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The Crystal and Molecular Structure of $[(C_4H_9)_4N]_2[Mo_2O_6(C_5H_4NCO_2)_2]$, a Complex Exhibiting the $[Mo_2O_6]^0$ Core

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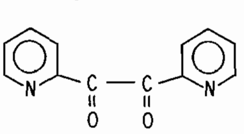
Polyoxomolybdate–carbonyl interactions are characterized by carbonyl insertion into a molybdenum–oxygen bond [1–3]. The synthesis of organo-oxomolybdates with acetyl [1], with diacetyl [2], and with diketal structures [3], depending upon the nature of the organic substrate, have been discussed in terms of acid–base pair binding sites and as models for substrate binding sites on solid oxide surfaces [4].

That the products of such molybdate–carbonyl reactions depend intimately upon the nature of the organic precursor is demonstrated by the isolation of the oxalatodimolybdate $[Mo_2O_4Cl_4(C_2O_4)]^{2-}$ from the reaction of $[Mo_8O_{26}]^{4-}$ with dichloroglyoxal [3] and the formation of the oxalatooctamolybdate $[Mo_8O_{16}(OCH_3)_8(C_2O_4)]^{2-}$ from the reaction of $[Mo_8O_{26}]^{4-}$ with rhodizonic acid [5]. These observations suggest that ligand dissociation will occur, subsequent to carbonyl insertion. In order to examine the generality of carbonyl insertion coupled with ligand dissociation in polyoxomolybdate–carbonyl chemistry, we have investigated the reaction of molybdate with 2,2′-dipyridil. The product of the reaction is the 2-pyridine carboxylate–dimolybdate $[(C_4H_9)_4N]_2[Mo_2O_6(C_5H_4NCO_2)_2]$, a species exhibiting the unusual $[Mo_2O_6]^0$ core.



2,2′ - dipyridil

The reaction of $[(C_4H_9)_4N]_2[Mo_2O_7]$ with 2,2′-dipyridil in methanol yields colorless translucent crystals of $[(C_4H_9)_4N]_2[Mo_2O_6(C_5H_4NCO_2)_2]$ in 45% yield. *Anal.* Calc. for $Mo_2O_{10}N_4C_{44}H_{80}$: C, 52.0; H, 7.87; N, 5.51. Found: C, 51.8; H, 7.72; N, 5.54%. The infrared spectrum is characterized by strong bands at 933 and 910 cm^{-1} assigned to ν_s(Mo=O) and ν_{as}(Mo=O), respectively, and a number of features in the 700 to 860 cm^{-1} range associated with the Mo_2O_2 bridge. The complex crystallizes in the monoclinic space group $P2_1/c$ with $a = 9.959(2)$ Å, $b = 13.708(3)$ Å, $c = 18.851(5)$ Å; $\beta = 100.76(2)°$, $V = 2528.4(10)$ Å^3, $D_{calc} = 1.33$ g cm^{-3} for $Z = 2$. Structure solution and refinement based on 2882 reflections with $F_o \geqslant 6\sigma(F_o)$ (Mo Kα radiation, λ = 0.71073 Å) converged at $R = 0.0545$.

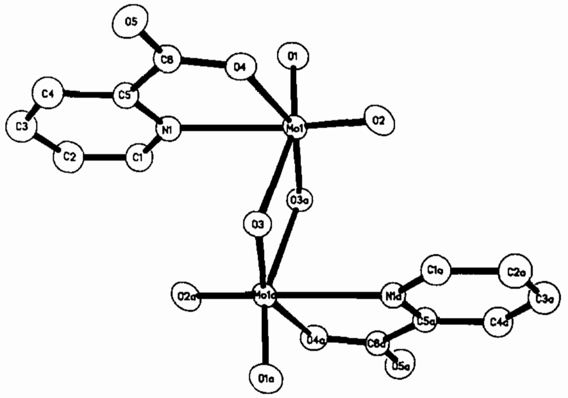


Fig. 1. ORTEP view of $[Mo_2O_6(C_5H_4NCO_2)_2]^{2+}$ showing the atom labeling scheme. Selected bond lengths (Å): Mo1–O1, 1.709(5), Mo1–O2, 1.713(4); Mo1–O3, 2.225(4); Mo1–O3a, 1.805(3); Mo1–O4, 2.139(4); Mo1–N1, 2.382(5); C6–O4, 1.294(7); C6–O5, 1.204(7); C5–C6, 1.504(8); C5–N1, 1.329(8); Mo1–Mo1a, 3.178(1). Angles (°): O1–Mo1–O3, 161.2(2); O4–Mo1–O3a, 151.2(2); O2–Mo1–N1, 159.3(2); O3–Mo1–O3a, 76.4(2); O4–Mo1–N1, 69.9(2); Mo1–O3–Mo1a, 103.6(1).

The structure of $[(C_4H_9)_4N]_2[Mo_2O_6(C_5H_4NCO_2)_2]$ is shown in Fig. 1, and selected bond lengths and angles are presented in the caption. The structure of the binuclear dinegative anionic complex consists of the unusual $[Mo_2O_6]^0$ core, ligated to two pyridinecarboxylate ligands. The Mo centers display $[MoO_5N]$ pseudo-octahedral geometry as a consequence of coordination to two mutually *cis* terminal oxo groups, two bridging oxo groups, a carboxylate oxygen donor, and a pyridine nitrogen donor of the pyridinecarboxylate ligand. One terminal oxo group of each molybdenum center is normal to the Mo_2O_2 bridge plane, adopting an *anti* configuration. Consequently, the second terminal oxo group must lie approximately in the Mo_2O_2 plane in order to adopt the preferred *cis* terminal dioxo configuration. The significant *trans* influence of the in-plane terminal oxo groups results in the lengthening of two opposite Mo-bridging oxo distances to 2.226(2) Å, compared to a distance of 1.805(2) Å for the Mo-bridging oxo distances *trans* to the carboxylate oxygen donor. The alternating long–short pattern of Mo–O distances within the Mo_2O_2 rhombus may be characteristic of the $[Mo_2O_6]^0$ core [6].

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Although oxo-coordination is ubiquitous for molybdenum species in the (V) and (VI) oxidation states, the common structural cores have been identified as $[MoO_2]^{2+}$, $[MoO_3]^0$ and $[Mo_2O_5]^{2+}$ for Mo(VI), and $[Mo_2O_3]^{4+}$ and $[Mo_2O_4]^{2+}$ for Mo(V) [7, 8]. The $[Mo_2O_6]^0$ core has now been documented in two cases, the title complex and $[Mo_2O_6\text{-}(tropolonate)_2]^{2+}$ [6]. The results suggest that bidentate monoanionic ligands with extensive π-delocalization throughout the chelate ring may stabilize the $[Mo_2O_6]^0$ core in non-aqueous solvents [9]. The core does not persist in aqueous media.

The pyridinecarboxylato ligand is formed in the course of the common carbonyl insertion of the reactant pyridil-carbonyl group into a molybdenum–oxygen bond. The resultant dipyridyl diketal, unlike the analogous phenanthrene diketal [3] which retains its integrity, undergoes C–C bond cleavage to give the pyridinecarboxylato unit. The C–C bond cleavage may be characteristic with species of this type as it has also been observed in the reaction of benzil with molybdate.

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