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Steven E. Diamond,* Andrew Szalkiewicz, Frank Mares*
Corporate Research Center, Allied Chemical Corporation
Morristown, New Jersey 07960

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Polyoxomolybdate-Hydrocarbon Interactions. Synthesis and Structure of the $\text{CH}_2\text{Mo}_4\text{O}_{15}\text{H}^{3-}$ Anion and Related Methylenedioxy-molybdates

Sir:

In light of the pronounced heterogeneous reactivity of molybdenum, tungsten, and vanadium oxides toward hydrocarbons,¹ it is somewhat surprising that no polyoxoanion clusters of these metals are known which contain hydrocarbon moieties bound to their surface oxygens. A recent study of the cobalt molybdate catalyzed selective oxidation of propylene to acrolein has provided evidence indicating that the rate-determining step is desorption of acrolein from the oxide catalyst surface.² As a logical starting point for the structural investigation of polyoxoanion-hydrocarbon interactions, we have therefore examined the solution reactivity of acrolein and other aldehydes toward polyoxomolybdates. We report here the isolation and characterization of several presumably isostructural $\text{RCHMo}_4\text{O}_{15}\text{H}^{3-}$ anions ($\text{R} = \text{C}_2\text{H}_5$, H , CH_3 , C_6H_5 , and CF_3), which contain RCH units bonded to the oxide surface of a tetranuclear polyoxomolybdate cluster.

Reaction of a large excess of acrolein with $[(n\text{-C}_4\text{H}_9)_4\text{N}]_2\text{Mo}_2\text{O}_7$ ³ in hydrated $\text{CH}_3\text{CN}-\text{CH}_2\text{Cl}_2$ solution at 0 °C, followed by addition of ether, results in the formation of a precipitate which analyzes⁴ as $[(n\text{-C}_4\text{H}_9)_4\text{N}]_3\text{C}_3\text{H}_4\text{Mo}_4\text{O}_{15}\text{H}$ (**1**) after purification by reprecipitation from CH_2Cl_2 with ether at 0 °C. Since attempts to obtain compound **1** in crystalline form have been unsuccessful owing to its instability in solution,⁵ the structure of **1** has been inferred from a more stable analogue, the formaldehyde adduct $[(n\text{-C}_4\text{H}_9)_4\text{N}]_3\text{CH}_2\text{Mo}_4\text{O}_{15}\text{H}$ (**2**),⁶ which is easily recrystallized from $\text{CH}_2\text{Cl}_2-\text{C}_6\text{H}_5\text{CH}_3$. Compounds **1** and **2** are assumed to contain isostructural anions since their IR spectra display

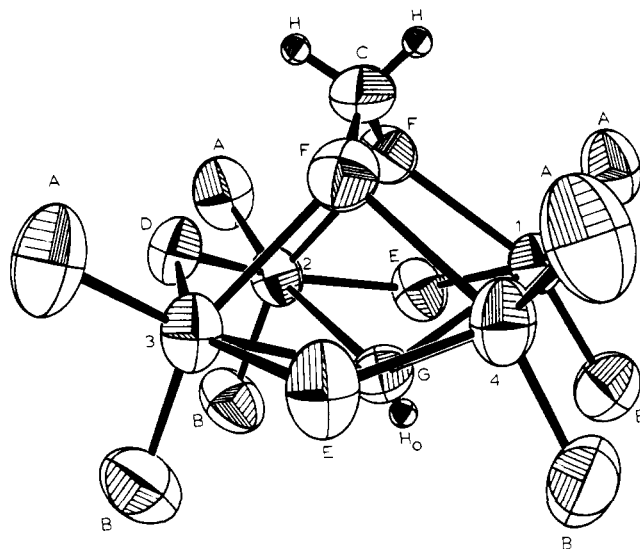


Figure 1. ORTEP drawing of the $\text{CH}_2\text{Mo}_4\text{O}_{15}\text{H}^{3-}$ anion as observed in single crystals of its $(n\text{-C}_4\text{H}_9)_4\text{N}^+$ salt. All nonhydrogen atoms are represented by thermal vibration ellipsoids drawn to encompass 50% of the electron density; the three hydrogen atoms are represented by arbitrarily small spheres for purposes of clarity. Molybdenum atoms are labeled with numbers and the 15 oxygen atoms are labeled according to the following scheme: A or B for the eight terminally bonded oxygens, D or E for the four doubly bridging oxygens, F for the two triply bridging oxygens, and G for the one hydroxyl oxygen. The carbon atom is designated by C and the hydrogen atoms by H's. The second doubly bridging O_D atom is hidden from view. The anion approximates C_{2v} site symmetry with C, O_G , and H_O ideally lying on the C_2 axis.

Table I. Average Molybdenum-Oxygen Distances for the $\text{CH}_2\text{Mo}_4\text{O}_{15}\text{H}^{3-}$ ion in $[(n\text{-C}_4\text{H}_9)_4\text{N}]_3\text{CH}_2\text{Mo}_4\text{O}_{15}\text{H}$

type ^a	distance, ^b Å
Mo-O _A }	1.702 (5, 5, 16, 8)
Mo-O _B }	1.905 (5, 4, 4, 4)
Mo-O _D	1.924 (5, 3, 5, 4)
Mo-O _E	2.194 (5, 5, 9, 4)
Mo-O _F	2.456 (5, 24, 34, 4)
Mo-O _G	

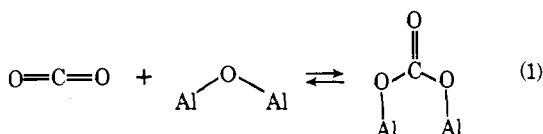
^a See Figure 1 for labeling scheme. ^b For explanation of numbers in parentheses, see ref 11.

several common features: a sharp OH absorption in the 3600-3650- cm^{-1} region, two C-O absorptions⁷ in the 990-1100- cm^{-1} region, and an identical pattern of Mo-O absorptions in the 550-950- cm^{-1} region.

A single-crystal X-ray diffraction study⁸ of **2** reveals that the compound contains discrete $\text{CH}_2\text{Mo}_4\text{O}_{15}\text{H}^{3-}$ anions (see Figure 1) which are structurally similar to the $(\text{CH}_3)_2\text{AsMo}_4\text{O}_{15}\text{H}^{2-}$ anion.⁹ Although the anion possesses no rigorous crystallographic symmetry, it approximates rather closely C_{2v} site symmetry with all four molybdenum atoms coplanar to within 0.004 Å. As an indication of the extent to which chemical and structural analogies might exist between polyoxoanion clusters such as $\text{CH}_2\text{Mo}_4\text{O}_{15}\text{H}^{3-}$ and solid oxide bound hydrocarbons, we note that the oxygen atoms are in the polyoxoanion approximate a hexagonal close-packed arrangement. Each A layer would ideally contain two O_A , two O_B , and an adjacent O_D atom while the B layer would correspond to the pseudomirror plane which passes through the two O_E , two O_F , and the O_G atoms. The $\text{CH}_2\text{Mo}_4\text{O}_{15}\text{H}^{3-}$ anion can thus be described as having CH_2 and H units bonded to opposite side surfaces of a close-packed oxygen array in which molybdenum atoms occupy octahedral interstices. Consideration of bonding interactions (see Table I), however, produces a different description where $\text{H}_2\text{CO}_2^{2-}$ and OH^- groups are

connected by weak ($>2.1 \text{ \AA}$) Mo–O bonds to opposite sides of an Mo_4O_{12} ring, yielding the structural formula¹⁰ $(\text{H}_2\text{CO}_2^{2-})(\text{OH}^-)(\text{Mo}_4\text{O}_{12})$. From this point of view, the $\text{CH}_2\text{Mo}_4\text{O}_{15}\text{H}^{3-}$ anion is seen to be an acetal derivative. The C–O distance of 1.393 (9, 9, 9, 2) \AA ¹¹ and the O–C–O angle of 115 (1)° are accordingly in good agreement with the corresponding values of 1.382 (4) \AA and 114.3 (7)° in dimethoxymethane.¹²

If one considers the $\text{CH}_2\text{Mo}_4\text{O}_{15}\text{H}^{3-}$ anion to be an aldehyde adduct, the H_2CO binding site can be viewed as an acid–base pair site consisting of two coordinatively unsaturated molybdenum centers and a basic oxygen atom. In this sense, the mode of H_2CO binding conforms to current models for substrate binding on solid oxide surfaces.¹³ There is, however, at present no spectroscopic evidence which indicates that aldehydes form surface acetals upon interaction with oxide surfaces. Unfortunately, the characteristic C–O IR absorptions for compound **1** and its analogues fall in the 990–1100- cm^{-1} range usually obscured by oxide lattice absorptions, and their IR spectroscopic observation would in many cases be difficult.¹⁴ IR studies of the interaction of CO_2 with α -alumina have provided strong evidence for surface binding of the closely related type shown in eq 1.¹⁵ It is therefore not unreasonable



to predict that H_2CO should interact in a similar fashion when suitable acid–base pair binding sites are available.

The formation of acetal molybdates such as compounds **1** and **2** appears to be quite general. Hydrated acetaldehyde, benzaldehyde, and trifluoroacetaldehyde all react with $[(n\text{-C}_4\text{H}_9)_4\text{N}]_2\text{Mo}_2\text{O}_7$ to form derivatives $\text{RCHMo}_4\text{O}_{15}\text{H}^{3-}$ as tetrabutylammonium salts.¹⁶ Attempts to synthesize ketal derivatives $\text{R}_2\text{CMo}_4\text{O}_{15}\text{H}^{3-}$ have thus far been unsuccessful. Reaction of hydrated acetone or hexafluoroacetone with tetrabutylammonium dimolybdate, for example, yields α - $[(n\text{-C}_4\text{H}_9)_4\text{N}]_4\text{Mo}_8\text{O}_{26}$ as the major product. Apparently, enolate and fluoroform formation prevail in the presence of the basic dimolybdate ion. We are currently examining these reactions in greater detail.

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- (5) The ^1H NMR spectrum of **1** in CD_2Cl_2 at 25 °C displays only free acrolein, water, and counterion resonances >5 min after dissolution.
- (6) Prepared by reacting excess formaldehyde hydrate with $[(n\text{-C}_4\text{H}_9)_4\text{N}]_2\text{Mo}_2\text{O}_7$ in CH_2Cl_2 at 25 °C and adding ether to obtain crude product.
- (7) Observed from KBr pellets at 1078 and 990 cm^{-1} for **1** and at 1075 and 1006 cm^{-1} for **2**. An isotope shift of $\sim 15 \text{ cm}^{-1}$ was observed for ^{18}O -enriched **2**.
- (8) Large, well-shaped single crystals of **2** obtained as described above are monoclinic, space group $P_{21/n}$ (an alternate setting of $P_{21/c}-C_{2h}^2$, No. 14) with $a = 17.066$ (2), $b = 16.469$ (3), $c = 28.420$ (4) \AA ; $\beta = 123.62$ (1)°; and $Z = 4$. Three-dimensional X-ray diffraction data (15 237 independent reflections having $2\theta_{\text{MoK}\alpha} < 55^\circ$) were collected on a computer-controlled four-circle Syntex P_1 autodiffractometer using graphite-monochromated $\text{Mo K}\alpha$ radiation and full (1° wide) ω scans. The four molybdenum atoms of the totally general-position asymmetric unit were located using direct methods (MULTAN); the remaining anionic and cationic nonhydrogen atoms

and the anionic hydrogen atoms were located by standard difference Fourier techniques. The resulting structural parameters have been refined to convergence ($R = 0.042$ for 6343 independent reflections having $2\theta_{\text{MoK}\alpha} < 43^\circ$ (the equivalent of 0.50 limit $\text{Cu K}\alpha$ sphere) and $I > 3\sigma(I)$) using unit-weighted full-matrix least-squares techniques with anisotropic thermal parameters for all 71 nonhydrogen atoms and isotropic thermal parameters for the 3 anionic hydrogens. Refinement is continuing with those reflections having $2\theta_{\text{MoK}\alpha} < 55^\circ$ and a model which includes isotropic cationic hydrogen atoms.

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- (17) Camille and Henry Dreyfus Teacher–Scholar.
- (18) Fellow of the Alfred P. Sloan Foundation, 1976–1978.

V. W. Day,*¹⁷ M. F. Fredrich

Department of Chemistry, University of Nebraska
Lincoln, Nebraska 68588

W. G. Klemperer,*¹⁸ R.-S. Liu

Department of Chemistry, Columbia University
New York, New York 10027

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An Unusual Rearrangement of Ajaconine: An Example of a "Disfavored" 5-Endo-Trigonal Ring Closure

Sir:

The structure of ajaconine (**1**), the major alkaloid of the seeds of *Delphinium ajacis* and *D. consolida*, was established elegantly by Dvornik and Edwards^{1,2} and was correlated³ subsequently with the known alkaloid atidine (**2**). Ajaconine was the first example of a C_{20} -diterpenoid alkaloid bearing an internal carbinolamine ether linkage (N–C–O–C) between C(7) and C(20). This communication reports an unusual rearrangement of ajaconine via a "disfavored" 5-endo-trig ring

