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Tritungsten(IV) Cluster Compounds with Hydroxo Ligands. Preparation and Structure of $[W_3O_2(O_2CCH_3)_6(H_2O)(OH)_2]\cdot 16H_2O$ and $[W_3O_2(O_2CCH_3)_6(H_2O)(OH)_2]\cdot KBr\cdot 15H_2O$

AVI BINO* and DAN GIBSON

Department of Inorganic and Analytical Chemistry, The Hebrew University of Jerusalem, 91904 Jerusalem, Israel

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Abstract

The trinuclear tritungsten(IV) cluster ion, $[W_3O_2(OAc)_6(H_2O)_3]^{2+}$ acts as a polyprotic acid in aqueous solution. If the pH of the solution is about 6, brown yellow crystals of $[W_3O_2(OAc)_6(H_2O)\cdot(OH)_2]\cdot 16H_2O$, **2**, are obtained. In the presence of KBr, crystals of the double salt, $[W_3O_2(OAc)_6(H_2O)(OH)_2]\cdot KBr\cdot 15H_2O$, **3**, precipitate upon evaporation of the solution. X-ray structural analyses of the two compounds revealed that compound **2** is monoclinic, space group $C2/m$ with a = 18.845(2) Å, b = 19.001(3) Å, c = 10.862(1) Å, β = 95.60(3)°, V = 3871(1) Å^3 and Z = 4. Compound **3** is monoclinic, space group $P2_1/c$ with a = 10.984(1) Å, b = 18.440(2) Å, c = 19.305(2) Å, β = 95.63(2)°, V = 3891(1) Å^3 and Z = 4. The structures were refined by a full-matrix least-squares technique, using 2996 and 3871 reflections to R values of 3.7% and 4.6% respectively. In both structures the presence of the two hydroxo ligands in the cluster causes a considerable increase in the W–W bond lengths relative to the triaqua complex. In **3**, the potassium cation is bonded to two hydroxo oxygen atoms from neighbouring clusters, forming infinite chains of $\cdot\cdot O(H)W_3O(H)\cdots K\cdots O(H)W_3O(H)\cdots$ units in the crystal.

Introduction

Trinuclear triangular metal cluster compounds of molybdenum and tungsten have been the subject of many structural studies in recent years. One particular group, having the general formula $[M_3X_2(O_2CR)_6L_3]^{n\pm}$, is obtained by the reaction of $M(CO)_6$ (M = Mo, W) with carboxylic acids [1–4] or by the reaction of Na_2MO_4 with Zn in acetic anhydride [5]. It was shown recently that clusters with the general formula $[M_3O_2(O_2CR)_6(H_2O)_3]^{2+}$ (M = Mo(IV), W(IV); R = CH_3, CH_2CH_3) undergo hydrolysis in aqueous solution [6–8] (eqn. (1)).

$$[M_3O_2(O_2CR)_6(H_2O)_3]^{2+} \rightleftharpoons \underset{\textbf{I}}{[M_3O_2(O_2CR)_6(H_2O)_2(OH)]^+} + H^+ \qquad (1)$$

The hydrolysis product, **I**, may react with the triaqua ion to form a 'dimer' of clusters bridged by a μ-H_3O_2 ligand [6–8]. This bridge is the result of a strong hydrogen bond between the OH ligand of one trimer and a H_2O ligand of another. An infinite chain of clusters, bridged by such $H_3O_2^-$ units is obtained when the concentration of **I** is relatively high. The concentration of the various polymeric species is therefore pH-controlled [8]. A further hydrolytic step is the deprotonation of a second H_2O ligand (eqn. (2))

$$[Mo_3O_2(O_2CR)_6(H_2O)_2(OH)]^+ \rightleftharpoons [M_3O_2(O_2CR)_6(H_2O)(OH)_2] + H^+ \qquad (2)$$

The structure of a Mo(IV) acetate complex, $[Mo_3O_2(OAc)_6(H_2O)(OH)_2]\cdot 16H_2O$, **1**, with two hydroxo ligands was recently reported [5]. In this structure, one OH and the H_2O ligand are disordered and therefore no accurate dimensions such as M–O distances are available. This compound was prepared by the hydrolysis of $[Mo_3O_2(OAc)_6(OAc)_3]^-$ in H_2O.

We now report the preparation and structure of two tungsten(IV) trinuclear clusters with two hydroxo ligands. The first, $[W_3O_2(OAc)_6(H_2O)(OH)_2]\cdot 16H_2O$, **2**, is the analogue of the molybdenum compound **1** and was found to be isostructural with it. The second is $[W_3O_2(OAc)_6(H_2O)(OH)_2]\cdot KBr\cdot 15H_2O$, **3**, in which the two OH ligands are distinct and no disorder exists in the crystal.

Experimental

Preparation of $[W_3O_2(O_2CCH_3)_6(H_2O)(OH)_2]\cdot 16H_2O$, 2

$W(CO)_6$ (1 g) in 100 ml of a 1:1 mixture of acetic acid and acetic anhydride were refluxed for

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*Author to whom correspondence should be addressed.

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TABLE I. Crystallographic Data.

Compound No.	2	3
formula	$C_{12}H_{54}O_{33}W_3$	$BrC_{12}H_{52}KO_{32}W_3$
FW	1278.09	1380.49
space group	$C2/m$	$P2_1/c$
a (Å)	18.845(2)	10.984(1)
b (Å)	19.001(3)	18.440(2)
c (Å)	10.862(1)	19.305(3)
β (deg)	95.60(3)	95.63(2)
V (Å^3)	3871(1)	3891(1)
Z	4	4
d(calcd) (g × cm^{-3})	2.201	2.365
μ (cm^{-1})	86.06	96.71
cryst size (mm)	0.2 × 0.2 × 0.15	0.25 × 0.20 × 0.15
range of 2θ (deg)	3–50	3–45
observations	$\pm h, k, l$	$\pm h, k, l$
syst. refl. absences	$h + k = 2n + 1$	$hol, l = 2n + 1$ $oko, k = 2n + 1$
no. of unique data	3512	5006
data with $F_o^2 > 3\sigma(F_o^2)$	2996	3871
no. of parameters	233	307
R	0.037	0.046
R_w	0.040	0.051
w	$(\sigma_F^2 + 0.000313\,F^2)^{-1}$	$(\sigma_F^2 + 0.00115\,F^2)^{-1}$

20 h. The resulting brown solution was diluted with H_2O (100 ml), warmed up to 80 °C for 1 h, and absorbed on a Dowex 50W-X2 (H^+ form) cationic exchange resin. The yellow band at the top of the column was eluted with a 0.25 M sodium oxalate solution. The yellow eluate was placed in an open beaker and yellow-brown crystals were deposited after several hours. The pH of this solution was ~6.

Preparation of $[W_3O_2(O_2CCH_3)_6(H_2O)(OH)_2]\cdot KBr\cdot 15H_2O$, *3*

The procedure is as in 2. A solution of 0.5 M KBr was used for the elution of the ion from the column and the pH of the eluate was adjusted to 6 by adding KOH. Yellow-brown crystals were obtained upon slow evaporation of the solution in an open beaker.

X-Ray Crystallography

A crystal of compound 2 was mounted inside a glass capillary tube above a column of the solution from which it was grown. A crystal of 3 was sealed with epoxy cement to the end of a glass fiber.

Data were collected for both compounds at 20 ± 2 °C on a Philips PW 1100 four-circle diffractometer. Mo K_α (λ = 0.71069 Å) radiation with a graphite crystal monochromator in the incident beam was used. The unit cell dimensions were obtained by a least-squares fit of 25 reflections in the range $12° < \theta < 16°$. Data were measured by using ω–2θ motion. Crystallographic data and other pertinent information are given in Table I. For each crystal Lorentz and polarization corrections were applied. Intensity data for 2 and 3 were corrected for absorption by the emperical ψ-scan method. Structure 2 was solved using the coordinates of the isostructural molybdenum compound 1 [5]. The heavy atom positions in 3 were obtained by using the results of MULTAN direct method analysis. Structure 2 was refined in space group $C2/m$ to convergence by using anisotropic thermal parameters for all non-hydrogen atoms except OW(12)*. Structure 3 was refined in space group $P2_1/c$ to convergence by using anisotropic thermal parameters for all non-hydrogen atoms, except the carbon atoms and oxygen atoms of the lattice water molecules.

The discrepancy indices $R = \Sigma\|F_o| - |F_c\|/\Sigma|F_o|$ and $R_w = [(\Sigma w|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$ are listed in Table I.

Results and Discussion

$[W_3O_2(OAc)_6(H_2O)(OH)_2]\cdot 16H_2O$, *2*

The atomic positional parameters are listed in Table II. Table III presents the important bond lengths and angles. Figure 1 shows the structure and the numbering scheme in the trinuclear cluster.

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*All crystallographic computing was done on a CYBER 74 Computer at the Hebrew University of Jerusalem, using the SHELX 1977 structure determination package.

TABLE II. Positional Parameters and e.s.d.s for **2**.

Atom	x	y	z
W(1)	0.19258(2)[a]	0.07257(2)	0.02194(3)
W(2)	0.16675(3)	0.00000	0.23541(4)
O(1)	0.1196(4)	0.00000	0.0588(7)
O(2)	0.2476(4)	0.00000	0.1260(7)
O(11)	0.2841(3)	0.0588(3)	−0.0722(6)
O(12)	0.1331(3)	0.0590(3)	−0.1507(5)
OW(1)	0.2042(3)	0.1653(3)	−0.0703(6)
OW(2)	0.1464(5)	0.00000	0.4133(7)
O(14)	0.2573(3)	0.1345(3)	0.1482(6)
O(15)	0.1067(3)	0.1347(3)	0.0689(5)
O(21)	0.0860(3)	0.0761(3)	0.2408(5)
O(22)	0.2376(3)	0.0763(3)	0.3188(6)
C(11)	0.3133(6)	0.00000	−0.095(1)
C(12)	0.3829(6)	0.00000	−0.154(1)
C(13)	0.1144(6)	0.00000	−0.200(1)
C(14)	0.0672(8)	0.00000	−0.320(1)
C(21)	0.0716(5)	0.1239(5)	0.1602(8)
C(22)	0.0084(5)	0.1727(5)	0.177(1)
C(23)	0.2682(5)	0.1235(5)	0.2638(9)
C(24)	0.3214(6)	0.1720(6)	0.339(1)
OW(3)	0.1563(4)	0.2839(4)	0.0314(7)
OW(4)	0.2288(4)	0.1418(4)	−0.3247(6)
OW(5)	0.2574(6)	0.00000	0.597(1)
OW(6)	0.3749(5)	0.3382(5)	0.5206(8)
OW(7)	0.50000	0.2618(8)	0.50000
OW(8)	0.3473(4)	0.2306(5)	0.7046(8)
OW(9)	0.4506(5)	0.1296(5)	0.0942(9)
OW(10)	0.1027(8)	0.50000	0.811(2)
OW(11)	0.0286(6)	0.3458(6)	0.324(1)
OW(12)	0.105(1)	0.474(2)	0.488(3)

[a] E.s.d.s in the least significant digits are shown in parentheses.

TABLE III. Important Bond Lengths (Å) and Angles (deg) for **2**.

Lengths			
W(1)–W(2)	2.7812(5)	W(2)–O(21)	2.105(5)
W(1)–W(1)'	2.7578(5)	W(2)–O(22)	2.114(6)
W(1)–O(1)	2.015(6)	O(11)–C(11)	1.280(8)
W(1)–O(2)	2.006(5)	O(12)–C(13)	1.276(7)
W(1)–O(11)	2.105(6)	O(14)–C(23)	1.27(1)
W(1)–O(12)	2.105(5)	O(15)–C(21)	1.26(1)
W(1)–OW(1)	2.049(5)	O(21)–C(21)	1.27(1)
W(1)–O(14)	2.103(6)	O(22)–C(23)	1.25(1)
W(1)–O(15)	2.105(6)	C(11)–C(12)	1.51(1)
W(2)–OW(2)	2.006(8)	C(13)–C(14)	1.50(1)
W(2)–O(1)	2.034(7)	C(21)–C(22)	1.54(1)
W(2)–O(2)	2.021(8)	C(23)–C(24)	1.53(1)
Angles			
W(1)–W(2)–W(1)'	59.44(1)	W(1)–O(1)–W(1)'	86.4(3)
W(1)–W(1)'–W(2)	60.28(1)	W(1)–O(2)–W(2)	87.4(3)
W(1)–O(1)–W(2)	86.8(3)	W(1)–O(2)–W(1)'	86.8(3)

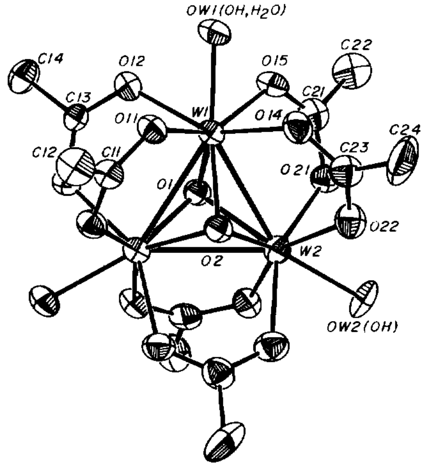

Fig. 1. The structure of $[W_3O_2(OAc)_6(H_2O)(OH)_2]$ in **2**. A plane of symmetry passes through OW(2), W(2), O(1), O(2) and C(11–14).

As mentioned, this structure is isostructural with its molybdenum analogue [5]. The neutral trimer is bisected by a crystallographic mirror plane with W(2) and the hydroxo oxygen OW(2), lying in the plane. The W(1)–OW(1) distance represents an average of M–OH and M–OH_2 bonds as in compound **1**.

The only notable difference between structures **1** and **2** is in one of the disordered lattice water molecules. In the molybdenum compound, **1**, there is one water oxygen, O(20), which is disordered among several positions which are partially occupied with occupancies of 0.1, 0.125, 0.175 and 0.1 [5]. The disorder scheme in **2** for OW(12) is less complex and it was located and refined in one defined position with an occupancy factor of 0.5. Table VI presents some relevant bond distances in the trinuclear clusters in **1**, **2** and **3** for comparison.

$[W_3O_2(OAc)_6(H_2O)(OH)_2]\cdot KBr\cdot 15H_2O$, 3

The atomic positional parameters are listed in Table IV; Table V presents the important bond lengths and angles in the neutral trinuclear cluster. Figure 2 shows the cluster and the labelling scheme.

With four molecules in the unit cell of space group $P2_1/c$, there is no crystallographic symmetry imposed upon the trinuclear cluster. The asymmetric unit contains one $[W_3O_2(OAc)_6(H_2O)(OH)_2]$ unit, one K^+, one Br^- and fifteen water molecules of crystallization. An elaborate network of hydrogen bonds exists between the H_2O and OH ligands and the H_2O molecules and the bromide ion in the lattice. The bromide anion is surrounded by four water molecules with Br···O distances in the range of 3.27–3.44 Å. The potassium ion is surrounded by eight oxygen atoms of neighbouring acetate and hydroxo ligands and water molecules. There are three K···O(OAc) and three K···OH_2 bonds in the range of 2.73–3.11 Å and two K···OH bonds (to the two hydroxo

TABLE IV. Positional Parameters and e.s.d.s for **3**.

Atom	*x*	*y*	*z*
W(1)	0.23664(5)[a]	0.19592(4)	0.35000(3)
W(2)	0.01781(6)	0.27073(3)	0.31359(3)
W(3)	0.01491(5)	0.12053(3)	0.32999(3)
Br(1)	0.6302(2)	0.4114(1)	0.1001(1)
K(1)	0.0792(4)	0.0219(2)	0.8076(2)
O(1)	0.0760(9)	0.2045(6)	0.3921(6)
O(2)	0.1047(9)	0.1881(5)	0.2706(5)
O(11)	0.3017(9)	0.2640(5)	0.2729(5)
O(12)	0.2678(9)	0.2841(6)	0.4194(5)
O(13)	0.2987(9)	0.1101(6)	0.2902(6)
O(14)	0.264(1)	0.1253(6)	0.4390(5)
O(21)	0.0962(9)	0.3453(6)	0.3892(5)
O(22)	0.1286(9)	0.3263(5)	0.2447(5)
O(23)	−0.1007(9)	0.2472(5)	0.2232(6)
O(24)	−0.1330(9)	0.2659(6)	0.3718(5)
O(31)	0.088(1)	0.0656(6)	0.4203(6)
O(32)	0.1210(8)	0.0481(5)	0.2731(5)
O(33)	−0.1353(9)	0.1450(5)	0.3856(5)
O(34)	−0.1058(9)	0.1268(6)	0.2367(6)
OW(1)	0.4188(8)	0.1977(5)	0.3726(5)
OW(2)	−0.074(1)	0.3626(6)	0.2895(6)
OW(3)	−0.0766(9)	0.0277(5)	0.3271(5)
C(1)	0.200(2)	0.338(1)	0.4260(9)
C(2)	0.244(2)	0.398(1)	0.4751(9)
C(3)	0.240(1)	0.3133(9)	0.2355(9)
C(4)	0.297(1)	0.3518(9)	0.1809(8)
C(5)	0.187(1)	0.0791(9)	0.4553(8)
C(6)	0.220(2)	0.038(1)	0.524(1)
C(7)	−0.174(1)	0.2067(9)	0.3982(9)
C(8)	−0.274(2)	0.215(1)	0.446(1)
C(9)	−0.134(1)	0.1840(9)	0.2027(8)
C(10)	−0.218(2)	0.177(1)	0.135(1)
C(11)	0.227(1)	0.0578(9)	0.2622(8)
C(12)	0.292(2)	0.008(1)	0.214(1)
OL(1)	0.658(1)	0.0452(8)	0.3024(7)
OL(2)	0.505(1)	0.1532(7)	0.8599(7)
OL(3)	0.150(1)	0.3247(7)	0.6293(7)
OL(4)	0.659(1)	0.1731(7)	0.7540(7)
OL(5)	0.337(1)	0.0364(8)	0.8205(7)
OL(6)	0.414(1)	0.3286(8)	0.6333(7)
OL(7)	0.943(1)	0.3990(7)	0.1390(7)
OL(8)	0.564(1)	0.3162(7)	0.7592(7)
OL(9)	0.626(1)	0.4293(8)	0.4622(8)
OL(10)	0.040(1)	0.2936(8)	0.0473(8)
OL(11)	0.519(1)	0.0503(8)	0.0852(8)
OL(12)	0.462(2)	0.227(1)	0.535(1)
OL(13)	1.004(2)	0.0533(9)	0.0851(9)
OL(14)	0.874(1)	0.4154(9)	0.4502(9)
OL(15)	0.528(1)	0.4392(8)	0.9207(8)

[a] E.s.d.s in the least significant digits are shown in parentheses.

ligands of different clusters) with the following distances: K···OW(2) 2.71(1) Å and K···OW(3) 2.75(1) Å. The K$^+$ ions serve as bridges between the clusters and form infinite chains of ··O(H)W$_3$O(H)···K···O(H)W$_3$O(H)·· units. The OW(2)–K–OW(3) angle

TABLE V. Important Bond Lengths (Å) and Angles (deg) for **3**.

Lengths			
W(1)–W(2)	2.8005(8)	W(2)–O(21)	2.12(1)
W(1)–W(3)	2.7980(8)	W(2)–O(22)	2.15(1)
W(1)–O(1)	2.02(1)	W(2)–O(23)	2.116(9)
W(1)–O(2)	2.008(9)	W(2)–O(24)	2.09(1)
W(1)–O(11)	2.12(1)	W(2)–OW(2)	2.00(1)
W(1)–O(12)	2.11(1)	W(3)–O(1)	2.03(1)
W(1)–O(13)	2.11(1)	W(3)–O(2)	2.015(9)
W(1)–O(14)	2.15(1)	W(3)–O(31)	2.11(1)
W(1)–OW(1)	2.006(9)	W(3)–O(32)	2.144(9)
W(2)–W(3)	2.7883(7)	W(3)–O(33)	2.10(1)
W(2)–O(1)	2.00(1)	W(3)–O(34)	2.13(1)
W(2)–O(2)	2.019(9)	W(3)–OW(3)	1.982(9)

W(2)–W(1)–W(3)	59.76(3)
W(2)–W(1)–O(1)	46.0(4)
W(2)–W(1)–O(2)	46.3(4)
W(2)–W(1)–O11)	82.6(3)
W(2)–W(1)–O(12)	82.1(4)
W(2)–W(1)–O(13)	123.6(4)
W(2)–W(1)–O(14)	123.4(4)
W(2)–W(1)–OW(1)	149.7(4)
W(3)–W(1)–O(1)	46.4(4)
W(3)–W(1)–O(2)	46.0(4)
W(3)–W(1)–O(11)	123.3(4)
W(3)–W(1)–O(12)	123.7(4)
W(3)–W(1)–O(13)	83.0(3)
W(3)–W(1)–O(14)	82.2(4)
W(3)–W(1)–OW(1)	150.5(4)
O(1)–W(1)–O(2)	74.0(5)
O(1)–W(1)–O(11)	127.4(5)
O(1)–W(1)–O(12)	77.3(5)
O(1)–W(1)–O(13)	128.3(5)
O(1)–W(1)–O(14)	77.4(5)
O(1)–W(1)–OW(1)	143.7(5)
O(2)–W(1)–O(11)	77.3(5)
O(2)–W(1)–O(12)	127.1(5)
O(2)–W(1)–O(13)	77.3(5)
O(2)–W(1)–O(14)	126.9(5)
O(2)–W(1)–OW(1)	142.3(5)
O(11)–W(1)–O(12)	86.5(5)
O(11)–W(1)–O(13)	85.5(5)
O(11)–W(1)–O(14)	152.1(5)
O(11)–W(1)–OW(1)	75.2(5)
O(12)–W(1)–O(13)	151.6(5)
O(12)–W(1)–O(14)	87.5(5)
O(12)–W(1)–OW(1)	76.3(5)
O(13)–W(1)–O(14)	87.0(5)
O(13)–W(1)–OW(1)	75.3(5)
O(14)–W(1)–OW(1)	77.0(5)
W(1)–W(2)–W(3)	60.06(3)
W(1)–W(2)–O(1)	45.7(4)
W(1)–W(2)–O(2)	45.9(4)
W(1)–W(2)–O(21)	82.0(4)
W(1)–W(2)–O(22)	82.2(3)
W(1)–W(2)–O(23)	123.4(3)
W(1)–W(2)–O(24)	122.7(4)
W(1)–W(2)–OW(2)	150.9(4)

(continued on facing page)

TABLE V. *(continued)*

W(3)–W(2)–O(1)	46.6(4)
W(3)–W(2)–O(2)	46.1(4)
W(3)–W(2)–O(21)	124.6(4)
W(3)–W(2)–O(22)	123.8(3)
W(3)–W(2)–O(23)	83.0(3)
W(3)–W(2)–O(24)	82.3(4)
W(3)–W(2)–OW(2)	149.0(4)
O(1)–W(2)–O(2)	73.5(5)
O(1)–W(2)–O(21)	78.0(5)
O(1)–W(2)–O(22)	126.5(5)
O(1)–W(2)–O(23)	128.6(5)
O(1)–W(2)–O(24)	77.0(5)
O(1)–W(2)–OW(2)	144.2(6)
O(2)–W(2)–O(21)	126.4(5)
O(2)–W(2)–O(22)	77.7(5)
O(2)–W(2)–O(23)	77.5(5)
O(2)–W(2)–O(24)	127.4(5)
O(2)–W(2)–OW(2)	142.3(5)
O(21)–W(2)–O(22)	84.5(5)
O(21)–W(2)–O(23)	151.2(5)
O(21)–W(2)–O(24)	87.3(5)
O(21)–W(2)–OW(2)	77.1(6)
O(22)–W(2)–O(23)	86.0(5)
O(22)–W(2)–O(24)	152.3(5)
O(22)–W(2)–OW(2)	75.8(4)
O(23)–W(2)–O(24)	88.8(4)
O(23)–W(2)–OW(2)	74.2(4)
O(24)–W(2)–OW(2)	75.8(4)
W(1)–W(3)–W(2)	60.18(2)
W(1)–W(3)–O(1)	46.2(3)
W(1)–W(3)–O(2)	45.8(3)
W(1)–W(3)–O(31)	82.4(3)
W(1)–W(3)–O(32)	82.6(3)
W(1)–W(3)–O(33)	122.6(3)
W(1)–W(3)–O(34)	123.4(3)
W(1)–W(3)–OW(3)	149.8(3)
W(2)–W(3)–O(1)	45.8(3)
W(2)–W(3)–O(2)	46.3(3)
W(2)–W(3)–O(31)	124.3(3)
W(2)–W(3)–O(32)	123.2(3)
W(2)–W(3)–O(33)	82.1(3)
W(2)–W(3)–O(34)	82.1(3)
W(2)–W(3)–OW(3)	150.0(3)
O(1)–W(3)–O(2)	73.3(4)
O(1)–W(3)–O(31)	78.5(4)
O(1)–W(3)–O(32)	127.8(4)
O(1)–W(3)–O(33)	76.4(4)
O(1)–W(3)–O(34)	126.8(4)
O(1)–W(3)–OW(3)	144.3(4)
O(2)–W(3)–O(31)	126.8(4)
O(2)–W(3)–O(32)	76.9(4)
O(2)–W(3)–O(33)	127.6(4)
O(2)–W(3)–O(34)	77.6(4)
O(2)–W(3)–OW(3)	142.4(4)
O(31)–W(3)–O(32)	86.6(4)
O(31)–W(3)–O(33)	86.4(4)
O(31)–W(3)–O(34)	151.7(4)
O(31)–W(3)–OW(3)	76.1(4)
O(32)–W(3)–O(33)	152.6(4)
O(32)–W(3)–O(34)	85.7(4)
O(32)–W(3)–OW(3)	75.4(4)
O(33)–W(3)–O(34)	88.0(4)
O(33)–W(3)–OW(3)	77.2(4)
O(34)–W(3)–OW(3)	75.6(4)

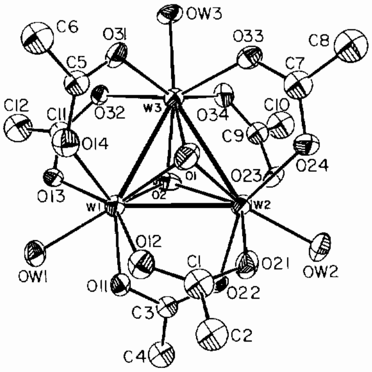

Fig. 2. View of [$W_3O_2(OAc)_6(H_2O)(OH)_2$] in 3. OW(2) and OW(3) are the hydroxo oxygen atoms.

TABLE VI. Structural Data for 1–3 and [$W_3O_2(OAc)_6(H_2O)_3$]$^{2+}$.

Compound	Bond Distances (Å)				
	(H_2O)M–M(OH_2)	(H_2O)M–M(OH)	(HO)M–M(OH)	M–OH_2	M–OH
[$Mo_3O_2(OAc)_6(H_2O)(OH)_2$]·$16H_2O$, 1^a	–	2.773(1)	2.796(1)^b	2.049(5)^c	1.979(7)
[$W_3O_2(OAc)_6(H_2O)(OH)_2$]·$16H_2O$, 2	–	2.7578(5)	2.7812(5)^b	2.049(5)^c	2.006(8)
[$W_3O_2(OAc)_6(H_2O)(OH)_2$]·KBr·$15H_2O$, 3	–	2.8005(8) 2.7980(8)	2.7883(7)	2.006(9)	2.00(1) 1.982(9)
[$W_3O_2(OAc)_6(H_2O)_3$](CF_3SO_3)$_2$^{d}	2.746(1)	–	–	2.132(6)	–

[a] Ref. 5. [b] Average between (HO)M–M(OH_2) and (HO)M–M(OH). [c] Average between M–OH and M–OH_2. [d] Ref. 9.

is 100.9(3)° and the W(2)–OW(2)–K and W(3)–OW(3)–K angles are 110.1(4)° and 105.8(4)° respectively.

The relative concentration of the triaqua, monohydroxo, dihydroxo and the postulated tri-hydroxo W_3 species is obviously pH-dependent. In this work the two dihydroxo compounds were prepared from solutions with pH ~ 6. This fact supports the assumption that the triaqua ion acts as a strong polyprotic acid. In the preparation of **2**, this pH was the result of the formation of $C_2O_4^{2-}/H_2C_2O_4$ buffer and in the preparation of **3** by the addition of KOH to neutralize the large excess of H^+ ions that were eluted from the column.

Compound **1** was prepared by a different route, *i.e.*, by hydrolizing $[Mo_3O_2(OAc)_6(OAc)_3]^-$ in H_2O [5]. Although the exact pH was not stated in that work it is reasonable to assume that under these conditions it was close to 6 and that the concentration of the dihydroxo species was relatively high.

The parameters that determine the metal–metal and metal–oxygen distances in the three dihydroxo clusters cannot be clearly deduced from the data of Table VI. In structures **1** and **2** the trinuclear units deviate significantly from threefold symmetry. Cotton, Dori *et al.* explained these deviations in the molybdenum compound, **1**, by assuming that the stronger the M–O (equatorial) bond is, the weaker will be the adjacent M–M bonds [5]. Accordingly, the distance (HO)-M–M(OH) should be longer than $(H_2O)M–M(OH)$ since M–OH bond (1.979 Å in **1**) is stronger than $M–OH_2$ (2.083–2.144 Å [4]). This pattern is retained in compound **2** but not in compound **3**. It can be seen from Table VI that in the latter the (OH)–W–W(OH) distance, 2.7883(5) Å, is shorter than the other two $(HO)W–W(OH_2)$ distances, 2.8005(5) Å and 2.7980(5) Å. In fact the three W–W bond lengths are very similar and are significantly longer than the W–W separation in the triaqua compound. 2.746(1) Å [9]. Another puzzling phenomenon in structure **3** is the fact that the $W–OH_2$ distance is almost as short as the other two W–OH distances, 2.006(9) Å *vs.* 2.00(1) Å and 1.982(9) Å. This distance is considerably shorter than the $W–OH_2$ distance in the triaqua complex, 2.132(6) Å [9]. These results suggest that M–M and M–O bonds are not exclusively determined by the nature of the equatorial ligands (OH^- or H_2O) but are susceptible to intermolecular forces such as hydrogen bonding and electrostatic interactions in the lattice. The trinuclear cluster in **3** co-crystallizes with KBr and the strong bonding between the two hydroxo oxygen atoms OW(2) and OW(3), and some of the bridging acetate oxygen atoms with the potassium cation, may cause considerable strain on the cluster and deform it. A similar phenomenon was observed in another trinuclear metal cluster, namely, $[Nb_3O_2(SO_4)_6(H_2O)_3]^{5-}$ in which the three Nb–Nb distances differ from each other (2.875 Å, 2.889 Å, 2.892 Å) due to asymmetric intermolecular forces [10].

An alternative explanation to the increase in the W–W distance in the dihydroxo trimer is based on the assumption that some of the extra negative charge in the cluster (relatively to the 2+ triaqua ion) flows to metal–metal molecular orbitals with anti-bonding nature.

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Supplementary Material

Tables of structure factors, thermal parameters, non-essential bond distances and angles for **2** and **3** (47 pages), are available from the authors.

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