Preparation of the new species $[W_3(\mu_3\text{-}O)(\mu\text{-}Cl)_2(\mu\text{-}O_2CMe)_4Cl_3]^-$ and $[Mo_3(\mu_3\text{-}O)(\mu\text{-}Cl)_4(\mu\text{-}O_2CMe)_2Cl_2(PMe_3)_2]^-$ that bracket, structurally, the very common $M_3(\mu_3\text{-}O)(\mu\text{-}X)_3(\mu\text{-}O_2CR_3)_3L_3$ type of cluster compound

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Abstract

Two new monocapped trinuclear molybdenum and tungsten clusters, which also contain different numbers of bridging halogen atoms and carboxylate groups, have been synthesized and characterized by X-ray diffraction, thus completing an entire series of monocapped trinuclear molybdenum and tungsten clusters with 1–6 bridging carboxylate ligands. Compound **1**, $(Et_4N)[W_3OCl_5(OAc)_4]\cdot 3CH_2Cl_2$, was obtained as a byproduct in the reaction of $(Et_4N)_3[W_2Cl_9]$ with acetic acid and acetic anhydride. Crystallographic data: space group $P2_12_12_1$, $a=12.795(3)$, $b=15.685(3)$, $c=19.436(3)$ Å, $V=3901(1)$ Å^3, $Z=4$, $R=0.037$. The W–W distances are 2.7280(7), 2.5754(8) and 2.5715(8) Å. The average oxidation state of the tungsten atoms is +3.33. Compound **2**, $(Et_4N)[Mo_3OCl_6(OAc)_2(PMe_3)_2]$, was synthesized by the reaction of $(Et_4N)[Mo_3OCl_6(OAc)_3]$ with Me_3SiCl and PMe_3 in THF. Crystallographic data: space group $Pna2_1$, $a=27.459(7)$, $b=13.660(5)$, $c=18.524(5)$ Å, $V=6948$ Å^3, $Z=8$, $R=0.052$. The Mo–Mo distances are 2.627(4), 2.546(3) and 2.631(6) Å. The entire series of monocapped trinuclear molybdenum and tungsten clusters with 0–6 μ-CH_3CO_2 groups is reviewed.

Introduction

There is, in principle, a series of seven structural prototypes for equilateral triangular $M_3(\mu_3\text{-}Y)$ based cluster compounds (generally, though not necessarily, Y is an oxygen atom). The central member, which contains a $M_3(\mu_3\text{-}Y)(\mu\text{-}X)_3(\mu\text{-}O_2CR)_3$ core, is most common [1]. The end members, one of which has six μ-O_2CR groups [2] and the other one no μ-O_2CR groups [3], are also known. Of the four possible intermediate structures, one has only a single example, i.e. the $[W_3(\mu_3\text{-}O)(\mu\text{-}O_2CCH_3)_5(\mu\text{-}OMe)(H_2O)_3]^{2+}$ ion [2a]. The entire series of prototype structures is shown schematically in Fig. 1 and opposite to each prototype structures is shown one example of a corresponding real compound. Two of these real examples have only recently been obtained in this laboratory and are described here. It will be seen that with the addition of these two new species, each member of the entire set of seven prototype structures is now represented by at least one real compound.

It should be stressed at the outset that we are thinking here in terms of structure only, and therefore there are two forms of heterogeneity in the compounds we are classifying structurally. (1) The identity of the μ_3-Y and μ-X atoms varies considerably, with O, CR, S, Cl, Br and OR, being possible occupants of these two types of structural position. (2) The number of cluster electrons can vary, with 6, 8 or even 9 being the preferred number depending on the identities of Y and X [5].

Experimental

As a precautionary measure because of possible instability of intermediates, all preparations were carried out under an atmosphere of argon, and standard Schlenk and vacuum line techniques were used. Solvents were dried and deoxygenated by refluxing over appropriate reagents before use. Acetic acid and acetic anhydride were purchased from Aldrich Co. Starting material $(Et_4N)[Mo_3OCl_6(OAc)_3]$ was prepared by the literature method [1c].

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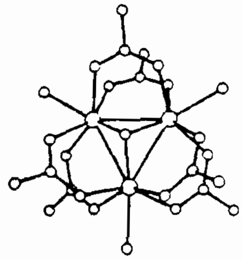
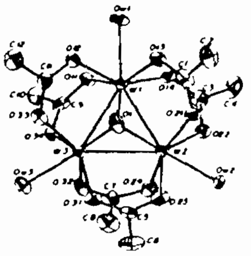


$M_3(O_2CR)_6$



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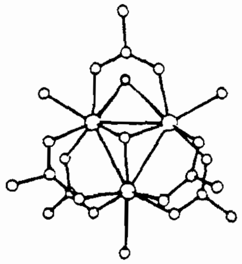

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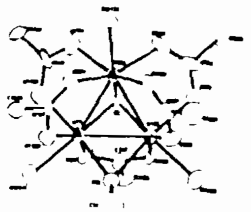

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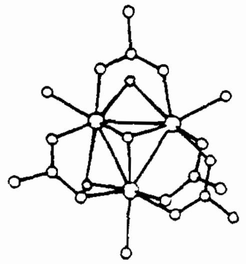

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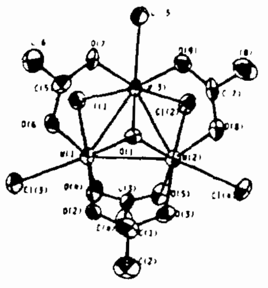

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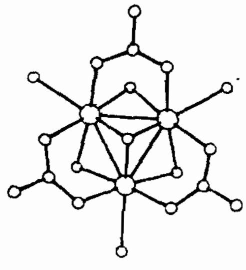
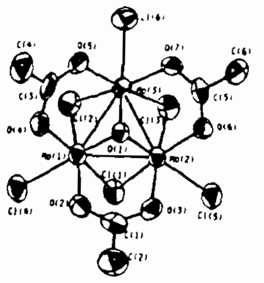


$M_3X_3(O_2CR)_3$



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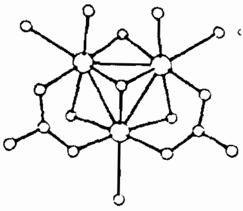
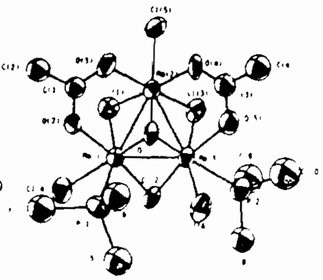


$M_3X_3(O_2CR)_2$



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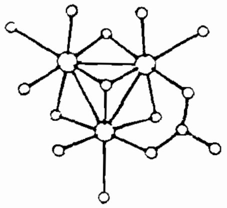
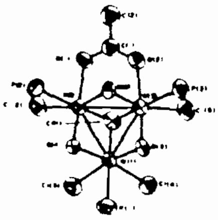


$M_3X_3(O_2CR)$



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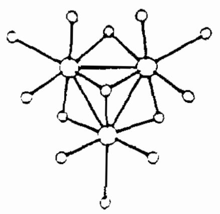
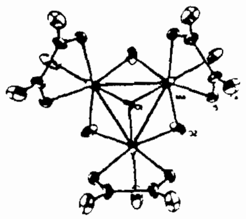


M_3X_3



Compound 7

Fig. 1. Seven prototype structures containing different numbers of bridging carboxylate ligands and a real example of each one. Compound 1: $[W_3O(OAc)_6(H_2O)_3]ZnCl_4\cdot 4H_2O$ [2a]. Compound 2: $[W_3O(OAc)_5(OMe)(H_2O)_3]ZnCl_4$ $7H_2O$ [2a]. Compound 3: $(Et_4N)[W_3OCl_5(OAc)_4]\cdot 3CH_2Cl_2$ (**1**). Compound 4: $(Bu_4N)[Mo_3OCl_6(OAc)_3]\cdot Me_2CO$ [1f]. Compound 5: $(Et_4N)[Mo_3OCl_6(OAc)_2(PMe_3)_2]$ (**2**). Compound 6: $W_3O_3Cl_5(OAc)(PBu_3)_3$ $0.5C_7H_8$ [4]. Compound 7. $Cs_3[Mo_3O_4(C_2O_4)_3(H_2O)_3]CF_3SO_3\cdot 3H_2O$ [3a].

Preparation of $(Et_4N)_3[W_2Cl_9]$

$(Et_4N)_3[W_2Cl_9]$ was prepared by electrolysis of $Na_2WO_4 \cdot 2H_2O$ with a minor modification of the literature method [6]. Na_2WO_4 (25 g) was dissolved in water (200 ml) and the solution was slowly added to an electrolytic cell which contained concentrated hydrochloric acid (300 ml) at 0 °C with rapid stirring. A slow flow of anhydrous hydrogen chloride 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 solution was formed. Then three molar equivalents of Et_4NCl were added. The mixture was then filtered, the filtrate was evaporated to dryness, and the solid was stored in a dry box.

Preparation of $(Et_4N)[W_3OCl_5(OAc)_4] \cdot 3CH_2Cl_2$ (1)

$(Et_4N)_3[W_2Cl_9]$ (10.0 g, 9.29 mmol) was placed in a three-neck flask and allowed to react with a mixture of acetic acid (60 ml) and acetic anhydride (15 ml) at 80 °C for 2 days. A mixture of a light brown solution and a red–purple precipitate was formed. The mixture was separated, the filtrate discarded, and the red–purple precipitate was treated with acetone. A purple solution and a red–brown precipitate were formed. Following filtration, purple crystals were obtained from the filtrate by layering with hexane. These were characterized by X-ray crystallography as $(Et_4N)[W_3OCl_6(OAc)_3] \cdot Me_2CO$ (yield *c.* 43%) [1c]. The red-brown precipitate was treated with dichloromethane to afford a red–brown solution, which was filtered and layered with hexane. Dark blue crystals were obtained after solvent diffusion. Yield *c.* 10%. These crystals were identified later by X-ray diffraction to be $(Et_4N)[W_3OCl_5(OAc)_4] \cdot 3CH_2Cl_2$ (**1**).

Preparation of $(Et_4N)[Mo_3OCl_6(OAc)_2(PMe_3)_2]$ (2)

The reaction of $(Et_4N)[Mo_3OCl_6(OAc)_3]$ (1.00 g, 1.22 mmol) with three molar equivalents of chlorotrimethylsilane (0.47 ml, 3.66 mmol) and trimethylphosphine (0.36 ml, 3.66 mmol) in 25 ml of THF resulted in the formation of a brown precipitate. After filtration the brown precipitate was dissolved in 20 ml of acetone. The acetone solution was then filtered and layered with hexane. Dark brown crystals, which have the formula as shown above, appeared after diffusion was complete. Yield *c.* 52%.

X-ray crystallography for $(Et_4N)[W_3OCl_5(OAc)_4] \cdot 3CH_2Cl_2$ (1)

A dark blue crystal suitable for X-ray diffraction experiments was mounted on the top of a quartz fiber. X-ray diffraction intensity data for the crystal were collected on an Enraf-Nonius CAD4 diffractometer under a nitrogen stream at −53 °C. The unit cell dimensions were determined from 25 reflections. During data collection, three intensity standards were monitored every 2 h, and no decay was observed during a total of 55.3 h of exposure to X-rays. Systematic absences determined the space group as $P2_12_12_1$. Three independent W atoms were found based on the solution of a Patterson function [7]. The remaining non-hydrogen atoms were then located and refined by a combination of least-squares refinements and difference Fourier syntheses. All these non-hydrogen atoms were refined anisotropically except those from an interstitial dichloromethane solvent molecule, which were refined isotropically in the final least-squares refinement.

The final residuals were $R = 0.037$ and $R_w = 0.048$ for the fit of 373 variables to 3642 data with $F_o^2 \geqslant 3\sigma(F_o^2)$. The residuals for the refinement of the alternative enantiomer were 0.043 and 0.054 for R and R_w, respectively, which was indicative of the correctness of the first choice. Pertinent crystallographic data are listed in Table 1, and the positional and thermal parameters are shown in Table 2.

X-ray crystallography for $(Et_4N)[Mo_3OCl_6(OAc)_2(PMe_3)_2]$ (2)

The intensity data were collected on a Rigaku AFC5R diffractometer. Systematic absences suggested two possible space groups $Pna2_1$ and $Pnma$, and both were tried. The acentric $Pna2_1$ was later fully confirmed by the successful solution and refinement of the structure. Positions of six crystallographically independent Mo atoms were obtained by the Patterson method [7]. The remaining non-hydrogen atoms were then located and refined by alternating least-squares refinements and difference Fourier syntheses. In order to keep an appropriate ratio of reflections (3042) to variables (440), only Mo, Cl, P and O atoms were refined anisotropically, and all the other non-hydrogen atoms were refined isotropically. The final residuals were 0.052 and 0.061 for R and R_w, respectively. No peaks with electron density larger than 0.95 e/Å^3 were found in the final difference Fourier map. Although there were two independent sets of trinuclear Mo molecules in the unit cell, there was no inversion or reflection that could connect them together to comply with a space group of higher symmetry. Crystallographic details are listed in Table 1, and the positional and thermal parameters are compiled in Table 3.

Results and discussion

Crystal structure of $(Et_4N)[W_3OCl_5(OAc)_4] \cdot 3CH_2Cl_2$ (1)

The results of X-ray crystallography show that the crystal structure consists of four formula units of $(Et_4N)[W_3OCl_5(OAc)_4] \cdot 3CH_2Cl_2$ per unit cell. The con-

TABLE 1. Crystallographic data for $(Et_4N)[W_3OCl_5(OAc)_4]\cdot 3CH_2Cl_2$ (**1**) and $(Et_4N)[(Mo_3OCl_6(OAc)_2)(PMe_3)_2]$ (**2**)

	1	**2**
Formula	$W_3Cl_{11}O_9NC_{19}H_{38}$	$Mo_3Cl_6P_2O_5NC_{18}H_{44}$
Formula weight	1366.05	917.04
Space group	$P2_12_12_1$	$Pna2_1$
a (Å)	12.795(3)	27.459(7)
b (Å)	15.685(3)	13.660(5)
c (Å)	19.436(3)	18.524(5)
V (Å^3)	3901(1)	6948(4)
Z	4	8
D_{calc} (g/cm^3)	2.175	1.753
Crystal size (mm)	0.50×0.20×0.25	0.35×0.30×0.20
Radiation	Mo Kα ($\lambda\alpha=0.71073$ Å)	Cu Kα ($\lambda\alpha=1.54184$ Å)
μ(Kα) (cm^{-1})	96.799 (Mo)	144.30 (Cu)
Data collection instrument	Enraf-Nonius CAD4	Rigaku AFC5R
Orientation reflections		
No. range (2θ) (°)	25, 30–37	25, 50–61
Temperature (°C)	−53	20
Scan method	ω–2θ	ω–2θ
Data collection range (2θ) (°)	4–46	4–116
No. unique data, total with $F_o^2>3\sigma(F_o^2)$	4253, 3642	5033, 3046
No. parameters refined	373	440
Transmission factors, max., min.	0.9928, 0.6794	1.0000, 0.7481
R^a, R_w^b	0.037, 0.048	0.052, 0.061
Quality-of-fit indicator^c	1.274	1.309
Largest shift/e.s.d. final cycle	0.002	0.01
Largest peak (e/Å^3)	1.696	0.949

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

figuration of the trinuclear tungsten cluster anion is shown in Fig. 2, and some important bond distances and angles are listed in Table 4. In the cluster anion, on one side of the triangular plane formed by the three tungsten atoms there are an oxygen atom capping the triangle and three acetate groups bridging the three edges of the triangle, while on the other side of the plane two chloride ions and another acetate group bridge the three edges. There are also three terminal chloride ions on the other side of the plane to complete an octahedral coordination environment for each tungsten atom.

It is easily seen from conventional electron bookkeeping that this is a d^8 system, in which the average oxidation state of the metal atoms is +3.33. Compared with the most common M_3X_{13} type [8] trinuclear molybdenum and tungsten clusters that contains three bridging atoms, e.g. $(Et_4N)[W_3(\mu_3\text{-}O)(\mu\text{-}Cl)_3(\mu\text{-}OAc)_3Cl_3]\cdot Me_2CO$ [1c], this structure belongs to an unprecedented M_3X_{14} type, and can be regarded as the product of substitution of one bridging atom in the above M_3X_{13} type compound by a fourth acetate group. As a consequence of such substitution, the coordination environment for each tungsten atom is seriously distorted, as can be seen from a sharp difference in the bond angles formed by the capping oxygen atom and the oxygen atoms of the two carboxylate groups that bridge the same W–W bond (W(1)–(W(2)) (79.0(4)° for O(1)–W(1)–O(2) versus 127.9(4)° for O(1)–W(1)–O(4), and 79.0(4)° for O(1)–W(2)–O(3) versus 129.1(4)° for O(1)–W(2)–O(5)). As another consequence, the former C_{3v} symmetry is reduced to a C_s symmetry, and the metal–metal bonding interactions may, therefore, be divided into two groups. The bond that is bridged by two acetate groups (2.7280(7) Å) is *c.* 0.15 Å longer than the other two that are related to each other by the mirror symmetry and each bridged by only one acetate group (2.5754(8) and 2.5715(8) Å). The average metal–metal bond distance is 2.63[7] Å, which is a little longer than that of the above M_3X_{13} type analogue (2.567[5] Å), which also has 8 d-electrons. Although a greater number of carboxylate groups may result in greater donation of electrons into antibonding metal–metal orbitals, as implied by molecular orbital calculations [9], the substitution of a bulkier carboxylate group for a chloride, and thus an increase in L–L repulsions, may also be expected to play a role. However, in spite of the perturbing effect of the fourth carboxylate group, a total of four pairs of M–M bonding electrons may still be assigned to this M_3X_{14} type structure, consistent with three short metal–metal bond lengths and the availability of four metal-based bonding molecular orbitals [5]. Apart from the perturbation of the metal–metal bonding interactions, other bonding interactions, such as $M\text{–}L_{capping}$, $M\text{–}L_{bridging}$ and $M\text{–}O_{OAc}$

TABLE 2. Positional and equivalent isotropic thermal parameters for $(Et_4N)[W_3OCl_5(OAc)_4]\cdot 3CH_2Cl_2$

Atom	x	y	z	B_{eq}[a] (Å^2)
W(1)	−0.11758(4)	0.83918(4)	0.78698(3)	1.73(1)
W(2)	0.09458(4)	0.83490(4)	0.80040(3)	1.79(1)
W(3)	−0.02733(4)	0.84302(4)	0.90538(3)	1.76(1)
Cl(1)	−0.1613(3)	0.9459(3)	0.8739(2)	2.45(8)
Cl(2)	0.1198(3)	0.9403(3)	0.8915(2)	2.64(8)
Cl(3)	−0.2830(3)	0.8671(3)	0.7294(2)	2.90(9)
Cl(4)	0.2754(3)	0.8568(3)	0.7656(2)	2.99(9)
Cl(5)	−0.0383(3)	0.8989(3)	1.0210(2)	3.00(9)
O(1)	−0.0194(9)	0.7574(6)	0.8297(5)	1.8(2)
O(2)	−0.0882(8)	0.7586(7)	0.7055(5)	1.9(2)
O(3)	0.0844(9)	0.7552(7)	0.7163(6)	2.3(2)
O(4)	−0.0824(9)	0.9443(7)	0.7271(7)	2.9(3)
O(5)	0.0874(9)	0.9412(7)	0.7369(6)	2.7(3)
O(6)	−0.2135(8)	0.7473(7)	0.8330(6)	2.1(2)
O(7)	−0.1434(8)	0.7606(7)	0.9379(6)	2.3(2)
O(8)	0.1713(8)	0.7381(7)	0.8571(6)	2.4(2)
O(9)	0.0711(8)	0.7546(7)	0.9492(5)	2.3(2)
C(1)	0.001(1)	0.7281(9)	0.6892(8)	2.5(3)
C(2)	0.004(2)	0.662(1)	0.634(1)	4.2(4)
C(3)	0.007(1)	0.974(1)	0.7158(8)	2.5(3)
C(4)	0.012(2)	1.055(1)	0.674(1)	4.1(5)
C(5)	−0.207(1)	0.725(1)	0.8945(8)	2.0(3)
C(6)	−0.276(1)	0.655(1)	0.9222(9)	3.4(4)
C(7)	0.141(1)	0.716(1)	0.9149(9)	2.3(3)
C(8)	0.196(2)	0.641(1)	0.9490(9)	3.8(4)
N	0.494(1)	0.6148(9)	0.7194(7)	2.8(3)
C(9)	0.574(2)	0.573(2)	0.672(1)	6.1(7)
C(10)	0.688(2)	0.608(2)	0.683(2)	10(1)
C(11)	0.388(2)	0.576(1)	0.701(1)	5.4(6)
C(12)	0.297(2)	0.611(2)	0.747(2)	6.3(7)
C(13)	0.518(2)	0.599(2)	0.796(1)	5.7(6)
C(14)	0.531(2)	0.499(1)	0.813(1)	4.6(5)
C(15)	0.489(2)	0.715(1)	0.713(2)	6.4(8)
C(16)	0.455(3)	0.739(2)	0.633(2)	7.9(9)
Cl(6)	0.0457(4)	0.6619(4)	1.1349(2)	4.1(1)
Cl(7)	−0.0731(5)	0.5691(4)	1.0319(3)	4.9(1)
C(17)	−0.066(2)	0.665(1)	1.079(1)	3.9(4)
Cl(8)	−0.0883(6)	0.3708(5)	0.9439(4)	6.9(2)
Cl(9)	−0.3041(7)	0.4152(6)	0.9659(4)	8.1(2)
C(18)	−0.219(2)	0.363(2)	0.913(1)	6.7(8)
Cl(10)	0.337(1)	0.583(1)	0.4979(8)	15.7(5)*
Cl(11)	0.158(3)	0.665(2)	0.474(1)	31(1)*
C(19)	0.228(2)	0.577(2)	0.442(2)	12(1)*

[a] Starred atoms were refined isotropically. Anisotropically refined atoms are given in the form of the equivalent isotropic displacement parameter defined as: $(4/3)[a^2\beta_{11}+b^2\beta_{22}+c^2\beta_{33}+ab(\cos\ \gamma)\beta_{12}+ac(\cos\ \beta)\beta_{13}+bc(\cos\ \alpha)\beta_{23}]$.

bond distances, do not seem to have changed significantly.

Crystal structure of $(Et_4N)[Mo_3OCl_6(OAc)_2(PMe_3)_2]$ (2)

X-ray crystallography has revealed another new type of molybdenum trinuclear cluster in $(Et_4N)[Mo_3OCl_6(OAc)_2(PMe_3)_2]$. There are two independent

TABLE 3. Positional and equivalent isotropic thermal parameters for $(Et_4N)[Mo_3OCl_6(OAc)_2(PMe_3)_2]$

Atom	x	y	z	B_{eq}[a] (Å^2)
Mo(1)	0.23493(7)	0.8588(2)	0.141	3.40(6)
Mo(2)	0.29080(8)	0.7317(2)	0.2084(3)	3.34(7)
Mo(3)	0.25753(7)	0.7005(2)	0.0771(2)	3.18(5)
Mo(4)	−0.00023(7)	0.2046(2)	0.2934(2)	3.37(5)
Mo(5)	−0.03707(8)	0.2389(2)	0.1647(3)	3.21(7)
Mo(6)	0.01817(7)	0.3670(2)	0.2281(2)	3.14(5)
Cl(1)	0.2135(3)	0.7888(6)	0.2573(5)	4.6(2)
Cl(2)	0.1731(3)	0.7596(5)	0.0788(7)	4.0(2)
Cl(3)	0.2445(2)	0.5858(6)	0.1780(5)	4.5(2)
Cl(4)	0.2456(3)	0.9791(6)	0.0493(5)	5.5(2)
Cl(5)	0.3068(3)	0.6598(6)	0.3270(5)	5.3(2)
Cl(6)	0.2229(3)	0.5724(6)	−0.0029(5)	5.2(2)
Cl(7)	0.0130(3)	0.0956(6)	0.1917(5)	5.0(2)
Cl(8)	0.0822(3)	0.2725(7)	0.2817(7)	5.0(2)
Cl(9)	0.0361(3)	0.3050(7)	0.1102(5)	5.0(2)
Cl(10)	0.0380(3)	0.0780(6)	0.3692(5)	6.1(2)
Cl(11)	−0.0557(3)	0.1669(7)	0.0467(5)	6.0(2)
Cl(12)	0.0103(3)	0.4836(6)	0.3279(5)	5.3(2)
P(1)	0.1596(3)	0.9688(7)	0.1692(5)	5.2(2)
P(2)	0.2846(3)	0.7687(7)	−0.0431(6)	4.2(2)
P(3)	−0.0249(3)	0.2698(7)	0.4162(6)	4.6(2)
P(4)	0.0899(3)	0.4811(7)	0.1976(5)	5.1(2)
O(1)	0.3001(5)	0.807(1)	0.117(1)	3.3(4)
O(2)	0.2765(7)	0.962(1)	0.206(1)	4.8(5)
O(3)	0.3283(6)	0.857(1)	0.251(1)	4.5(5)
O(4)	0.3530(6)	0.660(1)	0.178(1)	5.1(6)
O(5)	0.3232(6)	0.627(1)	0.067(1)	3.7(5)
O(6)	−0.0461(5)	0.305(1)	0.2595(9)	2.8(4)
O(7)	−0.0674(6)	0.125(1)	0.312(1)	4.1(5)
O(8)	−0.0997(5)	0.166(1)	0.206(1)	3.8(5)
O(9)	−0.0771(6)	0.356(2)	0.127(1)	4.4(5)
O(10)	−0.0265(6)	0.467(1)	0.176(1)	4.2(5)
C(1)	0.312(1)	0.940(2)	0.246(2)	4.3(6)*
C(2)	0.340(1)	1.024(2)	0.277(2)	5.7(8)*
C(3)	0.358(1)	0.626(2)	0.111(2)	3.8(6)*
C(4)	0.406(1)	0.578(2)	0.086(2)	4.5(6)*
C(5)	0.129(1)	1.013(2)	0.091(2)	6.2(8)*
C(6)	0.110(1)	0.929(3)	0.229(3)	9(1)*
C(7)	0.177(1)	1.077(3)	0.217(3)	10(1)*
C(8)	0.236(1)	0.836(3)	−0.098(2)	7.0(9)*
C(9)	0.312(1)	0.671(3)	−0.099(2)	6.2(8)*
C(10)	0.334(1)	0.857(3)	−0.040(2)	5.9(8)*
C(11)	−0.101(1)	0.123(2)	0.264(2)	3.9(6)*
C(12)	−0.149(1)	0.067(2)	0.281(2)	5.1(8)*
C(13)	−0.067(1)	0.447(2)	0.142(2)	4.0(6)*
C(14)	−0.098(1)	0.528(3)	0.107(2)	6.6(9)*
C(15)	0.020(1)	0.312(3)	0.473(2)	6.3(8)*
C(16)	−0.046(1)	0.172(2)	0.478(2)	5.7(8)*
C(17)	−0.079(1)	0.361(3)	0.419(2)	6.0(8)*
C(18)	0.125(1)	0.531(2)	0.267(2)	6.2(8)*
C(19)	0.142(1)	0.413(3)	0.147(3)	10(1)*
C(20)	0.071(2)	0.586(4)	0.150(3)	12(2)*
N(1)	0.5366(6)	0.285(2)	0.861(1)	2.8(4)*
N(2)	0.2898(8)	0.283(2)	0.017(1)	4.5(6)*
C(21)	0.542(1)	0.242(3)	0.788(1)	8(1)*
C(22)	0.521(2)	0.280(3)	0.717(2)	9(1)*
C(23)	0.541(1)	0.202(3)	0.912(2)	11(1)*
C(24)	0.590(1)	0.148(3)	0.912(2)	8(1)*

(continued)

TABLE 3 (*continued*)

Atom	x	y	z	$B_{eq}{}^{a}$ ($Å^2$)
C(25)	0.571(1)	0.367(3)	0.864(2)	12(1)*
C(26)	0.565(1)	0 392(3)	0 944(2)	9(1)*
C(27)	0 4849(7)	0.315(3)	0 866(2)	9(1)*
C(28)	0 442(1)	0 245(3)	0.849(2)	7(1)*
C(29)	0 299(1)	0.341(3)	0.083(2)	9(1)*
C(30)	0.279(2)	0.280(3)	0.147(2)	9(1)*
C(31)	0.243(1)	0.239(3)	−0.006(3)	11(1)*
C(32)	0.195(2)	0.297(5)	−0 004(4)	18(3)*
C(33)	0.326(2)	0.202(3)	0.013(3)	13(2)*
C(34)	0.332(2)	0.149(4)	−0.060(3)	12(2)*
C(35)	0.288(2)	0.349(4)	−0.046(3)	17(2)*
C(36)	0.335(1)	0.406(3)	−0.063(2)	8(1)*

[a] Starred atoms were refined isotropically. Anisotropically refined atoms are given in the form of the equivalent isotropic displacement parameter defined as: $(4/3)[a^2\beta_{11}+b^2\beta_{22}+c^2\beta_{33}+ab(\cos\gamma)\beta_{12}+ac(\cos\beta)\beta_{13}+bc(\cos\alpha)\beta_{23}]$.

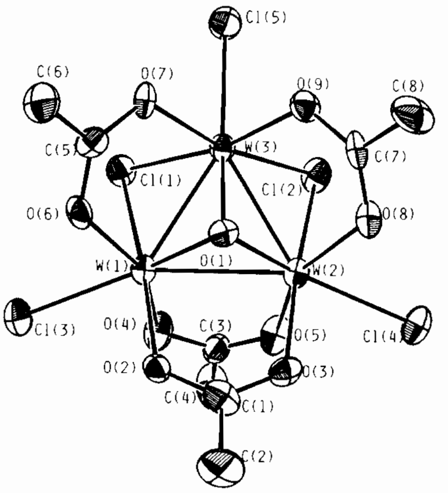


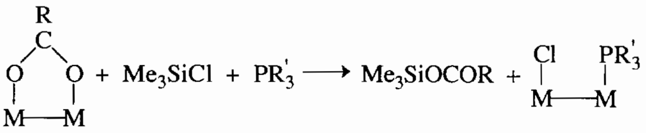
Fig. 2. Configuration of $[W_3OCl_5(OAc)_4]^-$. Thermal ellipsoids are shown at the 50% probability level.

molecules in an asymmetric unit of the unit cell. The configuration of one such molecule is shown in Fig. 3, and the other is basically similar. The central part of the cluster $Mo_3(\mu_3\text{-}O)(\mu\text{-}Cl)_3$ is an apex-deficient cubane-like skeleton. The six coordination sites that are *trans* to the three bridging chloride atoms are occupied by two bridging acetate groups, one chloride atom and a trimethylphosphine, while the three positions that are *trans* to the capping oxygen atom are filled by two chloride atoms and another trimethylphosphine. Although each Mo atom has a distorted octahedral coordination environment, the cluster anion as a whole has no symmetry at all. As a consequence of this lack of symmetry, the lengths of the six metal–metal bonds in these two cluster anions are all different (Table 5), 2.546(3), 2.627(4), 2.631(6), 2.577(4), 2.597(4) and 2.597(4) Å. It can be seen that the three metal atoms altogether have 9 d-electrons and the average oxidation state of the three Mo atoms is +3. The average metal–metal distance in this structure is 2.60[3] Å, which is quite comparable to those of other Mo clusters that also have 9 d-electrons, three bridging chloride atoms, but one more bridging acetate group (2.59–2.61 Å) [1]. However, the one metal–metal bond in each of the two independent molecules that is not bridged by the acetate groups is found to be the shortest (2.546(3) and 2.577(4) Å), which is quite unusual, considering that an acetate group has a small and flexible bite and should engender less L–L repulsion than two separate ligands such as chloride ions or phosphines. Thus the origin of shortening should be sought in the electronic structure. From the results of molecular orbital calculations [4], the ninth electron would enter a degenerate metal–metal antibonding orbital (20e), if C_{3v} symmetry prevailed. With the orbital degeneracy destroyed in this case, localization of the ninth electron in an orbital covering the two acetate-bridged Mo–Mo bonds may cause a small increase in the lengths of these two metal–metal bonds because of the antibonding character of the ninth electron, but no increase in the length of the remaining Mo–Mo bond. Except for the above unusual feature of the metal–metal bond distances, other bond parameters, such as $M\text{–}L_{capping}$, $M\text{–}L_{bridging}$ and $M\text{–}O_{OAC}$ bonds are all consistent with those of the more symmetrical analogues.

Remarks on the preparative chemistry

While we have accomplished the objective of supplying examples of the two previously unrealized prototype structures, it must be admitted that only in one case was this done by designed synthesis. Our isolation of a compound containing a $M_3X_2(O_2CR)_4$ unit, namely $(Et_4N)[W_3OCl_5(OAc)_4]$, was unplanned — a happy accident. Thus, there is still a need for further research to see if a deliberate synthesis of this type system can be devised.

On the other hand, our preparation of $(Et_4N)[Mo_3OCl_6(OAc)_2(PMe_3)_2]$ is an example of a deliberate synthesis based on a rational approach. The idea was to begin with a cluster having these $\mu\text{-}OAc^-$ groups and then replace one by Cl^-, employing the following well-established type of reaction [10]:



$$\underset{M\text{—}M}{\overset{R\\C}{O\quad O}} + Me_3SiCl + PR'_3 \longrightarrow Me_3SiOCOR + \underset{M\text{——}M}{\overset{Cl\qquad PR'_3}{|\qquad\quad |}}$$

This chemistry was partly successful, but the actual reaction was more complicated. The OAc group was removed, as planned, but, in addition, an unplanned

TABLE 4. Selected bond lengths (Å) and angles (°) for $[Et_4N][W_3OCl_5(OAc)_4]\cdot 3CH_2Cl_2$

Bond distances					
W(1)–W(2)	2.7280(7)	W(1)–O(6)	2.09(1)	W(2)–O(8)	2.12(1)
W(1)–W(3)	2.5754(8)	W(2)–W(3)	2.5715(8)	W(3)–Cl(1)	2.432(4)
W(1)–Cl(1)	2.443(4)	W(2)–Cl(2)	2.443(4)	W(3)–Cl(2)	2.438(4)
W(1)–Cl(3)	2.434(4)	W(2)–Cl(4)	2.435(4)	W(3)–Cl(5)	2.416(4)
W(1)–O(1)	1.98(1)	W(2)–O(1)	1.98(1)	W(3)–O(1)	1.99(1)
W(1)–O(2)	2.06(1)	W(2)–O(3)	2.06(1)	W(3)–O(7)	2.07(1)
W(1)–O(4)	2.07(1)	W(2)–O(5)	2.08(1)	W(3)–O(9)	2.06(1)
Bond angles					
W(2)–W(1)–W(3)	57.92(2)	Cl(2)–W(2)–O(1)	107.7(3)	Cl(1)–W(3)–O(7)	89.2(3)
Cl(1)–W(1)–Cl(3)	89.8(1)	Cl(2)–W(2)–O(3)	173.1(3)	Cl(1)–W(3)–O(9)	169.3(3)
Cl(1)–W(1)–O(1)	107.4(3)	Cl(2)–W(2)–O(5)	83.9(3)	Cl(2)–W(3)–Cl(5)	85.5(1)
Cl(1)–W(1)–O(2)	173.4(3)	Cl(2)–W(2)–O(8)	92.7(3)	Cl(2)–W(3)–O(1)	107.5(3)
Cl(1)–W(1)–O(4)	83.8(4)	Cl(4)–W(2)–O(1)	149.9(3)	Cl(2)–W(3)–O(7)	168.4(3)
Cl(1)–W(1)–O(6)	92.4(3)	Cl(4)–W(2)–O(3)	85.7(3)	Cl(2)–W(3)–O(9)	89.7(3)
Cl(3)–W(1)–O(1)	149.5(3)	Cl(4)–W(2)–O(5)	76.3(3)	Cl(5)–W(3)–O(1)	159.0(3)
Cl(3)–W(1)–O(2)	85.1(3)	Cl(4)–W(2)–O(8)	78.8(3)	Cl(5)–W(3)–O(7)	84.3(3)
Cl(3)–W(1)–O(4)	77.7(3)	O(1)–W(2)–O(3)	79.0(4)	Cl(5)–W(3)–O(9)	84.0(3)
Cl(3)–W(1)–O(6)	79.1(3)	O(1)–W(2)–O(5)	129.1(4)	O(1)–W(3)–O(7)	80.9(4)
O(1)–W(1)–O(2)	79.0(4)	O(1)–W(2)–O(8)	75.6(4)	O(1)–W(3)–O(9)	79.7(4)
O(1)–W(1)–O(4)	127.9(4)	O(3)–W(2)–O(5)	90.7(4)	O(7)–W(3)–O(9)	83.8(4)
O(1)–W(1)–O(6)	75.3(4)	O(3)–W(2)–O(8)	90.4(4)	W(1)–Cl(1)–W(3)	63.8(1)
O(2)–W(1)–O(4)	91.0(4)	O(5)–W(2)–O(8)	154.9(4)	W(2)–Cl(2)–W(3)	63.6(1)
O(2)–W(1)–O(6)	90.7(4)	W(1)–W(3)–W(2)	64.01(2)	W(1)–O(1)–W(2)	87.1(4)
O(4)–W(1)–O(6)	156.5(4)	Cl(1)–W(3)–Cl(2)	95.8(1)	W(1)–O(1)–W(3)	80.8(4)
W(1)–W(2)–W(3)	58.06(2)	Cl(1)–W(3)–Cl(5)	87.3(1)	W(2)–O(1)–W(3)	80.6(4)
Cl(2)–W(2)–Cl(4)	88.9(1)	Cl(1)–W(3)–O(1)	107.3(3)		

Numbers in parentheses are e.s.d.s in the least significant digit.

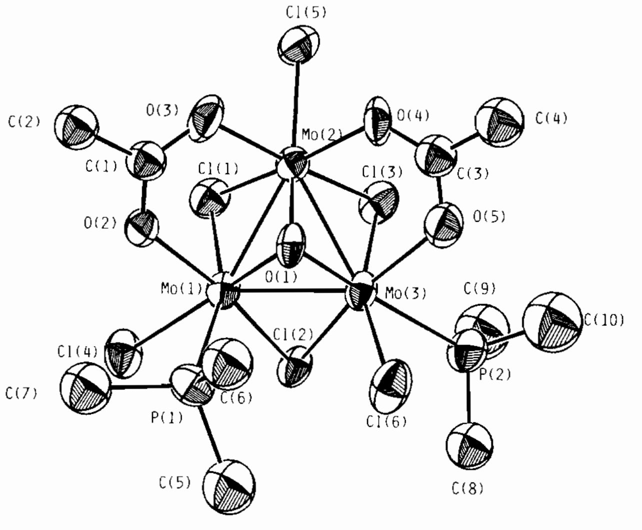


Fig. 3. Configuration of $[Mo_3OCl_6(OAc)_2(PMe_3)_2]^-$. Thermal ellipsoids are shown at the 50% probability level.

reduction occurred, so that the 8-electron cluster with which we started became a 9-electron cluster. Presumably, the reduction was caused by the excess PMe_3. Thus, even here, more work will be required to get the synthetic chemistry fully under control.

Another observation concerning the preparative chemistry is also worthy of mention. It will be noted in 'Experimental' that three equivalents of both Me_3SiCl and PMe_3 were used per molar equivalent of the Mo_3 starting material, and yet only one μ-OAc^- group was removed. This is a reproducible result, and even with larger excesses of the reagents and more severe conditions it proved impossible to remove another μ-OAc^- group. This is yet another puzzling aspect of the chemistry that will require further study.

Bridging carboxylate groups and metal–metal bonding interactions

It has been well documented that except for some bifunctional carboxylate groups, such as oxalate [3], carboxylate groups are good bridging ligands in the formation of transition metal clusters [11]. Paddle-wheel type tetracarboxylate compounds are one of the most important groups of multiply bonded dinuclear transition metal clusters. In the bicapped molybdenum and tungsten trinuclear cluster chemistry, hexacarboxylate compounds are also dominant. Now, with the two new compounds added to the category of molybdenum and tungsten trinuclear clusters, a complete series of monocapped molybdenum and tungsten clusters which contain from 0 to 6 bridging carboxylate groups on a trimer unit has been synthesized and characterized by X-ray diffraction. Important bond distances are com-

TABLE 5. Selected bond distances (Å) and bond angles (°) for $(Et_4N)[Mo_3OCl_6(OAc)_2(PMe_3)_2]$

Bond distances					
Mo(1)–Mo(2)	2.627(4)	Mo(2)–O(4)	2.05(2)	Mo(4)–O(7)	2.17(2)
Mo(1)–Mo(3)	2.546(3)	Mo(3)–Cl(2)	2.456(7)	Mo(5)–Mo(6)	2.597(4)
Mo(1)–Cl(1)	2.420(8)	Mo(3)–Cl(3)	2.464(9)	Mo(5)–Cl(7)	2.443(8)
Mo(1)–Cl(2)	2.464(9)	Mo(3)–Cl(6)	2.482(9)	Mo(5)–Cl(9)	2.424(8)
Mo(1)–Cl(4)	2.388(9)	Mo(3)–P(2)	2.53(1)	Mo(5)–Cl(11)	2.45(1)
Mo(1)–P(1)	2.607(9)	Mo(3)–O(1)	2.00(2)	Mo(5)–O(6)	1.99(2)
Mo(1)–O(1)	1.98(2)	Mo(3)–O(5)	2.07(2)	Mo(5)–O(8)	2.12(2)
Mo(1)–O(2)	2.17(2)	Mo(4)–Mo(5)	2.631(6)	Mo(5)–O(9)	2.07(2)
Mo(2)–Mo(3)	2.631(6)	Mo(4)–Mo(6)	2.577(4)	Mo(6)–Cl(8)	2.397(9)
Mo(2)–Cl(1)	2.436(8)	Mo(4)–Cl(7)	2.430(9)	Mo(6)–Cl(9)	2.394(9)
Mo(2)–Cl(3)	2.430(8)	Mo(4)–Cl(8)	2.455(8)	Mo(6)–Cl(12)	2.450(9)
Mo(2)–Cl(5)	2.45(1)	Mo(4)–Cl(10)	2.461(9)	Mo(6)–P(4)	2.575(9)
Mo(2)–O(1)	2.00(2)	Mo(4)–P(3)	2.54(1)	Mo(6)–O(6)	2.04(2)
Mo(2)–O(3)	2.14(2)	Mo(4)–O(6)	1.96(2)	Mo(6)–O(10)	2.07(2)
Bond angles					
Mo(2)–Mo(1)–Mo(3)	61.1(1)	Cl(3)–Mo(2)–O(4)	88.9(6)	Cl(7)–Mo(4)–Cl(10)	87.0(3)
Cl(1)–Mo(1)–Cl(2)	91.9(3)	Cl(5)–Mo(2)–O(1)	161.0(5)	Cl(7)–Mo(4)–P(3)	162.1(3)
Cl(1)–Mo(1)–Cl(4)	159.3(3)	Cl(5)–Mo(2)–O(3)	84.4(6)	Cl(7)–Mo(4)–O(6)	106.0(5)
Cl(1)–Mo(1)–P(1)	82.0(3)	Cl(5)–Mo(2)–O(4)	84.8(7)	Cl(7)–Mo(4)–O(7)	86.7(5)
Cl(1)–Mo(1)–O(1)	106.3(5)	O(1)–Mo(2)–O(3)	81.0(7)	Cl(8)–Mo(4)–Cl(10)	85.6(3)
Cl(1)–Mo(1)–O(2)	83.9(6)	O(1)–Mo(2)–O(4)	84.4(8)	Cl(8)–Mo(4)–P(3)	101.1(4)
Cl(2)–Mo(1)–Cl(4)	97.2(3)	O(3)–Mo(2)–O(4)	94.7(7)	Cl(8)–Mo(4)–O(6)	107.5(5)
Cl(2)–Mo(1)–P(1)	82.1(3)	Mo(1)–Mo(3)–Mo(2)	60.9(1)	Cl(8)–Mo(4)–O(7)	171.0(5)
Cl(2)–Mo(1)–O(1)	108.4(5)	Cl(2)–Mo(3)–Cl(3)	93.6(3)	Cl(10)–Mo(4)–P(3)	81.3(3)
Cl(2)–Mo(1)–O(2)	168.1(6)	Cl(2)–Mo(3)–Cl(6)	82.9(3)	Cl(10)–Mo(4)–O(6)	161.0(5)
Cl(4)–Mo(1)–P(1)	80.9(3)	Cl(2)–Mo(3)–P(2)	99.6(4)	Cl(10)–Mo(4)–O(7)	85.6(5)
Cl(4)–Mo(1)–O(1)	88.4(5)	Cl(2)–Mo(3)–O(1)	108.0(5)	P(3)–Mo(4)–O(6)	82.6(5)
Cl(4)–Mo(1)–O(2)	83.4(6)	Cl(2)–Mo(3)–O(5)	169.2(5)	P(3)–Mo(4)–O(7)	78.9(6)
P(1)–Mo(1)–O(1)	165.9(5)	Cl(3)–Mo(3)–Cl(6)	87.1(3)	O(6)–Mo(4)–O(7)	81.5(7)
P(1)–Mo(1)–O(2)	86.3(6)	Cl(3)–Mo(3)–P(2)	161.0(3)	Mo(4)–Mo(5)–Mo(6)	59.1(1)
O(1)–Mo(1)–O(2)	83.4(7)	Cl(3)–Mo(3)–O(1)	105.4(6)	Cl(7)–Mo(5)–Cl(9)	85.3(3)
Mo(1)–Mo(2)–Mo(3)	57.9(1)	Cl(3)–Mo(3)–O(5)	83.4(5)	Cl(7)–Mo(5)–Cl(11)	88.7(3)
Cl(1)–Mo(2)–Cl(3)	83.9(3)	Cl(6)–Mo(3)–P(2)	81.2(3)	Cl(7)–Mo(5)–O(6)	104.6(6)
Cl(1)–Mo(2)–Cl(5)	87.2(3)	Cl(6)–Mo(3)–O(1)	162.4(5)	Cl(7)–Mo(5)–O(8)	90.5(5)
Cl(1)–Mo(2)–O(1)	105.3(5)	Cl(6)–Mo(3)–O(5)	86.5(5)	Cl(7)–Mo(5)–O(9)	171.8(6)
Cl(1)–Mo(2)–O(3)	91.5(5)	P(2)–Mo(3)–O(1)	83.4(6)	Cl(9)–Mo(5)–Cl(11)	87.2(3)
Cl(1)–Mo(2)–O(4)	169.3(6)	P(2)–Mo(3)–O(5)	81.1(6)	Cl(9)–Mo(5)–O(6)	107.6(5)
Cl(3)–Mo(2)–Cl(5)	88.4(3)	O(1)–Mo(3)–O(5)	82.8(7)	Cl(9)–Mo(5)–O(8)	173.5(6)
Cl(3)–Mo(2)–O(1)	106.9(6)	Mo(5)–Mo(4)–Mo(6)	59.8(1)	Cl(9)–Mo(5)–O(9)	90.5(5)
Cl(3)–Mo(2)–O(3)	171.7(6)	Cl(7)–Mo(4)–Cl(8)	91.5(3)	Cl(11)–Mo(5)–O(6)	160.6(5)
Cl(11)–Mo(5)–O(8)	87.9(6)	Cl(9)–Mo(6)–Cl(12)	159.5(3)	Mo(1)–Cl(2)–Mo(3)	62.3(2)
Cl(11)–Mo(5)–O(9)	84.1(6)	Cl(9)–Mo(6)–P(4)	81.7(3)	Mo(2)–Cl(3)–Mo(3)	65.0(2)
O(6)–Mo(5)–O(8)	78.2(7)	Cl(9)–Mo(6)–O(6)	106.9(5)	Mo(4)–Cl(7)–Mo(5)	65.4(2)
O(6)–Mo(5)–O(9)	83.3(7)	Cl(9)–Mo(6)–O(10)	85.9(6)	Mo(4)–Cl(8)–Mo(6)	64.1(2)
O(8)–Mo(5)–O(9)	93.1(7)	Cl(12)–Mo(6)–P(4)	80.8(3)	Mo(5)–Cl(9)–Mo(6)	65.2(2)
Mo(4)–Mo(6)–Mo(5)	61.1(1)	Cl(12)–Mo(6)–O(6)	88.8(5)	Mo(1)–O(1)–Mo(2)	82.7(6)
Cl(8)–Mo(6)–Cl(9)	92.1(4)	Cl(12)–Mo(6)–O(10)	82.7(6)	Mo(1)–O(1)–Mo(3)	79.5(6)
Cl(8)–Mo(6)–Cl(12)	95.8(4)	P(4)–Mo(6)–O(6)	167.2(5)	Mo(2)–O(1)–Mo(3)	82.3(6)
Cl(8)–Mo(6)–P(4)	81.7(3)	P(4)–Mo(6)–O(10)	87.3(5)	Mo(4)–O(6)–Mo(6)	80.0(6)
Cl(8)–Mo(6)–O(6)	107.0(5)	O(6)–Mo(6)–O(10)	84.0(7)	Mo(5)–O(6)–Mo(6)	80.2(6)
Cl(8)–Mo(6)–O(10)	169.0(5)	Mo(1)–Cl(1)–Mo(2)	65.5(2)	Mo(4)–O(6)–Mo(5)	83.5(6)

Numbers in parentheses are e.s.d.s in the least significant digits.

piled in Table 6 for monocapped Mo_3 and W_3 cluster species in the order of increasing number of carboxylate groups.

It is possible to infer some rules of thumb concerning the influence of replacement of ligands on the metal–metal bonding interactions in the M_3X_{13} type structures [1b, 12b]. For example, replacement of a μ_3-O atom by a μ_3-S atom will increase the average Mo–Mo bond length by *c.* 0.1 Å. Upon replacement of three μ-Cl atoms by three μ-Br atoms the increase is only 0.02 Å, while for replacement of three μ-O atoms by three μ-S atoms the increase is 0.12–0.15 Å. Keeping

TABLE 6. Monocapped molybdenum and tungsten trinuclear compounds that contain bridging carboxylate ligands

Compounds	n_d[a]	M–M[b]	M–L_c[c]	M–O_b[d]	M–L_b[a]	Ref.
$W_3(\mu_3\text{-Cl})(\mu\text{-O})_3(OAc)Cl_4(CBu^n{}_3)_3$	6	2.608[9]	2.468[7]	2.150[3]	1.94[2]	11
$W_3S_4(OAc)(dtp)_3(py)$[f]	6	2.721[3]	2.343[2]	2.17[2]	2.298[5]	12a
$Mo_3S_4(O_2CEt)(dtp)_3(py)$	6	2.731[14]	2.335		2.288	12b
$Mo_3S_4(O_2CH)(dtp)_3(py)$	6	2.740[31]	2 332		2.287	12b
$Mo_3S_4(OAc)(dtp)_3(py)$	6	2.739[37]	2.334		2.293	12b
$(Et_4N)_2[Mo_3OCl_8(OAc)_2]$	8	2.599[14]	2.00[5]	2.09[4]	2.41[1]	13
$(Et_4N)[Mo_3OCl_6(OAc)_2(PMe_3)_2]$	9	2.602[32]	2.00[2]	2.11[5]	2.43[2]	
$[Mo_3(\mu_3\text{-CMe})Br_3(OAc)_3(H_2O)_3]ClO_4\cdot 4H_2O$	8	2.594[1]	2.013[5]	2.09[1]	2.595[7]	1b
$(Me_4N)[Mo_3OCl_6(OAc)_3]$ 2HOAc	8	2.570[3]	1.975[3]	2.063[4]	2.418[3]	1c
$(Et_4N)[W_3OCl_6(OAc)_3]\cdot Me_2CO$	8	2.567[5]	1.995[5]	2.065[6]	2.433[4]	1c
$[Mo_3OCl_3(OAc)_3(H_2O)_3](ClO_4)Cl$	8	2.550(2)	2.03(1)	2 065[3]	2.427[2]	1a
$(Bu^n{}_4N)[Mo_3OCl_6(OAc)_3]\cdot Me_2CO$	8	2 578[2]	1.980[3]	2.065[6]	2.415[3]	1d
$(Bu^n{}_4N)[Mo_3OBr_6(OAc)_3]\cdot Me_2CO$	8	2 597[2]	1.986[2]	2.072[8]	2.549[8]	1d
$(Et_4N)[Mo_3OCl_6(O_2CH)_3]$	8	2.573[2]	1.984	2.086	2.410	1e
$(Me_4N)[Mo_3OCl_6(O_2CH)_3]$	8	2.577[1]	1.982[1]	2.084	2.414	1e
$(Me_4N)[Mo_3O(\mu\text{-Br})_3Cl_3(O_2CH)_3]$	8	2.596[2]	1.976	2.089	2.545	1e
$(C_5H_7S_2)[Mo_3OCl_6(OAc)_3]$	8	2.577[7]	1.992[6]	2.075	2.419	1e
$(C_5H_7S_2)[Mo_3O(\mu\text{-Br})_3Cl_3(OAc)_3]$	8	2.594[8]	1 970[4]	2.076	2.549	1e
$(Et_4N)[Mo_3O(\mu\text{-Cl})_3X_3(OAc)_3]$[g]	8	2.577[5]	1.976	2 068	2.415	1e
$(Et_4N)[Mo_3OCl_6(O_2CEt)_3]$	8	2.576[1]	1.965	2.064	2.448	1e
$(Bu^n{}_4N)_2[Mo_3OCl_6(OAc)_3]\cdot Me_2CO$	9	2.604[9]	1.984[9]	2.113[7]	2.437[5]	1f
$(Bu^n{}_4N)[Mo_3OCl_5(OAc)_3(PMe_3)]\cdot 2THF$	9	2.592[31]	1.984[7]	2.099[6]	2.433[8]	1f
$Mo_3OCl_4(OAc)_3(PMe_3)_2$	9	2.589[18]	1.992[7]	2.10[1]	2.427[6]	1f
$[Mo_3OCl_4(OAc)_3(PMe_3)_2]\cdot THF$	9	2.591[17]	1.986[5]	2.090[9]	2.44[1]	1f
$Mo_3OCl_4(OAc)_3(THF)_2$	9	2.588[4]	1.98[1]	2.10[2]	2.44[1]	1g
$(Bu^n{}_4N)_2[Mo_3OBr_6(OAc)_3]\cdot Me_2CO$	9	2.624[14]	1.98[1]	2.11[2]	2.54[2]	1g
$[Mo_3OBr_3(OAc)_3(PMe_3)_3]BF_4$	9	2.613[11]	1.999[4]	2.10[1]	2.573[4]	1g
$(Et_4N)_2[W_3OCl_6(OAc)_3]$	9	2 591[15]	2.01[5]	2.12[3]	2.449[8]	1g
$(Et_4N)[W_3OCl_5(OAc)_4]\cdot 3CH_2Cl_2$	8	2.625[73]	1.983[5]	2.08[2]	2.439[5]	
$[W_3O(OAc)_5(OMe)(H_2O)_3]ZnCl_4\cdot 7H_2O$	8	2.622[90]	1.95[3]	2.08[2]		2a
$[W_3O(OAc)_6(H_2O)_3]ZnCl_4$ $4H_2O$	8	2.699[9]	1.98[1]	2.07[2]		2a
$[W_3O(OAc)_6(H_2O)_3]ZnBr_4\cdot 8H_2O$	8	2.710[7]	1.96[2]	2.07[1]		2b

[a] n_d denotes number of d-electrons. [b] Square brackets denote mean deviation from arithmatic mean. [c] L_c denotes capping ligands. [d] O_b denotes oxygen atoms from bridging carboxylate groups. [e] L_b denotes bridging atoms. [f] dtp denotes diethyldithiophosphate. [g] $X = 0.5$ (Cl + Br).

these factors in mind, from the data listed in the Table we can see a relationship between the number of carboxylate groups and the lengths of the metal–metal bonds.

The first five compounds are 6-electron clusters that have only one bridging carboxylate ligand. While the significance of the first one is not clear, in the other four, which have all been prepared by a substitution reaction of $M_3S_4(dtp)_4L$ ($M = Mo$, W; $L = H_2O$, py) by carboxylate groups [12] the average metal–metal distances are reduced by more than 0.1 Å, compared with the values 2.754[14] Å for $Mo_3S_4(dtp)_4(H_2O$ and 2.754[8] Å for $Mo_3S_4(dtp)_4(py)$. In all these d^6 structures the metal–metal bonds that are bridged by carboxylate groups are shorter than the other two without such a bridge. This is not surprising since RCO_2^- has a smaller bite than the $(RO)_2PS_2^-$ ligand.

In the d^8 systems the average metal–metal bond distances are *c.* 2.60 Å for molybdenum dicarboxylate trinuclear compounds and *c.* 2.58 Å for their tricarboxylate derivatives. The metal–metal bond that is not bridged by a carboxylate group in the dicarboxylate compound $(Et_4N)[Mo_3OCl_8(OAc)_2]$ is always longer than the other two [13]. It would appear that carboxylate groups enhance metal–metal bonding interactions in this type of cluster, and their small and flexible bites and small L–L repulsions (as compared with two monodentate ligands) may play an important role in this respect.

Upon addition of an electron to a d^8 system, the metal–metal distances show a small increase due to the antibonding character of the ninth electron, as was indicated by theoretical studies [5].

Beginning with the $M_3(\mu_3\text{-}X)(\mu\text{-}Y)_3(\mu\text{-}O_2CR)_3$ structure, each further increase in the number of bridging carboxylate groups will necessarily reduce the number of bridging halides, and the cluster type will change from M_3X_{13} to M_3X_{14}, and finally to M_3X_{16}, although each metal retains an octahedral coordination environment. It is seen that an increase in the number of carboxylate groups causes the average metal–metal bond distances to show a monotonic increase from 2.58 Å for the tricarboxylate clusters to the newly determined *c.* 2.63 Å for the tetracarboxylate structure, and to *c.* 2.71 Å for the hexacarboxylate ones. As mentioned above, both greater donation of electrons into antibonding metal–metal orbitals [9] and greater L–L repulsion from the greater number of carboxylate groups may contribute to this progressive increase in the metal–metal bond lengths.

It is also to be noted that while tungsten clusters display the whole range of carboxylate groups, no more than three bridging carboxylate groups have been found for any monocapped molybdenum cluster. Under similar reaction conditions attempts to prepare trinuclear molybdenum clusters with a larger number of carboxylate ligands have resulted, instead, in a number of very stable bicapped hexacarboxylate molybdenum trinuclear clusters with 4–6 d-electrons [11]. Despite the difference between molybdenum and tungsten in this respect, on the whole, they jointly maintain a narrow range of 2.55–2.74 Å for the metal–metal distances. The consistent occurrence of fairly strong metal–metal interactions in the monocapped carboxylate clusters implies that carboxylate groups are an excellent stabilizing factor in the formation of monocapped molybdenum and tungsten clusters with 6–9 d-electrons.

Supplementary material

Tables of positional parameters, bond lengths and angles, anisotropic thermal parameters, ORTEP drawings of unit cell contents for **1** and **2** (17 pages), and observed and calculated structure factors for **1** and **2** (35 pages) may be obtained from author F.A.C.

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References

1 (1) A Bino, F.A. Cotton and Z. Dori, *Inorg. Chim Acta, 33* (1979) L133, (b) A. Birnbaum, F.A. Cotton, Z. Dori, M. Kapon, D Marler, G.M. Reisner and W. Schwotzer, *J Am. Chem. Soc., 107* (1985) 2405; (c) F.A. Cotton, M. Shang and Z. Sun, *J Am Chem. Soc., 113* (1991) 3007; (d) F.A. Cotton, M. Shang and Z.S. Sun, *J. Cluster Sci., 3* (1992) 109; (e) Jia Huang, Jin Huang, M. Shang, X. Lin, H. Zhang and D Wu, *J Inorg Chem. (Chin.), 2* (1986) 27, (f) F.A. Cotton, M Shang and Z. Sun, *J Am. Chem Soc., 113* (1991) 6917; (g) F.A. Cotton, M. Shang and Z.S. Sun, *J. Cluster Sci, 3* (1992) 123.

2 (a) A Bino, F.A. Cotton, Z. Dori, M. Shaia-Gottlieb and M. Kapon, *Inorg Chem., 27* (1988) 3592; (b) M Ardon, F.A. Cotton, Z. Dori, A. Fang, M. Kapon, G.M. Reisner and M. Shaia, *J. Am Chem Soc, 104* (1982) 5394.

3 (a) E. Benory, A. Bino, D. Gibson, F.A. Cotton and Z. Dori, *Inorg Chem Acta, 99* (1985) 137; (b) F A Cotton, Z. Dori, R Llusar and W. Schwotzer, *J Am Chem Soc, 107* (1985) 6734.

4 F.A. Cotton, T.R. Felthouse and D.G. Lay, *Inorg Chem, 20* (1981) 2219.

5 F.A. Cotton and X Feng, *Inorg. Chem., 30* (1991) 3666

6 T. Moeller, *Inorg. Synth, 5* (1957) 139.

7 G M Sheldrick, *SHELXS-86*, program for X-ray crystal structure determination, University of Gottingen, Germany, 1986

8 A. Muller, R. Jostes and F A. Cotton, *Angew. Chem., Int Ed Engl, 19* (1980) 875.

9 B Bursten, F.A. Cotton, M.B. Hall and R.C. Najjar, *Inorg Chem, 21* (1982) 302

10 (a) F.A. Cotton, K.R. Dunbar and R. Poly, *Inorg. Chem, 25* (1986) 3700; (b) P.A. Agaskar and F.A. Cotton, *Inorg Chem, 23* (1984) 3383, (c) T.R Ryan and R E McCarley, *Inorg Chem., 21* (1982) 2072.

11 F.A. Cotton, *Polyhedron, 5* (1986) 3.

12 (a) Y. Zheng, H. Zhan and X. Wu, *Acta Crystallogr., Sect C, 45* (1989) 1424; (b) Jia Huang, Jin Huang, M. Shang, S. Lu, X. Lin, M Huang, H. Zhuang and J. Lu, *Pure Appl. Chem, 60* (1988) 1185

13 M. Shang, J. Huang and J. Lu, *Acta Crystallogr, Sect C, 40* (1984) 761.