

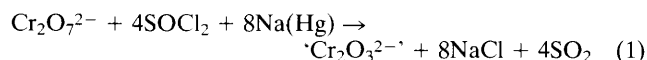
Synthesis of a Tetranuclear Chromium(III) Complex containing a Central μ_4 -Oxo and Two μ_3 -Sulphato Ligands: X-Ray Crystal Structure of $[\text{Ph}_4\text{P}]_3[\text{Cr}_4\text{O}(\mu_3\text{-SO}_4)_3(\mu\text{-Cl})_5\text{Cl}_4]\cdot\text{MeCN}$

William Clegg, R. John Errington,* David C. R. Hockless, Anthony D. Glen and David G. Richards

Department of Chemistry, The University, Newcastle upon Tyne NE1 7RU, UK

A tetranuclear chloroanion of chromium(III) has been synthesised by the non-aqueous reduction of dichromate in the presence of thionyl chloride; X-ray diffraction reveals a novel structure containing a μ_4 -oxo and two μ_3 -sulphato ligands.

During our investigations into the non-aqueous halogenation of early transition metal oxanions we have found that $(\text{Bu}^n_4\text{N})_2[\text{Cr}_2\text{O}_7]$ can be converted to $(\text{Bu}^n_4\text{N})[\text{CrO}_3\text{Cl}]$ in high yield by treatment with $\text{C}_2\text{O}_2\text{Cl}_2$. This prompted us to employ a strategy of halogenation and subsequent reduction as a possible general route to reduced polyoxoanions and we attempted the preparation of a Cr^{II} species using SOCl_2 as the chlorinating agent as in reaction (1). Hence, addition of SOCl_2



to a dichloromethane solution of $(\text{Bu}^n_4\text{N})_2[\text{Cr}_2\text{O}_7]$ over sodium-mercury amalgam with the stoichiometry indicated in reaction (1) produced a purple solution from which crystals were obtained after recrystallisation from $\text{CH}_2\text{Cl}_2\text{-Et}_2\text{O}$. It was evident from the IR spectrum and microanalysis results[†] that this compound was a chloroanion and not a polyoxoanion but its structure was not obvious. Although crystals of this Bu^n_4N^+ salt were unsuitable for an X-ray diffraction study, suitable crystals of $(\text{Ph}_4\text{P})_3[\text{Cr}_4\text{O}(\text{SO}_4)_2\text{Cl}_9]\cdot\text{MeCN}$ were obtained from the analogous reduction of $(\text{Ph}_4\text{P})_2[\text{Cr}_2\text{O}_7]$ in MeCN and the molecular structure of the anion is shown in Fig. 1 together with selected bond lengths and angles. A distorted tetrahedron of four chromium atoms containing a central μ_4 -oxide is capped on two faces by μ_3 -sulphato ligands and bridged along five edges by chlorines, with terminal chlorines completing the octahedral coordination geometry at each metal centre. The central oxygen has a distorted tetrahedral coordination with $\text{Cr}(1)\text{-O}(1)\text{-Cr}(3)$ and $\text{Cr}(2)\text{-O}(1)\text{-Cr}(4)$ angles of $131.6(2)$ and $112.5(2)^\circ$ respectively. The

interior O-S-O angles between coordinated oxygens of the sulphato ligands average 108.3° . The $\text{S-O}_{\text{terminal}}$ distances [$1.427(6)$ Å av.] are shorter than those for the coordinated oxygens [$1.489(8)$ Å av.]. Sulphate bands in the IR spectrum occur at 1275 and 1268 cm^{-1} (terminal S=O) and at 1058 , 1037 , 1015 and 984 cm^{-1} (coordinated S-O). Cr-Cl bands occur at 378 , 368 and 353 cm^{-1} .

To our knowledge this is the first structurally characterised complex containing two tridentate, triply bridging sulphato ligands and also the first example of an oxo-centred tetranuclear Cr^{III} complex. Apart from the oxocarboxylates, $[\text{M}_4\text{O}(\text{O}_2\text{CR})_6]$ ($\text{M} = \text{Be}, \text{Zn}, \text{Co}$ and Mn),¹ few compounds have been shown to contain central tetrahedral μ_4 -oxo ligands; structurally characterised examples being $[\text{Cu}_4\text{OCl}_6(\text{OPPh}_3)_4]$, $[\text{Pb}_6\text{O}(\text{OH})_6]^{4+}$, $\text{TlPb}_8\text{O}_4\text{Br}_9$,² and notably the Cr^{II} compound $[\text{Cr}_4(\mu_4\text{-O})(\text{C}_6\text{H}_4\text{CH}_2\text{NMe}_2)_4(\text{MeCO}_2)_2]^3$ in which the oxide ligand unites two Cr-Cr bonded fragments. It is more usual for Cr^{III} in the presence of potentially bidentate bridging ligands to form compounds with the well established trinuclear $[\text{M}_3\text{O}(\text{O}_2\text{CR})_6\text{L}_3]$ structure containing a planar μ_3 -oxide.¹ In this regard it is also worth noting the controversial proposal that the aquated $\text{Cr}_4(\mu_4\text{-O})(\mu\text{-OH})_5^{4+}$ unit is

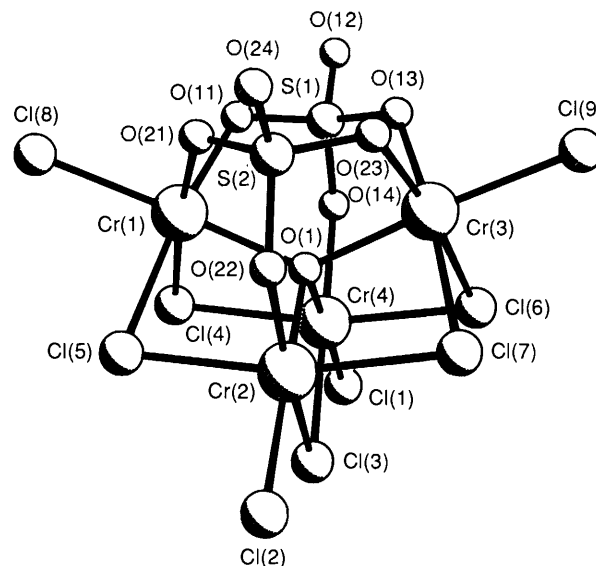


Fig. 1 Molecular structure and atom numbering scheme for $[\text{Cr}_4\text{O}(\text{SO}_4)_2\text{Cl}_9]^{3-}$. Selected mean bond distances (Å) and angles ($^\circ$) not included in the text: $\text{Cr}(1,3)\text{-O}(11,21,13,23)$ $1.976(4)$; $\text{-O}(1)$ $1.987(2)$; $\text{-Cl}(8,9)$ $2.268(10)$; $\text{-Cl}(4,5,6,7)$ $2.388(5)$; $\text{Cr}(2,4)\text{-O}(22,23)$ $1.987(4)$; $\text{-O}(1)$ $2.004(8)$; $\text{-Cl}(3)$ $2.387(8)$; $\text{-Cl}(1,2)$ $2.276(3)$; $\text{-Cl}(4,5,6,7)$ $2.345(7)$; $\text{Cr}(1)\cdots\text{Cr}(3)$ $3.623(3)$; $\text{Cr}(2)\cdots\text{Cr}(4)$ $3.333(3)$; $\text{Cr}(1,3)\cdots\text{Cr}(2,4)$ $3.127(6)$; $\text{Cr}(1,3)\text{-Cl}(4,5,6,7)\text{-Cr}(2,4)$ $82.7(4)$; $\text{Cr}(2)\text{-Cl}(3)\text{-Cr}(4)$ $88.6(1)$; $\text{Cr}(1,3)\text{-O}(11,21,13,23)\text{-S}(1,2)$ $126.2(5)$; $\text{Cr}(2,4)\text{-O}(22,14)\text{-S}(2,1)$ $123.2(2)$.

[†] Satisfactory microanalysis results consistent with $(\text{Bu}^n_4\text{N})_3[\text{Cr}_4\text{O}(\text{SO}_4)_2\text{Cl}_9]\cdot 2\text{Bu}^n_4\text{NCl}\cdot 2\text{CH}_2\text{Cl}_2$ (recrystallised from $\text{CH}_2\text{Cl}_2\text{-Et}_2\text{O}$), $(\text{Bu}^n_4\text{N})_3[\text{Cr}_4\text{O}(\text{SO}_4)_2\text{Cl}_9]\cdot \text{Bu}^n_4\text{NCl}\cdot 1,2\text{-C}_2\text{H}_4\text{Cl}_2$ (recrystallised from $1,2\text{-C}_2\text{H}_4\text{Cl}_2\text{-Et}_2\text{O}$), and $(\text{Ph}_4\text{P})_3[\text{Cr}_4\text{O}(\text{SO}_4)_2\text{Cl}_9]\cdot\text{MeCN}$ have been obtained.

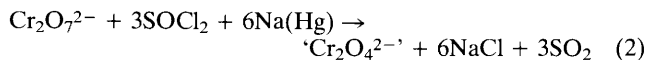
[‡] Crystal data for $(\text{Ph}_4\text{P})_3[\text{Cr}_4\text{O}(\text{SO}_4)_2\text{Cl}_9]\cdot\text{MeCN}$: $\text{C}_{74}\text{H}_{63}\text{Cl}_9\text{Cr}_4\text{N}_3\text{O}_{10}\text{P}_3\text{S}_2$, $M_r = 1753.4$, orthorhombic, $a = 12.829(1)$, $b = 21.593(2)$, $c = 28.315(2)$ Å, $U = 7844.0$ Å³, $Z = 4$, $D_c = 1.485\text{ g cm}^{-3}$, $F(000) = 3560$, $\mu(\text{Mo-K}\alpha) = 1.00\text{ mm}^{-1}$, $\lambda = 0.71073$ Å, space group $P2_12_12_1$. The structure was determined from 7935 unique absorption-corrected diffractometer data with $2\theta < 45^\circ$, and refined with anisotropic thermal parameters and constrained hydrogen atoms to $R = 0.0395$, $R_w = 0.0421$.

Crystal data for $(\text{Bu}^n_4\text{N})_3[\text{Cr}_4\text{O}(\text{SO}_4)_2\text{Cl}_9]$: $\text{C}_{48}\text{H}_{108}\text{N}_3\text{O}_9\text{S}_2\text{Cl}_9\text{Cr}_4$, $M_r = 1462.6$, monoclinic, $a = 13.496(2)$, $b = 11.734(4)$, $c = 23.418(4)$ Å, $\beta = 97.25(1)^\circ$, $U = 3678.9$ Å³, $Z = 2$, $D_c = 1.320\text{ g cm}^{-3}$, $F(000) = 1540$, $\mu(\text{Mo-K}\alpha) = 0.99\text{ mm}^{-1}$, $\lambda = 0.71073$ Å, space group $P2_1/c$. The structure was determined from 3353 unique absorption-corrected diffractometer data with $2\theta < 45^\circ$, and refined with anisotropic thermal parameters and constrained hydrogen atoms to $R = 0.0468$, $R_w = 0.0353$.

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.

one of the products of hydrolytic polymerisation of Cr^{III} ,⁴ a postulate that has been strongly criticised.⁵ Complexes containing μ_3 -sulphato ligands are rare, the only structurally characterised examples being $[\text{H}_2\text{Os}_3(\text{CO})_9(\text{SO}_4)]$,⁶ $[\text{Co}_3\text{Cl}(\text{CF}_3\text{CO}_2)_3(\text{SO}_4)(\text{dme})_3]$ (dme = 1,2-dimethoxyethane),⁷ and $[\text{Cu}_3(\text{L})_3(\text{OH})(\text{SO}_4)]$ (L = pyridine-2-carbaldehyde oximate).⁸

From a similar non-aqueous reduction (2) of $(\text{Bu}^n_4\text{N})_2[\text{Cr}_2\text{O}_7]$ designed to produce a Cr^{III} species, a green-brown crystalline product was obtained for which microanalysis



suggested the formulation $(\text{Bu}^n_4\text{N})_2[\text{Cr}_4\text{O}(\text{SO}_4)_2\text{Cl}_9]$, *i.e.* a mixed oxidation state $\text{Cr}^{\text{III}}_3\text{Cr}^{\text{IV}}$ compound, although the X-ray structure determination of a crystal selected from this sample showed it to be the Cr^{III}_4 compound, $(\text{Bu}^n_4\text{N})_3[\text{Cr}_4\text{O}(\text{SO}_4)_2\text{Cl}_9]$ with full occupancy of the Bu^n_4N^+ sites.[‡] Preliminary cyclic voltammetric studies of the purple Bu^n_4N^+ and Ph_4P^+ salts show an oxidation wave for both compounds at +0.55 V *vs.* the ferrocene-ferrocinium couple suggesting

that a mixed oxidation state complex containing Cr^{IV} might be accessible.

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