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Trinuclear Mo(IV) Cluster Ion with a Propylidyne Cap

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Recently the preparation and structure of a remarkable new class of organometallic trinuclear cluster compounds was reported [1–3]. The compounds, containing μ_3-ethylidyne capping groups, were obtained by the reaction of molybdenum hexacarbonyl with a mixture of acetic acid and acetic anhydride, followed by a suitable work-up. The general formula of the trimolybdenum cluster ions is

$$[Mo_3(\mu_3\text{-}X)(\mu_3\text{-}Y)(O_2CCH_3)_6(H_2O)_3]^{n+}$$

where X = CCH_3; Y = O, CCH_3 and n = 1, 2. The presence of the capping ethylidyne groups in these high valence molybdenum complexes was confirmed by a thorough X-ray crystallographic analysis and ^{13}C NMR studies [2]. The ^{13}C tracer study showed that the ethylidyne group arises by reduction of the acetate group. If an acetate salt is added to the $Mo(CO)_6/CH_3CO_2H/(CH_3CO_2)O$ reaction mixture, the main product obtained after the dilution of the solution with H_2O is $[Mo_3O(CCH_3)(OAc)_6(H_2O)_3]^+$. The oxidation state of the molybdenum atoms in this yellow-orange, diamagnetic ion is +4 and hence, six d electrons occupy the M–M molecular orbitals. The Mo–Mo distance, as found in the fluoroborate salt of this ion [2], is 2.752(1) Å. The three molybdenum atoms in this structure are triply bridged by one oxygen atom and one ethylidyne group above and below the triangle plane.

We now report that the reaction of molybdenum hexacarbonyl with a mixture of propionic acid/propionic anhydride followed by the chromatographic separation of the products, yields the propionato analogue of the mono-ethylidyne trinuclear cluster ion, namely, $[Mo_3O(CCH_2CH_3)(O_2CC_2H_5)_6(H_2O)_3]^+$. This new ion contains six bridging propionates and one propylidyne capping group.

Experimental

$Mo(CO)_6$ was refluxed for 4 h with a mixture of 1:4 propionic acid/propionic anhydride. The resulting dark brown solution was diluted with water and stirred for 2 h at *ca.* 100 °C. The solution was then absorbed on a DOWEX 50 W cation exchange column and eluted with 0.2 *M* $ZnBr_2$. A slow evaporation of the yellow-orange eluate yielded crystals of the same color.

TABLE I. Some Important Average Bond Lengths (A) in $[Mo_3O(CCH_2CH_3)(pr)_6(H_2O)_3][Zn_2Br_6]_{1/2}$.

Mo–Mo	2.742(4)	$Zn–Br_b$	2.47(1)
Mo–O(capping)	1.98(2)	$Zn–Br_t$	2.32(1)
Mo–C(capping)	2.05(4)		

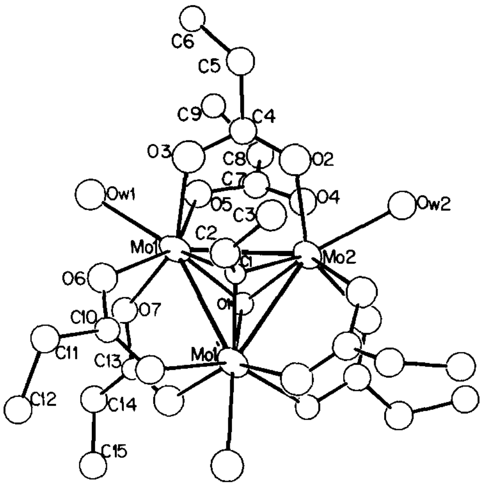

Fig. 1. The structure of $[Mo_3O(CCH_2CH_3)(O_2CC_2H_5)_6(H_2O)_3]^+$.

These crystals were found to belong to space group *C2/m* with *a* = 24.063(4) Å, *b* = 13.642(2) Å, *c* = 12.534(2) Å, β = 113.12(5)° and *Z* = 4. The structure was solved and the formula was shown to be $[Mo_3O(CCH_2CH_3)(O_2CC_2H_5)_6(H_2O)_3][Zn_2Br_6]_{1/2}$. The trinuclear cation *1*, has the structure shown in Fig. 1. A crystallographic mirror plane, perpendicular to the triangle, bisects the ion and passes through Mo(2), Ow(2), O(1), C(1), C(2), C(3) and all carbon atoms of the propionato groups bridging Mo(1) and Mo(1)'. The electronic absorption spectrum of *1* is identical with the spectrum of the acetato analogue $[Mo_3O(CCH_3)(OAc)_6(H_2O)_3]^+$, *2*. The dimensions of the $Mo_3O(CCH_2CH_3)$ central unit are similar to those found in *2* and are given in Table I. The 4+ charge of the four cluster cations in the unit cell is balanced by two units of $Zn_2\mathit{Br}_6^{2-}$ residing

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on a (two-fold) *2/m* crystallographic center. The $Zn_2Br_6^{2-}$ ion consists of two $ZnBr_4$ tetrahedra, sharing one edge. It is subjected to a two-fold disorder, the two bridging bromine atoms lie on the mirror plane while two terminal bromine atoms lie on a crystallogrpahic two-fold axis. The zinc atom and one terminal bromine atom occupy general positions and were refined with occupancy factors of 0.5. Some bond distances in the $Zn_2Br_6^{2-}$ unit are given in Table I. A detailed report on this structure and other products of the reaction between $Mo(CO)_6$ and propionic acid will be presented elsewhere.

Acknowledgement

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References

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