Supplementary Material Available: C–C distances (Table A) and bond angles (Table B) in phenyl groups and acetone molecules and tables of observed and calculated structure factors for $Mo_2(DPPM)_2NCS$ and $Mo_2(DPPM)_2Cl_4$ (29 pages). Ordering information is given on any current masthead page.

References and Notes

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(2) For leading references see: F. A. Cotton, *Chem. Soc. Rev.*, **4**, 27 (1975); *Acc. Chem. Res.*, **11**, 224 (1978).

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A New Class of Trinuclear Tungsten(IV) Cluster Compounds with W–W Single Bonds

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The reaction of tungsten hexacarbonyl with carboxylic acids, followed by suitable workup procedures, allows the isolation of compounds whose common feature is the presence of a $[W_3O_2(O_2CR)_6]^{2+}$ unit, to which three additional donors are coordinated. This consists of an equilateral triangle of tungsten atoms with oxygen atoms on the threefold axis above and below the triangle so that the W_3O_2 set of atoms defines a trigonal bipyramid. Each W–W edge is bridged by two bidentate carboxylato ions. Each tungsten atom is coordinated by an additional ligand, such as H_2O or an anion, and is therefore nine-coordinate, counting its neighboring tungsten atoms. The W–W distances, which are all about 2.75 Å, are consistent with the existence of W–W single bonds. Additional anions or cations are present as necessary for electroneutrality. Four compounds, all of which have been structurally characterized by X-ray crystallography, are reported here: **1**, $\{[W_3O_2(O_2CCH_3)_6](H_2O)_3\}(CF_3SO_3)_2$; **2**, $\{[W_3O_2(O_2CC_2H_5)_6](H_2O)_3\}(BF_4)_2\cdot 5.5H_2O$; **3**, $\{[W_3O_2(O_2CC(CH_3)_3)_6](O_2CC(CH_3)_3)_2(H_2O)\}(CH_3)_3CCO_2H$; **4**, $Cs\{[W_3O_2(O_2CCH_3)_6](CH_3CO_2)_3\}\cdot 3H_2O$. All four are yellow solids and are stable in air. The principal crystallographic data for each of the compounds are as follows: (**1**) monoclinic $C2/c$, $a = 19.798$ (5) Å, $b = 11.424$ (5) Å, $c = 15.079$ (5) Å, $\beta = 115.94$ (5)°, $V = 3067$ Å^3, $Z = 4$; (**2**) triclinic $P\bar{1}$, $a = 13.285$ (6) Å, $b = 12.614$ (5) Å, $c = 12.453$ (5) Å, $\alpha = 93.84$ (5)°, $\beta = 92.17$ (5)°, $\gamma = 102.37$ (5)°, $V = 2031$ Å^3, $Z = 2$; (**3**) orthorhombic $Pnnm$, $a = 16.159$ (3) Å, $b = 26.053$ (6) Å, $c = 16.941$ (3) Å, $V = 7132$ Å^3, $Z = 4$; (**4**) monoclinic $C2/c$, $a = 20.702$ (5) Å, $b = 12.987$ (2) Å, $c = 25.535$ (5) Å, β 92.61 (6)°, $V = 6858$ Å^3, $Z = 8$.

Introduction

Ever since the discovery that $Mo(CO)_6$ reacts with carboxylic acids to give yellow compounds[2] subsequently shown to be the dinuclear,[3] quadruply bonded[4] molecules $Mo_2(O_2CR)_4$, Figure 1A, efforts have been made[5,6] to prepare analogous tungsten compounds, but without any conclusive success. With several carboxylic acids, materials thought to be the $W_2(O_2CR)_4$ compounds were obtained[5] but none was obtained in crystalline form, so that X-ray crystallographic confirmation of such suggested structures is lacking.

In the case of acetic acid the only product previously isolated[5,6] was recognized to be an oxo compound and was probably trinuclear. Formulas such as $W_3O(O_2CCH_3)_9$,[5] $W_3O(O_2CCH_3)_8(OH)(H_2O)$,[6] and $W_3O(O_2CCH_3)_8(OH)(CH_3OH)$[6] were suggested. However, there has been no evidence for the details of these proposals and they were suggested by analogy with the well-known oxotrimetal hexacarboxylate structure, Figure 1B, exhibited by many transition-metal compounds.[7] An important characteristic of this structure is that the oxygen atom resides at the center of the equilateral triangle of metal atoms and thus prevents the metal atoms from approaching one another closely enough to form direct metal–metal bonds. Compounds with this structure are therefore *not* metal atom cluster compounds in the true sense of that term.[8]

The present work was undertaken with the purpose of understanding more fully what happens when an excess of acetic acid, or a mixture of the acid and its anhydride, reacts with $W(CO)_6$. The product isolated and discussed in the earlier investigations, which precipitates from the reaction mixture, contains only a small fraction of the total tungsten introduced and one obvious task was to determine the fate of the rest of the tungsten, which remained in solution. In this paper we report that essentially all of that remaining tungsten appears to be present in one form, namely, as a true trinuclear cluster, and that various compounds can be isolated depending on the workup procedure. We also report that with acids other than acetic, specifically propionic and pivalic, crystalline products containing the same type of trinuclear cluster can be isolated.

Experimental Section

Materials. $W(CO)_6$ was used as obtained from Pressure Chemical Co. All solvents and chemicals were reagent grade and were used without further purification.

Preparation of $\{[W_3O_2(O_2CCH_3)_6](H_2O)_3\}(CF_3SO_3)_2$ (1). $W(CO)_6$ (1 g, 2.8 mmol) was refluxed overnight with 100 mL of a 1:1 mixture of acetic acid and acetic anhydride. The yellow precipitate that formed upon cooling was filtered off. This substance is still under investigation. The resulting clear solution was diluted with 100 mL of H_2O and absorbed on a cation exchange column (Dowex 50W-X2) and eluted with 0.5 M CF_3SO_3H. Slow evaporation of the eluate gave beautiful yellow crystalline material whose elemental analysis suggested the formula $[W_3(O_2CCH_3)_6O_2(H_2O)_3](CF_3SO_3)_2$. Anal. Calcd for $W_3C_{14}O_{23}H_{24}F_6S_2$: C, 13.02; F, 8.83; H, 1.86; S, 4.96. Found: C, 13.01; F, 8.73; H, 2.20; S, 5.22.

Preparation of $\{[W_3O_2(O_2CCH_2CH_3)_6](H_2O)_3\}(BF_4)_2\cdot 5.5H_2O$ (2). This compound was prepared in a way analogous to the acetate

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Table I. Determination of the Oxidation State of Tungsten

compd	mg of sample	mmol of W	mL of 0.1 N $KMnO_4$ before Jones	mL of 0.1 N $KMnO_4$ after Jones	oxidn state[a]	
1	100	0.233	4.71	5.40	+3.9	3.9 ± 0.1
2	120	0.266	5.45	6.20	+3.9	3.9 ± 0.1
3	45	0.089	1.70	2.30	+4.2	*b*
4[c]	150	0.370	7.30	8.91	+4.0	4.0 ± 0.1

[a] The results of the first column are those from the measurement detailed. The second column gives the averages, with esd's, for three measurements. [b] This compound was measured only once. [c] The measurements were done with the triethylammonium salt of this compound.

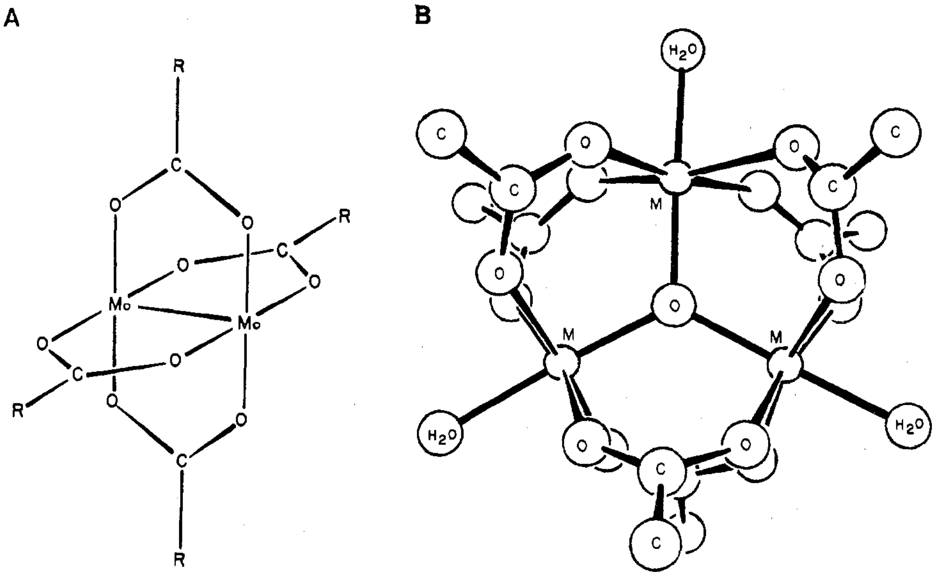

Figure 1. (A) $Mo_2(O_2CR)_4$ structure. (B) The previously known basic carboxylate trinuclear structure. The drawing is based on experimental data for the chromium acetate reported by S. C. Chang and G. A. Jeffrey, *Acta Crystallogr., Sect. B*, **26**, 673 (1970).

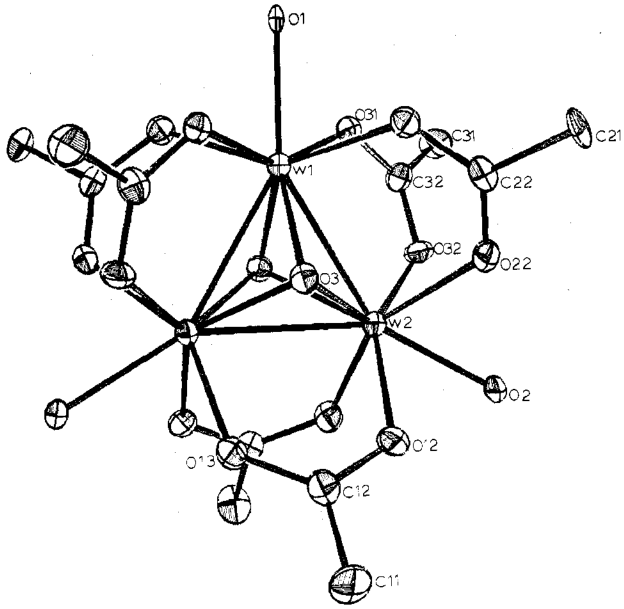

Figure 2. $[W_3O_2(O_2CCH_3)_6(H_2O)_3]^{2+}$ unit in compound **1**. Unnumbered atoms are related to numbered ones by a twofold rotation axis coincident with the O(1)–W(1) bond.

complex. The elution from the cation exchange column was carried out with 1 M HBF_4.

Preparation of $\{[W_3O_2(O_2CC(CH_3)_3)_6]((CH_3)_3CCO_2)_2(H_2O)\}\cdot(CH_3)_3CCOOH$ **(3).** $W(CO)_6$ (10.1 g, 0.28 mmol) was heated to 140 °C in 20 mL of pivalic acid in a sealed tube for 48 h. After several weeks of standing at room temperature, a few yellow crystals separated and these were used for the structure determination.

Preparation of $Cs\{[W_3O_2(O_2CCH_3)_6](CH_3CO_2)_3\}\cdot 3H_2O$ **(4).** $W(CO)_6$ (1 g, 2.8 mmol) was refluxed for 24 h under N_2 with 100 mL of acetic anhydride containing 0.4 g (4 mmol) of triethylamine. Upon cooling, yellow crystalline material separated out. Elemental

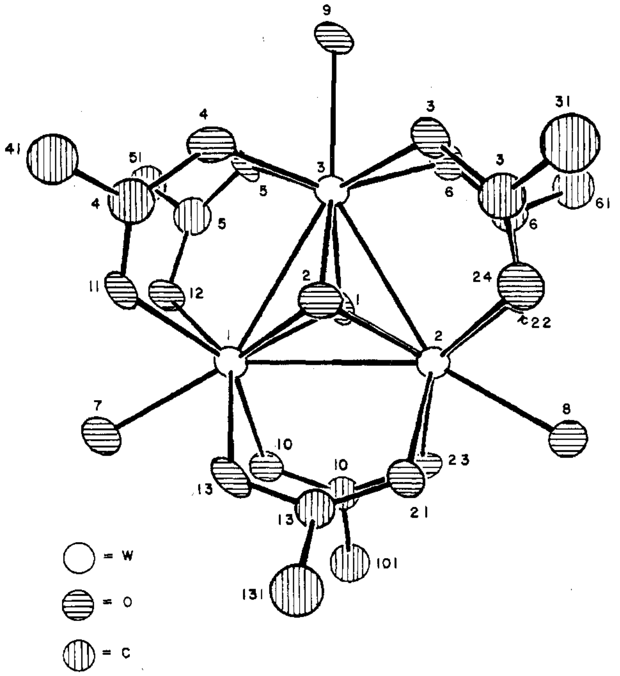

Figure 3. $[W_3O_2(O_2CC_2H_5)_6(H_2O)_3]^{2+}$ unit of compound **2**. The β-carbon atoms of the propionato groups have been omitted. Each atom is represented by its ellipsoid (or sphere) of thermal vibration, scaled to enclose 50% of its electron density. The numbering scheme used in Tables III and IV is defined.

Table II. Crystallographic Data

parameter	compound 1	2	3	4
space group	*C*2/*c*	$P\bar{1}$	*Pnnm*	*C*2/*c*
a, Å	19.798 (5)	13.285 (6)	16.159 (3)	20.702 (5)
b, Å	11.424 (5)	12.614 (5)	26.053 (6)	12.987 (2)
c, Å	15.079 (5)	12.453 (5)	16.941 (3)	25.535 (5)
α, deg	90.00	93.84 (5)	90.00	90.00
β, deg	115.94 (5)	92.17 (5)	90.00	92.61 (6)
γ, deg	90.00	102.37 (5)	90.00	90.00
V, $Å^3$	3067	2031	7132	6858
d, g/cm^3	2.82	2.13	1.4	2.52
Z	4	2	4	8
crystal size, mm	0.25 × 0.2 × 0.18	0.1 × 0.1 × 0.1	0.1 × 0.1 × 0.1	0.1 × 0.4 × 0.5
μ, cm^{-1}	121	90.1	51.7	117.89
no. of unique data	3900	5309	5218	5142
data of $F_o^2 > 3\sigma(F_o^2)$	3554[a]	3496	2026	3080
R_1 (anisotropic)	0.039	0.052	0.070	0.057
R_2 (anisotropic)	0.060	0.067	0.096	0.078
esd	1.23	1.35	1.76	1.68

[a] For this structure data with $F_o^2 > 2\sigma(F_o^2)$ were used.

Table III. Positional and Thermal Parameters for $[W_3O_2(O_2CC_2H_5)_6(H_2O)_3](BF_4)_2$[a]

atom	*x*	*y*	*z*	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
W(1)	0.28957 (7)	0.23030 (6)	0.12595 (7)	2.91 (3)	2.42 (3)	2.38 (3)	0.88 (3)	0.61 (3)	0.61 (3)
W(2)	0.11043 (7)	0.29729 (6)	0.16860 (7)	3.09 (3)	2.69 (3)	2.41 (3)	1.32 (3)	0.51 (3)	0.76 (3)
W(3)	0.22807 (7)	0.24319 (7)	0.33334 (7)	3.07 (3)	2.77 (3)	2.18 (3)	1.12 (3)	0.45 (3)	0.59 (3)
O(3)	0.199 (1)	0.384 (1)	0.412 (1)	4.7 (7)	4.6 (6)	2.9 (6)	2.8 (5)	1.0 (5)	0.6 (5)
O(4)	0.381 (1)	0.315 (1)	0.366 (1)	5.1 (7)	3.0 (6)	2.8 (6)	1.2 (5)	0.1 (6)	1.3 (5)
O(5)	0.272 (1)	0.096 (1)	0.338 (1)	3.0 (6)	2.9 (5)	2.3 (5)	0.9 (5)	1.7 (5)	0.4 (5)
O(6)	0.084 (1)	0.168 (1)	0.383 (1)	3.4 (6)	4.0 (6)	3.5 (6)	1.1 (5)	0.9 (6)	0.5 (5)
O(10)	0.198 (1)	0.144 (1)	−0.006 (1)	3.3 (6)	3.0 (6)	2.4 (6)	0.9 (5)	0.4 (5)	0.1 (5)
O(11)	0.436 (1)	0.306 (1)	0.198 (1)	3.3 (6)	4.7 (6)	2.7 (6)	1.8 (5)	1.6 (5)	0.9 (5)
O(12)	0.324 (1)	0.082 (1)	0.169 (1)	4.3 (6)	3.1 (6)	2.3 (6)	1.3 (5)	1.0 (5)	0.3 (5)
O(13)	0.312 (1)	0.361 (1)	0.028 (1)	3.2 (6)	3.4 (6)	2.9 (6)	0.0 (5)	1.7 (5)	0.6 (5)
O(21)	0.167 (1)	0.418 (1)	0.064 (1)	4.2 (6)	3.7 (5)	3.3 (6)	2.3 (5)	1.5 (5)	1.7 (5)
O(22)	−0.010 (1)	0.207 (1)	0.247 (1)	3.9 (6)	4.4 (6)	3.4 (6)	1.8 (5)	1.0 (6)	2.0 (5)
O(23)	0.054 (1)	0.199 (1)	0.030 (1)	4.1 (7)	3.2 (6)	2.9 (6)	0.4 (5)	−0.6 (6)	1.5 (5)
O(24)	0.102 (1)	0.427 (1)	0.280 (1)	5.4 (7)	2.8 (6)	4.2 (7)	1.8 (5)	0.5 (6)	−0.3 (6)
O(1)	0.162 (1)	0.162 (1)	0.196 (1)	3.2 (6)	2.9 (5)	2.9 (6)	1.6 (4)	1.3 (5)	0.5 (5)
O(2)	0.258 (1)	0.351 (1)	0.225 (1)	3.4 (6)	2.9 (6)	2.4 (6)	0.3 (5)	−0.3 (5)	−0.6 (5)
O(7)	0.395 (1)	0.193 (1)	0.015 (1)	4.9 (7)	5.0 (7)	3.9 (7)	2.6 (5)	1.9 (6)	1.9 (5)
O(8)	−0.018 (1)	0.350 (1)	0.116 (1)	4.3 (7)	5.7 (7)	3.7 (7)	2.5 (5)	0.9 (6)	1.9 (6)
O(9)	0.251 (1)	0.224 (1)	0.499 (1)	5.5 (7)	6.2 (7)	1.9 (6)	3.8 (5)	1.1 (5)	0.9 (5)

atom	*x*	*y*	*z*	*B*, $Å^2$	atom	*x*	*y*	*z*	*B*, $Å^2$
F(1)	0.875 (2)	0.748 (2)	0.350 (2)	9.4 (5)	C(6)	0.001 (2)	0.159 (2)	0.335 (2)	3.5 (5)
F(2)	0.804 (2)	0.565 (2)	0.319 (2)	10.9 (6)	C(10)	0.109 (2)	0.143 (2)	0.026 (2)	3.0 (4)
F(3)	0.941 (3)	0.638 (3)	0.236 (3)	18.1 (11)	C(13)	0.252 (2)	0.429 (2)	0.023 (2)	2.9 (4)
F(4)	0.818 (3)	0.682 (3)	0.192 (3)	16.8 (10)	C(31)	0.152 (2)	0.558 (2)	0.431 (2)	5.4 (6)
F(5)	0.536 (2)	0.132 (2)	0.319 (2)	12.9 (8)	C(32)	0.231 (4)	0.643 (4)	0.374 (4)	13.7 (16)
F(6)	0.701 (2)	0.221 (2)	0.365 (2)	11.2 (6)	C(41)	0.550 (2)	0.411 (2)	0.332 (2)	4.6 (5)
F(7)	0.636 (2)	0.058 (2)	0.415 (2)	15.2 (9)	C(42)	0.540 (3)	0.526 (3)	0.343 (3)	9.4 (10)
F(8)	0.584 (3)	0.190 (3)	0.475 (3)	18.1 (11)	C(51)	0.326 (2)	−0.065 (2)	0.287 (2)	4.4 (5)
O(202)	0.069 (1)	0.611 (1)	0.078 (1)	5.2 (4)	C(52)	0.366 (3)	−0.123 (3)	0.193 (3)	8.1 (9)
O(201)	0.595 (1)	0.840 (1)	0.417 (2)	6.3 (4)	C(61)	−0.099 (2)	0.091 (2)	0.375 (2)	4.9 (6)
O(203)	0.829 (2)	0.361 (2)	0.245 (2)	6.5 (5)	C(62)	−0.106 (3)	0.097 (3)	0.499 (3)	8.2 (9)
O(204)	0.547 (2)	0.116 (2)	0.081 (2)	9.9 (7)	C(101)	0.054 (2)	0.074 (2)	−0.129 (2)	4.6 (5)
O(205)	0.626 (2)	0.775 (2)	0.188 (2)	9.8 (7)	C(102)	−0.051 (2)	0.094 (2)	−0.163 (2)	5.7 (6)
O(206)	0.745 (4)	0.085 (4)	0.077 (4)	8.3 (13)	C(131)	0.292 (2)	0.526 (2)	−0.037 (2)	5.1 (6)
C(3)	0.148 (2)	0.447 (2)	0.369 (2)	4.0 (5)	C(132)	0.380 (4)	0.607 (4)	0.031 (4)	12.6 (14)
C(4)	0.454 (2)	0.340 (2)	0.295 (2)	4.1 (5)	B(1)	0.855 (2)	0.656 (2)	0.281 (3)	5.1 (7)
C(5)	0.302 (2)	0.046 (2)	0.264 (2)	3.9 (5)	B(2)	0.622 (5)	0.137 (5)	0.357 (5)	13.8 (18)

[a] The form of the anisotropic thermal parameter is $\exp[-{}^1/_4(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^* + 2B_{13}hla^*c^* + 2B_{23}hkb^*c^*)]$.

analysis suggested the formula $[(C_2H_5)_3NH][W_3(O_2CCH_3)_9O_2]$. Anal. Calcd for $W_3C_{24}H_{43}O_{20}N$: C, 23.67; H, 3.50; N, 1.15. Found: C, 23.52; H, 3.67; N, 1.21. Attempts to grow larger crystals for X-ray measurements were unsuccessful. This complex (0.2 g) was dissolved in a minimum amount of water containing CsCl. Slow evaporation of this solution yielded beautiful crystals of $Cs[W_3(O_2CCH_3)_9O_2]\cdot 3H_2O$ which were used for the structure analysis.

Determination of the Oxidation State of Tungsten. The procedure used was essentially the same as that described by Federov for tungsten determination.[11] A measured amount of each of the four compounds was dissolved in 100 mL of 2 M H_2SO_4 and then oxidized with a standardized solution of $KMnO_4$ to W(VI). Fourteen milliliters of concentrated H_3PO_4 was added and the resulting solution was stirred until completely clear. The clear solution was then reduced with a

Table IV. Bond Distances (Å) and Bond Angles (deg) for $[W_3O_2(O_2CC_2H_5)_6(H_2O)_3][BF_4]_2$

Bond Distances

W(1)-W(2)	2.749 (1)			O(3)-C(3)	1.29 (2)	O(4)-C(4)	1.34 (2)
W(1)-W(3)	2.743 (1)	W(2)-W(3)	2.742 (1)	O(24)-C(3)	1.23 (2)	O(11)-C(4)	1.25 (2)
W(1)-O(10)	2.10 (1)	W(2)-O(21)	2.11 (1)	C(3)-C(31)	1.55 (3)	C(4)-C(41)	1.43 (3)
W(1)-O(11)	2.12 (1)	W(2)-O(22)	2.07 (1)	C(31)-C(32)	1.56 (5)	C(41)-C(42)	1.48 (4)
W(1)-O(12)	2.11 (1)	W(2)-O(23)	2.07 (1)	O(5)-C(5)	1.21 (2)	O(6)-C(6)	1.22 (2)
W(1)-O(13)	2.10 (1)	W(2)-O(24)	2.09 (1)	O(12)-C(5)	1.31 (2)	O(22)-C(6)	1.30 (2)
W(1)-O(1)	1.98 (1)	W(2)-O(1)	2.01 (1)	C(5)-C(51)	1.54 (3)	C(6)-C(61)	1.53 (3)
W(1)-O(2)	2.01 (1)	W(2)-O(2)	2.01 (1)	C(51)-C(52)	1.51 (4)	C(61)-C(62)	1.55 (4)
W(1)-O(7)	2.11 (1)	W(2)-O(8)	2.06 (1)	O(10)-C(10)	1.20 (2)	O(13)-C(13)	1.30 (2)
W(3)-O(3)	2.08 (1)			O(23)-C(10)	1.31 (2)	O(21)-C(13)	1.24 (2)
W(3)-O(4)	2.05 (1)			C(10)-C(101)	1.56 (3)	C(13)-C(131)	1.48 (3)
W(3)-O(5)	2.06 (1)			C(101)-C(102)	1.52 (3)	C(131)-C(132)	1.56 (5)
W(3)-O(6)	2.08 (1)						
W(3)-O(1)	2.00 (1)			B(1)-F(1)	1.37 (3)	B(2)-F(5)	1.20 (6)
W(3)-O(2)	1.97 (1)			B(1)-F(2)	1.32 (3)	B(2)-F(6)	1.32 (6)
W(3)-O(9)	2.11 (1)			B(1)-F(3)	1.34 (4)	B(2)-F(7)	1.31 (6)
				B(1)-F(4)	1.29 (4)	B(2)-F(8)	1.72 (6)

Bond Angles

W(2)-W(1)-W(3)	59.90 (3)			W(1)-W(3)-W(2)	60.16 (3)		
-O(10)	82.3 (3)	W(3)-W(1)-O(10)	125.0 (3)	-O(4)	82.7 (3)	W(2)-W(3)-O(4)	123.5 (3)
-O(13)	83.0 (3)	-O(13)	123.9 (3)	-O(5)	82.6 (3)	-O(5)	124.5 (3)
-O(11)	124.0 (3)	-O(11)	83.6 (3)	-O(3)	124.2 (3)	-O(3)	83.2 (3)
-O(12)	124.9 (3)	-O(12)	83.3 (3)	-O(6)	125.0 (3)	-O(6)	82.4 (4)
-O(1)	47.0 (3)	-O(1)	46.7 (3)	-O(1)	46.2 (3)	-O(1)	47.1 (3)
-O(2)	47.0 (3)	-O(2)	45.9 (3)	-O(2)	47.2 (3)	-O(2)	47.2 (3)
-O(7)	150.2 (4)	-O(7)	149.9 (4)	-O(9)	150.3 (3)	-O(9)	149.5 (3)
O(10)-W(1)-O(11)	150.2 (4)			O(3)-W(3)-O(4)	85.4 (5)		
-O(12)	88.7 (4)	O(11)-W(1)-O(12)	86.3 (5)	-O(5)	150.4 (4)	O(4)-W(3)-O(5)	86.4 (5)
-O(13)	84.8 (4)	-O(13)	85.1 (5)	-O(6)	85.0 (5)	-O(6)	150.9 (5)
-O(1)	78.4 (5)	-O(1)	128.8 (5)	-O(1)	129.1 (5)	-O(1)	127.6 (5)
-O(2)	127.7 (5)	-O(2)	77.1 (5)	-O(2)	77.1 (5)	-O(2)	76.3 (5)
-O(7)	74.9 (5)	-O(7)	75.4 (5)	-O(9)	75.1 (5)	-O(9)	76.4 (5)
O(12)-W(1)-O(13)	150.2 (4)			O(5)-W(3)-O(6)	88.5 (5)		
-O(1)	77.9 (5)	O(13)-W(1)-O(1)	128.6 (5)	-O(1)	77.4 (4)	O(6)-W(3)-O(1)	78.8 (5)
-O(2)	127.4 (5)	-O(2)	78.0 (5)	-O(2)	128.1 (4)	-O(2)	127.7 (5)
-O(7)	74.2 (5)	-O(7)	76.0 (5)	-O(9)	75.3 (5)	-O(9)	74.5 (5)
O(1)-W(1)-O(2)	75.2 (5)			O(1)-W(3)-O(2)	75.8 (4)		
-O(7)	141.5 (5)	O(2)-W(1)-O(7)	143.3 (5)	-O(9)	142.0 (5)	O(2)-W(3)-O(9)	142.2 (5)
W(1)-W(2)-W(3)	59.94 (3)			W(1)-O(1)-W(2)	86.9 (4)	W(1)-O(2)-W(2)	86.0 (4)
-O(21)	83.2 (3)	W(3)-W(2)-O(21)	123.4 (4)	-W(3)	87.0 (5)	-W(3)	87.0 (5)
-O(23)	83.1 (4)	-O(23)	125.5 (3)	W(2)-O(1)-W(3)	86.2 (4)	W(2)-O(2)-W(3)	86.9 (5)
-O(22)	123.9 (3)	-O(22)	83.0 (3)	W(3)-O(3)-C(3)	124 (1)	W(3)-O(4)-C(4)	127 (1)
-O(24)	123.9 (4)	-O(24)	82.3 (4)	W(2)-O(24)-C(3)	126 (1)	W(1)-O(11)-C(4)	125 (1)
-O(1)	46.1 (3)	-O(1)	46.7 (3)	O(3)-C(3)-O(24)	124 (2)	O(4)-C(4)-O(11)	120 (2)
-O(2)	47.0 (3)	-O(2)	45.9 (3)	-C(31)	117 (2)	-C(41)	119 (2)
-O(8)	150.0 (4)	-O(8)	150.0 (4)	O(24)-C(3)-C(31)	119 (2)	O(11)-C(4)-C(41)	121 (2)
O(21)-W(2)-O(22)	151.0 (5)			C(3)-C(31)-C(32)	106 (2)	C(4)-C(41)-C(42)	111 (2)
-O(23)	85.7 (5)	O(22)-W(2)-O(23)	87.5 (5)	W(3)-O(5)-C(5)	127 (1)	W(3)-O(6)-C(6)	127 (1)
-O(24)	85.9 (5)	-O(24)	86.2 (5)	W(1)-O(12)-C(5)	122 (1)	W(2)-O(22)-C(6)	125 (1)
-O(1)	128.1 (4)	-O(1)	77.7 (5)	O(5)-C(5)-O(12)	125 (2)	O(6)-C(6)-O(22)	123 (2)
-O(2)	77.6 (5)	-O(2)	127.4 (5)	-C(51)	117 (2)	-C(61)	122 (2)
-O(8)	75.4 (5)	-O(8)	75.5 (5)	O(12)-C(5)-C(51)	118 (2)	O(22)-C(6)-C(61)	115 (2)
O(23)-W(2)-O(24)	150.3 (5)			C(5)-C(51)-C(52)	115 (2)	C(6)-C(61)-C(62)	115 (2)
-O(1)	78.9 (5)	O(24)-W(2)-O(1)	127.6 (5)	W(1)-O(10)-C(10)	126 (1)	W(1)-O(13)-C(13)	124 (1)
-O(2)	128.4 (5)	-O(2)	77.0 (5)	W(2)-O(23)-C(10)	124 (1)	W(2)-O(21)-C(13)	125 (1)
-O(8)	74.7 (5)	-O(8)	75.7 (5)	O(10)-C(10)-O(23)	125 (2)	O(13)-C(13)-O(21)	125 (2)
O(1)-W(2)-O(2)	74.5 (5)			O(10)-C(10)-C(101)	119 (2)	O(13)-C(13)-C(131)	115 (2)
-O(8)	142.9 (5)	O(2)-W(2)-O(8)	142.6 (5)	O(23)-C(10)-C(101)	117 (2)	O(21)-C(13)-C(131)	120 (2)
				C(10)-C(101)-C(102)	116 (2)	C(13)-C(131)-C(132)	111 (2)
				F(1)-B(1)-F(2)	117 (3)	F(5)-B(2)-F(6)	128 (6)
				-F(3)	112 (3)	-F(7)	117 (6)
				-F(4)	107 (3)	-F(8)	88 (4)
				F(2)-B(1)-F(3)	110 (3)	F(6)-B(2)-F(7)	113 (6)
				-F(4)	116 (3)	-F(8)	87 (4)
				F(2)-B(1)-F(4)	93 (3)	F(7)-B(2)-F(8)	84 (4)

Jones reductor column and the resulting green-brown solution was reoxidized with $KMnO_4$. The green-brown solution obtained from the Jones reductor has been shown by Fedorov[11] to contain a mixture of W(III) and W(IV) with an average oxidation state (OS) of +3.6. Consequently, the OS was determined from the ratio of MnO_4^- titer before and after the reduction using the equation

$$\mathrm{OS} = 6 - \frac{\text{mL of MnO}_4^- \text{ before Jones reductor}}{\text{mL of MnO}_4^- \text{ after Jones reductor}} \times 2.4$$

The experimental results are tabulated in Table I.

X-ray Data Collection. Data were collected for compounds **2**, **3**, and **4** on a Syntex $P\bar{1}$ automated four-circle diffractometer using Mo Kα (λ 0.71073 Å) radiation with a graphite-crystal monochromator in the incident beam. Fifteen strong, low-angle reflections were used to obtain an initial orientation matrix for a crystal. During the data collection the crystal was centered with 15 high-angle reflections from which the accurate cell constants were deduced. Data were collected at 22 ± 3 °C using the θ–2θ scan technique with a variable scan rate

Table V. Positional and Thermal Parameters for $\{[W_3O_2(O_2CC(CH_3)_3)_8(H_2O)]\}(CH_3)_3CCOOH^a$

atom	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
W(1)	0.1052 (1)	0.10292 (8)	0.0000 (0)	2.24 (7)	3.49 (9)	2.32 (8)	−0.2 (1)	0	0
W(2)	0.1948 (1)	0.19369 (9)	0.0000 (0)	2.45 (9)	3.5 (1)	2.98 (9)	0.0 (1)	0	0
W(3)	0.0231 (1)	0.19490 (9)	0.0000 (0)	2.23 (8)	3.4 (1)	3.10 (9)	0.20 (9)	0	0
O(1)	0.107 (1)	0.1648 (7)	0.069 (1)	3.0 (9)	2.7 (9)	6 (1)	−2 (1)	0 (1)	1.6 (9)
O(12)	0.193 (1)	0.0764 (9)	0.083 (1)	4 (1)	7 (1)	2 (1)	1 (1)	1.5 (9)	0 (1)
O(13)	0.108 (2)	0.0194 (12)	0.000 (0)	4 (1)	5 (2)	3 (1)	−2 (2)	0	0
O(21)	0.268 (1)	0.1539 (9)	0.086 (1)	3 (1)	3 (1)	6 (1)	−0 (1)	−1 (1)	−1 (1)
O(22)	0.306 (2)	0.2253 (11)	0.000 (0)	1 (1)	2 (1)	7 (2)	−1 (1)	0	0
O(23)	0.175 (1)	0.2486 (9)	0.085 (1)	4 (1)	3 (1)	4 (1)	1 (1)	1 (1)	1 (1)
O(31)	0.037 (1)	0.2531 (10)	0.083 (1)	2 (1)	7 (1)	3 (1)	0 (1)	0 (1)	−2 (1)
O(32)	−0.070 (2)	0.2359 (13)	0.000 (0)	5 (2)	4 (2)	5 (2)	−3 (1)	0	0
O(33)	−0.047 (1)	0.1613 (8)	0.089 (1)	1.1 (8)	4 (1)	4 (1)	1.6 (9)	0.1 (9)	0 (1)
atom	**x**	**y**	**z**	**B, Å²**	**atom**	**x**	**y**	**z**	**B, Å²**
O(11)	0.017 (1)	0.0841 (8)	0.087 (1)	2.2 (4)	C(13)	0.393 (4)	0.089 (2)	0.144 (3)	10.7 (16)
O(41)	0.244 (2)	−0.0175 (16)	0.000 (0)	6.3 (11)	C(14)	0.312 (3)	0.136 (2)	0.238 (3)	9.8 (16)
O(51)	−0.197 (2)	0.1984 (13)	0.000 (0)	4.5 (8)	C(34)	−0.117 (3)	0.046 (2)	0.187 (3)	6.4 (11)
O(61)	0.301 (2)	0.3111 (15)	0.000 (0)	6.1 (10)	C(35)	−0.131 (3)	0.142 (2)	0.221 (3)	9.0 (15)
O(71)	0.187 (2)	−0.0969 (14)	0.000 (0)	4.7 (8)	C(15)	0.280 (3)	0.032 (2)	0.191 (3)	8.5 (14)
C(11)	0.250 (2)	0.111 (1)	0.110 (2)	3.5 (8)	C(51)	−0.140 (4)	0.236 (3)	0.000 (0)	7.3 (20)
C(12)	0.301 (2)	0.091 (2)	0.184 (2)	5.3 (10)	C(52)	0.203 (0)	0.723 (0)	0.000 (0)	4.0 (0)
C(21)	0.102 (2)	0.261 (1)	0.109 (2)	4.4 (8)	C(61)	0.323 (4)	0.262 (2)	0.000 (0)	5.9 (16)
C(31)	−0.033 (2)	0.118 (1)	0.115 (2)	3.1 (8)	C(62)	0.427 (3)	0.279 (2)	0.000 (0)	2.8 (10)
C(33)	0.006 (2)	0.100 (2)	0.261 (3)	5.7 (10)	C(41)	0.251 (4)	−0.066 (2)	0.000 (0)	5.1 (14)
C(32)	−0.071 (2)	0.099 (2)	0.196 (3)	6.1 (11)	C(42)	0.349 (3)	−0.097 (2)	0.000 (0)	4.3 (13)
C(22)	0.107 (3)	0.303 (2)	0.182 (3)	8.0 (12)	C(43)	0.416 (4)	−0.045 (3)	0.000 (0)	7.7 (19)
C(23)	0.156 (4)	0.355 (2)	0.163 (4)	13.3 (22)	C(44)	0.150 (2)	0.371 (2)	0.417 (3)	6.2 (11)
C(24)	0.167 (4)	0.280 (3)	0.249 (5)	16.4 (26)	C(63)	0.464 (5)	0.332 (4)	0.000 (0)	12.3 (30)
C(25)	0.024 (3)	0.314 (2)	0.215 (3)	9.9 (17)	C(64)	0.453 (4)	0.256 (3)	0.071 (4)	13.8 (23)

[a] The form of the anisotropic thermal parameter is $\exp[-\frac{1}{4}(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^* + 2B_{13}hla^*c^* + 2B_{23}hkb^*c^*)]$.

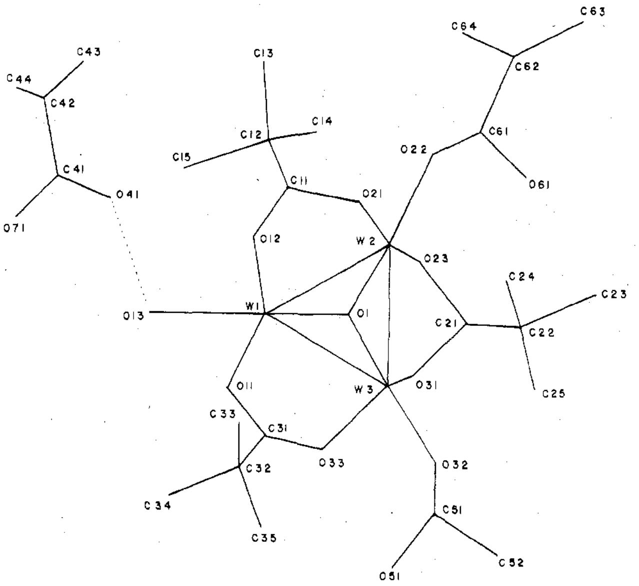

Figure 4. Projection of the asymmetric unit of compound **3** on the 001 plane, showing the atom numbering scheme. Atoms shown are those in or above the plane. Symmetry-related atoms below the plane have primed numbers, e.g., all atoms in the second set of three bridging pivalato groups, the other μ_3-O, (O(1)′), etc.

from 4.0 to 24.0°/min. The scan range was from 1° above to 1° below the 2θ values of the $K\alpha_1$ and $K\alpha_2$ lines. Stationary crystal/counter background counts were taken at each end of the 2θ scan range with a background to scan time ratio of 0.5. Three standard reflections were checked periodically. Crystallographic data and other pertinent information are given in Table II. For each crystal, Lorentz and polarization corrections were applied to the intensity data and for compound **4** the data were also corrected for absorption.

Solution and Refinement of the Structures.[12] The structures of **2** and **3** were solved by the heavy-atom method. A three-dimensional Patterson function yielded the positions of the W atoms. Difference Fourier maps based on the refined positions of the W atoms revealed the positions of the remaining nonhydrogen atoms. The positions and isotropic temperature factors of all nonhydrogen atoms were refined by three full-matrix least-squares cycles. The function minimized during the refinement was $\sum w(|F_o| - |F_c|)^2$, where $w = 4F_o^2/\sigma(F_o^2)^2$. A value of 0.07 was used for p in the calculation of σ.

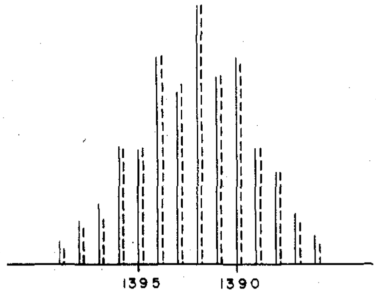

Figure 5. Parent ion multiplet for $[W_3O_2(O_2CCMe_3)_8]$ from compound **3** observed (full lines) in the mass spectrum. The dash lines show the calculated pattern based on the natural isotope distribution.

The final discrepancy indices defined as

$$R_1 = \sum||F_o| - |F_c||/|F_o|$$

$$R_2 = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$$

are listed in Table II. In the last three cycles of refinement the temperature factors of the W atoms and the oxygen atoms in the coordination sphere were refined anisotropically. Refinement was terminated when no parameter shifted by more than 0.6 times its estimated standard deviation. The largest peaks on the final difference Fourier maps were found to be associated with the tungsten atoms.

Intensity data for **4** were corrected for absorption by the empirical ψ-scan method. This was deemed necessary because of the shape and the size of the crystal. The positions of the three tungsten atoms were determined by direct methods using the MULTAN program. The highest peak on the difference Fourier map based on the positions of the three W atoms had coordinates of 0.50, 0.43, 0.75 which places Cs atoms

Table VI. Bond Distances (Å) and Bond Angles (deg) for $\{[W_3O_2(O_2CC(CH_3)_3)_8(H_2O)]\}(CH_3)_3CCOOH$

Bond Distances

W(1)-W(2)	2.773 (3)			O(23)-C(21)	1.28 (3)		
W(1)-W(3)	2.739 (3)	W(2)-W(3)	2.774 (2)	O(31)-C(21)	1.16 (3)		
W(1)-O(1)	2.00 (2)	W(2)-O(1)	1.99 (1)	C(21)-C(22)	1.64 (4)		
W(1)-O(11)	2.10 (2)	W(2)-O(21)	2.15 (2)	C(22)-C(23)	1.61 (6)		
W(1)-O(12)	2.12 (2)	W(2)-O(22)	1.98 (2)	C(22)-C(24)	1.60 (6)		
W(1)-O(13)	2.18 (2)	W(2)-O(23)	2.06 (2)	C(22)-C(25)	1.50 (5)		
W(3)-O(1)	1.96 (2)			O(22)-C(61)	1.00 (6)	O(32)-C(51)	1.12 (6)
-O(31)	2.08 (2)			C(61)-O(61)	1.32 (6)	C(51)-O(51)	1.35 (7)
-O(32)	1.85 (4)			C(61)-C(62)	1.74 (6)	C(51)-C(52)	1.50 (1)
-O(33)	2.07 (2)			C(62)-C(63)	1.50 (8)		
O(11)-C(31)	1.30 (3)	O(12)-C(11)	1.36 (3)	C(62)-C(64)	1.41 (6)		
O(33)-C(31)	1.22 (3)	O(21)-C(11)	1.22 (3)	O(71)-C(41)	1.31 (5)		
C(31)-C(32)	1.60 (4)	C(11)-C(12)	1.58 (4)	C(41)-O(41)	1.27 (5)		
C(32)-C(33)	1.66 (4)	C(12)-C(13)	1.64 (5)	C(41)-C(42)	1.78 (6)		
C(32)-C(34)	1.58 (4)	C(12)-C(14)	1.50 (5)	C(42)-C(43)	1.74 (6)		
C(32)-C(35)	1.54 (4)	C(12)-C(15)	1.59 (5)	C(42)-C(44)	1.62 (4)		

Bond Angles

W(2)-W(1)-W(3)	60.44 (5)			O(1)-W(3)-O(31)′	128.6 (7)		
-O(1)	45.7 (5)	W(3)-W(1)-O(1)	45.7 (5)	O(1)-W(3)-O(32)	142.8 (6)		
-O(11)	123.5 (5)	-O(11)	82.9 (5)	O(1)-W(3)-O(33)	76.9 (7)		
-O(12)	85.8 (5)	-O(12)	127.6 (6)	O(1)-W(3)-O(33)′	130.0 (7)	O(31)-W(3)-O(33)′	148.8 (7)
-O(13)	147.3 (7)	-O(13)	152.3 (7)	O(31)-W(3)-O(31)′	85 (1)	O(32)-W(3)-O(33)	78.5 (8)
O(1)-W(1)-O(1)′	72.2 (9)			O(31)-W(3)-O(32)	70.4 (9)	O(33)-W(3)-O(33)′	93 (1)
-O(11)	77.8 (7)			O(31)-W(3)-O(33)	82.9 (8)		
-O(11)′	127.8 (7)			W(1)-O(1)-W(2)	88.2 (8)		
-O(12)	81.9 (8)			W(1)-O(1)-W(3)	87.5 (7)		
-O(12)′	130.0 (8)			W(2)-O(1)-W(3)	89.3 (7)		
-O(13)	143.8 (5)			W(1)-O(11)-C(31)	121 (2)	W(1)-O(12)-C(11)	117 (2)
O(11)-W(1)-O(11)′	88.8 (9)			W(3)-O(33)-C(31)	123 (2)	W(2)-O(21)-C(11)	123 (2)
O(11)-W(1)-O(12)	85.0 (6)			O(11)-C(31)-O(33)	127 (3)	O(12)-C(11)-O(21)	130 (3)
O(11)-W(1)-O(12)′	147.5 (7)			O(11)-C(31)-C(32)	110 (3)	O(12)-C(11)-C(12)	113 (3)
O(11)-W(1)-O(13)	77.4 (7)			O(33)-C(31)-C(32)	122 (3)	O(21)-C(11)-C(12)	116 (3)
O(12)-W(1)-O(12)′	83.4 (9)			C(31)-C(32)-C(33)	105 (2)	C(11)-C(12)-C(13)	99 (3)
O(12)-W(1)-O(13)	70.1 (8)			C(31)-C(32)-C(34)	112 (3)	C(11)-C(12)-C(14)	107 (3)
W(1)-W(2)-W(3)	59.18 (9)			C(31)-C(32)-C(35)	104 (3)	C(11)-C(12)-C(15)	106 (3)
-O(1)	46.0 (5)	W(3)-W(2)-O(1)	45.0 (5)	C(33)-C(32)-C(34)	116 (3)	C(13)-C(12)-C(14)	100 (3)
-O(21)	82.8 (5)	-O(21)	123.7 (5)	C(33)-C(32)-C(35)	106 (3)	C(13)-C(12)-C(15)	101 (3)
-O(22)	146.1 (8)	-O(22)	154.7 (8)	C(34)-C(32)-C(35)	112 (3)	C(14)-C(12)-C(15)	138 (4)
-O(23)	120.6 (6)	-O(23)	80.4 (6)	W(2)-O(22)-C(61)	130 (4)	W(2)-O(23)-C(21)	123 (2)
O(1)-W(2)-O(1)′	73 (1)			O(22)-C(61)-O(61)	149 (6)	W(3)-O(31)-C(21)	119 (2)
-O(21)	78.7 (8)			O(22)-C(61)-C(62)	120 (6)	O(23)-C(21)-O(31)	132 (3)
-O(21)′	127.7 (7)			O(61)-C(61)-C(62)	91 (4)	O(23)-C(21)-C(22)	110 (3)
-O(22)	143.5 (5)			C(61)-C(62)-C(63)	128 (4)	O(31)-C(21)-C(22)	117 (3)
-O(23)	74.6 (7)			C(61)-C(62)-C(64)	100 (3)	C(21)-C(22)-C(23)	116 (3)
-O(23)′	124.5 (8)			C(63)-C(62)-C(64)	106 (3)	C(21)-C(22)-C(24)	109 (3)
O(21)-W(2)-O(21)′	86 (1)			C(64)-C(62)-C(64)′	117 (5)	C(21)-C(22)-C(25)	111 (3)
-O(22)	72.6 (7)			W(3)-O(32)-C(51)	145 (5)	C(23)-C(22)-C(24)	99 (4)
-O(23)	86.8 (8)			O(32)-C(51)-O(51)	133 (7)	C(23)-C(22)-C(25)	110 (4)
-O(23)′	154.3 (8)			O(32)-C(51)-C(52)	134 (7)	C(24)-C(22)-C(25)	110 (4)
O(22)-W(2)-O(23)	81.7 (8)			O(51)-C(51)-C(52)	93 (6)		
O(23)-W(2)-O(23)′	89 (1)			O(41)-C(41)-O(71)	122 (5)		
W(1)-W(3)-W(2)	60.38 (9)			O(41)-C(41)-C(42)	123 (5)		
-O(1)	46.7 (5)	W(2)-W(3)-O(1)	45.7 (5)	O(71)-C(41)-C(42)	115 (4)		
-O(31)	126.0 (6)	-O(31)	84.4 (5)	C(41)-C(42)-C(43)	101 (4)		
-O(32)	154 (1)	-O(32)	145 (1)	C(41)-C(42)-C(44)	104 (2)		
-O(33)	83.9 (5)	-O(33)	122.6 (5)	C(43)-C(42)-C(44)	112 (2)		
O(1)-W(3)-O(1)′	74 (1)			C(44)-C(42)-C(44)′	120 (4)		
O(1)-W(3)-O(31)	79.2 (8)						

at the fourfold special position (e) of the space group. The other four Cs atoms which are required to be present in order to achieve electroneutrality were found to occupy the (eightfold) general position with an occupancy factor of 0.5. Otherwise, the solution and refinement of the whole structure proceeded essentially as described for **2** and **3**.

Details of data collection and solution and refinement of the structure of **1** will appear elsewhere.[13]

Results

Compound 1. The detailed structural information for this compound will, as already noted, be presented elsewhere; only the average values of important types of bond lengths and angles will be presented here for comparison with the analogous results on the other three compounds. The structure of the $[W_3O_2(O_2CCH_3)_6(H_2O)_3]^{2+}$ unit in **1** is shown in Figure 2. This cluster unit resides on a crystallographic twofold axis collinear with the W(1)–O(1) bond.

Compound 2. A drawing of the cluster cation is presented in Figure 3. The atom numbering scheme is indicated. The β carbon atoms of each C_2H_5 group, which are omitted from this drawing for the sake of clarity, bear numbers 1 unit higher than those of the α carbon atoms to which they are attached; thus C(62) is attached to C(61), and so forth. The positional and thermal parameters for all atoms in **2** are listed in Table III, while Table IV gives the important bond lengths and angles. In this compound no crystallographic symmetry is imposed upon the $[W_3O_2(O_2CC_2H_5)_6(H_2O)_3]^{2+}$ unit.

Compound 3. The atomic positional and thermal parameters are listed in Table V and the bond distances and angles are given in Table VI. Figure 4 shows the numbering scheme. This structure is less fully refined than the others because it

Table VII. Positional and Thermal Parameters for $Cs[W_3O_2(O_2CCH_3)_9]^a$

atom	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
W(1)	0.22593 (5)	0.24116 (7)	0.65005 (4)	1.84 (4)	1.74 (4)	1.98 (4)	−0.04 (3)	−0.07 (3)	0.12 (3)
W(2)	0.33866 (5)	0.34460 (7)	0.62955 (4)	1.73 (4)	1.79 (4)	2.05 (4)	0.08 (4)	0.05 (3)	0.02 (3)
W(3)	0.22078 (5)	0.44200 (7)	0.61249 (4)	1.90 (4)	1.78 (4)	2.08 (4)	0.23 (3)	0.06 (3)	0.09 (3)
CS(1)	0.5000 (0)	0.4411 (3)	0.7500 (0)	3.9 (1)	6.6 (2)	3.4 (1)	−0.3 (4)	0.2 (1)	−0.7 (2)
CS(2)	0.5272 (3)	0.0278 (5)	0.5968 (4)	6.4 (3)	7.6 (3)	18.4 (6)	−0.1 (3)	−2.0 (4)	−1.5 (4)
O(1)	0.2588 (7)	0.310 (1)	0.5869 (5)	2.9 (8)	2.1 (6)	0.3 (6)	0.1 (6)	−0.2 (5)	0.4 (5)
O(2)	0.2351 (8)	0.125 (1)	0.3262 (6)	2.7 (7)	1.4 (6)	2.6 (7)	−0.4 (6)	0.7 (6)	0.2 (6)
O(29)	0.3480 (8)	0.045 (1)	0.3301 (6)	2.3 (7)	3.9 (8)	3.2 (7)	0.1 (7)	1.8 (6)	−0.8 (7)
O(8)	0.2432 (14)	0.970 (2)	0.7003 (13)	8 (2)	5 (1)	14 (2)	3 (1)	−2 (2)	3 (1)
O(11)	0.2301 (8)	0.378 (1)	0.3874 (6)	2.7 (8)	1.8 (6)	2.9 (8)	−0.2 (6)	−0.6 (6)	0.5 (6)
O(12)	0.2789 (8)	0.200 (1)	0.7184 (6)	2.4 (8)	2.6 (7)	1.9 (7)	0.2 (6)	−0.4 (6)	−0.4 (6)
O(13)	0.3438 (7)	0.200 (1)	0.3014 (6)	0.7 (6)	2.6 (7)	3.6 (8)	0.3 (6)	0.1 (6)	0.4 (6)
O(14)	0.3525 (8)	0.277 (1)	0.4052 (6)	2.5 (7)	2.0 (6)	2.9 (7)	−0.4 (6)	0.4 (6)	0.8 (6)
O(15)	0.3237 (8)	0.384 (1)	0.3259 (6)	2.5 (7)	1.8 (6)	3.1 (8)	−1.1 (6)	−1.1 (6)	−0.2 (6)
O(18)	0.4836 (12)	0.208 (2)	0.6552 (12)	5 (1)	6 (1)	12 (2)	2 (1)	2 (1)	2 (1)
O(21)	0.3561 (8)	0.410 (1)	0.5559 (6)	1.9 (7)	2.1 (7)	2.8 (7)	0.1 (6)	0.0 (6)	−0.4 (6)
O(22)	0.3621 (8)	0.204 (1)	0.5954 (6)	2.0 (7)	2.8 (7)	2.2 (7)	0.0 (6)	−0.6 (6)	1.0 (6)
O(23)	0.4366 (8)	0.355 (1)	0.6244 (7)	1.0 (7)	4.3 (9)	5.0 (9)	0.2 (7)	1.4 (6)	−0.1 (8)
O(24)	0.3687 (7)	0.284 (1)	0.7032 (6)	1.6 (7)	3.5 (7)	1.4 (6)	−0.1 (6)	0.1 (6)	−0.3 (6)
O(25)	0.6349 (8)	0.513 (1)	0.3380 (7)	3.1 (8)	2.6 (7)	3.0 (8)	−0.7 (7)	0.4 (7)	−0.9 (6)
O(31)	0.6672 (9)	0.067 (1)	0.5917 (7)	4.1 (9)	3.0 (7)	4.3 (8)	1.4 (7)	1.7 (7)	2.1 (7)
O(32)	0.7390 (8)	0.511 (1)	0.4567 (6)	3.7 (8)	2.5 (7)	1.3 (6)	0.1 (7)	0.7 (6)	−0.4 (6)
O(33)	0.7270 (9)	0.436 (1)	0.3500 (6)	3.7 (8)	1.7 (6)	3.2 (7)	0.2 (6)	0.9 (7)	−1.1 (6)
O(34)	0.3563 (8)	0.118 (1)	0.4353 (6)	3.5 (8)	2.0 (6)	2.8 (7)	1.1 (6)	−0.2 (7)	0.3 (6)
O(41)	0.6325 (16)	0.160 (2)	0.5211 (9)	15 (2)	6 (1)	5 (1)	3 (1)	−5 (1)	−1 (1)

atom	x	y	z	B, Å^2	atom	x	y	z	B, Å^2
O(42)	0.468 (1)	0.366 (2)	0.333 (1)	7.4 (6)	C(14)	0.427 (1)	0.238 (2)	0.4750 (11)	3.3 (5)
O(43)	0.521 (1)	0.175 (2)	0.363 (1)	7.2 (6)	C(15)	0.660 (1)	0.498 (2)	0.5258 (11)	3.7 (6)
O(44)	0.605 (1)	0.282 (2)	0.438 (1)	7.6 (7)	C(16)	0.671 (1)	0.437 (2)	0.3324 (9)	2.0 (4)
C(1)	0.542 (2)	0.322 (3)	0.5946 (16)	7.2 (10)	C(18)	0.649 (1)	0.968 (2)	0.4371 (10)	2.8 (5)
C(5)	0.368 (1)	0.530 (2)	0.3068 (9)	2.2 (5)	C(19)	0.637 (1)	0.208 (2)	0.7142 (11)	3.5 (6)
C(6)	0.591 (1)	0.083 (2)	0.2441 (11)	3.8 (6)	C(21)	0.317 (1)	0.464 (2)	0.5294 (9)	2.1 (4)
C(7)	0.679 (1)	0.514 (2)	0.6884 (12)	3.8 (6)	C(25)	0.335 (1)	0.233 (2)	0.7311 (10)	2.9 (5)
C(10)	0.363 (1)	0.113 (2)	0.2970 (9)	2.2 (5)	C(30)	0.645 (1)	0.343 (2)	0.3066 (10)	3.3 (6)
C(12)	0.484 (1)	0.289 (2)	0.6271 (10)	3.1 (5)	C(32)	0.375 (1)	0.206 (2)	0.4356 (9)	2.1 (4)
C(13)	0.327 (1)	0.127 (2)	0.5920 (9)	2.1 (4)	C(45)	0.726 (2)	0.221 (3)	0.5718 (15)	6.1 (9)
					C(46)	0.669 (2)	0.148 (2)	0.5578 (12)	4.7 (7)

[a] The form of the anisotropic thermal parameter is $\exp[-{}^1/_4(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^* + 2B_{13}hla^*c^* + 2B_{23}hkb^*c^*)]$.

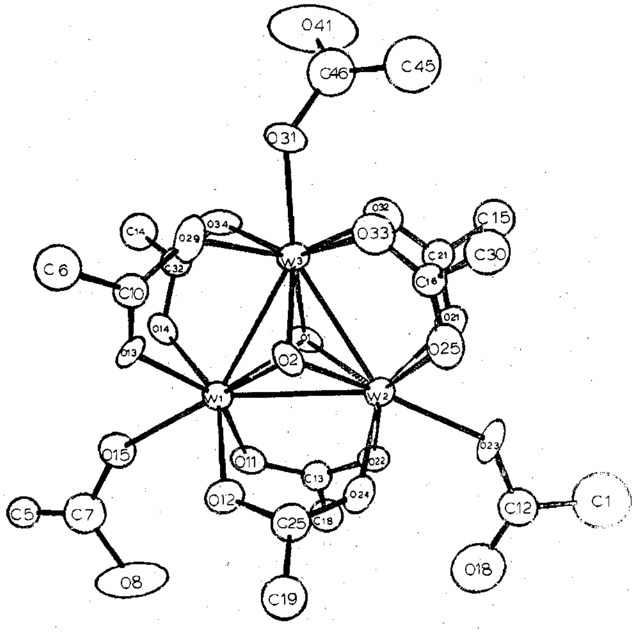

Figure 6. $[W_3O_2(O_2CCH_3)_6(OCOCH_3)_3]^-$ anion in compound **4**. Atoms are represented by ellipsoids or spheres of thermal vibration scaled to enclose 50% of their electron density and the numbering scheme used in Tables VII and VIII is defined.

is larger and less tractable, but it is not significantly different from the others in any essential respect.

In this case the cluster species is a neutral since the three radial coordination sites of the $[W_3O_2(O_2CC(CH_3)_3)_6]^{2+}$ unit are occupied by two pivalate anions and one water molecule, O(13) in Figure 4. The crystalline compound also contains one molecule of pivalic acid per W_3 unit and this, as shown in Figure 4, is hydrogen bonded to the coordinated water molecule. The $[W_3O_2(O_2CC(CH_3)_3)_6(O_2CC(CH_3)_3)_2]$ molecule is stable enough to be observed mass spectrometrically in the vapor at ca. 200 °C. Figure 5 shows the structure of the parent ion multiplet.

In the crystal, both the cluster complex and the pivalic acid molecule lie on a crystallographic mirror plane. The three tungsten atoms lie in the plane, as do a number of C and O atoms. In Figure 4 the methyl carbon atoms attached to C(52) are not shown because they are disordered and no model that refined satisfactorily was found. A complete list of the atoms that lie in the mirror plane at $Z = 0$ is as follows: W(1), W(2), W(3), O(13), O(22), O(32), O(41), O(51), O(61), C(71), C(51), C(52), C(61), C(62), C(41), C(42), C(43), C(63).

Compound 4. The atomic parameters are given in Table VII and the bond lengths and angles in Table VIII. Figure 6 shows the $[W_3O_2(O_2CCH_3)_6(O_2CCH_3)_3]^-$ anion, which has no crystallographic symmetry, and defines the numbering scheme.

The essential similarity of all of the structures is emphasized by the listing in Table IX of average values of the important and characteristic interatomic distances and angles for each of the structures. The averaging was done in accord with the requirements of ideal D_{3h} symmetry (e.g., three equivalent W–W distances, six equivalent W–(μ_3-O) distances, and so

Table VIII. Bond Distances (Å) and Bond Angles (deg) for $Cs[W_3O_2(O_2CCH_3)_9]$

Bond Distances

W(1)-W(2)	2.763 (1)			O(11)–C(13)	1.31 (2)	O(12)–C(25)	1.28 (2)
W(1)-W(3)	2.779 (1)	W(2)-W(3)	2.765 (1)	O(22)–C(13)	1.24 (2)	O(24)–C(25)	1.21 (2)
W(1)–O(1)	1.99 (1)	W(2)–O(1)	1.99 (1)	C(13)–C(18)	1.53 (3)	C(25)–C(19)	1.52 (3)
W(1)–O(2)	2.00 (1)	W(2)–O(2)	1.98 (1)	O(25)–C(16)	1.25 (2)	O(21)–C(21)	1.25 (2)
W(1)–O(11)	2.06 (1)	W(2)–O(21)	2.11 (1)	O(33)–C(16)	1.22 (2)	O(32)–C(21)	1.26 (2)
W(1)–O(12)	2.09 (1)	W(2)–O(22)	2.09 (1)	C(16)–C(30)	1.47 (3)	C(21)–C(15)	1.58 (3)
W(1)–O(13)	2.09 (1)	W(2)–O(23)	2.04 (1)	O(29)–C(10)	1.27 (2)	O(14)–C(32)	1.28 (2)
W(1)–O(14)	2.11 (1)	W(2)–O(24)	2.10 (1)	O(13)–C(10)	1.21 (2)	O(34)–C(32)	1.22 (2)
W(1)–O(15)	2.03 (1)	W(2)–O(25)	2.09 (1)	C(10)–C(6)	1.50 (3)	C(32)–C(14)	1.50 (3)
W(3)–O(1)	2.01 (1)	W(3)–O(32)	2.08 (1)				
W(3)–O(2)	1.98 (1)	W(3)–O(33)	2.12 (1)				
W(3)–O(29)	2.10 (1)	W(3)–O(34)	2.11 (1)				
W(3)–O(31)	2.03 (1)						

O(8)-C(7)	1.47 (3)	O(18)-C(12)	1.27 (3)	O(31)–C(46)	1.34 (3)
O(15)-C(7)	1.38 (3)	O(23)-C(12)	1.31 (2)	O(41)–C(46)	1.19 (3)
C(7)-C(5)	1.14 (3)	C(12)–C(1)	1.54 (4)	C(46)–C(45)	1.54 (4)

Bond Angles

W(2)-W(1)-W(3)	59.86 (3)			O(23)-W(2)–O(24)	80.1 (5)		
–O(1)	46.0 (3)	W(3)-W(1)–O(1)	46.2 (3)	–O(25)	74.1 (5)	O(24)-W(2)–O(25)	85.0 (5)
–O(2)	45.7 (3)	–O(2)	45.3 (4)	W(1)-W(3)-W(2)	59.78 (3)		
-O(11)	83.3 (3)	–O(11)	123.9 (3)	–O(1)	45.7 (3)	W(2)-W(3)–O(1)	45.9 (3)
-O(12)	82.4 (4)	–O(12)	122.7 (3)	–O(2)	45.9 (3)	–O(2)	45.7 (4)
–O(13)	123.1 (3)	–O(13)	81.1 (3)	–O(29)	81.4 (4)	–O(29)	123.3 (4)
–O(14)	123.9 (3)	–O(14)	82.0 (3)	–O(31)	148.8 (4)	–O(31)	151.3 (4)
-O(15)	152.8 (4)	–O(15)	147.4 (4)	–O(32)	124.1 (3)	–O(32)	83.4 (4)
O(1)-W(1)-O(2)	73.0 (5)			–O(33)	122.3 (4)	–O(33)	81.0 (4)
-O(11)	77.7 (5)	O(2)-W(1)–O(11)	128.0 (5)	–O(34)	82.6 (3)	–O(34)	124.1 (3)
-O(12)	127.3 (5)	–O(12)	77.3 (5)	O(1)-W(3)–O(2)	73.0 (5)		
-O(13)	126.0 (5)	–O(13)	77.4 (5)	–O(29)	125.7 (5)	O(2)-W(3)–O(29)	77.6 (5)
-O(14)	78.0 (5)	–O(14)	126.0 (5)	–O(31)	144.9 (5)	–O(31)	142.1 (6)
–O(15)	143.1 (5)	–O(15)	143.7 (5)	–O(32)	78.4 (4)	–O(32)	127.9 (5)
O(11)-W(1)–O(12)	88.2 (5)			–O(33)	125.8 (5)	–O(33)	76.4 (5)
–O(13)	152.1 (5)	O(12)-W(1)–O(13)	87.0 (5)	–O(34)	78.2 (5)	–O(34)	127.2 (5)
–O(14)	87.0 (5)	-O(14)	152.3 (5)	O(29)-W(3)–O(31)	74.8 (5)		
-O(15)	77.2 (5)	-O(15)	78.2 (5)	–O(32)	151.8 (5)	O(31)-W(3)–O(32)	77.0 (5)
O(13)-W(1)-O(14)	84.7 (5)			–O(33)	88.5 (5)	–O(33)	77.2 (6)
-O(15)	74.9 (5)	O(14)-W(1)–O(15)	74.2 (5)	–O(34)	85.1 (5)	–O(34)	75.7 (6)
W(1)-W(2)-W(3)	60.36 (3)			O(32)-W(3)–O(33)	86.9 (5)		
W(1)-W(2)-O(1)	46.0 (3)	W(3)-W(2)–O(1)	46.5 (3)	–O(34)	86.5 (5)	O(33)-W(3)–O(34)	152.9 (5)
–O(2)	46.2 (3)	-O(2)	45.6 (4)	W(1)–O(1)-W(2)	88.0 (4)	W(1)–O(2)-W(2)	88.0 (5)
–O(21)	123.1 (3)	–O(21)	82.0 (3)	-W(3)	88.1 (4)	-W(3)	88.7 (5)
-O(22)	82.4 (3)	–O(22)	123.6 (3)	W(2)-O(1)-W(3)	87.5 (4)	W(2)–O(2)-W(3)	88.7 (5)
–O(23)	153.3 (4)	–O(23)	146.2 (4)	W(1)–O(11)–C(13)	125 (1)	W(1)–O(12)–C(25)	124 (1)
-O(24)	82.4 (3)	–O(24)	122.3 (3)	W(2)–O(22)–C(13)	126 (1)	W(2)–O(24)–C(25)	125 (1)
–O(25)	124.3 (4)	–O(25)	82.5 (4)	O(11)–C(13)–O(22)	123 (2)	O(12)–C(25)–O(24)	125 (2)
O(1)-W(2)–O(2)	73.3 (5)			-C(18)	118 (2)	–C(19)	118 (2)
–O(21)	77.0 (5)	O(2)-W(2)–O(21)	126.6 (5)	O(22)–C(13)–C(18)	118 (2)	O(24)–C(25)–C(19)	117 (2)
–O(22)	77.1 (5)	–O(22)	127.7 (5)	W(2)–O(25)–C(16)	127 (1)	W(2)–O(21)–C(21)	125 (1)
–O(23)	141.5 (5)	–O(23)	144.9 (6)	W(3)–O(33)–C(16)	128 (1)	W(3)–O(32)–C(21)	125 (1)
–O(24)	127.6 (5)	–O(24)	76.6 (5)	O(25)–C(16)–O(33)	122 (2)	O(21)–C(21)–O(32)	125 (2)
–O(25)	127.8 (5)	–O(25)	78.0 (5)	O(25)–C(16)–C(30)	119 (2)	O(21)–C(21)–C(15)	116 (2)
O(21)-W(2)–O(22)	85.9 (4)			O(33)–C(16)–C(30)	119 (2)	O(32)–C(21)–C(15)	119 (2)
–O(23)	72.8 (5)	O(22)-W(2)–O(23)	77.3 (5)	W(3)–O(29)–C(10)	127 (1)	W(3)–O(34)–C(32)	126 (1)
-O(24)	152.9 (5)	-O(24)	89.1 (5)	W(1)–O(13)–C(10)	130 (1)	W(1)–O(14)–C(32)	125 (1)
-O(25)	86.7 (5)	-O(25)	151.3 (5)	O(29)-C(10)–O(13)	120 (2)	O(34)–C(32)–O(14)	125 (2)
				O(29)–C(10)–C(6)	118 (2)	O(34)–C(32)–C(14)	119 (2)
				O(13)–C(10)–C(6)	122 (2)	O(14)–C(32)–C(14)	117 (2)

W(1)–O(15)–C(7)	147 (1)	W(2)-O(23)–C(12)	135 (1)	W(3)–O(31)–C(46)	139 (1)
O(15)–C(7)–O(8)	117 (2)	O(23)-C(12)–O(18)	123 (2)	O(31)–C(46)–O(41)	124 (3)
-C(5)	120 (2)	–C(1)	112 (2)	–C(45)	112 (2)
O(8)–C(7)–C(5)	123 (2)	O(18)–C(12)-C(1)	125 (2)	O(41)–C(46)–C(45)	124 (3)

forth) for each compound. It is clear that the W_3O_2 nucleus is essentially invariant, and the last column of Table IX gives the dimensions of this unit averaged over all four compounds. Because of the requirements of D_{3h} symmetry, the W_3O_2 unit has only two independent variables, which may be any two of the three (W–W distance, W–O distance, W–O–W angle) listed.

Discussion

As far as we know, the central structure found in all of the compounds reported here is of a new type. It is compact and stable and it forms spontaneously under a variety of conditions. It is a true metal atom cluster species since there is a direct bond, evidently of order 1 (see later), between each pair of metal atoms.

The formal oxidation number of tungsten in these compounds is 4+. This is a relatively uncommon oxidation state for tungsten, especially in its aqueous chemistry where all ligand atoms are oxygen atoms. The discovery of these completely stable and easily handled compounds thus opens a new chapter in the aqueous chemistry of the element tungsten.

Table IX. Mean Values[a] of Important Bond Lengths (Å) in $[W_3O_2(O_2CR)_6L_3]^{2+}$ Clusters

bond	compound 1	2	3	4	grand average[b]
W–W	2.747 (1)	2.745 (3)	2.76 (1)	2.769 (6)	2.75 (1)
W–(μ_3-O)	2.000 (6)	2.00 (1)	1.98 (2)	1.99 (1)	2.00 (1)
W–O(μ-RCO_2)	2.07 (1)	2.09 (1)	2.05 (2)	2.10 (1)	2.09 (1)
W–O(H_2O)	2.128 (4)	2.09 (2)	2.18 (5)		2.11 (2)
W–O(RCO_2)			1.91 (2)	2.03 (1)	2.03

[a] Figures in parentheses are mean deviations from the mean.
[b] Grand averages are calculated omitting the less precise values for compound 3.

The stereochemistry of the tungsten atoms in these species is of particular interest. Each tungsten atom has a coordination number of 9, counting the neighboring tungsten atoms as well as the coordinated oxygen atoms. The geometry can be regarded as either a distorted capped square antiprism or a distorted tricapped trigonal prism. In the former, the capped square face is defined by the four oxygen atoms of bridging carboxylato groups and the capping atom is an oxygen atom, from water or from a nonbridging carboxylato anion, occupying one of the three radial sites in the plane of the W_3 triangle. Alternatively, if the coordination geometry is to be considered as a distorted form of the tricapped trigonal prism, the prism is defined by the four oxygen atoms of bridging carboxylato groups together with the two μ_3 oxygen atoms. The capping atoms, lying outside the vertical, rectangular faces of the trigonal prism are the other two tungsten atoms and the peripheral oxygen atom.

Each tungsten atom can be considered to have effectively 18 electrons in its valence shell. Each of the seven coordinated oxygen atoms is regarded as a two-electron donor and each W–W bond as an electron-pair (single) bond. Thus, from the oxygen atoms there are 14 electrons and from the two W–W single bonds there are 4 more.

The assignment of a bond order of unity to the W–W bonds is quite straightforward. That there are bonds between the metal atoms follows from the short distance between them, viz., 2.75 (1) Å. Since the formal oxidation number of the metal atoms is 4+, they have only two d electrons to use in forming W–W bonds, and, therefore, the two bonds formed cannot be more than single bonds.

The $W_3O_2(O_2CR)_6$ unit can be the basis for a varied family of compounds. First, the group R in the carboxylic acid is variable. Among the four compounds reported we have R = CH_3, C_2H_5, and $C(CH_3)_3$. Second, the radial coordination sites may be occupied by neutral or anionic ligands, or a mixture of both, to give cationic clusters as in compounds **1** and **2**, a neutral one as in **3**, or an anionic one as in **4**.

Further exploration of this class of compounds is clearly attractive. In addition to a number of things which can be done with the $W_3O_2(O_2CR)_6$ type cluster, there appears to be considerable promise that $Mo_3O_2(O_2CR)_6$ compounds and mixed Mo–W compounds can be isolated.

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Registry No. **1**, 67661-42-1; **2**, 67584-03-6; **3**, 67584-00-3; **4**, 67583-98-6; $W(CO)_6$, 14040-11-0; $[(C_2H_5)_3NH][W_3(O_2CCH_3)_9O_2]$, 67612-74-2.

Supplementary Material Available: Tables of observed and calculated structure factors for compounds **2**, **3**, and **4** (38 pages). Ordering information is given on any current masthead page.

References and Notes

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(8) Although the term *metal atom cluster* was introduced in 1963,[9] it was first explicitly pointed out that it should be used only for those polynuclear compounds in which "a finite group of metal atoms .... are held together mainly, or at least to a significant extent, by bonds directly between the metal atoms", in 1964.[10] The unfortunate tendency of many authors to call virtually any tri- or polynuclear complex, whether it has M–M bonds or not, a cluster is deplorable since the whole point of introducing the word cluster was to have a clear distinction from the ordinary, Wernerian polynuclear complexes.
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(12) Procedures for preliminary examination of crystals, determination of unit cell dimensions, and the collection and reduction of data were standard ones in this laboratory and have been described elsewhere. See, for example, F. A. Cotton, M. W. Extine, and G. W. Rice, *Inorg. Chem.*, **17**, 176 (1978). All computations were performed on a PDP 11/45 computer at the Molecular Structure Corp., College Station, Texas 77840, using software from the Enraf-Nonius structure determination package.
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