Cobalt(II) and Cobalt(III) Complexes of a Novel Homoleptic Thioether Cage

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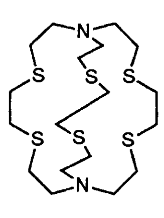
Low-spin hexadentate cobalt(II) and cobalt(III) complexes of the hexathioether cage (1,8-dimethyl-3,6,10,13,16,19-hexathiabicyclo[6.6.6]icosane) have been synthesised, their redox and spectral properties have been investigated, and the encapsulation of the cobalt(II) ion has been established by an X-ray crystal structure determination, which shows the metal ion to be coordinated to six thioether sulphur atoms at distances ranging from 2.265(3) to 2.354(2) Å.

Monodentate thioethers are generally rather poor ligands for first row transition metals.[1] The problem of low stability has in part been overcome by the use of multidentate, or in particular, macrocyclic thioethers.[2] Another possible way of conferring high stability on such metal ion complexes is to form a cage with six sulphur donor atoms oriented to bind to the metal. These cages have been sought for some time and until now have remained rather elusive. One large cryptand with six sulphur ligating atoms and two nitrogen donors in the cage has been described **1** but only a passing reference was made to the possibility of preparing metal complexes.[3] Also, since we have addressed the chelating ability of N_6 **2** and N_3S_3 **3** donor sets in such cages,[4] and noted their capacity to stabilise labile metal ions in complexes, different oxidation states, and to affect electron transfer properties, it was therefore relevant and important to address the same basic issues for the S_6 donor set. Furthermore, the coordinating ability of thioethers with later transition metals, potentially makes ligands of this type industrially and environmentally important for ion selection, detoxification, selective electrodes and other purposes.

We wish to report the synthesis of the novel cage (Me_2S_6sar,



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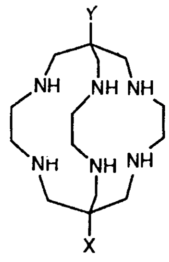

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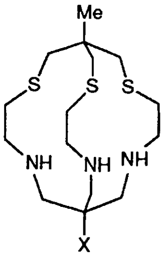

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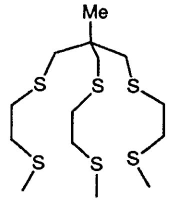

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4), containing six equivalent thioether donors, and the first fully encapsulated transition metal complex containing a homoleptic thioether donor set. Synthesis of **4** involves adaptation of the conventional synthesis for macrocyclic thioethers with a caesium carbonate mediated ring closure reaction[5] (Scheme 1), and will be the subject of a separate report. The ligand has been characterised by ^1H and ^{13}C NMR and chemical ionization mass spectroscopy.†

$[Co(Me_2S_6sar)](CF_3SO_3)_2$ was prepared by mixing a methanolic solution of $[Co(H_2O)_6](CF_3SO_3)_2$ with an equimolar solution of the ligand **4** in dichloromethane. Upon addition of diethyl ether, dark reddish-purple crystals suitable for an X-ray crystallographic analysis were deposited.‡ Notable features of this structure (see Fig. 1) include a $Co–S_6$ coordination sphere with four shorter bonds $[d(Co–S)_{av} = 2.272(7)$ Å] and two significantly longer bonds that are *trans* to each other [2.354(2) Å]. A similar elongation of two *trans* Co–S bonds has been observed in the crystal structure of $[Co([18]aneS_6)](picrate)_2$ $[d(Co–S)_{av} = 2.271(10)$ and 2.479(1) Å, respectively].[6] This elongation of two bonds is consistent with a low-spin formulation for the d^7 cobalt(II) which is expected to show a pronounced Jahn–Teller distortion in the strong field limit. The Co–S bond lengths are similar to those observed in other low-spin cobalt(II) thioether complexes. {The mean Co–S bond distance for $[Co([9]aneS_3)_2](BF_4)_2{\cdot}2MeNO_2$ is 2.321 Å}.[7] The geometry about the metal ion is close to octahedral and the twist angle between opposing trigonal faces of S_3 atoms is 60 °. The chelate rings containing the dimethylene linkages are all in the *lel*§ conformation, in contrast to the ob_3 and ob_2lel conformations reported for the related complexes of nickel(II) and cobalt(II), respectively with the supertripodal ligand **5**.[8,9] Some strain is evident in the bond angles between the 'cap' methyl group, the quaternary carbon and the methylene groups (104.6–105.4°), as well as the methylene–quaternary carbon–methylene units of the cap (112.6–114.8°), and the sulphur–methylene–quaternary carbon units (115.7–116.9°).

The magnetic susceptibility of the complex, 1.6 μ_B, determined in the solid state at 295 K using a vibrating magnetometer is consistent with a low-spin electron configuration, and compatible with values for related thioether systems $\{[Co(\mathbf{5})](BF_4)_2$ 1.67 μ_B;[9] $[Co([9]aneS_3)_2](BF_4)_2{\cdot}2MeNO_2$ 1.71 μ_B,[10] 1.82 μ_B[11]}.

The brick-red cobalt(III) complex was readily prepared by oxidation of the cobalt(II) complex in aqueous solution with $AgCF_3SO_3$, and was isolated as the triflate salt.¶ The diamagnetic nature and complete encapsulation of the metal are confirmed by the ^1H and ^{13}C NMR spectra which also show the average D_3 symmetry of the cation in solution (the protons of the CH_2 in the cap give rise to an AB doublet pair of signals, while the dimethylene protons produce an AA′BB′ multiplet; the ^{13}C spectrum contains only four resonances). Its electronic spectrum resembles that of the related N_3S_3 cage systems,[4,12] and is consistant with an octahedral coordination sphere, but the intensities of the bands in the visible region are considerably greater. This enhanced intensity of thioether donor systems has been observed previously, and attributed to 'intensity stealing' from the charge transfer bands.[13] The charge transfer bands are shifted to lower energy than their counterparts in the N_3S_3 systems,[4,12] but have similar intensities. Clearly, the thioether is a weaker ligand field than the amine, but the interelectronic repulsion parameter for the sulphur ligand is much lower than that for nitrogen.

Cyclic voltammetry in aqueous solution shows a well behaved, near-reversible (ΔE_p = 78 mV) cobalt (III)/(II) couple at 270 mV (*vs.* normal hydrogen electrode NHE); Pt or Au electrode, scan rates 20 and 100 mV s^{-1}, T = 295 K, μ = 0.1 mol dm^{-3}, $NaClO_4$). This is in contrast to the values observed for the N_6 cage $[Co(Me_2sar)]^{3+/2+}$ (−480 mV)[14]‖ and the N_3S_3 cage $[Co(capten)]^{3+/2+}$ (−70 mV)[12]‖ systems, and represents a stabilization of the cobalt(II) state of 750 mV compared with the N_6 analogue. The reduction potential for the $[Co([9]aneS_3)_2]^{3+/2+}$ couple in water has been determined as 420 mV *vs.* NHE[15] and the difference perhaps reflects the strain induced in expanding the cage relative to that in expanding the two facially coordinated macrocycles.

Of considerable interest is the electron self-exchange rate in the light of enhanced rates observed for the $[Co(N_6)]^{2+/3+}$ cages[16] compared with their non-cyclic analogues, and the additional enhancement for the $Co(N_3S_3)$ cages with respect to the $Co(N_6)$ cages.[17] The substantial increase in the self-exchange rate from the $Co(N_6)$ to the $Co(N_3S_3)$ system is

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† ^1H NMR (300MHz, $CDCl_3$) δ (*vs.* internal dioxane at 3.74 ppm) 1.07 (s, 6 H, Me), 2.95 (s, 12 H, CH_2S) and 3.01 (s, 12 H, CH_2S). $^{13}C\{H\}$ NMR (75MHz, $CDCl_3$) δ (*vs.* internal dioxane at 67.39 ppm) 24.68 (Me), 32.80, 41.52 (CH_2S) and 41.93 (quaternary C). Low resolution MS (CI) *m/e* 415.1 (calc. for $C_{16}H_{30}S_6$ 414.78), 387, 358, 193, 165 and 133.

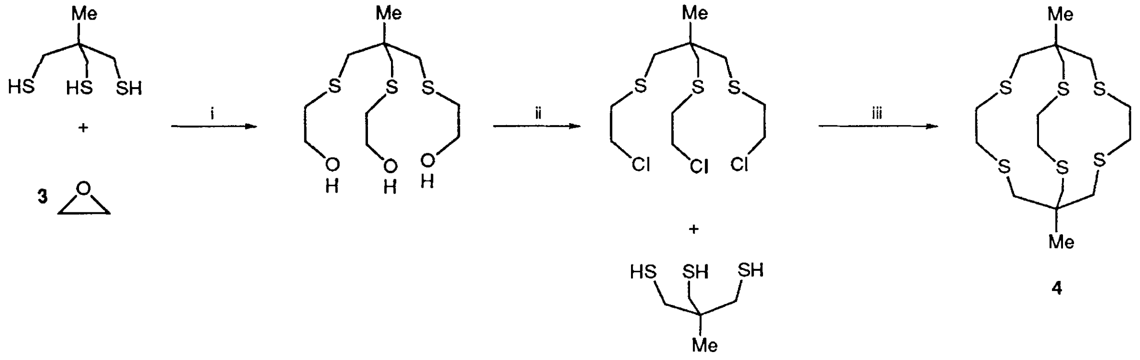
‡ Satisfactory C, H, S and F analyses were obtained.

Crystal and refinement data: $[Co(Me_2S_6sar)](CF_3SO_3)_2$ = $C_{18}H_{30}CoF_6O_6S_8$, M_r = 771.9. Monoclinic, *C*2/*c*, a = 19.350 (4), b = 8.669 (4), c = 17.679 (11) Å, β = 103.86 (4)°, U = 2879 Å^3. D_c (Z = 4) = 1.78 g cm^{-3}. $F(000)$ = 1580. μ(monochromatic Mo-$K\alpha$ radiation, λ = 0.7107$_3$ Å) = 11.6 cm^{-1} (Gaussian correction), specimen: 0.15 × 0.25 × 0.08 mm; $A^*_{min,max}$ = 1.09, 1.19. 2537 unique, diffractometer reflections to $2\theta_{max}$ = 50° ($2\theta/\theta$ scan mode), 1199 observed $[I > 3\sigma(I)]$. R_F = 0.046, R_w (statistical weights) = 0.044. Full-matrix least-squares refinement, anisotropic thermal parameters for the non-hydrogen atoms, $(x,y,z,U_{iso})_H$ constrained at estimates. The cation is disposed on a 2 crystallographic axis; the anion is rotationally disordered. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

§ For *lel* and *ob* terminology, see *Inorg. Chem.*, 1970, **9**, 1.

¶ Satisfactory C, H, S and F analyses were obtained. ^1H NMR (300MHz, $CDCl_3$) δ (*vs.* internal dioxane at 3.74 ppm) 1.45 (s, 6 H, Me), 3.01 (d, J 13.3 Hz, 6 H, C_qCH_2S), 3.20 (m, 6 H, SCH_2CH_2S), 3.43 (d, J 13.3 Hz, 6-H, C_qCH_2S) and 4.16 (m, 6 H, SCH_2CH_2S). $^{13}C\{H\}$ NMR (75MHz, $CDCl_3$) δ (*vs.* internal dioxane at 67.39 ppm) 28.64 (Me), 41.13, 41.99 (CH_2S) and 42.72 (quaternary C). Electronic spectrum in H_2O [λ_{max}, nm (ε_{max}, dm^3 cm^{-1} mol^{-1})]: 494 (2400), 380 (sh, ~2700), 322 (17 700), 244 (6500), 225 (6600).

‖ Me_2sar = **2** (X = Y = Me); capten = **3** (X = H); azacapten = 8-methyl-1,3,13,16-tetraaza-6,10,19-trithiabicyclo[6.6.6]icosane.



Scheme 1 *Reagents and conditions*: i, BzEt$_3$NOH; ii, SOCl$_2$; iii, Cs$_2$CO$_3$, dimethylformamide, 90 °C, 24 h

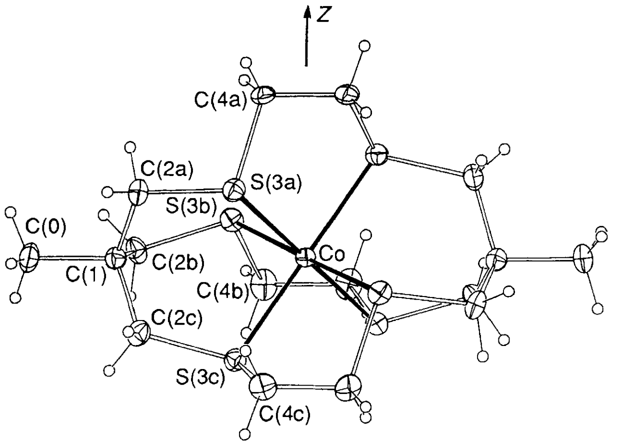


Fig. 1 ORTEP plot of the [Co(Me$_2$S$_6$sar)]$^{2+}$ cation; selected bond lengths (Å) and angles (°): Co–S(3a) 2.265 (3), Co–S(3b) 2.354 (2), Co–S(3c) 2.279 (3); S(3a)–Co–S(3b) 90.8 (1), S(3a)–Co–S(3c) 90.65 (9), S(3a)–Co–S(3a′) 89.4 (1), S(3a)–Co–S(3b′) 88.8 (1), S(3a)–Co–S(3c′) 179.4 (1), S(3b)–Co–S(3c) 91.9 (1), S(3b)–Co–S(3b′) 179.3 (1), S(3b)–Co–S(3c′) 88.6 (1), S(3c)–Co–S(3c′) 89.3 (1)

attributed to the low-spin condition in both oxidation states for the latter complex compared with the cobalt(II) high-spin, cobalt(III) low-spin couples of the N$_6$ cages.[17] This corresponds to a smaller change in Co–N(S) bond length with electron transfer, and reduced reorganization energy. The electron self-exchange rate constant for the [Co(Me$_2$S$_6$-sar)]$^{2+/3+}$ system has been measured by NMR line broadening techniques[18] and its value, 2.8 × 10^4 dm^3 mol^{-1} s^{-1} (T = 300 K, μ = 0.10 mol dm^{-3}), is to be compared with those obtained for [Co(azacapten)]$^{2+/3+}$ (2.2 × 10^4 dm^3 mol^{-1} s^{-1})[17]‖ and for [Co([9]aneS$_3$)$_2$]$^{2+/3+}$ (1.3 × 10^4, 1.6 × 10^5 dm^3 mol^{-1} s^{-1})[15,19] under similar conditions.

Clearly, the S$_6$ cage has stabilised the Co$^{\text{II}}$ oxidation state dramatically relative to the analogous N$_6$ cage, and [Co(Me$_2$-S$_6$sar)]$^{3+}$ should be useful as a modest oxidant. The Co$^{\text{II}}$ ion in the cage is kinetically inert with respect to dissociation in aqueous medium. The electron transfer rates are also faster (~10^4) for the Co$^{\text{II}}$/Co$^{\text{III}}$ couple than for the equivalent N$_6$ system. This type of molecule should be useful to garner the later transition metal ions, especially Ag, Au, Pd and Pt and we are currently extending the synthesis to the larger cage analogues.

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