A New Approach to Hexakis(thioether) Co-ordination: the Cobalt(II) Complex of 1,1,1-Tris[(2-methylthioethylthio)methyl]ethane

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The previously unreported ligand 1,1,1-tris[(2-methylthioethylthio)methyl]ethane (L) reacts with cobalt(II) to yield an octahedral complex in which the low-spin metal ion co-ordinates with six thioether sulphur atoms at distances that range from 2.241(4) to 2.501(4) Å, as shown by an *X*-ray crystal structure determination.

The confluence of our interest in thioether co-ordination chemistry and in three-dimensionally articulated ligands has recently led us to prepare 1,1,1-tris[(2-methylthioethylthio)methyl]ethane (L), a readily synthesised ligand that enforces hexakis(thioether) co-ordination on Ni^{II}.[1] We report herein the synthesis and structural characterisation of $[Co(L)]^{2+}$, a low-spin, octahedral complex of Co^{II}. In a broad context the present results suggest that other such ligands based upon carbon bridgeheads may provide a simple route to exceptionally strong chelating ligands with a variety of donor atoms.

Addition of the supertripodal ligand L (0.29 mmol) [prepared by reaction of the tritosylate of 1,1,1-tris(hydroxymethyl)ethane with sodium 2-methylthioethanethiolate in EtOH] to $[Co(EtOH)_6](BF_4)_2$ (0.29 mmol) in $MeNO_2$ gave a dark mauve solution that upon concentration *in vacuo* deposited mauve crystals (yield: 146 mg, 81%).† Recrystallisation from nitromethane by vapour diffusion of diethyl ether gave diffraction-quality crystals.‡

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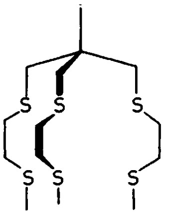
† Satisfactory analytical data were obtained.

‡ *Crystal data:* $C_{14}H_{30}B_2CoF_8S_6$, M_r 623.29, orthorhombic, space group $Pna2_1$, $a = 12.321(5)$, $b = 19.701(7)$, $c = 10.279(9)$ Å, $Z = 4$, $D_c = 1.65$ g cm^{-3}. A crystal (0.45 × 0.35 × 0.25 mm) was sealed in an *X*-ray capillary under nitrogen for crystallographic studies. An Enraf–Nonius CAD4 diffractometer with Mo-K_α radiation (0.71069 Å) was used in the ω–2θ mode for collection of 3168 unique data (excluding systematic absences) with $2\theta < 50°$. Four standard reflections measured every hour showed no decay. Calculations were performed with the CRYSTALS crystallographic programs on a VAX 11/750 computer, with atomic scattering factors from the usual source. The Co atom was found by Patterson synthesis, and the remaining atoms were found by Fourier difference syntheses and full matrix least-squares refinement based on 1383 data with $I > 3\sigma(I)$. At convergence $R = 5.88\%$ ($R_w = 7.10\%$) for 205 parameters. The highest peak in the difference map was 0.69 e/Å^3, and was found near a tetrafluoroborate group. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.



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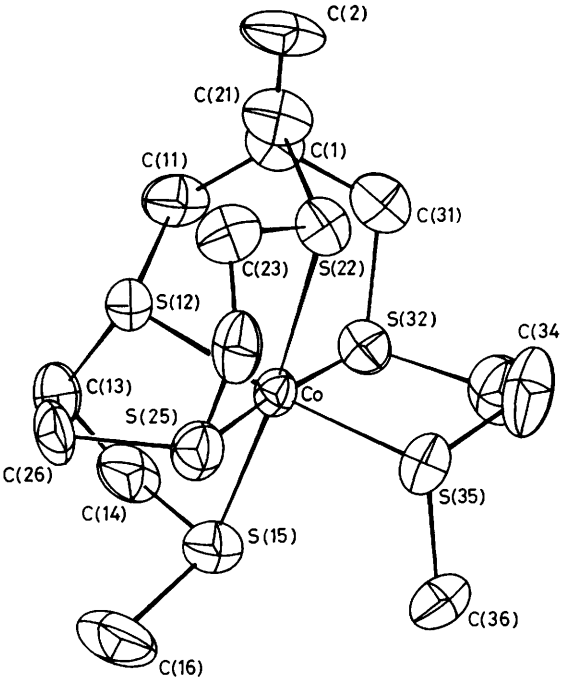

Figure 1. CHEMGRAF drawing of the $[Co(L)]^{2+}$ cation showing thermal ellipsoids at 50% probability level (hydrogen atoms are omitted for clarity).

In $[Co(L)](BF_4)_2$ (Figure 1) all six thioether groups of the ligand co-ordinate to the metal to give an essentially octahedral co-ordination sphere (trigonal twist angle 59.7°). Curiously, L assumes a different conformation here than in $[Ni(L)]^{2+}$, for which the 'ob_3'[2] form was found.[1] Here only two arms adopt the '*ob*' orientation; the third arm [C(21)–S(22)–C(23)–C(24)–S(25)–C(26)] assumes the '*lel*' orientation, and as a consequence the terminal methyl group of this arm suffers a short contact distance [C(16)–C(26) 3.78(2) Å].

Cobalt–sulphur bond distances range from 2.241(4) to 2.501(4) Å; as in $[Ni(L)]^{2+}$, M–S distances to the S atoms at the open end of the ligand exceed those at the closed end by *ca.* 0.03 Å. Co-ordination to six thioether groups results in a low-spin Co^{II} ion [$\mu(298\ K) = 1.67\ \mu_B$ both in CD_3NO_2 solution and in the solid state] that exhibits a severe Jahn–Teller distortion (>0.2 Å), with the two *trans* 'axial' Co–S distances [to S(15) and S(22)] of 2.501(4) and 2.451(4) Å, respectively, exceeding the four 'equatorial' ones, which range from 2.316(4) to 2.241(4) Å. These Co–S distances compare well with those found for the few other known hexakis(thioether)–cobalt(II) complexes, all of which have been reported within the last few years.[3,4]

Probably because of the Jahn–Teller distortion, intraligand bond angles in L show considerably more strain than in the analogous Ni^{II} complex. Bond angles from the unique methyl group to the three methylene groups average 105.5°, with one [∠C(2)–C(1)–C(31)] of 102.3(12)°. To accommodate the metal ion, bridgehead angles between methylene groups [*e.g.*, ∠C(11)–C(1)–C(21)] expand somewhat (average: 113.1°) from tetrahedral values, as do bond angles at methylene carbon atoms [*e.g.*, ∠C(1)–C(11)–S(12)], which average 113.4°.

The growing number of homoleptic thioether complexes of Co^{II} affords an opportunity to assess the effect of geometric deformations upon the redox thermodynamics of the low-spin $Co^{III/II}$ couple. In general thioether co-ordination strongly stabilises Co^{II} over Co^{III}, as in $[Co(18S6)]^{3+/2+}$ [E_0 +844 mV *vs.* normal hydrogen electrode (N.H.E.)],[3] $[Co(24S6)]^{3+/2+}$ (+894 mV *vs.* N.H.E.),[5] and $[Co(ttn)_2]^{3+/2+}$ (+864 mV *vs.* N.H.E.).[3]§ Cyclic voltammetric measurements at a glassy carbon electrode in $MeNO_2$ containing 0.1 M $Bu_4N^+BF_4^-$ show that the $[Co(L)]^{3+/2+}$ couple has a much lower redox potential, +633 mV *vs.* N.H.E., a value close to that found for $[Co(9S3)_2]^{3+/2+}$ (+680 mV *vs.* N.H.E.).[3,6] Geometric factors alone cause this shift of over 200 mV, since both co-ordination spheres comprise six thioethers. Comparable shifts have been reported by Rorabacher *et al.* for Cu–tetrakis(thioether) complexes.[7] The low values for the complexes of L and 9S3 indicate that both these ligands stabilise Co^{II} substantially less than 18S6 or $(ttn)_2$ do. This may be because L geometrically constrains the three donor atoms at the closed end to positions more commensurate with co-ordination to Co^{III} than Co^{II}. This observation clearly suggests a means by which redox potentials may be tuned over substantial ranges without modification of the co-ordination sphere of the metal ion.

In addition to emphasising the extent to which purely geometric factors can shift redox potentials of otherwise identical complexes, the present results demonstrate the efficacy of L as a means of enforcing a hexakis(thioether) environment on first-row ions. Furthermore, use of analogous procedures may provide similar ligands with other donor atoms.

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§ 9S3 = 1,4,7-Trithiacyclononane; 18S6 = 1,4,7,10,13,16-hexathiacyclo-octadecane; 24S6 = 1,5,9,13,17,21-hexathiacyclotetracosane; ttn = 2,5,8-trithianonane.