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Coordination Chemistry of Polyoxomolybdates with Squarate. Substitution of Monodentate and Bidentate Molybdate Subunits by $(C_4O_4)^{2-}$ Groups in the Preparation of $[(n\text{-}C_4H_9)_4N]_2[Mo_2(OMe)_2(NNPh)_4(C_4O_4)_2]\cdot 2CH_3OH$ from $[(n\text{-}C_4H_9)_4N]_2[Mo_2(OMe)_2(NNPh)_4(MoO_4)_2]$ and $[(n\text{-}C_4H_9)_4N]_4[Mo_4O_8(OMe)_2(C_4O_4)_2(C_4O_4H)_2]\cdot CH_3OH$ from $[(n\text{-}C_4H_9)_4N]_4[Mo_4O_8(OMe)_2(MoO_4)_2(HMoO_4)_2]$

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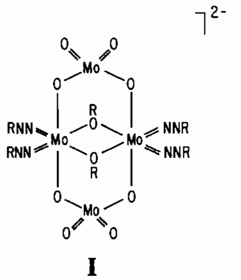
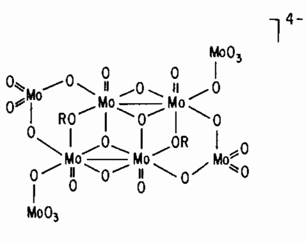
Coordination complexes of polyoxomolybdate anions are of contemporary interest as structural analogues for the interactions of small organic substrate molecules with metal oxide surfaces [1, 2]. In the course of our investigations of the pentamolybdate anion $[(MoO_4)_2\{Mo_3O_8(OMe)\}]^{3-}$ [3] we noted that the weakly coordinated $(MoO_4)^{2-}$ subunits were readily displaced by squarate ligands, $(C_4O_4)^{2-}$. The squarate anion exhibits marked similarities to the ligated $(MoO_4)^{2-}$ group: both are dianionic ligands capable of monodentate and bridging bidentate coordination modes and both exhibit ligand 'bite' distances of the order of 3.10 Å. Although this observation suggests that $(C_4O_4)^{2-}$ may displace $(MoO_4)^{2-}$ units in polyoxomolybdate species with retention of the structural core, examples of polyoxomolybdate structures exhibiting $(MoO_4)^{2-}$ units, attached by monodentate or bidentate coordination modes, are relatively rare. Two species exhibiting such structural subunits are the recently described $[(n\text{-}C_4H_9)_4N]_2[Mo_2(OR)_2(NNPh)_4(MoO_4)_2]$ (**I**), which displays bidentate bridging $(MoO_4)^{2-}$ units [4], and $[(n\text{-}C_4H_9)_4N]_4[Mo_4O_8(OMe)_2(MoO_4)_2(HMoO_4)_2]$ (**II**), which possesses both bidentate bridging $(MoO_4)^{2-}$ and terminal monodentate $(HMoO_4)^{1-}$ groups [5].



I



II

In this paper, we report the facile substitution of the weakly coordinated molybdate subunits of these structures by squarate ligands to give $[(n\text{-}C_4H_9)_4N]_2[Mo_2(OMe)_2(NNPh)_4(C_4O_4)_2]\cdot 2CH_3OH$ (**IIIa**) and $[(n\text{-}C_4H_9)_4N]_4[Mo_4O_8(OMe)_2(C_4O_4)_2(C_4O_4H)_2]\cdot CH_3OH$ (**IV**) from **I** and **II**, respectively.

Reaction of **I** with two equivalents of squaric acid in methanol, followed by addition of diethyl ether and standing for one week, yields violet crystals of $[(n\text{-}C_4H_9)N]_2[Mo_2(OCH_3)_2(NNPh)_4(C_4O_4)_2]\cdot 2CH_3OH$ (**IIIa**) in 40% yield. Satisfactory elemental analyses were found. IR (KBr, cm^{-1}): 1668 (m, $\nu(N{=}N)$; no bands in the 800–950 cm^{-1} region associated with $\nu(Mo{-}O)$ or $\nu(Mo{-}O{-}Mo)$. Reactions of $[(n\text{-}C_4H_9)_4N]_2[Mo_2(OR)_2(NNPh)_4(MoO_4)_2]$ ($R = -C_2H_5$, $-C_3H_7$) in the appropriate alcohol under similar conditions yield the analogous complexes $[(n\text{-}C_4H_9)_4N]_2[Mo_2(OR)_2(NNPh)_4(C_4O_4)_2]$ ($R = -C_2H_5$ (**IIIb**), $-C_3H_7$ (**IIIc**)). Crystal data for $C_{68}H_{106}N_{10}O_{12}Mo_2$ (**IIIa**): triclinic space group $P\bar{1}$, $a = 11.640(2)$, $b = 11.743(3)$, $c = 15.941(4)$ Å, $\alpha = 76.74(2)°$, $\beta = 73.18(1)°$, $\gamma = 71.68(1)°$, $V = 1957.1(11)$ Å^3, $Z = 1$, $D_{calc} = 1.27$ g cm^{-3}. A total of 5317 unique data having $2\theta \leq 45$ were collected on a Nicolet R3m/V diffractometer using graphite monochromated Mo Kα radiation ($\lambda = 0.71073$ Å) and a coupled θ(crystal)–2θ(counter) scan mode. The structure was solved by the Patterson method, and structural parameters were refined using full-matrix least-squares techniques to $R = 0.061$ and $R_w = 0.065$ for 3793 reflections having $F_o \geq 6\sigma(F_o)$. These refinement cycles employed anisotropic temperature factors for all non-hydrogen atoms. Calculated H atom positions were introduced in the final cycles of refinement, with the C–H bond distances set to 0.96 Å.

The structural analysis of **IIIa** revealed the binuclear structure illustrated in Fig. 1. The discrete binuclear molecular anion consists of the $[Mo_2(OMe)_2(NNPh)_4]^{2+}$ core with two bidentate $(C_4O_4)^{2-}$ moieties bridging the Mo centers. The structural parameters associated with the $[Mo_2(OMe)_2(NNPh)_4]^{2+}$ core are essentially identical to those previously reported for $[Mo_2(OMe)_2(NNPh)_4(MoO_4)_2]^{2-}$ [6] and for the class of binuclear complexes $[Mo_2(OMe)_2(NNPh)_4(L_1)_2(L_2)_2]$ [4, 5]. The $[MoO_4N_2]$ coordination geometry associated with the Mo centers of **IIIa** is similar in detail to the pseudo-octahedral Mo sites of **I**. The structural parameters observed for the squarate moiety indicate that the multiple bond character is localized at C(1)–C(2) and C(3)–O(3) and C(4)–O(4), such that the valence form **V** predominates, rather than the delocalized structure **VI** [7, 8].

The reaction of **II** (1 equiv.) with squaric acid (4 equiv.) in methanol, followed by careful addition of

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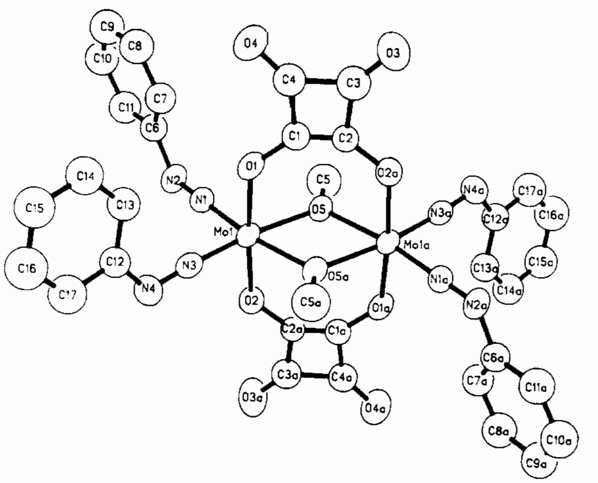
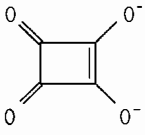
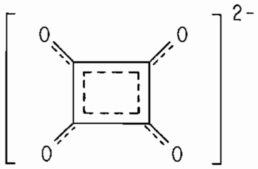


Fig. 1. Perspective view of the structure of $[Mo_2(OMe)_2(NNPh)_4(C_4O_4)_2]^{2-}$ (IIIa), showing the atom-labelling scheme. Selected bond lengths (Å) and angles (°): Mo(1)–O(1), 2.078(5); Mo(1)–O(2), 2.079(5); Mo(1)–O(5), 2.112(5); Mo(1)–N(1), 1.841(6); Mo(1)–N(3), 1.834(7); Mo(1)–O(5a), 2.114(6); N(1)–N(2), 1.217(7); N(3)–N(4), 1.239(8); C(1)–C(2), 1.175(10); C(2)–C(3), 1.442(10); C(1)–C(4), 1.441(10); C(3)–C(4), 1.479(12); C(1)–O(1), 1.363(9); C(2)–O(2a), 1.371(9); C(3)–O(3), 1.222(9); C(4)–O(4), 1.235(9); Mo(1)–N(1)–N(2), 176.5; Mo(1)–N(3)–N(4), 174.8(5); Mo(1)–O(1)–C(1), 132.4(4).



V



VI

ether, yields yellow translucent crystals of $[(n\text{-}C_4H_9)_4N]_4[Mo_4O_8(OCH_3)_2(C_4O_4)_2(C_4O_4H)_2]\cdot CH_3OH$ (IV) in 30% yield. Satisfactory elemental analysis was found. Crystal data for $C_{83}H_{154}N_4O_{27}Mo_4$ (IV): monoclinic space group $P2_1/n$, $a = 16.851(3)$, $b = 14.079(2)$, $c = 23.322(4)$ Å, $\beta = 107.07(1)$, $V = 5289.2(19)$ Å^3, $Z = 2$, $D_{calc} = 1.27$ g cm^{-3}; structure solution and refinement procedures were as for **IIIa**: 4613 reflections with $F_o > 6\sigma(F_o)$ (7410 collected) gave final discrepancy factors of $R = 0.0674$ and $R_w = 0.0734$.

The tetranuclear anionic cluster of **IV** is illustrated in Fig. 2. The tetranuclear core of the anion, provided by edge-sharing Mo octahedra, is identical to that previously observed for $[Mo_4O_8(OR)_2(HOR)_2Cl_4]^{2-}$ [4, 9] and $[Mo_4O_8(OMe)_2(MoO_4)_2(HMoO_4)_2]^{4-}$ (**II**) [6]. The structures of **II** and **IV** are related by the substitution of the monodentate $(HMoO_4)^{1-}$ and bidentate bridging $(MoO_4)^{2-}$ moities of **II**, by hydrogen squarate $(HC_4O_4)^{1-}$ and squarate ligands to give **IV**, while retaining the common $[Mo_4O_8(OR)_2]^{2+}$ core. As illustrated in Fig. 3, displacement of the four chloride ligands and the two peripheral methoxy groups of $[Mo_4O_8(OR)_2(HOR)_2Cl_4]^{2-}$ by four squarate ligands also generates the structure **IV**. The most unusual feature of the structure is the presence of monodentate hydrogen squarate ligands $(HC_4O_4)^{1-}$. The structural parameters are consistent with protonation at O(13).

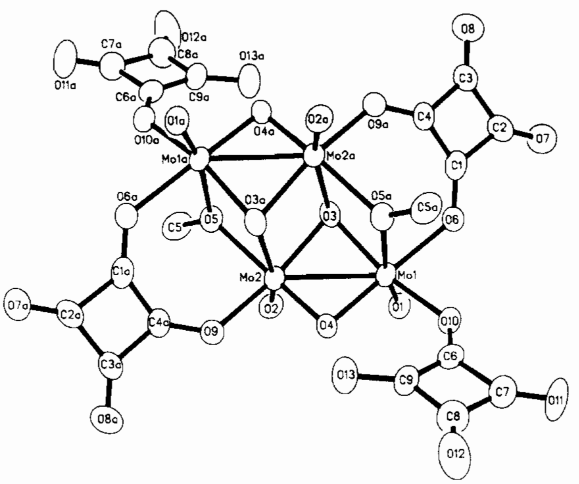


Fig. 2. Perspective view of the structure of $[Mo_4O_8(OMe)_2(C_4O_4)_2(HC_4O_4)_2]^{4-}$ (IV), showing the atom-labelling scheme. Selected bond lengths (Å) and angles (°): Mo(1)–Mo(2), 2.615(2); Mo(1)–O(1), 1.662(7); Mo(1)–O(3), 1.997(7); Mo(1)–O(4), 1.958(6); Mo(1)–O(5a), 2.217(6); Mo(1)–O(6), 2.097(6); Mo(1)–O(10), 2.068(8); Mo(2)–O(2), 1.670(7); Mo(2)–O(3), 1.991(6); Mo(2)–O(3a), 2.239(6); Mo(2)–O(4), 1.947(8); Mo(2)–O(5), 2.092(6); Mo(2)–O(9), 2.063(6); O(1)–Mo(1)–O(5a), 167.9(3); O(3)–Mo(1)–O(10), 157.5(3); O(4)–Mo(1)–O(6), 166.8(3); O(2)–Mo(2)–O(3a), 162.8(4); O(3)–Mo(2)–O(9), 159.3(3); O(4)–Mo(2)–O(5), 159.6(3).

It should be noted that the parent species (**II**) was incorrectly formulated by us as $[(n\text{-}C_4H_9)_4N]_4[Mo_4O_8(OMe)_2(MoO_4)_4]$ [5]. Complex **II** contains the tetranuclear Mo(V) core $[Mo_4O_8(OR)_2]^{2+}$ common to the structures of the $[Mo_4O_8(OR)_2(HOR)_2Cl_4]^{2-}$ species [4, 9] and to **IV**, rather than the mixed valence Mo(V)/Mo(VI) core $[Mo_4O_8(OR)_2]^{4+}$ as originally described [4, 5, 9]. The need to reformulate this complex as possessing the $[Mo_4O_8(OR)_2]^{2+}$ core is most convincingly presented by Lincoln and Koch [10].

The structural chemistry exhibited by the analogous series of complexes $[\{Mo_3O_8(OMe)\}(MoO_4)_2]^{3-}$ and $[Mo_3O_8(OMe)(C_4O_4)_2]^{3-}$, $[Mo_2(OR)_2(NNPh)_4(MoO_4)_2]^{2-}$ and $[Mo_2(OR)_2(NNPh)_4(C_4O_4)_2]^{2-}$, $[Mo_4O_8(OMe)_2(MoO_4)_2(HMoO_4)_2]^{4-}$ and $[Mo_4O_8(OMe)_2(C_4O_4)_2(HC_4O_4)_2]^{4-}$ suggests that the squarate moiety functions as an organic analogue of tetraoxomolybdate, $(MoO_4)^{2-}$. We are currently seeking to extend this analogy to other polyoxomolybdate coordination complexes which exhibit peripherally bound $(MoO_4)^{2-}$ subunits.

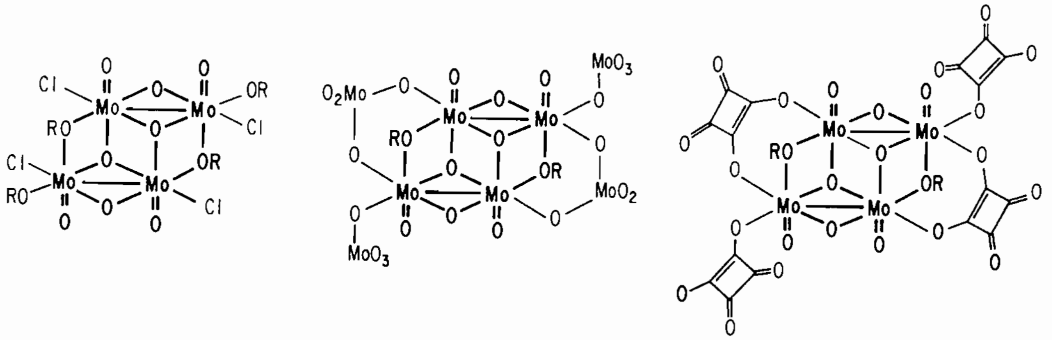


Fig. 3. Schematic illustrations of the structures of $[Mo_4O_8(OMe)_2(HOMe)_2Cl_4]^{2-}$, $[Mo_4O_8(OMe)_2(MoO_4)_2(HMoO_4)_2]^{4-}$ and $[Mo_4O_8(OMe)_2(C_4O_4)_2(HC_4O_4)_2]^{4-}$, highlighting the common $[Mo_4O_8(OMe)_2]^{2+}$ core.

Acknowledgement

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