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Crystal Structure of $[FeCr_2(\mu_3\text{-}O)(CH_3COO)_6(H_2O)_3]FeCl_4\cdot 2(CH_3)_2CO\cdot CH_3OH$

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Trinuclear complexes containing 3 antiferromagnetically coupled Cr_3 or Fe_3 ions have been investigated by several workers in an attempt to elucidate the mechanism of unpaired electron-spin interactions. Magnetic studies [1] and EPR studies [2] have confirmed the existence of mixed metal complexes with Cr_2FeO and Fe_2CrO groups and they have demonstrated that exchange interactions between the Fe atoms in mixed complexes are larger than in the Fe_3O group; the interpretation for Cr–Cr interactions is less clear. In order to determine more precise structure details of a complex triangulo-cation containing 2 types of metal atom Glowiak and co-workers [3] carried out an X-ray investigation on $[Cr_2FeO(CH_3CO_2)_6(H_2O)_3]NO_3\cdot CH_3COOH$. They found that the Cr and Fe atoms are statistically distributed in the triangulo-cations.

The only other crystal structure which has been published on a mixed Cr–Fe triangulo-system is our own work on the glycine analogue $[Fe_2CrO(glycine)_6(H_2O)_3](ClO_4)_7\cdot 6H_2O$ [4]. Of particular interest in this structure is the fact that the Fe_2Cr arrangement is *ordered.* The 4 symmetry-equivalent cations in each unit cell are arranged so that all of the $Cr–(\mu_3\text{-}O)$ bonds are aligned in 2 directions at only 35.4° to each other.

We have now determined the crystal structure of $[FeCr_2(\mu_3\text{-}O)(CH_3COO)_6(H_2O)_3]FeCl_4\cdot 2(CH_3)_2CO\cdot CH_3OH$ in an attempt to discover another example of a triangulo-structure with an ordered arrangement.

Experimental

The compound was prepared by refluxing (90 °C for 4 h) a mixture of $FeCl_3\cdot 6H_2O$ and $CrCl_3\cdot 6H_2O$ (2:1 molar ratio respectively) with $CH_3COONa\cdot 3H_2O$ (6 mol) in an ethanol–acetic acid solvent mixture (100 ml equivolume). The precipitated NaCl was filtered off and the filtrate was evaporated to dryness. The residue was dissolved in the minimum volume of a methanol–acetone solvent mixture (3:1 by volume) and the resulting solution was set aside at *ca.* 10 °C for 6 h. Almost black crystals suitable for X-ray studies were obtained (20% yield).

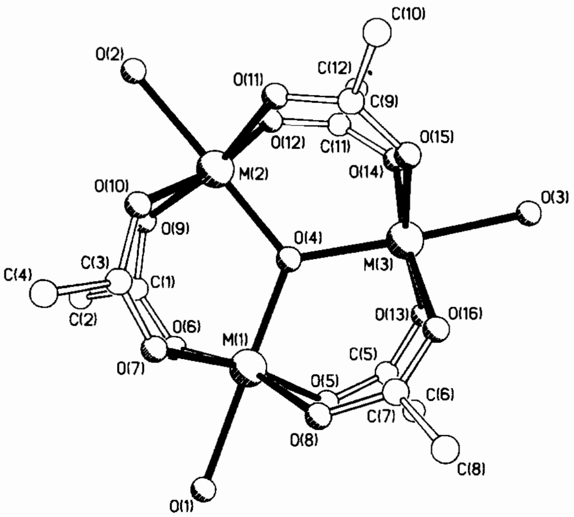

Fig. 1. Structure of the $[Fe_2Cr(\mu_3\text{-}O)(CH_3COO)_6(H_2O)_3]^+$ cation. Average bond lengths are $M–(\mu_3\text{-}O)$ = 1.891 Å, M–O (acetate) = 1.966 Å, $M–O(H_2O)$ = 2.069 Å.

M.P. 210 °C (dec.). *Anal.* Calcd. for $C_{19}H_{40}O_{19}Cl_4Fe_2Cr_2$: C, 24.51; H, 4.34; Fe, 12.01; Cr, 11.18%. Found: C, 24.02; H, 4.31; Fe, 11.24; Cr, 10.96%.

Crystal Data

$C_{19}H_{40}O_{19}Cl_4Fe_2Cr_2$, M = 930; black monoclinic crystals, space group $P2_1/c$, a = 10.164(1), b = 14.026(1), c = 27.371(3) Å, β = 94.29(2)°, V = 3891.1 Å^3, D_c = 1.581 g cm^{-3} for Z = 4, μ(Mo-Kα) = 15.04 cm^{-1}. Intensity data were collected on a Stoe-Siemens AED diffractometer with graphite-monochromated Mo-K radiation (λ = 0.71069 Å). The structure, solved by conventional Patterson and Fourier methods, was refined by full-matrix least-squares, assigning to all non-hydrogen atoms anisotropic thermal factors, using 6847 unique, absorption corrected reflections with $F > 4\sigma(F)$. Final reliability indices are R = 0.060 and R' = 0.074. Some average bond distances are reported in the caption of Fig. 1.*

Infrared spectra were examined for KBr discs on a PE Model 598 spectrometer. Electronic spectra were obtained from solids on a Unicam SP 1700. Electrochemical reduction and oxidation experiments were investigated with a basic potentiostat (250 mA) constructed within the Department, in conjunction

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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.

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with a Chemical Electronics Function Generator RB1.

Results and Discussion

The preparation was carried out in an attempt to prepare the mixed-metal $Fe_2Cr(\mu_3\text{-}O)$ triangulo-cation with a simple Cl^- anion. This is preferable to the potentially explosive compounds which contain ClO_4^- anions (*e.g.* the mixed-metal glycinate complex [4]). Elemental analysis on the black crystals gave a tolerable fit for $[Fe_2Cr(\mu_3\text{-}O)(CH_3COO)_6(H_2O)_3]Cl \cdot 2H_2O$ and the electronic spectrum showed bands characteristic of the $M_3(\mu_3\text{-}O)$ trimer unit (*i.e.* weak absorptions at 720, 695, 685, 695; main bands at 510, 444 nm). The IR spectrum of the black crystals did not reveal the presence of $FeCl_4^-$ anions because the IR active mode at *ca.* 378 cm^{-1} (ν_3) is not readily distinguishable from the ν_{sym} Fe–OH (330 cm^{-1}) and ν_{asym} Fe–OH (395 cm^{-1}) modes of the triangulo-cation [5, 6]. The IR active bending mode, ν_4, of $FeCl_4^-$ is expected to occur at *ca.* 136 cm^{-1} but this is beyond the range of our instrument.

Cyclic voltammetry measurements gave a clear indication that the complex contained two differently co-ordinated iron atoms. $FeCl_3$ (0.01 M) dissolved in MeCN shows a reversible oxidation-reduction wave at +0.125 V *vs.* s.c.e. while $[Fe(\mu_3\text{-}O)(CH_3COO)_6(H_2O)_3]^+CH_3COO^-$ dissolved in MeCN shows only an irreversible reduction wave at –0.25 V *vs.* s.c.e. The new crystalline complex under investigation, when dissolved in MeCN, exhibited both a reversible oxidation-reduction wave at +0.24 V *vs.* s.c.e. and an irreversible reduction wave at –0.15 V *vs.* s.c.e. The presence of a complex $FeCl_4^-$ anion was confirmed by an X-ray study. The structure of the $[FeCr_2(\mu_3\text{-}O)(CH_3COO)_6(H_2O)_3]^+$ cation is shown in Fig. 1 together with some average bond distances around the metal atoms. An important point is that the Cr and Fe atoms appear as a statistical mixture in the triangulo-structure. The refinement is hardly affected by treating all 3 metal atoms as Cr_3, Fe_3 or a statistical mixture. Thus the X-ray method alone does not unambiguously confirm the presence of a mixed-metal cationic species. This observation has a bearing on the earlier work of Glowiak and co-workers [3] who also reported a statistical distribution for $[Cr_2Fe(\mu_3\text{-}O)(CH_3COO)_6(H_2O)_3]NO_3 \cdot CH_3COOH$. The authors report the preparation of dark-red crystals (the usual colour for $Fe_3(\mu_3\text{-}O)$-triangulos *cf.* green for $Cr_3(\mu_3\text{-}O)$ triangulos). The mixed-metal triangulos are usually almost black and in the absence of elemental analysis we are not entirely convinced that they have prepared a mixed-metal cation.

The presence of acetone and methanol molecules in our mixed-metal complex emphasises the importance of solvent choice. The solvent molecules are hydrogen-bonded to the 3 coordinated water molecules present in the cationic structure.

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