–Co(1)–S(1)	90.91(11)	N(1)–Co(1)–Cl(1)	93.02(11)
N(1)–Co(1)–S(2)	176.51(12)	N(2)–Co(1)–Cl(1)	87.65(12)
N(2)–Co(1)–N(3)	174.27(14)	N(3)–Co(1)–Cl(1)	88.61(12)
N(2)–Co(1)–S(1)	94.39(12)	S(1)–Co(1)–Cl(1)	175.65(5)
N(2)–Co(1)–S(2)	88.92(11)	S(2)–Co(1)–Cl(1)	87.80(4)
N(3)–Co(1)–S(1)	89.64(11)		

for Co(III)–amine and Co(III)–alcohol bond lengths means that the oxygen atom in **2** cannot be distinguished from the nitrogen atoms based on coordination bond lengths alone. However, the oxygen atom can be distinguished by comparing the C–O bond length (1.463(9) Å) with the C–N bond lengths (1.485(3) Å average). The Co–S bond lengths (2.228(2), 2.219(2) Å) are similar to those for **1** (2.2159(13) Å).

The structures of the complex cations of endo-**3** and exo-**3** (Figs. 3 and 4(a) and (b), respectively) show a N₃S₂Cl donor set with the alcohol group not coordinated. The amine donors are
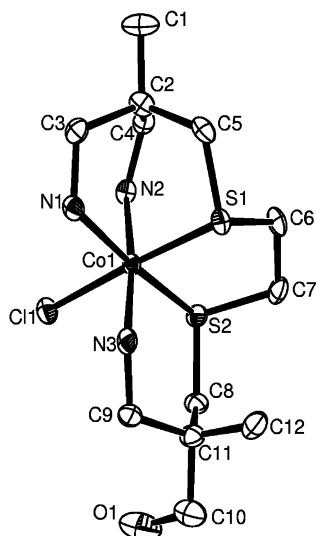
Fig. 3 ORTEP plot of the complex cation endo-**3** with crystallographic numbering. Probability ellipsoids of 30% are shown.
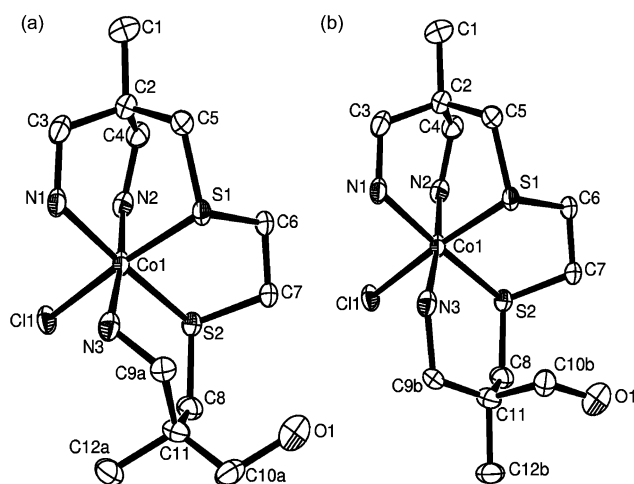
Fig. 4 (a) ORTEP plot of the complex cation exo-**3** – boat form, with crystallographic numbering. Probability ellipsoids of 30% are shown. (b) ORTEP plot of the complex cation exo-**3** – chair form, with crystallographic numbering. Probability ellipsoids of 30% are shown.

arranged meridonially as opposed to **2** where the amine donors adopt a facial conformation. The structure of endo-**3** consists of the complex cation, a chloride anion, a hexafluorophosphate anion and a water molecule positioned on a site of symmetry such that it has a unit cell occupancy of 50%. exo-**3** was crystallized as a mixed chloride/perchlorate salt, and the structure shows the complex cation disordered, with each form having a ~50% occurrence within the unit cell. In one structure, the six-membered chelate ring at the alcohol apex has a boat conformation while in the second form the same chelate ring has a chair conformation. The structures of endo- and exo-**3** are otherwise identical with the five-membered dithio-chelate rings having the lel form. As might be expected, the coordination spheres for endo- and exo-**3** exhibit very few differences in terms of bond lengths and bond angles (Tables 4 and 5, respectively). The Co–N bond lengths for both endo (1.973(5), 1.968(6), 1.986(6) Å) and exo (1.969(4), 1.973(4), 1.980(4) Å) isomers fall within the expected range for Co(III)–amine bonds (1.94–2.01 Å).[12–14,28] The Co–S bond length for the thioether trans to the chloride group (endo, 2.202(2) Å; exo, 2.2012(11) Å) is found to be slightly shorter in comparison to the Co–S bond for the thioether trans to an amine (endo, 2.2348(19) Å; exo, 2.2272(12) Å). These Co–S bonds are still within the typical range for Co(III)–thioether bond lengths (2.194(5)–2.275(3) Å).[12–14] The Co–Cl bond lengths for the endo (2.281(2) Å) and exo (2.2771(11) Å) isomers are in reasonable agreement with Co(III)–Cl bonds of similar complexes (2.237(4)–2.305(4) Å).[32,33]
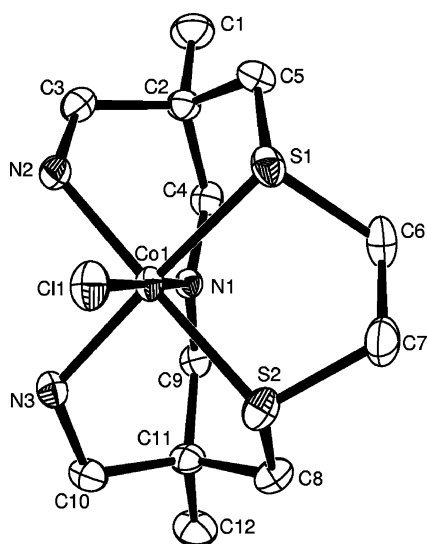
Complex **4** (Fig. 5) consists of a coordinated chloride and a pentadentate macrocyclic ligand coordinated to the cobalt centre through two primary amines, two thioethers and one imine donor. Two perchlorate anions and a water molecule make up the structure. The dmatue ligand has a cis arrangement with both methyleneamine arms positioned on the same side of the average plane of the macrocycle. The primary amine donors are coordinated trans to the thioether donors. The donors within the eleven-membered macrocyclic ring are co-ordinated facially and the chloride ion is positioned trans to the imine nitrogen. The imine bond is located between atoms N1 and C9. The Co–N$_{imine}$ bond (1.919(3) Å) (Table 6) is seen to be significantly shorter than the Co–N$_{amine}$ bonds (1.974(3),

Table 6 Selected interatomic distances (Å) and angles (°) for **4·(ClO₄)₂·H₂O**

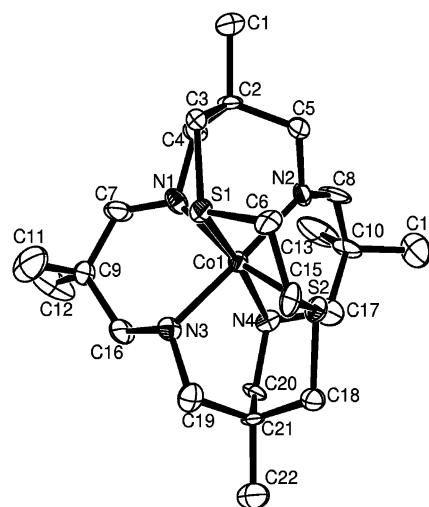|			
Co(1)–N(1)	1.919(3)	Co(1)–S(1)	2.2244(12)
Co(1)–N(2)	1.974(3)	Co(1)–S(2)	2.2345(12)
Co(1)–N(3)	1.975(3)	Co(1)–Cl(1)	2.2658(12)
N(1)–Co(1)–N(2)	90.67(13)	N(3)–Co(1)–S(2)	88.42(11)
N(1)–Co(1)–N(3)	88.22(13)	S(1)–Co(1)–S(2)	88.88(5)
N(1)–Co(1)–S(1)	92.60(10)	N(1)–Co(1)–Cl(1)	177.83(9)
N(1)–Co(1)–S(2)	94.45(10)	N(2)–Co(1)–Cl(1)	88.22(10)
N(2)–Co(1)–N(3)	94.16(14)	N(3)–Co(1)–Cl(1)	90.00(10)
N(2)–Co(1)–S(1)	88.48(10)	S(1)–Co(1)–Cl(1)	89.23(5)
N(2)–Co(1)–S(2)	174.34(10)	S(2)–Co(1)–Cl(1)	86.75(4)
N(3)–Co(1)–S(1)	177.23(11)		

Table 7 Selected interatomic distances (Å) and angles (°) for **5·(ClO₄)₃·2H₂O**

Co(1)–N(1)	2.026(10)	Co(1)–N(4)	2.025(8)
Co(1)–N(2)	1.991(9)	Co(1)–S(1)	2.248(3)
Co(1)–N(3)	1.989(9)	Co(1)–S(2)	2.225(3)
N(1)–C(7)	1.274(14)	N(2)–C(8)	1.232(14)
N(3)–C(16)	1.422(13)	N(4)–C(17)	1.439(14)
N(1)–Co(1)–S(1)	83.6(3)	N(3)–Co(1)–N(4)	86.6(4)
N(1)–Co(1)–S(2)	166.5(3)	N(3)–Co(1)–S(1)	85.2(3)
N(2)–Co(1)–N(1)	85.3(4)	N(3)–Co(1)–S(2)	98.0(3)
N(2)–Co(1)–N(4)	91.6(4)	N(4)–Co(1)–N(1)	105.2(4)
N(2)–Co(1)–S(1)	97.2(3)	N(4)–Co(1)–S(1)	168.0(3)
N(2)–Co(1)–S(2)	86.2(3)	N(4)–Co(1)–S(2)	85.5(3)
N(3)–Co(1)–N(1)	90.9(4)	S(2)–Co(1)–S(1)	87.04(12)
N(3)–Co(1)–N(2)	175.2(4)		

Fig. 6 ORTEP plot of the complex cation **5** with crystallographic numbering. Probability ellipsoids of 30% are shown.

distorted octahedron. Encapsulation of the coordination sphere shows a slight increase in both the Co–N$_{amine}$ (1.989(9) and 2.025(8) Å) and Co–S (2.225(3) and 2.248(3) Å) bond lengths in comparison with the precursor **1**. The Co–N$_{imine}$ bond lengths (1.991(9) and 2.026(10) Å) are similar to those reported for its N₆ analogue [17,18] and are distinctly longer than Co–N$_{imine}$ bonds of 1.90 Å in relatively unstrained ligand environments.[34,35] The Co–N$_{amine,\ imine}$ bonds *trans* to the thioether donors are ~0.03 Å longer than the corresponding Co–N$_{amine,\ imine}$ bonds *trans* to nitrogen donors indicating a possible *trans* influence exerted by the thioethers. This is not observed in **1** and may be a result of the strained nature of the macrobicyclic ligand. The six-membered amine/imine-chelate rings of **5** have a distorted chair conformation while those at the apices adopt the unsymmetrical skew boat conformation, as observed for **1**. Superimposition of the structures of **1** and **5** (Fig. 7) suggests that the amplector structure undergoes minimal rearrangement on encapsulation.
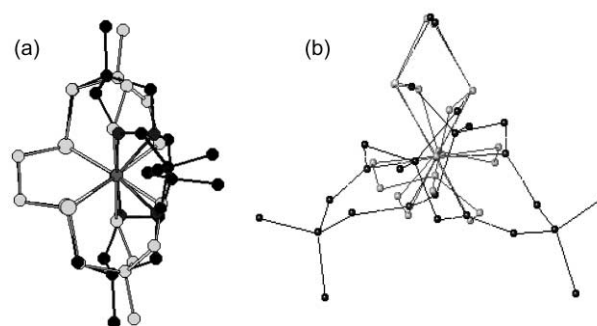
Fig. 7 An overlay of the structures of the complex cations of **1** and **5** (b) perpendicular and (b) parallel to the pseudo-C_3 axis. The S–Co–S bonds are overlaid.

¹³C and ¹H NMR

The ¹³C NMR spectrum of **1** displays a six-line spectrum with a single resonance for the methyl carbons and the quaternary carbons whilst two resonances are observed for the methylene carbons adjacent to the coordinated primary amines ($\delta_C \sim$ −21 ppm) and the coordinated thioethers ($\delta_C \sim$ −28 ppm).[9,13,14] Complex **2** displays a twelve-line ¹³C NMR spectrum. The resonance at δ_C −43.5 ppm for **2** can be assigned to the methyl group at the amine and thioether donor apex by comparison with the resonance for the methyl peaks in **1** (δ_C −43.2 ppm) while that at δ_C −45.3 ppm can be assigned to the methyl group at the oxygen donor apex. Similarly, the quaternary carbon resonances at the N₂S and NOS apices (δ_C −26.5 and −25.4


Fig. 5 ORTEP plot of the complex cation **4** with crystallographic numbering. Probability ellipsoids of 30% are shown.

1.975(3) Å). This is typical for cobalt(III)–imine bonds in relatively unstrained systems (1.905(5)–1.924(7) Å) consisting of linear or branched ligands.[34,35] However, Co(III)–N$_{imine}$ distances have been observed as long as 2.011 Å in a strained macrobicyclic system.[17] This suggests that there is little strain for the complex upon chelation. The Co–N$_{amine}$ (1.974(3), 1.975(3) Å), Co–S (2.2244(12), 2.2345(12) Å) and Co–Cl (2.2658(12) Å) distances are all within the typical ranges for these type of bonds.[32,33] The bond angles about the coordination sphere also suggests there is little coordinative strain as there is minimal distortion of donor atoms from octahedral geometry.

The structure of **5** consists of the molecular cation, three perchlorate anions and two water molecules. The complex cation (Fig. 6; selected bond lengths and angles Table 7) has a *lel₃* conformation (defined as the vectors between C7 and C16, C8 and C17, C6 and C15). Two *cis* imine bonds are located between atoms N1 and C7, and N2 and C8. The position of the donor atoms in the complex can be considered as a slightly

ppm, respectively) can be assigned by comparison with **1** (C_q: δ_C −26.5 ppm). The ^{13}C resonance for the methylene carbon adjacent to the coordinated oxygen (δ_C −1.0 ppm, pH 1.3) is shifted downfield relative to the resonances for the methylene carbons adjacent to primary amine donors, reflecting the higher electronegativity of oxygen compared to nitrogen. The resonance position is also dependent on pH. The ^1H NMR spectrum of **2** also shows the unsymmetric nature of the complex with distinct resonances observed for the methyl groups.

The ^{13}C NMR spectrum of *endo*-**3** exhibits twelve resonances, similar to the ^{13}C spectrum of **2** with only minor shifts observed for analogous resonances. For the *exo*-**3** complex the ^{13}C NMR spectrum exhibits ten resonances of a possible twelve with resonances due to methylenes adjacent to thioethers degenerate (δ_C −30.1 ppm). The resonance due to the methyl group at the NOS apex (δ_C −48.5 ppm) is shifted upfield in comparison to the analogous resonance for *endo*-**3** (δ_C −45.8 ppm) while that at the N_2S apex (δ_C −43.1 ppm) is similar to those of **1**, **2** and *endo*-**3** (δ_C −43.2, −43.5, −43.5 ppm, respectively). The resonances for the quaternary carbons for *exo*-**3** (δ_C −27.0, −26.6 ppm) and *endo*-**3** (δ_C −27.9, −24.3 ppm) cannot be readily distinguished on the basis of proximity to the oxygen donor. For each of these compounds there is no quaternary carbon chemical shift that is distinctly closer to that for **1** (δ_C −26.5 ppm) than the other quaternary carbon resonance. The resonance for the methylene carbon adjacent to the unbound alcohol group in *endo*- and *exo*-**3** (δ_C +3.1 and + 2.6 ppm, respectively) display a downfield shift in comparison with the resonance of the methylene carbon adjacent to the coordinated alcohol group in **2** (δ_C −1.0 ppm, pH 1.3). The ^{13}C chemical shifts of the methylene carbons adjacent to coordinated primary amines and coordinated thioethers in both the *endo*- and *exo*-**3** complexes are typical for nitrogen–thioether complexes.[12–14] ^1H NMR spectra, obtained in D_2O, give no indication of the formation of an aqua species by substitution of the coordinated chloride ion.

Complex **4** displays a resonance in the twelve-line ^{13}C NMR spectrum assigned to the imine carbon (δ_C +121.8 ppm).[17,18] The resonance attributed to the methylene carbon adjacent to the imine nitrogen (δ_C −5.8 ppm) is shifted markedly downfield relative to that assigned to the coordinated primary amines (δ_C −24.4, −20.6 ppm). The resonance at δ_C −18.5 ppm is due to the quaternary carbon in proximity to the imine bond while the other quaternary carbon is assigned to the resonance at δ_C −25.9 ppm. The resonances for the methyl (δ_C −44.4, −43.6 ppm) and methylene carbons adjacent to thioethers (δ_C −31.4, −29.2, −27.9, −26.5 ppm) do not shift substantially from those observed for **1**. The ^1H NMR spectrum of **4** displays two distinct methyl resonances (δ_H 1.19, 1.57 ppm) and an α-imine proton resonance at δ_H 7.98 ppm.

The encapsulated complex **5** displays a twenty-line ^{13}C NMR spectrum indicative of an unsymmetric molecule in solution. The resonances observed for the methyl carbons (δ_C −43.0, −42.9, −42.8, −42.6, −42.4 ppm; two accidentally degenerate), methylene carbons adjacent to thioethers (δ_C −29.1, −28.7, −27.0 ppm; degenerate δ_C −29.1 ppm), methylene carbons adjacent to secondary amines (δ_C −9.5, −8.1, −6.5, −6.3 ppm), imine nitrogens (δ_C +0.7, +1.0 ppm) and methine carbons (δ_C +123.6, +125.6 ppm) appear typical.[9,13,14,17,18]

Redox behaviour

The cyclic voltammogram of **1** (aqueous 0.1 M $NaClO_4$, glassy carbon working electrode) showed metal-based irreversible redox processes (−0.37 V). For **2** under the same conditions metal based irreversible redox couples were observed although the cathodic peak for the $Co^{3+/2+}$ redox couple (E_c −96 mV: 100 mV s^{-1}) was shifted to less negative potentials in comparison to **1** (E_c −330 mV: pH 1.5, 100 mV s^{-1}) reflecting the more facile

reduction of the Co(III) to Co(II) on replacement of an amine with a alcohol donor. The redox behaviour of **2** was found to be pH dependent where increasing the pH incrementally to 5.5 caused a decrease in the intensity of the $Co^{3+/2+}$ cathodic peak until no metal-based cathodic peak was observed within the limits of the solvent.

The cyclic voltammogram of **5** (aqueous 0.1 M NaCl, pH 1.4, glassy carbon working electrode) exhibited quasi-reversible behaviour (ΔE = 77 mV, 10 mV s^{-1}, i_c/i_a = 1.0; ΔE = 165 mV, 500 mV s^{-1}, i_c/i_a = 1.0). The quasi-reversible behaviour is in contrast to the irreversible redox characteristics of **1** under the same conditions, reflecting the enhanced stability of the macrobicyclic complexes (Fig. 8). The potential of the **5**$^{3+/2+}$ couple ($E_{1/2}$ +245 mV, *vs*. SHE) falls between those reported for the cobalt complexes of Me_8tricosatrieneN_6 and Me_5tricosatrieneN_6 (+400 mV and −160 mV, *vs*. SHE, respectively).[17,18] Replacement of N donors with thioethers in the case of the sarcophagine complexes causes a positive shift in metal centred redox potentials ([Co(MeN$_6$sar)]$^{3+/2+}$ −484 mV; [Co(MeN$_3$-S$_3$sar)]$^{3+/2+}$ −104 mV; *vs*. SHE).[36] For the complexes of the enlarged encapsulating ligands, Me_6docosadieneN_4S_2, Me_8tricosatrieneN_6 and Me_5tricosatrieneN_6, the position of the metal centred redox potential is predominantly influenced by steric factors due to the methyl substituents on each encapsulating arm rather than the composition of the donor set.[17,18]
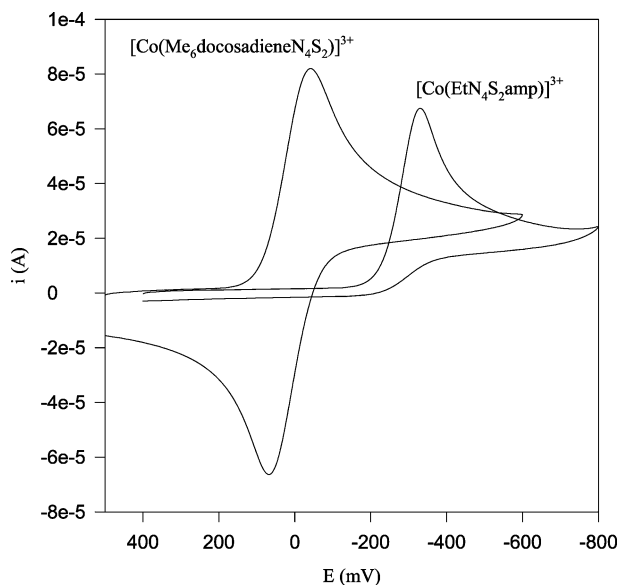

Fig. 8 Cyclic voltammograms of **5** (pH 1.4, I = 0.1 M NaCl) and **1** (pH 1.5, I = 0.1 M NaClO$_4$) 100 mV s^{-1}, glassy carbon working electrode, *vs*. Ag/AgCl.

UV-Visible spectroscopy

The room-temperature solution visible absorption spectra of Co(III) low-spin d^6 systems characteristically exhibit two spin-allowed transitions. For **1** the $^1A_{1g} \longrightarrow {}^1T_{1g}$ transition is clearly observed (21140 cm^{-1}) whilst the higher energy $^1A_{1g} \longrightarrow {}^1T_{2g}$ d–d transition was observed as a clearly defined shoulder (28800 cm^{-1}) on a much more intense charge-transfer band. The spin-forbidden transitions were not observed in the room-temperature solution spectra. At 14 K in a Nafion film the higher energy $^1A_{1g} \longrightarrow {}^1T_{2g}$ absorption becomes more pronounced. In order to locate the spin-forbidden transitions ($^1A_{1g} \longrightarrow {}^3T_{1g}$ (13800 cm^{-1}) and $^1A_{1g} \longrightarrow {}^3T_{2g}$ (17400 cm^{-1})) at 11 K highly concentrated solutions and stacked Nafion films were required (Fig. 9).

The perturbation expressions corrected for configuration interaction which can be used to uniquely determine the spectroscopic parameters $10Dq$, B and C when the spin for-bidden transitions are observed, and assuming O_h symmetry are,[13,37]
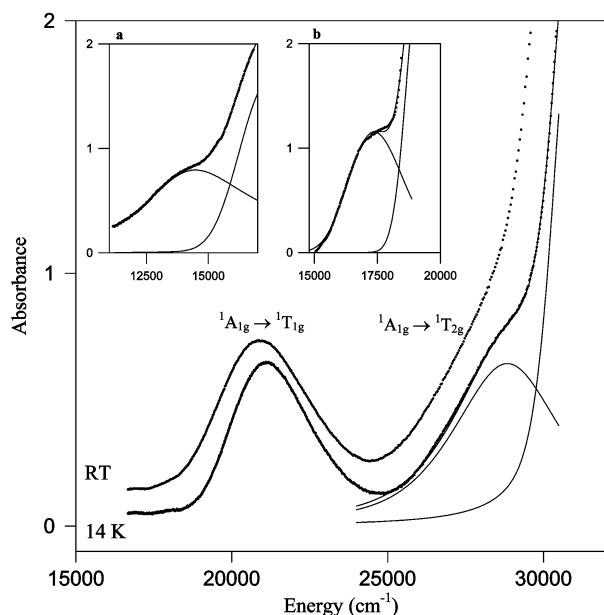
Fig. 9 Nafion film UV-visible absorption spectrum of **1** spin allowed bands at room temperature and 14 K with calculated fit for the $^1A_{1g} \longrightarrow {}^1T_{2g}$ transition at 14 K. (Inset (a) $^1A_{1g} \longrightarrow {}^3T_{1g}$ transition with calculated fit at 14 K. Inset (b) $^1A_{1g} \longrightarrow {}^3T_{2g}$ transition with calculated fit at 14 K.)

$$E(^1A_{1g} \longrightarrow {}^1T_{1g}) = 10Dq - C + (5BC + 7B^2 + C^2)/5Dq$$
$$E(^1A_{1g} \longrightarrow {}^1T_{2g}) = 10Dq - C + 16B + (3BC - 27B^2 + C^2)/5Dq$$
$$E(^1A_{1g} \longrightarrow {}^3T_{1g}) = 10Dq - 3C + (5BC - 11B^2 + C^2)/5Dq$$
$$E(^1A_{1g} \longrightarrow {}^3T_{2g}) = 10Dq - 3C + 8B + (3BC - 21B^2 + C^2)/5Dq$$
$$(1)$$

For **1** the best fit parameters for $10Dq$ (22570 cm^{-1}), B (551 cm^{-1}) and C (3500 cm^{-1}; $C/B = 6.4$) were obtained from the observed band positions in the low-temperature spectra. The values obtained may be compared with the values determined from a complete d^6 ligand field calculation for **1** ($10Dq \sim 23400$ cm^{-1}, $B = 553$ cm^{-1}, $C = 3680$ cm^{-1}), assuming C_{2v} symmetry.[38] The results $C \approx 6B$ and $10Dq \sim 22000$ cm^{-1} are consistent with those obtained previously for mixed donor thioether–nitrogen ligands (Table 8) and consistent with arguments that C/B ratio is approximately 6 compared with 4.8 for the free ion.[4,13,14,39] The magnitude of $10Dq$ for **1** supports previous observations that this parameter is relatively insensitive for mixed nitrogen–thioether cobalt(III) complexes.[4,13,14]

The UV-visible absorption spectra of **2** were obtained in aqueous solution at room temperature, and Nafion films at room temperature and at ~14 K. The absorption due to the $^1A_{1g} \longrightarrow {}^1T_{1g}$ transition is clearly observed in solution (pH 2.05: 21000 cm^{-1}) but the $^1A_{1g} \longrightarrow {}^1T_{2g}$ transition is completely obscured by a charge-transfer band and cannot be resolved even with low temperature studies (~14 K). The Nafion film UV-visible absorption spectra at low temperature (~14 K) did not resolve bands due to the $^1A_{1g} \longrightarrow {}^3T_{1g}$ and $^1A_{1g} \longrightarrow {}^3T_{2g}$ spin-forbidden transitions, hence a complete analysis of ligand field parameters for **2** was not possible. Splitting of the $^1A_{1g} \longrightarrow {}^1T_{1g}$ transition due to the low symmetry of the complex was not observed, although the band was found to exhibit a pH dependence in aqueous solution.

The room-temperature solution UV-visible absorption spectrum of *endo*-**3** shows the lower energy d–d transition $^1A_{1g} \longrightarrow {}^1T_{1g}$ at 18760 cm^{-1}. The higher energy $^1A_{1g} \longrightarrow {}^1T_{2g}$ transition is observed as a distinct shoulder on an intense charge-transfer band and band analysis of the spectrum suggests that the band maximum occurs at 26880 cm^{-1}. No spin-forbidden bands were observed in the room-temperature solution absorption spectrum. The ligand field parameters $10Dq$ and B determined from the perturbation expressions for the energies of the d–d

Table 8 Spectrophotometric parameters for Co(III) complexes of nitrogen–thioether ligands[a]

Ligand	Donor set	$E(^1A_{1g} \longrightarrow {}^1T_{1g})$	$E(^1A_{1g} \longrightarrow {}^1T_{2g})$	$E(^1A_{1g} \longrightarrow {}^3T_{1g})$	$E(^1A_{1g} \longrightarrow {}^3T_{2g})$	$10Dq$	B	C/B	Ref.
(NH$_3$)$_6$	N$_6$	21200	29550	13000	17200	22400	621	6.1	45
(en)$_3$	N$_6$	21500	29600	13700	17500	23000	583	6.4	45
sen	N$_6$	21400	29400	–	–	22710	587	b	22
AMN$_5$SsarH$^+$	N$_5$S	20660	28330	13750	17500	21950	557	5.8	14
(daes)$_2$	N$_4$S$_2$	20600	28100	–	–	21900	549	b	13
N$_4$S$_2$	N$_4$S$_2$	20800	27950	–	–	22140	516	b	13
AZAN$_4$S$_2$sar	N$_4$S$_2$	20450	27500	–	–	21770	509	b	13
AMN$_4$S$_2$sarH$^+$	N$_4$S$_2$	20450	27700	–	–	21750	526	b	13
EtN$_4$S$_2$amp	N$_4$S$_2$	21140	28800	13800	17400	22570	551	6.4	c
N$_3$S$_3$	N$_3$S$_3$	20860	27280	14535	17625	23360	452	6.7	4
AMN$_3$S$_3$sarH$^+$	N$_3$S$_3$	20460	26960	14145	17240	21920	459	6.6	4

[a] All parameters are given in cm^{-1}. [b] $C = 6B$ assumed. [c] This work.

transitions, corrected for configuration interaction and assuming $C = 6B$, were $10Dq = 19650$ cm^{-1} and $B = 619$ cm^{-1}. The $10Dq$ for *endo*-**3** is somewhat less than the $10Dq$ values for mixed donor nitrogen–thioether complexes. The Racah parameter B for *endo*-**3** is greater than those of **1** and $[Co(N_4S_2)]^{3+}$ (551 and 516 cm^{-1}, respectively)[4] suggesting greater ionic character of the Co–Cl bond and the higher covalent character of the Co–S bond relative to the cobalt(III)-amine bond.

The solution UV-visible absorption spectrum of **4** in aqueous solution shows both spin allowed d–d transitions ($^1A_{1g} \longrightarrow {}^1T_{2g}$, 26880 cm^{-1}; $^1A_{1g} \longrightarrow {}^1T_{1g}$, 20660 cm^{-1}) expected for low spin Co(III) complexes. Spin-forbidden transitions were not observed under these conditions. The $^1A_{1g} \longrightarrow {}^1T_{1g}$ band is asymmetric and can be fitted to two band components at 21000 cm^{-1} and 18830 cm^{-1}, with the intensity of the former approximately twice that of the latter. The low symmetry of **4** causes the triply degenerate $^1T_{1g}$ state to be split into its three lower symmetry components. The observation of only two bands within the $^1A_{1g} \longrightarrow {}^1T_{1g}$ transition, one being twice the intensity of the other, suggests that two of the lower symmetry states derived from the $^1T_{1g}$ state are degenerate or near-degenerate. When the weighted average of the energies of the band components for the $^1A_{1g} \longrightarrow {}^1T_{1g}$ (20285 cm^{-1}) transition is used for the determination of ligand field and Racah parameters of **4**, $10Dq$ is determined as 21610 cm^{-1} and B as 472 cm^{-1}.

The room-temperature solution UV-visible absorption spectrum of **5** shows two spin-allowed transitions with the higher energy $^1A_{1g} \longrightarrow {}^1T_{2g}$ clearly seen as a shoulder on an intense charge-transfer band. The Nafion film spectrum at low temperature shows the spin-allowed transitions at 19380 and 26450 cm^{-1}; no spin-forbidden transitions were detected. The electronic spectrum of **5** is similar to that of $[Co(Me_8tricosatrieneN_6)]^{3+}$ with spin allowed transitions at 19310 and 27250 cm^{-1}, but is markedly different in comparison to $[Co(Me_5tricosatrieneN_6)]^{3+}$ (21370 and 29150 cm^{-1}) the latter thought to have optimal Co^{III}N$_6$ geometry.[16,17] Assuming $C = 6B$, gives $10Dq = 20580$ cm^{-1} and $B = 516$ cm^{-1} for **5**. In comparison with the spectrophotometric parameters of other N$_6$ expanded encapsulated Co(III) complexes, ($[Co(Me_8tricosatrieneN_6)]^{3+}$, $B = 597$ cm^{-1}; $[Co(Me_5tricosatrieneN_6)]^{3+}$, $B = 568$ cm^{-1}) B is distinctly lower for **5** (516 cm^{-1}) reflecting the higher covalency of Co–thioether bonds. The ligand field parameter $10Dq$ may correlate to the size of the encapsulating cavity of these large macrobicyclic ligands. Thus the larger encapsulating cavities Me$_6$docosadieneN$_4$S$_2$, Me$_8$tricosatrieneN$_6$ give $10Dq$ values of similar magnitude (20580 and 20330 cm^{-1}, respectively) while the smaller cavity of Me$_5$tricosatrieneN$_6$ has a larger $10Dq$ value (22700 cm^{-1}).[16,17]

Conclusion

A relatively versatile synthetic methodology has been developed for the synthesis of a ligand in which bifurcations of the chain occur at atoms other than donor atoms. A range of by-products has also been characterized. The cobalt(III) complex has been characterized and elaborated to form a new encapsulated complex. Subsequent work will report the development of the synthetic strategy resulting in a range of amplector and encapsulating type ligands.

Experimental

Physical measurements

^{1}H, ^{13}C[^{1}H] and ^{13}C DEPT NMR spectra were recorded with a Bruker AC200F 200 MHz or a Bruker AV400 400 MHz spectrometer on internal lock. Chemical shifts for the ^{1}H NMR spectra (CDCl$_3$ and d$_4$-methanol) are reported in parts per million (δ) as positive downfield of the internal reference tetramethylsilane. In D$_2$O, the chemical shifts are reported as

positive downfield of the internal reference sodium 2,2-dimethyl-2-silapentane-5-sulfonate. The chemical shifts of ^{13}C NMR spectra (D$_2$O) are reported in parts per million (δ) as positive downfield and negative upfield of the internal reference 1,4-dioxane.[10,13,14] ^{13}C NMR spectra recorded in CDCl$_3$ and d$_4$-methanol were referenced to the CDCl$_3$ resonance at 77 ppm or the d$_4$-methanol resonance at 49 ppm. For NMR assignments quaternary and aromatic carbons are denoted by C$_q$ and Ar, respectively. The tosyl and phthalimide groups are abbreviated at tos and phth, respectively.

Low-resolution ESI mass spectra were obtained using a Finnigan MAT 900 XL mass spectrometer and methanol–water (40 : 60) solutions of the metal complexes. Spectra were recorded varying the capillary and skimmer potentials (50–200 V) so as to optimize the intensity of the signals obtained.

Cyclic voltammetry was performed with a Metrohm 757VA Computrace electrochemical analyzer using a standard three-electrode system with a glassy carbon or platinum working electrode, a platinum auxillary electrode and a Ag/AgCl/KCl reference electrode. Aqueous solutions (metal complex, 5 × 10^{-3} M; 0.1 M NaClO$_4$) were employed. Scan rates were varied from 5 to 600 mV s^{-1}.

Solution and Nafion film UV-visible spectra were recorded as described previously.[4] Where necessary, peak positions were determined using Peakfit[40] obtaining a correlation coefficient (R^2) greater than 0.997.

Syntheses

1,3-(Dimethylmethylenedioxy)-2-methyl-2-hydroxymethyl-propane and 1,3-(dimethylmethylenedioxy)-2-methyl-2-(methylene-*p*-tolylsulfonyl)propane were prepared as described previously.[19]

2,9-Bis(3,3-dimethyl-2,4-dioxocyclohexanyl)-4,7-dithiadecane. To a solution of sodium metal (10.72 g, 0.47 mol) dissolved in dry ethanol (600 cm^3) was added 1,2-ethanedithiol (20.0 g, 0.21 mol) and the solution stirred for five minutes. 1,3-(Dimethyl-methylenedioxy)-2-methyl-2-(methylene-*p*-toluenesulfonyl)-propane (133.6 g, 0.42 mol) was added and the solution heated at reflux for 6 h. Upon cooling, the white precipitate of sodium tosylate was removed by filtration and the solvent was removed from the filtrate under reduced pressure. The residue was dissolved in CHCl$_3$ (300 cm^3) and the solution was washed with water (3 × 100 cm^3). The organic layer was separated, dried over Na$_2$SO$_4$, filtered and the solvent removed under reduced pressure leaving a yellow oil (86.9 g, quantitative). ^{13}C NMR (CDCl$_3$): δ_C 19.1 (–CH$_3$); 20.5, 26.8 (CH$_3$–C$_q$); 34.0, 38.6 (–CH$_2$–S); 34.0 (C$_q$); 67.9 (–CH$_2$–O); 97.8 (C$_q$–O). ^{1}H NMR (CDCl$_3$): δ_H 0.86 (–CH$_3$, s); 1.40, 1.42 (CH$_3$–C$_q$O, s); 2.78 (–CH$_2$–S, s); 3.64 (–CH$_2$–O, dd).

2,2,9,9-Tetra(hydroxymethyl)-4,7-dithiadecane. 2,9-Bis(3,3-dimethyl-2,4-dioxocyclohexanyl)-4,7-dithiadecane (86.9 g) was dissolved in ethanol (400 cm^3) and heated at reflux. Concentrated HCl (20 cm^3) was added and the reflux continued for 10 min. Upon cooling the solvent was removed under reduced pressure. The black residue was allowed to stand overnight to solidify. The solid was triturated in ethanol and filtered to give a white solid (41.5 g, 60.6%). The filtrate was retained, the solvent removed, and the trituration repeated until no further product was obtained. Analysis. Calc. for C$_{12}$H$_{26}$O$_4$S$_2$: C, 48.3; H, 8.78%. Found: C, 48.2; H, 9.11%. ^{13}C NMR (d$_4$-methanol): δ_C 18.9 (–CH$_3$); 34.9, 38.3 (–CH$_2$–S); 42.2 (C$_q$); 67.1 (–CH$_2$–O). ^{1}H NMR (d$_4$-methanol): δ_H 0.90 (–CH$_3$, s); 2.61 (–CH$_2$–S, s); 2.74 (–CH$_2$–S, s); 3.45 (–CH$_2$–O, s).

2,2,9,9-Tetra(methylene-*p*-toluenesulfonyl)-4,7-dithiadecane. 2,2,9,9-Tetra(hydroxymethyl)-4,7-dithiadecane (32.5 g, 0.11 mol) was dissolved in dry pyridine (200 cm^3) and cooled in an

ice-bath. To this stirred solution, *p*-toluenesulfonyl chloride (93.6 g, 0.49 mol) dissolved in dry pyridine (250 cm^3) was added dropwise over 2 h. The reaction mixture was allowed to warm to room temperature and stirring maintained for 48 h. The mixture was poured into a solution of concentrated HCl (275 cm^3), water (350 cm^3) and methanol (700 cm^3) to precipitated an off-white solid which was extracted in CHCl$_3$ (3 × 300 cm^3) and the extracts combined and washed with water (2 × 300 cm^3). The CHCl$_3$ solution was separated, dried over Na$_2$SO$_4$, filtered and the solvent was removed under reduced pressure leaving an orange oil. The oil was triturated with boiling ethanol, the solution cooled to 5 °C for 24 h and filtered to give a white solid (79.8 g, 80.0%). Analysis. Calc. for C$_{40}$H$_{50}$O$_{12}$S$_6$: C, 52.5; H, 5.51%. Found: C, 52.6; H, 5.61%. ^{13}C NMR (CDCl$_3$): δ_C 18.1 (–CH$_3$); 21.5 (CH$_3$-tos); 33.8, 36.3 (–CH$_2$–S); 39.5 (C$_q$); 71.4 (–CH$_2$–O); 127.8, 129.9 (Ar–H); 132.0, 145.1 (Ar–). ^{1}H NMR (CDCl$_3$): δ_H 0.91 (–CH$_3$, s); 2.45 (CH$_3$-tos, s); 2.49, 2.54 (–CH$_2$–S, s); 3.83 (–CH$_2$–O, dd); 7.54 (Ar–H, dd).

2,2,9,9-Tetra(methylenephthalimido)-4,7-dithiadecane.

2,2,9,9-Tetra(methylene-*p*-toluenesulfonyl)-4,7-dithiadecane (40.0 g, 0.044 mol) and potassium phthalimide (35.6 g, 0.19 mol) were suspended in diethylene glycol dimethyl ether (150 cm^3) and the mixture heated at 150°C for 18 h. The cooled solution was poured into water (600 cm^3) to precipitate a brown oil. The mixture was allowed to stand for 24 h and was filtered to yield a pale brown solid. The solid was dissolved in CHCl$_3$ (600 cm^3), dried over Na$_2$SO$_4$, filtered and the solvent removed under reduced pressure to give a pale brown oil. The oil was triturated in warm ethanol and the solution filtered to yield an off-white solid (20.5 g, 57.2%). ^{13}C NMR (CDCl$_3$): δ_C 21.0 (–CH$_3$); 34.4 (–CH$_2$-phth); 41.2, 45.2 (–CH$_2$–S); 43.0 (C$_q$); 123.4, 134.1(Ar–H); 131.9 (Ar–); 168.9 (C=O). ^{1}H NMR (CDCl$_3$): δ_H 1.07 (–CH$_3$, s); 2.69, 2.72 (–CH$_2$–S, s); 3.79 (–CH$_2$-phth, s); 7.78 (Ar–H, m).

2,2,9,9-Tetra(methyleneamine)-4,7-dithiadecane

(EtN$_4$S$_2$amp). 2,2,9,9-Tetra(methylenephthalimido)-4,7-dithiadecane (12.5 g) was suspended in ethanol (200 cm^3) and heated at reflux. Hydrazine hydrate (31 cm^3) was added to the refluxing solution. Over a period of 5 min the solution became clear then a dense white precipitate formed. The reflux was maintained for 2 h. The solution was cooled in an ice-bath and concentrated HCl (40 cm^3) was added dropwise. The mixture was heated at reflux for a further 40 min, then cooled and the solvent removed under reduced pressure. The residue was dissolved in water (200 cm^3) and the solution filtered. The filtrate was made strongly alkaline with KOH and the product was extracted in CHCl$_3$ (3 × 100 cm^3). The CHCl$_3$ extracts were combined, dried over Na$_2$SO$_4$, filtered and the solvent was removed under reduced pressure to yield a yellow oil (4.22 g, 96%). The product was used for preparation of the cobalt(III) complex without further purification.

Metal complex syntheses

CAUTION: Although the perchlorate salts described in this work do not appear to be sensitive to shock or heat these materials, like all perchlorates, should be treated with caution.

[Co(EtN$_4$S$_2$amp)]Cl(ClO$_4$)$_2$ (1·Cl(ClO$_4$)$_2$). Cobaltous nitrate hexahydrate (9.0 g) in methanol (200 cm^3) was added dropwise to the stirred crude EtN$_4$S$_2$amp (9.0 g) dissolved in methanol (200 cm^3). A stream of air was bubbled through the ligand solution for the duration of the addition and continued for a further 3 h. The solvent was removed under reduced pressure, the residue dissolved in water and the solution filtered. The filtrate was diluted to 2 L and loaded onto Dowex cation exchange resin (50W × 2 (200–400 mesh) H$^+$ form). The column was washed with water, then 1 M HCl to elute minor

products. The major red band was eluted with 3 M HCl. The solvent was removed from the eluent under reduced pressure to give a red solid which was dissolved in water (750 cm^3) and loaded onto Sephadex C-25 cation exchange resin (Na$^+$ form). The column was washed with water, then 0.2 M NaCl to elute a large rose coloured band which was collected in fractions. Elution with 0.3 M NaCl resulted in a major orange band. The orange eluent was collected and loaded onto Dowex cation exchange resin, and the column washed with water and 1 M HCl. The orange band was eluted with 3 M HCl and the solvent was removed under reduced pressure to yield an orange solid (1.7 g, 12%). The solid was dissolved in a minimum of water and NaClO$_4$ added until an orange precipitate formed. The precipitate was filtered and crystallised from warm water. Analysis. Calc. for [C$_{12}$H$_{30}$N$_4$S$_2$Co]Cl(ClO$_4$)$_2$: C, 24.5; H, 5.14; N, 9.53%. Found: C, 24.2; H, 5.12; N, 9.31. UV-visible spectrum [λ_{max}/nm (ε_{max}/L mol^{-1} cm^{-1}) in H$_2$O]: 479 (346), 359 (304), 287 (16600), 237 (14600). ^{13}C NMR (D$_2$O): δ_C –43.2 (–CH$_3$); –28.4, –27.5 (–CH$_2$–S); –26.5 (C$_q$); –22.1, –20.1 (CH$_2$–N). ^{1}H NMR (D$_2$O): δ_H 1.05 (–CH$_3$, s); 2.2–3.9 (–CH$_2$–, m). ESI-MS: Calc. for [Co(EtN$_4$S$_2$amp)]$^{3+}$ – H$^+$ + ^{35}ClO$_4$$^-$, *m/z* 451; Found, *m/z* 451 (100%). Calc. for [Co(EtN$_4$S$_2$amp)]$^{3+}$ – 2H$^+$, *m/z* 351; Found, *m/z* 351 (80%).

[Co(Et(HO)N$_3$S$_2$amp)]Cl(ClO$_4$)$_2$ (2·Cl(ClO$_4$)$_2$). During the purification of the crude product from the synthesis of **1** [Co(EtN$_4$S$_2$amp)]$^{3+}$ on Sephadex cation exchange resin with 0.2 M NaCl a final red–brown fraction was collected. The red–brown eluent was loaded on Dowex cation exchange resin (50W × 2 (200–400 mesh) H$^+$ form) and the column was washed with 1 M HCl. The product was eluted with 3 M HCl to separate two bands, a minor initial band and a larger second band. The solvent removed from the eluent under reduced pressure to yield a red solid. The solid was dissolved in a minimum volume of aqueous NaClO$_4$ solution. Slow evaporation over several days resulted in dark red–brown crystals (0.3 g, 1.7%). Analysis. Calc. for [C$_{12}$H$_{29}$N$_3$OS$_2$Co]Cl(ClO$_4$)$_2$: C, 24.5; H, 4.96; N, 7.14%. Found: C, 23.9; H, 4.87; N, 6.89%. UV-visible spectrum (H$_2$O, pH 2.05) [λ_{max}/nm (ε_{max}/L mol^{-1} cm^{-1})]: 476 (287). ^{13}C NMR (D$_2$O, pH 1.3): δ_C –45.3 (–CH$_3$, N/O donor apex); –43.5 (–CH$_3$, N/N donor apex); –28.7, –27.4, –27.4, –26.6 (–CH$_2$–S); –26.5 (C$_q$, N/N donor apex); –25.4 (C$_q$, N/O donor apex); –22.8, –20.1, –19.7 (–CH$_2$–N); –1.0 (–CH$_2$–O). ^{1}H NMR (D$_2$O, pH 2.1): δ_H 0.97, 1.06 (–CH$_3$); 1.8–4.0 (–CH$_2$–, m). ESI-MS: Calc. for [Co(Et(HO)N$_3$S$_2$amp)]$^{3+}$ – H$^+$ + ^{35}ClO$_4$$^-$, *m/z* 452; Found, *m/z* 452 (77%). Calc. for [Co(Et(HO)N$_3$S$_2$amp)]$^{3+}$ – 2H$^+$, *m/z* 352; Found, *m/z* 352 (99%).

***endo*-[Co(Et(HO)N$_3$S$_2$amp)Cl]Cl(ClO$_4$) (*endo*-3·Cl(ClO$_4$)).** From the purification of the crude product from the [Co(EtN$_4$-S$_2$amp)]$^{3+}$ eluted from Sephadex cation exchange resin with 0.2 M NaCl the initial section of the rose coloured band was collected. The rose coloured eluent was loaded onto Dowex cation exchange resin (50W × 2 (200–400 mesh) H$^+$ form) and the column washed with water and 1 M HCl. Elution with 3 M HCl resulted in the separation of minor red/pink bands and the separation of two bands, a pink/purple band followed by a red/pink band (see below) which were collected separately. The solvent was removed from the pink/purple eluent and the purple residue was dissolved in a minimum of water and NaClO$_4$ was added. Purple crystals formed within 24 h. Analysis. Calc. for [C$_{12}$H$_{29}$N$_3$OS$_2$ClCo]Cl(ClO$_4$): C, 26.55; H, 5.76; N, 7.74%. Found: C, 26.35; H, 5.41; N, 7.51%. The sample was recrystallised in water with the addition of NH$_4$PF$_6$ resulting in a purple product (0.3 g, 1.7%). UV-visible spectrum (H$_2$O) [λ_{max}/nm (ε_{max}/L mol^{-1} cm^{-1})]: 533 (345), 290 (12600), 217 (12500). ^{13}C NMR (D$_2$O): δ_C –45.8 (–CH$_3$, O apex); –43.5 (–CH$_3$, N/N donor apex); –33.3, –32.8, –30.0, –26.5 (–CH$_2$–S); –27.9, –24.3 (C$_q$); –23.1, –22.6, –21.4 (–CH$_2$–N); +3.1 (–CH$_2$–O). ^{1}H NMR (D$_2$O): δ_H 1.04, 1.08 (–CH$_3$, s), 3.38 (–CH$_2$–O, dd),

2.0–3.7 (–CH$_2$–, m). ESI-MS Calc. for [Co(Et(HO)N$_3$S$_2$amp)]$^{3+}$ − 2H$^+$, m/z 352; Found, m/z 352 (100%).

***exo*-[Co(Et(HO)N$_3$S$_2$amp)Cl]Cl(ClO$_4$) (*exo*-3·Cl(ClO$_4$)).** The solvent was removed from the red/pink eluent under reduced pressure. The red solid was dissolved in a minimum of water and NaClO$_4$ was added. The solution was allowed to slowly evaporate over several days to give red crystals (<0.01 g, <0.01%). Analysis. Calc. for [C$_{12}$H$_{29}$N$_3$OS$_2$ClCo]Cl(ClO$_4$): C, 27.46; H, 5.57; N, 8.00%. Found: C, 26.29; H, 5.61; N, 7.59%. ^{13}C NMR (D$_2$O): δ_C −48.5 (–CH$_3$, O apex); −43.1 (–CH$_3$, N/N donor apex); −30.1, −26.9 (–CH$_2$–S); −27.0, −26.6 (C$_q$); −22.2, −21.8, −20.4 (–CH$_2$–N); +2.6 (–CH$_2$–O).

[Co(dmatue)Cl](ClO$_4$)$_2$·H$_2$O (4·(ClO$_4$)$_2$·H$_2$O). The first fraction of the rose coloured solution eluted from Sephadex with 0.2 M NaCl was collected and loaded onto Dowex cation exchange resin (50W × 2 (200–400 mesh) H$^+$ form). The Dowex column was washed with 1 M HCl and elution with 3 M HCl gave a red–pink solution first followed by some minor bands. The red-pink eluent was collected separately and the solvent was removed under reduced pressure to give a red residue. The residue was dissolved in a minimum of water and NaClO$_4$ was added to afford red crystals (<0.01 g, <0.01%). Analysis. Calc. for [C$_{12}$H$_{25}$N$_3$S$_2$ClCo](ClO$_4$)$_2$·H$_2$O: C, 24.56; H, 4.64; N, 7.16%. Found: C, 24.27; H, 4.60; N, 7.01%. UV-visible spectrum (H$_2$O) [λ_{max}/nm (ε_{max}/L mol^{-1} cm^{-1})]: 484 (280), 372 (390), 281 (13000), 256 (12000). ^{13}C NMR (D$_2$O): δ_C −44.4, −43.6 (–CH$_3$); −31.4, −29.2, −27.9, −26.5 (–CH$_2$–S); −25.9 (C$_q$); −24.4, −20.6 (–CH$_2$–N); −18.5 (C$_q$ (imine)); −5.8 (–CH$_2$–N=); +121.8 (–CH=N). ^{1}H NMR (D$_2$O): δ_H 1.19, 1.57 (–CH$_3$, s), 2.4–3.7 (–CH$_2$–, m), 7.98 (–CH=N, s). ESI-MS: Calc. for [Co(dmatue)]$^{3+}$ + ^{35}Cl$^−$, m/z 184; Found, m/z 184 (100%).

[Co(Me$_6$docosadieneN$_4$S$_2$)](ClO$_4$)$_3$·2H$_2$O (5·(ClO$_4$)$_3$·2H$_2$O). 1 (as its chloride salt) (1.0 g) was dissolved in dimethylformamide (70 cm^3) with an excess of NaClO$_4$ with stirring. The solution was filtered. To the filtrate was added isobutyraldehyde (10 cm^3), paraformaldehyde (0.32 g) and triethylamine (7.6 cm^3) in quick succession with stirring. After stirring for 1 h, the reaction was quenched with acetic acid. The solution was poured into water (1 L) and filtered. The filtrate was diluted to 2 L and loaded onto Dowex cation exchange resin (50W × 2 (200–400 mesh) H$^+$ form). The column was washed with water and 1 M HCl to elute a minor pink band. The major band was eluted with 3 M HCl. The solvent was removed from the eluent under reduced pressure. The residue was dissolved in water (1 L) and loaded onto Sephadex C-25 cation exchange resin (Na$^+$ form). The column was washed with water slightly acidified with HCl (pH 4). A major pink band was eluted with 0.2 M NaCl acidified with HCl (pH 4) followed by a series of minor orange bands. The pink eluent was loaded onto Dowex cation exchange resin. The column was washed with 1 M HCl and the product was eluted with 3 M HCl. The solvent was removed from the eluent to yield a dark pink solid (0.15 g, 11.6%). The solid was dissolved in a minimum of water and NaClO$_4$ was dissolved in the solution. The solution was allowed to stand to produce dark pink crystals. Analysis. Calc. for [C$_{22}$H$_{42}$N$_4$S$_2$Co](ClO$_4$)$_3$·2H$_2$O: C, 32.27; H, 5.65; N, 6.83%. Found: C, 31.80; H, 5.25; N, 6.24%. UV-visible spectrum [λ_{max}/nm (ε_{max}/L mol^{-1} cm^{-1}) in H$_2$O]: 515 (630), 378 (450, sh), 310 (15000). ^{13}C NMR (D$_2$O, acidified with HCl): δ_C −43.0, −42.9, −42.8, −42.6, −42.4 (–CH$_3$); −29.1, −28.7, −27.0 (–CH$_2$–S); −28.2, −27.2, −25.6, −24.3 (C$_q$); −9.5, −8.1, −6.5, −6.3 (–CH$_2$–N), +0.7, +1.0 (–CH$_2$–N=); +123.6, +125.6 (–CH=N). ^{1}H NMR (D$_2$O, acidified with HCl): δ_H 1.21, 1.27, 1.32, 1.34, 1.38 (–CH$_3$, s); 2.1–3.9 (–CH$_2$–, m); 7.83, 8.30 (–CH–N=, s). ESI-MS: Calc. for [Co(Me$_6$docosadieneN$_4$S$_2$)]$^{3+}$ − 2H$^+$, m/z 483; Found, m/z 483 (100%).

Crystal structure determinations

For diffractometry the crystals were mounted onto glass fibres with Supa Glue. Lattice parameters were determined by least squares fits to the setting parameters of 25 independent reflections, measured and refined with an Enraf-Nonius CAD4 diffractometer using graphite-monochromated Mo-Kα radiation. The structures were solved by heavy-atom methods (direct methods) and refined using full-matrix least squares on F^2. Programs used were SHELXS-86[41] or SIR-92[42] for solution, SHELXL-93[43] for refinement and ORTEP[44] for plotting. Crystal data are given in Table 1. The geometries of the molecules are shown in Figs. 2–6 together with atomic numbering schemes. Selected bond lengths and bond angles are given in Tables 2–7.

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See http://www.rsc.org/suppdata/dt/b3/b304914k/ for crystallographic data in CIF or other electronic format.

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