

Potentials of tungsten-containing clusters are 0.20 V more negative than those of their molybdenum analogues. This property, together with the lability of coordinated solvent molecules, leads to the possibility that reduced clusters in the presence of a protic source may be able to bind and effect reductive transformations of nitrogenase substrates. This matter and other structural, electronic, and reactivity features of individual MFe_3S_4 -type clusters are under investigation.

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Registry No. 6-Mo, 80766-33-2; 6-W, 80766-32-1; 7-Mo, 82281-65-0; 7-W, 82247-33-4; 8-Mo, 82247-35-6; 8-W, 82247-36-7; 8-Mo-DMSO, 82190-37-2; 9-Mo, 82247-34-5; 10-Mo, 82190-40-7; 10-W, 82190-41-8; 11-Mo, 82190-39-4; $(Et_4N)_3[Mo_2Fe_7S_8(SET)_{12}]$, 73589-29-4; $(Et_4N)_3[W_2Fe_7S_8(SET)_{12}]$, 73589-28-3.

Supplementary Material Available: Crystal structure data for $(Et_4N)_4[Mo_2Fe_6S_8(SET)_6(Pr_2cat)_2]$, thermal parameters of the anion (Table S-I), positional and thermal parameters of the cations (Table S-II), and calculated and observed structure factors (Table S-III) (28 pages). Ordering information is given on any current masthead page.

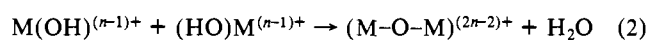
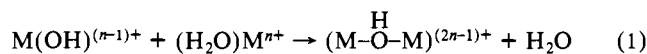
The Hydrogen Oxide Bridging Ligand ($H_3O_2^-$). 1. Dimerization and Polymerization of Hydrolyzed Trinuclear Metal Cluster Ions

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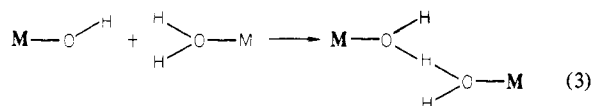
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Abstract: Trinuclear metal cluster ions of molybdenum and tungsten undergo hydrolysis in aqueous solutions. By the addition of various counterions such as Cl^- , Br^- , I^- , and NCS^- to this solution several hydrolysis products with different degrees of polymerization have been crystallized. The preparation and X-ray structural characterization of six new compounds are reported; full structural details are presented for two compounds. The two compounds are isomorphous having the formula $\{[M_3O_2(O_2CC_2H_5)_6(H_2O)_2]_2(H_3O_2)\}Br \cdot 6H_2O$, in compound **1**, $M = Mo$, and in **2**, $M = W$. They crystallized in space group $P\bar{1}$ with the following cell dimensions: **1**, $a = 14.358$ (4) Å, $b = 12.114$ (3) Å, $c = 11.402$ (2) Å, $\alpha = 111.08$ (2)°, $\beta = 105.69$ (3)°, $\gamma = 66.74$ (2)°, $V = 1680$ (2) Å³, and $Z = 1$; **2**, $a = 14.316$ (3) Å, $b = 12.115$ (2) Å, $c = 11.423$ (2) Å, $\alpha = 111.14$ (2)°, $\beta = 105.59$ (2)°, $\gamma = 66.59$ (2)°, $V = 1677$ (2) Å³, and $Z = 1$. Dimerization and polymerization occur by formation of a hydrogen oxide ligand ($H_3O_2^-$), bridging between two metal atoms of adjacent cluster ions. The $H_3O_2^-$ unit appearing in structures **1** and **2** is symmetric with an O-O separation of 2.52 (1) Å and 2.50 (1) Å, respectively.

$M(OH)^{(n-1)+}$, the primary product of hydrolysis of a metal aquo ion $M(OH_2)^{n+}$, often undergoes condensation reactions to form hydrolytic dimers and polymers.¹ It is generally assumed that the metal atoms in these dimers and polymers are bridged by μ -hydroxo or μ -oxo ligands.^{2,3} These bridges are formed by elimination of a water molecule from a pair of ions (eq 1 and 2).



This work reveals the existence of a different kind of bridging by means of a new ligand, the μ -hydrogen oxide ligand, $H_3O_2^-$. Bridging by this ligand may be accomplished by formation of a strong hydrogen bond between the hydroxo ligand of one metal ion and the water ligand of the other ion. Formation of this $H_3O_2^-$ bridge does not require the elimination of a water molecule (eq 3).



(1) Burgess, J. "Metal Ions in Solution"; E. Horwood: Chichester, 1978; pp 290-305.

(2) Cotton, F. A.; Wilkinson, G. "Advanced Inorganic Chemistry", 4th ed.; Wiley: New York, 1980; pp 152-153.

(3) Baes, C. F., Jr.; Mesmer, R. E. "The Hydrolysis of Cations"; Wiley: New York, 1976; pp 419-421.

Recent work on trinuclear clusters of the early transition elements in aqueous solution showed the existence of triangular species with a new type of structure, namely, M_3X_{17} shown in Figure 1.⁴⁻⁶ Molybdenum, tungsten, and niobium form a variety of M_3X_{17} triangular clusters all of which have the general formula $[M_3(\mu_3-X)_2(\mu-B)_6(H_2O)_3]^{n\pm}$ ($X = O, CCH_3$; $B = O_2CR, SO_4$). Clusters of group 6 metals are obtained by reaction of the hexacarbonyls with carboxylic acids.^{4,5} The niobium cluster is obtained by the reduction of Nb(V) in sulfuric acid.⁶

Almost all of the reports on the M_3X_{17} clusters dealt with two major aspects: (a) the preparation and (b) the structural characterization of these species.

The present work is part of a project exploring the chemistry of the M_3X_{17} metal clusters in aqueous solution including the substitution and electron-transfer reactions.

In a preliminary communication we reported the discovery of the complex ion $\{[M_3O_2(O_2CC_2H_5)_6(H_2O)_2]_2(H_3O_2)\}^{3+}$ ($M = Mo$,

(4) (a) Bino, A.; Ardon, M.; Maor, I.; Kaftory, M.; Dori, Z. *J. Am. Chem. Soc.* **1976**, *98*, 7093-7095. (b) Bino, A.; Cotton, F. A.; Dori, Z. *Ibid.* **1981**, *103*, 243-244. (c) Bino, A.; Cotton, F. A.; Dori, Z.; Kolthammer, B. W. S. *Ibid.* **1981**, *103*, 5779-5784. (d) Ardon, M.; Bino, A.; Cotton, F. A.; Dori, Z.; Kapon, M.; Kolthammer, B. W. S. *Inorg. Chem.* **1981**, *20*, 4083-4090. (e) Ardon, M.; Bino, A.; Cotton, F. A.; Dori, Z.; Kaftory, M.; Reisner, G. *Ibid.* **1982**, *21*, 1912.

(5) (a) Bino, A.; Cotton, F. A.; Dori, Z.; Koch, S.; Kuppers, H.; Millar, M.; Sekutowski, J. C. *Inorg. Chem.* **1978**, *17*, 3245-3253. (b) Bino, A.; Hesse, K.-F.; Kuppers, H. *Acta Crystallgr., Sect. B* **1980**, *B36*, 723-725.

(6) (a) Bino, A. *J. Am. Chem. Soc.* **1980**, *102*, 7990-7991. (b) Bino, A. *Inorg. Chem.* **1982**, *21*, 1917.

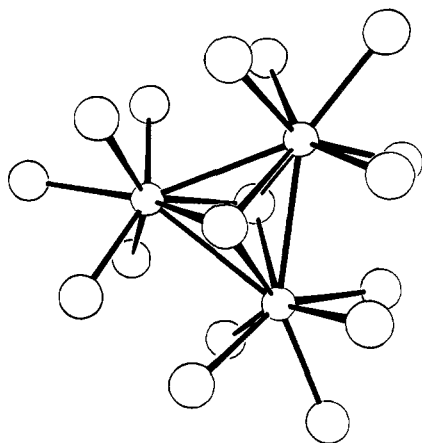


Figure 1. A general representation of the M_3X_{17} structure.

W) in which two triangular metal clusters are bridged by a μ - H_3O_2 ligand.⁷ This bridging ligand may play an important role, not only in the solid-state and solution chemistry of metal clusters but also in the hydrolysis of many other metal ions, such as simple aquo ions in solution.

With the purpose of determining the factors governing the occurrence of the $H_3O_2^-$ moiety in the solid state and the relationship with species in aqueous solution, we have synthesized a series of new compounds, all of which contain one or more bridging $H_3O_2^-$ ligands.

In a series of papers, these compounds will be described in detail. In the first paper we report the preparation and structure of six compounds, two of which will be described in detail. Structural results on the bridging $H_3O_2^-$ unit are presented here for the first time.

Experimental Section

Preparation of $[[Mo_3O_2(O_2CC_2H_5)_6(H_2O)_2](H_3O_2)]Br_3 \cdot 6H_2O$ (1). $Mo(CO)_6$ (1 g) was refluxed overnight with 100 mL of a 1:2 mixture of propionic acid and propionic anhydride. The resulting dark brown solution was diluted with 200 mL of H_2O and stirred on a hot plate at 70 °C for over 1 h. The solution was filtered and absorbed on a cation-exchange column (Dowex 50W-X2). The column was washed with a solution of KBr (0.2 M). The red band, remaining on the column, was eluted with 0.5 M KBr. Red crystals were obtained by slow evaporation of the eluate.

Preparation of $[W_3O_2(O_2CC_2H_5)_6(H_2O)_2](H_3O_2)]Br_3 \cdot 6H_2O$ (2). This compound was prepared in a way analogous to the Mo complex (1) using $W(CO)_6$. Anal. Calcd for $W_6Br_3O_{40}C_{36}H_{83}$: W, 44.16; Br, 9.60; C, 17.30; H, 3.32. Found: W, 44.4; Br, 9.85; C, 17.44; H, 3.13.

Preparation of $[Mo_3O_2(O_2CC_2H_5)_6(H_2O)_2](H_3O_2)]I_3 \cdot 6H_2O$ (3) and $[W_3O_2(O_2CC_2H_5)_6(H_2O)_2](H_3O_2)]I_3 \cdot 6H_2O$ (4). These compounds were prepared in the same way as 1 and 2, respectively, but the elution from the column was carried out with 0.5 M KI.

Preparation of $[W_3O_2(O_2CC_2H_5)_6(H_2O)_2](H_3O_2)]NCS$ (5). A 100-mg sample of 2 was dissolved in H_2O (15 mL). KNCS (0.75 g) was added, and the solution was placed in an open beaker. After a few hours, deep yellow-brown crystals were deposited.

Preparation of $[W_3O_2(O_2CC_2H_5)_6(H_2O)_2]Cl_2 \cdot H_2O$ (6). The same procedure as for 2. The yellow ion was eluted with 0.5 M KCl. The aqueous solution of 6 is strongly acidic. The pH of a solution of 4 mM is approximately 3.0.

Alternative Preparation of 2, 4, and 5. Compound 6 may be used as a starting material for the synthesis of these compounds. An excess of the appropriate salt KX ($X = Br, I, NCS$) is added to a concentrated aqueous solution of 6. The respective compounds precipitate upon evaporation of the solution.

X-ray Crystallography. Data were collected for compounds 1 and 2 on a PW 1100 Philips four-circle computer-controlled diffractometer. $Mo K\alpha$ ($\lambda = 0.71069 \text{ \AA}$) 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 $12^\circ < \theta < 16^\circ$. Data were measured by using a ω - 2θ motion. The scan width, $\Delta\omega$, for each reflection was 1° with scan time of 20 s. background mea-

Table I. Crystallographic Data

	1 ^a	2 ^b
space group	$P\bar{1}$	$P\bar{1}$
<i>a</i> , Å	14.358 (4)	14.316 (3)
<i>b</i> , Å	12.114 (3)	12.115 (2)
<i>c</i> , Å	11.402 (2)	11.423 (2)
α , deg	111.08 (2)	111.14 (2)
β , deg	105.69 (3)	105.59 (2)
γ , deg	66.74 (2)	66.59 (2)
<i>V</i> , Å ³	1680 (2)	1677 (2)
<i>d</i> (calcd), g cm ⁻³	1.95	2.48
<i>d</i> (exptl), g cm ⁻³	1.96 ± 0.01	2.49 ± 0.01
<i>Z</i>	1	1
μ , cm ⁻¹	28.07	116.54
range of 2θ , deg	3→52	3→55
no. of unique data	6521	7517
data with $F_o^2 > 3\sigma(F_o^2)$	3960	5276
<i>R</i> ₁	0.048	0.062
<i>R</i> ₂	0.053	0.072

^a 1, $[Mo_3O_2(O_2CC_2H_5)_6(H_2O)_2-(H_3O_2)-Mo_3O_2(O_2CC_2H_5)_6-(H_2O)_2]Br_3 \cdot 6H_2O$. ^b 2, $[W_3O_2(O_2CC_2H_5)_6(H_2O)_2-H_3O_2-W_3O_2(O_2CC_2H_5)_6(H_2O)_2]Br_3 \cdot 6H_2O$.

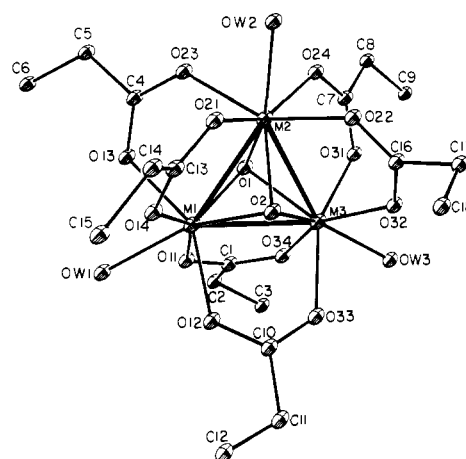


Figure 2. The labeling scheme of structures 1 and 2. For the sake of clarity all atoms were given an arbitrary isotropic thermal parameters of $U_{11} = 0.02 \text{ \AA}^2$. OW_3 is the oxygen atom of the $H_3O_2^-$ -bridging ligand.

surements were made at both limits of each scan. Crystallographic data and other pertinent information are given in Table I. For each crystal, Lorentz and polarization corrections were applied. Intensity data for 1 and 2 were corrected for absorption by the empirical ψ -scan method. The heavy-atom positions in 1 were obtained from a three-dimensional Patterson function, and the structure was refined⁸ in space group $P\bar{1}$ to convergence. All propionate hydrogen atoms and coordinated water hydrogen atoms including the two of the $H_3O_2^-$ ligand were located from the difference Fourier map. The 30 propionate hydrogen atoms were introduced at calculated positions (which were found to correspond to those found from the difference map), and the six coordinated water hydrogen atoms were introduced in the positions obtained from the difference Fourier map. Only those two in the $H_3O_2^-$ unit, H(1) and H(2), were refined; the other 34 hydrogen atoms in the structure were introduced as fixed contributions to F.

Anisotropic thermal parameters were used for all molybdenum, bromine, and oxygen atoms and isotropic ones for the carbon atoms and for H(1) and H(2). The positions of all non-hydrogen atoms of 2 were taken from 1. Anisotropic thermal parameters were used for all tungsten, bromine, and oxygen atoms and isotropic ones for all carbon atoms.

The discrepancy indices, $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$ and $R_2 = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2}$, are listed in Table I. The final difference map in both structures showed no peaks of structural significance. Lists of all observed and calculated structure factors are available as supplementary material. Details of data collection, solution, and refinement of the structures of 3–6 will appear elsewhere.

(8) 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 Standard Deviations^a for **1**

atom	x	y	z	atom	x	y	z
Mo(1)	0.35307 (6)	0.13578 (8)	0.17044 (7)	OW(5)	0.6063 (7)	0.244 (1)	0.2880 (9)
Mo(2)	0.20617 (6)	0.24760 (8)	0.32832 (7)	OW(6)	0.2816 (7)	0.4926 (8)	0.6501 (8)
Mo(3)	0.17784 (6)	0.06851 (8)	0.10030 (7)	C(1)	0.3787 (8)	-0.1415 (9)	0.0648 (9)
Br(1)	0.8506 (1)	0.2125 (1)	0.3197 (1)	C(2)	0.446 (1)	-0.277 (1)	0.034 (1)
Br(2)	0.50000 (0)	0.50000 (0)	0.50000 (0)	C(3)	0.395 (1)	-0.366 (2)	-0.052 (2)
O(1)	0.2883 (4)	0.0703 (6)	0.2521 (5)	C(4)	0.4282 (8)	0.173 (1)	0.452 (1)
O(2)	0.2037 (4)	0.2301 (6)	0.1468 (5)	C(5)	0.505 (1)	0.168 (1)	0.569 (1)
O(11)	0.4247 (5)	-0.0599 (6)	0.1019 (7)	C(6)	0.613 (1)	0.124 (1)	0.552 (1)
O(12)	0.3273 (5)	0.1308 (7)	-0.0211 (6)	C(7)	0.1289 (7)	0.0525 (9)	0.3329 (9)
O(13)	0.4539 (5)	0.1322 (6)	0.3424 (6)	C(8)	0.1023 (8)	-0.014 (1)	0.402 (1)
O(14)	0.3486 (5)	0.3214 (6)	0.2139 (6)	C(9)	0.065 (1)	-0.121 (1)	0.318 (1)
O(21)	0.2309 (5)	0.4108 (6)	0.3411 (6)	C(10)	0.2505 (8)	0.108 (1)	-0.102 (1)
O(22)	0.0522 (5)	0.3424 (6)	0.2746 (6)	C(11)	0.236 (1)	0.121 (1)	-0.232 (1)
O(23)	0.3355 (5)	0.2239 (7)	0.4688 (6)	C(12)	0.293 (2)	0.180 (2)	-0.256 (2)
O(24)	0.1510 (5)	0.1510 (6)	0.3983 (6)	C(13)	0.2872 (8)	0.417 (1)	0.278 (1)
O(31)	0.1284 (5)	0.0079 (6)	0.2155 (5)	C(14)	0.273 (1)	0.547 (1)	0.277 (1)
O(32)	0.0295 (5)	0.2016 (6)	0.0903 (6)	C(15)	0.335 (1)	0.553 (2)	0.199 (2)
O(33)	0.1860 (5)	0.0768 (7)	-0.0775 (6)	C(16)	-0.0012 (8)	0.309 (1)	0.1694 (9)
O(34)	0.2835 (5)	-0.1134 (6)	0.0506 (6)	C(17)	-0.104 (1)	0.399 (1)	0.131 (1)
OW(1)	0.4963 (5)	0.1151 (7)	0.1324 (7)	C(18)	-0.093 (2)	0.479 (3)	0.074 (3)
OW(2)	0.1547 (5)	0.3764 (7)	0.4969 (6)	H(1)	0.00000 (0)	0.00000 (0)	0.00000 (0)
OW(3)	0.0897 (5)	-0.0310 (7)	-0.0217 (6)	H(2)	0.109 (9)	-0.06 (1)	-0.08 (1)
OW(4)	0.9941 (6)	0.3718 (7)	0.5679 (7)				

^a Estimated standard deviations in the least significant digits are shown in parentheses.

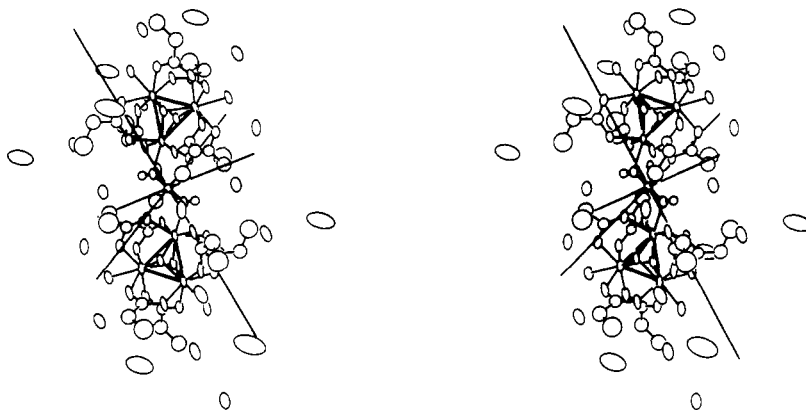


Figure 3. A stereoview of the unit cell of $\{[\text{Mo}_3\text{O}_2(\text{O}_2\text{CC}_2\text{H}_5)_6(\text{H}_2\text{O})_2]_2(\text{H}_3\text{O}_2)\}\text{Br}_3 \cdot 6\text{H}_2\text{O}$

Results

Compound 1. $\{[\text{Mo}_3\text{O}_2(\text{O}_2\text{CC}_2\text{H}_5)_6(\text{H}_2\text{O})_2]_2(\text{H}_3\text{O}_2)\}\text{Br}_3 \cdot 6\text{H}_2\text{O}$. The atomic positional parameters are listed in Table II while Table III gives the important bond lengths and angles. The thermal parameters and the calculated positional parameters of the propionato and coordinated water hydrogen atoms are listed in a table included in the supplementary material. Figure 2 shows the numbering scheme in **1** and **2** while Figure 3 gives a stereoview of the contents of the entire unit cell.

With $Z = 1$ in the space group $P\bar{1}$ there is only half a $\{[\text{Mo}_3\text{O}_2(\text{O}_2\text{CC}_2\text{H}_5)_6(\text{H}_2\text{O})_2]_2(\text{H}_3\text{O}_2)\}^{3+}$ ion in the asymmetric unit, with the other half related to it by a crystallographic inversion center at 0, 0, 0. There are three bromide anions in the cell two of which occupy general positions and one resides on a crystallographic inversion center at $1/2, 1/2, 1/2$.

The hydrogen oxide ion and its dimensions are shown in Figure 4. Both H(1) and H(2) were located from the difference Fourier map; H(1) was found on the crystallographic inversion center at 0, 0, 0. The thermal parameters of H(1) and H(2) and the positional parameters of H(2) were included in the least-squares refinement. The isotropic thermal vibration parameter, U_{11} , of H(1) and H(2) were refined to the reasonable values of 0.10 (6) and 0.06 (4) \AA^2 , respectively. The value of 0.7 (1) \AA for the OW(3)–H(2) distance is acceptable for such a structural study using X-ray data.⁹ More accurate values for the dimensions of

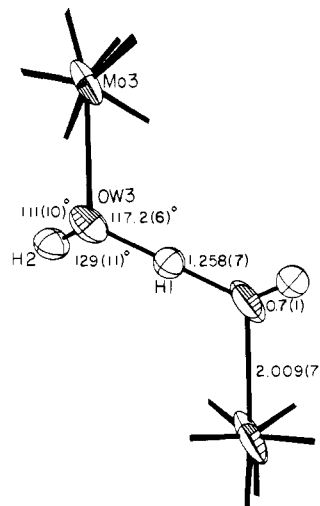


Figure 4. The structure and dimensions of the Mo–O(H)HO(H)–Mo portion in **1**. Only Mo–O bonds are depicted in the coordination sphere of the metal atoms. H(1) and H(2) were given an arbitrary isotropic thermal parameters of $U_{11} = 0.02 \text{ \AA}^2$ for the sake of clarity.

the H_3O_2^- unit may be obtained by neutron diffraction, and we are attempting to grow suitable crystals of **1** for such a study.

Compound 2. $\{[\text{W}_3\text{O}_2(\text{O}_2\text{CC}_2\text{H}_5)_6(\text{H}_2\text{O})_2]_2(\text{H}_3\text{O}_2)\}\text{Br}_3 \cdot 6\text{H}_2\text{O}$. This compound and **1** are isostructural. The atomic positional

(9) Hamilton, W. C.; Ibers, J. A. "Hydrogen Bonding in Solids"; W. A. Benjamin: New York, 1968; pp 49–52.

Table III. Important Bond Lengths (Å) and Angles (Deg) for 1

Bond Lengths			
Mo(1)-Mo(2)	2.751 (1)	Mo(2)-O(23)	2.097 (6)
-Mo(3)	2.774 (1)	-O(24)	2.093 (9)
-O(1)	1.985 (8)	-OW(2)	2.092 (6)
-O(2)	1.988 (5)	Mo(3)-O(1)	2.007 (5)
-O(11)	2.113 (6)	-O(2)	1.993 (7)
-O(12)	2.097 (7)	-O(31)	2.092 (8)
-O(13)	2.102 (6)	-O(32)	2.106 (5)
-O(14)	2.100 (8)	-O(33)	2.102 (7)
-OW(1)	2.116 (8)	-O(34)	2.099 (5)
Mo(2)-Mo(3)	2.775 (1)	-OW(3)	2.009 (7)
-O(1)	1.993 (5)	OW(3)-OW(3)	2.52 (1)
-O(2)	1.995 (6)	-H(1)	1.258 (7)
-O(21)	2.092 (9)	-H(2)	0.7 (1)
-O(22)	2.085 (5)		
Bond Angles			
Mo(2)-Mo(1)-Mo(3)	60.29 (3)	O(2)-Mo(2)-O(21)	77.7 (3)
-O(1)	46.4 (3)	-O(22)	78.4 (3)
-O(2)	46.4 (2)	-O(23)	126.9 (3)
-O(11)	124.5 (2)	-O(24)	127.4 (3)
-O(12)	125.4 (3)	-OW(2)	142.9 (3)
-O(13)	82.9 (2)	O(21)-Mo(2)-O(22)	85.4 (3)
-O(14)	82.2 (2)	-O(23)	85.0 (3)
-OW(1)	149.7 (3)	-O(24)	150.6 (4)
Mo(3)-Mo(1)-O(1)	46.3 (2)	-OW(2)	74.9 (3)
-O(2)	45.9 (2)	O(22)-Mo(2)-O(23)	149.9 (4)
-O(11)	82.4 (2)	-O(24)	85.5 (3)
-O(12)	83.3 (2)	O(22)-Mo(2)-OW(2)	75.0 (4)
-O(13)	125.5 (2)	O(23)-Mo(2)-O(24)	89.0 (3)
-O(14)	122.9 (2)	-OW(2)	74.9 (4)
-OW(1)	150.0 (3)	O(24)-Mo(2)-OW(2)	75.7 (3)
O(1)-Mo(1)-O(2)	73.8 (3)	Mo(1)-Mo(3)-Mo(2)	59.43 (3)
-O(11)	78.1 (3)	-O(1)	45.7 (1)
-O(12)	128.0 (3)	-O(2)	45.7 (2)
-O(13)	79.3 (3)	-O(31)	123.5 (2)
-O(14)	127.5 (3)	-O(32)	122.2 (2)
-OW(1)	142.8 (3)	-O(33)	82.0 (2)
O(2)-Mo(1)-O(11)	126.8 (3)	-O(34)	82.9 (2)
-O(12)	79.0 (3)	-OW(3)	151.8 (2)
-O(13)	127.8 (3)	Mo(2)-Mo(3)-O(1)	45.9 (3)
-O(14)	77.0 (3)	-O(2)	45.9 (2)
-OW(1)	143.6 (3)	-O(31)	81.8 (2)
O(11)-Mo(1)-O(12)	84.3 (4)	-O(32)	81.5 (2)
-O(13)	88.6 (4)	-O(33)	124.0 (2)
-O(14)	151.7 (3)	-O(34)	123.2 (2)
-OW(1)	75.3 (3)	-OW(3)	148.8 (3)
O(12)-Mo(1)-O(13)	149.1 (3)	O(1)-Mo(3)-O(2)	73.2 (3)
-O(14)	86.5 (3)	-O(31)	77.9 (3)
-OW(1)	74.9 (3)	-O(32)	126.4 (3)
O(13)-Mo(1)-O(14)	85.7 (3)	-O(33)	126.2 (3)
-OW(1)	74.2 (3)	-O(34)	77.4 (3)
O(14)-Mo(1)-OW(1)	76.5 (4)	-OW(3)	143.9 (3)
Mo(1)-Mo(2)-Mo(3)	60.27 (3)	O(2)-Mo(3)-O(31)	126.4 (3)
-O(1)	46.1 (1)	-O(32)	76.4 (3)
-O(2)	46.2 (2)	-O(33)	78.1 (3)
-O(21)	82.9 (3)	-O(34)	127.4 (3)
-O(22)	124.6 (2)	-OW(3)	142.8 (3)
-O(23)	82.3 (2)	O(31)-Mo(3)-O(32)	86.2 (3)
-O(24)	124.8 (3)	-O(33)	152.3 (3)
-OW(2)	149.3 (2)	-O(34)	87.2 (3)
Mo(3)-Mo(2)-O(1)	46.3 (2)	-OW(3)	75.6 (3)
-O(2)	45.9 (2)	O(32)-Mo(3)-O(33)	88.1 (3)
-O(21)	123.5 (2)	-O(34)	153.1 (3)
-O(22)	83.2 (3)	-OW(3)	75.8 (4)
-O(23)	125.5 (3)	O(33)-Mo(3)-O(34)	85.7 (3)
-O(24)	82.9 (2)	-OW(3)	76.8 (3)
-OW(2)	150.4 (2)	O(34)-Mo(3)-OW(3)	77.2 (4)
O(1)-Mo(2)-O(2)	73.5 (3)	Mo(1)-O(1)-Mo(2)	87.5 (3)
-O(21)	128.0 (3)	-Mo(3)	88.0 (2)
-O(22)	128.2 (3)	Mo(2)-O(1)-Mo(3)	87.9 (3)
-O(23)	79.3 (3)	Mo(1)-O(2)-Mo(2)	87.3 (3)
-O(24)	78.6 (3)	-Mo(3)	88.4 (3)
-OW(2)	143.6 (3)	Mo(2)-O(2)-Mo(3)	88.2 (2)
		Mo(3)-OW(3)-H(1)	117.2 (6)
		-H(2)	111 (10)
		H(1)-OW(3)-H(2)	129 (11)

parameters are listed in Table IV. Tables of thermal parameters and bond lengths and angles are included in the supplementary material.

Compounds 3 and 4. $[\{M_3O_2(O_2CC_2H_5)_6(H_2O)_2\}_2(H_3O_2)]I_3 \cdot 6H_2O$ ($M = Mo, W$). These two compounds form isomorphous crystals. They crystallize in the triclinic space group $P\bar{1}$ with $Z = 2$. The asymmetric unit contains an entire $[\{M_3O_2(O_2CC_2H_5)_6(H_2O)_2\}_2(H_3O_2)]^{3+}$ ion; hence there is no crystallographic symmetry imposed on this ion as in **1** or **2**. There are six iodide anions in the cell. The geometry and dimensions of the $3+$ cation in **3** ($M = Mo$) and **4** ($M = W$) are essentially identical with those found in **1** and **2**, respectively. The detailed structural information of **3** and **4** will be presented elsewhere.

Compound 5. $[W_3O_2(O_2CC_2H_5)_6(H_2O)(H_3O_2)]NCS$. In this compound, each triangular W_3 cluster is bridged by two $H_3O_2^-$ ligands to two adjacent clusters forming an infinite chain in the lattice. The asymmetric unit of space group $P2_1/c$ contains one $[W_3O_2(O_2CC_2H_5)_6(H_2O)(H_3O_2)]^+$ ion and one NCS^- anion. The detailed structure will be presented elsewhere.

Compound 6. $[W_3O_2(O_2CC_2H_5)_6(H_2O)_3]Cl_2 \cdot H_2O$. The $[W_3O_2(O_2CC_2H_5)_6(H_2O)_3]^{2+}$ unit is essentially identical with that found in the fluoroborate salt $[W_3O_2(O_2CC_2H_5)_6(H_2O)_3] \cdot (BF_4)_2 \cdot 5.5H_2O$.^{5a} The $2+$ charge is balanced by two chloride anions in the lattice. The detailed structure will be presented elsewhere.

Discussion

The existence of the hydrogen oxide anion, $H_3O_2^-$, has been postulated for a long time¹⁰ but only recently has the first structural characterization of this species been accomplished.¹¹ The compound $Na_2[(C_2H_5)_3(CH_3)N][Cr(PhC(S)=N(O))_3] \cdot \frac{1}{2}NaH_3O_2 \cdot 18H_2O$, described by Raymond et al., has been crystallized from an alkaline solution and is the first example of a crystalline substance containing the "hydrated hydroxide", $H_3O_2^-$, ion as a *discrete entity* in a crystal lattice. This species is the primary hydration product of OH^- with a symmetric $O \cdots H \cdots O$ bond and $O-O$ separation of 2.29 Å. The central $H_3O_2^-$ ion is surrounded by four additional water molecules, each forming a hydrogen bond to a lone pair on one of the oxygen atoms of the $H_3O_2^-$ ion.

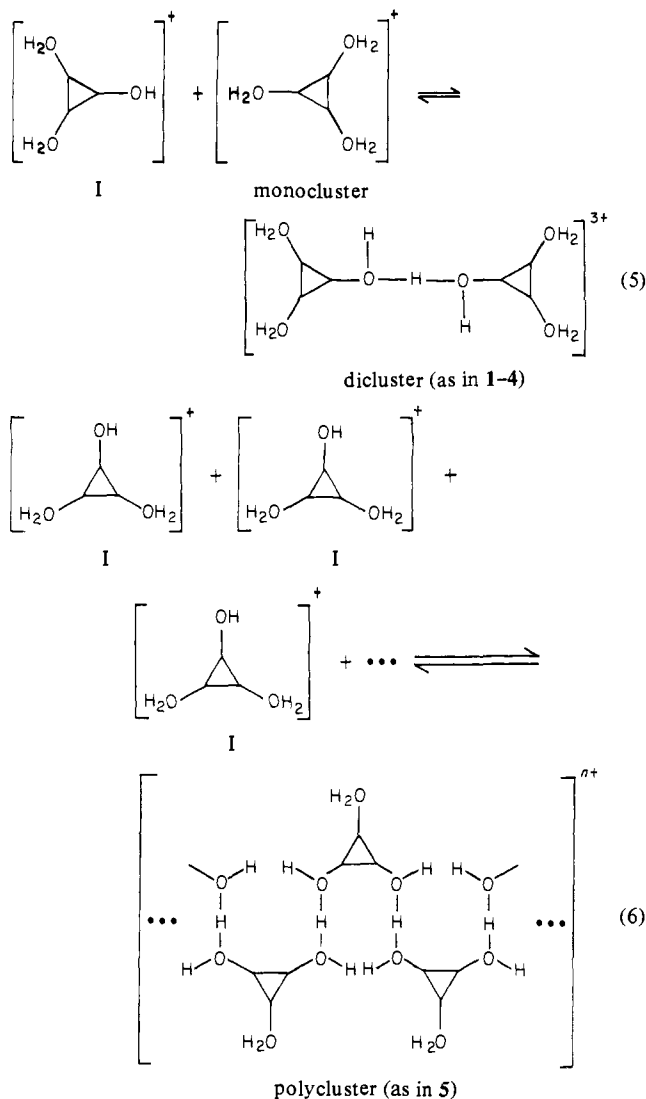
In the present work we describe a series of compounds that contain a hydrogen oxide *bridging ligand* between two metal atoms. These compounds have been crystallized from acidic solutions.

The bridging $H_3O_2^-$ unit in compounds **1** (Figure 4) and **2** is symmetric just as the discrete unit in Raymond's compound. In all three cases it resides on a crystallographic inversion center, and in **1** the central hydrogen atom is located on the inversion center. The structural differences between the $H_3O_2^-$ unit in Raymond's compound and those found in our series are the following (a) the four electron pairs on each of the $H_3O_2^-$ oxygen atoms in the free ion are engaged in bonds to hydrogen atoms (two covalent $O-H$ bonds and two long-range hydrogen bonds) while in the bridging $H_3O_2^-$ ligands only three electron pairs are utilized as can be seen in Figure 4. (b) The $O-O$ separation in the coordinated unit is significantly longer (2.52 Å in **1** and 2.50 Å in **2**) than the 2.29 Å reported by Raymond.¹¹ These differences are due to the fact that the oxygen atoms of the $H_3O_2^-$ ligand are coordinated to the metal atoms, donating a pair of electrons to the metal orbitals and hence becoming more positively charged.

The replacement of one water ligand in the M_3 cluster by an $H_3O_2^-$ ligand causes a considerable distortion of the equilateral triangle of metal atoms. Table V shows the $M-M$ bond distances in compounds **1** and **2** as compared with **6** and those found in $[W_3O_2(O_2CC_2H_5)_6(H_2O)_3](BF_4)_2$ ^{5a} and $[Mo_3O_2(O_2CC_2H_5)_6$

(10) (a) Zundel, G. "The Hydrogen Bond, Recent Developments in Theory and Experiment. Structure and Spectroscopy"; Shuster, P.; Zundel, G.; Sandorfy, C.; Eds.; North-Holland Publishing Co.: Amsterdam, 1979; Vol. II, Chapter 15. (b) Gennick, I.; Harmon, K. M.; Hartwig, J. *Inorg. Chem.* **1977**, *16*, 2241-2248. (c) Harmon, K. M.; Gennick, I. *Ibid.* **1975**, *14*, 1840-1845. (d) Harmon, K. M.; Gennick, I. *J. Mol. Struct.* **1977**, *39*, 39-49.

(11) (a) Abu-Dari, K.; Raymond, K. N.; Freyberg, D. P. *J. Am. Chem. Soc.* **1979**, *101*, 3688-3689. (b) Abu-Dari, K.; Freyberg, D. P.; Raymond, K. N. *Inorg. Chem.* **1979**, *18*, 2427-2433.



of a *dicluster* consisting of one H_3O_2^- and three X^- anions becomes more favorable with Br^- and I^- than with Cl^- .¹³ The NCS^- ion is even larger than Br^- or I^- and the energy gained by hydrogen bonding of this ion in the lattice is even smaller. Therefore the solubilities of both the *mono-* and the *dicluster* thiocyanates are large enough to enable the precipitation of the *polycluster* ion

(13) The BF_4^- and the CF_3SO_3^- salts of $[\text{M}_3\text{O}_2(\text{O}_2\text{CC}_2\text{H}_5)_6(\text{H}_2\text{O})_3]^{2+}$ crystallize as *monoclusters*^{5a,46} due to the extensive network of strong hydrogen bonds surrounding these anions.

present in solution by NCS^- . In this salt (5) the 2+ charge of the W_3 cluster is balanced by one NCS^- and one (two halves) H_3O_2^- ligand.

Is the existence of H_3O_2^- -bridged "dimers" and "polymers" in equilibrium with hydrolyzed "monomers" in solution a phenomenon limited only to trinuclear metal clusters?

As we mentioned before, no substantial differences exist between a water ligand in a metal cluster coordination and a water ligand bound to a mononuclear metal ion (such as Fe^{3+} or Al^{3+}). Therefore it is quite possible that the existence of H_3O_2^- -bridged polymer ions is a general phenomenon in aqueous solutions of many metal ions. The fact that other salts containing the hydrogen oxide bridging ligand have not been crystallized before may be due to their high solubility. Even in systems containing species such as $[\text{M}_3(\mu_3\text{-O})_2(\mu\text{-L})_6(\text{H}_2\text{O})_3]^{2+}$, H_3O_2^- -bridged clusters crystallized only with $\text{L} = \text{O}_2\text{CC}_2\text{H}_5$ and not with smaller μ_2 -ligands such as acetates.^{4c}

All the dimeric and polymeric hydrolysis products of metal ions that are believed to be bridged by μ -hydroxo or μ -oxo bridges are formed in reactions much slower than the reaction forming the mononuclear hydroxo species $\text{M}(\text{OH})^{(n-1)+}$. If polymeric species with H_3O_2^- bridges, as suggested in this work, do exist in aqueous solution, they are probably formed from the mononuclear species by an "instantaneous" (diffusion-controlled) reaction because their formation requires only a hydrogen bond formation and does not involve any metal-ligand bond breaking. In contrast to this very rapid reaction, the rate of formation of dimers and polymers bridged by $\mu\text{-OH}$ or $\mu\text{-O}$ ligands is slower by many orders of magnitude since these reactions require breaking of M-L bonds.¹⁴

Another important difference between the $\mu\text{-H}_3\text{O}_2^-$ -bridged polymers and the $\mu\text{-OH}$ or $\mu\text{-O}$ species is the metal to metal separation. $\mu\text{-H}_3\text{O}_2^-$ bridging is characterized by an M-M separation of ca. 5.6 Å. This is much longer than in any $\mu\text{-OH}$ or $\mu\text{-O}$ complex.¹ Investigating the existence of μ -hydrogen oxide bridged polymers in aqueous solutions of ordinary metal ions is not an easy task. We intend to employ suitable techniques such as EXAFS and X-ray scattering experiments to this end.

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Registry No. 1, 79417-66-6; 2, 79716-36-2; 3, 82044-75-5; 4, 82044-76-6; 5, 82044-77-7; 6, 82065-72-3; $\text{Mo}(\text{CO})_6$, 13939-06-5; $\text{W}(\text{CO})_6$, 14040-11-0.

Supplementary Material Available: Tables of structure factors of 1 and 2, thermal parameters of 1 and 2, bond distances and angles in the propionato ligands in 1, calculated positions of the hydrogen atoms in 1, and bond distances and angles in 2 (64 pages). Ordering information is given on any current masthead page.

(14) For example, the first-order rate constant of the reaction $\text{Fe}_2(\text{OH})_2^{4+} \rightleftharpoons \text{Fe}(\text{OH})^{2+}$ was estimated to be 0.4 s^{-1} (ref 3, p 234).