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Crystal and Molecular Structure of the Six-Electron-Reduced Form of Metatungstate $Rb_4H_8[H_2W_{12}O_{40}]\cdot{\sim}18H_2O$: Occurrence of a Metal–Metal Bonded Subcluster in a Heteropolyanion Framework

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The crystal structure of the rubidium salt of the six-electron-reduced form of metatungstate $Rb_4H_8[H_2W_{12}O_{40}]\cdot{\sim}18H_2O$ has been determined. Crystal data are as follows: cubic, space group *Fm*3*m*, a = 22.051 (5) Å, Z = 8. The structure was refined by using 392 observed independent reflections to a conventional weighted R factor of 0.074. The reduced anion exhibits the well-known Keggin structure, but the tungsten atom can occupy two different positions in the WO_6 octahedra, with statistical disorder. For the complete structure, nine tungsten atoms occupy the usual position for a Keggin structure while the three others have been displaced by 0.48 Å in the direction of the center of a W_3O_{13} group. These results are interpreted as a consequence of the formation of a $W^{IV}{}_3O_{13}$ cluster.

Introduction

It is well-known that metatungstate $H_2W_{12}O_{40}{}^{6-}$ and heteropolyanions $XW_{12}O_{40}{}^{n-}$ with the Keggin structure can be reduced to brown forms which are different from the usual "heteropoly blues".[1,2] In these compounds, the number of electrons introduced by reduction is always a multiple of 6, and it has been suggested by one of us[1] that these electrons are not uniformly distributed over the whole structure but form $W^{IV}{}_3O_{13}$ groups. This assumption is supported in part by an ESCA study[3] showing the presence of W^{VI} and W^{IV} in these compounds with the exception of W^V. A crystallographic study appeared useful since marked differences in bond lengths are expected when W^{VI} is replaced by W^{IV}. Here we report the crystal structure of the rubidium salt of the six-electron-reduced form of metatungstate, which is formulated as $Rb_4H_8[H_2W^{IV}{}_3W^{VI}{}_9O_{40}]\cdot{\sim}18H_2O$ according to the previous ESCA study.[3] More reduced species failed to crystallize. Despite the existence of a crystallographic disorder, the results obtained here are consistent with the hypothesis expressed above and give additional support to the presence of $W^{IV}{}_3O_{13}$ clusters in this compound.

Experimental Section

Sodium metatungstate (0.0124 mol L^{-1}) was reduced on a mercury cathode at −0.53 V vs. SCE in 0.5 mol L^{-1} HCl. The electrolysis was stopped when 6 faradays/mol of metatungstate had passed through the circuit. To one volume of the resulting brown-violet solution, a mixture of 0.6 volume of a molar sodium acetate solution and 0.2 volume of a rubidium chloride solution (0.4 mol L^{-1}) was added. The final pH was ca 4. Dark brown cubic crystals appeared after 1 night. They were rapidly washed with water and dried with acetone. Anal. Calcd for $Rb_4H_8[H_2W_{12}O_{40}]\cdot 18H_2O$: Rb, 9.71; W, 62.64. Found: Rb, 9.80; W, 61.87. Reduction degree, by cerium titration: 5.83 e/mol. The purity of the sample was checked by polarography. The number of crystallization water molecules has been obtained by thermogravimetry with an uncertainty of ±1 water molecule.

Structural Study

The single crystal was a cube of approximate dimensions 0.12 × 0.12 × 0.10 mm stuck with a small dot of Araldite in a Lindemann tube. Precession and Laue photographs showed a cubic symmetry with Laue class *m*3*m*. Systematic extinctions yielded three possible space groups: the centrosymmetric *Fm*3*m* and the two noncentrosymmetric $F\bar{4}3m$ and *F*432. The *Fm*3*m* group was retained after examination of the statistical tests. The lattice parameter was obtained from a least-squares refinement of the setting angles of six strong reflections centered manually on a four-circle diffractometer: a = 22.051 (5) Å. The calculated density for eight formula units $Rb_4H_8[H_2W_{12}O_{40}]\cdot 18H_2O$ per unit cell was 4.36 g cm^{-3}, which agrees with the experimental value 4.43 g cm^{-3}, obtained by picnometry in cyclohexane.

A total of 537 independent reflections with Bragg angles lower than 25° were recorded at room temperature on an automatic four-circle diffractometer, using graphite-monochromatized Mo Kα radiation (λ = 0.710 69 Å). The $\theta/2\theta$ scan technique was used with a scan rate of 0.55° min^{-1}. The crystal–focus distance was 225 mm and the crystal–counter distance was 235 mm. Two reference reflections were monitored every 50 reflections and found to be constant. All intensities were corrected from counting losses and Lorentz polarization. Each structure factor was assigned a standard deviation $\sigma = \Delta I/2F$, where ΔI was the error on the integrated intensity.

Of the 537 reflections, 145 with $F_o < 2\sigma$ were not included in subsequent calculations.

Computations were performed by using standard programs[4] on a C I I IRIS 80. Scattering factors were taken from ref 14b, including $\Delta f'$ and $\Delta f''$ for rubidium and tungsten. The agreement factors were defined by $R = \sum(|F_o - |F_c||)/\sum|F_o|$ and $R_w = \{\sum(w|F_o - |F_c||)^2/\sum(w|F_o|)^2\}^{1/2}$ and the quantity minimized was $\sum(w|F_o - |F_c||)^2$ by full-matrix inversion. The weighting scheme used was $w = 1/\sigma$.

Structure Solution and Refinement

Since the unit cell contained 96 tungsten atoms, they were searched in special positions of the *Fm*3*m* space group. A Patterson map was calculated and tungsten atoms were found on mirror planes (k position). There was only one independent tungsten atom. This generated the arrangement of eight Keggin anions described as type D crystal structure in Evans' classification.[5] At this stage, the weighted R_w factor was 0.251. A Fourier map revealed the presence of rubidium atoms in positions d and e as well as the four independent oxygen atoms constituting the tungsten octahedral environment: O_A, O_B, O_C, and O_D in Evans' nomenclature.[5] In order to account for the stoichiometry of the salt and the relative intensities of Fourier peaks, it was necessary to assign occupation probabilities of $^5/_6$ and $^1/_2$ for Rb d and Rb e, respectively. A least-squares cycle with these values as variables proved them to be correct. The R_w factor dropped then to 0.150. A difference Fourier map then revealed a strong peak near the position of the tungsten atom and in the general direction of the O_A oxygen. This was interpreted as an indication of the existence of a second tungsten position, with statistical disorder. A least-squares refinement with these positions occupied with probabilities 0.75 and 0.25 yielded a marked decrease in R_w down to 0.112.[7] The possibility that the peak

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Table I. Atomic Coordinates with Their Standard Deviations[a]

atom	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
$W_1(W^{VI})$	0.3621 (2)	0.3621 (2)	0.2558 (3)	2.4 (1)	2.4 (1)	2.0 (2)	−0.4 (1)	0.2 (1)	0.2 (1)
Rb d	0.0	0.25	0.25	1.8 (4)	5.2 (4)	5.2 (4)	0.0	0.0	0.6 (6)
Rb e	0.295 (1)	0.0	0.0	7 (1)	1.8 (4)	1.8 (4)	0.0	0.0	0.0
O_A	0.292 (1)	0.292 (1)	0.292 (1)	1.0[b]					
O_D	0.415 (1)	0.415 (1)	0.240 (1)	4.0 (9)	4.0 (9)	2 (2)	−2 (1)	−0.8 (8)	−0.8 (8)
O_C	0.409 (1)	0.3179 (8)	0.3179 (8)	5 (2)	2.1 (8)	2.1 (8)	0.2 (8)	0.2 (8)	0 (1)
O_B	0.383 (2)	0.299 (1)	0.200 (1)	7 (2)	2.4 (9)	2.4 (9)	−2 (1)	2 (1)	−1 (1)
$W_2(W^{IV})$	0.3506 (5)	0.3506 (5)	0.2704 (8)	2.4 (4)	2.4 (4)	2.0 (6)	−0.9 (4)	0.7 (2)	0.7 (2)
O_1	0.50	0.380 (1)	0.380 (1)	3.2 (8)[b]					

[a] Thermal parameters enter the following expression for the temperature factor: $\exp[-0.25(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^* + 2B_{13}hla^*c^* + 2B_{23}klb^*c^*)]$. [b] Isotropic value of B.

Table II. Bond Lengths in $W^{VI}O_6$ and $W^{IV}O_6$ Octahedra

$W^{VI}O_6$ octahedra		$W^{IV}O_6$ octahedra	
W_1-O_A	2.32 (2)	W_2-O_A	1.88 (2)
W_1-O_B	1.905 (5)	W_2-O_B	2.04 (1)
W_1-O_C	1.97 (2)	W_2-O_C	1.80 (3)
W_1-O_D	1.69 (2)	W_2-O_D	2.13 (2)
$W_1 \cdots W_2$[a]	0.48 (1)		
W_1-W_1[b]	3.312 (7)	W_2-W_2	2.50 (2)

[a] Apparent distance between W_1 and W_2. [b] Metal–metal distances inside a W_3O_{13} group.

Table III. Bond Angles in $W^{VI}O_6$ and $W^{IV}O_6$ Octahedra[a]

$W^{VI}O_6$ octahedra		$W^{IV}O_6$ octahedra	
O_D-W_1-O_B	101.3 (8)	O_D-W_2-O_B	83.9 (8)
O_D-W_1-O_C	97 (1)	O_D-W_2-O_C	88 (1)
O_D-W_1-O_A	171 (1)	O_D-W_2-O_A	176 (1)
O_B-W_1-O_B'	87.4 (2)	O_B-W_2-O_B'	80.2 (6)
O_B-W_1-O_C	87.3 (5)	O_B-W_2-O_C	87.8 (5)
O_B-W_1-O_C'	161.3 (7)	O_B-W_2-O_C'	166.5 (8)
O_B-W_1-O_A	84.7 (2)	O_B-W_2-O_A	93.6 (4)
O_C-W_1-O_C'	91 (1)	O_C-W_2-O_C'	103 (1)
O_C-W_1-O_A	76.9 (9)	O_C-W_1-O_A	93.5 (9)

[a] Symmetry code: unprimed atoms x, y, z; primed atoms y, x, z.

appearing on the Fourier difference map could be due to a strongly anisotropic thermal motion of the first tungsten atom is unlikely for the following reasons: (i) only one such peak was observed, on one side only of the tungsten position, and (ii) a refinement with one tungsten atom only and anisotropic parameters gave a higher R_w value, 0.120. The next difference Fourier map revealed several weak peaks between the anions, revealing the existence of crystallization water molecules. Only one of these, O_1 in position i, could be efficiently refined. It was found, by refining the occupation probability, that this position was fully occupied, corresponding to six H_2O per formula unit. The other peaks could not been refined, and it is believed that the remaining 12 water molecules are highly disordered, as frequently happens in heteropolyanion structures, especially those of type D.[6] This disorder is probably responsible of the relatively high final R values.

In the final cycles, all atoms were refined anisotropically except O_1 and O_A. For the latter atom, an attempt to refine anisotropically led to anomalous thermal components. Only an isotropic refinement was possible, which led to a low value of the thermal parameter. This is not very surprising since this oxygen atom is embedded inside the polyanion so that its vibration amplitude is low and anisotropic refinement is meaningless. Three reflections with large $|F_o - |F_c||$ differences were dropped out since they displayed also very asymmetrical background counts. The absorption correction was performed: The linear absorption coefficient was 32.8 mm^{-1} and the absorption coefficient ranged from 0.019 to 0.094. It was checked that the two equivalent reflections 800 and 080 gave identical structure factors after this correction.

The final R values were as follows: unweighted $R = 0.096$ and weighted $R_w = 0.074$.

Atomic parameters with their estimated standard deviations are listed in Table I, bond distances are given in Table II, and bond angles are given in Table III.

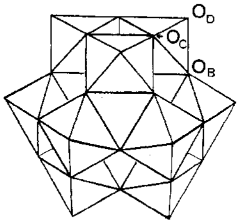

Figure 1. The Keggin structure. Only three W_3O_{13} groups are represented, for clarity. See Figure 2 for the definition of the different oxygen atoms.

Discussion

The $H_8[H_2W_{12}O_{40}]^{4-}$ ion has retained the original Keggin structure of the parent oxidized form[8] and, to our knowledge, this is the first time it is confirmed by a complete crystallographic study. While this structural retention has never been seriously questioned in the case of the first reduced species ("heteropoly blues"), there still remained some doubt for the higher reduction stages. The usual arrangement of four W_3O_{13} groups is thus found, each group resulting from the association of three edge-sharing WO_6 octahedra (see Figure 1). The 12 WO_6 octahedra are crystallographically equivalent owing to the high symmetry of the *Fm*3*m* space group. However, two types of metal sites are found with a crystallographic disorder. This is interpreted in the following way: For the complete structure, there are nine sites of type 1 in which the tungsten would be present as W^{VI} and three sites of type 2 in which the tungsten would be present as W^{IV}. These two types of sites are distant of 0.48 Å. The nine type 1 sites would make three $W^{VI}{}_3O_{13}$ groups and the three type 2 sites would make a $W^{IV}{}_3O_{13}$ group. In type 1 sites, the tungsten coordination is identical with the one observed in other iso- or heteropolyanions: The W^{VI} ion, which would be able to "rattle" in the octahedral hole owing to its small size, is actually locked in an off-center position as a consequence of the presence of strong W–O_D π bonds. (See table of W–O distances and Figure 2 with the definitions of the different oxygen atoms.)

By contrast, in type 2 sites, the tungsten atom has moved mainly toward O_A, since the W–O_A distance is reduced by 0.45 Å. This can be attributed to the breaking of W–O_D π bonds with simultaneous protonation of O_D oxygens. (Let us recall that $H_2W_{12}O_{40}{}^{6-}$ as well as $SiW_{12}O_{40}{}^{4-}$ reduced with six electrons contain three nontitrable protons.[2,9]) However the W_1–W_2 vector makes an angle of 21° with the W_1–O_A direction, showing that there is also a component of the dis-

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(7) Strictly speaking, the displacement of tungsten atoms must be accompanied by some displacement of the oxygen atoms, but this did not appear on Fourier maps. This effect is expected to be very small since the Keggin structure can be viewed as a close-packed array of oxygen atoms with tungsten atoms occupying octahedral holes.

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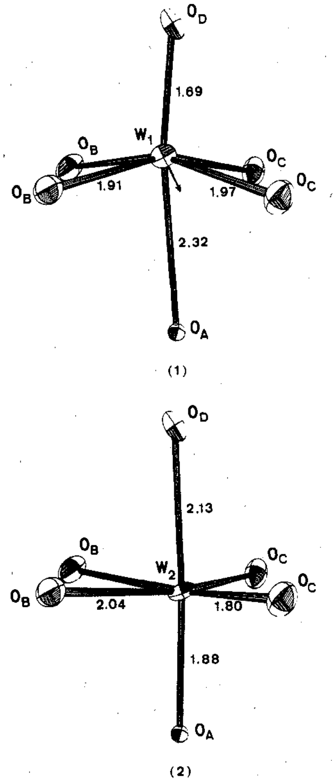

Figure 2. Comparison of bond lengths in sites 1 ($W^{VI}O_6$) and 2 ($W^{IV}O_6$). O_D designates the unshared outermost oxygen, O_A is one of the central oxygen atoms, O_B are bridging octahedra belonging to different W_3O_{13} groups, and O_C are bridging the octahedra of a same W_3O_{13} group. The arrow shows the direction of the W_1–W_2 displacement.

placement toward the center of a W_3O_{13} group (see Figure 2). This is also reflected in the W_2O_C distances which have decreased to 1.80 Å, while the W_2O_B distances have increased to 2.04 Å. Thus there seems to be a tendency for the tungsten atoms to move toward the other tungsten atoms of a same W_3O_{13} group, and we think that the driving force for this process is the building up of a $W^{IV}{}_3O_{13}$ cluster-like group, which necessitates that the three tungsten atoms occupying sites 2 are those belonging to the same W_3O_{13} group. If this is assumed, the W–W distances are found to be 3.31 Å in the three normal groups (which is in the usual range for this type of structure) and 2.50 Å in the type 2 group. This value is strikingly similar to the one (2.51 Å) observed by Mattes[10] in the $W^{IV}{}_3O_4F_9{}^{5-}$ ion exhibiting the same general structure with three edge sharing octahedra.

Of course the present study does not definitively prove the existence of $W^{IV}{}_3O_{13}$ clusters in reduced polyanion and it will be necessary for that to find a compound in which the crystallographic disorder is absent. However it gives a strong additional support to this assumption. A further argument comes from the existence of a brown 6-electron-reduced form of $Nb_2W_4O_{19}{}^{4-}$.[11] This ion is a cis isomer,[12] and its only structural analogy with the metatungstate ion is the possibility of finding three WO_6 octahedra disposed exactly like in a W_3O_{13} group. Finally let us recall that we have shown elsewhere[1] how the cluster hypothesis can account for the final reduction stage of metatungstate, with 32 electrons per mole, that is 8 electrons per W_3O_{13} group. The electronic structure of this kind of cluster with 6 or 8 electrons can be accounted for by Cotton's molecular orbital scheme.[13,14a,15]

Registry No. $Rb_4H_8[H_2W_{12}O_{40}]\cdot 18H_2O$, 74231-08-6; $Na_6H_2W_{12}O_{40}$, 12141-67-2.

Supplementary Material Available: A listing of structure factor amplitudes (3 pages). Ordering information is given on any current masthead page.

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Crystal and Molecular Structure of Trichlorobis(4-cyanopyridine-N^1)iron(III): A Rare Example of a MX_3L_2 Trigonal-Bipyramidal Complex of Iron(III)

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The crystal and molecular structure of the high-spin five-coordinate $FeCl_3(4\text{-cpy})_2$ complex has been determined from three-dimensioned X-ray diffraction data. The complex crystallizes in the monoclinic system of space group $P2_1/c$, with the cell dimensions $a = 11.84$ (1) Å, $b = 10.067$ (5) Å, $c = 12.92$ (1) Å, $\beta = 96.6$ (1)°, $Z = 4$ for $d_{calcd} = 1.60$ g cm^{-3}, and $d_m = 1.60$ g cm^{-3}. The structure described by 181 variable parameters was refined by full-matrix least-squares methods to conventional and weighted R values of 0.05 and 0.053, respectively, based on 2381 data with $F > 3\sigma(F)$. The coordination polyhedron around iron(III) is a trigonal bipyramid. The three vertices of the equatorial plane are occupied by Cl atoms while the pyridine ring nitrogens complete the environment. The Fe–Cl bond distances are 2.204 (1), 2.216 (1), and 2.229 (1) Å and the axial Fe–N bond distances are 2.232 (3) and 2.213 (3) Å, respectively. The electronic and infrared spectra are also discussed.

Introduction

The coordination chemistry of iron(III) with nitrogen-containing ligands has received a great deal of attention because of the biological implications of iron. As a part of our interest in this chemistry, we have studied the products of the reaction of iron(III) chloride on cyanopyridine (cpy) in nonaqueous solvents.[1] The 2-, 3-, and 4-cyanopyridines have two potential donor sites, (i) the pyridine ring nitrogen and (ii) the nitrile nitrogen; a competition between those nitrogen

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