  Bull. Chem. Soc. Jpn., 60, 4285—4290 (1987)

Structural Retention of Decatungstates upon Photoreduction

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(Received January 26, 1987)

The crystal structures of oxidized and photoreduced decatungstates are compared. Three specimens of decatungstate complexes were prepared in mixed solvents of H_2O-CH_3CN and were characterized by X-ray diffraction. Unit cell parameters are as follows: $(C_6H_{16}N)_4[W_{10}O_{32}]\cdot 2CH_3CN$; DECA M_r=2841.4, monoclinic, $P2_1/n$, a=14.617(2), b=17.783(3), c=11.755(2) Å, β=100.27(2)°, V=3006.5(9) Å^3, Z=2; $(C_6H_{16}N)_4[H_{1.5}W_{10}O_{32}]\cdot 8H_2O$; RED1 M_r=2905.4, monoclinic, $P2_1/n$, a=15.902(3), b=12.233(2), c=15.673(4) Å, β=93.76(2)°, V=3042(1) Å^3, Z=2; $Na_4[H_{1.8}W_{10}O_{32}]\cdot 14H_2O$; RED2 M_r=2696.7, monoclinic, $C2/m$, a=16.123(5), b=12.636(3), c=12.168(4) Å, β=117.40(2)°, V=2202(1) Å^3, Z=2; There is no obvious change in the anion frame among the three decatungstate complexes. Photoreduced decatungstates may coordinate protons which neutralize excess charge injected into anions. It is concluded that the structure of $W_{10}O_{32}$ is not largely altered up to two-electron reduction.

The photochemical properties of polyoxometalates in both solutions and solid states have been investigated.[1,2] To characterize the reduced polyoxometalates produced as a results of a photoredox reaction, it was decided to carry out a study of the crystal structure of photoreduced polyoxometalates. There have been only a few reports on the crystal structures of such reduced polyoxometalates as $(C_3H_{10}N)_4[Mo_{13}O_{40}]_{0.33}[H_4Mo_{12}O_{40}]_{0.67}$, $Rb_4H_8[H_2W_{12}O_{40}]\cdot 18H_2O$, and $Ca_{0.5}H_6PMo_{12}O_{40}\cdot 18H_2O$.[3-5] This paper describes the crystal structures of photoreduced decatungstates which are useful for catalytic H_2 production from water and organic substances.

The decatungstate anions, $[W_{10}O_{32}]^{4-}$[6] are stable in an acidic media and exhibit electrochemically reversible oxidation-reduction steps.[7] We prepared single crystals of two specimens of photoreduced decatungstates from H_2O-CH_3CN mixed solvents, and carried out X-ray diffraction studies.

Experimental

$(C_6H_{16}N)_4[W_{10}O_{32}]\cdot 2CH_3CN$; DECA. 3 g of $Na_2WO_4\cdot 2H_2O$ was dissolved in 40 cm^3 of water. The solution pH was adjusted to 1 using $HClO_4$. The solution was stirred at 80 °C for 30 min. Pale-yellow precipitates were obtained upon adding 20 cm^3 of a 2 mol dm^{-3} diisopropylammonium perchlorate aqueous solution and filtering. The precipitates were washed with water and diethyl ether and then recrystallized from a mixed solvent of H_2O-CH_3CN (1 : 4 v/v (pH 2)). Pale-yellow crystals were grown after 1—2 days.

$(C_6H_{16}N)_4[H_{1.5}W_{10}O_{32}]\cdot 8H_2O$; RED1. 1.8 g of the DECA powder was dissolved in 20 cm^3 mixed solvent of H_2O-CH_3CN (1 : 4 v/v (pH 2)). The solution was irradiated for 20 h by a use of a 500-W superhigh pressure mercury lamp in combination of a cut filter (λ>300 nm) under an argon atmosphere. Dark-blue crystals were grown from the photolyte at 5 °C within 2—3 days. The analysis of W^v in the blue crystals was achieved by $KMnO_4$ titration under an argon atmosphere and gave the composition of 1.5-electron reduction.

$Na_4[H_{1.8}W_{10}O_{32}]\cdot 14H_2O$; RED2. 5 g of $Na_2WO_4\cdot 2H_2O$ was dissolved in 20 cm^3 of H_2O. The solution pH was adjusted to 1 using $HClO_4$. The solution was stirred at 80 °C for 60 min and then 20 cm^3 of 2 mol dm^{-3} monoisopropylammonium perchlorate aqueous solution and 160 cm^3 of CH_3CN were added together. After cooling at room temperature, the solution was irradiated for 20 h in the same manner with RED1. Dark-blue platelike crystals were obtained from the solution at room temperature. The $KMnO_4$-titration analysis yielded a composition of 1.8 electron reduction per molecule.

X-Ray Structure Analysis. [DECA] The preliminary unit-cell dimensions and the space group were obtained from the oscillation and Weissenberg photographs. Systematic absences were k=2n+1 for 0k0 and h+l=2n+1 for h0l. The cell parameters were refined by least-squares on the basis of 15 independent 2θ values in the range 22°<2θ<29°. Crystallographic data are summarized in Table 1.

A crystal of 0.2×0.2×0.3 mm, sealed in a glass capillary, was mounted on a Rigaku AFC-4 diffractometer. Intensity data were collected up to 2θ=55° using Mo$K\alpha$ radiation monochromated by graphite. The ω—2θ scan technique was applied with a scan rate of 8° (2θ) min^{-1}. Three standard reflections, measured every 50 reflections, showed a variation in intensity of less than 2%. A total of 6898 reflections were measured, of which 5776 with $|F_o|>3\sigma(F_o)$ were used for the analysis. Correction was made for Lorentz and polarization factors, but neither for absorption nor extinction. The positions of the W atoms were obtained by a direct method using

Table 1. Crystallographic Data for Three Crystals

	DECA	RED1	RED2
M_r	2841.4	2905.4	2696.7
a/Å	14.617(2)	15.902(3)	16.123(5)
b/Å	17.783(3)	12.233(2)	12.636(3)
c/Å	11.755(2)	15.673(4)	12.168(4)
β/°	100.27(2)	93.76(2)	117.40(2)
V/Å^3	3006.5(9)	3042(1)	2202(1)
Space group	$P2_1/n$	$P2_1/n$	$C2/m$
Z	2	2	2
D_x/g cm^{-3}	3.14	3.17	4.07
D_m/g cm^{-3}	3.13	3.15	4.05
μ(Mo $K\alpha$)/cm^{-1}	183.5	181.4	280.9

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MULTAN78.[8] Other C, N, and O atoms appeared on successive Fourier maps. The structure was refined by using a the block diagonal least-squares program called HBLS.[9] Anisotropic temperature factors were applied to all the atoms except O (15) and C (42), whose factors turned out to non-positive definite. No hydrogen atoms were found on the difference map and, thus, not included in the calculation. The weighting scheme was $w=\{\sigma^2(|F_o|)+(C|F_o|)^2\}^{-1}$, where C was 0.06. In the final difference map, maximum and minimum electron densities were 5.2 and 4.3 e Å^{-3} within 1.5 Å around a W atom. The final R and R_W values became 0.090 and 0.110 for 5776 reflections. Final positional and thermal parameters are given in Table 2. The atomic scattering factors, including anomalous dispersion terms, were taken from International Tables for X-Ray Crystallography.[10] Calculations were carried out on the FACOM-HITAC system M-180 and M-280 computer at this Institute.

[RED1]: Experimental details were similar to those for [DECA]. Systematic absences were $k=2n+1$ for $0k0$ and $h+l=2n+1$ for $h0l$. The cell parameters were refined using 18 independent 2θ values in the range $18°<2\theta<29°$. A crystal of 0.3×0.3×0.2 mm was used for data collection. A total of 6980 reflection were obtained, of which 6001 were $|F_o|>3\sigma(F_o)$. In a least-squares refinement with the program HBLS, the anisotropic temperature factors of 15 non-W atoms was shown to be non-positive definite. These atoms were refined with isotropic temperature factors. The C value in the weighting scheme was 0.08. A considerably high residual peak of 11.4 e Å^{-3} appeared near one of the W atoms (ca. 0.9 Å) and ±3.6 e Å^{-3} around the other W atoms. A refinement based on a disordered model was unsuccessful. The final R and R_w were 0.127 and 0.159 for 6001 reflections, respectively. Final positional and thermal parameters are shown in Table 3.

[RED 2]: Experimental detailes were similar to those for

Table 2. Atomic Coordinates with the Equivalent Isotropic and Isotropic Thermal Parameters (Å^2) for DECA

$B_{eq}=4/3\sum_i\sum_j B_{ij}a_ia_j$

Atom	x	y	z	B_{eq} or B/Å^2
W(1)	26752(6)	97320(5)	91268(8)	1.8
W(2)	7753(6)	107049(5)	81231(7)	1.8
W(3)	6635(6)	88798(5)	83663(8)	1.9
W(4)	15990(6)	90219(6)	111076(8)	2.1
W(5)	17128(6)	108438(5)	108345(8)	2.0
O(1)	377(1)	961(1)	876(1)	2.3
O(2)	61(1)	1131(1)	695(1)	2.9
O(3)	36(1)	815(1)	746(1)	3.2
O(4)	197(1)	839(1)	1220(2)	4.3
O(5)	232(1)	1152(1)	1165(2)	3.6
O(6)	209(1)	1041(1)	799(1)	1.9
O(7)	197(1)	895(1)	824(2)	2.8
O(8)	269(1)	907(1)	1041(1)	2.2
O(9)	287(1)	1052(1)	1019(1)	1.9
O(10)	43(1)	976(1)	743(1)	1.9
O(11)	103(1)	840(1)	984(1)	2.0
O(12)	195(1)	1000(1)	1181(1)	2.2
O(13)	135(1)	1134(1)	938(1)	2.2
O(14)	−55(1)	904(1)	879(1)	1.8
O(15)	37(1)	921(1)	1139(1)	1.9(3)*
O(16)	125(1)	989(1)	961(1)	1.5
N(1)	547(1)	873(1)	887(2)	2.0
C(10)	546(2)	853(2)	764(2)	3.7
C(11)	457(3)	814(2)	706(3)	4.2
C(12)	560(2)	931(2)	703(2)	2.6
C(20)	534(2)	804(2)	963(2)	2.6
C(21)	623(2)	759(2)	990(3)	2.9
C(22)	524(3)	838(2)	1079(3)	5.5
N(2)	255(1)	1083(1)	576(2)	2.4
C(30)	226(2)	1020(2)	491(2)	3.4
C(31)	122(2)	1008(2)	476(3)	4.2
C(32)	286(3)	955(2)	522(3)	5.1
C(40)	208(2)	1164(2)	550(2)	3.4
C(41)	252(2)	1210(2)	654(4)	4.9
C(42)	235(3)	1195(2)	436(3)	5.2(7)*
N(AN1)	457(2)	1116(2)	602(2)	4.7
C(AN1)	524(2)	1151(2)	622(3)	4.3
C(AN2)	601(2)	1201(2)	631(4)	5.4

Multiplied by 10^5 for W atoms, 10^3 for O, N, and C atoms. Atoms with asterisk were refined with the isotropic temperature factor.

Table 3. Atomic Coordinates with the Equivalent Isotropic and Isotropic Thermal Parameters (Å^2) for RED1

$B_{eq}=4/3\sum_i\sum_j B_{ij}a_ia_j$

Atom	x	y	z	B_{eq} or B/Å^2
W(1)	8147(7)	33066(9)	−3515(7)	1.4
W(2)	903(7)	12859(9)	−16074(7)	1.4
W(3)	−10737(7)	19818(9)	−436(7)	1.4
W(4)	5675(7)	16512(9)	13003(7)	1.4
W(5)	17534(7)	9154(9)	−2564(7)	1.4
O(1)	107(1)	471(2)	−52(1)	1.8(3)*
O(2)	1(1)	137(2)	−269(1)	2.0
O(3)	−203(1)	259(2)	−1(1)	2.4
O(4)	76(2)	202(2)	235(2)	2.8(4)*
O(5)	279(1)	72(2)	−35(1)	1.7
O(6)	52(1)	283(2)	−144(1)	1.5(3)*
O(7)	−48(1)	351(2)	−29(1)	1.4(3)*
O(8)	84(1)	319(2)	85(1)	1.3(3)*
O(9)	183(1)	260(2)	−41(1)	1.8(3)*
O(10)	−98(1)	182(2)	−119(2)	2.2
O(11)	−61(1)	207(2)	112(2)	2.7(4)*
O(12)	163(1)	114(2)	94(2)	2.1
O(13)	125(1)	96(2)	−144(1)	2.8
O(14)	−139(1)	51(2)	10(1)	1.5
O(15)	22(1)	17(2)	140(1)	1.9
O(16)	35(1)	155(1)	−14(1)	1.2(3)*
N(1)	144(2)	446(2)	235(2)	2.8
C(10)	79(2)	534(3)	247(2)	2.9
C(11)	−4(3)	477(4)	253(3)	4.0(8)*
C(12)	108(3)	597(4)	320(3)	5.1
C(20)	235(2)	468(3)	220(2)	3.1
C(21)	245(3)	554(4)	144(3)	4.7(9)*
C(22)	280(4)	378(6)	210(4)	7.0(14)*
N(2)	323(2)	361(2)	−124(2)	2.9
C(30)	408(2)	326(3)	−85(3)	3.9
C(31)	478(3)	398(5)	−102(4)	4.0(10)*
C(32)	392(4)	330(5)	18(4)	4.7(12)*
C(40)	319(2)	342(3)	−222(2)	3.1
C(41)	307(3)	220(4)	−244(3)	4.5(9)*
C(42)	238(4)	416(5)	−255(4)	6.9(14)*
O(W1)	−353(3)	182(3)	−107(2)	6.9
O(W2)	427(2)	−61(3)	−28(2)	5.9
O(W3)	−303(3)	427(4)	73(3)	7.1
O(W4)	101(3)	232(4)	−384(3)	9.4

Multiplied by 10^5 for W atoms, 10^3 for O, N, and C atoms. Atoms with asterisk were refined with the isotropic temperature factor.

Table 4. Atomic Coordinates with the Equivalent Isotropic and Isotropic Thermal Parameters (Å²) for RED2

$B_{eq}=4/3\sum_i\sum_j B_{ij}a_ia_j$

Atom	x	y	z	B_{eq} or B/Å²
W(1)	27866(8)	50000	29531(10)	1.6
W(2)	6687(8)	50000	27628(10)	1.6
W(3)	12315(5)	68234(6)	13073(7)	1.5
W(4)	18000(8)	50000	−1519(10)	1.5
O(1)	393(2)	500	413(2)	2.2
O(2)	40(2)	500	395(2)	2.5
O(3)	139(1)	818(1)	149(1)	2.7
O(4)	233(2)	500	−113(2)	2.1(4)*
O(5)	208(1)	500	385(2)	1.8
O(6)	250(1)	648(1)	262(1)	1.8
O(7)	299(1)	500	149(2)	1.5(3)*
O(8)	81(1)	648(1)	249(1)	1.7
O(9)	169(1)	651(1)	15(1)	1.8
O(10)	−56(1)	500	140(2)	1.4
O(11)	0	674(2)	0	1.8
O(12)	125(1)	500	133(2)	1.5
Na(1)	376(1)	500	−133(1)	2.8
Na(2)	0	653(2)	500	6.3
O(W1)	−94(2)	190(2)	173(2)	5.0
O(W2)	464(3)	500	96(7)	10.1
O(W3)	−52(2)	805(3)	582(3)	6.9
O(W4)	139(2)	652(3)	651(3)	7.7

Multiplied by 10^5 for W atoms, 10^3 for O, N, and C atoms. Atoms with asterisk were refined with the isotropic temperature factor.

[DECA]. Systematic absences were at $h+k=2n+1$. The space group was assigned to be $C2m$ or $C2/m$. The refinement of the structure on the latter gave a reasonable result. The cell parameters were refined with 15 reflections of $18°<2\theta<30°$. A crystal of 0.35×0.25×0.12 mm was used for data collection. The intensities were gradually decrease to 92% in the data collection. An absorption correction was made using the program DABEX.[11] The correction factors were from 1.421 to 1.817. The positions of W atoms were obtained by a direct method with MULTAN 78. The Na and O atoms appeared on the successive Fourier maps. The structure was refined by a full-matrix least-squares method with the SHELX 76 program.[12] Two oxygen atoms, O(4) and O(7), revealed non-positive definite and refined isotropically. The weighting scheme employed was $w=\{\sigma^2(|F_o|)+0.002869\times(|F_o|)^2\}^{-1}$. In the final difference map, a maximum and minimum height of 11.0 and −7.4 e Å^{-3}, respectively, appeared around one of the W atoms for distances of less than 1.4 Å. Final R and R_w became 0.084 and 0.098 for 2499 reflections, respectively. Final positional and thermal parameters are given in Table 4.†††

Results

Structure of Decatungstate. The approximate geometries of the decatungstate anions in the three crystals (DECA, RED1 and RED2) are similar to one another and to that found in the crystal of tributylammonium salts.[6] Figure 1 shows the numbering of the atoms.

It is composed of ten WO_6 octahedra sharing edges

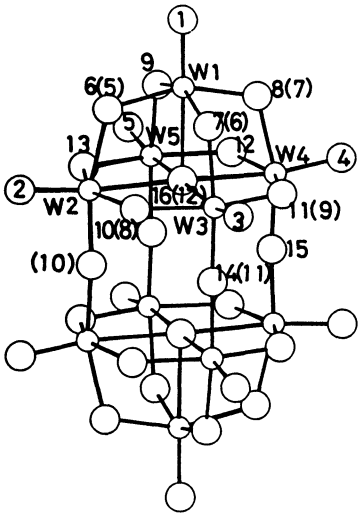

Fig. 1. The molecular structure of the decatungstate (DECA, RED1, and RED2) anions with the numbering on the atoms. Numbers in the bracket were given to RED2.

Table 5. Bond Distances (Å) in Decatungstate Anions (DECA, RED1, and RED2)

	DECA	RED1	RED2	
W(1)-O(1)	1.74(2)	1.78(2)	W(1)-O(1)	1.74(3)
W(2)-O(2)	1.74(2)	1.70(2)	W(2)-O(2)	1.69(3)
W(3)-O(3)	1.69(2)	1.70(3)	W(3)-O(3)	1.73(2)
W(4)-O(4)	1.72(2)	1.71(2)	W(4)-O(4)	1.75(3)
W(5)-O(5)	1.69(2)	1.68(2)		
W(1)-O(6)	1.89(2)	1.84(2)	W(1)-O(5)	1.91(2)
W(2)-O(6)	2.02(2)	2.02(2)	W(2)-O(5)	2.04(2)
W(1)-O(7)	1.92(2)	2.07(2)	W(1)-O(6)	1.92(2)
W(3)-O(7)	1.95(2)	2.14(2)	W(3)-O(6)	1.98(2)
W(1)-O(8)	1.91(2)	1.88(2)	W(1)-O(7)	1.96(2)
W(4)-O(8)	1.92(2)	2.06(2)	W(4)-O(7)	2.04(2)
W(1)-O(9)	1.87(2)	1.84(2)	W(2)-O(8)	1.93(2)
W(5)-O(9)	2.05(2)	2.07(2)	W(3)-O(8)	1.91(2)
W(2)-O(10)	1.90(2)	1.98(2)	W(3)-O(9)	1.91(2)
W(3)-O(10)	1.91(2)	1.82(2)	W(4)-O(9)	1.96(2)
W(3)-O(11)	1.92(2)	1.92(2)		
W(4)-O(11)	1.92(2)	1.95(2)		
W(4)-O(12)	1.95(2)	1.93(2)		
W(5)-O(12)	1.89(2)	1.92(2)		
W(5)-O(13)	1.91(2)	1.96(3)		
W(2)-O(13)	1.94(2)	1.90(3)		
W(3)-O(14)	1.94(2)	1.89(2)	W(2)-O(10)	1.91(2)
W(5)-O(14)	1.85(2)[a]	1.86(2)[b]	W(4)-O(10)	1.87(2)[c]
W(4)-O(15)	1.91(2)	1.90(2)	W(3)-O(11)	1.89(2)
W(2)-O(15)	1.88(2)[a]	1.89(2)[b]		
W(1)-O(16)	2.27(1)	2.30(2)	W(1)-O(12)	2.35(2)
W(2)-O(16)	2.28(1)	2.33(2)	W(2)-O(12)	2.33(2)
W(3)-O(16)	2.38(1)	2.34(2)	W(3)-O(12)	2.30(2)
W(4)-O(16)	2.33(1)	2.26(3)	W(4)-O(12)	2.34(2)
W(5)-O(16)	2.25(1)	2.38(2)		

a) Symmetry code (−x, 2−y, 2−z). b) Symmetry code (−x, −y, −z). c) Symmetry code (−x, y, −z).

†††The complete F_o-F_c data, anisotropic thermal parameters, bond distances of diisopropylammonium cations and acetonitrile in DECA and of the diisopropylammonium cations of RED1 and bond angles are deposited as Document No. 8756 at the Office of the Editor of Bull. Chem. Soc. Jpn.

and corners and has a pseudo point symmetry D_{4h}. Bond distances of the decatungstate in the three crystals are given in Table 5.

The corresponding bonds agreed with one another within the three crystals. There are three types of W-O bonds; terminal, bridging and central bonds. The terminal W-O bond, in which an oxygen atom has only one bond with a W atom, has a distance of 1.68—1.78 Å. The bridging W-O bond distance ranges from 1.84 to 2.07 Å, since the oxygen atom makes bonds with two W atoms. The central O atom has five bonds with the surrounding W atoms and the central W-O bond distances are 2.25—2.38 Å.

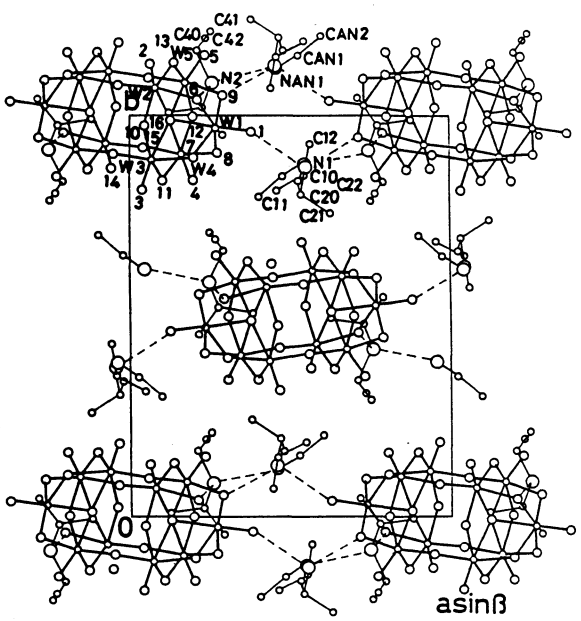

Fig. 2. The crystal structure of DECA viewed along the c axis. The hydrogen bonds are drawn with broken lines.

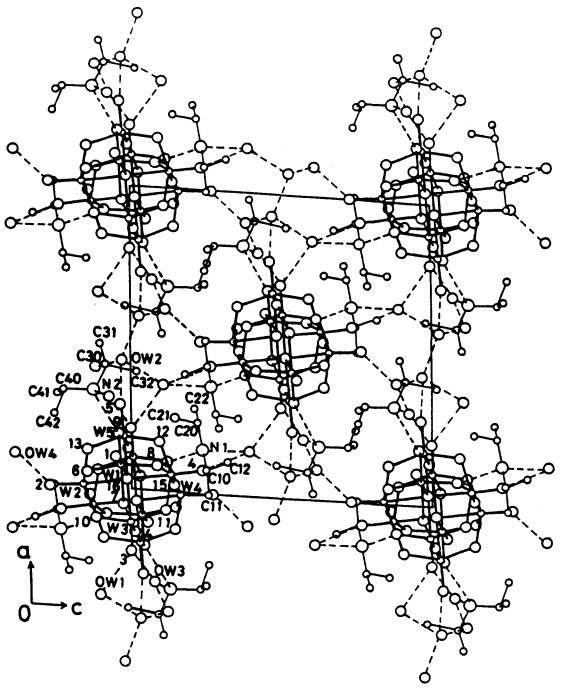

Fig. 3. The crystal structure of RED1 viewed along the b axis. The hydrogen bonds are drawn with broken lines.

Crystal Structure and Hydrogen-Bonding Scheme. The crystal structure of DECA viewed along the c axis is shown in Fig. 2.

The decatungstate anion in DECA is located at a center of symmetry. There are two diisopropylammonium cations and one CH_3CN solvent molecule per half an anion. One of the cations, N(1), makes two hydrogen bonds with O(1) and O(9) and links the anions along the *a*-axis. Another cation, N(2), has two hydrogen bonds with O(6) and the CH_3CN molecule. The distances of the hydrogen bonds are listed in Table 6. Figure 3 shows the crystal structure of RED1 viwed along the b-axis.

The decatungstate anion in RED1 also lies at a center of symmetry. Two cations and four water molecules take part in the three-dimensional hydrogen network; N(1) makes two hydrogen bonds with O(8) and O(W1), and N(2) has two bonds with O(9) and O(W3). Each water molecule has three or four hydrogen bonds with the anions and cations and with other water molecules.

Figure 4 shows the crystal structure of RED2 viewed along the b-axis. The decatungstate anion is at the position of symmetry $2/m$.

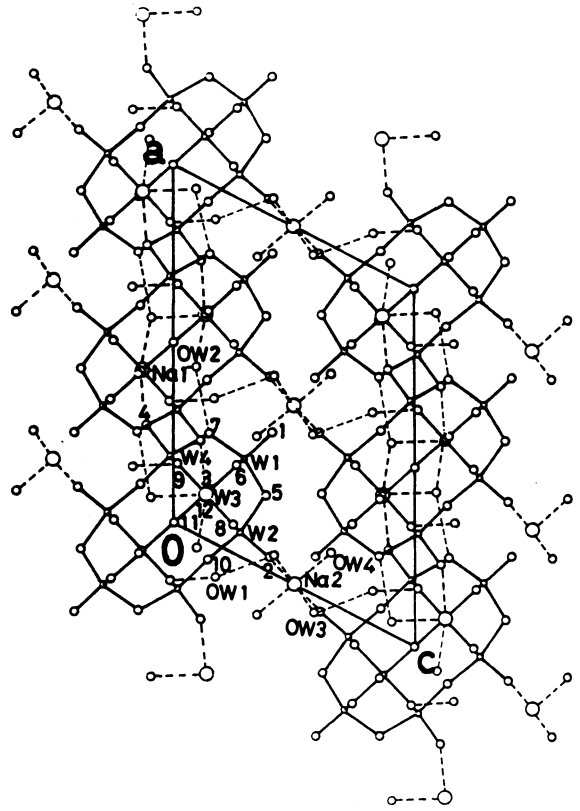

Fig. 4. The crystal structure of RED2 viewed along the b axis. Interactions among the oxygen atoms of the polyanions, water molecules and Na are shown with broken lines.

Table 6. Hydrogen Bond Distances (Å) in DECA and RED1, and Intermolecular Distances among the Oxygen Atoms of the Polyanions and Water Molecules, and Na in RED2

[DECA]		
N(1)-O(1)	2.93(3)	
N(1)-O(9)*	2.81(3)	*(1−x, 2−y, 2−z)
N(2)-O(6)	2.92(3)	
N(2)-O(AN1)	2.97(4)	
[RED1]		
N(1)-O(8)	2.94(4)	
N(1)-O(W1)*	2.93(5)	*(1/2+x, 1/2−y, 1/2+z)
N(2)-O(9)	2.93(4)	
N(2)-O(W3)*	2.73(5)	*(−x, 1−y, −z)
O(W1)-O(3)	2.96(5)	
O(W1)-O(4)*	3.02(5)	*(−1/2+x, 1/2−y, −1/2+z)
O(W1)-O(W2)*	2.90(6)	*(−x, −y, −z)
O(W2)-O(5)	2.85(4)	
O(W2)-O(W2)*	2.85(8)	*(1−x, −y, −z)
O(W2)-O(W4)*	2.90(7)	*(1/2−x, −1/2+y, −1/2−z)
O(W3)-O(3)	2.89(5)	
O(W3)-O(W4)*	2.58(7)	*(−1/2+x, 1/2−y, 1/2+z)
O(W4)-O(2)	2.75(6)	
[RED2]		
Na(1)-O(4)	2.44(3)	
Na(1)-O(W2)	2.48(8)	
Na(1)-O(W2)*	2.40(8)	*(1−x, 1−y, −z)
Na(2)-O(2)	2.56(4)	
Na(2)-O(W3)	2.49(5)	
Na(2)-O(W4)	2.14(5)	
O(W1)-O(9)*	2.87(3)	*(−x, 1−y, −z)
O(W1)-O(W3)*	2.82(5)	*(−x, 1−y, 1−z)
O(W2)-O(7)	3.01(9)	

The Na(1) cation interacts with O(3), O(4), and O(W2). The two Na(1) cations are bridged by the two O(W2) atoms and they make a tetragon. This tetragon unit connects the anion along the a- and b-axes. The Na(2) cation has octahedral interaction with O(2), O(W3), and O(W4). The two Na(2) cations are also bridged by two O(2) atoms of the neighboring anions. These octahedral units are stacked and make a column along the b-axis. This column connects the anions along the b- and c-axes. The intermolecular distances are given in Table 6.

Discussion

The structure of the decatungstate anion is not obviously changed by two-electron photoreduction. Electrochemical six-electron reduction of metatungstate $[H_2W_{12}O_{40}]^{6-}$ yields dark-brown crystals and the structural frame of the metatungstate anion is retained during the reduction.[4] However, the W-O bond distances are obviously changed by a six-electron reduction: each of the tungsten atoms in the WO_6 octahedra of a certain W_3O_{13} group is positioned with a shifting to a cavity center of the anion, resulting in a longer bond length between terminal oxygen and tungsten atoms compared to these of the WO_6 sites of other W_3O_{13} groups. Such a structural distortion induced by the six-electron reduction has been explained by a localization of six electrons within the specific edge-shared W_3O_{13} group of the metatungstate frame which consists of four W_3O_{13} groups with corner-shared bonding.

The photoreduced decatungstates of RED1 and RED2 consist of a mixture of protonated one- and two-electron reduced species, since flash photolysis of $[(C_4H_9)_4N]_4[W_{10}O_{32}]$ in CH_3CN, revealed that $[W_{10}O_{32}]^{5-}$ is produced by electron transfer from $[(C_4H_9)_4N]^+$ to $[W_{10}O_{32}]^{4-}$ and that upon protonation $[HW_{10}O_{32}]^{4-}$ (with $pK_a \approx 3.7$ in CH_3CN-H_2O of 9:1 v/v) suffers from the disproportionation to a protonated two-electron reduced species, $[H_2W_{10}O_{32}]^{4-}$, as summarized by Eqs. 1—3:[13,14]

$$[W_{10}O_{32}]^{4-} + [(C_4H_9)_4N]^+ \xrightarrow{h\nu} [W_{10}O_{32}]^{5-} + [N(C_4H_9)_3\cdot]^+ + H^+ + \text{1-butene}, \quad (1)$$

$$[W_{10}O_{32}]^{5-} + H^+ \rightleftarrows [HW_{10}O_{32}]^{4-}, \quad (2)$$

and

$$2[HW_{10}O_{32}]^{4-} \rightarrow [H_2W_{10}O_{32}]^{4-} + [W_{10}O_{32}]^{4-}. \quad (3)$$

Furthermore, it has been reported that the paramagnetic electron in the photoreduced decatungstate solid is delocalized over the anion by a large extent, compared with the six-electron reduced metatungstate.[2] The large degree of the electron-delocalization results in a decrease in the structural distortion due to a decrease in the formal electron density on a single WO_6 octahedron, leading to no obvious difference of the anion frame between the oxidized and photoreduced decatungstates (up to two-electron reduction). An X-ray structural analysis of the photoreduced decatungstates reveals the presence of four $[((CH_3)_2CH)_2NH_2]^+$ or Na^+ cations per decatungstate anion. This provides the compositions $(C_6H_{16}N)_4[H_xW_{10}O_{32}]\cdot 8H_2O$ and $Na_4[H_xW_{10}O_{32}]\cdot 14H_2O$. In conjunction with the result of the W^V analysis, in order to maintain electrical neutrality, therefore, the photoreduced species can be formulated as $(C_6H_{16}N)_4[H_{1.5}W_{10}O_{32}]\cdot 8H_2O$ and $Na_4[H_{1.8}W_{10}O_{32}]\cdot 14H_2O$, respectively. It must be recalled that the structure of $[(C_2H_5)_3NH]_3(H_3O)[Mo_8O_{26}]$ revealed the presence of one oxonium in addition to three $[(C_2H_5)_3NH]^+$, as cations.[15] The crystals of complexes of RED1 and RED2 incorporate several water molecules to form a complicated hydrogen-bonding network among the anions and water molecules. This enabled us to deduce the presence of aquahydrogen cations in the crystal; from the fact that the oxidized decatungstate has no water molecule in the crystal, it is inferred that the photoreduction of the decatungstates accompanies the incorporation of aquahydrogen cations for a conpensation of excess charges injected into the anion.

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