

Synthesis, structure and magnetism of the oxalato-bridged chromium(III) complex $[\text{NBu}^n_4]_4[\text{Cr}_2(\text{ox})_5] \cdot 2\text{CHCl}_3 \dagger$

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The binuclear complex $[\text{NBu}^n_4]_4[\text{Cr}_2(\text{ox})_5] \cdot 2\text{CHCl}_3$ has been prepared by an ion-exchange procedure employing Dowex 50WX2 cation-exchange resin in the *n*-butylammonium form and potassium tris(oxalato)chromate(III). The dimeric complex was characterised by a crystal structure determination: monoclinic, space group *C2/c*, $a = 29.241(7)$, $b = 15.192(2)$, $c = 22.026(5)$ Å, $\beta = 94.07(1)^\circ$, $Z = 4$. The magnetic susceptibility (300–4.2 K) indicated that the chromium(III) sites were antiferromagnetically coupled ($J = -3.1 \text{ cm}^{-1}$).

Amongst other more elaborate ligands employed in the search for molecular based magnetic materials,^{1–6} the oxalate ligand ($\text{C}_2\text{O}_4^{2-}$) has been employed extensively. Major emphasis in studies employing this ligand is associated with the formation of network structures, particularly when it is bridging two metal centres. In this regard the simple chromium(III) complex potassium tris(oxalato)chromate(III), $\text{K}_3[\text{Cr}(\text{ox})_3]$, has been utilised widely; it is an attractive precursor because of its D_3 symmetry, the η^3 character, the simplicity of its preparation, and, as well, the oxalate bridge is a good mediator in both antiferromagnetic and ferromagnetic interactions in complexes of the type Cr–L–M (where L is oxalate, Cr and M are different metal ions, or Cr^{III} and Cr^{II}).^{7–12} Typical examples of these mixed-metal systems include the complexes $\{[\text{PPh}_4][\text{MnCr}(\text{ox})_3]\}_n$ and $\{\text{NBu}^n_4[\text{MCr}(\text{ox})_3]\}_x$ ($M = \text{Mn}^{2+}$, Fe^{2+} , Co^{2+} , Ni^{2+} , Cu^{2+} or Zn^{2+}).^{9,13} These complexes, designed so as to assume a three-dimensional structure of alternately arrayed chromium(III) and metal(II) ions, are of interest because within these extended states an antiferromagnetic interaction between the adjacent metal-ion pairs leads to a ferrimagnetic state because of non-compensation of the local spins.⁹

Although there are reports of structurally characterised compounds,¹³ one of the suggested drawbacks in using the tris(oxalato)chromate(III) ion is that lattices based on it are poorly crystalline.¹⁴ In an attempt to prepare an analogue of the tris(oxalato)chromate(III) anion expected to be soluble in organic solvents with the anticipation of more control over crystallisation of subsequent products, we sought a synthetic approach to permit ready interchange of the K^+ cation.^{10,15–20}

Experimental

Tetrabutylammonium bromide (Aldrich Chemical Company) was used as received; $\text{K}_3[\text{Cr}(\text{ox})_3] \cdot 3\text{H}_2\text{O}$ was prepared using a literature method.²¹

Preparation of $[\text{NBu}^n_4]_4[\text{Cr}_2(\text{ox})_5] \cdot 2\text{CHCl}_3$

A Dowex cation-exchange resin (50WX2, 200–400 mesh, H⁺ form) was preconditioned by washing with distilled water, 1 M HCl, and then distilled water until the pH of the eluent was identical to that of distilled water. The resin was washed with an aqueous solution (2 dm³) of 0.1 M tetrabutylammonium bromide, then distilled water until no more halide was detected in the

eluent. The salt $\text{K}_3[\text{Cr}(\text{ox})_3] \cdot 3\text{H}_2\text{O}$ (1.0 g, 2.05 mmol) was dissolved in a small volume of distilled water and placed onto the Dowex resin in a narrow band. The column was eluted using distilled water, the single band collected and the solvent removed using a rotary evaporator. The oil which resulted was dissolved in ethanol, and the solvent again removed under reduced pressure. The crude product was purified by chromatography on a silica column (Davisil, 4–20 μm, 60 Å, 3.5 × 8 cm). The single band eluted from the silica with ethanol was collected, filtered and the ethanol removed under vacuum leaving a purple-green solid. Crystals suitable for X-ray crystallography were grown by solvent diffusion (hexane–chloroform) and filtered off (0.15 g, 14%) {Found: C, 52.0; H, 8.6; N, 3.1. $[\text{NBu}^n_4]_4[\text{Cr}_2(\text{ox})_5] \cdot 2\text{CHCl}_3$ requires C, 52.0; H, 8.5; N, 3.2%}.

The synthesis was repeated using Dowex 50WX8 cation-exchange resin in the $\text{NBu}^n_4^+$ form.

Crystallography

Crystal data. $\text{C}_{76}\text{H}_{146}\text{Cl}_6\text{Cr}_2\text{N}_4\text{O}_{20}$, $M = 1752.93$, monoclinic, space group *C2/c*, $a = 29.241(7)$, $b = 15.192(2)$, $c = 22.026(5)$ Å, $\beta = 94.07(1)^\circ$, $U = 9760(4)$ Å³, $Z = 4$, $D_c = 1.194 \text{ g cm}^{-3}$, $\lambda(\text{Mo-K}\alpha) = 0.71073$ Å, $F(000) = 3768$, $0.50 \times 0.20 \times 0.10$ mm, $T = 293(2)$ K, $\mu(\text{Mo-K}\alpha) = 0.448 \text{ mm}^{-1}$, $R = 0.0871$, $wR2 = 0.2444$, goodness of fit 1.026; $R(F_o) = \sum ||F_o| - |F_c|| / \sum |F_o|$, $wR2(F_o)^2 = [\sum w(F_o^2 - F_c^2) / (\sum w F_o^2)]^2$, $w = [\sigma^2(F_o^2) + (0.1752P)^2 + 12.12P]^{-1}$ where $P = \frac{1}{3} [\max(F_o^2, 0) + 2F_c^2]$.

Data collection, structure solution and refinement. For diffractometry the green-purple crystal was mounted on a glass fibre with SuperGlue. Lattice parameters at 293(2) K were determined by least-squares fits to the setting parameters of 25 independent reflections, measured and refined on an Enraf-Nonius CAD4 diffractometer using graphite-monochromated Mo-K α radiation employing the θ scan technique. A total of 6013 independent reflections were recorded in the range $1.51 < \theta < 24.97^\circ$, 1974 of which were considered observed ($I > 2\sigma$) and used in solution of the structure. The structure was solved by heavy-atom methods, and refined using full-matrix least squares on F^2 , anisotropic for all non-hydrogen atoms. Programs used were SHELXS²² and SHELXL 93²³ for solution and refinement, respectively, and PLATON²⁴ for plotting. CCDC reference number 186/788.

Magnetic studies

Magnetic susceptibility studies were made using a Quantum

† Non-SI unit employed: $\mu_B \approx 9.27 \times 10^{-24} \text{ J T}^{-1}$.

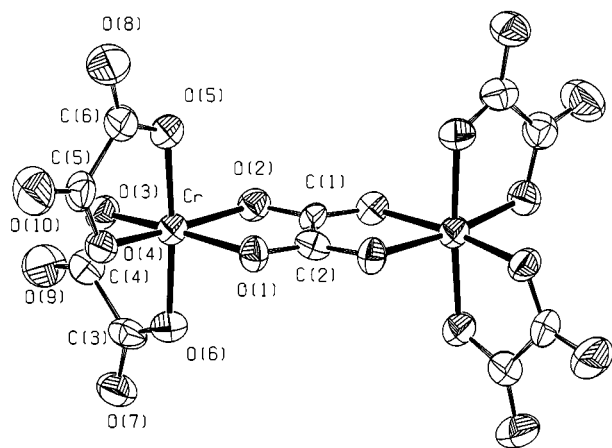


Fig. 1 Structure of the complex anion $[\text{Cr}_2(\text{ox})_5]^{4-}$ with relevant atoms labelled. 30% Probability ellipsoids are shown

Design MPMS SQUID magnetometer with an applied field of 1 T. The powdered sample was contained in a calibrated gelatine capsule which was held in the centre of a soda straw fixed to the end of the sample rod. The magnetisation values of the instrument were calibrated against a standard palladium sample, supplied by Quantum Design, and also chemical calibrants such as $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ and $[\text{Ni}(\text{en})_3][\text{S}_2\text{O}_3]$ (en = ethane-1,2-diamine).

Results and Discussion

In an attempt to prepare the *n*-butylammonium salt, $[\text{NBu}_4]_3[\text{Cr}(\text{ox})_3]$, an aqueous solution of $\text{K}_3[\text{Cr}(\text{ox})_3] \cdot 3\text{H}_2\text{O}$ was passed through a Dowex 50WX2 (200–400 mesh) resin (NBu_4^+ form). The product isolated was the μ -oxalato dimer $[\text{NBu}_4]_4[(\text{ox})_2\text{Cr}(\mu\text{-ox})\text{Cr}(\text{ox})_2]$, viz. $[\text{NBu}_4]_4[\text{Cr}_2(\text{ox})_5]$. Crystals were obtained by hexane diffusion into a chloroform solution of the complex. A purification step employing chromatography on silica was introduced to remove a colourless product which crystallised along with the chromium dimer in the chloroform–hexane diffusion. A unit cell from a crystal produced prior to the introduction of the silica purification step was identical to that produced from a crystal obtained after the introduction of the extra purification step. With a Dowex 50WX8 cation-exchange resin (NBu_4^+ form) in place of the Dowex 50WX2 resin, the $[\text{NBu}_4]_4[\text{Cr}_2(\text{ox})_5]$ dimer was again isolated.

The preparation of $[\text{NBu}_4]_3[\text{Cr}(\text{ox})_3]$ has been reported previously, in one case by reaction of $[\text{Cr}(\text{ox})_3]^{3-}$ as its strychnine salt with tetrabutylammonium iodide with subsequent removal of the precipitated strychnine iodide,¹⁹ and secondly by an ion-exchange procedure with Dowex 50WX8 cation-exchange resin in the NBu_4^+ form.²⁰

The mechanism by which the dimeric species forms in the present case has not been elucidated although reaction on the ion-exchange resin in the presence of NBu_4^+ ion appears crucial as we have not been able to form the dimer complex in reactions in which either of these is omitted. Based on previous studies on the reactions of $[\text{Cr}(\text{ox})_3]^{3-}$ in aqueous and acidic solution, the intermediacy of the diaqua complex $[\text{Cr}(\text{ox})_2(\text{H}_2\text{O})_2]^{-25,26}$ or a five-co-ordinate complex $[\text{Cr}(\text{ox})_2\{\text{OC}(\text{O})\text{C}(\text{O})\text{O}\}]^{3-27-30}$ might be anticipated. Both intermediates have been predicted to result in the $[\text{Cr}(\text{ox})_3]^{3-}$ complex after anation and intramolecular ring closure, following substitution by oxalate, respectively. However, reaction of $\text{K}_3[\text{Cr}(\text{ox})_3]$ and *cis*- $\text{K}[\text{Cr}(\text{ox})_2(\text{H}_2\text{O})_2]$ in aqueous solution at 298 K and subsequent separation of the reaction products on an anion-exchange column resulted in the isolation of the starting materials.

The structure of $[\text{NBu}_4]_4[\text{Cr}_2(\text{ox})_5] \cdot 2\text{CHCl}_3$ consists of the tetrabutylammonium cation, the complex anion $[\text{Cr}_2(\text{ox})_5]^{4-}$ and two solvent molecules (Fig. 1). There are four dimers in the unit cell, sixteen tetrabutylammonium cations, and eight lattice

Table 1 Bond lengths (Å) and angles (°) for $[\text{NBu}_4]_4[\text{Cr}_2(\text{ox})_5] \cdot 2\text{CHCl}_3$

Cr–O(4)	1.923(7)	Cr–O(3)	1.929(7)
Cr–O(5)	1.949(7)	Cr–O(6)	1.952(7)
Cr–O(1)	2.034(7)	Cr–O(2)	2.036(7)
O(1)–C(2)	1.240(10)	O(2)–C(1)	1.254(11)
O(3)–C(4)	1.296(14)	O(4)–C(5)	1.276(13)
O(5)–C(6)	1.297(14)	O(6)–C(3)	1.275(14)
O(7)–C(3)	1.245(13)	O(8)–C(6)	1.233(13)
O(9)–C(4)	1.202(14)	O(10)–C(5)	1.220(13)
C(1)–C(2)	1.55(2)	C(3)–C(4)	1.54(2)
O(4)–Cr–O(3)	93.1(3)	O(4)–Cr–O(5)	83.7(3)
O(3)–Cr–O(5)	93.0(3)	O(4)–Cr–O(6)	93.3(3)
O(3)–Cr–O(6)	83.5(3)	O(5)–Cr–O(6)	175.4(3)
O(4)–Cr–O(1)	93.2(3)	O(3)–Cr–O(1)	172.0(3)
O(5)–Cr–O(1)	92.6(3)	O(6)–Cr–O(1)	91.2(3)
O(4)–Cr–O(2)	172.9(3)	O(3)–Cr–O(2)	92.5(3)
O(5)–Cr–O(2)	91.7(3)	O(6)–Cr–O(2)	91.6(3)
O(1)–Cr–O(2)	81.5(3)	C(2)–O(1)–Cr	113.4(10)
C(1)–O(2)–Cr	112.1(11)	C(4)–O(3)–Cr	115.4(8)
C(5)–O(4)–Cr	114.4(8)	C(6)–O(5)–Cr	113.5(8)
C(3)–O(6)–Cr	112.8(7)	O(2)–C(1)–O(2 ¹)	126(2)
O(2)–C(1)–C(2)	117.1(11)	O(1)–C(2)–C(1)	115.8(11)
O(1)–C(2)–O(1 ¹)	128(2)	O(7)–C(3)–O(6)	126.7(12)
O(7)–C(3)–C(4)	117.0(14)	O(6)–C(3)–C(4)	116.3(12)
O(9)–C(4)–O(3)	123.9(12)	O(9)–C(4)–C(3)	124.2(13)
O(3)–C(4)–C(3)	111.9(13)	O(10)–C(5)–O(4)	124.3(13)
O(10)–C(5)–C(6)	120.9(13)	O(4)–C(5)–C(6)	114.7(11)
O(8)–C(6)–O(5)	123.6(13)	O(8)–C(6)–C(5)	122.9(14)
O(5)–C(6)–C(5)	113.4(11)		

Symmetry operation I: $-x, y, -z + \frac{1}{2}$.

chloroform molecules. Selected bond distances and angles for the complex anion are given in Table 1. The structural details of the disordered cations will not be addressed further.

The complex anion, $[\text{Cr}_2(\text{ox})_5]^{4-}$, has two chromium metal centres bridged by a planar bis(didentate) oxalate ligand, each co-ordinated to two other terminal didentate oxalate ligands. The dimer can potentially exist in either the *racemic* ($\Delta, \Delta; \Lambda, \Lambda$) or *meso* form, however, the crystal structure is of the *racemic* isomer. The complex has crystallographic C_2 symmetry, the two-fold axis being coincident with the C(1)–C(2) bond of the oxalate bridge. Each chromium ion is six-co-ordinate; the geometry is that of a distorted octahedron with the O–Cr–O angles in the range 83.7(3)–93.3(3)°, larger than those reported for the $\text{K}_3[\text{Cr}(\text{ox})_3] \cdot 3\text{H}_2\text{O}$ complex [81.9(1)–82.5(1)°].¹⁵ For the chelating oxalate ligands the O–Cr–O angles are 83.7(3) and 83.5(3)° whilst for the bridging ligand the angle is 81.5(3)°. For the terminal oxalate groups the Cr–O lengths are within the range 1.923(7)–1.952(7) Å, shorter than those observed in $\text{K}_3[\text{Cr}(\text{ox})_3] \cdot 3\text{H}_2\text{O}$ [Cr–O_{av} 1.969(13) Å]¹⁵ and $\text{CaK}[\text{Cr}(\text{ox})_3] \cdot 5\text{H}_2\text{O}$ (Cr–O_{av} 1.970 Å).³¹ The Cr–O bond lengths for the bridging oxalate ligand are longer [2.034(7)–2.036(7) Å] than those of the terminal oxalates. The bridging oxalate ligand is essentially planar [O(2)–C(1)–C(2)–O(1) 0.8°] and the distance between the two chromium centres is 5.32 Å.

The $[(\text{ox})_2\text{M}(\mu\text{-ox})\text{M}(\text{ox})_2]^{n-}$ structural unit has been observed previously for $\text{M} = \text{Ni}^{2+}$, the *racemic* isomer of the complex $[\text{H}_3\text{dien}]_2[\text{Ni}_2(\text{ox})_5] \cdot 12\text{H}_2\text{O}$ (dien = diethylenetriamine) being structurally characterised.³² Two interesting features related to the oxalate bridge arise in the structure of the nickel complex, neither of which are features of the structure of the analogous chromium complex. First $[\text{Ni}_2(\text{ox})_5]^{6-}$ has D_2 point symmetry with four identical C–O bonds. Additionally the bridge is not planar, with a distortion arising from twisting around the C(2)–C(2¹) bond, with a dihedral angle of 9.2(3)°.³²

The infrared spectrum of $[\text{NBu}_4]_4[\text{Cr}_2(\text{ox})_5]$ shows evidence of both didentate {1700 [$\nu_{\text{asym}}(\text{CO})$], 1678 [$\nu_{\text{asym}}(\text{CO})$], 1384 [$\nu_{\text{sym}}(\text{CO})$], 884 cm^{-1} [$\nu_{\text{sym}}(\text{CO})$]} and bridging {1655 [$\nu_{\text{asym}}(\text{OCO})$], 1357 [$\nu_{\text{sym}}(\text{OCO})$], 804 cm^{-1} [$\delta(\text{CO})$]} oxalate co-ordination.^{32–36}

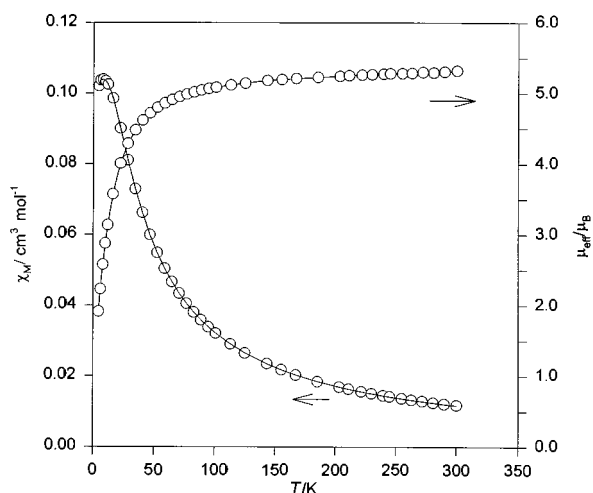


Fig. 2 Plot of χ_M and μ_{eff} vs. T for $[\text{NBu}^n_4]_4[\text{Cr}_2(\text{ox})_5] \cdot 2\text{CHCl}_3$. The solid line represents the best least-squares fit to the experimental data using the parameters given in the text

The visible spectrum in aqueous solution showed peaks at 422 and 568 nm attributed to the spin-allowed ${}^4\text{A}_2 \rightarrow {}^4\text{T}_1$ and ${}^4\text{A}_2 \rightarrow {}^4\text{T}_2$ transitions, respectively. Two low-energy bands at 689 and 697 nm correspond to the spin-forbidden spin-flip ${}^4\text{A}_2 \rightarrow {}^2\text{E}$ transitions. It has been observed previously that, in mono- and di-meric chromium(III) complexes, spin-allowed and -forbidden d-d bands are essentially at the same positions, although the intensity gain of the spin-flip ${}^4\text{A}_2 \rightarrow {}^2\text{E}$ spin-forbidden transitions though co-operative exchange interactions in the dimer may be substantial.³⁷⁻³⁹ The gain in intensity is dependent upon the magnitude of the coupling between the two nuclei.³⁷⁻⁴⁰

Magnetic susceptibility data on a powdered sample of $[\text{NBu}^n_4]_4[\text{Cr}_2(\text{ox})_5]$ were collected in the temperature range 4.5–300 K. A plot of $\chi_M T$ vs. T shows a steep increase with increasing T , indicating antiferromagnetic interaction between the chromium(III) centres.⁴¹ At 298 K for two uncoupled chromium(III) ions the theoretical effective magnetic moment is $5.48 \mu_B$ ($S = \frac{3}{2}$, $g = 2$) close to that observed, $5.32 \mu_B$.

For a dinuclear metal complex exchange coupling may be described by the Hamiltonian, $\mathcal{H} = -2JS_1 \cdot S_2$, where J is the bilinear exchange coupling constant. A biquadratic term (j) which absorbs the effect of a temperature dependence in the bilinear exchange coupling constant⁴² is often introduced to the Hamiltonian; j is typically smaller than 5% of the magnitude of J .⁴³ The exchange coupling for chromium(III) dimers is thus often described by the modified Hamiltonian $\mathcal{H} = -2JS_1 \cdot S_2 - j(S_1 \cdot S_2)^2$ ($S_1 = S_2 = \frac{3}{2}$). The best fit to the data yielded $J = -3.1 \text{ cm}^{-1}$, $j = -0.03 \text{ cm}^{-1}$, $p = 0.08$ and $g = 2.01$ ($R = 7.2 \times 10^{-7}$) where the term p takes into account a monomeric impurity. The function minimised in curve fitting was $R = \sum(\chi_M^{\text{obs}} - \chi_M^{\text{calc}})^2 / \sum(\chi_M^{\text{obs}})^2$. Without taking into account the biquadratic term, the best fit to the data yielded $J = -3.1 \text{ cm}^{-1}$, $p = 0.09$ and $g = 2.01$ ($R = 1.9 \times 10^{-6}$). The experimental and calculated magnetic susceptibilities including the biquadratic term, and the magnetic moment (μ_{eff}) per dimer, are displayed in Fig. 2.

For the $[\text{NBu}^n_4]_4[\text{Cr}_2(\text{ox})_5]$ dimer the t_{2g} orbitals on both octahedral chromium(III) ions are half filled. Possible orbital exchange interactions are reduced by symmetry to four types $[xy-xy, yz-yz(xz-xz), yz-xy(xy-yz), xz-xy, xy-xz]$ and $yz-xz(xz-yz)$. The main contribution to the antiferromagnetic exchange would be from the xy orbitals situated in the plane of the bridging network of both chromium(III) ions,⁴⁴ essentially through occupied oxalate molecular orbitals of π character.^{45,46} The situation for the $[\text{Cr}_2(\text{ox})_5]^{4-}$ complex can be contrasted with that of $[\text{Ni}_2(\text{ox})_5]^{6-}$ with the unpaired electrons in the d_{z^2} and $d_{x^2-y^2}$ orbitals and strong interactions with the oxalate

σ orbitals resulting in large antiferromagnetic coupling ($J = -22.8 \text{ cm}^{-1}$).^{32,47-49}

μ -Oxalato-dimetal complexes of varying structural complexity are known. Homodinuclear dimeric complexes such as $[(\text{N}_4)\text{M}(\mu\text{-C}_2\text{O}_4)\text{M}(\text{N}_4)]$ [$\text{M} = \text{Mn}^{\text{II}}, \text{Fe}^{\text{II}}, \text{Co}^{\text{II}}, \text{Ni}^{\text{II}}, \text{Cu}^{\text{II}}$ or Zn^{II} ; (N_4) = a tetradentate ligand],⁴⁹ mixed valence $[\text{NBu}^n_4]_4[\text{M}_2(\text{ox})_3]$ ($\text{M} = \text{Cr}^{\text{II}}/\text{Cr}^{\text{III}}$ or $\text{Fe}^{\text{II}}/\text{Fe}^{\text{III}}$) complexes with proposed layer structures,^{10,14} $[\text{Fe}(\text{bipy})_3]_n^{2n+}[\text{Fe}_2(\text{ox})_3]_n^{2n-}$ an iron(II) complex with a three dimensional polymeric anionic network (bipy = 2,2'-bipyridyl),⁵⁰ and the dimeric $[\text{H}_3\text{dien}]_2[\text{Ni}_2(\text{ox})_5] \cdot 12\text{H}_2\text{O}$ complex³² are previous examples. The complex $[\text{NBu}^n_4]_4[\text{Cr}_2(\text{ox})_5]$ represents a further addition to the latter structural type of homodinuclear (μ -oxalato) complex.

Acknowledgements

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