Preparation and Crystal Structure of Potassium Salt of the Binuclear Molybdenum(III) Complex, μ-Acetato-di-μ-hydroxo-μ(*NN′*) ethylenediaminetetra-acetato-bis[molybdenum(III)], K[$Mo_2(OH)_2(O_2CMe)(C_{10}H_{12}O_8N_2)$]

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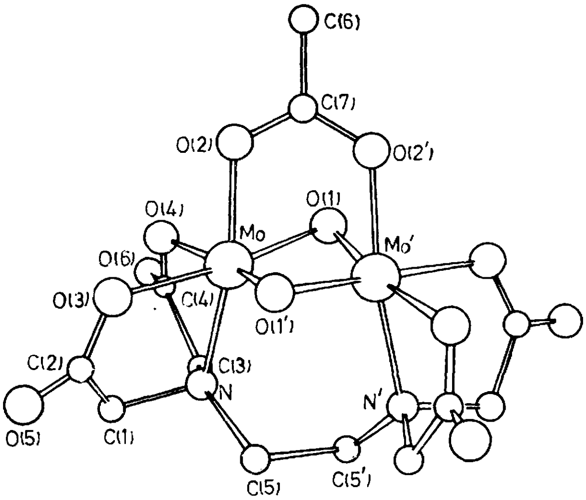
Summary A clarification of the preparative procedure and the first crystal structure of a binuclear molybdenum(III) complex, K[$Mo_2(OH)_2(O_2CMe)(C_{10}H_{12}O_8N_2)$], are reported; the metal atoms are bridged by two oxygens (as OH^-), acetate, and edta, and metal–metal bonding (2·43 Å) is apparent.

The procedure previously described[1] for the preparation of the ethylenediaminetetra-acetate (edta $\equiv Y^{4-}$) binuclear complex of molybdenum(III), KH[$Mo_2O_2(H_2O)_2Y$], has given instead the complex K[$Mo_2(OH)_2(O_2CMe)Y$],$x$$H_2O$, $x = 0$ and 2 (I), in which 1 mol of the acetate buffer is incorporated. Complex (I) has also been prepared in good yield (*ca.* 65%) by Zn–Hg reduction of the molybdenum(V) dimer, $Na_2[Mo_2O_4Y]$,[2] in acetate–acetic acid buffer. Without acetate, but with the pH maintained in the range 3—4 with HCl, both procedures yield a water-insoluble molybdenum(III) product (II), which analyses for [$Mo_2(OH)_2$-$(H_2O)_2Y$]. Both (I) and (II) are diamagnetic. The i.r. and u.v.–visible spectra of (I) are closely similar to those previously reported.[1] Derivatives with formate and two thiocyanates co-ordinated in place of the acetate have been prepared.[3] Complex (I) is stable in air for only limited periods (few hours), and in water it reacts rapidly with oxygen to give the molybdenum(V) product $[Mo_2O_4Y]^{2-}$. With azide and hydrazine at pH > *ca.* 6 a maroon molybdenum(IV)–edta product is obtained.

The *X*-ray crystal structure of the anhydrous form of (I) has been determined by Patterson and Fourier syntheses and refined by full-matrix least-squares method to a final *R* index of 0·06.[4] The complex crystallises in the orthorhombic system, space group *Fdd*2, with cell dimensions

$a = 7{\cdot}486$, $b = 25{\cdot}463$, $c = 20{\cdot}133$ Å, and $Z = 8$. The anion lies on a crystallographic two-fold rotation axis, and contains two molybdenum atoms, each co-ordinated by six ligands in a distorted octahedral environment (Figure). The two octahedra share a common edge containing two bridging oxygen atoms, which are assumed to be protonated to give the anion a uninegative charge. An unusual feature is the presence of two other bridging groups which complete the co-ordination sphere, *viz.* a hexadentate edta and a bidentate acetate group.



The Mo–O(2), Mo–O(3) and Mo–O(4) bond lengths of 2·14, 2·13, and 2·11 Å respectively do not differ significantly between themselves or from other Mo–O (carboxy) bonds in molybdenum(v) and molybdenum(vi) complexes.[5–7] The Mo–O(1) and Mo–O(1′) bond distances of 2·05 and 2·03 Å respectively are 0·1 Å longer than the corresponding values found in the Mo^{V} dioxo-bridged complexes,[5] and are consistent with the di-μ-hydroxo-structure. The Mo–N bond length of 2·18 Å is much shorter than the value of 2·45 Å found in for example $[Mo^{V}_2O_2S_2Y]^{2-}$.[5] It has been suggested that the lengthening of the Mo–N bond in the latter arises at least in part from the *trans*-effect of the terminal oxo-groups. No corresponding lengthening would be expected in the case of the molybdenum(iii) complex. The Mo–Mo′ distance of 2·43 Å is the shortest yet observed in a molybdenum complex with *O*-atom bridges, and indicates a strong-metal bond. Comparable distances are 2·569 Å in $[Mo^{V}_2O_4(\text{cysteine})_2]^{2-}$,[8] 2·541 Å in $[Mo^{V}_2O_4(\text{oxalate})_2(H_2O)_2]^{2-}$ and 2·552 Å in $[Mo^{V}_2O_4(\text{histidine})_2]$.[9]

The deviations from 90° of the bond angles subtended at the molybdenum range from −15 to +16°. The largest distortions are shown by the N–Mo–O(1) and N–Mo–O(1′) angles and these are caused by the nitrogen atoms being held apart by the ethylene bridge. The strong metal–metal bond results in an O(1)–Mo–O(1′) angle of 105°.

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