Synthesis and X-Ray Structure of a Formylated Octamolybdate Cluster $[(HCO)_2(Mo_8O_{28})]^{6-}$

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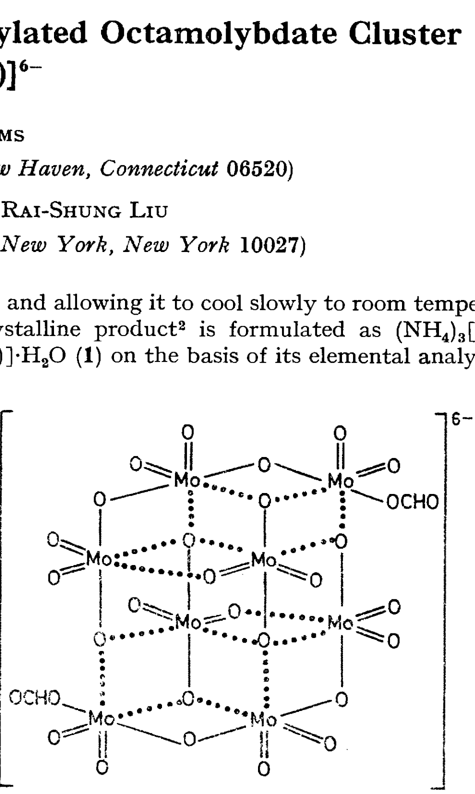
Summary Reaction of formic acid with aqueous $(NH_4)_6$-$[Mo_7O_{24}]$ yields the compound $(NH_4)_3[(HCO)(Mo_4O_{14})]\cdot H_2O$ which has been shown by X-ray crystallography to contain the discrete $[(HCO)_2(Mo_8O_{28})]^{6-}$ anion; this anion is related to the $[H_2Mo_8O_{28}]^{6-}$ anion by replacement of its surface-bound protons with formyl groups.

SINCE the selectivity of ternary groups 5a and 6a transition metal oxides as catalysts for the partial oxidation of hydrocarbons appears to depend upon the ease with which surface carboxylates are formed, the dissociative absorption of carboxylic acids on oxide surfaces has recently received renewed attention.[1] Little structural information is available, however, owing to the difficulty of characterizing surface-bound species. We have therefore attempted to isolate carboxylated molybdate clusters which might serve as models of surface complexes, and report here the synthesis and structure of a formylated octamolybdate cluster $[(HCO)_2(Mo_8O_{28})]^{6-}$. This anion is the first example of a carboxylated metal oxide cluster to be reported in the literature.

Slow addition of HCO_2H (0·8 ml) to a solution of $(NH_4)_6$-$[Mo_7O_{24}]\cdot 4H_2O$ (5 g) in water (13 ml) at 25 °C without stirring yields a supersaturated solution from which clear, colourless crystals are deposited after warming the solution to 45 °C and allowing it to cool slowly to room temperature. The crystalline product[2] is formulated as $(NH_4)_3[(HCO)$-$(Mo_4O_{14})]\cdot H_2O$ (**1**) on the basis of its elemental analysis and i.r. spectrum which displays strong C–O absorptions at 1612 and 1265 cm^{-1} characteristic of weakly bound, unidentate carboxylate groups.[3]



(1)

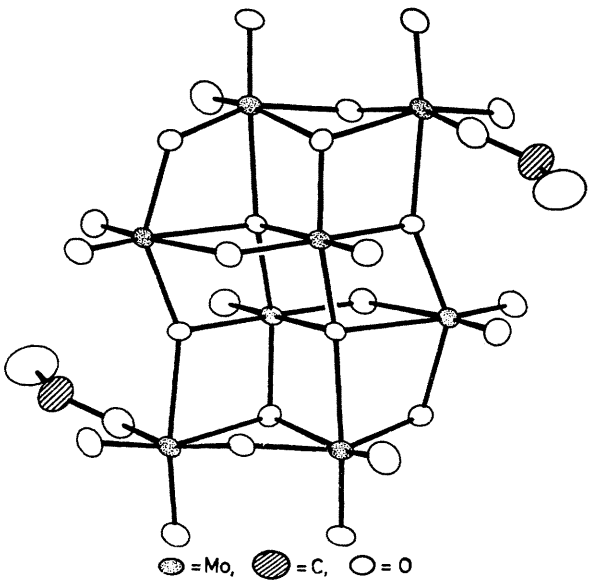


FIGURE. Structure of the centrosymmetric $[(HCO)_2(Mo_8O_{28})]^{6-}$ anion. All atoms shown are represented by thermal vibration ellipsoids drawn to encompass 50% of the electron density.

Crystal data: $C_2H_{30}Mo_8N_6O_{32}$, $M = 1417{\cdot}8$, monoclinic, space group $P2_1/n$ (C^5_2h), $a = 11{\cdot}816(3)$, $b = 8{\cdot}379(4)$, $c = 16{\cdot}802(4)$ Å, $\beta = 93{\cdot}49(2)°$, $U = 1660{\cdot}5(16)$ Å^3, $D_c = 2{\cdot}835$ g cm^{-3}, $Z = 2$, μ(Mo-K_α) = 29·78 cm^{-1}, λ(Mo-K_α) = 0·71073 Å. Diffraction data were collected on an Enraf-Nonius CAD-4 diffractometer. No absorption correction was applied. The structure was solved by a combination of Patterson, difference-Fourier, and least-squares refinement techniques using the Enraf-Nonius SDP program library on a Digital PDP 11/45 computer. The final R value was 5·1% for 3382 reflections with $F_0^2 > 3\sigma(F_0^2)$ obtained in the 2θ range 0—55°. All non-hydrogen atoms were treated anisotropically except the N atoms and the O atoms of the water of hydration which were given isotropic temperature factors. The hydrogen atoms were not located.†

As shown in the Figure, compound (**1**) contains discrete, crystallographically centrosymmetric $[(HCO)_2(Mo_8O_{28})]^{6-}$ anions. Viewed as a derivative of the hypothetical $[Mo_8O_{28}]^{8-}$ anion, the anion has the same structural configuration as the protonated species $[H_2Mo_8O_{28}]^{6-}$ [4] and its condensation polymer $(Mo_8O_{27}{}^{6-})_\infty$.[5] Like the $[H_2Mo_8O_{28}]^{6-}$ anion in $[C_3H_{10}N]_6[H_2Mo_8O_{28}]\cdot 2H_2O$,[4,6] the $[(HCO)_2(Mo_8O_{28})]^{6-}$ anion is photosensitive, becoming red-brown upon exposure to light.

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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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