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

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The synthesis of the hexadentate ligand 2,2,9,9-tetra(methyleneamine)-4,7-dithiadecane (EtN₃Samp) 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(EtN₃Samp)]⁺ (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(OH)N₃Samp) and an eleven-membered pendant arm macroyclic ligand 6,10-dimethyl-6,10-bis(methyleneamine)-1,4-dithia-8-azaacyclooctadec-7-one (dmature). The complexes [Co(EOtN₃Samp)]⁺ (2), in which the alcohol is coordinated to the metal ion, and [Co(dmature)Cl]⁺ (3) were isolated and characterized. Et(OH)N₃Samp also undergoes complexation with cobalt(III) to produce two isomers endo-[Co(EOtN₃Samp)Cl]⁺ (endo-3) and exo-[Co(EOtN₃Samp)Cl]⁺ (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 isobutyaldehyde, 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)[(ClO₄)₂]·2H₂O (Co(Me₆docosadieneN₃Samp)}]⁺ (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 1A₁g → 1T₄g and 1A₁u → 1T₂g and spin forbidden 1A₁g → 3T₂g and 1A₁u → 3T₄g 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(Me₆tricosatrieneN₃)⁺] and [Co(Me₆tricosatrieneN₃)⁺].

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. Numerical 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. One ligand topology described by Lions was that in which bifurcations of the chain occur at atoms other than donor atoms. Our interest in this particular ligand topology arises from the intrinsic chemistry, and that of the metal complexes formed from them. 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(methyleneamine)-4,7-dithiadecane (EtN₃Samp) 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.

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 EtN₃Samp (2,2,9,9-tetra(methyleneamine)-4,7-dithiadecane) the prefix Et denotes the ethyl hinge and N₃Samp refers to the tetraamine–dithioether donor set of the ligand. The same nomenclature applies for the major synthetic by-product Et(OH)N₃Samp (2,9,9-tris(methyleneamine)-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 (S₃) denote the donor atoms of the hinge moiety. The nomenclature employed to describe the encapsulated complex
Me₆docasadieneN₅S₂ 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 EtN₅S₅amp was synthesized by a reaction sequence (Scheme 1) in which 1,3-(dimethylmethyleneoxy)-2-methyl-2-(methylene-p-toluenesulfonyl)propane 19 is reacted with the sodium salt of 1,2-ethanediol. 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.22 We have found that multidentate ligands of this type cannot easily be purified; distillation invariably results in pyrolysis and chromatographic methods are relatively inefficient.5,9,10,14 The most convenient manner in which to produce a pure sample of the ligand is to prepare and characterize the cobalt(III) complex.8,9,10,14

Reaction of EtN₅S₅amp with cobalt(0) and oxygen resulted in the major product [Co(EtN₅S₅amp)Cl]2⁻ (1-Cl⁻) 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)N₅S₅amp)Cl]2⁻ (2-Cl⁻), a complex with a N₂O₅ chromophore where the HO is bound to the metal ion. The precursor for the Et(HO)N₅S₅amp 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-dioxy-N₂O₅ was isolated in the synthesis of tannin (1,1,1-tris(aminomethyl)ethane).23 A spectrophotometric pH titration of 2 in water (0.1 M Et₄NClO₄ pH 2–5) showed that the position of λₘₐₓ shifts to higher wavelengths with increasing pH (476 nm at pH 2; 494 nm at pH 5). Titration with acid (0.1 M Et₄NClO₄ pH 5–2) using the same solution shows the reversibility of this protonation process. The average fit to the data23 for the forward and back titrations provides a pKₐ of 2.8(1). Similar shifts in the 1Aₐ → 1Tₐ transition are observed on the deprotonation of Co(III) aminooalcohol complexes,24 and are assigned to the deprotonation of a coordinated alcohol group to a coordinated O⁻ species.

The ligand Et(OH)N₅S₅amp can function as a pentadentate ligand (N₂S₂ 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(OH)N₅S₅amp)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)N₅S₅amp)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. tenn; 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 cyclooctane to cyclooctane.25 Thus, formation of the aldehyde may arise from Et(HO)N₅S₅amp by reaction with Co⁺⁺ 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-C₂ axis, through the four primary amine donors, in a similar manner to the encapsulation reactions of [Co(tame)]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 C₃ axis.9,10,14,26 The imine cage complex [Co(Me₆docasadieneN₅S₂)²⁺ (5) was synthesized from a metal template strategy using 1 with parafomraldehyde in the presence of isobutyrualdehyde 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 (NaBH₄ 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 (let) to the pseudo-C₂ axis and the remaining six-membered chelate rings all adopt the unsymmetrical skew boat conformation.
Table 1 Crystal data

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<th>b (Å)</th>
<th>c (Å)</th>
<th>α (°)</th>
<th>β (°)</th>
<th>γ (°)</th>
<th>V (Å³)</th>
<th>D (g cm⁻³)</th>
<th>µ (cm⁻¹)</th>
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<td>89.5760</td>
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<td>18.1023</td>
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<td>2442.3(6)</td>
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<td>14.0794</td>
<td>18.1023</td>
<td>8.1363</td>
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<td>90.0466</td>
<td>89.5760</td>
<td>2442.3(6)</td>
<td>1.726</td>
<td>0.0584</td>
<td>0.0000</td>
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<td>0.0588</td>
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Table 2 Selected interatomic distances (Å) and angles (°) for 1-(ClO₄)₂H₂O

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<td>2.2159(13)</td>
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<tr>
<td>Co(1)–S(1)</td>
<td>1.987(4)</td>
<td>2.2159(13)</td>
</tr>
<tr>
<td>N(1)–Co(1)–N(1)</td>
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<td>89.0(1)</td>
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<tr>
<td>N(1)–Co(1)–S(1)</td>
<td>89.0(1)</td>
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<tr>
<td>N(1)–Co(1)–S(1)</td>
<td>89.0(1)</td>
<td>89.0(1)</td>
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For 1 (crystal data, Table 1) the Co–N and Co–S bond lengths (1.987(4) and 2.2159(13) Å, respectively (Table 2)) are similar to those reported for the hexadentate complex [Co(N₂S₂)]⁺⁺⁺ (N₂S₂ = 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), and appear typical of the normal range of Co–N and Co–S bond lengths for cobalt(nii) complexes of this type (Co–N: 1.94–2.01 Å; Co–S: 2.194(5)–2.275(3) Å). 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(nii) bonds with alcohol groups in multidentate ligands (1.898(1)–1.979(8) Å). The similar ranges...
Table 3: Selected interatomic distances (Å) and angles (°) for 2-Cl(ClO₄)₂

<table>
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<td>Co(1)-N(2)</td>
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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 N₅S₃Cl donor set with the alcohol group not coordinated. The amine donors are arranged meridionally 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 lefthanded conformation. 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 (1.975(3), 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). The Co–S bond length for the thioether bond (endo, 2.202(2) Å; exo, 2.191(2) Å) is found to be slightly shorter in comparison to the Co–S bond for the thioether bond 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). 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 (2.32(14)–2.305(4) Å). The Co–N₅S₃Cl bonds of complex 3 exhibit very few differences in terms of bond lengths and bond angles (Tables 4 and 5). The Co–N₅S₃Cl bonds (1.919(3) Å) (Table 6) are seen to be significantly shorter than the Co–N₅S₃Cl bonds (1.974(3),...
Table 6 Selected interatomic distances (Å) and angles (°) for 4-(ClO₄)₂·H₂O

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

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![ORTEP plot of the complex cation 5](image)

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

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 lel₁ 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 distorted octahedron. Encapsulation of the coordination sphere shows a slight increase in both the Co–Nₐₐₐₐ distances (1.989(9) Å and 2.026(8) Å) and Co–S (2.248(3) Å and 2.225(3) Å) bond lengths in comparison with the precursor 1. The Co-Nₐₐₐₐ bonds (1.991(9) Å and 2.026(8) Å) are similar to those reported for its Nₐₐₐₐ analogue[13,14] and are distinctly longer than Co-Nₐₐₐₐ bonds of 1.90 Å in relatively unstrained ligand environments[14,15]. The Co–Nₐₐₐₐ bonds trans to the thiourea donors are ~0.03 Å longer than the corresponding Co–Nₐₐₐₐ bonds trans to nitrogen donors indicating a possible trans influence exerted by the thiourea. 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 amplerceptor structure undergoes minimal rearrangement on encapsulation.

**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(n)-amine bonds in relatively unstrained systems (1.905(5)–1.924(7) Å) consisting of linear or branched ligands[14,15]. However, Co(n)–Nₐₐₐₐ 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–Nₐₐₐₐ (1.974(3), 1.975(3) Å), Co–S (2.2244(12), 2.2348(12) Å) and Co–Cl (2.2658(12) Å) distances are all within the typical ranges for these type of bonds[13,14]. The bond angles about the coordination sphere also suggests there is little coordinative strain as there is minimal distortion of the imine/amide bonds 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 lel₁ 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 distorted octahedron. Encapsulation of the coordination sphere shows a slight increase in both the Co–Nₐₐₐₐ distances (1.989(9) Å and 2.026(8) Å) and Co–S (2.225(3) Å and 2.248(3) Å) bond lengths in comparison with the precursor 1. The Co–Nₐₐₐₐ bonds (1.991(9) Å and 2.026(8) Å) are similar to those reported for its Nₐₐₐₐ analogue[13,14] and are distinctly longer than Co–Nₐₐₐₐ bonds of 1.90 Å in relatively unstrained ligand environments[14,15]. The Co–Nₐₐₐₐ bonds trans to the thiourea donors are ~0.03 Å longer than the corresponding Co–Nₐₐₐₐ bonds trans to nitrogen donors indicating a possible trans influence exerted by the thiourea. 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 amplerceptor 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-C₇ 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 (δC ~ –21 ppm) and the coordinated thioureas (δC ~ –28 ppm).5,13,14 Complex 2 displays a twelve-line 13C NMR spectrum. The resonance at δC ~ 43.5 ppm for 2 can be assigned to the methyl group at the amine and thiourea donor apex by comparison with the resonance for the methyl peaks in 1 (δC ~ 43.2 ppm) while that at δC ~ 45.3 ppm can be assigned to the methyl group at the oxygen donor apex. Similarly, the quaternary carbon resonances at the Nₐₐₐₐ and Nₐₐₐₐ/Sₐₐₐₐ apices (δC ~ 26.5 and ~25.4
ppm, respectively) can be assigned by comparison with 1 (C; δC = 26.5 ppm). The 13C resonance for the methylene carbon adjacent to the coordinated oxygen (δC = 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 13C NMR spectrum of endo-3 exhibits twelve resonances, similar to the 13C spectrum of 2 with only minor shifts observed for analogous resonances. For the exo-3 complex the 13C NMR spectrum exhibits ten resonances of a possible twelve with resonances due to methylenes adjacent to thioethers degenerate (δC = 30.1 ppm). The resonance due to the methyl group at the NOS apex (δC = 48.5 ppm) is shifted upfield in comparison to the analogous resonance for endo-3 (δC = 45.8 ppm) while that at the N2S apex (δC = 43.1 ppm) is similar to those of 1, 2 and endo-3 (δC = 43.2, 43.5, 43.5 ppm, respectively). The resonances for the quaternary carbons for exo-3 (δC = 27.0, 26.6 ppm) and endo-3 (δC = 27.9, 26.3 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 (δC = 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 (δC = 31.3 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 (δC = 1.0 ppm, pH 1.3). The 13C 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 D2O, 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 13C NMR spectrum assigned to the imine carbon (δC = 121.8 ppm).16 The resonance attributed to the methylene carbon adjacent to the imine nitrogen (δC = 5.8 ppm) is shifted markedly downfield relative to that assigned to the coordinated primary amines (δC = 24.4, 20.6 ppm). The resonance at δC = 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 δC = 25.9 ppm. The resonances for the methyl (δC = 24.4, 13C ppm) and methylene carbons adjacent to thioethers (δC = 31.4, 29.2, 43.5 ppm, respectively) do not shift substantially from those observed for 1. The 1H NMR spectrum of 4 displays two distinct methyl resonances (δH = 1.19, 1.57 ppm) and an α-imine proton resonance at δH = 7.98 ppm.

The encapsulated complex 5 displays a twenty-line 13C NMR spectrum indicative of an unsymmetric molecule in solution. The resonances observed for the methyl carbons (δC = 43.0, 42.9, 42.8, 42.6, 42.4 ppm; two accidentally degenerate), methylene carbons adjacent to thioethers (δC = 29.1, 28.7, 27.0 ppm; degenerate δC = 29.1 ppm), methylene carbons adjacent to secondary amines (δC = 1.3, 29.1 ppm, methylene carbons (δC = 43.6, 123.6, +1.0 ppm) appear typical.17-19

Redox behaviour

The cyclic voltammogram of 1 (aqueous 0.1 M NaClO4, 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(III/II) redox couple (EC = 96 mV; 100 mV s−1) was shifted to less negative potentials in comparison to 1 (EC = 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(III/II) 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, IL/IL = 1.0; ΔE = 165 mV, 500 mV s−1, IL/IL = 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+2− couple (E1/2 = 245 mV, vs. SHE) falls between those reported for the cobalt complexes of Me2tricosaatrieneN5 and Me2(tricasatrieneN5 (+400 mV and –160 mV, vs. SHE, respectively).17 Replacement of N donors with thioethers in the case of the sarcophagine complexes causes a positive shift in metal centred redox potentials ([Co(MeN5S2)]2+ −484 mV; [Co(MeN5S,S)]2+ −104 mV; vs. SHE). For the complexes of the enlarged encapsulating ligands, Me2docosadieneN5, Me2tricosatrieneN5 and Me2tricosatrieneN5, 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

UV-Visible spectroscopy

The room-temperature solution visible absorption spectra of Co(II) low-spin d6 systems characteristically exhibit two spin-allowed transitions. For 1 the 1A4g −→ 1T4g transition is clearly observed (21140 cm−1) whilst the higher energy 1A4g −→ 1T2g 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 1A4g −→ 1T4g absorption becomes more pronounced. In order to locate the spin-forbidden transitions (1A4g −→ 1T2g (18000 cm−1) and 1A4g −→ 1T4g (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-forbidden transitions are observed, and assuming O4h symmetry are.20-24

![Graph](image-url)

Fig. 8 Cyclic voltammograms of 5 (pH 1.4, f = 0.1 M NaCl) and 1 (pH 1.5, f = 0.1 M NaClO4) 100 mV s−1, glassy carbon working electrode, vs. Ag/AgCl.

3698 | Dalton Trans., 2003, 3693-3703

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Fig. 9  Nafion film UV-visible absorption spectrum of 1 spin allowed bands at room temperature and 14 K with calculated fit for the $^2A_g \rightarrow ^4T_{2g}$ transition at 14 K. (Inset (a) $^1A_g \rightarrow ^4T_{1u}$ transition with calculated fit at 14 K.)

\[
\begin{align*}
E(1A_g \rightarrow 1T_{2g}) &= 10Dq - C + (5BC + 7B^2 + C^2)/5Dq \\
E(1A_g \rightarrow 1T_{1u}) &= 10Dq - C + 16B + (3BC - 27B^2 + C^2)/5Dq \\
E(1A_g \rightarrow 1T_{1g}) &= 10Dq - 3C + (5BC - 11B^2 + C^2)/5Dq \\
E(1A_g \rightarrow 1T_{2g}) &= 10Dq - 3C + 8B + (3BC - 21B^2 + C^2)/5Dq
\end{align*}
\]

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$^7$ ligand field calculation for 1 ($10Dq = 23400$ cm$^{-1}, B = 553$ cm$^{-1}, C = 3680$ cm$^{-1}$), assuming $C_{3v}$ symmetry.\(^4\)

The results $C \approx 6B$ and $10Dq \approx 22000$ 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.\(^4,13,14,19\)

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 $^1A_g \rightarrow ^1T_{2g}$ transition is clearly observed in solution (pH 2.05: 21000 cm$^{-1}$) but the $^1A_g \rightarrow ^3T_{1g}$ 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 $^1A_g \rightarrow ^3T_{1g}$ and $^1A_g \rightarrow ^3T_{2g}$ spin-forbidden transitions, hence a complete analysis of ligand field parameters for 2 was not possible. Splitting of the $^1A_g \rightarrow ^3T_{1g}$ 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 $^1A_g \rightarrow ^1T_{1g}$ at 18760 cm$^{-1}$. The higher energy $^1A_g \rightarrow ^1T_{2g}$ 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>
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<th>Ligand</th>
<th>Donor set</th>
<th>Transition</th>
<th>$E(1A_g \rightarrow ^1T_{2g})$</th>
<th>$E(1A_g \rightarrow ^3T_{1g})$</th>
<th>$E(1A_g \rightarrow ^3T_{2g})$</th>
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<td>27700</td>
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Table 8  Spectrophotometric parameters for Co(ii) complexes of nitrogen-thioether ligands.

All parameters are given in cm$^{-1}$; $C/B = 6.4$ assumed. 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(S)\(_5\))]\(^{2+}\) (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 (\(\Delta A_{eg} = \Delta A_{tg}\) 28880 cm\(^{-1}\); \(\Delta A_{eg} = \Delta A_{tg}\) 20660 cm\(^{-1}\)) expected for low spin Co(III) complexes. Spin-forbidden transitions were not observed under these conditions. The \(\Delta A_{eg} \rightarrow \Delta A_{tg}\) 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 \(\Delta A_{tg}\) state to be split into its three lower symmetry components. The observation of only two bands within the \(\Delta A_{eg} \rightarrow \Delta A_{tg}\) transition, one being twice the intensity of the other, suggests that two of the lower symmetry states derived from the \(\Delta A_{eg}\) state are degenerate or near-degenerate. With the exception of the energies of the bands of the Co(III) complexes, \(\Delta A_{eg} \rightarrow \Delta A_{tg}\) transitions 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 \(\Delta A_{eg} \rightarrow \Delta A_{tg}\) 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\(^{-1}\), corrected for con

**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 amphoteric 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 \(d_6\)-methanol) are reported in parts per million (\(\delta\)) 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 (\(\delta\)) 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 \(d_6\)-methanol were referenced to the CDCl\(_3\) resonance at 7 ppm or the \(d_6\)-methanol resonance at 49 ppm. For NMR assignments quaternary and aromatic carbons are denoted by C\(_4\) and Ar, respectively. The tosyl and pthalimide groups are abbreviated as tos and pth, respectively.

Low solution 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 auxiliary electrode and a Ag/AgCl/KCl reference electrode. Aqueous solutions (metal complex, 5 × 10\(^{-4}\) 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\(^4\) 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-toluenesulfonyl)propane were prepared as described previously.\(^1\)

2.9-Bis(3,3-dimethyl-2,4-dioxycyclohexanoyl)-4,7-dithiadeacane.

To a solution of sodium metal (10.72 g, 0.47 mol) dissolved in dry ethanol (600 cm\(^3\)) was added 1.2-ethanethiol (20.0 g, 0.21 mol) and the solution stirred for five minutes. 1,3-(Dimethylmethylenedioxy)-2-methyl-2-(methylene-p-toluenesulfonyl)-propane (133.6 g, 0.42 mol) 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\(_3\)): \(\delta_{13} 19.1\) (–CH\(_3\)); 20.5, 26.8 (CH\(_2\)-C\(_3\)-O); 34.0, 38.6 (–CH\(_2\)-S); 34.0 (C\(_2\)); 67.9 (–CH\(_2\)-O); 97.8 (C\(_3\)-O). \(^1\)H NMR (CDCl\(_3\)): \(\delta_{1}\) 0.86 (–CH\(_3\), s); 1.40, 1.42 (CH\(_2\)-C\(_3\)-O), s; 2.78 (–CH\(_2\)-S), s; 3.64 (–CH\(_2\)-O, dd).

2.9,9,9-Tetra(hydroxymethyl)-4,7-dithiadeacane. 2.9-Bis(3,3-dimethyl-2,4-dioxycyclohexanoyl)-4,7-dithiadeacane (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\(_3\)H\(_8\)O\(_3\)S\(_2\): C: 48.3; H: 8.8%. Found: C: 48.2; H: 9.1%. \(^{13}\)C NMR (dm6-methanol): \(\delta_{13} 18.9\) (–CH\(_3\)); 34.9, 38.3 (–CH\(_2\)-S); 42.2 (C\(_2\)); 67.1 (–CH\(_2\)-O). \(^1\)H NMR (dm6-methanol): \(\delta_{1}\) 0.90 (–CH\(_3\), s); 2.61 (–CH\(_2\)-S, s); 2.74 (–CH\(_2\)-S, s); 3.45 (–CH\(_2\)-O, s).

2.9,9,9-Tetra(methylene-p-toluenesulfonyl)-4,7-dithiadeacane. 2.9,9,9-Tetra(hydroxymethyl)-4,7-dithiadeacane (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 cm³) 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 cm³) and the extracts combined and washed with water (2 × 300 cm³). The CHCl₃ solution was separated, dried over Na₂SO₄, and the solvent was removed under reduced pressure leaving an orange oil. The oil was triturated with boiling ethanol, the solution cooled to 50°C for 24 h and filtered to give a white solid which was extracted in CHCl₃ (3 × 300 cm³) and the mixture heated at 150°C for 18 h. The cooled solution was poured into water (600 cm³) to precipitate a brown oil. The mixture was allowed to stand for 24 h and was filtered to yield a pale brown solid. The residue was dissolved in CHCl₃ (600 cm³), dried over Na₂SO₄, filtered, and the solvent removed under reduced pressure to give a pale brown oil. The heterogeneous mixture was triturated in warm ethanol and the solution filtered to yield an off-white solid (20.5 g, 57.2%). ¹³C NMR (CDCl₃): δ₁ 21.0 (–CH₃); 41.2, 45.2 (–CH₂–S); 43.0 (Cₛ); 123.4, 134.1 (Ar–H); 168.9 (C=O). ¹H NMR (CDCl₃): δ₁ 1.07 (–CH₃); 2.69, 2.72 (–CH₂–S, s); 3.79 (–CH₂–S, s); 7.78 (Ar–H, m).

2.2.9.9-Tetra(methylene phosphalimido)-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 cm³) and the mixture heated at 150°C for 18 h. The cooled solution was poured into water (600 cm³) to precipitate a brown oil. The mixture was allowed to stand for 24 h and was filtered to yield a pale brown solid. The residue was dissolved in CHCl₃ (600 cm³), dried over Na₂SO₄, 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%). ¹³C NMR (CDCl₃): δ₁ 21.0 (–CH₃); 41.2, 45.2 (–CH₂–S); 43.0 (Cₛ); 123.4, 134.1 (Ar–H); 168.9 (C=O). ¹H NMR (CDCl₃): δ₁ 1.07 (–CH₃); 2.69, 2.72 (–CH₂–S, s); 3.79 (–CH₂–S, s); 7.78 (Ar–H, m).

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(Et₃N)₂(SAMP)]Cl(ClO₄)₂ (2-Cl(ClO₄)₂). During the purification of the crude product from the synthesis of [Co(Et₃N)₂(SAMP)]⁺ on Sephadex cation exchange resin with 0.2 M NaCl a final red–brown fraction was collected. The red–brown eluant was loaded on Dowex cation exchange resin (50 × 2 (200–400 mesh) H⁺ form) and the column was washed with 1 M HCl. The product was eluted with 3 M HCl and the solvent removed under reduced pressure to yield a red solid. The solid was dissolved in a minimum volume of aqueous NaClO₄ solution. Slow evaporation over several days resulted in dark red–brown crystals (0.3 g, 1.7%). Analysis. Calc. for [Et₃N]⁺Cl⁺Na⁺ClO₄⁻: C, 24.5; H, 4.96; N, 7.14%. Found: C, 23.9; H, 4.87; N, 6.89%. UV–visible spectrum (H₂O, pH 2.05) [ε₂₅₀/nm (ε₂₅₀/nmol L⁻¹ cm⁻¹)]: 476 (287). ¹³C NMR (D₂O, pH 1.3): δ₁ 45.3 (–CH₂–S, N donor apex); –43.5 (–CH₂–S, N donor apex); –28.7, –27.4, –27.4, –26.6 (–CH₂–S); –26.5 (Cₛ/N donor apex); –25.4 (Cₛ/N donor apex); –22.8, –20.1, –19.7 (–CH₂–S); –1.0 (–CH₂–S). ¹H NMR (D₂O, pH 2.1): δ₁ 0.97, 1.06 (–CH₃); 1.8–4.0 (–CH₂–S, m). ESI–MS: Calc. for [Co(Et₃N)₂(SAMP)]⁺ [M⁺] + H⁺ + ClO₄⁻, m/z: 452; Found, m/z 452 (77%). Calc. for [Co(Et₃N)₂(SAMP)]⁺ [M⁺] + H⁺ + ClO₄⁻, m/z: 351; Found, m/z 351 (80%).

[endo-Co(Et₃N)₂(SAMP)]Cl(ClO₄)₂ (endo-3-Cl(ClO₄)₂). From the purification of the crude product from the [Co(Et₃N)₂(SAMP)]⁺ eluted from Sephadex cation exchange resin with 0.2 M NaCl the initial section of the rose coloured band was collected. The rose coloured eluant was loaded onto Dowex cation exchange resin (50 × 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 eluant and the purple residue was dissolved in a minimum of water and NaClO₄ was added. Purple crystals formed within 24 h. Analysis. Calc. for [Et₃N]⁺Cl⁺Na⁺ClO₄⁻: C, 26.5; H, 5.76; N, 7.74%. Found: C, 26.8; H, 5.41; N, 6.15%. ¹H NMR (D₂O): δ₁ 0.97, 1.06 (–CH₃); 1.8–4.0 (–CH₂–S, m). ESI–MS: Calc. for [Endo-Co(Et₃N)₂(SAMP)]⁺ [M⁺] + H⁺ + ClO₄⁻, m/z: 452; Found, m/z 452 (77%). Calc. for [Endo-Co(Et₃N)₂(SAMP)]⁺ [M⁺] + H⁺ + ClO₄⁻, m/z: 351; Found, m/z 351 (80%).

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2.0–3.7 (–CH₂– m), m/z 352; Found, m/z 352 (100%).

exo-[Co(Et)(HO)NS₄amp]Cl(ClO₄)₂ (exo-3-Cl(CIO₄)₅). The solvent was removed from the red/pink eluent under reduced pressure. The red solid was dissolved in a mixture of water and NaClO₄ was added. The solution was allowed to slowly evaporate over several days to give red crystals (<0.01 g, <0.01%). Analysis. Calc. for [C₄H₅N₅S₄ClO₄][ClO₄]·H₂O: C, 24.56; H, 2.64; N, 7.16%. Found: C, 24.27; H, 4.60; N, 7.01%. Analysis for [C₄H₅N₅S₄ClO₄][ClO₄]·H₂O: C, 24.27; H, 4.60; N, 7.01%.

Crystal structure determinations

For x-ray crystallography the crystals were mounted on glass fibres with Supa Glue. Lattice parameters were determined by least squares fit 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 F². Programs used were SHELXS-86 [41] and 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.

CCDC reference numbers 209636–209641.

References and notes


27. lel, and ob refer to limiting conformations of five-membered chelate rings in which the C-C axis is respectively parallel and oblique to the (pseudo) C₃ axis of the complex cation. See, Inorg. Chem., 1970, 9, 1.


43 G. M. Sheldrick, SHELXL-93, A program for crystal structure determination, University of Göttingen, 1993.