$Os_3(CO)_8(PPh_3)(\mu_3\text{-}S)_2$. Indeed, when the reaction is performed under a CO atmosphere, the yield of **2** is greatly increased. The tendency to form mixed-metal clusters in the reaction of **1** with $Pt(PPh_3)_2C_2H_4$ is to be contrasted with the reaction of $Os_3(CO)_{12}$ with $Pt(PR_3)_4$ compounds, which yields only the phosphine-substituted derivatives $Os_3(CO)_{12-x}(PR_3)_x$ ($x = 1, 2$).[29]

Although the reaction of iron chalcogenide analogues of **1**, $Fe_3(CO)_9(\mu_3\text{-}E)_2$ (E = S, Te), does yield mixed-metal clusters upon reaction with $Pt(PPh_3)_2C_2H_4$, in these cases the iron cluster undergoes fragmentation and yields the diiron complexes $Fe_2(CO)_6(\mu_3\text{-}E)_2Pt(PPh_3)_2$.[30]

Compounds **2** and **3** are both 64-electron clusters. Thus, for all the metal atoms to obey the effective atomic number rule the cluster should contain only four metal–metal bonds, as is observed. In contrast, however, the isoelectronic compounds $Os_4(CO)_{12}(\mu_3\text{-}S)_2$[27] and $Os_3W(CO)_{12}(PMe_2Ph)(\mu_3\text{-}S)_2$[18] both contain butterfly clusters of four metal atoms that have five metal–metal bonds. These compounds alternatively adhere to the bonding requirements of the polyhedral skeletal electron pair (PSEP) theory. Compounds **2** and **3** could adopt analogous structures that obey the PSEP theory simply by forming a bond between osmium Os(1) and the platinum atom but instead opt for the more open electron-precise structure that is observed.

Acknowledgment. This work was supported by the National Science Foundation. NMR studies were supported by Grant No. CHE-7916210 to the Northeast Regional NSF-NMR Facility form the National Science Foundation. We thank Engelhard Industries for a loan of osmium tetroxide.

Registry No. **1**, 72282-40-7; **2**, 92763-25-2; **3**, 93403-89-5; $Pt(PPh_3)_2C_2H_4$, 12120-15-9; $Os_3(CO)_8(PPh_3)(\mu_3\text{-}S)_2$, 93403-90-8; Os, 7440-04-2; Pt, 7440-06-4.

Supplementary Material Available: Tables of structure factor amplitudes and hydrogen atom parameters for both structure analyses (34 pages). Ordering information is given on any current masthead page.

---

[29] Bruce, M. I.; Shaw, G.; Stone, F. G. A. *Chem. Commun.* **1971**, 1288.

[30] Bogan, L. E., Jr.; Lesch, D. A.; Rauchfuss, T. B. *J. Organomet. Chem.* **1983**, *250*, 429.

Contribution from the Department of Chemistry and Laboratory for Molecular Structure and Bonding, Texas A&M University, College Station, Texas 77843, and Department of Chemistry, The Technion-Israel Institute of Technology, Haifa, Israel

Synthesis and Structure of New Trinuclear Cluster Compounds $[M_3(\mu_3\text{-}O)_2(O_2CC_3H_7)_6(H_2O)_3]^{2+}$ (M = Mo, W). Comparison of Mo and W Bond Radii as a Function of M–M Bond Order

F. ALBERT COTTON,*[1a] ZVI DORI,[1b] DAVID O. MARLER,[1a] and WILLI SCHWOTZER[1a]

Received January 25, 1984

The autoclave reaction at 160 °C of butyric acid with either $W(CO)_6$ or $Mo_2(O_2CMe)_4$ leads, after suitable workup, to compounds containing the trinuclear cluster cations $[M_3(\mu_3\text{-}O)_2(O_2CC_3H_7)_6(H_2O)_3]^{2+}$ (M = W, Mo). The compounds have been fully characterized by spectroscopic methods as well as by a crystal structure determination. $[W_3O_2(O_2CC_3H_7)_6(H_2O)_3](CF_3SO_3)_2\cdot 2H_2O$ (**1**) is monoclinic, with $C2/c$, $a = 24.434$ (4) Å, $b = 23.628$ (5) Å, $c = 20.790$ (4) Å, $\beta = 124.61$ (1)°, and $Z = 8$. Crystals of $[Mo_3O_2(O_2CC_3H_7)_6(H_2O)_3](ClO_4)_2\cdot 3H_2O$ (**2**) are cubic, with $P2_13$, $a = 16.272$ (3) Å, and $Z = 4$. Bond distances and angles in both compounds along with those determined on similar compounds establish that there is a consistent difference of 0.016 [3] Å between the W–W and Mo–Mo bond lengths, with the W–W bonds being the shorter ones. This bond radius relationship, $r(Mo)/r(W) > 1$, is probably general for long (ca. 2.70 Å) M–M bonds and for single M–X bonds, whereas for M–M triple and quadruple bonds the ratio is <1. The value of unity is apparently encountered in the range 2.70–2.50 Å.

Introduction

As part of our continuing investigation of triangular trinuclear cluster compounds of molybdenum and tungsten,[2] we are always interested in preparative methods that allow preparation of new compounds or the preparation of known compounds more efficiently. As a general proposition, the use of an autoclave (pressure bomb) to contain a mixture of a carboxylic acid and some lower valent compound of the metal seemed to have practical advantages. For example, if the metal carbonyl, $Mo(CO)_6$ or $W(CO)_6$, is to be used as a starting material, an open, refluxing system is very messy to operate since the volatile carbonyl must be mechanically (manually) returned to the pot at frequent intervals. While the problem is tractable with a lower boiling acid (e.g., acetic acid (118 °C) or propionic acid (141 °C)), it becomes very bothersome with higher boiling acids. Actually, the use of a sealed reaction container for reactions with $W(CO)_6$ was first described in 1971,[3] but the results were inconclusive because the proper workup procedures employing cation-exchange resins were not then in use. Indeed, a secondary goal in the present work was to show that a representative compound reported in ref 3, when suitably worked up, is a $[W_3O_2(O_2CR)_6L_3]^{2+}$ compound. We have also further tested the possibility of using $Mo_2(O_2CCH_3)_4$ rather than $Mo(CO)_6$ as a starting material[4] with only the carboxylic acid as the oxidizing agent to obtain the $[M_3O_2(O_2CR)_6(H_2O)_3]^{2+}$ ion. Finally, with the additional structural results available from this work, we have examined how the ratio of bond radii for molybdenum and tungsten varies with the lengths of the bonds.

---

[1] (a) Texas A&M University. (b) The Technion-Israel Institute of Technology.

[2] See, for example: Birnbaum, A.; Cotton, F. A.; Dori, Z.; Marler, D. O.; Reisner, G. M.; Schwotzer, W.; Shaia, M. *Inorg. Chem.* **1983**, *22*, 2723. See also references cited in Table VI.

[3] Cotton, F. A.; Jeremic, M. *Synth. Inorg. Met.-Org. Chem.* **1971**, *1*, 265.

[4] Ardon, M.; Bino, A.; Cotton, F. A.; Dori, Z.; Kaftory, M.; Reisner, G. *Inorg. Chem.* **1982**, *21*, 1912.

0020-1669/84/1323-4738$01.50/0

Table I. Crystallographic Parameters

formula	$[W_3(\mu_3\text{-}O)_2(O_2CC_3H_7)_6(H_2O)_3]$-$(CF_3SO_3)_2\cdot 2H_2O$	$[Mo_3(\mu_3\text{-}O)_2(O_2CC_3H_7)_6(H_2O)_3]$-$(ClO_4)_2\cdot 3H_2O$
fw	1494.36	1149.41
space group	$C2/c$	$P2_13$
syst abs	hkl ($h + k = 2n$), $h0l$ ($l = 2n$)	$h00$ ($h = 2n$)
a, Å	24.434 (4)	16.272 (3)
b, Å	23.628 (5)	16.272 (3)
c, Å	20.790 (4)	16.272 (3)
α, deg	90.0	90.0
β, deg	124.61 (1)	90.0
γ, deg	90.0	90.0
V, Å^3	9883 (2)	4308 (3)
Z	8	4
d_{calcd}, g/cm^3	2.009	1.772
cryst size, mm	0.2 × 0.2 × 0.2	0.3 × 0.3 × 0.4
μ, cm^{-1}	72.97	91.68
data colln instrum	Enraf-Nonius CAD-4	Syntex P$\bar{1}$
radiation (monochromated in incident beam)	Mo Kα	Cu Kα
no. of orientation reflcns, range (2θ)	25, $10° \leq 2\theta \leq 20°$	15, $40° \leq 2\theta \leq 55°$
temp, °C	23 ± 2	5 ± 2
scan method	θ–2θ	θ–2θ
data colln range (2θ), deg	$2° \leq 2\theta \leq 40°$	$6° \leq 2\theta \leq 115°$
no. of unique data total with $F_o^2 > 3\sigma(F_o^2)$	5948; 3298	1009; 940
no. of parameters refined	366	184
exptl transmissn factors: max, min	1.0, 0.672	1.0, 0.613
R^a	0.053	0.061
$R_w{}^b$	0.070	0.079
quality-of-fit indicator^c	1.773	1.873
largest shift/esd, final cycle	<0.5	<0.5
largest peak, e/Å^3	<1.0	<1.0

[a] $R = \Sigma \|F_o\| - |F_c\|/\Sigma |F_o|$. [b] $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w |F_o|^2]^{1/2}$; $w = 1/\sigma(|F_o|^2)$. [c] Quality of fit $= [\Sigma w(|F_o| - |F_c|)^2/(N_{\text{observns}} - N_{\text{parameters}})]^{1/2}$.

Table II. Positional Parameters and Their Estimated Standard Deviations for 1

atom	x	y	z	B,[a] Å^2	atom	x	y	z	B,[a] Å^2
W(1)	0.95087 (4)	0.30073 (5)	0.01987 (4)	4.64 (2)	O(32)	0.9140 (7)	0.380 (1)	0.1762 (9)	10.7 (7)
W(2)	0.97591 (4)	0.25155 (5)	−0.08028 (4)	4.45 (2)	O(33)	0.7393 (9)	0.3317 (8)	0.4502 (9)	8.9 (7)
W(3)	0.84937 (4)	0.25094 (5)	−0.11559 (4)	4.51 (2)	O(34)	0.8205 (8)	0.3289 (9)	0.145 (1)	9.9 (7)
S(1)	0.8655 (3)	0.3712 (3)	0.1892 (3)	5.8 (2)	O(51)	0.633 (1)	0.354 (1)	0.327 (1)	12 (1)
S(2)	0.6976 (3)	0.3701 (4)	0.3869 (4)	7.8 (3)	O(52)	0.730 (1)	0.394 (1)	0.352 (1)	12.3 (9)
F(1)	0.653	0.468	0.375	17.4 (9)*	O(60)	0.6700 (7)	0.2601 (9)	0.4919 (9)	8.1 (6)
F(2)	0.753	0.450	0.485	22 (1)*	O(61)	0.6917 (8)	0.1725 (8)	0.6783 (8)	8.0 (6)
F(3)	0.662	0.415	0.459	23 (1)*	C(1)	0.8974 (9)	0.142 (1)	−0.141 (1)	5.0 (7)
F(4)	0.267	0.073	0.657	18.0 (9)*	C(2)	0.895 (1)	0.083 (1)	−0.158 (1)	8.5 (8)*
F(5)	0.295	0.063	0.589	22 (1)*	C(11)	0.863 (1)	0.276 (1)	−0.248 (1)	5.0 (7)
O(1)	0.9141 (6)	0.3126 (7)	−0.0928 (6)	4.8 (4)	C(12)	0.833 (1)	0.295 (1)	−0.331 (1)	5.9 (6)*
O(2)	0.9351 (6)	0.2229 (7)	−0.0255 (7)	5.2 (4)	C(13)	0.873	0.339	−0.333	14 (1)*
O(3)	0.9526 (6)	0.1664 (7)	−0.1191 (7)	5.1 (4)	C(14)	0.891	0.387	−0.292	17 (2)*
O(4)	0.8513 (6)	0.1656 (7)	−0.1461 (7)	5.2 (4)	C(21)	1.071 (1)	0.227 (1)	0.088 (1)	5.7 (8)
O(15)	0.9851 (6)	0.3440 (8)	0.1251 (7)	5.9 (5)	C(22)	1.129 (1)	0.192 (1)	0.159 (1)	7.3 (7)*
O(16)	1.0589 (6)	0.2193 (7)	0.0209 (7)	5.7 (4)	C(23)	1.150 (2)	0.144 (3)	0.131 (3)	19 (2)*
O(17)	0.9046 (6)	0.2616 (7)	0.0668 (6)	5.4 (4)	C(31)	0.856 (1)	0.229 (1)	0.029 (1)	5.5 (7)
O(21)	1.0382 (6)	0.2585 (7)	0.1046 (7)	5.9 (5)	C(32)	0.828 (1)	0.201 (1)	0.073 (1)	7.4 (7)*
O(22)	1.0416 (6)	0.2315 (7)	−0.1086 (7)	5.2 (4)	C(33)	0.879	0.178	0.144	15 (1)*
O(23)	0.9260 (6)	0.2712 (7)	−0.1991 (7)	5.4 (4)	C(34)	0.910	0.124	0.126	20 (2)*
O(24)	0.8232 (6)	0.2697 (7)	−0.2278 (6)	5.2 (4)	C(41)	0.822 (1)	0.366 (1)	−0.077 (1)	5.7 (7)
O(25)	1.0332 (6)	0.3231 (7)	−0.0557 (7)	5.2 (4)	C(42)	0.784 (1)	0.416 (1)	−0.090 (1)	7.0 (7)*
O(26)	0.8799 (7)	0.3647 (7)	−0.0137 (7)	6.1 (5)	C(43)	0.751	0.429	−0.163	27 (3)*
O(27)	1.0139 (6)	0.3633 (7)	0.0256 (6)	5.4 (4)	C(44)	0.803	0.460	−0.179	19 (2)*
O(28)	0.7986 (6)	0.3230 (7)	−0.1209 (7)	5.9 (5)	C(51)	1.0389 (9)	0.365 (1)	−0.013 (1)	5.6 (7)
O(29)	0.7476 (6)	0.2281 (8)	−0.1912 (7)	5.9 (5)	C(52)	1.075 (1)	0.418 (1)	−0.013 (2)	9.0 (9)*
O(30)	0.8239 (6)	0.2207 (7)	−0.0418 (7)	5.7 (4)	C(60)	0.697	0.453	0.443	19 (2)*
O(31)	0.8859 (8)	0.3710 (9)	0.2685 (8)	8.0 (6)	C(61)	0.336	0.027	0.676	7.6 (7)*

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

Experimental Section

Preparations. $[W_3(\mu_3\text{-}O)_2(O_2CC_3H_7)_6(H_2O)_3](CF_3SO_3)_2\cdot 2H_2O$ (1). A mixture of $W(CO)_6$ (2.0 g), butyric acid (30 mL), and butyric anhydride (3 mL) was placed in a Parr general purpose autoclave, Model 4751. The reaction mixture was heated at 160 °C for 48 h, cooled, and diluted with 200 mL of 95% ethanol. After the unreacted $W(CO)_6$ had been filtered off, the solution was chromatographed on a Dowex 50W-X2 cation-exchange column that had been prepared with ethanol. The adsorbed yellow band was eluted with a 2 M ethanolic solution of CF_3SO_3H. Yellow crystals were obtained by slow evaporation of the eluate; yield ca. 40%.

$[Mo_3(\mu_3\text{-}O)_2(O_2CC_3H_7)_6(H_2O)_3](ClO_4)_2\cdot 3H_2O$ (2). A mixture of 30 mL of butyric acid, 3 mL of butyric anhydride, and 2 g of $Mo_2(O_2CCH_3)_4$ was heated in an autoclave for 36 h at 160 °C. After dilution with ethanol and chromatographic workup following the procedure described above for the tungsten compound, well-formed

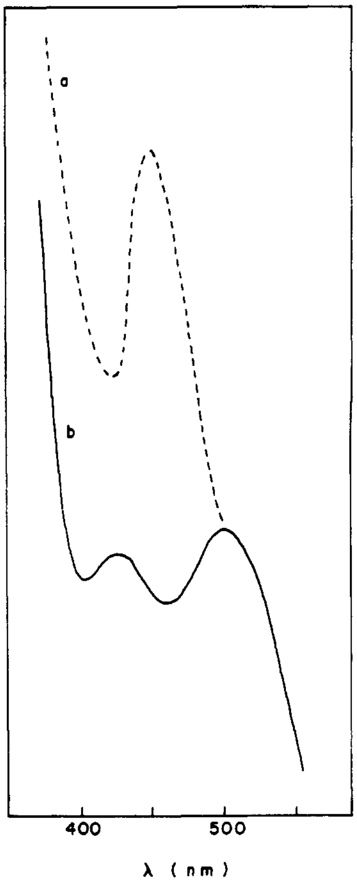

Figure 1. Visible absorption spectra of the $[W_3O_2(O_2CC_3H_7)_6(H_2O)_3]^{2+}$ (a) and $[Mo_3O_2(O_2CC_3H_7)_6(H_2O)_3]^{2+}$ (b) ions. For numerical data (λ, $\bar{\nu}$, ε) see the Experimental Section.

Table III. Positional Parameters and Their Estimated Standard Deviations for **2**

atom	x	y	z	B,[a] Å^2
Mo	0.67838 (8)	0.11267 (8)	0.24876 (9)	1.98 (3)
O(1)	0.8640 (7)	0.8640 (7)	0.8640 (7)	3.4 (3)
O(2)	0.7771 (9)	0.7771 (9)	0.7771 (9)	2.9 (2)
O(3)	0.7127 (9)	0.6995 (8)	0.9006 (9)	3.4 (3)
O(4)	0.3417 (8)	0.3274 (9)	0.5209 (8)	3.3 (3)
O(5)	0.6794 (9)	0.3595 (7)	0.3440 (8)	2.8 (3)
O(6)	0.2626 (9)	0.4441 (7)	0.5778 (8)	2.9 (3)
C(11)	0.753 (1)	0.639 (1)	0.874 (1)	3.7 (5)
C(21)	0.378 (1)	0.736 (1)	−0.008 (1)	2.7 (4)
C(22)	0.249 (1)	0.409 (1)	0.090 (1)	3.5 (4)
O(7)	0.2993 (8)	0.5020 (8)	0.1899 (8)	3.1 (3)
C(12)	0.614 (2)	0.288 (1)	0.054 (1)	3.9 (5)
C(24)	0.688 (2)	0.377 (2)	0.616 (2)	5.7 (7)
C(23)	0.659 (2)	0.294 (2)	0.643 (1)	4.6 (6)
C(13)	0.677 (2)	0.527 (2)	0.803 (2)	5.8 (7)
C(14)	0.582 (2)	0.770 (2)	0.609 (2)	6.6 (8)
Cl(1)	0.4998 (3)	0.4998 (3)	0.4998 (3)	3.2 (1)
Cl(2)	−0.0073 (4)	−0.0073 (4)	−0.0073 (4)	3.6 (1)
O(20)	0.410 (1)	0.482 (2)	−0.004 (1)	8.4 (7)
O(21)	0.044 (1)	0.044 (1)	0.044 (1)	5.1 (3)
O(23)	0.554 (2)	0.468 (1)	0.436 (1)	8.7 (7)
O(31)	0.436 (1)	0.388 (1)	0.205 (1)	4.4 (4)
O(22)	0.552 (1)	0.552 (1)	0.552 (1)	8.2 (5)

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

red crystals of the perchlorate salt were obtained by slow evaporation; yield ca. 80%.

NMR Spectroscopy. ^{1}H NMR spectra were measured on a Varian XL-200 PFT spectrometer at ambient temperature and are presented in Table V.

Table IV. Selected Bond Distances and Angles[a]

A. $[W_3(\mu_3\text{-}O)_2(O_2CC_3H_7)_6(H_2O)_3](CF_3SO_3)_2\cdot 2H_2O$

Distances, Å

W(1)-W(2)	2.741 (1)	W(2)-O(3)	2.12 (1)
-W(3)	2.744 (1)	-O(16)	2.07 (1)
-O(1)	1.995 (9)	-O(22)	2.06 (1)
-O(2)	2.002 (13)	-O(23)	2.10 (1)
-O(15)	2.11 (1)	-O(25)	2.07 (1)
-O(17)	2.08 (1)	W(3)-O(1)	2.00 (1)
-O(21)	2.09 (1)	-O(2)	1.97 (1)
-O(26)	2.10 (1)	-O(4)	2.12 (1)
-O(27)	2.09 (1)	-O(24)	2.09 (1)
W(2)-W(3)	2.742 (1)	W(3)-O(28)	2.07 (1)
-O(1)	2.00 (1)	-O(29)	2.12 (1)
-O(2)	2.01 (1)	-O(30)	2.08 (1)

Angles, deg

W(1)-W(2)-W(3)	60.05 (3)	W(2)-O(1)-W(3)	86.7 (4)
-O(1)-W(2)	86.7 (3)	W(1)-O(2)-W(2)	86.1 (3)
-W(3)	86.8 (3)	-W(3)	87.4 (3)
		W(2)-O(2)-W(3)	87.1 (3)

B. $[Mo_3(\mu_3\text{-}O)_2(O_2CC_3H_7)_6(H_2O)_3](ClO_4)_2\cdot 3H_2O$

Distances, Å

Mo(1)-Mo(1′)	2.762 (2)	Mo(1)-O(4)	2.10 (1)
-O(1)	2.032 (2)	-O(5)	2.102 (9)
-O(2)	1.980 (4)	-O(6)	2.078 (9)
-O(3)	2.08 (1)	-O(7)	2.10 (1)

Angles, deg

Mo(1)-Mo(1′)-Mo(1′)	60.00 (0)	Mo(1)-O(2)-Mo(1′)	88.39 (6)
-O(1)-Mo(1)	85.57 (6)		

[a] A complete list of bond distances and angles is available as supplementary material.

Table V. ^{1}H Chemical Shifts[a] and Coupling Constants for the $[M_3(\mu_3\text{-}O)_2(O_2CC_3H_7)_6(H_2O)_3]^{2+}$ Ions

metal	δ	mult	
Mo	0.795	triplet	^3J = 7.3 Hz
	1.582	sextet	
	2.463	triplet	
W	0.781	triplet	^3J = 7.3 Hz
	1.560	sextet	
	2.509	triplet	

[a] Spectra were recorded in Me_2SO-d_6 at 24 ± 1 °C. Chemical shifts are reported relative to Me_4Si.

Electronic Spectra. The spectra were recorded on a Cary 17D spectrometer in ethanolic solution and are shown in Figure 1 The tungsten complex shows a single peak located at 448 nm ($\bar{\nu}$ = 22.3 × 10^3 cm^{-1}, ε = 829 M^{-1} cm^{-1}). The molybdenum analogue shows two peaks, at 540 nm ($\bar{\nu}$ = 19.8 × 10^3 cm^{-1}, ε = 537 M^{-1} cm^{-1}) and at 423 nm ($\bar{\nu}$ = 23.6 × 10^3 cm, ε = 494 M^{-1} cm^{-1}).

X-ray Crystallographic Procedures. The crystallographic work followed procedures that have previously been described.[5] While the molybdenum compound **2** did not involve any unusual problems, the W compound **1** showed disorder at the anionic sites as well as at the terminal carbon atoms of the butyrate groups, and one CF_3SO_3 fluorine atom could be located in a difference Fourier map. Consequently, as indicated in Table II, the positions of five F and eight C atoms were not refined. An extended account of the handling of each structure is available in the supplementary material. Many of the relevant data are summarized in Table I. The atomic positions for compounds **1** and **2** are listed in Tables II and III, respectively. The structure factors are available as supplementary material.

Results and Discussion

The autoclave reactions work very well, giving compounds **1** and **2** in isolated yields of 40% and 80%, respectively. Our results suggest that the autoclave procedure is one of general applicability, at least with aliphatic carboxylic acids.

---

[5] See, for example: Bino, A.; Cotton, F. A.; Fanwick, P. E. *Inorg. Chem.* **1979**, *18*, 3558.

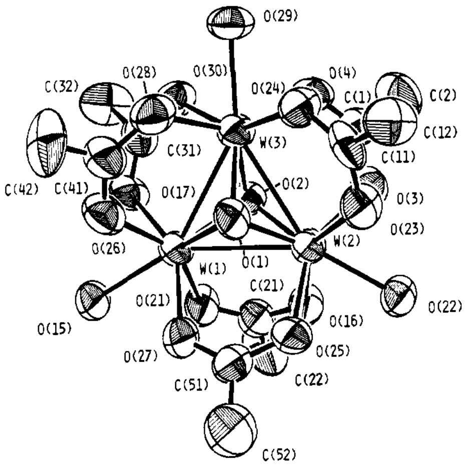

Figure 2. $[W_3(\mu_3\text{-}O)_2(O_2CC_3H_7)_6(H_2O)_3]^{2+}$ cation in compound **1**. The β- and γ-carbon atoms of the propyl groups are omitted. Atoms are represented by their thermal ellipsoids at the 50% probability level, and the atom-labeling scheme is defined.

The present study indicates that the previously made[3] tungsten compounds, which were not previously well characterized, are of the bi-oxo-capped type. We have not further investigated the primary products of the autoclave reaction since, in the absence of crystallographic results, there is nothing to add to the data of ref 3. In light of the fact that all the products were diamagnetic (from NMR chemical shifts) it seems reasonable to assume that 6-electron bi-oxo-capped trinuclear units are formed during the reaction, possibly with carboxylato or hyroxylato rather than water ligands in axial positions.

From the reaction of $W(CO)_6$ with butyric acid the $[W_3(\mu_3\text{-}O)_2(O_2CC_3H_7)_6(H_2O)_3]^{2+}$ cation was successfully crystallized as the trifluoromethanesulfonate salt. Table IV contains the important bond distances and angles while Figure 2 depicts the core of the trinuclear unit and defines the atom-labeling scheme. During refinement some of the terminal carbon atoms were crystallographically poorly defined, but the ^1H NMR spectrum in Me_2SO solution eliminates any doubts regarding their chemical nature.

When we found that the perchlorate salt of the molybdenum analogue, **2**, forms crystals of cubic symmetry, we pessimistically anticipated a disorder problem. Much to our surprise all atoms conformed with the high-symmetry requirements of the space group. Figure 3 shows an ORTEP drawing of the cation with the atom-labeling scheme, and Table IV presents important bond lengths and angles. The trinuclear unit resides around a threefold axis, which is the only crystallographically imposed symmetry element. There are strong hydrogen bonds (O···O = 2.543 (6) Å) between the axial water molecules and lattice water molecules. In the tungsten compound there are two such interactions (O···O = 2.596 (9), 2.605 (8) Å).

The ^1H NMR spectra of both of the cluster cations, as summarized in Table V, indicate that the cations are diamagnetic and that all carboxylato C_3H_7 groups are equivalent. They thus supply support for the the assigned formulas, wherein the capping groups are both oxygen atoms and the charges are 2+ in each case.

Table VI compares important distances in the two butyrate cluster cations with those in analogous $[M_3O_2(O_2CR)_6(H_2O)_3]^{n+}$ species. Although the individual distances differ in a statistical sense, there is no obvious correlation between the bond lengths and the nature of the carboxylic acid. It seems justified to average the values of the Mo–Mo distances for the five molybdenum compounds and the W–W distances in the three tungsten compounds, which leads to the values 2.760 [2] and 2.744 [2] Å, respectively. Thus, in this type of compound we find that the single-bond radius of molybdenum is ca. 0.008 [2] Å greater than that of tungsten. The difference is a small one, and we do not wish to overemphasize it. However, it should be noted that it does appear to be statistically valid and it is opposite in sign to what might have been expected. Thus, the Pauling R_1 values[6] differ by 0.008 in the opposite direction, and for triple and quadruple bonds it is always found that in homologous compounds the tungsten triple- or quadruple-bond radius appears to be ca. 0.04 Å *greater* than that of molybdenum.

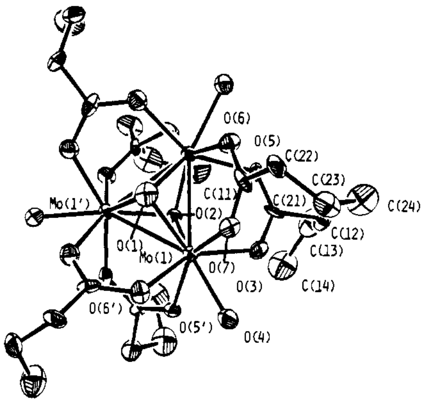

Figure 3. $[Mo_3(\mu_3\text{-}O)_2(O_2CC_3H_7)_6(H_2O)_3]^{2+}$ cation in compound **2**. It possesses crystallographic C_3 symmetry. Atoms are represented by their thermal ellipsoids at the 30% probability level, and the atom-labeling scheme is defined.

The relationship between the molybdenum and tungsten bond radii may be expected to vary with the bond orders. It has already been pointed out[7] that for the triple and quadruple metal–metal bonds a factor comes into play that is less important or unimportant at greater internuclear distances: namely, the fact that the tungsten atom has a core population (68 electrons) that is nearly twice as great as that of the molybdenum atom (36 electrons). At the very short distances characteristic of the triple and quadruple bonds the core–core repulsions are so much greater for W_2 units that the internuclear distances are increased by ca. 0.080 Å. However, at single-bond distances, i.e., ca. 2.75 Å, core–core repulsions may have ceased to differ significantly and the M–M distances will depend only on the properties of the orbitals that are used to form the bonds. These orbitals would, of course, be expected to be very similar for molybdenum and tungsten, but a slight difference might exist in either direction, depending on just what mix of atomic orbitals is used to form the bonds, since different valence shell atomic orbitals will be subject to different relativistic effects and these latter are far more important for tungsten than for molybdenum.

It may be noted that the relationship $r(Mo) > r(W)$ for single M–M bonds is also found in a comparison of the molecules $Mo_2Cl_4(O\text{-}i\text{-}Pr)_6$,[8] where Mo–Mo = 2.731 (1) Å, and $W_2Cl_4(OEt)_6$,[9] where W–W = 2.715 (1) Å. However, this comparison suffers from the possible steric effect of changing from OEt to O-*i*-Pr and perhaps also from the fact that the molybdenum structure was done at ca. 100 K while the tungsten structure was done at ca. 300 K. It has also been

---

(6) Pauling, L. "The Nature of the Chemical Bond", 3rd ed.; Cornell University Press: Ithaca, New York, 1960; p 403.

(7) Cotton, F. A.; Walton, R. A. "Multiple Bonds between Metal Atoms"; Wiley: New York, 1982; pp 349–351.

(8) Chisholm, M. H.; Kirkpatrick, C. C.; Huffman, J. C. *Inorg. Chem.* **1981**, *20*, 871.

(9) Cotton, F. A.; DeMarco, D.; Kolthammer, B. W. S.; Walton, R. A. *Inorg. Chem.* **1981**, *20*, 3048.

Table VI. Comparison of Distances (Å) in Eight $[M_3O_2(O_2CR)_6(H_2O)_3]Z$ Compounds

M	R	Z	M-M	M-(μ_3-O)	M-O_2CR	M-OH_2	ref
Mo	CH_3	$Br_2 \cdot H_2O$	2.766 (2)	2.004 [6]	2.093 [3]	2.083 [10]	*b*
Mo	CH_3	$(CF_3SO_3)_2$	2.759 (1)	1.994 (5)	2.082 [7]	2.129 (6)	*c*
Mo	C_2H_5	$(CF_3SO_3)_2 \cdot CF_3SO_3H \cdot 4H_2O$	2.752 [2]	1.984 [4]	2.090 [4]	2.144 [4]	*b*
Mo	C_3H_7	$(ClO_4)_2 \cdot 3H_2O$	2.762 (2)	2.006 [3]	2.090 [6]	2.102 (9)	*f*
Mo	C_6H_5	$(ClO_4)_2 \cdot HClO_4 \cdot 3CH_3CH_2OH$	2.761 [1]	1.983 [6]	2.081 [6]	2.123 [6]	*d*
W	CH_3	$(CF_3SO_3)_2$	2.746 (1)	2.011 (5)	2.085 [7]	2.132 (6)	*e*
W	C_2H_5	$(BF_4)_2 \cdot 5.5H_2O$	2.745 [2]	2.000 [4]	2.090 [10]	2.090 [20]	*e*
W	C_3H_7	$(CF_3SO_3)_2 \cdot 2H_2O$	2.742 [1]	1.999 [5]	2.090 [4]	2.096 [8]	*f*

[a] Parentheses indicate esd of one value; brackets indicate $\{(\Sigma\Delta_i^2)/(n(n-1))\}^{1/2}$ for several values whose unweighted arithmetic average is given. [b] Ardon, M.; Bino, A.; Cotton, F. A.; Dori, Z.; Kaftory, M.; Reisner, G. *Inorg. Chem.* **1982**, *21*, 1912. [c] Cotton, F. A.; Dori, Z.; Marler, D. O.; Schwotzer, W. *Inorg. Chem.* **1983**, *22*, 3104. [d] Cotton, F. A.; Dori, A.; Marler, D. O.; Schwotzer, W. *Inorg. Chem.*, in press. [e] Bino, A.; Cotton, F. A.; Dori, Z.; Koch, S.; Küppers, H.; Millar, M.; Sekutowski, J. C. *Inorg. Chem.* **1978**, *17*, 3245. [f] This work.

observed previously that even in homologous compounds containing quadruple bonds, for the metal to ligand bonds, those formed by molybdenum are systematically ca. 0.03 Å longer than those formed by tungsten.[10]

There are tentative indications that as the M–M bonds become stronger and shorter, the radius ratio, $r(\mathrm{Mo})/r(\mathrm{W})$, changes or has already changed from >1 to <1 by the time bond lengths of about 2.50 Å are reached. One pair of structures supporting this are the $[M_3O_4F_9]^{5-}$ ions[11,12] for which we have Mo–Mo = 2.505 (?) Å and W–W = 2.514 (1) Å. Another interesting pair are the $M_2(O\text{-}i\text{-}Pr)_6(py)_2(CO)$ molecules for which the M–M distances are Mo=M = 2.486 (2) Å at ca. 100 K[13] and 2.487 (1) Å at ca. 300 K[14] and W=W = 2.499 (3) Å[13] at ca. 100 K. It is useful to know that the temperature does not appear to affect such metal–metal bond lengths.

Acknowledgment. We thank the National Science Foundation and the U.S.-Israel Binational Science Foundation for support.

Registry No. **1**, 93503-86-7; **2**, 93530-02-0; $W(CO)_6$, 14040-11-0; $Mo_2(O_2CCH_3)_4$, 14221-06-8.

Supplementary Material Available: Details of the crystallography and listings of bond distances, anisotropic thermal parameters, bond angles, and observed and calculated structure factors (43 pages). Ordering information is given on any current masthead page.

---

(10) Cotton, F. A.; Extine, M. W.; Felthouse, T. R.; Kolthammer, B. W. S.; Lay, D. C. *J. Am. Chem. Soc.* **1981**, *103*, 4040.

(11) Mattes, R.; Mennemann, K. *Z. Anorg. Allg. Chem.* **1977**, *437*, 175.

(12) Müller, A.; Ruck, A.; Dartmann, M.; Reinsch-Vogell, U. *Angew. Chem.* **1981**, *93*, 493.

(13) Chisholm, M. H.; Huffman, J. C.; Leonelli, J.; Rothwell, I. P. *J. Am. Chem. Soc.* **1982**, *104*, 7030.

(14) Cotton, F. A.; Schwotzer, W. *Inorg. Chem.* **1983**, *22*, 387.