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Hydrogen **Oxide (H_3O_2) Bridge Formation in Trinuclear Metal Cluster Systems. The Structure of $[W_3O_2(O_2CCH_3)_6(H_2O)(H_3O_2)]$ NCS·H_2O**

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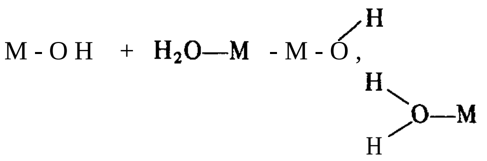
The formation of μ-H_3O_2 bridges between trinuclear metal clusters was shown in ions such as $\{[M_3O_2(pr)_6(H_2O)_2]_2(H_3O_2)\}^{3+}$ (I) and $[M_3O_2(pr)_6(H_2O)(H_3O_2)]^+$(2) where M = Mo(IV), W(IV) and pr = $O_2CCH_2CH_3$ [1–3]. This bridge is the result of a strong hydrogen bond between an OH ligand of one trimer and an H_2O ligand of another:



In **1,** there is a '**dimer**' of clusters bridged by one $H_3O_2^-$ unit and 2 is a 'polymer' of clusters bridged by this unit [2, 3].

The occurrence of such bridges between metal atoms in the solid state was first attributed to the size of the bulky hexapropionato trinuclear cluster and to the presence of various counter ions in the crystal [2]. Later it was shown that the major factor that determines the relative concentration of the various polymeric hydrolysis products is the H^+ ion concentration [3].

In this work we examine the influence of the cluster size on the H_3O_2 bridge formation. We report the preparation and structure of the acetato analogue of the 'polycluster', namely, the compound $[W_3O_2(O_2CCH_3)_6(H_2O)(H_3O_2)]$ NCS·H_2O (3).

Experimental

Yellow-brown crystals of 3 were obtained by the dissolution of $[W_3O_2(OAc)_6(H_2O)_3](CF_3SO_3)_2$ (0.05 g), prepared by a literature method [4], in 10 ml of 0.5 M KNCS and slow evaporation of the solution.

The crystals were found to belong to the monoclinic space-group $P2_1/c$ *with* a = 10.577(1) A, b = 16.748(2) Å, c = 15.479(2) Å, β = 110.64(3)° and V = 2566(1) Å^3 and Z = 4. A total of 3641 reflections were collected in the range of 3” < 2θ < 45°, of which 2822 were found to have Z > $3\sigma(I)$ and were used in refining of the structural parameters. The structure was relined by least-squares methods to a conventional ***R*** factor of 4.65%.

Results and Discussion

The positional parameters are listed in Table I, and Table II presents some important bond distances and angles. Figure 1 shows the trinuclear cluster and the numbering scheme.

TABLE I. Positional Parameters and e.s.d.s for $[W_3O_2(OAc)_6(H_2O)(H_3O_2)]$NCS·$H_2O$.[a]

Atom	*x*	Y	z
W(1)	0.04488(8)	0.13670(5)	0.21832(5)
W(2)	0.05794(8)	−0.02420(5)	0.26240(6)
W(3)	0.27383(7)	0.04974(5)	0.23497(6)
S(1)	0.6151(8)	0.8032(5)	0.8236(8)
O(1)	0.172(1)	0.0715(7)	0.3193(8)
O(2)	0.081(1)	0.0388(7)	0.1562(8)
O(11)	0.078(1)	0.1835(8)	0.1016(9)
O(12)	−0.151(1)	0.1042(8)	0.1300(9)
O(13)	0.186(1)	0.2247(8)	0.2902(9)
O(14)	−0.041(1)	0.1460(8)	0.3233(9)
O(21)	−0.138(1)	−0.0251(7)	0.1657(9)
O(22)	0.208(1)	−0.0755(8)	0.3736(9)
O(23)	−0.032(1)	0.0153(8)	0.356(1)
O(24)	0.105(1)	−0.1131(8)	0.1847(9)
O(31)	0.264(1)	0.1127(8)	0.1159(9)
O(32)	0.371(1)	0.1523(9)	0.305(1)
O(33)	0.385(1)	−0.0169(9)	0.3501(9)
O(34)	0.278(1)	−0.0542(8)	0.161(1)
OW(1)	−0.064(1)	0.2414(8)	0.1899(9)
OW(2)	−0.028(1)	−0.1237(8)	0.293(1)
OW(3)	0.472(1)	0.0464(8)	0.2292(9)
N(1)	0.590(3)	0.692(2)	0.844(2)
C(1)	0.312(2)	0.218(1)	0.320(1)
C(2)	0.404(2)	0.283(1)	0.370(2)
C(3)	0.332(2)	−0.064(1)	0.395(1)
C(4)	0.429(2)	−0.103(1)	0.482(2)
C(5)	−0.199(2)	0.032(1)	0.119(1)
C(6)	−0.336(2)	0.020(1)	0.046(2)
C(7)	−0.052(2)	0.089(1)	0.3720)
C(8)	-0.100(3)	0.108(2)	0.452(2)
C(9)	0.194(2)	−0.114(1)	0.150(1)
C(10)	0.211(2)	−0.184(1)	0.093(1)
C(11)	0.172(2)	0.161(1)	0.075(1)
C(12)	0.178(2)	0.197(1)	-0.014(2)
CN(1)	0.504(3)	0.738(2)	0.832(2)
DL(1)	0.680(3)	−0.052(2)	0.314(2)

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

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TABLE II. Important Bond Lengths (A) and Angles (deg.) for $[W_3O_2(OAc)_6(H_2O)(H_3O_2)]NCS\cdot H_2O$.

Lengths			
W(1)-W(2)	2.771(1)	W(2)-O(21)	2.09(1)
W(l)-W(3)	2.759(1)	W(2)-O(22)	2.07(1)
W(2)-W(3)	2.759(1)	W(2)-O(23)	2.10(1)
W(l)-O(1)	1.99(1)	W(2)-O(24)	2.08(1)
W(l)-O(2)	2.01(1)	W(2)-OW(2)	2.03(1)
W(l)-O(11)	2.11(1)	W(3)-O(1)	2.00(1)
W(1)-O(12)	2.12(1)	W(3)-O(2)	1.98(1)
W(1)-O(13)	2.12(1)	W(3)-O(31)	2.09(1)
W(1)-O(14)	2.13(1)	W(3)-O(32)	2.10(1)
W(1)-OW(1)	2.06(1)	W(3)-O(33)	2.08(1)
W(2)-O(1)	2.01(1)	W(3)-O(34)	2.09(1)
W(2)-O(2)	2.04(1)	W(3)-OW(3)	2.13(1)
OW(1)-OW(2)	2.44(2)		
Angles			
W(3)-W(l)-W(2)		59.85(3)	
W(3)-W(2)-W(1)		59.85(3)	
W(l)-W(3)-W(2)		60.30(3)	

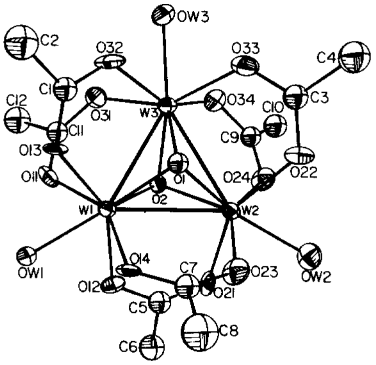

Fig. 1. The $[W_3O_2(OAc)_6(H_2O)(H_3O_2)_{2/2}]^+$ ion in 3 and the labeling scheme. OW(l) and OW(2) form the $H_3O_2^-$ bridges with the neighbouring clusters.

The asymmetric unit contains one $[W_3O_2(OAc)_6(H_2O)(H_3O)_2)_{2/2}]^+$ unit (where $(H_3O_2)_{2/2}$ denotes two doubly shared $H_3O_2^-$ bridges) and one NCS^- anion. The 2+ charge of the $[W_3O_2(OAc)_6]^{2+}$ unit is balanced by one NCS^- and one (two halves) $H_3O_2^-$ unit. Figure 2 shows how the trimers are linked together by $H_3O_2^-$ bridges, forming infinite chains in the crystal.

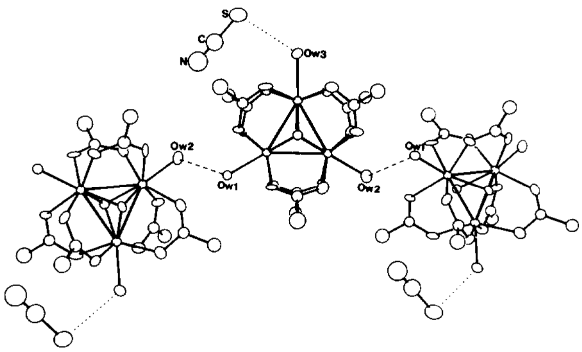

Fig. 2. Infinite chain of $\cdots H_3O_2{-}W_3{-}H_3O_2{-}W_3\cdots$ units in 3. The O···H···O bonds in the $H_3O_2^-$ units are represented by dashed lines. Hydrogen bond between the thiocyanate ion and the H_2O ligand OW(3) are represented by dotted lines.

The oxygen atoms of the $H_3O_2^-$ unit, OW(l) and OW(2), are not symmetry related and the short O··· 0 distance, 2.44(2) A is the result of the 2_1 symmetry element, transferring 0W(2) to the proximity of OW(l) of a neighbouring trimer. This distance is within the range of 2.44-2.52 Å found in other H_3O_2 units bridging trinuclear clusters [2,3] and is identical with the O··.·0 (H_3O_2) separation found in the propionato analogue, 2 [3]. We attribute this fact to the strong O···H···O interaction that exists in these two compounds. To preserve this interaction in 2, the clusters move away from each other in order to accommodate the bulkier propionato ligands. As a result, the chains in 2 deviate from a linear arrangement, much more than in 3, the O···O–W–W–O··· 0 chain in 2 being approximately sinusoidal [3].

The results presented here support the assumption that formation of H_3O_2 bridges is mainly pH-dependent, and that the size of the bridged clusters play only a minor role [3].

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References

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