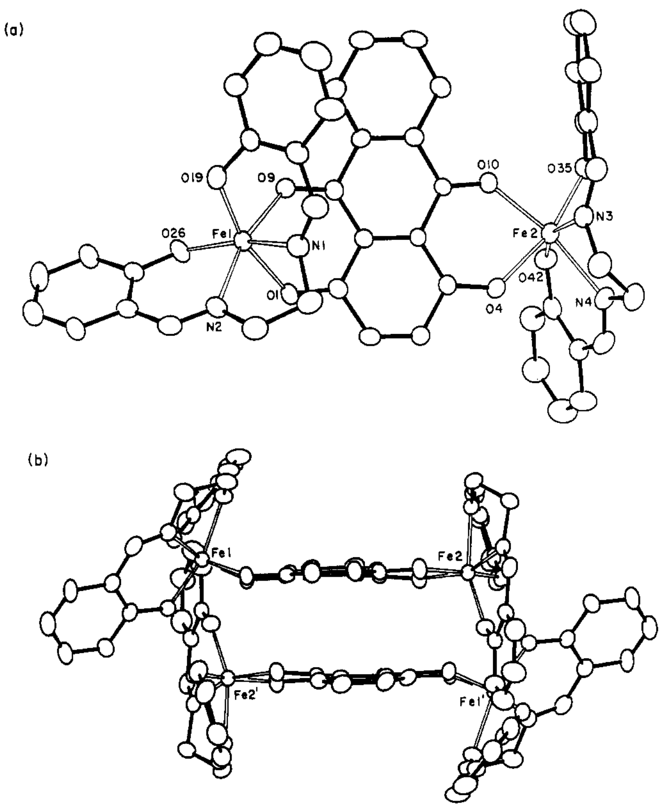

Figure 2. ORTEP plots of $[Fe(salen)]_2Qz$ with thermal ellipsoids at the 30% probability level with hydrogen atoms omitted for clarity: (a) plot showing the geometry of the complex; (b) plot showing the stacking interaction between the quinizarin moieties of inversion-related pairs of complexes.

the atoms of the six-membered chelate ring with quinizarin are coplanar to within ±0.048 (6) Å. However, Fe(1) is displaced 0.627 (1) Å from the plane defined by the other five atoms (±0.011 (6) Å) of its corresponding six-membered chelate ring in a direction toward N(1). This displacement can be viewed as a result of rotating the equatorial plane defined by atoms O(1), O(9), O(19), and N(2) by ca. 24° about an axis containing O(1) and O(9).

The difference between the disposition of the iron centers appears to be due to the fact that inversion-related pairs of molecules exist in the solid state as stacked dimers. The quinizarin planes of the dimers, required by symmetry to be parallel, are separated by a distance of slightly less than 3.4 Å, where the overlap involves the non-oxygen bearing ends of the fused ring systems. The equatorial plane of each Fe(1) atom is tipped away from the inversion related molecule. Even in the presence of this distortion, there are van der Waals contacts between the halves of the dimer, which involve atoms of nonequivalent salen ligands. Thus, the stacking interaction appears to preclude equivalence of the two iron centers. The association of two quinizarin ligands may be similar to the self-association of molecules of daunorubicin that has previously been observed for solutions of this drug.[39-42] The π-complex described is apparently strong enough to drive Fe(1) out of plane and may be responsible for the observation of two LMCT transitions in the electronic absorption spectrum of the compound if it persists in solution.

Acknowledgment. We gratefully acknowledge funding in support of this research from Abbott Laboratories, Abbott Park, IL.

Supplementary Material Available: Atomic coordinates for non-hydrogen atoms (Table S1), anisotropic thermal parameters (Table S2), hydrogen atom parameters (Table S3), and bond lengths and bond angles (Table S4) (13 pages); a table of observed and calculated structure factor amplitudes (25 pages). Ordering information is given on any current masthead page.

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Synthesis and Characterization of a Trinuclear Polyoxomolybdate Containing a Reactive $[MoO_3]$ Unit, $[(n\text{-}C_4H_9)_4N]_2[Mo_3O_7(CH_3C(CH_2O)_3)_2]$, and Its Conversion to the Methoxy Derivative $[(n\text{-}C_4H_9)_4N][Mo_3O_6(OCH_3)(CH_3C(CH_2O)_3)_2]$

Sir:

The effectiveness of early-transition-metal oxides as heterogeneous catalysts,[1-4] together with the difficulty of characterizing surface-bound intermediates for these systems, has prompted a number of investigations of the coordination chemistry of analogous polyoxoanion derivatives with organic substrate molecules.[5,6] Structurally characterized examples of polyoxomolybdate complexes incorporating simple organic substrate units include $[Mo_8O_{26}(HCO_2)_2]^{6-}$,[7] $[Mo_8O_{24}(OCH_3)_4]^{4-}$,[8] $[Mo_4O_{14}(OH)CH_2]^{3-}$,[9] and $[Mo_4O_8(OC_2H_5)_2(CH_3C(CH_2O)_3)_2]$,[10] while detailed studies of polyoxoanion interconversions have been reported for systems based on $[Nb_2W_4O_{19}H]^{3-}$[11] and $[MoO_2(OR)(P_3O_9)]^{2-}$.[12] In common with the vast majority of polyoxometalate structures,[13] the metal centers of these coordination complexes exhibit ligation to a number of bridging oxygen donors and either to two terminal oxo groups or to a single terminal oxo unit, to give the $[MO_2]^{2+}$ or $[MO]^{4+}$ core, respectively. Although molybdenum bound to three terminal oxo groups ($[MoO_3]$) and weakly bound to the bulk by additional bridging oxo interactions provides a reasonable

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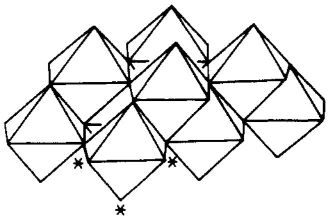

Figure 1. Arrangement of octahedra in molybdenum trioxide. Asterisks denote terminal oxo group positions for a potential chain-terminating Mo site.

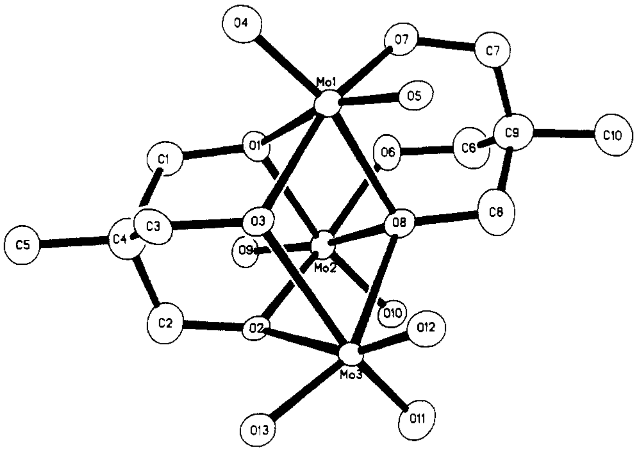

Figure 2. ORTEP view of the structure of $[Mo_3O_7(hmmp)_2]^{2-}$ (anion of I), showing the atom-labeling scheme. Selected bond lengths (Å) and angles (deg): Mo1–O1 = 2.152 (2), Mo1–O3 = 2.050 (2), Mo1–O4 = 1.695 (3), Mo1–O5 = 1.682 (3), Mo1–O7 = 1.954 (3), Mo1–O8 = 2.252 (2), Mo1–O1 = 2.169 (2), Mo2–O2 = 2.121 (2), Mo2–O6 = 1.898 (3), Mo2–O8 = 2.260 (3), Mo2–O9 = 1.715 (3), Mo2–O10 = 1.682 (2), Mo3–O2 = 2.318 (2), Mo3–O3 = 2.298 (2), Mo3–O8 = 2.359 (2), Mo3–O11 = 1.715 (3), Mo3–O12 = 1.677 (3), Mo3–O13 = 1.754 (3); O3–Mo3–O11 = 155.6 (1), O2–Mo3–O12 = 158.8 (1), O8–Mo3–O13 = 151.5 (1).

possibility for a surface Mo site in a solid oxide (Figure 1), there are relatively few examples of structures containing the $[MoO_3]$ unit, and these are largely limited to mononuclear species that are invariably unstable in solution[14-17] and to the binuclear $[Mo_2O_7]^{2-}$.[18] When present in polynuclear species, such as $[Mo_{10}O_{34}]^{8-}$[19] and $[Mo_8O_{24}(OCH_3)_2]^{4-}$,[20] the $[MoO_3]$ moiety is associated with the cluster as part of a corner-sharing $[MoO_4]^{2-}$ tetrahedron and readily dissociated in chemical transformations. The absence of stable polyanion species containing addenda MO_6 octahedra with more than two terminal oxygen atoms was first noted by Lipscomb[21] and has been rationalized in terms of the strong trans influence of the M–O(terminal) bonds which would result in the dissociation of *fac* $[MO_3]$ groups attached to the structure by weak bonds.[6] As part of our investigations of alkoxypolyoxomolybdate coordination chemistry, we have prepared the novel trinuclear polyoxomolybdate $[(n\text{-}C_4H_9)_4N]_2[Mo_3O_7(CH_3C(CH_2O)_3)_2]$ (I), containing a reactive $[MoO_3]$ moiety, and studied its conversion to the methoxy derivative $[(n\text{-}C_4H_9)_4N][Mo_3O_6(OCH_3)(CH_3C(CH_2O)_3)_2]$ (II) and to related alkoxy species. Complex I represents the first example of a solution-stable polyoxometalate coordination complex to violate "Lipscomb's principle".

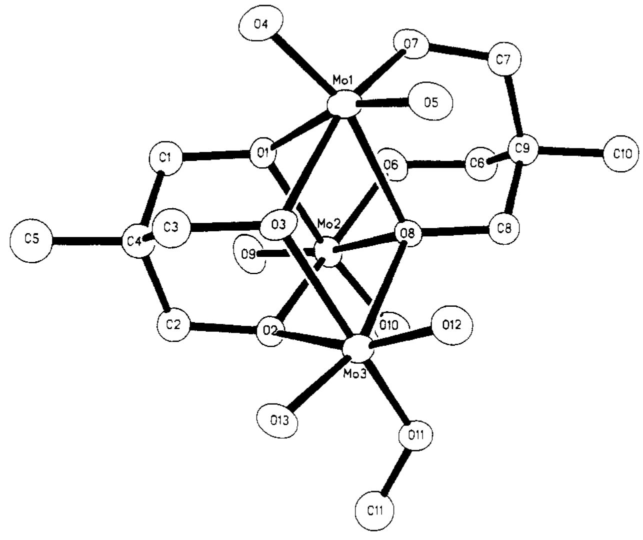

Figure 3. ORTEP view of the structure of $[Mo_3O_6(OCH_3)(hmmp)_2]^-$ (anion of II) showing the atom-labeling scheme. Selected bond lengths (Å) and angles (deg): Mo1–O1 = 2.149 (6), Mo1–O3 = 2.088 (6), Mo1–O4 = 1.686 (7), Mo1–O5 = 1.696 (7), Mo1–O7 = 1.883 (7), Mo1–O8 = 2.297 (5), Mo2–O1 = 2.178 (6), Mo2–O2 = 2.068 (6), Mo2–O6 = 1.883 (7), Mo2–O8 = 2.261 (6), Mo2–O9 = 1.712 (7), Mo2–O10 = 1.697 (7), Mo3–O2 = 2.240 (6), Mo3–O3 = 2.127 (6), Mo3–O8 = 2.266 (6), Mo3–O11 = 1.874 (7), Mo3–O12 = 1.696 (6), Mo3–O13 = 1.695 (7); O3–Mo3–O11 = 159.5 (3), O2–Mo3–O12 = 158.6 (3), O8–Mo3–O13 = 158.2 (3).

Reaction of $[(n\text{-}C_4H_9)_4N]_4[Mo_8O_{26}]$[22] with 2-(hydroxymethyl)-2-methyl-1,3-propanediol (H_3hmmp; 4 equiv) in acetonitrile, followed by addition of ether and standing at room temperature for 1 week, yields thin plates of $[(n\text{-}C_4H_9)_4N]_2[Mo_3O_7(hmmp)_2]\cdot 0.5(C_2H_5)_2O$ (I).[23] The structure of the anion in I, determined by X-ray diffraction, is shown in Figure 2, and selected bond lengths and angles are presented in the caption.

The discrete trinuclear anion $[Mo_3O_7(hmmp)_2]^{2-}$ exhibits the usual $[MoO_6]$ pseudooctahedral geometry for the Mo centers, with a number of unusual structural features. There are two distinct Mo geometries: Mo1 and Mo2 each coordinate to two terminal oxo ligands and complete their coordination requirements through ligation to bridging and terminal alkoxy donors, while the Mo3 center displays three terminal oxo groups and additional ligation to three bridging alkoxy oxygens. The two hmmp ligands are inequivalent; one provides three doubly bridging alkoxy donors, O1, O2, and O3, while the second exhibits a triply bridging oxygen, O8, and two terminal alkoxy groups, O6 and O7. The oxygen donors are arranged in two layers sandwiching a central Mo_3 triangle. The metrical parameters associated with the $[MoO_3]$ moiety indicate that the Mo3–O(terminal) bond distances are inequivalent. For previously described structures containing the $[MoO_3]$ moiety,[14-16] the average Mo–terminal oxo group bond length is 1.737 (9) Å with a range of 1.731 (6)–1.749 (6) Å. In contrast, the average of the Mo3–O11 and Mo3–O12 distances is significantly shorter at 1.696 (3) Å, while the Mo3–O13 distance of 1.754 (3) Å is somewhat longer than expected. However, the ^{17}O NMR spectrum of I reveals only two resonances associated with terminal oxo groups in the 850–950 ppm range, indicating that the observed structural inequivalence of the Mo–O distances for Mo3 represents a solid-state effect.

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(23) Anal. Calcd for $[(C_4H_9)_4N]_2[Mo_3O_7(hmmp)_2]\cdot 0.5(C_2H_5)_2O$, $C_{44}H_{95}N_2O_{13.5}Mo_3$: C, 45.7; H, 8.22; N, 2.42. Found: C, 45.6; H, 8.03; N, 2.45. IR (KBr pellet, cm^{-1}): 2912 (vs), 1460 (s), 1397 (m), 1119 (m), 1040 (vs), 988 (m), 932 (vs), 917 (vs), 901 (vs), 640 (s), 600 (m), 530 (m), 490 (m), 332 (m). Crystal data: monoclinic, space group $P2_1/n$, with a = 12.775 (2) Å, b = 24.867 (4) Å, c = 19.421 (6) Å, β = 94.47 (1)°, V = 6149.2 (11) $Å^3$, Z = 4, and D(calc) = 1.25 g cm^{-3}. Structure solution and refinement based on 5916 reflections with $F_o \geq 6\sigma(F_o)$ (Mo Kα, λ = 0.71073 Å) converged at R = 0.0257.

The $[Mo_3O_7(hmmp)_2]^{2-}$ anion of I reacts with chloroacetic acid, trimethyloxonium tetrafluoroborate, and diethyl sulfate according to reaction 1 to yield $[Mo_3O_6(OR)(hmmp)_2]^-$ derivatives.[24]

$$[Mo_3O_7(hmmp)_2]^{2-} \xrightarrow[-X]{RX} [Mo_3O_6(OR)(hmmp)_2]^- \qquad (1)$$

II^-: $R = CH_3$; $X = (CH_3)_2OBF_4$
III^-: $R = H$; $X = ClCH_2CO_2$
IV^-: $R = CH_2CH_3$; $X = CH_3CH_2OSO_3$

Crystal structure analysis of $[(n\text{-}C_4H_9)_4N][Mo_3O_6(OCH_3)(hmmp)_2]$ (II)[25] revealed the discrete trinuclear anion illustrated in Figure 3. The structure of the anion is analogous to that of I with a terminal oxo group of Mo3 replaced by a methoxy ligand. Substitution of the π-bonding oxo group by a methoxy group, a ligand of negligible trans influence, results in shortening of the Mo3–O3 distance from 2.298 (2) Å in I to 2.127 (6) Å in II and a general shortening of the Mo3–O(alkoxy) distances from an average of 2.325 (3) Å in I to an average of 2.211 (7) Å in II.

Protonation of I yields the acid $[Mo_3O_7H(hmmp)_2]^-$ (anion of III), which in turn may be used as a precursor in condensation reactions with alcohols ROH ($R = CH_3$, CH_3CH_2, and $(CH_3)_2CH$) to yield the esters $[Mo_3O_6(OR)(hmmp)_2]^-$, of which II is the structural prototype. Although these features of the chemistry are similar to those observed for $[Nb_2W_4O_{19}]^{4-}$[11] and $[MoO_3(P_3O_9)]^{3-}$,[12] attempts to isolate the corresponding anhydride $[(Mo_3O_6(hmmp)_2)_2O]^{2-}$ were unsuccessful, yielding rather the polynuclear species $[Mo_4O_8(OR)_2(hmmp)_2]$ or $[Mo_8O_{20}(OR)_4(hmmp)_2]^{2-}$.[20]

Transformation of coordinated alkoxide groups to the oxidation or dehydration products, aldehydes (or ketones) or alkenes, respectively, may be effected by thermal degradation of the complexes. Thermal decomposition of II in nitrobenzene at 180 °C yields a mixture of methanol, dimethyl ether, formaldehyde, and water as the major gaseous products, while thermal decomposition of the ethoxy derivative IV yields a mixture of acetaldehyde and ethanol. Both thermal oxidations are consistent with heterolytic pathways,[8,12,26] previously described for reactions of this type. We are currently investigating the photochemical degradation of these complexes and synthetic extensions of $[Mo_3O_7(hmmp)_2]^{2-}$ as a support for organometallic moieties.

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Supplementary Material Available: Tables of atomic coordinates, bond lengths, bond angles, and thermal parameters for I and II (12 pages); tables of observed and calculated structure factors (34 pages). Ordering information is given on any current masthead page.

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(24) Anal. Calcd for $[(C_4H_9)_4N][Mo_3O_6(OCH_3)(hmmp)_2]$ (II), $C_{27}H_{57}NO_{13}Mo_3$: C, 36.4; H, 6.40; N, 1.57. Found: C, 36.2; H, 6.29; N, 1.50. Calcd for $[(C_4H_9)_4N][Mo_3O_6(OH)(hmmp)_2]$ (III), $C_{26}H_{55}NO_{13}Mo_3$: C, 35.6; H, 6.27; N, 1.60. Found: C, 35.3; H, 6.11; N, 1.43. Calcd for $[(C_4H_9)_4N][Mo_3O_6(OCH_2CH_3)(hmmp)_2]$ (IV), $C_{28}H_{59}NO_{13}Mo_3$: C, 37.1; H, 6.52; N, 1.55. Found: C, 37.5; H, 6.66; N, 1.43.

(25) Crystal data: monoclinic, space group $P2_1/n$, with $a = 10.908$ (2) Å, $b = 25.674$ (5) Å, $c = 13.059$ (2) Å, $\beta = 96.35$ (2)°, $V = 3635.6$ (12) Å^3, $Z = 4$, D(calc) = 1.62g cm^{-3}. Structure solution and refinement based on 3143 reflections with $F_o \geq 6\sigma(F_o)$ (Mo Kα, $\lambda = 0.71073$ Å) converged at $R = 0.0491$.

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