

## Synthesis and Structure of $(\text{PPh}_4)_2\text{Na}[\text{Cr}_3(\text{SCH}_2\text{CH}_2\text{O})_6]$ containing a Linear Chromium(III) Trimer with Terminal Thiolate and Bridging Alkoxide Linkages

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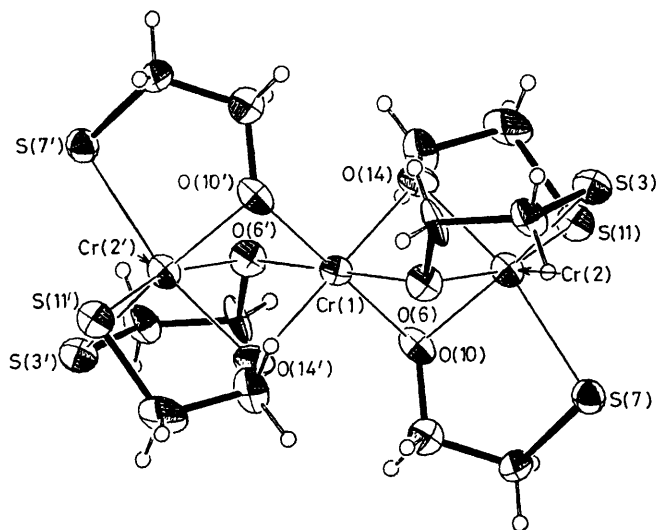
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$(\text{PPh}_4)_2\text{Na}[\text{Cr}_3(\text{SCH}_2\text{CH}_2\text{O})_6] \cdot 2\text{EtOH}$  has been obtained from the reaction of  $\text{CrCl}_3(\text{THF})_3$  (THF = tetrahydrofuran) with  $\text{HSCH}_2\text{CH}_2\text{OH} \cdot 2\text{NaOEt}$  in EtOH; the anion is the first example of a linear chromium(III) trimer and contains antiferromagnetically-coupled metal centres with an  $S = 3/2$  ground state.

Our recent interest in the thiolate chemistry of the early transition metals has concentrated on manganese(III)<sup>1,2</sup> and vanadium(III)<sup>3</sup> and (IV).<sup>3,4</sup> We have now extended our studies to include chromium(III), whose thiolate chemistry has hitherto been essentially unexplored. We have started to investigate its reactions with a variety of thiolates, and herein

report the product obtained from the use of the bifunctional ligand 2-hydroxyethanethiol ( $\text{hetH}_2$ ), which has yielded an interesting trimeric species  $[\text{Cr}_3(\text{het})_6]^{3-}$ .

All operations were carried out under a dinitrogen atmosphere employing standard Schlenk techniques. An ethanolic reaction mixture containing  $\text{CrCl}_3(\text{THF})_3$  (THF = tetrahydro-



**Figure 1.** The structure of  $[\text{Cr}_3(\text{het})_6]^{3-}$  showing the atom labelling scheme. Carbon atoms are numbered consecutively from S to O; thus, one ligand is S(7)–C(8)–C(9)–O(10). Cr(1) lies on the centre of symmetry.

furan),<sup>5</sup> 2-hydroxyethanethiol, and NaOEt in the molar ratio 1:3:6, respectively, yielded an intense blue–green solution and a fine white solid (NaCl). After 2 h, the solid was removed by filtration and  $\text{PPh}_4\text{Br}$  added to the filtrate to yield slowly large green prisms of  $(\text{PPh}_4)_2\text{Na}[\text{Cr}_3(\text{het})_6] \cdot 2\text{EtOH}$ ; this material was found suitable for structural studies. With product identity established, reaction solutions containing a Cr:het<sup>2-</sup> ratio of 1:2 were also found to yield the same product. Non-optimised yields of approximately 43% have been obtained to date.

**Crystal data:**  $\text{C}_{64}\text{H}_{76}\text{O}_8\text{P}_2\text{S}_6\text{NaCr}_3$ ,  $M_r = 1406.61$ , monoclinic, space group  $P2_1/n$ ,  $Z = 4$ ,  $a = 23.605(24)$ ,  $b = 17.390(14)$ ,  $c = 17.668(20)$  Å,  $\beta = 107.09(4)^\circ$ ,  $U = 6931.98$  Å<sup>3</sup>,  $t = -155^\circ\text{C}$ , crystal dimensions  $0.05 \times 0.20 \times 0.20$  mm; data were collected in the range  $6^\circ \leq 2\theta \leq 45^\circ$ . The structure was solved by a combination of direct methods and Fourier techniques, and refined by full-matrix least-squares. The asymmetric unit contains two independent and essentially identical anions, both lying on inversion centres located at the central Cr atom, two  $\text{PPh}_4^+$  cations, one  $\text{Na}^+$  ion, and two EtOH molecules, one of which is seriously disordered. Because of the large number of independent atoms and the disorder problem, all hydrogens were ignored, and only the anion, two P, and one Na atom were refined anisotropically; all other atoms were refined isotropically. 4350 Unique reflections with  $F > 3.0\sigma(F)$  were refined to conventional values of  $R$  and  $R_w$  of 10.98 and 10.75%, respectively.†

The structure of  $[\text{Cr}_3(\text{het})_6]^{3-}$  is shown in Figure 1. The molecule contains three  $\text{Cr}^{\text{III}}$  atoms arranged in a linear fashion with Cr(1) lying on a centre of symmetry; the Cr(2')–Cr(1)–Cr(2) angle is thus exactly  $180^\circ$ . At each end of the molecule, three het<sup>2-</sup> ligands provide three terminal thiolate [S(3), S(7), and S(11)] and three  $\mu_2$ -alkoxide [O(6),

O(10), and O(14)] linkages, the oxygen atoms bridging to the central Cr(1). The metals are thus six-co-ordinate with the central and outside metals possessing an  $\text{O}_6$  and  $\text{O}_3\text{S}_3$  co-ordination environment, respectively, and trigonally distorted octahedral geometry. The unit as a whole is composed of three face-sharing octahedra. The symmetry of the molecule is  $S_6$ , with the  $S_6$  axis coincident with the  $\text{Cr}_3$  axis. The Cr–S bond lengths are in the range 2.356(6)–2.369(6) Å, similar to those found in  $[\text{Cr}(\text{en})(\text{SCH}_2\text{CH}_2\text{COO})]^{+}$  [2.337(2) Å; en = ethylenediamine]<sup>6</sup> and  $[\text{Cr}(\text{L-cys})_2]^{-}$  [2.416(1) Å; L-cys = L-cysteine dianion],<sup>7</sup> which are both six-co-ordinate. The Cr–O bond lengths are of two distinct types: Cr(1)–O values are in the range 1.968(11)–1.989(12) Å while Cr(2,2')–O lengths are noticeably longer, being in the range 2.023(13)–2.041(12) Å.

The Cr  $\cdots$  Cr separations are unusually short for this oxidation state, being 2.677(4) and 2.684(4) Å for the two independent anions. The associated Cr–O–Cr angles are in the range  $83.7(5)$ – $84.4(5)^\circ$ . Comparison can be made with known  $\text{Cr}^{\text{III}}$  dimers containing two or three bridging groups. With two hydroxo-<sup>8</sup> or alkoxo-bridges,<sup>9</sup> Cr  $\cdots$  Cr separations are in the range 2.9–3.1 Å and Cr–O–Cr angles in the range  $95$ – $104^\circ$ . With three halide bridges<sup>10</sup> no Cr  $\cdots$  Cr separation less than 3 Å has ever been seen. Short Cr  $\cdots$  Cr separations [2.642(2) Å] and acute Cr–O–Cr angles [ $84.1(3)^\circ$ ] are seen also in  $[\text{Cr}_2(\text{OH})_3(\text{Me}_3[9]\text{ane-N}_3)_2]^{3+}$  ( $\text{Me}_3[9]\text{ane-N}_3 = 1,4,7$ -trimethyl-1,4,7-triazacyclononane),<sup>11</sup> containing three  $\mu_2$ -OH groups, suggesting these properties may be a consequence of systems containing three bridging oxo-groups. However, more examples must be studied to test the generality of this observation.

Chromium(II) is well known<sup>12</sup> to form metal–metal bonds but the radial contraction of chromium(III) d-orbitals due to the higher oxidation level makes the possibility of direct orbital overlap less likely. That is not to say, however, that the metals are non-interacting. Variable temperature solid-state magnetic susceptibility studies on powdered samples in the range 2–300 K have shown that the  $\text{Cr}^{\text{III}}$  atoms are antiferromagnetically-coupled, presumably via a bridge-mediated superexchange mechanism. At 300 K the effective magnetic moment is  $4.77 \mu_B$  per  $\text{Cr}_3$  unit ( $2.75 \mu_B$  per Cr), significantly less than expected for isolated  $d^3$  centres ( $6.71 \mu_B$  per  $\text{Cr}_3$ ,  $3.87 \mu_B$  per Cr). The moment decreases with decreasing temperature to  $\sim 3.7 \mu_B$  per  $\text{Cr}_3$  at  $\sim 75$  K, below which it is relatively constant. The trimer thus possesses an  $S = 3/2$  ground state. Least-squares fitting of the data to the magnetic susceptibility expression derived for a linear  $\text{Cr}^{\text{III}}$  trimer† has been carried out to quantify the strength of the exchange interaction. The values obtained for the exchange parameters  $J$  and  $J'$  are  $-37.7$  and  $0 \text{ cm}^{-1}$ , respectively.

The trimer  $[\text{Cr}_3(\text{het})_6]^{3-}$  represents the first linear trinuclear chromium(III) system.  $[\text{Cr}_3\text{O}(\text{O}_2\text{CMe})_6(\text{H}_2\text{O})_3]^{+13}$  and  $[\text{Cr}_3\text{O}(\text{nic})_6]^{+}$  (nicH = nicotinic acid)<sup>14</sup> possess the oxo-capped triangular structure characteristic of 'basic carboxylates'. The nearest precedent to  $[\text{Cr}_3(\text{het})_6]^{3-}$  is the mixed-valence (II,III,III) trimer  $\text{cp}_2\text{Cr}_3(\text{O}_2\text{C}\cdot\text{CF}_3)_6$  (cp = cyclopentadienyl)<sup>15</sup> containing an approximately linear  $\text{Cr}_3$  unit with a central Cr(II). Cr  $\cdots$  Cr distances in this molecule are 3.717(1) Å.

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† The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

‡ The spin Hamiltonian used is  $\hat{H} = -2[J_{12}\hat{S}_1\hat{S}_2 + J_{12'}\hat{S}_1\hat{S}_{2'} + J_{22'}\hat{S}_2\hat{S}_{2'}]$  where  $S_1 = S_2 = S_{2'} = 3/2$ ,  $J' = J_{22'}$ , and  $J = J_{12} = J_{12'}$ , by symmetry. Full details of the susceptibility measurements and the derived magnetic susceptibility expression will be reported in due course.

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