Enforced Coordination of Chromium(III) to a Thioether Donor in an Encapsulated Complex

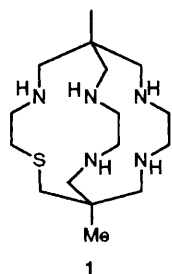James I. Bruce,[a] Lawrence R. Gahan,*[a] Trevor W. Hambley[b] and Robert Stranger[a]

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The synthesis, structure and preliminary spectroscopic and electrochemical properties of a hexadentate chromium(III) complex of a mixed sulfur–nitrogen containing ligand, with the 3-thia-6,10,13,16,19-pentaazabicyclo[6.6.6]icosane macrobicyclic structure, are reported.
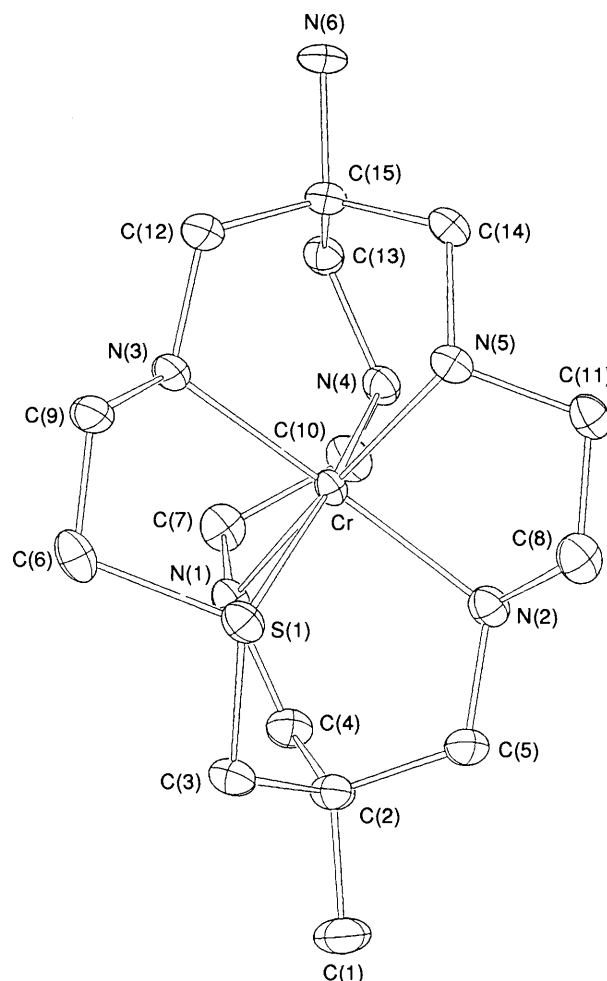
The coordination chemistry of encapsulating ligands such as 3,6,10,13,16,19-hexaazabicyclo[6.6.6]icosane (N_6sar),[1–4] 3,13-dithia-6,10,16,19-tetraazabicyclo[6.6.6]icosane (N_4S_2sar)[5] and 3,13,16-trithia-6,10,19-triazabicyclo[6.6.6]icosane (N_3S_3sar)[6] has been extensively investigated. The ligands impose high stability and significantly influence the redox chemistry and spectroscopic properties of the complexes formed with transition metal ions.[1–12]

Of particular interest is the potential for encapsulating ligands to impose an unexpected coordination geometry and donor environment on a metal ion.[13,14] With this in mind, the possibility of enforced thioether coordination to chromium(III) through the use of an encapsulating ligand containing both nitrogen and sulfur donors seemed worthy of investigation. We report the synthesis of a chromium(III) complex of an encapsulating ligand based on the 3-thia-6,10,13,16,19-penta-

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azabicyclo[6.6.6]icosane ligand structure, **1**, containing the N$_5$S donor set (AMN$_5$Ssar).[15] The complex, [Cr(AMN$_5$S-sarH)]Br$_4$, was prepared by adding CrCl$_3$·H$_2$O to an equi-molar amount of a warm dimethyl sulfoxide solution of the ligand, in the presence of zinc metal. No precautions were taken to protect the complex during the synthesis and the product was isolated after the usual chromatographic purifica-tion procedures (Dowex 50W-X2 cation exchange resin, elution with 3 mol dm^{-3} HCl; Sephadex C-25 cation exchange resin, elution with 0.3 mol dm^{-3} NaCl; removal of solvent under reduced pressure, 40 °C). Crystallisation from aqueous NaBr solution resulted in yellow–orange crystals of the complex [Cr(AMN$_5$SsarH)]Br$_4$·3H$_2$O suitable for an X-ray crystallographic analysis.†‡ The presence of a Cr–S bond [2.399(2) Å] was confirmed by the structural analysis (see Fig. 1). The Cr–N bond lengths in [Cr(AMN$_5$SsarH)]$^{4+}$ [average 2.067(5) Å] are similar to those reported for [Cr(diAMN$_6$-sar)]$^{3+}$ [average 2.070(3) Å],[16] a complex of the hexaamine encapsulating ligand 1,8-diamino-3,6,10,13,16,19-hexaazabi-cyclo[6.6.6]icosane,[4] and [Cr(NH$_3$)$_6$]$^{3+}$ [2.064(3) Å].[17] For [Cr(AMN$_5$SsarH)]$^{4+}$ the five-membered chelate rings con-taining the donor atoms are in the *lel$_2$ob* conformation.[18] The E–C$_{chelate}$ (E = NH or S) torsion angles, *e.g.* C(4)–N(1)–C(7)–C(10), are typical for the *lel* and *ob* conformations.[19] In contrast, for the [Cr(diAMN$_6$sar)]$^{3+}$ complex the chelate rings are in the *lel$_3$* conformation.[16] Previously reported examples of structurally characterised complexes containing a chro-mium–thioether bond are predominately of the type (CO)$_n$-CrL (n = 3,4,5), formally chromium(0), the range of Cr–S bond distances being 2.346(2)–2.458(2) Å, with a significant π component to the bond.[20] For [Cr(AMN$_5$SsarH)]$^{4+}$ the oxidation state of the metal ion is formally 3+, the unusual Cr–S bond being maintained by the encapsulating nature of the ligand and the five Cr–N bonds. Chromium(III) complexes of 1,4,7-trithiacyclononane (ttcn) have been reported but not structurally characterised.[21]

The magnetic moment of [Cr(AMN$_5$SsarH)]$^{4+}$, 4.00 μ$_B$ (297 K), was determined in aqueous solution,[22] and is very similar to those determined for other chromium(III)-thioether complexes [Cr(ttcn)Cl$_3$], 4.1 μ$_B$, and [Cr(ttcn)(SO$_3$CF$_3$)$_3$], 3.9 μ$_B$.[21] These values are consistently higher than those reported for the hexaamine complexes [Cr(diAMN$_6$sar)]$^{3+}$ (3.74 μ$_B$),[16] [Cr(diAMN$_6$sarH$_2$)]$^{5+}$ (3.80 μ$_B$)[16] and [Cr(en)$_3$]$^{3+}$ (3.83

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† Satisfactory microanalytical data were obtained.

‡ *Crystal data:* [Cr(AMN$_5$SsarH)]Br$_4$·3H$_2$O, C$_{15}$H$_{35}$CrN$_6$SBr$_4$·3H$_2$O, M = 757.20, a = 10.680(3), b = 17.668(11), c = 14.905(8) Å, β = 109.78(3)°, monoclinic, space group $P2_1/c$, Z = 4, D_c = 1.901 g cm^{-3}, $F(000)$ = 1508, λ (Mo-Kα) = 0.71069 Å, Gaussian absorption corrections, T_{max} = 0.353, T_{min} = 0.213. Solution by direct methods using SHELXS-86[26] and refinement by full-matrix least-squares analysis (SHELX-76).[27] Br(4) is disordered over two sites with occupancies 0.82 : 0.18. When the minor site is not occupied by Br it is occupied by water molecule O(1). There is also correlated disorder of the minor sites O(1'), O(1'') and O(1*). Final R = 0.038, R_w = 0.040 [2987 F with F > 5σ (F)]. Maximum excursions in final difference map 0.7 and −0.8 e Å^{-3}. 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.

Fig. 1 ORTEP plot of the [Cr(AMN$_5$SsarH)]$^{4+}$ cation: selected bond lengths (Å) and angles (°): Cr–S(1) 2.399(2), Cr–N(1) 2.074(5), Cr–N(2) 2.056(5), Cr–N(3) 2.092(5), Cr–N(4) 2.049(5), Cr–N(5) 2.062(5); N(1)–Cr–S(1) 87.9(1), N(2)–Cr–S(1) 86.3(1), N(2)–Cr–N(1) 93.6(2), N(3)–Cr–S(1) 84.3(1), N(3)–Cr–N(1) 94.6(2), N(3)–Cr–N(2) 167.2(2), N(4)–Cr–S(1) 171.4(1), N(4)–Cr–N(1) 84.2(2), N(4)–Cr–N(2) 97.5(2), N(4)–Cr–N(3) 93.1(2), N(5)–Cr–S(1) 103.9(1), N(5)–Cr–N(1) 167.8(2), N(5)–Cr–N(2) 84.0(2), N(5)–Cr–N(3) 89.9(2), N(5)–Cr–N(4) 84.2(2).

μ$_B$).[23] Since the addition of a single thioether donor brings about a significant increase in the magnetic moment from the spin only value of 3.87 μ$_B$, it is likely that the orbital contribution arises from mixing of the orbitally non-degener-ate ^{4}A$_{2g}$ groundstate with the low energy Cr–S ligand-to-metal charge transfer transition.

Cyclic voltammetry of [Cr(AMN$_5$SsarH)]$^{4+}$ in aqueous solution shows a chromium(III)/(II) couple (ΔE = 88 mV) at −920 mV (*vs.* Ag/AgCl); glassy carbon electrode, scan rate 100 mV s^{-1}, T = 294 K, 0.1 mol dm^{-3} NaClO$_4$. In contrast [Cr(diAMN$_6$sar)]$^{3+}$ and the protonated analogue [Cr(diAMN$_6$sarH$_2$)]$^{5+}$, exhibit quasi-reversible chromium-(III)/(II) couples at −1.35 and −1.04 V, respectively, [*vs.* saturated (KCl) calomel electrode, hanging mercury drop electrode, scan rate 50 mV s^{-1}].[16]

The electronic spectrum of [Cr(AMN$_5$SsarH)]$^{4+}$ in aqueous solution exhibits [λ$_{max}$ cm^{-1} (ε/dm^3 cm^{-1} mol^{-1})] 21 230 (229) and 28 170 (131) assigned to the ^{4}T$_{2g}$ ← ^{4}A$_{2g}$ and ^{4}T$_{1g}$(F) ← ^{4}A$_{2g}$ transitions, respectively. The 400 cm^{-1} splitting of the ^{4}T$_{2g}$ ← ^{4}A$_{2g}$ transition observed in the absorption spectrum of the [Cr(diAMN$_6$sar)]$^{3+}$ complex[16] was not apparent for the thioether complex [Cr(AMN$_5$SsarH)]$^{4+}$. However, as shown in [Cr(en)$_3$]$^{3+}$, this splitting is more likely the result of a Fano-antiresonance structure associated with the interaction

between the broad spin-allowed $^4T_{2g}$ state and the sharp spin-forbidden $^2T_{2g}$ state, rather than low symmetry splitting effects.[24]

On the basis of the observed band positions for the spin-allowed $^4T_{2g} \leftarrow {^4A_{2g}}$ and $^4T_{1g}(F) \leftarrow {^4A_{2g}}$ transitions, ligand-field parameters of $B = 680$, $Dq = 2120$ cm^{-1} and $B = 660$, $Dq = 2200$ cm^{-1} are calculated for $[Cr(AMN_5SsarH)]^{4+}$ and $[Cr(diAMN_6sar)]^{3+}$, respectively. The apparent increase in the Racah B parameter on replacement of a nitrogen donor with a thioether donor is unexpected and may well be the result of the non-inclusion of the $^4T_{1g}(P) \leftarrow {^4A_{2g}}$ transition in the ligand-field analysis. Unfortunately, at room temperature this transition is obscured by the low energy charge-transfer bands. Other studies of mixed nitrogen and thioether donor complexes of nickel(II) and cobalt(III) indicate that B is reduced between 30–40 cm^{-1} for each thioether donor present.[5,25]

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