The Synthesis and Characterization of Two Novel Octanuclear Mixed-metal Clusters: $[CrM_3O_4(O_2CEt)_8]_2Na_2$(M=Mo,W)

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Two novel insoluble octanuclear mixed-metal clusters with a centrosymmetric $[M_3O_4CrCrO_4M_3]^{14+}$ (M=Mo,W) core have been synthesized and characterized; a strong absorption near zero magnetic field in the EPR spectrum of the CrW_3 cluster is unexpectedly observed.

Triangular, trinuclear species with an $M_3O_4^{4+}$(M=Mo,W) core have received much attention.[1–13] Herein, we describe two octanuclear mixed-metal clusters formulated as $[CrM_3O_4(O_2CEt)_8]_2Na_2$(M=Mo, **1**; M=W, **2**), in which the two $[M_3O_4(O_2CEt)_8]^{4-}$ units, resulting from reaction of Na_2MO_4 with $Cr(CO)_6$ in propionic anhydride solution, are trapped by two chromium ions to form the octanuclear anion with the centrosymmetric $[M_3O_4CrCrO_4M_3]^{14+}$ core. This core has a similar composition to that in the double cubane-type $[Mo_3S_4CoCoS_4Mo_3]^{8+}$ cluster reported by Shibahara *et al.*,[14] but the two $M_3X_4^{4+}$ units are linked differently.

Preparation of the molybdenum compound **1** was carried out in air. A mixture of $Cr(CO)_6$, $Na_2MoO_4{\cdot}2H_2O$ and propionic anhydride was heated at 120 °C for two days. After

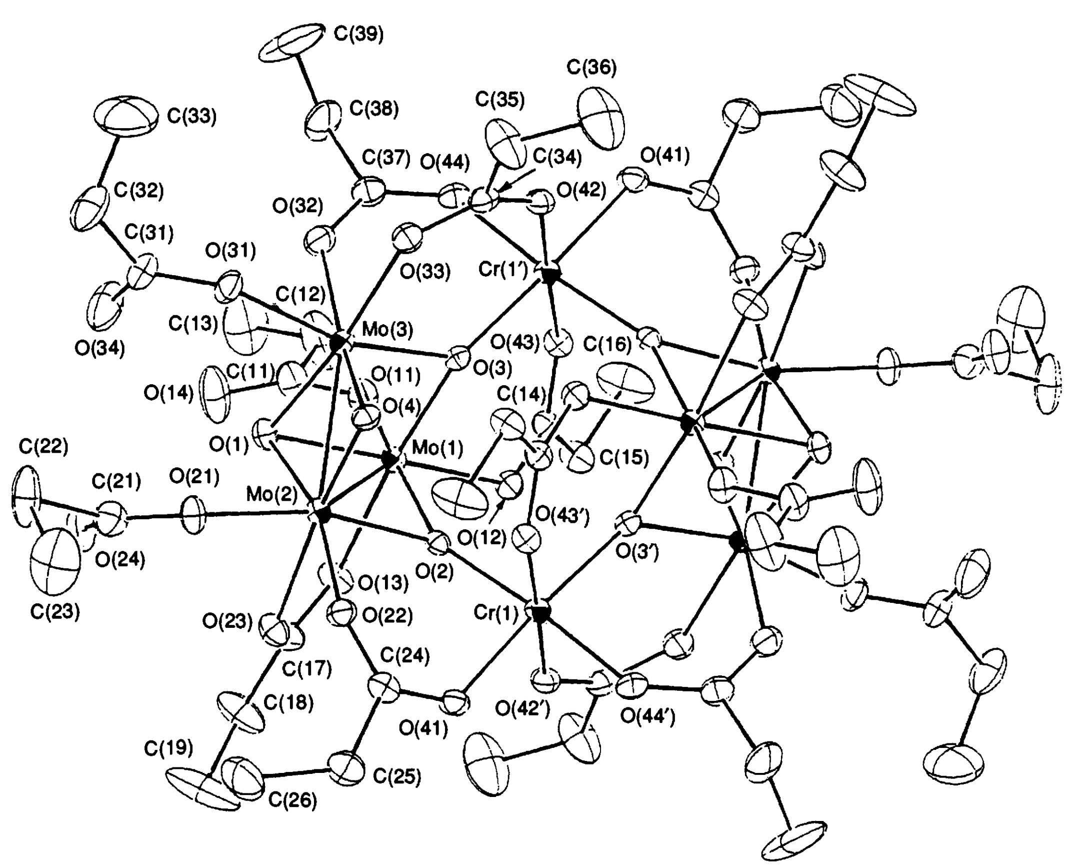

Fig. 1 Perspective view of the anion $[CrMo_3O_4(O_2CEt)_8]_2^{2-}$.

Selected bond lengths (Å) in cluster **1** (M=Mo), **2** (M=W): M(1)–M(2), 2.5108(8), 2.5177(8); M(1)–M(3), 2.5289(9), 2.5361(8); M(2)–M(3), 2.5203(8), 2.5402(9); M(1)–O(1), 2.019(4), 2.056(8); M(1)–O(2), 1.956(4), 1.982(8); M(1)–O(3), 1.934(4), 1.958(8); M(2)–O(1), 2.015(4), 2.039(8); M(2)–O(2), 1.963(4), 1.972(8); M(2)–O(4), 1.901(4), 1.928(9); M(3)–O(1), 2.044(4), 2.082(9); M(3)–O(3), 1.954(4), 1.975(7); M(3)–O(4), 1.913(4), 1.925(8); Cr(1)–O(2), 1.959(4), 1.943(8); Cr(1)–O(3′), 1.935(2), 1.916(8); average bond lengths: M–O (terminal $EtCO_2$), 2.013(4), 2.012(9); M–O (bridging $EtCO_2$) 2.114(4), 2.110(8), Cr–O($EtCO_2$), 1.973(5), 1.986(9).

being cooled, well-formed, black crystals of compound **1**, were obtained. The tungsten compound **2** was prepared similarly using $Na_2WO_4{\cdot}2H_2O$. The two clusters are air stable and are insoluble in water, organic solvents, such as, *N,N′*-dimethylformamide, EtOH, MeCN and tetrahydrofuran, and acids and bases.

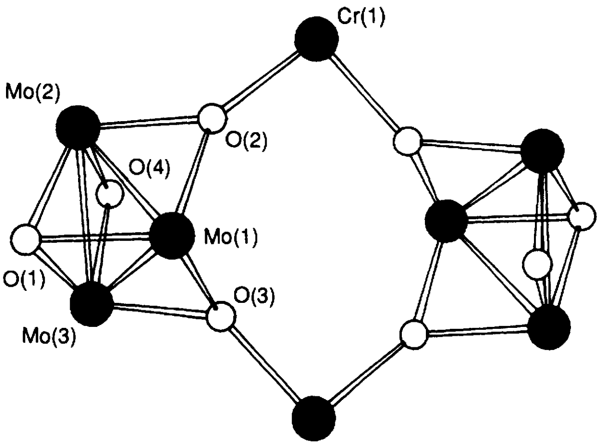

Fig. 2 Structure of $[Mo_3O_4CrCrO_4Mo_3]^{14+}$ core

The X-ray structural analyses† have revealed the existence of the octanuclear centrosymmetric anion of $[(EtCO_2)_8M_3O_4CrCrO_4M_3(O_2CEt)_8]^{2-}$ (M=Mo,W), in which the two $[M_3O_4(O_2CEt)_8]^{4-}$ units are joined by two Cr atoms through four Cr–μ_3O (from μ_2O atoms in both the Mo_3 units) and eight Cr–O_{ca} (bridging $EtCO_2$) bonds as shown in Fig. 1 (M=Mo). The inner part of the anion, the $[Mo_3O_4CrCrO_4Mo_3]^{14+}$ core, is given in Fig. 2. Clusters **1** and **2** are isostructural with each other.

The $[Mo_3O_4(O_2CEt)_8]^{4-}$ unit is similar to other Mo_3O_4 species except that one propionic bridge spans an Mo–Mo

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† *Crystal data* for **1**: $Cr_2Mo_6O_{40}C_{48}H_{80}Na_2$, M_r = 2022.7, triclinic, space group, $P\bar{1}$, a = 12.984(5), b = 13.977(6), c = 12.319(8) Å, α = 109.59(4), β = 117.66(4), γ = 90.48(4)°, V = 1829.1 Å^3, Z = 1, D_c = 1.84 g cm^{-3}, μ = 13.5 cm^{-1}, $F(000)$ = 1010, crystal dimensions 0.2 × 0.3 × 0.1, λ(Mo-Kα) = 0.71076 Å, $2\theta_{max}$ = 50°, RIGAKU AFC5R diffractometer, $\omega/2\theta$ scan, scan speed 16° min^{-1}, scan width 1.313 + 0.35 tanθ, the structure analyses are based on 4597(**1**), 4762(**2**) observed reflections with $I > 3\sigma(I)$; the intensities were corrected for absorption using empirical scan data, Lorentz and polarization factors. The structures were solved by direct methods using MULTAN11/82 and refined by full-matrix least-squares techniques with anisotropic thermal parameters for all non-hydrogen atoms (442 variables), final R = 0.040, R_w = 0.046, where weighting scheme $w = 1/[\sigma(F_o)^2 + (0.020 \times F_o)^2 + 1.00]$. $(\Delta/\sigma)_{max}$ = 0.07, $(\Delta/\rho)_{max}$ = 0.54 e Å^{-3}, S = 1.00, all calculations were performed on a VAX 785 computer using SDP package, scattering factors are taken from international tables.

2: $Cr_2W_6O_{40}C_{48}H_{80}Na_2$, M_r = 2550.2, triclinic, space group $P\bar{1}$, a = 12.961(8), b = 14.015(5), c = 12.312(6) Å, α = 109.75(3), β = 117.56(4), γ = 90.51(5)°, V = 1829.2 Å^3, Z = 1, D_c = 2.32 g cm^{-3}, μ = 99.8 cm^{-1}, $F(000)$ = 1202, crystal dimensions 0.2 × 0.3 × 0.05. Experimental details as for **1**, with scan width 0.945 + 0.35 tanθ. R = 0.040, R_w = 0.046, $(\Delta/\sigma)_{max}$ = 0.02, $(\Delta/\rho)_{max}$ = 0.54 e Å^{-3}, S = 0.99.

Atomic coordinates, bond lengths and angles, and thermal parameters for both compounds have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

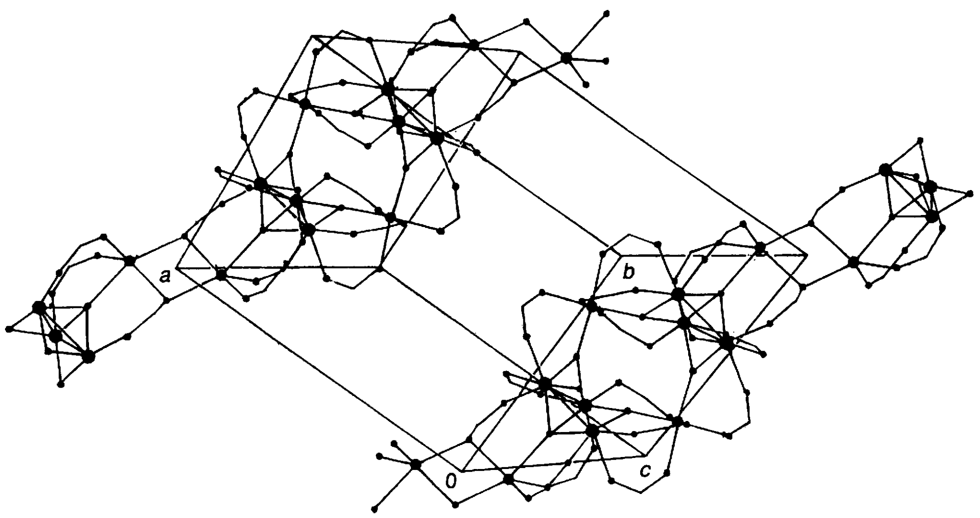

Fig. 3 Chain structure of $[CrM_3O_4(O_2CEt)_8]_2Na_2$(M=Mo, W), for clarity the Et groups are omitted

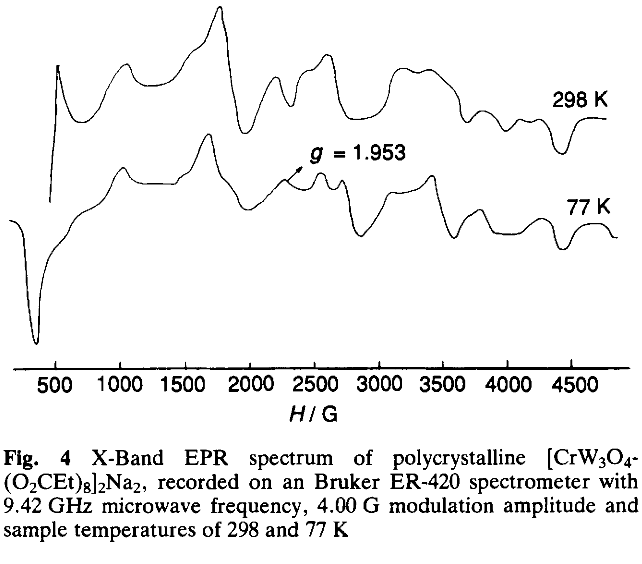

Fig. 4 X-Band EPR spectrum of polycrystalline $[CrW_3O_4(O_2CEt)_8]_2Na_2$, recorded on an Bruker ER-420 spectrometer with 9.42 GHz microwave frequency, 4.00 G modulation amplitude and sample temperatures of 298 and 77 K

edge. Each Mo atom is coordinated to three bridging oxygen [one μ_2O and two μ_3O atoms for Mo(2) and Mo(3), three μ_3O atoms for Mo(1)], one O_t(terminal $EtCO_2$) and two O_{ca}(bridging $EtCO_2$) oxygen atoms in a deformed octahedral arrangement. Each Cr atom is also bonded to six oxygen atoms, including one μ_3O, three O_{ca} atoms from one Mo_3 unit and one μ_3O, one O_{ca} atom from the other, to form an octahedron. At the centre of the structure (Fig. 2) is a near planar $Mo_2Cr_2O_4$ eight-membered ring lying on the crystallographic centric site (1, 0.5, 0.5). The deviations of the eight atoms from the least-squares plane defined by them range from 0.038(1) to 0.318(4) Å, with an average of 0.144 Å. As shown in Fig. 2, the two Cr atoms are bonded to four bridging oxygen atoms in both of the Mo_3 units to form four nearly planar $CrMo_2O$ units similar to the CrW_2O ones found in $W_3(OCH_2Bu^t)O_3Cr_3(O_2CBu^t)_{12}$.[15]

Bond lengths and angles of the $Mo(W)_3O_4$ unit in the two octanuclear anions are similar to those in the discrete M_3O_4 species reported previously. Only the Mo(W)–μ_3O (derived from μ_2O atoms in both the M_3 units) average bond lengths, 1.952(4) Å [1.972(8) Å], are significantly longer than the corresponding M–μ_2O ones [*e.g.* Mo–μ_2O, 1.908(7);[4] W–μ_2O, 1.911 Å[6]]. The Cr–Mo(Cr–W) bond distances fall in the range of 3.583(1)–3.775(1) Å [3.584(1)–3.767(1) Å], indicative of the absence of Cr–M bonding. The small range of the Cr–O distances of 1.935(4)–1.980(5) Å [1.916(8)–1.997(9) Å] clearly indicates Cr^{III}, rather than Cr^{II}, which would be expected to show a much larger range because of Jahn–Teller distortion.[16] Room temperature molecular moments of $5.21(2^{-\frac{1}{2}}) = 3.69\ \mu_B$ per Cr atom in both of the clusters are near to that expected for a magnetically isolated d^3 ion (3.87 μ_B). Thus, by deduction the formal oxidation state per Mo atom is IV. This is also suggested by a comparison of the average Mo–Mo(W–W) distances, 2.5198(5) Å [2.5313(8) Å] in **1** (**2**) *vs.* 251(1) Å[5] in $[Mo_3O_4(EDTA)_{3/2}]_2^{4-}$ and 2.534 Å[6] in $W_3O_4(NCS)_9^{5-}$.

Each Na atom in cluster **1** and **2** is coordinated to five oxygen atoms (one capping O, three O_t atoms from one anion and one O_t atom from another) in a distorted trigonal bipyramidal arrangement with an unexpected short Na–O average distance of about 2.31 Å, which indicates that the Na–O interactions may contain covalent bonding to some extent. The cluster anions are connected by Na atoms to constitute a chain structure, with Na_2O_2 four-membered cycles at the crystallographic centric site (0,0,0) as shown in Fig. 3. In view of their chain structures, short Na–O distances and insolubilities we believe that **1** and **2** are best regarded as new metal cluster materials in extended arrays rather than discrete ionic complexes.

The EPR spectrum of the CrW_3 cluster **2**, shown in Fig. 4, has an unexpectedly strong nonresonant absorption near zero magnetic field. Such an absorption is believed to be characteristic of the superconducting state of Cu–O[17] and $Gd_xLa_{1-x}Al_2$[18] and directly related to the behaviour of the superconducting clusters.[19] This low-field absorption may be related to the chain structure and the strong delocalization of electrons indicated by this very complicated EPR spectrum, which shows many more signals than that of $Cr^{III}{}_3O(MeCO_2)_6(H_2O)_3{}^+$.[20] The latter shows only one signal at room temperature (triplet at 20.4 K) near 3000 G.

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