chromium(IV) or EPR silent chromium(V) species, with a significantly larger extinction coefficient than the chromium(VI) glutathione thioester; however, we have no other spectroscopic evidence for such an intermediate. McAuley and Olatunji have tentatively assigned a peak at ~420–430 nm with an extinction coefficient of $\sim 1.25 \times 10^3\ \mathrm{M^{-1}\ cm^{-1}}$ to the chromium(VI) thioester formed from glutathione and hydrogen chromate.[45] They determined the following equilibrium:

$$\mathrm{GSH} + [(\mathrm{HO})\mathrm{CrO_3}]^- \overset{K_1}{\rightleftharpoons} [(\mathrm{GS})\mathrm{CrO_3}]^- + \mathrm{H_2O} \tag{5}$$

$$K_1 = 1440\ \mathrm{M^{-1}} \text{ at } T = 25\ ^\circ\mathrm{C}$$

Under their conditions of large excess ligand-to-metal ratios, the absorbance from hydrogen chromate at 350 nm was no longer observable, once the putative thioester had formed. However, the ^{17}O NMR results clearly indicate that under our conditions unreacted chromium(VI) remains in the reaction mixture. Connett and Wetterhahn[8] have also reported a chromium(VI) thioester formed from the reaction of chromate and glutathione at pH = 7.4. The UV–visible absorption spectrum observed is quite similar to that obtained under the conditions reported herein. However, the NMR data obtained at pH* = 8.0 show no $\mathrm{GSCrO_3^-}$ complex but rather different glutathione–chromium complexes (data not shown).

Summary

On the basis of extensive NMR studies, we conclude that the most likely structure for the product of the reaction of glutathione and dichromate is a monodentate thiolate chromium(VI)–glutathione complex, $\mathrm{GSCrO_3^-}$, which has been proposed previously.[6,8,10,13] The formation of this thiolate complex is unexpected, as glutathione possesses a number of other possible chromium(VI) binding sites. Chromium(VI) is considered a "hard" acid and sulfur a "soft" base, and therefore the "expected" preferred site of chromium(VI) binding to glutathione would be a carboxylate or possibly the amine group.[14] However, the reactivity of the thiolate of glutathione with chromium(VI) seems to outweigh these potential thermodynamic considerations of metal–ligand stability. Most of the previous metal–thiolate complexes of glutathione have been low-valent metal species.[9] We have presented evidence for a high-valent metal–thiolate complex formed from the reaction of dichromate with glutathione, i.e., $\mathrm{GSCrO_3^-}$. Several of the low-valent metal–thiolate complexes are not sensitive to the state of protonation of the thiol ($\mathrm{p}K_\mathrm{a} = 8.93$).[9] In contrast, we have seen little evidence of reaction between chromium(VI) and glutathione over pH 9.[46] This is in agreement with Connett and Wetterhahn's hypothesis that the proton on the thiol plays an important role in the formation of the $\mathrm{GSCrO_3^-}$ complex.[8]

The initial species of chromium(VI) appears to be important in thioester formation. Chromate/hydrogen chromate will form chromium(V) complexes with glutathione quite readily, as shown by the wealth of EPR data; however, we have no evidence for the formation of $\mathrm{GSCrO_3^-}$ thioester with chromate as the initial species of chromium(VI). We hypothesize that the lability of chromate/hydrogen chromate as a leaving group from dichromate assists in the formation of the $\mathrm{GSCrO_3^-}$ thioester. In comparison, the leaving group from chromate or hydrogen chromate would be oxide/hydroxide or hydroxide/water, and therefore redox processes appear to be favored over ligand substitution reactions of chromate/hydrogen chromate with glutathione. Further studies are being undertaken to identify the species formed at higher ratios of glutathione to chromium(VI).

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Preparations, Structures, and Properties of $\mathrm{M_3X_{13}}$ Type Molybdenum and Tungsten Trimers with Eight Cluster Electrons

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Abstract: The reactions of $\mathrm{MoCl_3{\cdot}3H_2O}$ and $\mathrm{(Et_4N)_3W_2Cl_9}$ with excess amounts of a mixture of acetic anhydride and acetic acid or 1 M hydrochloric acid solution of acetic acid, followed by suitable workup procedures, result in the isolation of complexes whose common feature is the presence of a $\mathrm{[M_3OCl_6(OAc)_3]^-}$ unit. This unit consists of an equilateral triangle of tungsten and molybdenum atoms with one capping oxygen atom above the triangle plane. Each M–M edge is bridged by an acetate group (above the plane) and a chloride ligand (below the plane). Each metal atom is further linked with a terminal chloride atom so that a distorted octahedral coordination environment is completed. The average oxidation state of the metal atoms for these two complexes is 3.33, and eight d electrons are delocalized over the $\mathrm{M_3}$ cluster. The average metal–metal bond distances for these two complexes are 2.570 (2) and 2.567 (1) Å, respectively. Additional cations are present as necessary for electroneutrality. Two such complexes have been structurally characterized by X-ray diffraction with the following crystallographic data: $\mathrm{(Me_4N)[Mo_3(\mu_3\text{-}O)(\mu\text{-}Cl)_3(\mu\text{-}OAc)_3Cl_3]{\cdot}2HOAc}$ (**1**), orthorhombic *Pnma*, $a = 7.684$ (2) Å, $b = 13.856$ (3) Å, $c = 28.495$ (4) Å, $V = 3034$ (1) Å^3, $Z = 4$, $R = 0.034$, $R_w = 0.041$; $\mathrm{(Et_4N)[W_3(\mu_3\text{-}O)(\mu\text{-}Cl)_3(\mu\text{-}OAc)_3Cl_3]{\cdot}Me_2CO}$ (**2**), monoclinic, $P2_1/c$, $a = 13.996$ (2) Å, $b = 15.999$ (4) Å, $c = 14.031$ (3) Å, $\beta = 98.01$ (1)°, $V = 3110$ (1) Å^3, $Z = 4$, $R = 0.034$, $R_w = 0.047$.

Introduction

The chemistry of triangular M–M bonded cluster compounds of molybdenum and tungsten has been extensively studied in recent years.[1] One of the structural types (though there are others[2-5]) is often designated the $\mathrm{M_3X_{13}}$ type. It consists of three $\mathrm{MX_6}$ octahedra fused together so that each octahedron shares one X

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[1] Cotton, F. A. *Polyhedron* **1986**, *5*, 3.

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with both of the others (X_0), and there are three shared edges, X_0–X_1, X_0–X_2, and X_0–X_3. This arrangement may also be described as an equilateral triangle of metal atoms with a capping atom (X_0) above and three edge-bridging atoms below (X_1, X_2, X_3) as well as three more ligand atoms on each metal atom, arranged so as to complete the local octahedron. It has been shown[6,7] that for this type of cluster the molecular orbitals that are chiefly concerned with metal–metal interaction are of the following types, where we list them in increasing order of energy: $1a_1$ 1e $2a_1$ 2e 3e $1a_2$.

For the particular case of $M_3O_4X_9$ systems, the $1a_1$ and 1e orbitals are strongly M–M bonding in character, while the $2a_1$ orbital is nonbonding or weakly antibonding, and the remaining ones are all antibonding. These theoretical results suggest that this type of cluster should achieve maximum stability when six electrons are available to enter cluster orbitals but should continue to be stable if there are seven or eight. This prediction is supported by the fact that until 1984 virtually all known M_3X_{13} species with M = Mo or W were six-electron species. There were also some electrochemical data[8,9] showing that the addition of two electrons (in one case, apparently three electrons) is possible, but only one eight-electron, M_3X_{13} compound, containing molybdenum, has been reported and structurally characterized. This first compound, reported in 1979 by Bino, Cotton, and Dori,[10] contained the cation $[Mo_3(\mu_3\text{-}O)(\mu\text{-}Cl)_3(\mu\text{-}OAc)_3(H_2O)_3]^{2+}$. Another such species, $[Mo_3(\mu_3\text{-}CCH_3)(\mu\text{-}Br)_3(\mu\text{-}OAc)_3(H_2O)_3]^+$, was described from this laboratory in 1985.[11] A Chinese group has also reported a couple of closely related compounds with a cluster core $Mo_3(\mu_3\text{-}O)(\mu_2\text{-}X)_3$ (X = Cl, Br)[12,13b] and presented a survey of nine such compounds that have all been characterized structurally (Mo–Mo distances in the range 2.55–2.60 Å),[14] although except for those mentioned above the details have not been published.

No tungsten analogue to this type of molybdenum compound (Mo_3X_{13} with eight cluster electrons) has previously been mentioned in the literature. The monocapped tungsten cluster cation,[5] $[W_3(\mu_3\text{-}O)(OAc)_6(H_2O)_3]^{2+}$ is somewhat different and is best regarded as a modified form of the bicapped $M_3(\mu_3\text{-}X)_2(O_2CR)_6L_3$ structure, where one capping atom is absent.

We report here the detailed preparative procedures for compounds containing the homologous $[M_3(\mu_3\text{-}O)(\mu\text{-}Cl)_3(\mu\text{-}OAc)_3Cl_3]^-$ ions with M = Mo and W. The latter is the first such tritungsten cluster to be reported.

Experimental Section

All manipulations were carried out under an atmosphere of dry oxygen-free argon by using Schlenk techniques, unless otherwise noted. Solvents were dried and deoxygenated by refluxing over appropriate reagents before use. Anhydrous hydrogen chloride and a 1 M solution of hydrochloric acid in acetic acid were purchased from Aldrich Co. Acetic acid was purchased from J. T. Baker Inc. Acetic anhydride and $Na_2WO_4{\cdot}2H_2O$ were purchased from Mallinckrodt Co.

Starting Materials. $MoCl_3{\cdot}3H_2O$ was prepared according to a previously reported[15] procedure. The $(Et_4N)_3W_2Cl_9$ stock solution was prepared by electrolysis of $Na_2WO_4{\cdot}2H_2O$[16] with a minor modification: Na_2WO_4 (25 g) was dissolved in water (200 mL), and then the solution was slowly added into an electrolytic cell which contained concentrated hydrochloric acid (300 mL) at 0 °C with rapid stirring. A slow flow of anhydrous hydrogen chloride gas was introduced during electrolysis (lead foil cathode, graphite plate anode, current density 3 A/dm^2). The electrolysis was carried out until a brown-green mixture was formed. Then 3 molar equiv of Et_4NCl were added. The mixture was filtered, and the filtrate was stored in a sealed three-necked flask.

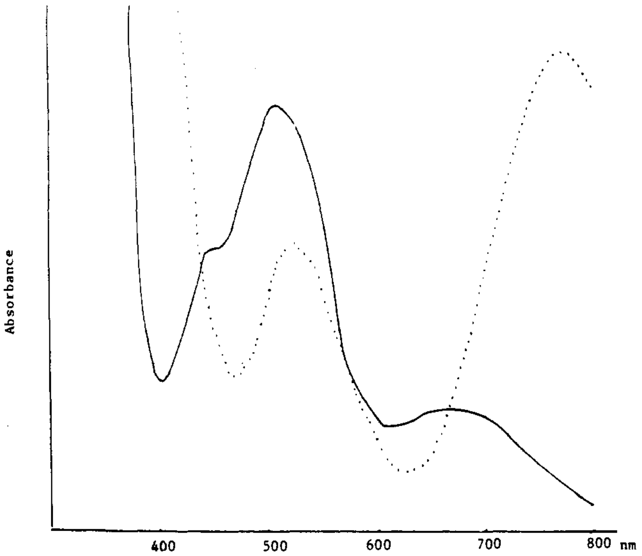

Figure 1. The electronic spectra of compound **1** and **2** (dashed line).

Preparation of $(Me_4N)[Mo_3(\mu_3\text{-}O)(\mu\text{-}Cl)_3(\mu\text{-}OAc)_3Cl_3]{\cdot}2HOAc$ (1). $MoCl_3{\cdot}3H_2O$ (0.50 g, 2.0 mmol) was placed in a flask and allowed to react with 15 mL of a mixture of acetic acid and acetic anhydride (4:1) at 80 °C for 1 day. Then tetramethylammonium chloride (0.078 g, 0.67 mmol) was added. The mixture was stirred for 10 more minutes at 80 °C and filtered through a layer of Celite. After the solution was cooled to room temperature, dark brown crystals were formed, which appeared green under a polarizing microscope. Solid samples are stable in air for several days: yield 0.20 g (45%).

Preparation of $(Et_4N)[W_3(\mu_3\text{-}O)(\mu\text{-}Cl)_3(\mu\text{-}OAc)_3Cl_3]{\cdot}Me_2CO$ (2). Twenty-five milliliters of the stock solution which contains 2.12 mmol of $(Et_4N)_3W_2Cl_9$ was loaded into a three-necked flask and evaporated to dryness. The solid was then allowed to react with 25 mL of a solvent mixture of acetic anhydride and a 1 M hydrochloric acid solution of acetic acid (1:3) at 80 °C for 1 day. A red-brown precipitate was formed. After filtration, the precipitate was redissolved in acetone, layered with hexane, and kept at 0 °C. Red crystals grew slowly over a period of several days: yield ca. 0.40 g (24%).

^{1}H NMR Spectroscopy. The proton NMR spectra of both **1** and **2** in acetone-d_6 were measured on a Varian XL-200 NMR spectrometer. In **1** four sets of peaks are at 3.44 ppm (t, 12 H, Me_4N^+, $^2J_{H-N}$ = 0.52 Hz), 2.83 ppm (s, 2 H, CH_3COOH), 2.39 ppm (s, 9 H, CH_3COO^-), and 1.92 ppm (s, 6 H, CH_3COOH). Also, in **2** four sets of peaks are at 3.50 ppm (q, 8 H, $(CH_3CH_2)_4N^+$, $^3J_{H-H}$ = 7.3 Hz), 2.46 (s, 9 H, CH_3COO^-), 2.08 ppm (s 6 H, $(CH_3)_2CO$), and 1.39 (tt, 12 H, $(CH_3CH_2)_4N^+$, $^3J_{H-H}$ = 7.3 Hz, $^3J_{H-N}$ = 1.9 Hz).

Electronic Spectroscopy. The electronic spectra of **1** and **2** were obtained on a Cary-17 spectrophotometer. They are shown in Figure 1. The principal features (nm) are **1** 495, 640, and 450 (sh); **2** 526 and 760. While the spectra of the two complexes have not been assigned, they can be used to identify them.

IR Spectroscopy. The IR spectra of **1** and **2** were recorded on a Perkin-Elmer 783 spectrophotometer. The observed absorption peaks of **1** (Nujol mull, KBr plates) were at 563 (w), 595 (w), 620 (m), 630 (m), 682 (s), 738 (m), 800 (m), 948 (s), 1025 (m), 1295 (s), 1450 (s), 1705 (s), 1745 (w), 1778 (w), 1635 (w), and 3400 (w) cm^{-1}. Under similar conditions of measurement **2** showed the following absorptions: 295 (m), 312 (m), 348 (s), 535 (m), 575 (m), 598 (w), 620 (m), 687 (s), 731 (m), 785 (m), 1000 (m), 1030 (w), 1050 (m), 1094 (w), 1170 (m), 1220 (m), 1350 (w), and 1695 (s) cm^{-1}.

Electrochemical Measurements. The cyclic voltammogram was recorded on a BAS-100 Electronic Analyzer in the range −1.8 to 1.8 V for **1** and −1.5 to 1.5 V for **2** with sweep rates 20–200 mV/s. Platinum electrodes were used as the auxiliary electrode and working electrode, and

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Table I. Crystallographic Data for Compound **1** and Compound **2**

	1	**2**
formula	$Mo_3Cl_6O_9NC_{14}H_{29}$	$W_3Cl_6O_8NC_{17}H_{35}$
formula weight	887.93	1184.76
space group	*Pnma*	$P2_1/c$
a, Å	7.684 (2)	13.996 (2)
b, Å	13.856 (3)	15.999 (4)
c, Å	28.495 (4)	14.031 (3)
β, deg		98.09 (1)
V, Å^3	3033 (2)	3111 (2)
Z	4	4
d_{calc}, g/cm^3	1.944	2.530
radiation (monochromated in incident beam)	Mo Kα (λ_α = 0.71073 Å)	
temp, °C	−58	20
R	0.034	0.033
R_w	0.041	0.047

Table II. Positional and Equivalent Isotropic Thermal Parameters for $(Me_4N)[Mo_3OCl_6(OAc)_3]\cdot 2HOAc$[a]

atom	x	y	z	B (Å^2)
Mo(1)	0.1787 (1)	0.250	0.04477 (3)	3.10 (2)
Mo(2)	0.29031 (8)	0.15742 (6)	0.11697 (2)	3.42 (1)
O(1)	0.0961 (8)	0.250	0.1102 (2)	3.2 (2)
Cl(1)	0.4014 (3)	0.3731 (2)	0.03902 (6)	4.13 (5)
Cl(2)	0.5519 (4)	0.250	0.1305 (1)	4.47 (7)
Cl(3)	0.1678 (4)	0.250	−0.03992 (9)	4.07 (7)
Cl(4)	0.4468 (3)	0.0194 (2)	0.14539 (7)	5.13 (5)
O(2)	−0.0083 (6)	0.1429 (4)	0.0403 (2)	3.5 (1)
O(3)	0.0895 (6)	0.0628 (4)	0.1031 (2)	3.6 (1)
C(1)	−0.0211 (9)	0.0758 (6)	0.0704 (3)	3.5 (2)
C(2)	−0.166 (1)	0.0072 (7)	0.0666 (3)	5.0 (2)
O(4)	0.2140 (7)	0.1698 (4)	0.1859 (2)	4.2 (1)
C(3)	0.184 (2)	0.250	0.2062 (4)	4.4 (3)
C(4)	0.109 (2)	0.250	0.2542 (4)	6.5 (4)
N(1)	0.311 (1)	0.750	0.0969 (3)	4.1 (2)
C(5)	0.478 (2)	0.750	0.1257 (5)	6.4 (4)
C(6)	0.169 (2)	0.750	0.1290 (5)	14.0 (9)
C(7)	0.307 (2)	0.8326 (9)	0.0649 (5)	11.4 (4)
O(5)	0.303 (2)	0.6546 (6)	0.2443 (3)	15.8 (4)
O(6)	0.3343 (9)	0.6546 (5)	0.3194 (2)	7.5 (2)
C(8)	0.354 (1)	0.5056 (9)	0.2806 (4)	8.0 (3)
C(9)	0.330 (2)	0.6124 (9)	0.2809 (3)	7.7 (3)

[a] Anisotropically refined atoms are given in the form of the equivalent isotropic displacement parameter defined as $(^4/_3)[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos\gamma)\beta_{12} + ac(\cos\beta)\beta_{13} + bc(\cos\alpha)\beta_{23}]$.

Table III. Positional and Equivalent Isotropic Thermal Parameters for $(Et_4N)[W_2OCl_6(OAc)_3]\cdot Me_2CO$[a]

atom	x	y	z	B (Å^2)
W(1)	0.23937 (3)	0.05228 (3)	0.25932 (3)	2.577 (8)
W(2)	0.39687 (3)	0.13601 (3)	0.27011 (3)	2.579 (8)
W(3)	0.24281 (3)	0.19129 (3)	0.16858 (3)	2.665 (9)
Cl(1)	0.3891 (2)	−0.0105 (2)	0.2237 (2)	3.73 (6)
Cl(2)	0.1845 (2)	0.0634 (2)	0.0874 (2)	3.62 (6)
Cl(3)	0.3920 (2)	0.1729 (2)	0.1007 (2)	4.00 (6)
Cl(4)	0.1720 (2)	−0.0882 (2)	0.2484 (2)	4.11 (6)
Cl(5)	0.5703 (2)	0.1262 (2)	0.2779 (2)	4.02 (6)
Cl(6)	0.1813 (2)	0.2643 (2)	0.0236 (2)	4.58 (7)
O(1)	0.2700 (4)	0.1668 (5)	0.3096 (4)	2.7 (1)
O(2)	0.2798 (5)	0.0274 (5)	0.4036 (4)	3.2 (2)
O(3)	0.4173 (4)	0.1012 (5)	0.4133 (4)	2.8 (1)
O(4)	0.1061 (5)	0.0922 (5)	0.2899 (5)	3.3 (2)
O(5)	0.1104 (5)	0.2129 (5)	0.2128 (5)	3.2 (2)
O(6)	0.4223 (5)	0.2582 (4)	0.3107 (5)	3.1 (2)
O(7)	0.2874 (5)	0.3076 (4)	0.2221 (5)	3.2 (2)
C(1)	0.3537 (8)	0.0617 (7)	0.4524 (7)	3.2 (2)
C(2)	0.3671 (9)	0.0523 (8)	0.5619 (7)	4.0 (3)
C(3)	0.0738 (7)	0.1627 (7)	0.2712 (7)	2.9 (2)
C(4)	−0.0089 (8)	0.1948 (8)	0.3173 (8)	3.8 (3)
C(5)	0.3611 (8)	0.3165 (7)	0.2875 (8)	3.5 (2)
C(6)	0.377 (1)	0.4006 (8)	0.333 (1)	5.0 (3)
N	0.2580 (6)	0.7199 (6)	0.4776 (6)	3.3 (2)
C(7)	0.1667 (9)	0.6863 (9)	0.4177 (9)	5.0 (3)
C(8)	0.094 (1)	0.646 (1)	0.479 (1)	6.4 (4)
C(9)	0.3161 (9)	0.6496 (8)	0.5322 (8)	4.3 (3)
C(10)	0.351 (1)	0.5820 (9)	0.4676 (9)	5.3 (3)
C(11)	0.3137 (9)	0.7617 (8)	0.4031 (8)	4.6 (3)
C(12)	0.408 (1)	0.803 (1)	0.451 (1)	7.5 (4)
C(13)	0.2354 (9)	0.7806 (8)	0.5540 (8)	4.2 (3)
C(14)	0.177 (1)	0.8550 (9)	0.517 (1)	6.4 (4)
O(8)	0.1658 (8)	0.5329 (7)	0.2440 (8)	7.6 (3)
C(15)	0.1151 (8)	0.4704 (9)	0.238 (1)	4.8 (3)
C(16)	0.099 (1)	0.419 (1)	0.324 (1)	6.7 (4)
C(17)	0.065 (1)	0.441 (1)	0.145 (1)	6.4 (4)

[a] Anisotropically refined atoms are given in the form of the equivalent isotropic displacement parameter defined as $(^4/_3)[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos\gamma)\beta_{12} + ac(\cos\beta)\beta_{13} + bc(\cos\alpha)\beta_{23}]$.

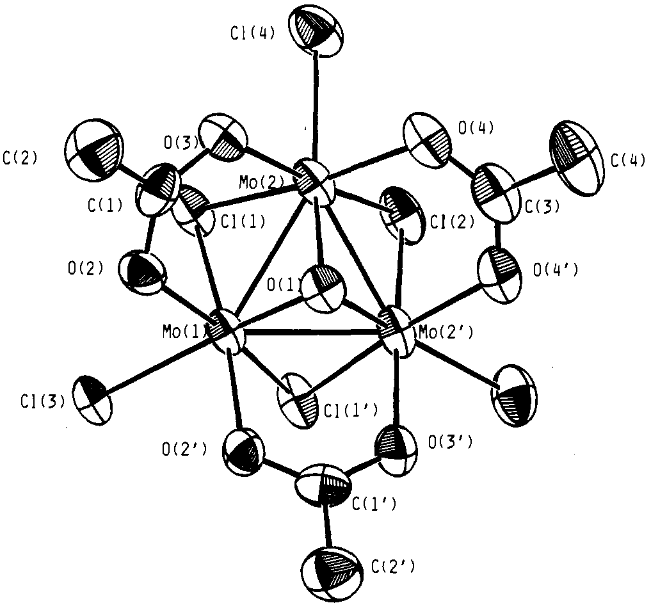

Figure 2. ORTEP drawing of anion of **1**. The thermal ellipsoids are at 50% probability.

a Ag/AgCl electrode was used as the reference electrode. The solution 0.2 M tetrabutylammonium tetrafluoroborate and 10^{-3} M of the trimer in acetonitrile was degassed with a nitrogen flow for at least 5 min prior to making measurements.

X-ray Crystallography. The procedural details and basic crystallographic characteristics have been fully described elsewhere.[17] Because the complexes are air stable, no special precautions were taken when mounting the crystals. The crystals typically were mounted on the top of thin glass fibers with the use of epoxy cement.

The diffraction data for **1** were collected on an Enraf-Nonius CAD-4 diffractometer in a cold stream of nitrogen at −58 ± 1 °C by using graphite-monochromated Mo Kα (λ_α = 0.71073 Å) radiation. Data reduction was carried out by standard methods with the use of well-established computational procedures.[18] The coordinates of the two crystallographically independent molybdenum atoms in **1** were obtained by the Patterson method (SHELX-86) in the space group *Pnma* which was later fully confirmed (as against $Pna2_1$, which is also consistent with the observed systematic absences) by the successful location of other atoms and refinement of the structure. After all non-hydrogen atoms were refined anisotropically to an R value of 0.042, a difference Fourier synthesis revealed all the hydrogen atoms, which were then assigned thermal parameters 1.3 times the equivalent isotropic thermal parameters of their corresponding bonded atoms. In the final refinement these hydrogen atoms were included in the calculation of the structure factors but not refined. Basic information pertaining to the crystal parameters and structure refinement is summarized in Tables I and II.

The diffraction data of **2** were again collected on the Enraf-Nonius CAD-4 diffractometer but at 20 °C. The space group was uniquely assigned as $P2_1/c$ according to the systematic absences. The coordinates of the three crystallographically independent tungsten atoms were obtained by the Patterson method (SHELX-86). Difference Fourier maps based on the refined positions of the tungsten atoms revealed the positions

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[18] Crystallographic computing was done on a local area VAX cluster, employing the VAX/VMS V4.6 computer and Enraf-Nonius SDP software.

Table IV. Selected Interatomic Distances (Å) and Angles in (deg) for $(Me_4N)[Mo_3OCl_6(OAc)_3]\cdot 2HOAc$

atom1	atom2	distance	atom1	atom2	distance	atom1	atom2	distance
Mo(1)	Mo(2)	2.572 (1)	Mo(2)	O(1)	1.977 (5)	O(5)	H(O5)	1.413
Mo(1)	O(1)	1.970 (7)	Mo(2)	Cl(1)	2.417 (2)	O(5)	C(9)	1.21 (1)
Mo(1)	Cl(1)	2.422 (2)	Mo(2)	Cl(2)	2.416 (2)	O(6)	C(9)	1.24 (1)
Mo(1)	Cl(3)	2.415 (3)	Mo(2)	Cl(4)	2.400 (3)	O(6)	H(O6)	1.322
Mo(1)	O(2)	2.069 (5)	Mo(2)	O(3)	2.063 (5)	O(5)	O(5′)	2.64 (1)
Mo(2)	Mo(2′)	2.566 (1)	Mo(2)	O(4)	2.058 (5)	O(6)	O(6′)	2.64 (1)

atom1	atom2	atom3	angle	atom1	atom2	atom3	angle	atom1	atom2	atom3	angle
Mo(2)	Mo(1)	Mo(2′)	59.84 (3)	O(1)	Mo(2)	Cl(1)	106.9 (2)	Cl(2)	Mo(2)	O(4)	92.3 (2)
O(1)	Mo(1)	Cl(1)	107.0 (1)	O(1)	Mo(2)	Cl(2)	107.4 (1)	Cl(4)	Mo(2)	O(3)	86.2 (2)
O(1)	Mo(1)	Cl(3)	159.2 (2)	O(1)	Mo(2)	Cl(4)	158.1 (2)	Cl(4)	Mo(2)	O(4)	83.5 (2)
O(1)	Mo(1)	O(2)	80.5 (2)	O(1)	Mo(2)	O(3)	80.2 (2)	O(3)	Mo(2)	O(4)	91.3 (2)
Cl(1)	Mo(1)	Cl(1′)	89.56 (8)	O(1)	Mo(2)	O(4)	79.8 (2)	Mo(1)	O(1)	Mo(2)	81.3 (2)
Cl(1)	Mo(1)	Cl(3)	87.53 (7)	Cl(1)	Mo(2)	Cl(2)	86.91 (8)	Mo(2)	O(1)	Mo(2′)	80.9 (2)
Cl(1)	Mo(1)	O(2′)	172.5 (1)	Cl(1)	Mo(2)	Cl(4)	89.62 (8)	Mo(1)	Cl(1)	Mo(2)	64.21 (6)
Cl(1)	Mo(1)	O(2)	88.9 (1)	Cl(1)	Mo(2)	O(3)	88.6 (1)	Mo(2)	Cl(2)	Mo(2′)	64.15 (7)
Cl(3)	Mo(1)	O(2)	85.1 (1)	Cl(1)	Mo(2)	O(4)	173.1 (2)	O(5)	C(9)	O(6)	122. (1)
O(2)	Mo(1)	O(2′)	91.6 (2)	Cl(2)	Mo(2)	Cl(4)	87.27 (7)	O(5)	H(O5)	O(5′)	138.5 (8)
Mo(1)	Mo(2)	Mo(2′)	60.08 (2)	Cl(2)	Mo(2)	O(3)	172.1 (1)	O(6)	H(O6)	O(6′)	175.6 (4)

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

Table V. Metal–Metal Bond Distances of Eight-Electron Trinuclear Complexes for Which Complete Structure Reports are Published

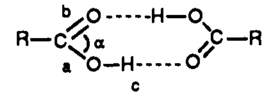
complexes	distances	ref
$[Mo_3OCl_3(OAc)_3(H_2O)_3]^{2+}$	2.550 (2)	10
$[Mo_3OCl_8(OAc)_2]^{2-}$	2.599 (14)	12
$[Mo_3OBr_3(OAc)_3Cl_3]^-$	2.594 (6)	13a
$[Mo_3(CCH_3)Br_3(OAc)_3(H_2O)_3]^+$	2.594 (1)	11

of the remaining non-hydrogen atoms. These atoms were refined anisotropically in the final least-squares refinement. More information concerning the crystal parameters and structure refinement of **2** is summarized in Tables I and III.

Results and Discussion

The crystal structure of **1** consists of four formula units of $[Me_4N][Mo_3(\mu_3\text{-}O)(\mu\text{-}Cl)_3(\mu\text{-}OAc)_3Cl_3]\cdot 2HOAc$ per unit cell. An ORTEP diagram, Figure 2, shows the structure of the molybdenum trinuclear anion, in which the three molybdenum atoms form a triangle. The anion resides on a crystallographic plane of symmetry that contains Mo(1) and the capping oxygen atom and bisects the Mo(2)–Mo(2′) bond. One capping oxygen atom and three bridging acetate groups are above the plane of the triangle and three chlorine atoms below it. Each Mo atom has a pseudooctahedral coordination environment. The average oxidation state for molybdenum atoms is 3.33. Table IV lists selected bond distances and bond angles of the trimer. The bond distances between molybdenum atoms are 2.572, 2.572, and 2.566 Å, with a mean value of 2.570 [2] Å. The structure of **1** closely resembles that of the trimer cation of $[Mo_3OCl_3(OAc)_3(H_2O)_3]ClO_4Cl$[10] except for the three terminal ligands and is essentially the same as that of the anion in $[C_5H_7S_2][Mo_3OCl_6(OAc)_3]$[13] as indicated in Table V. The acetic acid dimer formed in compound **1** is noteworthy because, although many other carboxylic acids[19] form such dimers in their crystalline forms, crystalline acetic acid does not. Instead, it forms infinite, hydrogen-bonded chains, which have been very thoroughly characterized by X-ray[20a] and neutron[20b] crystallography. The acetic acid dimer in compound **1** has dimensions very similar to those in the other dimers, as shown in Table VI.

Table VI. Some Important Dimensions in Carboxylic Acid Dimers



acid	*a*, Å	*b*, Å	*c*, Å	α, deg
acetic (this work)	1.24 (1)	1.21 (1)	2.64 (1)	122 (1)
propionic	1.31 (1)	1.23 (1)	2.64 (1)	122 (1)
butyric	1.32 (2)	1.20 (2)	2.62 (2)	123 (1)
valeric	1.35 (2)	1.26 (2)	2.63 (2)	118 (1)
(−)-malic	1.31 (1)	1.22 (1)	2.62 (1)	123.3 (3)
α-*trans*-cinnamic	1.29 (1)	1.25 (1)	2.634 (2)	123.1 (1)
(4-chlorophenyl)acetic	1.289 (2)	1.218 (1)	2.554 (1)	122.8 (1)
(3,4-dimethoxyphenyl)-propiolic	1.31 (1)	1.22 (1)	2.67 (1)	

The crystal structure of **2** has four formula units of $(Et_4N)[W_3(\mu_3\text{-}O)(\mu\text{-}Cl)_3(\mu\text{-}OAc)_3Cl_3]\cdot Me_2CO$. There is no crystallographic symmetry imposed on this complex. The structure of the tungsten trinuclear anion is shown in Figure 3, and selected bond distances and bond angles are listed in Table VII. The anion of this complex is homologous to that in **1** with substitution of molybdenum by tungsten. Three tungsten atoms form an essentially equilateral triangle with metal–metal bonding distances 2.566, 2.566, and 2.568 Å and a mean value of 2.567 [1] Å. Each W atom is coordinated by six ligands with a distorted octahedral

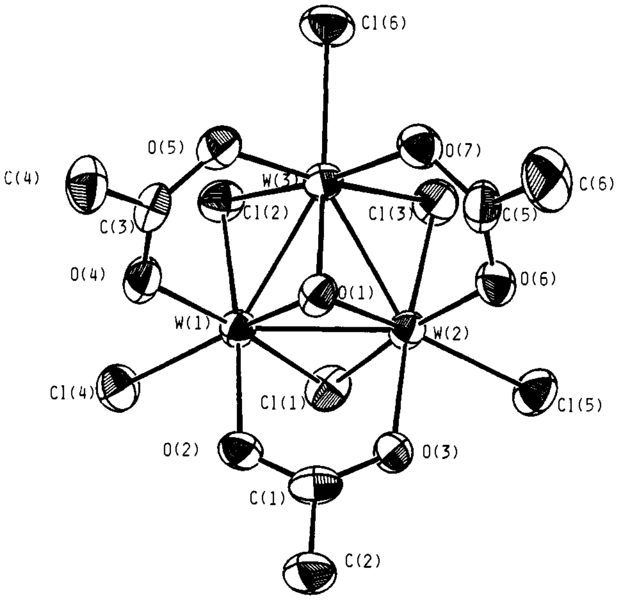


Figure 3. ORTEP drawing of anion of **2**. The thermal ellipsoids are at 50% probability.

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Table VII. Selected Bond Distances (Å) and Bond Angles (deg) for $(Et_4N)[W_3OCl_6(OAc)_3]\cdot Me_2CO$[a]

atom1	atom2	distance	atom1	atom2	distance	atom1	atom2	distance
W(1)	W(2)	2.566 (1)	W(1)	O(4)	2.072 (7)	W(2)	O(6)	2.054 (7)
W(1)	W(3)	2.566 (1)	W(2)	W(3)	2.568 (1)	W(3)	Cl(2)	2.427 (3)
W(1)	Cl(1)	2.438 (3)	W(2)	Cl(1)	2.432 (3)	W(3)	Cl(3)	2.431 (3)
W(1)	Cl(2)	2.432 (2)	W(2)	Cl(3)	2.440 (3)	W(3)	Cl(6)	2.398 (3)
W(1)	Cl(4)	2.433 (3)	W(2)	Cl(5)	2.420 (3)	W(3)	O(1)	2.001 (6)
W(1)	O(1)	1.988 (7)	W(2)	O(1)	1.995 (6)	W(3)	O(5)	2.065 (7)
W(1)	O(2)	2.062 (6)	W(2)	O(3)	2.066 (6)	W(3)	O(7)	2.070 (7)

atom1	atom2	atom3	angle	atom1	atom2	atom3	angle	atom1	atom2	atom3	angle
W(2)	W(1)	W(3)	60.06 (2)	Cl(1)	W(2)	Cl(5)	87.5 (1)	Cl(2)	W(3)	O(5)	91.5 (2)
Cl(1)	W(1)	Cl(2)	89.27 (9)	Cl(1)	W(2)	O(1)	107.7 (2)	Cl(2)	W(3)	O(7)	173.1 (2)
Cl(1)	W(1)	Cl(4)	86.7 (1)	Cl(1)	W(2)	O(3)	89.8 (2)	Cl(3)	W(3)	Cl(6)	87.3 (1)
Cl(1)	W(1)	O(1)	107.7 (2)	Cl(1)	W(2)	O(6)	172.6 (2)	Cl(3)	W(3)	O(1)	108.0 (2)
Cl(1)	W(1)	O(2)	89.8 (2)	Cl(3)	W(2)	Cl(5)	87.16 (9)	Cl(3)	W(3)	O(5)	174.0 (2)
Cl(1)	W(1)	O(4)	173.6 (2)	Cl(3)	W(2)	O(1)	107.9 (2)	Cl(3)	W(3)	O(7)	91.1 (2)
Cl(2)	W(1)	Cl(4)	86.5 (1)	Cl(3)	W(2)	O(3)	173.5 (2)	Cl(6)	W(3)	O(1)	158.4 (2)
Cl(2)	W(1)	O(1)	107.9 (2)	Cl(3)	W(2)	O(6)	91.1 (2)	Cl(6)	W(3)	O(5)	86.7 (2)
Cl(2)	W(1)	O(2)	172.7 (2)	Cl(5)	W(2)	O(1)	158.4 (2)	Cl(6)	W(3)	O(7)	85.6 (2)
Cl(2)	W(1)	O(4)	90.9 (2)	Cl(5)	W(2)	O(3)	86.4 (2)	O(1)	W(3)	O(5)	77.8 (3)
Cl(4)	W(1)	O(1)	159.3 (2)	Cl(5)	W(2)	O(6)	85.2 (2)	O(1)	W(3)	O(7)	79.1 (3)
Cl(4)	W(1)	O(2)	86.2 (2)	O(1)	W(2)	O(3)	78.6 (3)	O(5)	W(3)	O(7)	88.7 (3)
Cl(4)	W(1)	O(4)	86.9 (2)	O(1)	W(2)	O(6)	79.3 (3)	W(1)	Cl(1)	W(2)	63.58 (7)
O(1)	W(1)	O(2)	79.3 (3)	O(3)	W(2)	O(6)	89.5 (3)	W(1)	Cl(2)	W(3)	63.76 (7)
O(1)	W(1)	O(4)	78.4 (3)	W(1)	W(3)	W(2)	59.96 (2)	W(1)	Cl(3)	W(3)	63.64 (7)
O(2)	W(1)	O(4)	89.2 (3)	Cl(2)	W(3)	Cl(3)	88.1 (1)	W(1)	O(1)	W(2)	80.2 (3)
W(1)	W(2)	W(3)	59.98 (2)	Cl(2)	W(3)	Cl(6)	87.5 (1)	W(1)	O(1)	W(3)	80.1 (2)
Cl(1)	W(2)	Cl(3)	88.7 (1)	Cl(2)	W(3)	O(1)	107.7 (2)	W(2)	O(1)	W(3)	80.0 (2)

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

coordination environment. The average oxidation state of tungsten atoms is 3.33. The cation and the interstitial solvent molecule in **2** are Et_4N^+ and acetone instead of Me_4N^+ and acetic acid as in **1**.

The IR spectra data of both complexes correspond quite well with the structures derived from the X-ray analysis. According to assignments by Lu and co-workers,[21] molybdenum trimers containing a capping oxygen atom with eight electrons generally display a medium absorption band at 740–690 cm^{-1}. In **1**, the absorption occurs near 738 cm^{-1}, as in its analogue $[C_5H_7S_2][MO_3OCl_6(OAc)_3]$. Strong absorptions at 3300, 1705, and 948 cm^{-1} may be assigned to the stretching, bending, and rocking modes associated with O–H bonds.[22] A strong absorption at 1285 cm^{-1} is a characteristic absorption peak of a C–O stretching vibration of carboxylic acid dimers and thus consistent with the presence of the acetic acid dimer. In **2**, no peaks appeared in the positions which are assigned to the dimeric acetic acid. Absorptions at 1695 and 1170 cm^{-1} are characteristic of C=O stretching and C–C–C coupled stretching and bending modes in the acetone molecule.[23]

The proton NMR data of **1** and **2** are listed in the Experimental Section where assignments were given. These are in full accord with the crystallographic results.

Cyclic voltammograms showed significant differences between **1** and **2**. In **1** only one quasi-reversible reduction potential at −0.13 V (the separation between oxidation and reduction wave is 0.16 V) was found, while **2** showed a reversible reduction wave at −0.90 V (the separation is 0.10 V) and a reversible oxidation wave at 1.1 V (separation is 0.10 V). The CV results imply that the molybdenum trimer with acetate ligands and eight d electrons might be reduced to a molybdenum trimer with nine d electrons but cannot easily be oxidized to one with seven or six d electrons, while the tungsten trimer might be either oxidized to a trimer with six or seven electrons or reduced to one with nine electrons. Compared with its molybdenum analogue, the tungsten trimer has more versatile redox behavior although the two anions are structurally very similar. Paffett and co-workers have investigated the electrochemical properties of $Mo_3O_4(H_2O)_9{}^{4+}$ and the oxalato derivative in acidic media.[7] They found that these $Mo_3O_4{}^{4+}$ trimers with six electrons could be reversibly reduced to two trimeric species in two separated steps, first giving a molybdenum trimer with eight d electrons ($Mo_2{}^{III}Mo^{IV}$) and then one with nine d electrons ($Mo_3{}^{III}$). Obviously, the CV behavior of **1** is different from that reported by Paffett. The exact reason for the difference is not quite clear, but, certainly, the change from Mo_3O_4 to Mo_3OCl_3 must be of importance.

In summary, the present work reveals several important but previously unrecognized characteristics of M_3X_{13} type cluster species. (1) The relative stabilities of different oxidation levels (that is, the number of cluster electrons) are strongly affected by the nonmetal atoms incorporated in the central M_3X_4 core. Replacement of three μ-O atoms by three μ-Cl appears to favor eight-electron over six-electron populations. (2) In spite of a close structural similarity between homologous molybdenum and tungsten species, the redox behavior can be markedly different. As a result of the observations reported here, we consider it worthwhile to explore theoretically the way in which the preferred number of cluster electrons may depend on (a) the types of nonmetal atoms closely associated with the cluster (e.g., O_4 compared to OCl_3) and (b) the metal atoms in the cluster (i.e., Mo vs W). We hope to report the results of such studies in the future.

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Supplementary Material Available: Tables of positional parameters, bond lengths, bond angles, and anisotropic displacement parameters and ORTEP drawings of unit cell contents for **1** and **2** (15 pages); tables of observed and calculated structure factors for **1** and **2** (26 pages). Ordering information is given on any current masthead page.

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