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A LINEAR TRINUCLEAR CHROMIUM(III) COMPLEX WITH MIXED THIOLATE/ALKOXIDE LIGATION: PREPARATION AND PROPERTIES OF $(PPh_4)_2(Na)[Cr_3(SCH_2CH_2O)_6]$

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Abstract—The reaction between $CrCl_3(THF)_3$, NaOEt and 2-hydroxyethanethiol ($hetH_2$) gave the complex $(PPh_4)_2Na[Cr_3(het)_6]$ (**1**) as a highly crystalline solid in good yield. Analytical data and structural characterization show the presence also of solvate molecules, one of which is an EtOH group, and another which may be a second EtOH or a H_2O molecule hydrogen-bonded to an Et_2O group; the true formulation is thus **1**·2EtOH or **1**·EtOH·H_2O·Et_2O, or a combination. Complex **1**·EtOH·solvent crystallizes in monoclinic space group $P2_1/n$ with (at $-155°C$): $a = 23.605(24)$, $b = 17.390(14)$, $c = 17.668(20)$ Å, $\beta = 107.09(4)°$, $Z = 4$ and $V = 6931.98$ Å^3. The structure was solved and refined using 4350 unique data with $F > 3.0\sigma(F)$ collected in the range $6° \leqslant 2\theta \leqslant 45°$. Final values of $R(R_w)$ were 10.98 (10.75)%. The high values of $R(R_w)$ are a consequence of the limited number of strong reflections and the large number of independent atoms arising from the presence of two independent PPh_4^+ cations and two independent anions, both lying on inversion centres. As a result, not all atoms were refined anisotropically; the uncertainty in the identity of the disordered second solvate molecule was also detrimental. The two anions are essentially superimposable. The three chromium(III) atoms are linearly disposed ($Cr \cdots Cr$, ~2.7 Å) with each Cr_2 pair bridged by oxygen atoms from three het^{2-} groups whose sulphur atoms are terminally ligated. The inversion centre at the central chromium leads to idealized S_6 symmetry with distorted octahedral geometry at each metal. Variable-temperature, solid-state magnetic susceptibility data were collected in the temperature range 2–300 K. The effective magnetic moment, μ_{eff} per Cr_3, decreases from 4.77 μ_B at 299.9 K to 3.71 μ_B at 75.0 K, is then almost constant to 8.0 K and then decreases to 3.16 μ_B at 2.08 K. The data were least-squares fit to the theoretical expression derived for isotropic exchange

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interactions between three $S = 3/2$ centres. The fitting parameters were found to be $J = -37.7\ \mathrm{cm}^{-1}$, $J' = 0\ \mathrm{cm}^{-1}$ and $g = 1.90$, where J refers to interactions between adjacent chromium(III) centres and J' to the interaction between the terminal chromium(III) centres. The metals are thus antiferromagnetically coupled and the complex has an $S = 3/2$ ground state. The structure of the anion of **1** is compared to that found for the $[Cr_3(E_4)_6]^{3-}$ (E = Se, Te) complexes which also possess a linear Cr_3 unit and tetra-atomic chelating ligands.

Over the last few years, we have been involved in developing the thiolate chemistry of the early transition metals. Much of our work to-date has been concentrated on manganese[1] and vanadium,[2] and a variety of species of different nuclearities and oxidation levels have been obtained. Technical advantage has resulted from the use of either chelating or sterically-bulky thiolate ligands to inhibit polymerization and lead to tractable materials. The use of ethane-1,2-dithiolate (edt^{2-}) has been particularly beneficial. With vanadium(III), an unusual tetra-bridged, metal–metal bonded species $[V_2(edt)_4]^{2-}$ results.[2,3] The unusual nature of the vanadium(III) species prompted us to wonder what the product with chromium(III) would be. As reported by others,[3b] chromium(III) forms a complex with the empirical formula $\{(NMe_4)[Cr(edt)]\}_n$ that could not be obtained in a form suitable for crystallography. Our own efforts along these lines with the same anion proved equally fruitless. In the hope of obtaining better crystals, the related chelate 2-hydroxyethanethiol ($hetH_2$)[4] was employed, and the product was successfully characterized as $[Cr_3(het)_6]^{3-}$, suggesting the edt^{2-} complex may be of similar nuclearity and structure. More importantly, however, $[Cr_3(het)_6]^{3-}$ turned out to be the first example of a linear Cr_3^{III} unit, and it has been reported in preliminary form.[5] The prototypical nature of this complex also prompted magnetochemical studies, and the full details of this combined work are described herein.

EXPERIMENTAL

Syntheses

All manipulations were carried out under a dinitrogen atmosphere using standard anaerobic techniques and apparatus. Solvents were degassed by repeated vacuum/nitrogen cycles. Reagents were obtained commercially and used as received except $CrCl_3(THF)_3$, which was prepared as described elsewhere.[6]

Sodium metal (0.50 g, 21.7 mmol) was dissolved in EtOH (80 cm^3) with stirring and 2-hydroxyethanethiol (0.75 cm^3, 10.7 mmol) added by syringe. The septum cap on the flask was then briefly removed under a positive pressure of nitrogen, solid $CrCl_3(THF)_3$ (2.0 g, 5.3 mmol) was added in one portion, and the septum cap replaced and the flask subjected to vacuum/nitrogen cycles to remove any admitted air. The solid slowly dissolved on stirring to give a deep, blue–green solution and a fine white powder of NaCl. After stirring the solution for 2 h at room temperature, solid PPh_4Br (4.5 g, 10.7 mmol) was added as above and the solution stirred for a further 10 min. The solution was filtered and the filtrate allowed to sit undisturbed for 3 days at room temperature. Large dark green, rectangular-shaped crystals were obtained. These were collected by filtration, washed with 1 : 1 $EtOH/Et_2O$ (3×7 cm^3) and dried *in vacuo*; yield 40–45% based on chromium. The same procedure employing an increased het^{2-} : Cr ratio of 3 :1 gave the same product in comparable yield. A sample from a reaction employing the latter ratio provided the crystal employed for the X-ray structural investigation. Found: C, 54.7; H, 5.9; P, 4.4. Calc. for $C_{60}H_{64}O_6P_2S_6NaCr_3 \cdot C_2H_5OH \cdot H_2O$: C, 54.0; H, 5.3; P, 4.5. Calc. for $C_{60}H_{64}O_6P_2S_6NaCr_3 \cdot (C_2H_5OH)_2$: C, 54.6; H, 5.4; P, 4.4. Calc. for $C_{60}H_{64}O_6P_2S_6NaCr_3 \cdot C_2H_5OH \cdot H_2O \cdot (C_2H_5)_2O$: C, 54.6; H, 5.7; P, 4.3%.

X-ray crystallography and structure solution

Data were collected on a Picker four-circle diffractometer using standard low-temperature facilities; details of the diffractometry, low-temperature facilities and computational procedures employed by the Molecular Structure Centre are available elsewhere.[7] Data collection parameters are summarized in Table 1. A systematic search of a limited hemisphere of reciprocal space located a set of diffraction maxima with monoclinic symmetry and systematic absences corresponding to the unique monoclinic space group $P2_1/n$, an alternate

Table 1. Crystallographic data for complex **1**

$C_{62}H_{72}O_8P_2S_6NaCr_3$[a]
$M_r = 1378.53$
$a = 23.605(24)$ Å
$b = 17.390(14)$ Å
$c = 17.668(20)$ Å
$\beta = 107.09(4)°$
$V = 6931.98$ Å^3
$Z = 4$
$\rho_{calc.} = 1.321$ g cm^{-3}
$\mu = 7.226$ cm^{-1}

Space group $P2_1/n$
$T = -155°C$
$\lambda = 0.71069$ Å
Range $6° \leqslant 2\theta \leqslant 45°$
Unique data 9045
Observed data 4350
$F > 3.0\sigma(F)$
$R = 10.98\%$
$R_W = 10.75\%$

[a] For the formulation $(PPh_4)_2Na[Cr_3(het)_6] \cdot EtOH \cdot H_2O$.

setting of $P2_1/c$. Following data collection, routine data processing and averaging of equivalent reflections, a set of 9045 unique reflections was obtained, of which 4350 were considered observed based on the $F > 3.0\sigma(F)$ criterion. The structure was solved by a combination of direct methods (MULTAN) and standard Fourier techniques. The asymmetric unit consists of two independent anions, each lying on a centre of inversion, one sodium and two PPh_4^+ cations situated in general positions, one well-behaved EtOH solvate molecule and atoms assigned to a second solvate molecule. Because of the large number of independent atoms and the small number of observed reflections, only the non-hydrogen atoms of the anions, the sodium and the two phosphorus atoms were refined with anisotropic thermal parameters. The PPh_4^+ carbon atoms and the non-hydrogen atoms of the well-behaved EtOH molecule were refined isotropically. At this point, a difference Fourier map was used to identify the second solvate molecule. One peak was a reasonable distance from the sodium for assignment as an oxygen atom, O(54), and it refined well as such. In addition, there were six peaks clustered near O(54), but the closest was at 3.134 Å. These peaks were included as carbon atoms with isotropic thermal parameters in the final refinement cycles. Due to limitations imposed by the number of data and independent atoms, a search for a better fitting model for the poorly-behaved second solvate group(s) was not considered warranted. No hydrogen atoms were included in the final cycles. Final discrepancy indices are included in Table 1. The formula and molecular weight in Table 1 are those for $(PPh_4)_2Na[Cr_3(het)_6] \cdot EtOH \cdot H_2O$, the formulation employing only those atoms in the structure solution which are well-behaved and are at chemically-reasonable distances (*vide infra*).

Other measurements

Variable-temperature magnetic susceptibility data were collected on a Series 800 VTS-50 SQUID susceptometer operating at a magnetic field strength of 10 kG. Diamagnetic corrections were estimated from Pascal's constants for the formula **1** $\cdot EtOH \cdot H_2O$ and subtracted from the experimental susceptibility data to obtain the molar paramagnetic susceptibility of the compound. This was then least-squares fit[8] to the appropriate theoretical expression. Solution magnetic moments were obtained in $(CD_3)_2SO$ using the Evans NMR method on a Bruker 300 MHz instrument; a co-axial NMR tube was employed and the frequency separation was measured for the two peaks of the hexamethyldisiloxane internal reference. A diamagnetic correction (Pascal's constants) was employed.

RESULTS AND DISCUSSION

Synthesis and structure

The procedure to complex **1** involves readily-available starting materials and leads to good yields of crystalline product. Treatment of $CrCl_3(THF)_3$ with two or more equiv. of $2Na/hetH_2$ leads to fairly rapid formation of a blue–green solution from which the product slowly crystallizes on addition of a PPh_4^+ salt. Even in the presence of sufficient phosphonium salt, the crystalline material contained one Na^+ cation, which can be rationalized as due to lattice energy effects; the Na^+ is interacting with the anion as will be described below. The formation of a bridged 2 : 1 ligand : chromium product is a consequence of the preference of the alkoxide oxygens to bridge rather than occupy terminal positions; the formation of non-mononuclear products with het^{2-} has also been observed by us in vanadium(IV) chemistry.[4]

The crystal structure and the analytical data for complex **1** indicate the presence of solvate molecules bound to the Na^+ cation. One molecule is clearly an EtOH, refining well albeit with fairly large thermal parameters. The other molecule is less clear. One atom, O(54), is 2.378 Å from the Na^+, similar to 2.289 Å for the Na—O(EtOH) interaction. Six other peaks, refined as carbon atoms, were also located and one possible interpretation is that these belong to severely disordered ethyl carbons of a second EtOH group. However, none is within 3 Å of O(24) and while this may be an artifact of the model, it is also possible that it is not EtOH. An alternative possibility is that the six peaks are from a disordered Et_2O molecule that is hydrogen-bonded to a H_2O molecule [O(24)]. Based on analytical data, the formulations $1 \cdot 2EtOH$ and $1 \cdot EtOH \cdot H_2O \cdot Et_2O$ are both equally acceptable, or indeed a combination of the two.

The structure of the anion is shown in Figs 1 and 2 and selected structural parameters are listed in Table 2. The complex contains two independent anions, each lying on an inversion centre. The two anions are distinguished in Table 2 by the A and B suffixes. Each anion consists of a linear array of three chromium(III) atoms with Cr···Cr separations of 2.677(4) and 2.684(4) Å for anions A and B. Each pair of chromium atoms is bridged by three μ-oxygen atoms from three het^{2-} ligands whose sulphur atoms are terminally ligated. The unit thus consists of three face-sharing octahedra, with the central Cr1 possessing a CrO_6 ligation environment and Cr2 and Cr2′ possessing a CrO_3S_3 environment. The bridges are distinctly asymmetrical, the O—Cr1 distances 1.968(11)–1.989(12) Å being noticeably shorter than O–Cr2 distances, 2.023(13)–2.041(12) Å. All Cr—S distances are essentially identical, 2.023(13)–2.041(12) Å. The inversion centre at Cr1 and the disposition of the chelate rings affords idealized S_6 symmetry to the anions, and a view approximately down the S_6 axis is provided in Fig. 2.

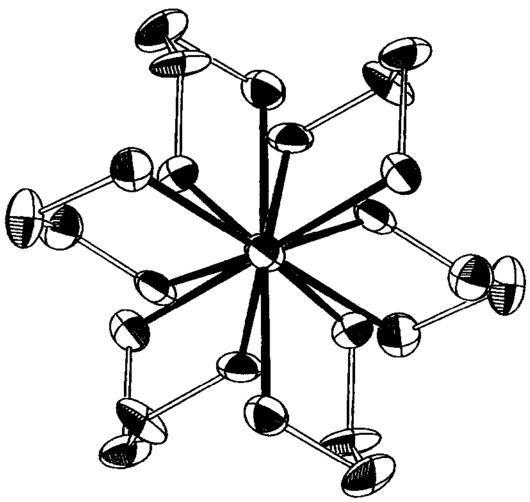

Fig. 2. View of the anion of complex **1** approximately down the Cr_3 axis emphasizing the idealized S_6 symmetry.

The structures of the two independent anions are extremely similar (Table 3) and also extremely similar to that reported for $[Cr_3(E_4)_6]^{3-}$ (E = Se, Te)[9] where E_4^{2-} serves to replace the similarly tetra-atomic SCCO backbone of het^{2-} in **1**. The $[Cr_3(E_4)_6]^{3-}$ ions also lie on inversion centres and have idealized S_6 symmetry. Selected structural parameters of **1** and $[Cr_3(E_4)_6]^{3-}$ are compared in Table 3. The major difference is the Cr···Cr separations which are much shorter in **1** (~2.68 Å) than in the chalcogenide-bridged species (>3.2 Å). Note, however, that the Cr1—X_b—Cr_2 angle in the $[Cr_3(E_4)_6]^{3-}$ complexes is slightly *more* acute (~77.5°) than in **1** (~84°) suggesting the increased Cr···Cr separations in the former are merely the consequence of the larger bridging atoms and the correspondingly longer Cr—X_b distances.

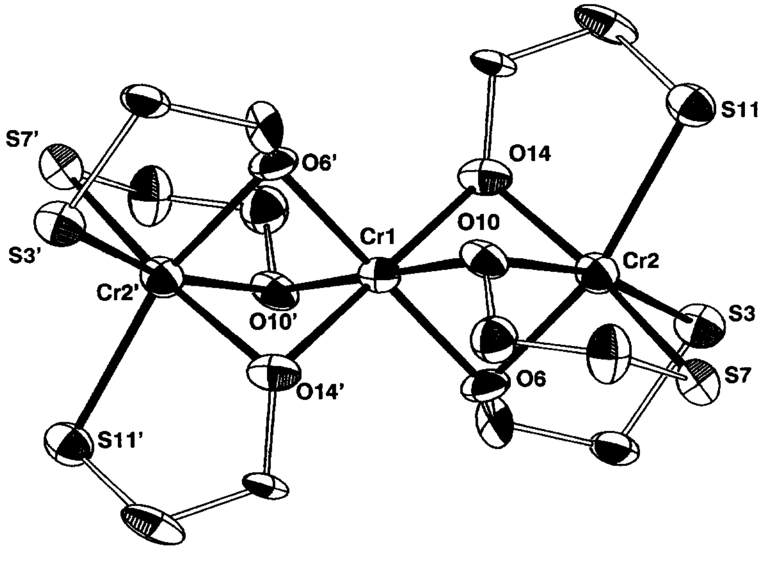

Fig. 1. ORTEP representation of one of the independent anions of complex **1** at the 50% probability level. Primed and unprimed atoms are related by the inversion centre at Cr1. Carbon atoms are numbered consecutively from S to O.

Table 2. Selected bond distances (Å) and angles (deg)

		Bonds	
Cr(1A)···Cr(2A)	2.677(4)	Cr(1B)···Cr(2B)	2.684(4)
Cr(1A)—O(6A)	1.968(11)	Cr(1B)—O(6B)	1.985(12)
Cr(1A)—O(10A)	1.968(12)	Cr(1B)—O(10B)	1.971(11)
Cr(1A)—O(14A)	1.989(12)	Cr(1B)—O(14B)	1.970(11)
Mean	1.975(10)	Mean	1.975(7)
Cr(2A)—S(3A)	2.365(6)	Cr(2B)—S(3B)	2.367(6)
Cr(2A)—S(7A)	2.358(6)	Cr(2B)—S(7B)	2.358(6)
Cr(2A)—S(11A)	2.369(6)	Cr(2B)—S(11B)	2.356(6)
Mean	2.364(5)	Mean	2.360(5)
Cr(2A)—O(6A)	2.030(12)	Cr(2B)—O(6B)	2.023(13)
Cr(2A)—O(10A)	2.027(11)	Cr(2B)—O(10B)	2.025(12)
Cr(2A)—O(14A)	2.023(13)	Cr(2B)—O(14B)	2.041(12)
Mean	2.027(3)	Mean	2.030(8)
		Angles	
O(6A)—Cr(1A)—O(10A)	98.3(5)	O(6B)—Cr(1B)—O(10B)	99.4(5)
O(6A)—Cr(1A)—O(14A)	80.6(5)	O(6B)—Cr(1B)—O(14B)	81.4(5)
O(10A)—Cr(1A)—O(14A)	98.2(5)	O(10B)—Cr(1B)—O(14B)	81.9(5)
Mean	92.4(83)	Mean	87.6(84)
S(3A)—Cr(2A)—S(7A)	94.28(21)	S(3B)—Cr(2B)—S(7B)	96.72(23)
S(3A)—Cr(2A)—S(11A)	95.67(21)	S(3B)—Cr(2B)—S(11B)	95.48(24)
S(7A)—Cr(2A)—S(11A)	97.66(21)	S(7B)—Cr(2B)—S(11B)	95.93(23)
Mean	95.87(139)	Mean	96.04(51)
S(3A)—Cr(2A)—O(6A)	86.7(4)	S(3B)—Cr(2B)—O(6B)	85.6(4)
S(3A)—Cr(2A)—O(14A)	98.8(4)	S(3B)—Cr(2B)—O(10B)	98.4(4)
S(7A)—Cr(2A)—O(6A)	99.0(4)	S(7B)—Cr(2B)—O(10B)	87.0(4)
S(7A)—Cr(2A)—O(10A)	86.9(4)	S(7B)—Cr(2B)—O(14B)	98.5(4)
S(11A)—Cr(2A)—O(10A)	98.6(3)	S(11B)—Cr(2B)—O(6B)	98.2(4)
S(11A)—Cr(2A)—O(14A)	84.6(4)	S(11B)—Cr(2B)—O(14B)	86.5(4)
Mean	92.4(64)	Mean	92.4(60)
S(3A)—Cr(2A)—O(10A)	165.4(3)	S(3B)—Cr(2B)—O(14B)	164.3(4)
S(7A)—Cr(2A)—O(14A)	166.5(4)	S(7B)—Cr(2B)—O(6B)	165.4(4)
S(11A)—Cr(2A)—O(6A)	162.9(4)	S(11B)—Cr(2B)—O(10B)	165.4(4)
Mean	164.9(15)	Mean	165.0(5)
O(6A)—Cr(2A)—O(10A)	78.8(5)	O(6B)—Cr(2B)—O(10B)	78.5(5)
O(6A)—Cr(2A)—O(14A)	78.4(5)	O(6B)—Cr(2B)—O(14B)	78.8(5)
O(10A)—Cr(2A)—O(14A)	79.6(5)	O(10B)—Cr(2B)—O(14B)	78.9(5)
Mean	78.9(5)	Mean	78.7(2)
Cr(1A)—O(6A)—Cr(2A)	84.0(4)	Cr(1B)—O(6B)—Cr(2B)	84.1(5)
Cr(1A)—O(10A)—Cr(2A)	84.1(4)	Cr(1B)—O(10B)—Cr(2B)	84.4(4)
Cr(1A)—O(14A)—Cr(2A)	83.7(5)	Cr(1B)—O(14B)—Cr(2B)	84.0(4)
Mean	83.9(2)	Mean	84.2(2)

The short Cr···Cr separation (~2.68 Å) in **1** appears to be a consequence of the three RO^- bridges. As noted above, three chalcogenide (Se, Te) bridges give >3 Å separations in trinuclear species, as do the $(\mu\text{-}O)(\mu\text{-}O_2CR)_2$ bridges across each chromium pair in the triangular $[Cr_3O(O_2CR)_6]^+$-containing species.[10,11] For dinuclear chromium(III) species, single O^{2-} or OH^- bridges give very long (>3.6 Å) separations and large (135°) Cr—O—Cr angles,[12] whereas two OH^- or OR^- bridges give Cr···Cr separations in the *ca* 2.9–3.1 Å and Cr—O—Cr angles in the *ca* 95–104° range.[13] Only in the complex $[LCr(\mu\text{-}OH)_3CrL]^{3+}$ (L = 1,4,7-trimethyl-1,4,7-triazacyclononane)[14] are the Cr···Cr separations [2.642(2) Å] and Cr—O—Cr angles [84.1(3)°] comparable to those in **1**. Similarly, short M···M separations are found in $[(NH_3)_3Co(OH)_3$

Table 3. Structural comparisons (Å, deg) between complex **1** and $[Cr_3(E_4)_6]^{3-}$ (E = Se, Te)

Parameter[a,b]	1(A)	1(B)	E = Se	E = Te
Cr···Cr	2.677(4)	2.684(4)	3.207	3.41(1)
Cr1—X_b	1.975	1.975	2.587	2.734
Cr2—X_b	2.027	2.030	2.530	2.744
Cr2—X_t	2.364	2.360	2.467	2.689
Cr1—X_b—Cr2	83.9	84.2	77.6	77.3

[a] Cr1 and Cr2 labelled as in Fig. 1; for $[Cr_3(E_4)_6]^{3-}$, the central and terminal chromium atoms were originally labelled Cr2 and Cr1, respectively.

[b] Quoted values represent the mean of S_6 symmetry-related parameters: b = bridging, t = terminal, X = O, S, Se or Te.

$Co(NH_3)_3]^{3+}$ [2.565(6) Å][15] and mixed valence $[LFe(OH)_3FeL]^{2+}$ [2.509(6) Å].[16]

The Na^+ cation in **1** is ligated to oxygen atoms O(S1) and O(S4) of the two solvent groups, and is also bound to four sulphur atoms, S7 and S11 of anion A, and S3 and S7 of anion B. The Na···S interactions are in the range 2.842–3.02 Å, typical for Na···S(thiolate) interactions.[17] The Na^+ ion is distorted octahedral and serves to link the two independent anions and give an extended network in the solid state.

One would not expect the Na^+ anion interactions within the solid state to remain intact on dissolution in good donor solvents such as MeCN or DMSO. However, to probe whether the anion maintains its trinuclear nature in solution, a magnetic moment determination in $(CD_3)_2SO$ was performed (Evans method). For a ~1.6 mM solution at 22.6°C, a magnetic moment of 4.68 μ_B per Cr_3 (2.70 μ_B per Cr) was obtained. This is similar to the solid-state value of 4.77 μ_B (*vide infra*) supporting retention of the trinuclear structure in solution. Disruption into mononuclear units would be expected to give 3.87 μ_B per Cr (d^3 spin-only value).

The visible spectrum of complex **1** has been recorded in DMF solution. Two broad bands are observed at wavelengths of 504 and 671 nm with extinction coefficients (ε_M/Cr_3; L mol^{-1} cm^{-1}) of 560 and 505, respectively. These features resemble those expected for isolated chromium(III) ions in near-octahedral fields and may be assigned to the $^4A_{2g} \rightarrow {}^4T_{1g}$ and $^4A_{2g} \rightarrow {}^4T_{2g}$ transitions.[10] Interpretation of the electronic spectra of weakly exchange-coupled metal aggregates in terms of the *d–d* transitions of the individual metal ions has been shown to be an acceptable approximation.[10] Particularly related to the present case are the spectra of trinuclear $Cr_3O(O_2CMe)_6(H_2O)_3{}^+$; these are also antiferromagnetically coupled (*vide infra*) and display spectra very similar to that of **1**.[10] The two inequivalent types of chromium(III) environments in **1** and the significant lowering of symmetry from octahedral are probably the cause of the broadness in the bands of **1**; the bands representing envelopes of several components. The exchange interactions are almost certainly the origin of the intensity enhancements seen for **1**, the ε_M values being somewhat higher than normally observed for chromium(III).

Magnetic susceptibility studies

Variable-temperature solid-state magnetic susceptibility studies were performed on powdered samples in the temperature range 2–300 K. The formulation **1**·EtOH·H_2O was employed in calculating the moles of material employed; use of other formulations as described above affects the values given below only slightly ($\leqslant$1%), comparable with the intrinsic experimental and fitting uncertainties. The effective magnetic moment per trinuclear complex, μ_{eff}/Cr_3, decreases from 4.77 μ_B at 299.9 K to 3.71 μ_B at 75.0 K, is then almost constant, decreasing to only 3.54 μ_B at 8.0 K, and then decreases more sharply to 3.16 μ_B at 2.08 K (Fig. 3). The 299.9 K value corresponds to 2.75 μ_B per chromium, significantly less than the spin-only value for a chromium(III) (d^3) centre (3.87 μ_B) and indicating the presence of intramolecular antiferromagnetic exchange interactions. The approximate plateau in the μ_{eff} vs T plot is suggestive of an $S = 3/2$ ground state (spin-only value, 3.87 μ_B/Cr_3).

The general spin-Hamiltonian describing the isotropic exchange interaction for a linear trinuclear complex is given by eq. (1).

$$\hat{H} = -2(J_{12}\hat{S}_1\cdot\hat{S}_2 + J_{12'}\hat{S}_1\cdot\hat{S}_{2'} + J_{22'}\hat{S}_2\cdot\hat{S}_{2'}) \quad (1)$$

The pairwise magnetic exchange interactions

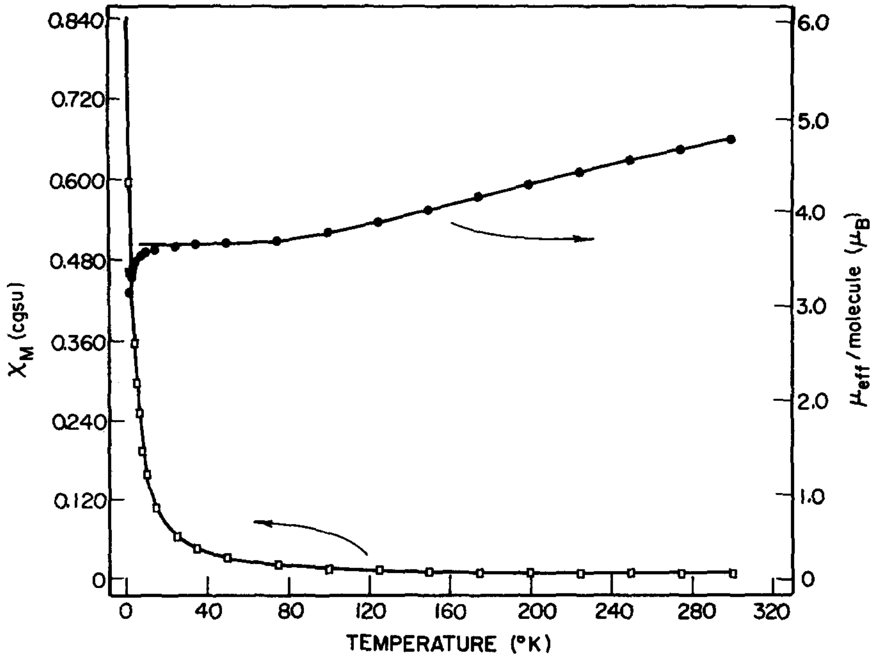

Fig. 3. Plots of the molar paramagnetic susceptibility, χ_M (□), and effective magnetic moment per trinuclear complex, μ_{eff}/Cr_3 (●), vs temperature for a polycrystalline sample of complex **1** · EtOH · H_2O. The solid lines result from a least-square fit of the data to the appropriate theoretical expression. See the text for fitting parameters.

between the central Cr1 and each of the terminal atoms Cr2 and Cr2′ must be identical by symmetry, such that $J_{12} = J_{12'} = J$. The spin-Hamiltonian of eq. (1) can therefore be simplified so that in eq. (2),

$$\hat{H} = -2J(\hat{S}_1 \cdot \hat{S}_2 + \hat{S}_1 \cdot \hat{S}_{2'}) - 2J'(\hat{S}_2 \cdot \hat{S}_{2'}), \quad (2)$$

where $J' = J_{22'}$. For complex **1**, $S_1 = S_2 = S_{2'} = 3/2$. The eigenvalues of the spin-Hamiltonian [eq. (2)] can be determined by using the Kambe vector coupling method[18a] with the coupling scheme $\hat{S}^* = \hat{S}_2 + \hat{S}_{2'}$, and $\hat{S}_T = \hat{S}^* + \hat{S}_1$. The energies of the spin states, which are eigenfunctions of the Hamiltonian in this coupling scheme, are given by eq. (3), where $S = S_1 = S_2 = S_{2'} = 3/2$. The overall degeneracy of this spin system is 64, made up of 12 spin states ranging from $S_T = 1/2$ to 9/2.

$$E = -J[S_T(S_T+1) - S^*(S^*+1) - S(S+1)] \\ -J'[S^*(S^*+1) - 2S(S+1)] \quad (3)$$

A theoretical expression for the molar paramagnetic susceptibility χ_M vs temperature dependence was derived using eq. (3) and the Van Vleck equation;[18b] this expression was employed to fit the experimental χ_M vs T data, and a fit was obtained with $J = -37.7$ cm^{-1}, $J' = 0$ cm^{-1} and $g = 1.90$, with temperature-independent paramagnetism (TIP) held constant at 200×10^{-6} cgsu. No paramagnetic impurity correction term (PAR) was needed. The fit is shown as a solid line in Fig. 3. The zero value of J' is reasonable given the large separation between Cr2 and Cr2′. The ground state with these values of J and J' is a quartet $S_T = 3/2$ state with a doublet $S_T = 1/2$ first excited state and a sextet $S_T = 5/2$ second excited state at ~113 cm and ~189 cm^{-1} in energy above the $S_T = 3/2$ ground state. The $S_T = 3/2$ ground state is thus fairly isolated from the nearest excited states, and this rationalizes the plateau observed in Fig. 3 in the 8–75 K temperature range, essentially all molecules being in the ground state. The sharp decrease in μ_{eff} below 8.0 K is not predicted by the theoretical model employed (Fig. 3). This low-temperature behaviour may be due to either zero field splitting (ZFS) within the $S_T = 3/2$ ground state or to *intermolecular* antiferromagnetic exchange interactions. ZFS with a positive ZFS parameter D would yield a decrease in the observed value of μ_{eff} as the higher M_S states of the $S_T = 3/2$ manifold become depopulated with decreasing temperature. Alternatively, the Na^+ cation linking the anions (*vide supra*) could be mediating weak inter-anion antiferromagnetic exchange interactions which would again decrease μ_{eff} at very low temperatures. Since these effects, whatever their origin, only manifest themselves in the very low temperature region, it was not considered warranted or necessary to pursue a more sophisticated model.

The sign and magnitude of the exchange interactions observed for complex **1** may be compared to those determined for many other di- and trinuclear chromium(III) complexes. In the vast majority of cases, dinuclear Cr_2^{III} complexes have been found to exhibit intramolecular antiferromagnetic exchange interactions with J values in the -0.6 to -55.5 cm^{-1} range.[13] In very few cases have weak ($J = 2.2$ cm^{-1}) ferromagnetic interactions been observed.[19] For triply-bridged Cr_2^{III} species, antiferromagnetic interactions have again been observed; for the $[Cr(\mu\text{-}X)_3Cr]^{3+}$-containing complexes ($X = Cl^-$, Br^-), J values are in the 0 to -8 cm^{-1} range.[20] In contrast, $[LCr(OH)_3CrL]^{3+}$ has a significantly stronger antiferromagnetic exchange interaction ($J = -64$ cm^{-1})[21] consistent with the three shorter Cr—O bonds and better π-bonding oxygen bridges facilitating the super-exchange interaction. For trinuclear systems, antiferromagnetic interactions have been observed in the triangular $[Cr_3(\mu_3\text{-}O)]^{7+}$-containing species with J values in the -9.3 to -19.7 cm^{-1} range.[10] The value of $J = -37.7$ cm^{-1} determined for complex **1** is thus reasonable in both sign and magnitude, the relatively strong nature of the interaction being consistent with the number of bridging oxygen atoms between each Cr_2 pair.

Additional comparison can be made between complex **1** and three other linear Cr_3^{III} species. Two of these $[Cr_3(E_4)_6]^{3-}$ (E = Se, Te) were described above; the third is $Cr_3(lig)_2$ (lig = 1,5-diphenyl-1,3,5-pentanetrionato) which has not been structurally characterized but is assumed linear due to ligand restrictions.[22] In all four complexes, exchange interactions between adjacent chromium(III) ions are antiferromagnetic but the J value for complex **1** (-37.7 cm^{-1}) is significantly greater than those for the E = Se (-10.8 cm^{-1}), E = Te (-5.3 cm^{-1}) and lig^{2-} (-6.0 cm^{-1}) complexes. Again, these differences are consistent with the differing nature and number of bridging atoms. Interestingly, only for complex **1** does the least-squares fit give a $J' = 0$ value for interactions between the terminal chromium(III) atoms; for the other complexes J' is in the range $+1.44$ to -1.35 cm^{-1}.

Supplementary material available. Complete listings of atomic coordinates, thermal parameters, bond distances and angles, the derived susceptibility vs temperature equation, and experimental and calculated magnetic susceptibility data (10 pages): tables of observed and calculated structure factors (12 pages). Ordering information is given on any current masthead page.

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