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Trinuclear Mo–Mo-Bonded Cluster Cation with One Oxygen Atom Cap and One Ethylidyne Cap

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Abstract: The compound $[Mo_3(\mu_3\text{-}O)(\mu_3\text{-}CCH_3)(O_2CCH_3)_6(H_2O)_3]BF_4{\cdot}9H_2O$ has been prepared and thoroughly characterized by a variety of physical measurements, including a complete X-ray crystallographic structure determination. It crystallizes in space group $Pmn2_1$ with $Z = 2$ and the following unit cell dimensions: $a = 11.140$ (1) Å, $b = 7.939$ (1) Å, $c = 20.297$ (3) Å, $V = 1795.1$ (7) Å^3. The cation resides on the crystallographic mirror plane but has C_{3v} symmetry within experimental error, with the following important mean distances: Mo–Mo, 2.752 (1) Å; Mo–(μ_3-O), 1.983 (4) Å; Mo–CCH_3, 2.044 (7) Å; Mo–O(acetate), 2.12 (1) Å; Mo–O(H_2O), 2.164 (4) Å. The compound is diamagnetic and exhibits well-resolved ^1H and ^{13}C NMR spectra completely consistent with the proposed structure. ^{13}C tracer study shows that the ethylidyne group arises by reduction of the acetate group. The bonding in the trimolybdenum cluster can be described as three Mo–Mo bonds of order 1.

Although a reaction of molybdenum hexacarbonyl with a carboxylic acid was first described more than 20 years ago,[2] only now are we beginning to fathom the complexity and diversity of this class of reactions. Attention has, from the beginning, tended to focus mainly on the reaction with acetic acid. After some initial misapprehensions,[2-4] the isolated yellow product was correctly identified,[5] and the presence in it of a quadruple bond was recognized. In this way one of the major strands in the fabric of the now large field of multiple bonds between metal atoms[7,8] came into existence. For many years, however, attention was entirely riveted on this particular product and the reaction was studied and modified only with a view of securing the best possible yield of $Mo_2(O_2CCH_3)_4$. In pursuit of this objective reaction conditions were changed.[9-13] Instead of the pure acid, or a mixture of the acid and the acid anhydride, higher boiling solvents, especially diethylene glycol dimethyl ether (diglyme) but also decalin, 1,2-dichlorobenzene, and toluene, have been used. In this way yields of 80% or better have been achieved.

However, let us return our attention to the primeval reaction of $Mo(CO)_6$ with an excess of glacial acetic acid, or a mixture of the acid and the anhydride. From such a reaction only a fraction of the molbydenum introduced, 10–20% depending on details, is recovered as $Mo_2(O_2CCH_3)_4$, which precipitates. The important question of what becomes of the rest of the molybdenum remained without any answer until a few years ago, when efforts were initiated to determine what compounds might be obtainable from the dark green-brown supernatant liquid above the precipitated $Mo_2(O_2CCH_3)_4$.

As we have already announced in a preliminary communication,[14] very novel trinuclear molybenum complexes of the general type $[Mo_3(\mu_3\text{-}X)(\mu_3\text{-}Y)(O_2CCH_3)_6(H_2O)_3]^{n+}$ may be obtained from these solutions. We now begin a series of papers in which these substances will be described in as much detail as we now have available on them. As we have noted, three major types have been recognized, differing in the capping groups μ_3-X and μ_3-Y: (1) those with X = Y = O; (2) those with X = Y = CCH_3; (3) those with X = O and Y = CCH_3. We begin our series of detailed reports by describing a compound of the third class, namely, one that incorporates both the relatively common capping oxygen atom and the novel capping ethylidyne group.

Table I. Crystallographic Data and Enraf-Nonius CAD-4 Data Collection Parameters

formula	$Mo_3F_4O_{25}C_{14}BH_{45}$
M	988.12
space group	$Pmn2_1$
a, Å	11.140 (1)
b, Å	7.939 (1)
c, Å	20.297 (3)
V, Å^3	1795.1 (8)
Z	2
ρ(calcd), g cm^{-3}	1.828
cryst size, mm	0.3 × 0.3 × 0.4
μ(Mo Kα), cm^{-1}	11.25
radiation	graphite-monochromated Mo Kα (λ = 0.71073 Å)
scan type	ω–2θ
scan width ($\Delta\omega$), deg	$0.80 + 0.35 \tan\theta$
aperature width, mm	$1.50 + 1.00 \tan\theta$
prescan rejection limit	2.0 (0.5σ)
prescan acceptance limit	0.02 (50σ)
max scan speed, deg min^{-1}	20.12
max counting time, s	30
collection range	$+h, +k, +l$, $0° < 2\theta < 50°$
no. of unique data	1712
no. of data, $I \geq 3\sigma(I)$	1631
p	0.05
X-ray exposure time, h	15
no. of variables	234
R_1	0.032
R_2	0.041
esd	1.38
largest parameter shift[a]	0.09
largest peak,[b] e Å^{-3}	0.28

[a] Final refinement cycle. [b] Largest peak in final difference Fourier map.

Experimental Section

Preparation and Isolation. A single-necked 50-mL flask was charged with 2.0 g (7.58 mM) of $Mo(CO)_6$, 20 mL of CH_3COOH, 10 mL of $(CH_2CO)_2O$, and 1.5 mL of $(CH_3CH_2)_3N$. The flask was fitted with a condenser and the mixture heated at reflux, in air, for 24 h during which time a brown supernatant liquid and a yellow precipitate formed. The

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(1) (a) The Hebrew University, Jerusalem. (b) Texas A&M University. (c) The Technion-Israel Institute of Technology, Haifa.

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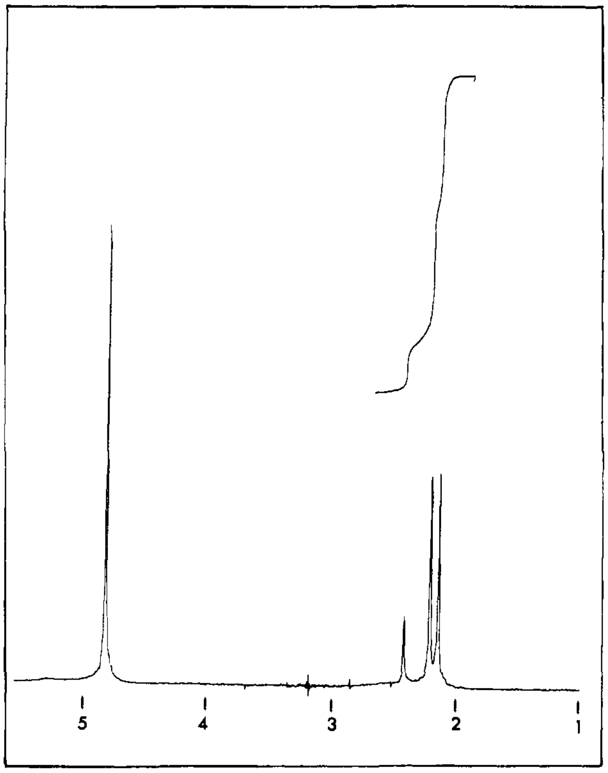

Figure 1. The ^1H NMR spectrum of $[Mo_3(O)(CCH_3)(O_2CCH_3)_6(H_2O)_3]BF_4 \cdot 9H_2O$ in D_2O at 360 MHz. The chemical shift scale is parts per million downfield from $Na[(CH_3)_3SiCD_2CD_2CO_2]$ (TSP).

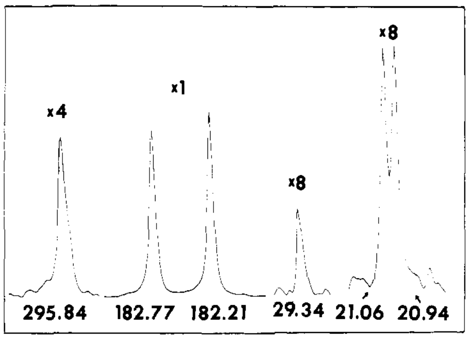

Figure 2. The $^{13}C\{^1H\}$ NMR spectrum, at the natural abundance level, of $[Mo_3(O)(CCH_3)(O_2CCH_3)_6(H_2O)_3]BF_4 \cdot 9H_2O$ in D_2O at 96 MHz. Chemical shifts are in parts per million downfield from the methyl carbon atoms of TSP. True relative intensities are obtained by applying the indicated multiplicative factors to the lines shown.

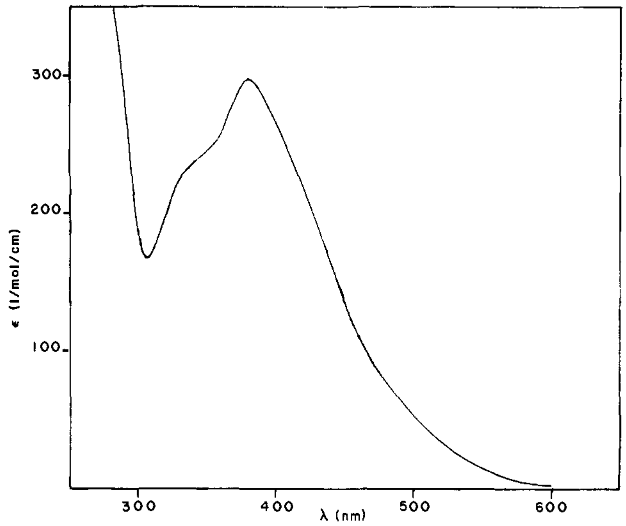

Figure 3. Electronic absorption spectrum of the $[Mo_3(O)(CCH_3)(O_2CCH_3)_6(H_2O)_3]^+$ ion.

yellow microcrystalline solid, $Mo_2(O_2CCH_3)_4$ (0.30 g, 19%), was removed by filtration, and the filtrate was placed in an open beaker. After 48 h a red-brown solid had precipitated. The solid was collected, rinsed with acetone and ether, and dried in a desiccator over P_2O_5, to yield 1.1 g of an orange powder.

A red aqueous solution of the red-brown solid was poured onto a 2 × 2 cm cation-exchange column (Dowex 50W-X2) and a bright red band formed on the resin. After the column was washed with water, it was eluted with 0.2 M HBF_4, developing an intense orange-red band. This band was collected and the resulting solution slowly evaporated in air to produce well-formed orange-red crystals of the compound $[Mo_3(O)(CCH_3)(O_2CCH_3)_6(H_2O)_3]BF_4 \cdot 9H_2O$.

X-ray Crystallography. Although crystals of this material were readily available, their proclivity to lose water and, hence, crystallinity presented difficulities. Several crystals of large size were used initially to determine the characteristics of the unit cell and to establish the systematic absences. Finally, a crystal of dimensions 0.3 × 0.3 × 0.4 mm, mounted on the end of a thin glass fiber, was used for data collection. Twenty-five reflections in the range $13° \leq \theta \leq 16°$ were located by using the automatic search routine on an Enraf-Nonius CAD-4 automated diffractometer. Least-squares analysis of the setting angles produced the unit cell parameters (Table I) and an orientation matrix for data collection. Standard data collection routines have been reported previously[15] and specific CAD-4 parameters used in this study are given in Table I. A total of 1712 unique observations were measured in the range $0° < 2\theta \leq 50°$.

During data collection, the intensities of three standard reflections measured every 30 min of X-ray exposure time showed a linear isotropic decrease at a rate of 1%/h over a period of 15 h. A linear decay correction was applied to the intensity data as well as the standard Lorentz and polarization corrections.

Structure Refinement.[16] The systematic absences, $h,0,l$, $h + l = 2n$, suggested the two space groups $Pmmn$ or $Pmn2_1$. A Rogers–Phillips–Howell test for acentricity proved ambiguous so refinement was initiated in the centric group. The molybdenum atom positions were found by a combination of Patterson and direct methods. Subsequent difference Fourier syntheses and refinement of positions for other atoms indicated that the centric group was not appropriate. A transformation to $Pmn2_1$ was made, and determination and refinement of all atomic positions using alternating difference Fourier maps and least-squares calculations proceeded readily. Toward the end of refinement, least-squares analysis of an enantiomorphic model led to significantly better results and these new positional parameters were adopted. The final model, including anisotropic thermal parameters for all 31 atoms, was indicative of the well-behaved complex showing no disorder and refined to values of $R_1 = 0.032$ and $R_2 = 0.041$, where $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$ and $R_2 = [\sum(|F_o| - |F_c|)^2/\sum|F_o|^2]^{1/2}$. Other pertinent crystallographic data are contained in Table I.

Final positional and thermal parameters are presented in Table II. Lists of observed and calculated structure factors are available as supplementary material.

NMR Spectra. The ^1H NMR spectrum was run at 360 MHz in D_2O. Chemical shifts are given downfield from the methyl protons of TSP, $Na[(CH_3)_3SiCD_2CD_2CO_2]$, as standard. The spectrum, shown in Figure 1, has the following features (ppm, relative intensity, assignment): (1) 4.709, 6.63, ^1H in the D_2O; (2) 2.400, 1.000, CCH_3; (3) 2.195, 2.986 O_2CCH_3; (4) 2.128, 3.027, O_2CCH_3.

The $^{13}C\ \{^1H\}$ spectrum, again in D_2O with TSP as the standard for chemical shifts, was run at 96 MHz with ^{13}C at the natural abundance level. It has six features, as shown in Figure 2.

Electrolytic Conductance. Using a standard undergraduate apparatus, calibrated with potassium chloride solution, a 1.05×10^{-2} M solution in water, at 25 °C, gave an equivalent conductance, Λ, of 109 $\Omega^{-1}\ cm^2\ mol^{-1}$. This is consistent with dissociation as a M^+X^- electrolyte on comparison with standards such as KCl ($\Lambda_o = 150$ at 25 °C).

Electronic Spectrum. This was measured on an aqueous solution by using a Cary 17D spectrometer at 25 °C and is shown in Figure 3. Numerical values for the peaks in nanometers (ε in l $mol^{-1}\ cm^{-1}$) are 457 (shoulder, 116), 379 (298), and 340 (shoulder, 227).

^{13}C-Enrichment Studies. A number of studies employing ^{13}C-enriched starting materials have been done. We shall be concerned here only with those in which ^{13}C-enriched acetic acid was used to confirm the source

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(16) All crystallographic computing was performed on a PDP 11/45 computer at the Molecular Structure Corp., College Station, TX, employing the Enraf-Nonius Structure determination package.

Table II. Positional and Thermal Parameters and Their Estimated Standard Deviations for $[Mo(O)(CCH_3)(O_2CCH_3)_6(H_2O)_3]BF_4 \cdot 9H_2O^{a,b}$

atom	*x*	*y*	*z*	*B*(1,1)	*B*(2,2)	*B*(3,3)	*B*(1,2)	*B*(1,3)	*B*(2,3)
Mo(1)	−0.12358 (4)	−0.08116 (5)	−0.10156 (0)	1.30 (2)	2.15 (2)	2.18 (2)	0.11 (1)	0.00 (2)	0.14 (2)
Mo(2)	0.00000 (0)	−0.21935 (9)	0.00261 (5)	1.47 (2)	2.27 (2)	2.09 (2)	0	0	0.25 (3)
F(1)	−0.5000 (0)	−0.244 (2)	−0.9621 (6)	21 (2)	13.2 (8)	7.7 (6)	0	0	5.9 (5)
F(2)	−0.5000 (0)	−0.228 (2)	−0.8540 (7)	18 (1)	14.1 (9)	7.3 (6)	0	0	1.9 (7)
F(3)	−0.4095 (9)	−0.423 (2)	−0.9028 (7)	10.4 (5)	27 (1)	14.9 (9)	8.6 (6)	0.6 (7)	6.3 (8)
O(1)	0.0000 (0)	−0.2602 (7)	−0.0936 (3)	1.4 (2)	2.3 (2)	2.2 (2)	0	0	−0.0 (2)
O(2)	0.0000 (0)	−0.3380 (10)	0.0983 (4)	3.2 (3)	5.8 (4)	2.5 (3)	0	0	1.6 (3)
O(3)	−0.2925 (4)	−0.0157 (6)	−0.1479 (2)	1.4 (2)	3.6 (2)	3.7 (2)	0.6 (2)	−0.3 (2)	0.5 (2)
Ow(4)	−0.5000 (0)	−0.1357 (11)	−0.0939 (5)	1.8 (2)	6.7 (4)	5.5 (4)	0	0	1.3 (4)
Ow(5)	−0.3196 (7)	−0.2678 (9)	−0.2652 (4)	4.8 (3)	7.1 (3)	5.8 (3)	−0.8 (3)	0.1 (3)	−1.0 (3)
Ow(6)	−0.5000 (0)	−0.4112 (14)	−0.1833 (5)	5.1 (5)	9.0 (6)	5.0 (5)	0	0	0.5 (4)
Ow(7)	0.0000 (0)	−0.9583 (18)	−0.8163 (6)	9.4 (8)	11.8 (8)	5.5 (5)	0	0	−3.4 (5)
Ow(8)	−0.3790 (11)	0.2296 (16)	−0.2278 (7)	9.3 (6)	19.8 (6)	22.6 (7)	−4.7 (5)	−7.5 (5)	16.3 (5)
Ow(9)	−0.1999 (7)	−0.4323 (9)	0.1678 (4)	5.1 (3)	7.9 (4)	6.1 (3)	−0.4 (3)	0.5 (3)	2.4 (3)
O(21)	−0.1357 (4)	−0.4087 (5)	−0.0061 (3)	1.9 (2)	2.8 (2)	3.5 (2)	−0.2 (1)	0.3 (2)	0.6 (2)
O(22)	−0.2324 (4)	−0.2957 (5)	−0.0906 (2)	1.5 (2)	2.8 (2)	3.6 (2)	0.0 (1)	−0.1 (2)	0.6 (2)
O(31)	−0.1350 (4)	−0.0988 (6)	0.0591 (3)	2.7 (2)	3.4 (2)	2.7 (2)	0.4 (2)	0.5 (2)	0.0 (2)
O(32)	−0.2355 (4)	0.0084 (6)	−0.0250 (2)	2.0 (2)	3.0 (2)	3.2 (2)	0.4 (2)	0.3 (2)	−0.2 (2)
O(41)	−0.0995 (4)	0.1608 (5)	−0.1437 (2)	2.4 (2)	2.5 (2)	3.5 (2)	0.3 (2)	−0.3 (2)	0.8 (2)
O(51)	−0.0997 (4)	−0.1538 (6)	−0.2019 (2)	1.6 (2)	3.7 (2)	2.2 (2)	0.1 (2)	−0.1 (2)	−0.0 (2)
C(6)	0.0000 (0)	0.0167 (11)	−0.0379 (5)	2.1 (3)	2.3 (3)	2.3 (3)	0	0	0.6 (3)
C(21)	−0.2163 (6)	−0.4100 (7)	−0.0484 (4)	1.2 (2)	2.7 (2)	3.3 (3)	0.1 (2)	0.4 (2)	0.3 (2)
C(22)	−0.2987 (7)	−0.5599 (9)	−0.0501 (5)	2.8 (3)	3.2 (3)	6.2 (4)	−1.0 (3)	−0.7 (3)	1.1 (3)
C(31)	−0.2211 (6)	−0.0120 (9)	0.0354 (3)	2.8 (3)	3.0 (2)	2.5 (2)	−0.1 (3)	0.5 (2)	−0.4 (2)
C(32)	−0.3030 (7)	0.0722 (10)	0.0828 (5)	3.4 (3)	6.1 (4)	3.9 (3)	2.1 (3)	0.9 (3)	−0.5 (3)
C(41)	0.0000 (0)	0.2311 (12)	−0.1572 (5)	2.8 (4)	2.7 (4)	3.0 (4)	0	0	0.1 (3)
C(42)	0.0000 (0)	0.3996 (14)	−0.1890 (7)	3.8 (5)	3.3 (4)	5.1 (6)	0	0	0.5 (4)
C(51)	0.0000 (0)	−0.1810 (11)	−0.2309 (5)	3.0 (4)	2.2 (3)	2.1 (3)	0	0	0.5 (3)
C(52)	0.0000 (0)	−0.2500 (15)	−0.2980 (5)	2.6 (4)	5.7 (5)	2.3 (4)	0	0	−0.2 (4)
C(61)	0.0000 (0)	0.1898 (10)	−0.0059 (6)	2.7 (4)	2.0 (3)	4.0 (4)	0	0	−0.7 (4)
B	−0.5000 (0)	−0.335 (3)	−0.909 (1)	4.4 (8)	12 (1)	5.3 (8)	0	0	3.4 (9)

[a] The form of the anisotropic thermal parameter is $\exp[-0.25\{h^2a^2B(1,1) + k^2b^2B(2,2) + l^2c^2B(3,3) + 2hkabB(1,2) + 2hlacB(1,3) + 2klbcB(2,3)\}]$, where *a, b,* and *c* are reciprocal lattice constants. [b] Estimated standard deviations in the least significant digits are shown in parentheses.

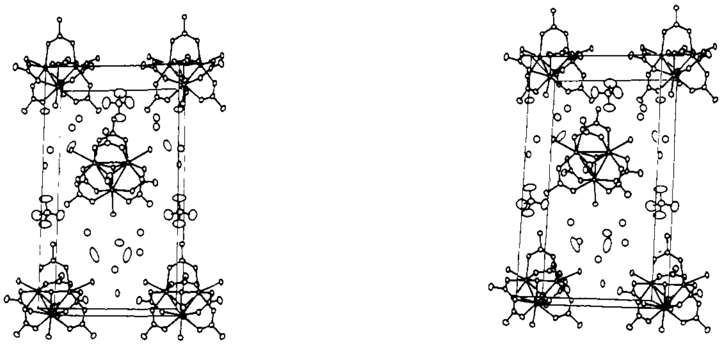

Figure 4. A stereoview of the unit cell of $[Mo_3(O)(CCH_3)(O_2CCH_3)_6(H_2O)_3]BF_4 \cdot 9H_2O$.

of the ethylidyne group. A 1-g sample of 90% enriched acetic acid (either at C(1) or C(2)) purchased from Merck was diluted with 6 mL of isotopically normal CH_3CO_2H, 3 mL of $(CH_3CO)_2O$, and 0.5 mL of $(C_2H_5)_3N$. The reaction with 0.65 g of $Mo(CO)_6$ and isolation of product were carried out according to the procedure described above for the ordinary preparation of the compound. The NMR spectra (50 MHz) showed equal degrees of transfer of ^{13}C from $^{13}CH_3CO_2H$ to both CH_3CO_2 and CH_3C groups in the product. For $CH_3{}^{13}CO_2H$ substantial transfer to both CH_2CO_2 and CH_3C positions was also observed. The results are not sufficiently accurate to allow us to say whether these transfers were quantitative.

Results

Crystal Structure. The crystal structure of this compound has been refined very successfully. The crystallographic unit cell is shown in Figure 4, and the cation, with the atomic labelling scheme, is depicted in Figure 5. Table III gives the bond lengths and bond angles. Both the cation and the BF_4^- anion reside on the crystallographic mirror plane. The numbering of the fluorine atoms in the anion is such that F(1) and F(2) lie in the mirror plane (along with B) while F(3) and F(3)′ lie on opposite sides of it. As is usual, high thermal motion and/or some disorder of the BF_4^- ions leads to sizable errors in the distances and angles.

The trinuclear cation is found to have C_{3v} symmetry within the esd's. The two crystallographically independent types of Mo–Mo bond are equal within experimental error at 2.752 (1) Å and so too are all other bond lengths that are chemically equivalent though crystallographically distinct. The mean distances from the metal atoms to the capping atoms are similar, with the mean Mo–(μ_3-O) distance being 1.983 (4) Å and the mean Mo–(μ_3-CCH_3) distance being 2.044 (7) Å. The $Mo_3(O)(CCH_3)$ central unit thus forms a slightly distorted trigonal bipyramid with mean angles at the O and C capping atoms of 87.9 (2)° and 84.6 (3)°, respectively.

The molybdenum atoms in this structure each form nine bonds in the type of arrangement that Pauling has predicted from hybridization of all nine (five d, three p, one s) valence shell orbitals.[17] There is first a basal set of four bonds, two Mo–Mo and two to the capping atoms. Then, in a staggered orientation relative to the basal set is an equatorial set of four bonds to the oxygen atoms of acetate ions. Finally, there is an axial bond to the water molecule. It is interesting that the Mo–O(H_2O) bonds (mean length 2.164 (4) Å) are only slightly longer than the Mo–O-

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[17] Pauling, L. *Proc. Nat. Acad. Sci. U.S.A.* **1975**, *72*, 3799, 4200.

Table III. Bond Distances and Bond Angles for $[Mo_3(O)(CCH_3)(O_2CCH_3)_6(H_2O)_3]BF_4 \cdot 9H_2O$

A. Bond Distances (Å) in Cation

Mo(1)-Mo(1′)	2.753 (1)	C(21)-O(21)	1.243 (8)	Mo(2)-O(1)	1.980 (7)	C(31)-O(31)	1.275 (9)
Mo(2)	2.751 (1)	O(22)	1.261 (7)	O(2)	2.159 (7)	O(32)	1.247 (7)
O(1)	1.985 (4)	C(22)	1.504 (9)	O(21)	2.139 (4)	C(32)	1.48 (1)
O(3)	2.167 (4)	C(41)-O(41)	1.271 (6)	O(31)	2.119 (4)	C(51)-O(51)	1.275 (6)
O(22)	2.104 (4)	C(41)	1.49 (1)	C(6)	2.047 (8)	C(52)	1.47 (1)
O(32)	2.116 (5)	C(6)-C(61)	1.52 (1)				
O(41)	2.120 (4)						
O(51)	2.134 (4)						
C(6)	2.042 (7)						

B. Bond Angles (Deg) in Cation

Mo(1′)-Mo(1)-Mo(2)	59.98 (1)	O(32)-Mo(1)-O(41)	93.8 (2)	O(2)-Mo(2)-O(31)	73.2 (2)
O(1)	46.1 (1)	O(51)	150.0 (2)	O(21′)	76.6 (2)
O(3)	150.3 (1)	C(6)	78.7 (2)	O(31′)	73.2 (2)
O(22)	125.2 (1)	O(41)-Mo(1)-O(51)	81.0 (2)	C(6)	139.6 (3)
O(32)	126.1 (1)	C(6)	79.9 (3)	O(21)-Mo(2)-O(31)	82.0 (2)
O(41)	82.7 (1)	O(51)-Mo(1)-C(6)	128.5 (2)	O(21′)	89.9 (2)
O(51)	82.8 (1)	Mo(1)-O(41)-C(41)	126.5 (5)	O(31′)	149.7 (2)
C(6)	47.6 (2)	O(41)-C(41)-O(41′)	121.4 (8)	C(6)	127.6 (2)
Mo(2)-Mo(1)-O(1)	46.0 (2)	C(42)	119.3 (4)	O(31)-Mo(2)-O(21′)	149.7 (2)
O(3)	149.7 (1)	Mo(1)-O(51)-C(51)	126.5 (4)	O(31′)	90.4 (3)
O(22)	83.4 (1)	O(51)-C(51)-O(51′)	121.1 (8)	C(6)	78.7 (2)
O(32)	82.2 (1)	C(52)	119.4 (4)	O(21′)-Mo(2)-O(31′)	82.0 (2)
O(41)	127.5 (1)	Mo(1)-C(6)-Mo(1′)	84.8 (3)	C(6)	127.6 (2)
O(51)	124.3 (1)	Mo(1)-C(6)-Mo(2)	84.6 (3)	O(31′)-Mo(2)-C(6)	78.7 (2)
Mo(2)-Mo(1)-C(6)	47.8 (2)	Mo(1)-Mo(2)-O(1)	46.1 (1)	Mo(1)-O(22)-C(21)	125.0 (4)
O(1)-Mo(1)-O(3)	144.0 (2)	O(2)	149.94 (2)	Mo(2)-O(21)-C(21)	125.0 (4)
O(22)	79.1 (2)	O(21)	82.1 (1)	O(21)-C(21)-O(22)	124.5 (5)
O(32)	126.1 (2)	O(31)	83.1 (1)	C(22)	117.6 (6)
O(41)	126.4 (2)	O(21′)	124.8 (2)	O(22)-C(21)-C(22)	117.9 (6)
O(51)	78.3 (2)	O(31′)	126.2 (1)	Mo(1)-O(32)-C(31)	127.1 (5)
C(6)	75.7 (3)	C(6)	47.6 (2)	Mo(2)-O(31)-C(31)	125.1 (4)
O(3)-Mo(1)-O(22)	74.9 (2)	O(1)-Mo(2)-O(2)	144.7 (3)	O(31)-C(31)-O(32)	122.5 (6)
O(32)	74.1 (2)	O(21)	78.7 (2)	C(32)	117.5 (6)
O(41)	73.6 (2)	O(31)	127.4 (2)	O(32)-C(31)-C(32)	120.0 (7)
O(51)	76.0 (2)	O(21′)	78.7 (2)	Mo(1)-O(1)-Mo(1′)	87.8 (2)
C(6)	140.3 (2)	O(31′)	127.4 (2)	Mo(1)-O(1)-Mo(2)	87.9 (2)
O(22)-Mo(1)-O(32)	81.7 (2)	C(6)	75.7 (3)	Mo(1)-C(6)-C(61)	127.9 (4)
O(41)	148.2 (2)	O(2)-Mo(2)-O(21)	76.6 (2)	Mo(2)-C(6)-C(61)	131.0 (6)
O(51)	87.4 (2)				
C(6)	129.1 (3)				

C. Bond Distances (Å) and Angles (Deg) in Anion

B-F(1)	1.30 (2)	F(1)-B-F(2)	109 (2)	F(2)-B-F(3)	105 (1)
F(2)	1.40 (3)	F(3)	113 (1)	F(3)-B-F(3)′	109 (3)
F(3)	1.24 (2)				

D. Bond Distances (Å) for Hydrogen Bonding Contacts

O(2)-Ow(9)	2.741 (8)	Ow(4)-Ow(6)	2.84 (1)	F(1)-Ow(4)	2.81 (2)	Ow(8)-Ow(9)	2.80 (1)
O(3)-Ow(4)	2.730 (6)	Ow(5)-Ow(6)	2.85 (1)	F(3)-Ow(9)	2.74 (1)	Ow(5)-Ow(7)	2.89 (1)
O(3)-Ow(8)	2.71 (1)	Ow(5)-Ow(9)	2.75 (1)	Ow(8)-Ow(8)*	2.70 (3)		

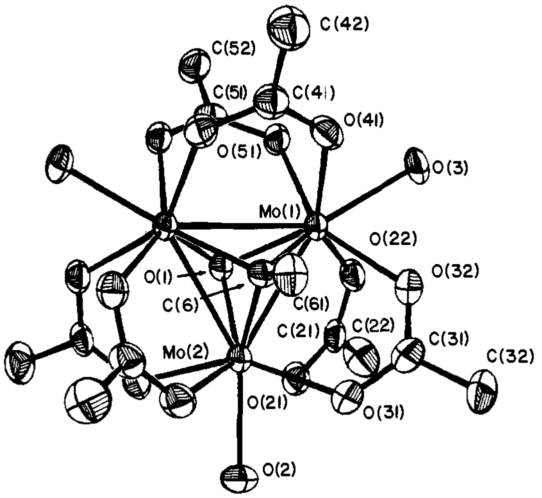

Figure 5. The $[Mo_3(O)(CCH_3)(O_2CCH_3)_6(H_2O)_3]^+$ ion and the atom-labeling scheme. Unlabeled atoms are related to labeled ones by the mirror plane. Each atom is represented by its ellipsoid of thermal motion at the 40% level.

(acetate) bonds, which have a mean length of 2.12 (1) Å.

The Hydrogen-Bonding Network. The closest contacts between the cationic cluster and the lattice water molcules occur at the cluster water molecules. There is a complex hydrogen-bonding network which incorporates these sites along with all of the lattice water molecules and the BF_4^- counterions. Contact distances are listed in part D of Table III. The most interesting interaction involves two lattice water molecules, Ow(4) and Ow(9), the two coordinated water ligands, O(2) and O(3), and F(1) and F(3) of the counterion. The contacts among these atoms are all roughly 2.7 Å, and, including the regular bonding contacts for O(2), Mo(2), Mo(1), O(3) and F(1), B, F(3), well-defined nine membered rings of nonhydrogen atoms are formed which connect all the anions and cations into an infinite array.

A second interaction which links together all of the cations involves again the coordinated water ligands as well as Ow(9) and Ow(8). It includes a more direct link by using an intermolecular bridge of O(3), Ow(8), Ow(8)*, and O(3)* and a direct O(3)–Ow(4)–O(3)* connection. The acetate oxygen atoms and the capping oxygen, O(1), make no external contacts shorter than 3.30 Å.

NMR Spectra. The proton and carbon NMR spectra, shown in Figures 1 and 2, offer strong testimony that the compound is diamagnetic[18] and that it retains the same structure in solution. Because there are different capping groups on each side of the Mo_3 plane, the acetate groups are divided into two sets of three. This is seen in the ^1H spectrum, Figure 1, which shows the expected three methyl resonances, for the one CCH_3 and the three O_2CCH_3 groups of each type, in the intensity ratio of 1:3:3.

The $^{13}C\{^1H\}$ spectrum alone is virtually conclusive. The six features are shown in Figure 2. At 29.34, 21.06, and 20.94 ppm in the intensity ratio of 1:3:3, we find the $\mathrm{C}C\mathrm{H_3}$ and two $\mathrm{O_2C}C\mathrm{H_3}$ signals. At 182.77 and 182.21 ppm we find the two $\mathrm{O_2}C\mathrm{CH_3}$ signals, and at 295.84 ppm there is a line attributable to $C\mathrm{CH_3}$. Because of drastic differences in NOE's and T_1's, intensity ratios have no significance except within the sets of resonances for chemically similar carbon atoms, i.e., the three types of $C\mathrm{H_3}$ and the two types of $\mathrm{O_2}C\mathrm{CH_3}$ nuclei. It is significant that the chemical shift difference for the two types of $\mathrm{O_2}C\mathrm{CH_3}$ atoms, 0.56 ppm, is considerably greater than that between the two types of $\mathrm{O_2C}C\mathrm{H_3}$ atoms, 0.12 ppm. This is consistent with the former being much closer to the central $Mo_3(O)(CCH_3)$ group where they are more strongly affected by the fact that the capping groups are different.

The chemical shifts for the $C\mathrm{H_3}$ and $\mathrm{O_2}C\mathrm{CH_3}$ carbon atoms are in the known ranges for such carbon atoms[19] and require no further comment. The downfield position of the resonance for the ethylidyne carbon atom, $C\mathrm{CH_3}$, is not inconsistent with previous observations. In a variety of trinuclear metal carbonyl type cluster compounds with (μ-CR) groups the capping carbon atom has been seen in the range 263–346 ppm.[20]

Discussion

Preparation. As we have indicated in our preliminary communication[14] three main types of trimolybdenum cluster compounds (i.e., $Mo_3(\mu_3\text{-}O)_2$, $Mo_3(\mu_3\text{-}CCH_3)_2$, and $Mo_3(\mu_3\text{-}O)(\mu_3\text{-}CCH_3)$ types) can be obtained from the reactions of $Mo(CO)_6$ with glacial acetic acid or a mixture of the acid and its anhydride, depending on (a) the conditions under which the reaction itself is conducted and (b) the way in which the workup of the reaction products is carried out. In each of the full papers, of which this is the first, these crucial matters will be fully explained and discussed. We turn now to the preparation of the (O,CCH_3)-capped compounds.

The preparative procedure given in the Experimental Section calls for the addition of a base, triethylamine, to the $CH_3CO_2H/(CH_3CO)_2O$ reaction medium. Some compounds containing the O,CCH_3-type complex ion were originally obtained as very minor products from the reaction mixture with no base present. However, the addition of base provides as good a procedure as we know for making compounds containing the $[Mo_3(O)(CCH_3)(O_2CCH_3)_6(H_2O)_3]^+$ ion. It may be mentioned here that acids other than HBF_4 may be used to elute the cation-exchange column and in this way other well-defined crystalline, hydrated salts of the same cation may be obtained.

To return, however, to the preparative reaction itself, it was found that bases other than Et_3N are also efficient in favoring the formation of the O,CCH_3-type cluster and it was concluded from this that the bases might all be acting in the same simple way, namely, to generate acetate ions. For a test of this, the reaction was run with addition of 1–2 g of sodium acetate and no other base and found to work quite well. We can, therefore, state that the preparation can be perfectly well carried out with any number of modifications of the procedure given in which 1–2 g of some other base (e.g., pyridine) or 1–2 g of NaO_2CCH_3 are used instead of triethylamine.

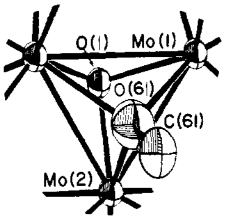

Figure 6. The central portion of the cation as refined to convergence with the capping CCH_3 group treated as OCH_3.

Authenticating the Ethylidyne Group. In the initial stages of this work, the identification of the capping atoms posed a problem. In the earliest preliminary communication[21] on a trinuclear compound derived from the type of reaction used here, it was believed that the capping groups were alkoxides. Consequently, in the earliest stages of our work on this compound we believed that the capping groups were O and OC_2H_5. It soon became clear, however, that no trace of a β-carbon atom could be found crystallographically and the structure was, therefore, refined with O and OCH_3 as capping groups. However, this led to several inconsistencies. Some of these have to do with reconciling the analytical data and the density measurements with this formula. They have been outlined in our preliminary note with specific reference to two related compounds. The present compound does not provide a good test case in these respects because the large amount of water of crystallization and the tendency of the crystals to effloresce introduce uncertainty into analytical data and the density measurements.

There are, however, five features of this particular compound that are indicative of the unacceptability of the O,OCH_3 formulation of it, quite apart from any reference to related compounds. One has to do with the question of where the OCH_3 group would come from. The idea of an OCH_2CH_3 group arising from reduction of the acetic acid is obvious and sensible, but one has to invoke some far from obvious molecular rearrangements to generate OCH_3 groups.

A second consideration has to do with the electronic structure. If the capping groups are O and OCH_3, the mean oxidation number of the molybdenum atoms is +10/3, and this leaves 18 − 10 = 8 electrons to be accomodated in the molecular orbitals of the $[Mo_3]^{10+}$ cluster. Now, in this structure, each metal atom forms seven bonds to ligands, leaving only two orbitals to be used in the cluster. These two orbitals per metal atom just suffice to form three Mo–Mo bonding orbitals and three Mo–Mo antibonding orbitals.[22] When six electrons are placed in the bonding orbitals, there are still two electrons to be accommodated and only Mo–Mo or Mo–ligand antibonding orbitals to put them in. While it can hardly be said that this situation affords a conclusive indication that something has to be wrong, it is cogently unsatisfying and caused us much concern.

A third aspect of the O,OCH_3 model that caused concern was the final, refined $O\text{–}CH_3$ distance, 1.51 (2) Å. This is considerably longer than would be expected for such a bond, which ought to have a length of about 1.43 Å.[23] While some reduction from 1.51 Å might result if a correction for thermal vibration were applied (perhaps 0.01–0.02 Å), the observed bond length would be difficult to rationalize for an $O\text{–}CH_3$ bond.

However, the thing that not only convinced us conclusively the O,OCH_3 formulation had to be wrong but also indicated where the right answer had to lie was an anomaly in the refined structure. We show in Figure 6 the central part of the cation after the O,OCH_3 model was fully refined. Note that the O-capping atom, O(1), which really is an oxygen atom, has refined to give a small vibrational ellipsoid, as would be expected. The other "oxygen" atom, O(61), however, has a thermal ellipsoid even larger than

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[18] The diamagnetism was confirmed by a bulk susceptibility measurement, using the Faraday method; this gave a value of $-(250 \pm 50) \times 10^{-6}$ cgs units, which may be compared with an estimated value, based on conventional diamagnetic contributions of the constituent atoms, of $-(300 \pm 50) \times 10^{-6}$ cgs units.

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[22] A detailed discussion of the bonding in trinuclear cluster compounds of molybdenum and tungsten will be presented later in this series of papers.

[23] *Spec. Publ.—Chem. Soc.* **1965**, *No. 18*, 520s.

that of the pendant carbon atom, which ought to have a greater amount of vibrational motion and hence a larger vibrational ellipsoid. This is physically unreasonable and suggest that too much electron density has been assigned to the atom called O(61). By calling it a carbon atom, C(6), which is the only chemically acceptable alternative, we obtain the physically satisfying result already shown in Figure 5, where the two capping atoms, O(1) and C(6), have thermal ellipsoids of essentially equal size, with that of the terminal carbon atom C(61) being much larger.

If we change the OCH_3^- to CCH_3^{3-}, we then raise the mean oxidation number of molbydenum to +4. This leaves only $18 - 12 = 6$ electrons to be placed in cluster molecular orbitals, and these suffice exactly to provide the three Mo–Mo single bonds. Thus, the electronic structure difficulty is resolved. Further, it is a lot easier to imagine CCH_3^{3-} (formally) as a reduction product of the acetic acid than OCH_3^-. Also, the final, refined $C-CH_3$ bond length of 1.51 (1) Å is entirely acceptable.

Finally, there is a fifth form of evidence favoring the O,CCH_3 model. Having changed the crystallographic model, albeit modestly, by introducing the carbon atom for the oxygen atom, we observed a decrease in R values from 0.033 and 0.043 to 0.032 and 0.041 for R_1 and R_2, respectively. Concurrently, there was an improvement in the goodness-of-fit parameter from 1.43 to 1.38.

These arguments, together with the evidence that in related compounds there were also μ_3-CCH_3 groups, left no real doubt that we were dealing with a μ_3-CCH_3 group. However, direct evidence was deemed necessary and this was provided by the ^{13}C NMR spectrum, as shown in Figure 2. In addition to the signals for the other five types of carbon atom, that would be present for the O,OCH_3 formulation, we find an additional signal in a region where the *C*CH_3 resonance might reasonably be expected.

The CCH_3-capping group, or similar C–X capping groups, have been observed often in the past.[20,24] However, in all these previous cases, the compounds have been of the metal carbonyl and/or organometallic types that characteristically have a nonaqueous chemistry and are more or less unstable toward water, air, and oxidizing agents. The remarkable characteristics of the compound described here, and related ones with CCH_3 capping groups, is that they are prepared and handled in aqueous, oxidizing conditions.

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Supplementary Material Available: A table of observed and calculated structure factors (7 pages). Ordering information is given on any current masthead page.

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Micellar Catalysis of Dephosphorylation by Benzimidazolide and Naphth-2,3-imidazolide Ions

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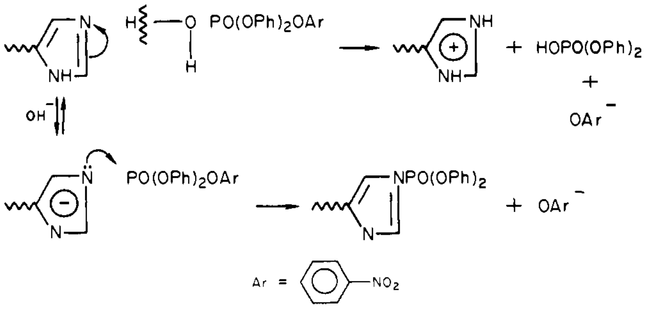
Abstract: The reactions of *p*-nitrophenyl diphenyl phosphate (*p*-NPDPP) with benzimidazolide and naphth-2,3-imidazolide ion are strongly catalyzed by micelles of cetyltrimethylammonium bromide (CTABr). The maximum rate enhancements are 2.5×10^3 and ca. 1.5×10^4 for benzimidazole and naphth-2,3-imidazole, respectively. The first-order rate constants go through maxima with increasing [CTABr], and for [CTABr] > 10^{-3} M the rate–surfactant profile is accommodated by a pseudophase model which relates rates in the micelles to the concentrations of micellar bound reactants, with the second-order rate constants in the micelle being similar to those in water. The imidazolide ions are phosphorylated by *p*-NPDPP and the phosphoryl intermediates can react with *p*-nitrophenoxide ion, regenerating starting material, or can go forward to product.

Imidazole derivatives are effective deacylating agents,[2] and their reactions with carboxylic esters are speeded by micellized surfactants.[3] The rate enhancements are especially large when the imidazole moiety is covalently bound to the surfactant head group, and these systems have been studied intensively.[3b,c]

Scheme I



Imidazole mediated dephosphorylation has not been studied widely, in either the absence or presence of micelles. Imidazole

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