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The Hydrogen Oxide Bridging Ligand ($H_3O_2^-$). 2. Effect of the Hydrogen Ion Concentration

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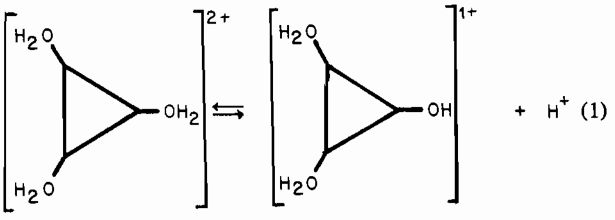
The trinuclear M(IV) cluster ion $[M_3O_2(pr)_6(H_2O)_3]^{2+}$ (M = Mo, W; pr = $O_2CC_2H_5$) undergoes extensive hydrolysis in aqueous solution and produces hydroxo species. Dimerization and polymerization of these clusters proceed via formation of the hydrogen oxide bridging ligand, μ-$H_3O_2^-$. This ligand is formed by a strong hydrogen bond between the hydroxo ligand of one cluster and an aquo ligand of another. In solution, all species exist in equilibrium and their relative concentration is pH dependent. Different crystalline products have been obtained by varying the hydrogen ion concentration of solutions containing the trinuclear cluster ion $[M_3O_2(pr)_6(H_2O)_3]^{2+}$, M = Mo, W (in 0.5 M KNCS). When the H^+ concentration is 1 M, crystals of $[W_3O_2(pr)_6(H_2O)_3](NCS)_2$ (**1**) are deposited. At $[H^+]$ = 0.05 M crystals of $\{[W_3O_2(pr)_6(H_2O)_2]_2(H_3O_2)\}(NCS)_3 \cdot H_2O$ (**2**) and of its molybdenum analogue $\{[Mo_3O_2(pr)_6(H_2O)_2]_2(H_3O)\}(NCS)_3 \cdot H_2O$ (**3**) are obtained. When no acid is added, crystals of $[W_3O_2(pr)_6(H_2O)(H_3O_2)]NCS$ (**4**) are obtained. Crystals of the four compounds were subjected to a detailed X-ray structural analysis. Compound **1** forms monoclinic crystals, space group $P2_1/c$, with a = 17.953 (3) Å, b = 18.923 (3) Å, c = 10.034 (2) Å, β = 94.59 (2)°, V = 3398 (1) Å^3, and Z = 4. Compound **2** forms triclinic crystals, space group $P\bar{1}$, with a = 11.334 (2) Å, b = 17.393 (3) Å, c = 9.011 (2) Å, α = 98.63 (3)°, β = 110.48 (3)°, γ = 100.09 (2)°, V = 1595 (1) Å^3, and Z = 1. Compound **3** is isostructural with **2** with a = 11.347 (2) Å, b = 17.399 (3) Å, c = 9.004 (2) Å, α = 98.69 (3)°, β = 110.57 (3)°, γ = 100.15 (3)°, and V = 1594 (1) Å^3. Compound **4** forms monoclinic crystals, space group $P2_1/c$, with a = 14.842 (2) Å, b = 13.611 (2) Å, c = 16.432 (2) Å, β = 111.29 (2)°, V = 3093 (1) Å^3, and Z = 4. Compound **1** contains discrete $[W_3O_2(pr)_6(H_2O)_3]^{2+}$ units (monocluster). The 2+ charge of the cation is balanced by two NCS^- anions. In **2** and **3** two trinuclear clusters are bridged by a μ-$H_3O_2^-$ ligand and the 3+ charge of the dicluster is balanced by three NCS^- ions. Structure **4** consists of infinite chains of triangular W_3 clusters (polycluster); each μ-$H_3O_2^-$ ligand bridges two adjacent clusters. The O---O separations in the $H_3O_2^-$ unit in compounds **2**, **3**, and **4** are 2.46 (1), 2.52 (1), and 2.44 (1) Å, respectively.

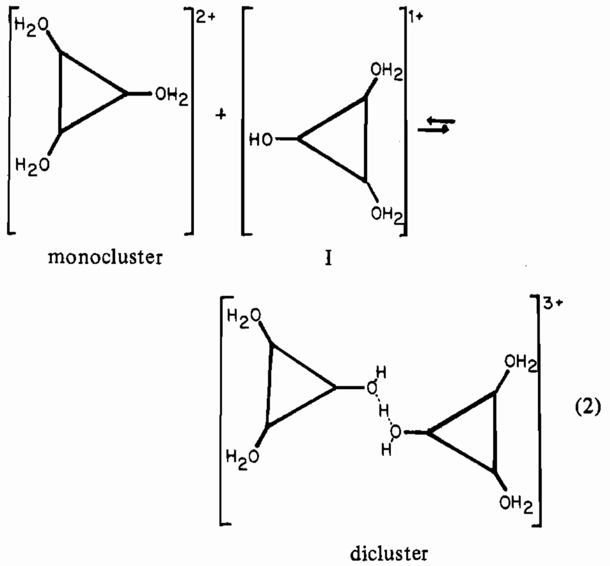
Introduction

The formation of the trinuclear cluster ion $[W_3O_2(pr)_6(H_2O)_3]^{2+}$ (pr = $O_2CC_2H_5$) was reported several years ago.[1] This ion was prepared by the reaction of $W(CO)_6$ with propionic acid followed by isolation of this species by ion-exchange chromatography. The yellow fluoroborate salt of this ion, $[W_3O_2(pr)_6(H_2O)_3](BF_4)_2 \cdot 5^1/_2H_2O$, was prepared by elution of the 2+ cation from an ion-exchange column with aqueous HBF_4 and slow evaporation of the eluant.[1] The molybdenum analogue, $[Mo_3O_2(pr)_6(H_2O)_3]^{2+}$, was prepared by the reaction of $Mo(CO)_6$ or $Mo_2(OAc)_4$ with propionic acid.[2,3]

Recently,[2] we have shown that salts of the ion $[M_3O_2(pr)_6(H_2O)_3]^{2+}$ (M = W, Mo) ("monocluster") are extensively hydrolyzed in aqueous solution by the deprotonation of a coordinated water ligand as in eq 1 (where the μ_3-O and propionato ligands are omitted—see Figure 1). Dimerization and polymerization of hydrolyzed cluster ions in solution was shown to be accomplished by the hydrogen oxide bridging ligand, $H_3O_2^-$. This ligand is formed by a strong hydrogen bond between the hydroxo ligand in I ($[M_3O_2(pr)_6(H_2O)_2(OH)]^+$) and the water ligand of another ion. The reaction of I with a monocluster produces a "dimer" or "dicluster" in which the two clusters are bridged by an $H_3O_2^-$ ligand as in eq 2.[2] Similarly, the reaction of several I ions with each other may form a polymeric chain ("polycluster") as in eq 3. We have shown that salts of diclusters or polyclusters are precipitated from an aqueous solution of a monocluster salt by the addition of certain counterions. Whereas counterions such as BF_4^-, $CF_3SO_3^-$, and Cl^- precipitated salts of monoclusters, Br^- and I^- precipitated salts of diclusters and NCS^- precipitated salts of polyclusters. It was suggested that both the dicluster and polycluster ions exist in solution in equilibrium with species I as in reactions 2 and 3.



monocluster I



dicluster

For a given total metal concentration, the relative concentrations of these species should be pH dependent. At low pH the monocluster predominates, at a higher pH (~p*K*) the dicluster should reach maximum concentration, and at still

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(1) Bino, A.; Cotton, F. A.; Dori, Z.; Koch, S.; Kuppers, H.; Millar, M.; Sekutowski, J. C. *Inorg. Chem.* **1978**, *17*, 3245–3253.

(2) (a) Bino, A.; Gibson, D. *J. Am. Chem. Soc.* **1981**, *103*, 6741–6742. (b) Bino, A.; Gibson, D. *Ibid.* **1982**, *104*, 4383–4388.

(3) Ardon, M.; Bino, A.; Cotton, F. A.; Dori, Z.; Kaftory, M.; Reisner, G. *Inorg. Chem.* **1982**, *21*, 1912.

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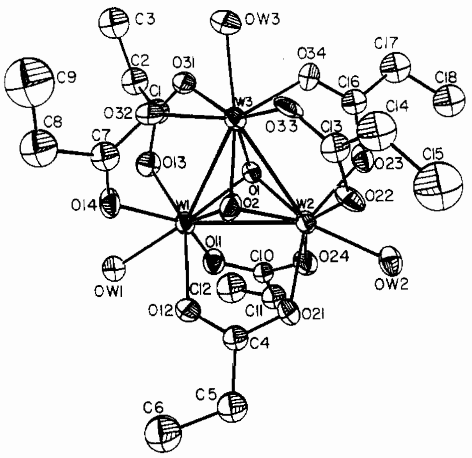
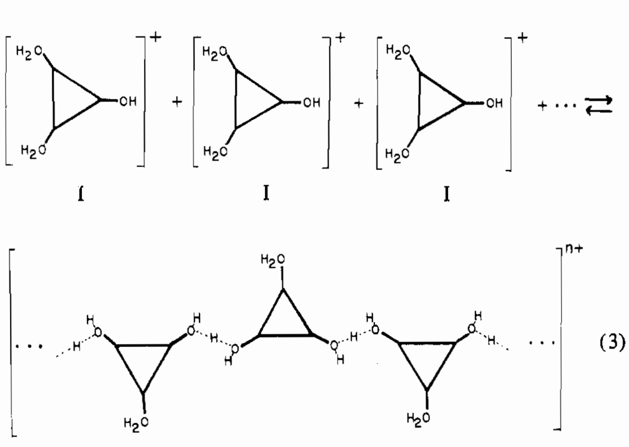


Figure 1. Labeling scheme of structures **1**, **2**, and **3**. In **2** and **3**, OW2 is the oxygen atom of the $H_3O_2^-$ bridging ligand.

Table I. Crystallographic Data

	1[a]	2[b]	3[c]	4[d]
space group	$P2_1/c$	$P\bar{1}$	$P\bar{1}$	$P2_1/c$
a, Å	17.953 (3)	11.334 (2)	11.347 (2)	14.842 (2)
b, Å	18.923 (3)	17.393 (3)	17.399 (3)	13.611 (2)
c, Å	10.034 (2)	9.011 (2)	9.004 (2)	16.432 (3)
α, deg		98.63 (3)	98.69 (3)	
β, deg	94.59 (2)	110.48 (3)	110.57 (3)	111.29 (2)
γ, deg		100.09 (2)	100.15 (3)	
V, Å^3	3398 (1)	1595 (1)	1594 (1)	3093 (1)
Z	4	1	1	4
μ, cm^{-1}	98.85	105.00	21.01	107.9
range of 2θ, deg	3–46	3–45	3–46	3–45
no. of unique data	4677	4123	4354	4012
data with $F_o^2 > 3\sigma(F_o^2)$[e]	3724	3508	3298	3385
R_1	0.058	0.038	0.049	0.035
R_w	0.070	0.044	0.058	0.039

[a] 1: $[W_3O_2(pr)_6(H_2O)_3](NCS)_2$; monocluster.
[b] 2: $\{[W_3O_2(pr)_6(H_2O)_2]_2(H_3O_2)\}(NCS)_3\cdot H_2O$; dicluster.
[c] 3: $\{[Mo_3O_2(pr)_6(H_2O)_2]_2(H_3O_2)\}(NCS)_3\cdot H_2O$; dicluster.
[d] 4: $[W_3O_2(pr)_6(H_2O)(H_3O_2)]NCS$; polycluster. [e] Refinement on $|F|$.



polycluster (3)

higher pH the equilibrium in solution should shift toward the polycluster ion. If this scheme is correct, it should be possible, at least in principle, to obtain salts of mono-, di-, and polyclusters by varying the pH of the solution. In order to eliminate the specific effects of different counterions on the system, all solutions should contain the *same* counterion.

This work reports the achievement of this aim by the use of thiocyanate as a counterion. The preparation and the structural characterization by an X-ray analysis of thiocyanate salts belonging to the three types mentioned above are reported.

We shall describe the following four compounds: $[W_3O_2(pr)_6(H_2O)_3](NCS)_2$ (**1**) (monocluster); $\{[W_3O_2(pr)_6(H_2O)_2]_2(H_3O_2)\}(NCS)_3\cdot H_2O$ (**2**) and its molybdenum analogue $\{[Mo_3O_2(pr)_6(H_2O)_2]_2(H_3O_2)\}(NCS)_3\cdot H_2O$ (**3**) (diclusters); $[W_3O_2(pr)_6(H_2O)(H_3O_2)]NCS$ (**4**) (polycluster).

Experimental Section

Preparations. The starting material for all compounds is the dicluster bromide salt $\{[M_3O_2(pr)_6(H_2O)_2]_2(H_3O_2)\}Br_3\cdot 6H_2O$ (M = W or Mo), prepared as described in part 1.[2b] The different products are obtained when 25-mg samples are dissolved in 5 mL of 0.5 M KNCS solutions of varying acidities.

$[W_3O_2(pr)_6(H_2O)_3](NCS)_2$ (1). A sample of the dicluster bromide salt of tungsten is dissolved in a solution of 0.5 M KNCS and 1 M HCl. The yellow solution is placed in an open beaker. Yellow-brown crystals are deposited after 24 h.

Table II. Positional Parameters and Estimated Standard Deviations for 1[a]

atom	x	y	z	atom	x	y	z
W(1)	0.29134 (5)	0.07442 (5)	0.12519 (9)	N(1)	0.298 (1)	0.090 (1)	0.567 (3)
W(2)	0.21947 (5)	−0.05239 (4)	0.15502 (9)	N(2)	0.172 (1)	−0.132 (1)	0.550 (2)
W(3)	0.24470 (5)	−0.00390 (4)	−0.09666 (9)	C(1)	0.216 (1)	0.155 (1)	−0.108 (2)
S(1)	0.3941 (4)	0.2020 (4)	0.5185 (8)	C(2)	0.192 (2)	0.220 (2)	−0.177 (4)
S(2)	0.0935 (5)	−0.2247 (4)	0.701 (1)	C(3)	0.127 (2)	0.215 (2)	−0.277 (4)
O(1)	0.1912 (7)	0.0358 (7)	0.055 (1)	C(4)	0.356 (1)	−0.025 (1)	0.344 (2)
O(2)	0.3115 (9)	−0.0232 (7)	0.068 (1)	C(5)	0.414 (2)	−0.039 (2)	0.456 (3)
O(11)	0.2207 (8)	0.1080 (7)	0.268 (1)	C(6)	0.396 (2)	−0.099 (2)	0.548 (4)
O(12)	0.3600 (7)	0.0377 (7)	0.286 (1)	C(7)	0.401 (1)	0.060 (1)	−0.091 (2)
O(13)	0.2504 (8)	0.1578 (7)	0.012 (2)	C(8)	0.472 (1)	0.072 (1)	−0.147 (3)
O(14)	0.3886 (9)	0.8887 (8)	0.022 (2)	C(9)	0.522 (2)	0.124 (2)	−0.076 (4)
O(21)	0.3032 (8)	−0.0658 (7)	0.312 (1)	C(10)	0.173 (1)	0.068 (1)	0.318 (2)
O(22)	0.1143 (8)	−0.0773 (7)	0.062 (2)	C(11)	0.122 (1)	0.106 (1)	0.410 (2)
O(23)	0.2539 (8)	−0.1487 (8)	0.077 (2)	C(12)	0.069 (2)	0.055 (2)	0.480 (3)
O(24)	0.1660 (8)	0.0046 (7)	0.294 (1)	C(13)	0.094 (1)	−0.065 (1)	−0.058 (2)
O(31)	0.2090 (8)	0.0961 (7)	−0.172 (1)	C(14)	0.013 (1)	−0.080 (1)	−0.111 (2)
O(32)	0.3522 (8)	0.0236 (8)	−0.155 (2)	C(15)	−0.028 (1)	−0.125 (1)	−0.008 (3)
O(33)	0.1339 (9)	−0.0388 (8)	−0.142 (1)	C(16)	0.274 (1)	−0.158 (1)	−0.038 (3)
O(34)	0.2753 (8)	−0.1082 (7)	−0.126 (1)	C(17)	0.303 (2)	−0.231 (1)	−0.072 (3)
OW(1)	0.343 (1)	0.1685 (8)	0.207 (2)	C(18)	0.342 (2)	−0.235 (2)	−0.199 (4)
OW(2)	0.1782 (9)	−0.1285 (8)	0.278 (2)	CS(1)	0.336 (1)	0.136 (1)	0.549 (3)
OW(3)	0.2366 (8)	−0.0134 (7)	−0.304 (1)	CS(2)	0.140 (1)	−0.171 (1)	0.614 (3)

[a] Estimated standard deviations are given by the numbers in parentheses, which correspond to the least significant digits of the adjacent parameters.

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

W(1)-W(2)	2.752 (1)	W(1)-O(13)	2.05 (1)	W(2)-O(21)	2.10 (1)	W(3)-O(1)	2.01 (1)
-W(3)	2.749 (1)	-O(14)	2.12 (1)	-O(22)	2.09 (1)	-O(2)	2.00 (1)
-O(1)	2.01 (1)	-OW(1)	2.15 (1)	-O(23)	2.10 (1)	-O(31)	2.12 (1)
-O(2)	1.98 (1)	W(2)-W(3)	2.758 (1)	-O(24)	2.06 (1)	-O(32)	2.12 (1)
-O(11)	2.08 (1)	-O(1)	1.99 (1)	-OW(2)	2.07 (1)	-O(33)	2.11 (1)
-O(12)	2.07 (1)	-O(2)	2.01 (1)			-O(34)	2.08 (1)
						-OW(3)	2.08 (1)

W(2)-W(1)-W(3)	60.19 (3)	O(12)-W(1)-O(13)	149.0 (6)	O(2)-W(2)-O(21)	78.1 (6)	O(1)-W(3)-O(2)	74.5 (6)
-O(1)	46.2 (4)	-O(14)	87.8 (6)	-O(22)	127.8 (6)	-O(31)	77.7 (5)
-O(2)	46.8 (4)	-OW(1)	76.4 (6)	-O(23)	78.5 (6)	-O(32)	128.0 (6)
-O(11)	82.8 (4)	O(13)-W(1)-O(14)	84.4 (6)	-O(24)	126.5 (6)	-O(33)	77.4 (5)
-O(12)	83.0 (4)	-OW(1)	72.5 (6)	-OW(2)	142.8 (6)	-O(34)	127.6 (5)
-O(13)	125.6 (4)	O(14)-W(1)-OW(1)	74.4 (6)	O(21)-W(2)-O(22)	150.7 (6)	-OW(3)	142.2 (6)
-O(14)	125.2 (4)	W(1)-W(2)-W(3)	59.84 (3)	-O(23)	87.6 (6)	O(2)-W(3)-O(31)	127.1 (6)
-OW(1)	151.2 (4)	-O(1)	46.9 (4)	-O(24)	84.3 (6)	-O(32)	76.8 (6)
W(3)-W(1)-O(1)	46.9 (4)	-O(2)	45.8 (4)	-OW(2)	74.8 (6)	-O(33)	127.9 (6)
-O(2)	46.5 (4)	-O(21)	82.7 (4)	O(22)-W(2)-O(23)	85.4 (6)	-O(34)	78.2 (6)
-O(11)	123.8 (4)	-O(22)	124.2 (4)	-O(24)	88.2 (6)	-OW(3)	143.2 (6)
-O(12)	125.0 (4)	-O(23)	124.3 (4)	-OW(2)	75.9 (6)	O(31)-W(3)-O(32)	86.5 (6)
-O(13)	83.8 (4)	-O(24)	82.3 (4)	O(23)-W(2)-O(24)	151.0 (6)	-O(33)	87.1 (6)
-O(14)	83.2 (4)	-OW(2)	149.7 (4)	-OW(2)	75.4 (6)	-O(34)	151.0 (6)
-OW(1)	148.6 (4)	W(3)-W(2)-O(1)	46.7 (4)	O(24)-W(2)-OW(2)	75.6 (6)	-OW(3)	74.1 (5)
O(1)-W(1)-O(2)	74.9 (6)	-O(2)	46.3 (4)	W(1)-W(3)-W(2)	59.97 (3)	O(32)-W(3)-O(33)	151.5 (6)
-O(11)	76.9 (6)	-O(21)	124.4 (4)	-O(1)	47.0 (4)	-O(34)	86.4 (6)
-O(12)	127.5 (5)	-O(22)	82.8 (4)	-O(2)	45.9 (4)	-OW(3)	74.9 (6)
-O(13)	79.4 (6)	-O(23)	82.8 (4)	-O(31)	82.5 (4)	O(33)-W(3)-O(34)	85.8 (6)
-O(14)	128.6 (6)	-O(24)	124.5 (4)	-O(32)	82.2 (4)	-OW(3)	76.6 (6)
-OW(1)	141.7 (6)	-OW(2)	150.4 (4)	-O(33)	124.3 (4)	O(34)-W(3)-OW(3)	76.9 (6)
O(2)-W(1)-O(11)	128.3 (5)	O(1)-W(2)-O(2)	74.7 (5)	-O(34)	124.2 (4)	W(1)-O(1)-W(2)	86.8 (5)
-O(12)	78.5 (6)	-O(21)	128.0 (5)	-OW(3)	148.0 (4)	-W(3)	86.1 (5)
-O(13)	128.6 (6)	-O(22)	77.3 (5)	W(2)-W(3)-O(1)	46.1 (4)	W(2)-O(1)-W(3)	87.2 (5)
-O(14)	78.5 (6)	-O(23)	127.8 (6)	-O(2)	46.6 (4)	W(1)-O(2)-W(2)	87.4 (6)
-OW(1)	143.4 (6)	-O(24)	77.8 (6)	-O(31)	123.8 (4)	-W(3)	87.6 (6)
O(11)-W(1)-O(12)	85.8 (6)	-OW(2)	142.5 (6)	-O(32)	123.5 (4)	W(2)-O(2)-W(3)	87.1 (6)
-O(13)	86.3 (6)			-O(33)	82.6 (4)		
-O(14)	150.1 (6)			-O(34)	83.1 (4)		
-OW(1)	75.8 (6)			-OW(3)	152.0 (4)		

Table IV. Positional Parameters and Estimated Standard Deviations for **2**[a]

atom	x	y	z	atom	x	y	z
W(1)	0.14890 (6)	0.30680 (3)	0.39883 (7)	N(1)	0.306 (2)	0.695 (1)	0.589 (2)
W(2)	0.08811 (5)	0.15540 (3)	0.45211 (7)	C(1)	0.277 (1)	0.2985 (9)	0.156 (2)
W(3)	0.32351 (6)	0.21299 (3)	0.42959 (7)	C(2)	0.291 (2)	0.314 (1)	0.001 (2)
S(1)	0.8045 (5)	0.4380 (3)	0.3237 (6)	C(3)	0.431 (2)	0.323 (1)	0.013 (2)
O(1)	0.1387 (9)	0.1978 (5)	0.283 (1)	C(4)	0.023 (1)	0.2893 (8)	0.642 (2)
O(2)	0.2353 (9)	0.2533 (5)	0.574 (1)	C(5)	−0.032 (2)	0.3190 (9)	0.762 (2)
O(11)	−0.0419 (9)	0.2751 (6)	0.233 (1)	C(6)	−0.001 (2)	0.411 (1)	0.815 (2)
O(12)	0.0707 (9)	0.3368 (6)	0.572 (1)	C(7)	0.428 (2)	0.3888 (9)	0.602 (2)
O(13)	0.200 (1)	0.3304 (6)	0.204 (1)	C(8)	0.538 (2)	0.462 (1)	0.717 (2)
O(14)	0.3149 (9)	0.3985 (5)	0.544 (1)	C(9)	0.671 (3)	0.451 (2)	0.770 (3)
O(21)	0.019 (1)	0.2144 (5)	0.613 (1)	C(10)	−0.123 (1)	0.2079 (8)	0.201 (2)
O(22)	0.2072 (9)	0.1161 (5)	0.648 (1)	C(11)	−0.259 (2)	0.1928 (9)	0.077 (2)
O(23)	0.0905 (9)	0.0514 (5)	0.304 (1)	C(12)	−0.273 (2)	0.246 (1)	−0.045 (2)
O(24)	−0.095 (1)	0.1521 (6)	0.272 (1)	C(13)	0.331 (1)	0.1267 (9)	0.697 (2)
O(31)	0.3440 (9)	0.2554 (6)	0.234 (1)	C(14)	0.405 (2)	0.096 (1)	0.843 (2)
O(32)	0.4583 (9)	0.3218 (6)	0.574 (1)	C(15)	0.324 (2)	0.056 (1)	0.924 (3)
O(33)	0.3968 (9)	0.1630 (6)	0.628 (1)	C(16)	0.180 (1)	0.0413 (9)	0.249 (2)
O(34)	0.281 (1)	0.0970 (6)	0.288 (1)	C(17)	0.160 (2)	−0.036 (1)	0.134 (2)
OW(1)	0.095 (1)	0.4171 (6)	0.366 (1)	C(18)	0.043 (2)	−0.102 (1)	0.117 (2)
OW(2)	−0.0324 (9)	0.0631 (5)	0.483 (1)	CS(1)	0.261 (2)	0.640 (1)	0.626 (2)
OW(3)	0.504 (1)	0.1980 (6)	0.435 (1)	CN(1)	0.535 (3)	0.029 (2)	0.498 (4)
S(2)	0.657 (1)	0.0707 (9)	0.481 (2)	OL(1)	0.744 (5)	0.101 (3)	0.460 (6)

[a] Estimated standard deviations are given by the numbers in parentheses, which correspond to the least significant digits of the adjacent parameters.

$\{[W_3O_2(pr)_6(H_2O)_2]_2(H_3O_2)\}(NCS)_3\cdot H_2O$ (2) and $\{[Mo_3O_2(pr)_6(H_2O)_2]_2(H_3O_2)\}(NCS)_3\cdot H_2O$ (3). The corresponding starting material is dissolved in a solution of 0.5 M KNCS and 0.05 M HCl. Yellow-brown crystals of **2** and deep red crystals of **3** are deposited after slow evaporation of the corresponding solution in an open beaker.

$[W_3O_2(pr)_6(H_2O)(H_3O_2)]NCS$ (4). No acid is added to the KNCS solution. Yellow-brown crystals are deposited after several hours.

X-ray Crystallography. Data were collected for all compounds on a Philips PW1100 four-circle computer-controlled diffractometer. Mo Kα ($\lambda = 0.71069$ 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 a ω–2θ motion. The scan width, $\Delta\omega$, for each reflection was 1° with scan time of 20 s. Background measurements 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**, **2**, and **4** were corrected for absorption by the empirical ψ-scan method. The heavy-atom positions in **1** and **4** were obtained by using the results of MULTAN direct-method analysis.[4] Both

Table V. Important Bond Lengths (Å) and Angles (deg) for **2**

W(1)-W(2)	2.7595 (7)
-W(3)	2.7457 (9)
-O(1)	1.986 (9)
-O(2)	1.995 (9)
-O(11)	2.071 (8)
-O(12)	2.09 (1)
-O(13)	2.10 (1)
W(1)-O(14)	2.097 (7)
-OW(1)	2.15 (1)
W(2)-W(3)	2.7688 (9)
-O(1)	2.00 (1)
-O(2)	2.012 (7)
-O(21)	2.10 (1)
W(2)-O(22)	2.106 (9)
-O(23)	2.09 (1)
-O(24)	2.121 (9)
-OW(2)	2.04 (1)
W(3)-O(1)	1.993 (8)
-O(2)	2.01 (1)
-O(31)	2.08 (1)
W(3)-O(32)	2.114 (8)
-O(33)	2.08 (1)
-O(34)	2.094 (9)
-OW(3)	2.09 (1)
OW(2)-OW(2)	2.46 (1)

W(2)-W(1)-W(3)	60.39 (2)
-O(1)	46.5 (3)
-O(2)	46.7 (4)
-O(11)	83.9 (3)
-O(12)	82.6 (3)
-O(13)	124.0 (3)
-O(14)	126.0 (3)
-OW(1)	148.4 (3)
W(3)-W(1)-O(1)	46.5 (4)
-O(2)	47.0 (3)
-O(11)	125.7 (3)
-O(12)	124.3 (3)
-O(13)	82.9 (3)
-O(14)	83.7 (2)
-OW(1)	151.1 (3)
O(1)-W(1)-O(2)	74.9 (5)
-O(11)	79.2 (5)
-O(12)	127.7 (4)
-O(13)	77.6 (4)
-O(14)	128.4 (4)
-OW(1)	143.9 (5)
O(2)-W(1)-O(11)	128.9 (4)
-O(12)	77.3 (4)
-O(13)	128.6 (4)
-O(14)	79.3 (5)
-OW(1)	141.2 (5)
O(11)-W(1)-O(12)	85.1 (5)
-O(13)	86.2 (5)
-O(14)	147.9 (4)
-OW(1)	73.8 (5)
O(12)-W(1)-O(13)	150.8 (4)
-O(14)	87.5 (5)
-OW(1)	73.7 (4)
O(13)-W(1)-O(14)	85.2 (5)
-OW(1)	77.1 (4)
O(14)-W(1)-OW(1)	74.2 (5)
W(1)-W(2)-W(3)	59.56 (2)
-O(1)	46.0 (3)
-O(2)	46.2 (3)
-O(21)	82.9 (3)
-O(22)	123.5 (3)
-O(23)	123.3 (3)
-O(24)	81.7 (3)
-OW(2)	152.8 (3)
W(3)-W(2)-O(1)	46.0 (4)
-O(2)	46.5 (3)
-O(21)	124.6 (4)
-O(22)	82.1 (3)
-O(23)	82.4 (3)
-O(24)	123.7 (3)
-OW(2)	147.6 (3)
O(1)-W(2)-O(2)	74.2 (5)
-O(21)	127.3 (4)
-O(22)	126.8 (4)
-O(23)	77.3 (4)
-O(24)	77.7 (4)
-OW(2)	142.5 (5)
O(2)-W(2)-O(21)	78.0 (4)
-O(22)	77.3 (4)
-O(23)	127.6 (4)
-O(24)	126.3 (4)
-OW(2)	143.2 (5)
O(21)-W(2)-O(22)	88.0 (4)
-O(23)	151.3 (4)
-O(24)	84.2 (5)
-OW(2)	77.5 (4)
O(22)-W(2)-O(23)	86.2 (4)
-O(24)	152.5 (4)
-OW(2)	74.8 (5)
O(23)-W(2)-O(24)	88.0 (5)
-OW(2)	73.9 (4)
O(24)-W(2)-OW(2)	77.7 (4)
W(1)-W(3)-W(2)	60.05 (2)
-O(1)	46.3 (3)
-O(2)	46.5 (3)
-O(31)	83.1 (3)
-O(32)	82.8 (3)
-O(33)	124.8 (3)
-O(34)	124.4 (4)
-OW(3)	149.6 (3)
W(2)-W(3)-O(1)	46.3 (3)
-O(2)	46.5 (4)
-O(31)	124.7 (3)
-O(32)	124.4 (2)
-O(33)	83.4 (3)
-O(34)	82.8 (3)
-OW(3)	150.4 (3)
O(1)-W(3)-O(2)	74.4 (5)
-O(31)	78.5 (4)
-O(32)	127.6 (4)
-O(33)	128.3 (4)
-O(34)	78.2 (5)
-OW(3)	143.5 (5)
O(2)-W(3)-O(31)	128.0 (4)
-O(32)	77.9 (4)
-O(33)	78.3 (4)
-O(34)	127.8 (4)
-OW(3)	142.1 (6)
O(31)-W(3)-O(32)	85.1 (5)
-O(33)	149.7 (4)
-O(34)	87.3 (4)
-OW(3)	75.0 (4)
O(32)-W(3)-O(33)	86.9 (5)
-O(34)	150.6 (4)
-OW(3)	74.7 (5)
O(33)-W(3)-O(34)	85.4 (5)
-OW(3)	74.6 (4)
O(34)-W(3)-OW(3)	75.9 (5)
W(1)-O(1)-W(2)	87.6 (4)
-W(3)	87.3 (5)
W(2)-O(1)-W(3)	87.7 (5)
W(1)-O(2)-W(2)	87.0 (5)
-W(3)	86.5 (4)
W(2)-O(2)-W(3)	86.9 (5)

Table VI. Positional Parameters and Estimated Standard Deviations for **4**[a]

atom	*x*	*y*	*z*
W(1)	0.18305 (4)	0.89359 (4)	0.07259 (4)
W(2)	0.35871 (4)	0.79947 (4)	0.14990 (4)
W(3)	0.34170 (4)	1.00021 (4)	0.17249 (4)
O(1)	0.2754 (7)	0.8813 (7)	0.1959 (6)
O(2)	0.3131 (6)	0.9133 (7)	0.0675 (6)
O(11)	0.1275 (7)	0.7699 (7)	0.1123 (7)
O(12)	0.1757 (6)	0.8084 (7)	−0.0354 (6)
O(13)	0.1131 (6)	0.9777 (7)	0.1396 (6)
O(14)	0.1583 (6)	1.0121 (7)	−0.0123 (6)
O(21)	0.2679 (7)	0.6909 (8)	0.1728 (7)
O(22)	0.3170 (7)	0.7301 (7)	0.0260 (7)
O(23)	0.4413 (7)	0.8057 (8)	0.2838 (6)
O(24)	0.4862 (7)	0.8444 (7)	0.1332 (7)
O(31)	0.2857 (7)	1.0998 (7)	0.0684 (6)
O(32)	0.2428 (7)	1.0595 (7)	0.2243 (7)
O(33)	0.4716 (6)	1.0037 (8)	0.1505 (7)
O(34)	0.4297 (7)	0.9665 (8)	0.3009 (7)
OW(1)	0.0342 (6)	0.8906 (7)	−0.0069 (7)
OW(2)	0.4389 (7)	0.6752 (7)	0.1736 (7)
OW(3)	0.4005 (7)	1.1349 (7)	0.2229 (7)
C(1)	0.457 (1)	0.881 (1)	0.330 (1)
C(2)	0.514 (2)	0.880 (2)	0.429 (1)
C(3)	0.549 (2)	0.788 (2)	0.466 (2)
C(4)	0.178 (1)	0.698 (1)	0.1543 (9)
C(5)	0.125 (1)	0.611 (2)	0.174 (1)
C(6)	0.073 (2)	0.553 (2)	0.090 (2)
C(7)	0.213 (1)	1.088 (1)	−0.000 (1)
C(8)	0.189 (1)	1.166 (1)	−0.069 (1)
C(9)	0.111 (2)	1.137 (2)	−0.155 (1)
C(10)	0.240 (1)	0.749 (1)	−0.039 (1)
C(11)	0.225 (1)	0.699 (1)	−0.123 (1)
C(12)	0.118 (1)	0.682 (1)	−0.178 (1)
C(13)	0.513 (1)	0.932 (1)	0.133 (1)
C(14)	0.602 (1)	0.949 (1)	0.110 (1)
C(15)	0.640 (1)	1.053 (1)	0.122 (1)
C(16)	0.156 (1)	1.036 (1)	0.2028 (9)
C(17)	0.100 (1)	1.079 (1)	0.254 (1)
C(18)	0.158 (2)	1.095 (2)	0.351 (1)
S(1)	0.2620 (4)	0.1673 (4)	0.6780 (5)
N(1)	0.085 (1)	0.251 (1)	0.582 (1)
CS(1)	0.163 (1)	0.216 (1)	0.625 (1)

[a] Estimated standard deviations are given by the numbers in parentheses, which correspond to the least significant digits of the adjacent parameters.

structures **1** and **4** were refined[5] in space group $P2_1/c$ to convergence by using anisotropic thermal parameters for all tungsten, sulfur, and oxygen atoms and isotropic ones for the nitrogen and carbon atoms.

The heavy-atom positions in **2** were obtained from a three-dimensional Patterson function. The positions of all non-hydrogen atoms of **3** were taken from **2**. In **2** and **3**, anisotropic thermal parameters were used for all tungsten, molybdenum, and oxygen atoms and one of the sulfur atoms, S(1), and isotropic parameters were used for the rest of the non-hydrogen atoms. One of the NCS^- groups and the uncoordinated H_2O in **2** and **3** are in twofold disorder. The NCS^- unit resides on a crystallographic inversion center at $^1/_2$, 0, $^1/_2$. The inversion center is located midway between the C and the N atoms. This disordered atom, CN, was refined isotropically as a carbon atom with an occupancy factor of 1.083. The sulfur atom was refined isotropically with an occupancy factor of 0.5. Since the oxygen atom of the

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(4) Main, P.; Hull, S. E.; Lessinger, L.; Germain, G.; Declercq, J. P.; Woolfson, M. M. "MULTAN 78: A System of Computer Programs for the Automatic Solution of Crystal Structures for X-ray Diffraction Data"; Universities of York and Louvain: York, England, and Louvain, Belgium, 1978.

(5) All crystallographic computing was done on a Cyber 74 computer at the Hebrew University of Jerusalem, with the SHELX 1977 structure determination package.

Table VII. Important Bond Lengths (Å) and Angles (deg) for 4

W(1)-W(2)	2.7653 (7)
-W(3)	2.7456 (7)
-O(1)	1.999 (8)
-O(2)	1.980 (9)
-O(11)	2.08 (1)
-O(12)	2.09 (1)
-O(13)	2.11 (1)
W(1)-O(14)	2.076 (9)
-OW(1)	2.120 (8)
W(2)-W(3)	2.7812 (7)
-O(1)	2.00 (1)
-O(2)	2.006 (9)
-O(21)	2.12 (1)
-O(22)	2.12 (1)
W(2)-O(23)	2.096 (8)
-O(24)	2.10 (1)
-OW(2)	2.023 (9)
W(3)-O(1)	2.00 (1)
-O(2)	2.007 (9)
-O(31)	2.103 (9)
-O(32)	2.11 (1)
W(3)-O(33)	2.09 (1)
-O(34)	2.090 (9)
-OW(3)	2.069 (9)
S(1)-CS(1)	1.57 (1)
N(1)-CS(1)	1.21 (2)
OW(2)-OW(3)	2.44 (1)

W(2)-W(1)-W(3)	60.62 (2)
-O(1)	46.4 (3)
-O(2)	46.5 (3)
-O(11)	84.0 (3)
-O(12)	83.3 (3)
-O(13)	125.0 (3)
-O(14)	125.2 (3)
-OW(1)	150.7 (3)
W(3)-W(1)-O(1)	46.7 (3)
-O(2)	46.9 (3)
-O(11)	126.3 (4)
-O(12)	124.8 (3)
-O(13)	63.0 (3)
-O(14)	84.0 (3)
-OW(1)	148.7 (3)
O(1)-W(1)-O(2)	74.6 (4)
-O(11)	79.5 (5)
-O(12)	128.3 (4)
-O(13)	78.6 (4)
-O(14)	129.4 (4)
-OW(1)	143.2 (4)
O(2)-W(1)-O(11)	128.8 (4)
-O(12)	77.9 (4)
-O(13)	128.5 (4)
-O(14)	78.7 (4)
-OW(1)	142.2 (4)
O(11)-W(1)-O(12)	85.0 (4)
-O(13)	87.1 (4)
-O(14)	147.7 (5)
-OW(1)	74.6 (4)
O(12)-W(1)-O(13)	149.6 (5)
-O(14)	85.3 (4)
-OW(1)	75.2 (4)
O(13)-W(1)-O(14)	85.9 (4)
-OW(1)	74.4 (4)
O(14)-W(1)-OW(1)	73.2 (4)
W(1)-W(2)-W(3)	59.34 (2)
-O(1)	46.2 (4)
-O(2)	45.7 (3)
-O(21)	81.4 (3)
-O(22)	82.4 (3)
-O(23)	123.9 (3)
-O(24)	123.3 (3)
-OW(2)	150.0 (3)
W(3)-W(2)-O(1)	46.0 (3)
-O(2)	46.1 (3)
-O(21)	124.5 (3)
-O(22)	123.8 (3)
-O(23)	82.3 (3)
-O(24)	82.0 (3)
-OW(2)	150.6 (4)
O(1)-W(2)-O(2)	73.9 (4)
-O(21)	78.6 (4)
-O(22)	127.1 (5)
-O(23)	77.7 (5)
-O(24)	126.6 (4)
-OW(2)	142.4 (4)
O(2)-W(2)-O(21)	125.2 (5)
O(2)-W(2)-O(22)	77.7 (4)
-O(23)	127.1 (4)
-O(24)	77.6 (4)
-OW(2)	143.7 (4)
O(21)-W(2)-O(22)	82.9 (4)
-O(23)	90.5 (5)
-O(24)	152.4 (4)
-OW(2)	75.6 (4)
O(22)-W(2)-O(23)	151.7 (4)
-O(24)	88.1 (4)
-OW(2)	76.0 (5)
O(23)-W(2)-O(24)	85.1 (5)
-OW(2)	75.7 (5)
O(24)-W(2)-OW(2)	76.9 (4)
W(1)-W(3)-W(2)	60.04 (2)
-O(1)	46.6 (4)
-O(2)	46.1 (3)
-O(31)	81.6 (3)
-O(32)	82.6 (3)
-O(33)	123.6 (3)
-O(34)	125.0 (3)
-OW(3)	148.5 (3)
W(2)-W(3)-O(1)	46.1 (3)
-O(2)	46.1 (3)
-O(31)	123.5 (3)
-O(32)	122.7 (3)
-O(33)	82.2 (3)
-O(34)	82.3 (3)
-OW(3)	151.4 (3)
O(1)-W(3)-O(2)	73.9 (4)
-O(31)	126.9 (5)
-O(32)	76.6 (4)
-O(33)	126.9 (4)
-O(34)	78.4 (5)
-OW(3)	143.5 (4)
O(2)-W(3)-O(31)	77.4 (4)
-O(32)	127.8 (4)
-O(33)	77.6 (4)
-O(34)	126.8 (4)
-OW(3)	142.5 (4)
O(31)-W(3)-O(32)	87.4 (4)
-O(33)	87.8 (4)
-O(34)	151.7 (4)
-OW(3)	74.9 (5)
O(32)-W(3)-O(33)	152.2 (4)
-O(34)	87.0 (4)
-OW(3)	75.7 (4)
O(33)-W(3)-O(34)	84.4 (4)
-OW(3)	84.4 (4)
O(34)-W(3)-OW(3)	76.8 (5)
W(1)-O(1)-W(2)	87.4 (4)
-W(3)	86.6 (4)
W(2)-O(1)-W(3)	87.9 (4)
W(1)-O(2)-W(2)	87.8 (3)
-W(3)	87.0 (3)
W(2)-O(2)-W(3)	87.7 (4)
S(1)-CS(1)-N(1)	177 (2)

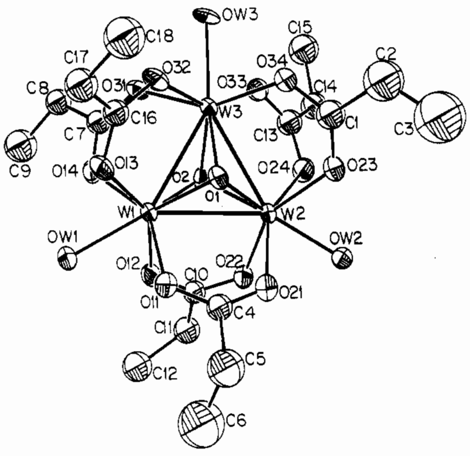

Figure 2. The $[W_3O_2(pr)_6(H_2O)(H_3O_2)_{2/2}]^+$ ion in **4** and the labeling scheme. OW2 and OW3 form the $H_3O_2^-$ bridges with neighboring clusters.

uncoordinated water molecule, OL(1), was hydrogen bonded to the N terminus of the NCS^- ion, it was refined isotropically with an occupancy factor of 0.5.

The discrepancy indices $R_1 = \sum||F_o|| - |F_c||/\sum|F_o|$ and $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|]^{1/2}$ are listed in Table I. In all structures the final difference map showed no peaks of structural significance. Lists of all observed and calculated structure factors are available as supplementary material.

Results

$[W_3O_2(pr)_6(H_2O)_3](NCS)_2$ (1). The atomic positional parameters are listed in Table II, while Table III presents the important bond lengths and angles. Figure 1 shows the structure and the numbering scheme of the trinuclear cation. 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 $[W_3O_2(pr)_6(H_2O)_3]^{2+}$ unit and two NCS anions. The geometry and the dimensions of the trinuclear cation are essentially identical with

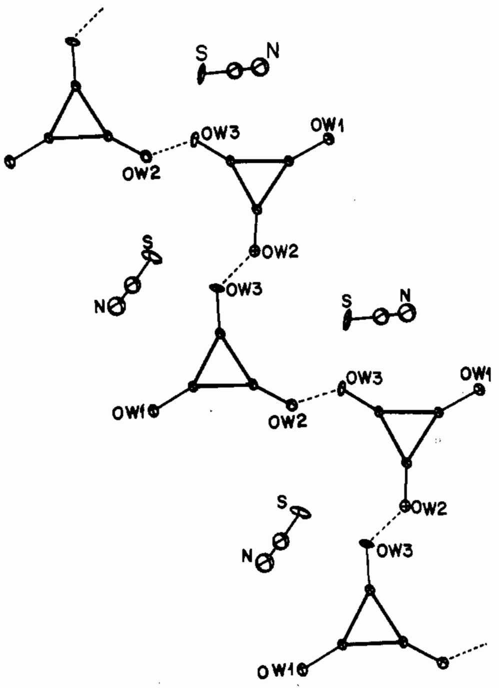

Figure 3. Infinite chain of the polycluster in **4**. The μ_3-oxygen atoms and propionate ligands were omitted for the sake of clarity. The O···H···O bonds in the $H_3O_2^-$ ligands are represented by dotted lines.

Table VIII. Structural Data for **1**-**4** and Other $[M_3O_2(pr)_6(H_2O)_3]^{2+}$ Salts

			bond dist,[a] Å					
compd	type	M	M(1)-M(2)	M(1)-M(3)	M(2)-M(3)	M-O(H_2O)	M-O(H_3O_2)	O-O($H_3O_2^-$)
$[W_3O_2(pr)_6(H_2O)_3](NCS)_2$ (1)	monocluster	W	2.752 (1)	2.749 (1)	2.758 (1)	2.10 (3)		
$\{[W_3O_2(pr)_6(H_2O_2)_2]_2(H_3O_2)\}(NCS)_3\cdot H_2O$ (2)	dicluster	W	2.760 (1)	2.746 (1)	2.769 (1)	2.12 (3)	2.04 (1)	2.46 (1)
$\{[Mo_3O_2(pr)_6(H_2O)_2]_2(H_3O_2)\}(NCS)_3\cdot H_2O$ (3)	dicluster	Mo	2.775 (1)	2.757 (1)	2.784 (1)	2.13 (3)	2.01 (1)	2.52 (1)
$[W_3O_2(pr)_6(H_2O)(H_3O_2)]NCS$ (4)	polycluster	W	2.765 (1)	2.746 (1)	2.781 (1)	2.12 (1)	2.02 (1) 2.07 (1)	2.44 (1)
$[W_3O_2(pr)_6(H_2O)_3](BF_4)_2$[1]	monocluster	W	2.749 (1)	2.743 (1)	2.742 (1)	2.09 (1)		
$[Mo_3O_2(pr)_6(H_2O)_3](CF_3SO_3)_2$[3]	monocluster	Mo	2.755 (1)	2.748 (1)	2.754 (2)	2.15 (1)		
$\{[Mo_3O_2(pr)_6(H_2O)_2]_2(H_3O_2)\}Br_3\cdot 6H_2O$[2b]	dicluster	Mo	2.751 (1)	2.774 (1)	2.775 (1)	2.10 (1)	2.009 (7)	2.52 (1)
$\{[W_3O_2(pr)_6(H_2O)_2]_2(H_3O_2)\}Br_3\cdot 6H_2O$[2b]	dicluster	W	2.743 (1)	2.759 (1)	2.763 (1)	2.11 (1)	1.99 (1)	2.50 (1)

[a] For M-M bond distances, numbers in parentheses are esd's occurring in the last significant figures. For M-O and O-O bonds crystallographically equivalent distances have been averaged and the numbers in parentheses are the mean deviations from the mean.

those found in the fluoroborate salt $[W_3O_2(pr)_6(H_2O)_3](BF_4)_2\cdot 5.5\ H_2O$.[1] The average W-W and W-O (H_2O) distances are listed in Table VIII along with the corresponding distances in **2**-**4** and other $[M_3O_2(pr)_6(H_2O)_3]^{2+}$ salts. The three coordinated water ligands in the cluster are hydrogen bonded to the NCS anions through the S or N terminus with the normal O···S and O···N distances of 3.23-3.27 (1) and 2.61-2.87 (1) Å, respectively.

$\{[M_3O_2(pr)_6(H_2O)_2]_2(H_3O_2)\}(NCS)_3\cdot H_2O$ (M = W, Mo) (2, 3). These two compounds are isostructural. The atomic positional parameters of **2** are listed in Table IV while Table V gives the important bond lengths and angles. Figure 1 shows the numbering scheme in **2** and **3**. The atomic positional and thermal parameters and the bond lengths and angles in **3** are included in the supplementary material.

With $Z = 1$ in space group $P\bar{1}$ there is only half a $\{[M_3O_2(pr)_6(H_2O)_2]_2(H_3O_2)\}^{3+}$ ion in the asymmetric unit, with the other half related to it by a crystallographic inversion center at 0, 0, $^1/_2$. There are three thiocyanate anions in the cell, two that occupy general positions and one that resides on a crystallographic inversion center at $^1/_2$, 0, $^1/_2$. As mentioned above, this NCS^- ion is subjected to a twofold disorder. The geometry and the dimensions of the $\{[M_3O_2(pr)_6(H_2O)_2]_2(H_3O_2)\}^{3+}$ unit in **2** (M = W) and in **3** (M = Mo) are essentially identical with those found in the bromide salts of these cations.[2] In all cases the $H_3O_2^-$ unit resides on a crystallographic inversion center. The O···O distances in the $H_3O_2^-$ units and the M-M, M-O(H_2O), and M-O($H_3O_2^-$) distances in **2** and **3** are listed in Table VIII.

$[W_3O_2(pr)_6(H_2O)(H_3O_2)]NCS$ (4). The atomic positional parameters are listed in Table VI. Table VII presents the important bond lengths and angles. Figure 2 shows the numbering scheme.

With four molecules in the unit cell of space group $P2_1/c$, there is no crystallographic symmetry imposed upon the cluster. The asymmetric unit contains one $[W_3O_2(pr)_6(H_2O)(H_3O_2)_{2/2}]^+$ unit (where $(H_3O_2)_{2/2}$ denotes two doubly shared bridging hydrogen oxide ligands) and one NCS^- anion. The 2+ charge of the $[W_3O_2(pr)_6]^{2+}$ unit in this compound is balanced by one NCS^- and one (two halves) $H_3O_2^-$ ligand. As can be seen in Figure 3, each W_3 triangle is linked to two adjacent clusters by two μ-$H_3O_2^-$ units, forming infinite chains in the lattice. Each NCS^- ion in the lattice is hydrogen bonded through both ends, cross-linking adjacent chains. The nitrogen atom is bonded to the water ligand with an N-OW(1) separation of 2.58 (1) Å, and the sulfur atom is bonded to one of the oxygen atoms, OW(3), of the $H_3O_2^-$ ligand with an S-OW(3) separation of 3.30 (1) Å. The three angles around OW(3) are as follows: W(3)-OW(3)-S = 119.7 (5)°, W-OW(3)-OW(2) = 130.0 (6)°, and S-OW(3)-OW(2) = 110.1 (5)°. The angle W(2)-OW(2)-OW(3) is 132.9 (6)°. The W-W, W-O(H_2O), W-O(H_3O_2), and O···O(H_3O_2) distances are given in Table VIII. The oxygen atoms of the $H_3O_2^-$ unit in this structure, OW(3) and OW(2), are not symmetry related. It is the 2_1 symmetry element that transfer OW(3) to the proximity of OW(2) of another cluster.

Discussion

Preparation. In part 1 of this series[2b] the tendency of various counterions to precipitate di- and polycluster salts was related to their relative contribution to the crystal energies by hydrogen bond formation. Among the ions investigated (BF_4^-, $CF_3SO_3^-$, Cl^-, Br^-, I^-, and NCS^-), the thiocyanate ion was shown to be the best counterion for polycluster salt precipitation and was chosen as the common counterion for the series of salts prepared in this work. A similar series of salts may perhaps be obtained with I^- or Br^- but not with BF_4^- or $CF_3SO_3^-$, due to the strong hydrogen bonds formation by the latter in the lattice. The preparative procedures for the compounds described here were deduced from the scheme presented in the Introduction (eq 1-3). The positive preparative results of these deductions support this scheme. It is to be expected that in a high acid concentration, i.e., 1 M, the aquo ion (monocluster) predominates and will be precipitated. The fact that from solutions with an acid concentration of 0.05 M dicluster salts are obtained suggests that in this acidity the concentration of the hydroxo species, I, is relatively high (not necessarily optimal). This observation is in a good agreement with the assumption that the aquo ion (monocluster) acts as a strong acid.[2b] At still higher pH, obtained by dissolution of the crystalline dicluster salt in 0.5 M KNCS, the polycluster ion predominates and is precipitated preferentially.

Comparison and Correlation of Structures. We now have a total of six accurately measured structures, containing the $H_3O_2^-$ bridging unit, three of which are described here. The short O···O distances in the $H_3O_2^-$ unit as found in all these compounds (2.44-2.52 Å) clearly indicate the presence of a strong hydrogen bond. Since it was impossible to point out the positions of the hydrogen atoms in the $H_3O_2^-$ units in compounds **2**, **3**, and **4** with use of the X-ray data, we cannot conclude that the O···H···O bonds are symmetric. However, in compounds **2** and **3** the $\{[Mo_3O_2(pr)_6(H_2O)_2]_2(H_3O_2)\}^{3+}$ unit is essentially identical with the corresponding one in the bromide salts described in part 1. In all three of these cases the $H_3O_2^-$ unit resides on a crystallographic inversion center, a fact that indicates that the unit may be symmetric. This assumption is further supported by the fact that the central hydrogen atom in the bromide salt of the molybdenum dicluster is located on the inversion center.[2b] In the case of the polycluster, compound **4**, it is not obvious that the $H_3O_2^-$ unit is symmetric since the two W-O(H_3O_2) distances are not identical (2.023 (9) and 2.069 (9) Å). The $H_3O_2^-$ moiety can be regarded, therefore, as either a symmetric H–O⋯H⋯O–H or an asymmetric H–O–H⋯O–H unit. In both cases the bridging unit is the result of a strong hydrogen bond between a hydroxo ligand of one trimer and an aquo ligand of another.

The M–O(H_3O_2) distances in structures **2**–**4** are considerably shorter than the M–O(H_2O) distances (see Table VIII). The shorter M–O(H_3O_2) distance is caused by the displacement of the metal atom toward the negatively charged $H_3O_2^-$ unit. As a result of this displacement, the equilateral triangles are slightly distorted. This distortion leads to isosceles triangles in **2** and **3** (as in the corresponding bromide salts reported in part 1) and to a completely asymmetric triangle in **4**.

It was suggested that $H_3O_2^-$ bridges may be a general phenomenon existing also between a pair of mononuclear metal ions such as $M(H_2O)^{n+}$ and $M(OH)^{(n-1)+}$ (part 1).[2b] Efforts are being made to obtain crystalline products of such species.

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Registry No. **1**, 87869-35-0; **2**, 87861-53-8; **3**, 87861-55-0; **4**, 82044-77-7; $\{[W_3O_2(pr)_6(H_2O)_3]_2(H_3O_2)\}Br_3{\cdot}6H_2O$, 79716-36-2; $\{[Mo_3O_2(pr)_6(H_2O)_3]_2(H_3O_2)\}Br_3{\cdot}6H_2O$, 79417-66-6.

Supplementary Material Available: Tables of structure factors of **1**–**4**, thermal parameters of **1**–**4**, positional parameters and bond distances and angles in **3**, and bond distances and angles in the propionate ligands in **1**, **2**, and **4** (100 pages). Ordering information is given on any current masthead page.

Notes

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Interactions between Metal Chelate Electrolytes of 1,10-Phenanthroline and Nitrobenzene in Water: Crystal and Molecular Structure of the Nitrobenzene Solvate of Tris(1,10-phenanthroline)iron(II) Iodide Dihydrate

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The nature of solute–solvent interactions of transition metal chelate electrolytes of 1,10-phenanthroline (phen) has long been of interest, especially in connection with racemization,[1] salting-in,[2] and resolution of optical isomers.[3]

A salting-in of nitrobenzene by the $[Fe(phen)_3]^{2+}$ ion was found to be abnormally large.[2] From the nitrobenzene-saturated aqueous solution of the chelate, we isolated the nitrobenzene solvate, $[Fe(phen)_3]I_2{\cdot}2H_2O{\cdot}C_6H_5NO_2$.[4] Moreover, a significant effect of a trace amount of nitrobenzene on the racemization of $[Fe(phen)_3]^{2+}$ in aqueous solutions[5] was observed, indicating a specific interaction between the chelate cations and nitrobenzene. On account of the bulkiness and aromaticity, the chelate cations were assumed to behave as a hydrophobic solute reinforcing the structure of water.[2,6] Thus, these results may be ascribed to the coupled action of the water structural effect and ion-dipole and/or van der Waals interactions to attract such molecules as nitrobenzene with π-electron systems. However, it is still necessary to explain the geometrical mode of the direct interaction between the attracted molecules and the chelate cations: whether this is governed by ion-dipole or van der Waals interactions if the molecule is polar like nitrobenzene. To get information concerning the nature of the interactions involved, the crystal structure of the nitrobenzene solvate was investigated.

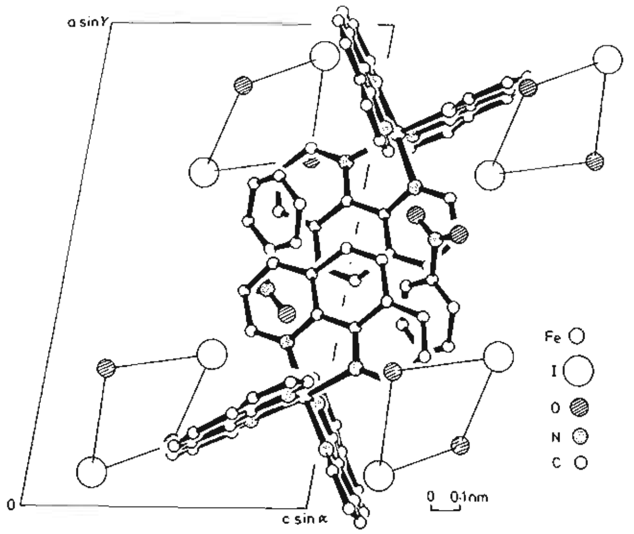

Figure 1. Crystal packing viewed along the *b* axis.

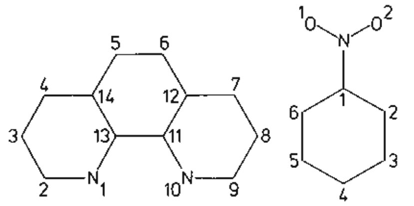

Figure 2. Labeling scheme of the phenanthroline ligands and nitrobenzene molecules.

Experimental Section

Dark red triclinic crystals were isolated from nitrobenzene-saturated aqueous solutions of the chelate as described previously.[4] The intensities and cell dimensions were measured on a RIGAKU AFC-5 four-circle diffractometer with Mo Kα radiation ($\lambda = 0.7107$ Å) monochromated by a graphite plate at -40.0 ± 0.5 °C. The size of crystal used for the X-ray measurement was $0.30 \times 0.19 \times 0.21$ mm^3. No systematic absence suggested the possible space group $P1$ or $P\bar{1}$, but the former was eliminated because the intensity statistics showed the presence of an inversion center. Crystal data: fw = 1009.4, triclinic, $a = 16.917$ (7) Å, $b = 12.350$ (6) Å, $c = 10.590$ (5) Å, $\alpha = 114.47$ (3)°, $\beta = 80.96$ (4)°, $\gamma = 97.55$ (4)°, $V = 1983$ Å^3, space

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