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Structural characterization of the brown six-electron-reduced form of dodecatungstoborate, $K_5[BW_{12}O_{37}(H_2O)_3]\cdot13.5H_2O$

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Prolonged photolysis of aqueous solutions containing α-$K_5[BW_{12}O_{40}]\cdot9H_2O$ **1** and MeOH at pH 0.1 led to the formation of the diamagnetic six-electron-reduced species $K_5[BW_{12}O_{37}(H_2O)_3]\cdot13.5H_2O$ **2**, *via* successive disproportionations between the protonated two-electron reduced species $[H_2BW_{12}O_{40}]^{5-}$. Single-crystal X-ray diffraction analyses of colourless crystals of **1** and dark brown crystals of **2** showed that six electrons contribute to the formation of a trigonal edge-shared $W^{IV}{}_3O_{13}$ group of α-Keggin framework and approximate C_{3v} symmetry. The edge-shared $W^{IV}{}_3$ triad contains terminal aqua ligands with a mean bond length of 2.15(4) Å on each W^{IV} atom which is linked by W^{IV}–W^{IV} bonds [mean 2.543(3) Å]. The aqua ligand is also bound to lattice water and neighbouring anion oxygen atoms by hydrogen bonds. The magnitude of the O(terminal)–W–O(μ) bond angles for each WO_6 octahedron can be associated with the asymmetry of the axial W–O bond distances, due to the electrostatic repulsive interaction of μ-O atoms with terminal-O and μ_4-O atoms. The contraction ($\approx$0.77 Å) of the W $\cdots$ W distances due to the W^{IV}–W^{IV} bond formation in the $W^{IV}{}_3$ triad is concerted, pushing atom B down ($\approx$0.4 Å) toward the corner-shared $W^{VI}{}_3$ triad. As a result, an expansion ($\approx$0.03 Å) of the $W^{VI} \cdots W^{VI}$ distances in the corner-shared $W^{VI}{}_3$ triad occurs with a shortening ($\approx$0.4 Å) in B $\cdots$ W^{VI} distances, and is accompanied by slight elongations ($<$ 0.07 Å) in both the $W^{VI} \cdots W^{VI}$ distances in the edge-shared $W^{VI}{}_3$ triad and $W^{VI} \cdots W^{IV}$ distances between the corner-sharing $W^{VI}O_6$ and $W^{IV}O_6$ octahedra.

It is well known that $[H_2W_{12}O_{40}]^{6-}$, $[BW_{12}O_{40}]^{5-}$, $[SiW_{12}O_{40}]^{4-}$ and other α-Keggin structural heteropolyoxotungstates can be reduced electrochemically or photochemically to the brown six-electron reduction species which are different from the usual heteropoly blues corresponding to one- or two-electron reduction species.[1-4] In the brown species it has been suggested that these electrons lead to the formation of the edge-sharing octahedral $W^{IV}{}_3O_{13}$ group, in which the W^{IV} atoms are linked by W^{IV}–W^{IV} bonds and the terminal oxygens become protonated to form water molecules. This assumption is supported by the crystal structure of the brown species of metatungstate formulated as $Rb_4H_8[H_2W^{IV}{}_3W^{VI}{}_9O_{40}]\cdot\approx18H_2O$, although the resolution obtained is limited by orientational disorder:[5] the space group of the crystal ($Z = 8$) is $Fm\bar{3}m$ which allows only one independent W atom in the anion. The X-ray analysis of the brown metatungstate implies the presence of two kinds of tungsten positions which were attributed to W^{IV} and W^{VI} atoms, in which the W atoms are disordered with occupancy factors of $\frac{1}{4}$ and $\frac{3}{4}$, respectively. The configurations of the W^{IV} and W^{VI} atoms were not determined and the presence of the $W^{IV}{}_3O_{13}$ group was only indirectly suggested. In order to prove the existence of the $W^{IV}{}_3O_{13}$ group in the brown species it is essential to find a compound in which the crystallographic disorder is absent. Here, we report a complete structure of the potassium salt of the six-electron-reduced form of α-$[BW_{12}O_{40}]^{5-}$, which is formulated as $K_5[BW_{12}O_{37}(H_2O)_3]\cdot13.5H_2O$. This compound can be obtained by the photoredox reaction of $[BW_{12}O_{40}]^{5-}$ and alcohols in acidic media:[3] in highly acidic solutions (pH $<$ 2) protonation of the one-electron reduced species, $[BW_{12}O_{40}]^{6-}$ ($pK_a \approx 1.5$ for $[HBW_{12}O_{40}]^{5-}$), formed in the redox reaction between $[BW_{12}O_{40}]^{5-}$ and MeOH, occurs, followed by successive disproportionations to the six-electron-reduced species. The ^{183}W NMR spectrum of $[BW_{12}O_{37}(H_2O)_3]^{5-}$ consists of three simple lines at δ 1412.3, -109.8 and -128.3 with an intensity ratio of 1 : 1 : 2. Each of the lines is shifted downfield relative to a simple resonance at δ -129.5 for the oxidized parent $[BW_{12}O_{40}]^{5-}$.[4,6] The line at δ 1412.3, shifted strongly downfield, has been assigned to three W^{IV} atoms in the $W^{IV}{}_3O_{13}$ group where six electrons will be localized preferentially, probably due to bond strengthening as a result of the formation of three W^{IV}–W^{IV} bonds in the $W^{IV}{}_3O_{13}$ group. The crystal structural analysis of the six-electron brown species $K_5[BW_{12}O_{37}(H_2O)_3]\cdot13.5H_2O$ should be also useful for the confirmation of the W^{IV}–W^{IV} bonding.

Experimental

Preparation and chemical analysis

The salt $Na_{10}[SiW_9O_{34}]\cdot18H_2O$ was prepared as described previously[7] and $K_5[BW_{12}O_{40}]\cdot9H_2O$ **1** was synthesized and crystallized according to a published procedure.[8] All other reagents were of at least analytical grade used without further purification. Diamagnetic $K_5[BW_{12}O_{37}(H_2O)_3]\cdot13.5H_2O$ **2** was prepared according to the photochemical method[3] and crystallized as follows: complex **1** (0.3 g, 0.09 mmol) was dissolved in water (20 cm^3) in a quartz tube (40 cm^3), HCl was added to adjust the pH to 0.1, and then MeOH (5 cm^3) was added. The resulting solution was irradiated for 3 d under an atmosphere of nitrogen using a 500 W superhigh-pressure mercury lamp. Potassium chloride (0.5 g, 6.8 mmol) and α-$Na_{10}[SiW_9O_{34}]\cdot18H_2O$ (0.25 g, 0.1 mmol) were added to the dark brown photolyte and kept at 4 °C. Dark brown single parallelepiped crystals (0.13 g) of **2** were precipitated within 1 d. The increase in the ionic strength of the photolyte by additional electrolytes such as $Na_{10}[SiW_9O_{34}]\cdot18H_2O$, $Eu(NO_3)_3\cdot6H_2O$, and $PhP(O)(OH)_2$ seems to be important for crystallization of the brown reduced species. The six-electron reduction in **2** was confirmed by potentiometric titration under an atmosphere of nitrogen and the potential of a platinum indicator electrode *vs.* Ag–AgCl reference electrode at open circuit was measured by a TOA Electronics IM-5S ion meter: a known volume of ammonium iron(II) sulfate was added to **2** in 4 mol dm^{-3} H_2SO_4

to clarify the endpoint of the titration and the tungsten(IV) content was determined using a standard solution of $KMnO_4$. The extent of reduction in **2** was 5.5 ± 0.1. The IR and Raman spectra were recorded on JASCO FT/IR-5000 and Jobin-Yvon T6400 Raman spectrophotometers, respectively.

Crystallography

Crystals were sealed in Lindemann glass capillaries and mounted on a Rigaku AFC-5 diffractometer equipped with graphite-crystal-monochromatized Mo-Kα ($\lambda = 0.710\,69$ Å) radiation. The intensities were collected by ω–2θ scans at a 2θ scan rate of 8° min^{-1} at room temperature. The orientation matrix and cell dimensions were obtained from the setting angles of 25 centred reflections in the range $2\theta = 20.0$–24.7 and 20.1–25.0° for complexes **1** and **2**, respectively. No significant decay in intensity of three standard reflections recorded after every 100 was observed. The W atom positions for **1** and **2** were determined by direct methods using MITHRIL[9] and SAPI 91,[10] respectively. Atoms K, O and B were located from difference syntheses. Lorentz and polarization factors were applied and an absorption correction by use of DIFABS[11] after isotropic refinement for **1**, and on the basis of Ψ scans of three reflections[12] for **2**. The correction factors applicable to $|F_o|$ were 0.80–1.46 and 0.15–1.00 for **1** and **2**, respectively. Subsequently in **1** the W, and in **2** the W and K atoms were refined with anisotropic thermal parameters. Refinements for all non-H atoms were carried out (on *F*) using the full-matrix least-squares method. The quantity minimized was $\Sigma w(|F_o| - |F_c|)^2$. Attempts to refine potassium and crystal-water oxygen atoms, with various combinations of site-occupancy factors, were performed. A summary of crystal data for **1** and **2** is shown in Table 1. The weighting scheme employed was $w^{-1} = \sigma^2(F_o)$, where $\sigma^2(I_o) = \sigma^2(I_{counting}) + (0.007\ I_o)^2$ and $\sigma^2(I_o) = \sigma^2(I_{counting}) + (0.042\ I_o)^2$ for **1** and **2**, respectively. The maximum and minimum heights in the final difference synthesis were 5.8 and −2.5 e $Å^{-3}$ around K(1) and K(2) atoms at distances of 1.0 and 1.2 Å in **1**, respectively [7.0 and −6.4 e $Å^{-3}$ around W(12) and W(6) at 1.1 and 0.9 Å in **2**, respectively]. All calculations were carried out on a Micro VAX II computer using the TEXSAN software package.[13]

Complete atomic coordinates, thermal parameters and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1996, Issue 1.

Results and Discussion

Structure of $K_5[BW_{12}O_{40}]\cdot 9H_2O$ 1

The unit cell of $K_5[BW_{12}O_{40}]$ consists of crystallographically distinct molecules (**1a** and **1b**); two and four, respectively, formulated as $K_5[BW_{12}O_{40}]\cdot 9H_2O$ which occupy sites of crystallographic symmetry 222 (D_2) and 2 (C_2), respectively. Fig. 1 shows views of **1a** and **1b** and their crystal packing in the cell. The $[BW_{12}O_{40}]^{5-}$ anions in **1** exhibit the α-Keggin structure with T_d symmetry, in which the W^{VI} atoms occupy the vertices of a cuboctahedron. Tables 2 and 3 show atomic coordinates and selected bond distances and angles, respectively. The structures of molecules **1a** and **1b** were identical but the location of K^+ or crystal water relative to the anion was different between the two. Fig. 2 shows the dimensions of the edge-shared W_3O_{13} units in molecules **1a** and **1b**. Two kinds of W ··· W distances are observed; one [3.304(3)–3.324(3) Å] with an average of 3.313(3) Å between W atoms of a W_3O_{13} unit and the other [3.633(3)–3.659(3) Å] with an average of 3.645(3) Å between W atoms of adjacent W_3O_{13} units. The W=O, W–O(μ) and W–O(μ_4) bond distances are 1.66(3)–1.79(5), 1.82(3)–1.96(4) and 2.33(3)–2.47(3) Å, respectively, indicating the expected trend of increasing W–O bond length for one- < two- < four-co-ordinate oxygens. The W–O(μ_4) distances are elongated as a consequence of the *trans* influence of the terminal W=O oxide ligands. The asymmetric feature of the axial W–O bond distances provides a large displacement of O=W–O(μ) bond angles [96(1)–105(2), average 100(2)°] from 90° due to the electrostatic repulsive interaction among axial and equatorial O atoms, as demonstrated by the fact that O(μ) ··· O(terminal) distances [2.67(5)–2.84(6), average 2.77(6) Å] for every WO_6 octahedral site are nearly equivalent to O(μ) ··· O(μ_4) distances [2.60(5)–2.95(4), average 2.80(5) Å]. The central B atom is in a tetrahedral position with mean B–O bond length of 1.49(6) Å. These geometrical parameters are in the range of those observed in other Keggin polyoxoanions.[14] The site occupancy

Table 1 Crystal and refinement data for complexes **1** and **2**

	1	2
Formula	$H_{18}BK_5O_{49}W_{12}$	$H_{33}BK_5O_{53.5}W_{12}$
M	3215	3302
Crystal symmetry	Orthorhombic	Triclinic
Space group	*C*222	$P\bar{1}$
a/Å	19.055(3)	11.803(4)
b/Å	33.004(6)	12.064(4)
c/Å	12.439(2)	18.790(6)
α/°		86.55(3)
β/°		80.55(3)
γ/°		63.42(3)
U/Å^3	7823(2)	2360(2)
Z	6	2
D_c/g cm^{-3}	4.094	4.646
μ/cm^{-1}	268.796	297.124
F(000)	8388	2898
Crystal size/mm	0.15 × 0.15 × 1.8, plate	0.3 × 0.2 × 0.1, plate
Data collection range/°	$5 \leqslant 2\theta \leqslant 55$	$5 \leqslant 2\theta \leqslant 55$
h,k,l Ranges	0–25, 0–43, 0–17	−13 to 15, 0–15, ±24
No. data measured	4897	11 383
No. unique data	4895	10 869
No. observed data [$\lvert F\rvert > 3.0\sigma(F)$]	3491	5700
No. variables	249	371
R	0.058	0.081
R'	0.062	0.090
Goodness of fit, *S*	1.88	2.09
Maximum shift/error	0.117	0.021

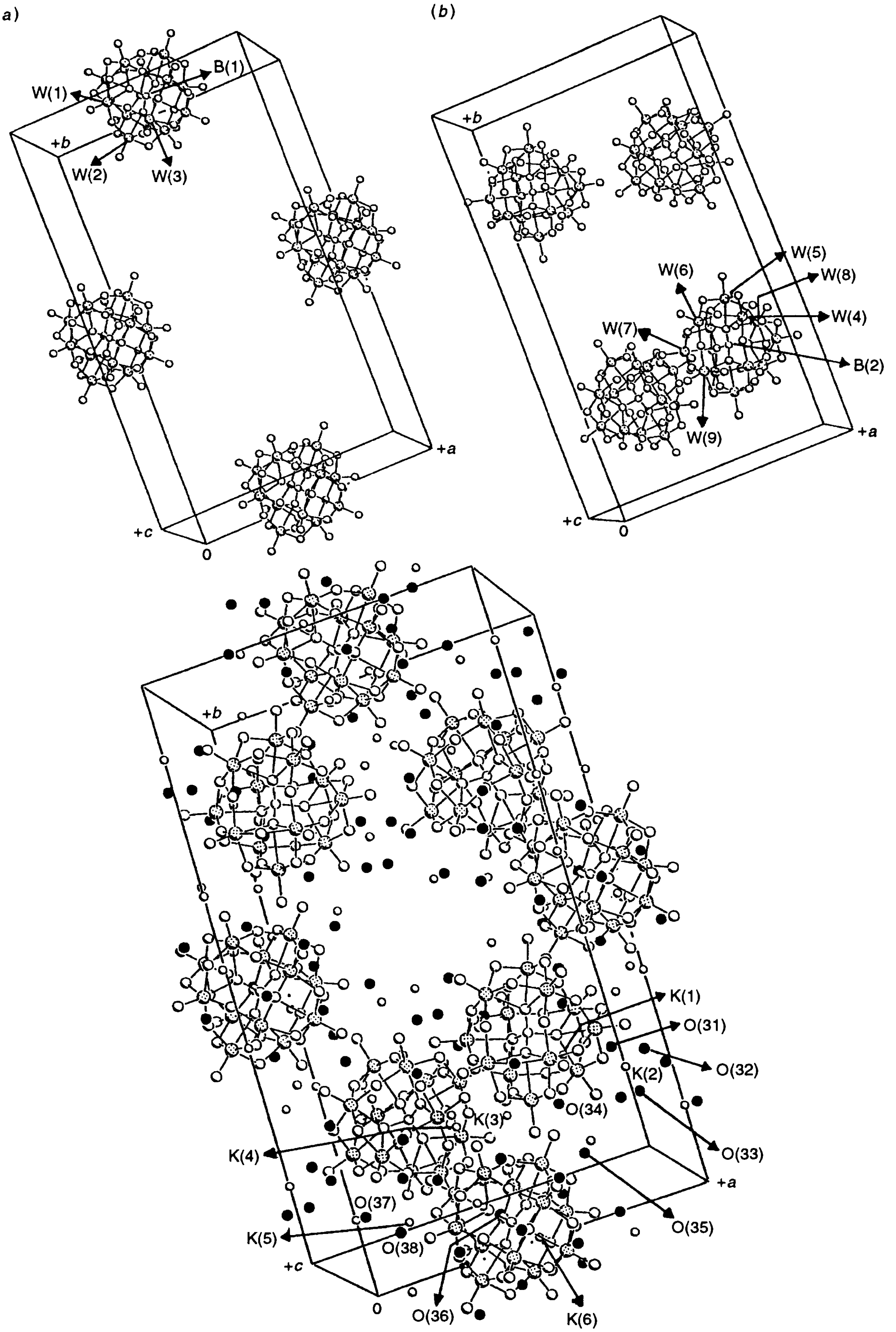

Fig. 1 Anion stackings of the crystallographically distinct molecules **1a** (*a*) and **1b** (*b*) and the crystal packing (*c*) of complex **1** with atom labelling. The black circles are lattice-water oxygen atoms

of atom K(6) is fixed at 0.5 throughout the structure refinements, since the short distance [1.12(9) Å] of K(6)··· K(6^{III}) (symmetry code III: *x*, −*y*, −*z*) may be brought about by the disordered structure of the two K atoms.

Structure of $K_5[BW_{12}O_{37}(H_2O)_3]\cdot 13.5H_2O$ 2

The structure of complex **2** consists of discrete cations and $[BW_{12}O_{37}(H_2O)_3]^{5-}$ anions, with water molecules of crystallization occupying the void volumes. The anion in **2** lies

Table 2 Atomic coordinates for complex **1** with estimated standard deviations (e.s.d.s) in parentheses

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
W(1)	0.370 4(1)	0.003 73(6)	−0.302 7(2)	O(14)	0.445(2)	−0.032(1)	−0.252(3)
W(2)	0.371 6(1)	−0.075 21(5)	−0.509 2(2)	O(15)	0.444(2)	−0.089(1)	−0.409(3)
W(3)	0.506 1(1)	−0.074 01(5)	−0.301 8(2)	O(16)	0.456(1)	0.025 0(8)	−0.430(3)
W(4)	0.857 9(1)	0.290 01(6)	0.031 3(2)	O(17)	0.865(2)	0.341 1(9)	−0.045(3)
W(5)	0.798 5(1)	0.351 85(6)	−0.157 3(2)	O(18)	0.728(2)	0.362(1)	−0.046(3)
W(6)	0.690 6(1)	0.316 75(6)	0.030 4(2)	O(19)	0.778(2)	0.312(1)	0.102(3)
W(7)	0.573 0(1)	0.276 64(6)	−0.175 6(2)	O(20)	0.670(2)	0.263(1)	0.076(3)
W(8)	0.864 0(1)	0.283 96(6)	−0.364 4(2)	O(21)	0.588(2)	0.233(1)	−0.074(3)
W(9)	0.679 5(1)	0.313 03(7)	−0.363 8(2)	O(22)	0.855(2)	0.322 8(8)	−0.254(3)
				O(23)	0.720(2)	0.344(1)	−0.253(3)
K(1)	0.75	0.25	0.297(4)	O(24)	0.623(2)	0.309 8(9)	−0.078(3)
K(2)	1.0	0.132(2)	1.0	O(25)	0.944(2)	0.261(1)	−0.289(3)
K(3)	0.551 6(6)	0.183 6(4)	0.333(1)	O(26)	0.771(2)	0.297(1)	−0.406(3)
K(4)	0.5	0.132 3(5)	1.0	O(27)	0.591(2)	0.316(1)	−0.285(3)
K(5)	0.197(2)	0.069(1)	0.340(4)	O(28)	0.855(2)	0.233(1)	−0.439(3)
K(6)	0.5	0	0.045(3)	O(29)	0.767(2)	0.284(1)	−0.093(3)
				O(30)	0.811(2)	0.241 3(8)	−0.239(2)
O(1)	0.308(2)	−0.006(1)	−0.208(3)				
O(2)	0.312(2)	−0.111(1)	−0.486(4)	O(31)	0.890(2)	0.234(1)	0.321(4)
O(3)	0.491(2)	−0.110 8(8)	−0.206(3)	O(32)	1.0	0.196(2)	0.5
O(4)	0.922(2)	0.300 6(8)	0.122(3)	O(33)	0.933(4)	0.149(2)	0.332(9)
O(5)	0.820(2)	0.402(1)	−0.184(3)	O(34)	0.704(2)	0.173(1)	0.335(5)
O(6)	0.646(2)	0.344(1)	0.128(3)	O(35)	0.710(3)	0.098(2)	0.161(7)
O(7)	0.488(2)	0.288(1)	−0.154(4)	O(36)	0.407(2)	0.061(1)	0.007(5)
O(8)	0.910(2)	0.311(1)	−0.458(3)	O(37)	1.067(7)	0.111(4)	1.24(1)
O(9)	0.662(2)	0.351(1)	−0.462(4)	O(38)	0.265(6)	0	1.0
O(10)	0.579(2)	−0.044(1)	−0.228(3)				
O(11)	0.580(2)	−0.101 7(8)	−0.376(3)	B(1)	0.5	0	−0.5
O(12)	0.320(2)	0.045(1)	−0.384(3)	B(2)	0.750	0.250	−0.13(1)
O(13)	0.343(2)	−0.033 4(9)	−0.409(3)				

Table 3 Selected bond distances (Å) and angles for complex **1**

W(1)–O(1)	1.71(3)	W(2)–O(2)	1.66(3)	W(3)–O(3)	1.73(3)	W(4)–O(4)	1.70(3)
W(1)–O(10$^{\text{II}}$)	1.90(3)	W(2)–O(11$^{\text{IV}}$)	1.91(3)	W(3)–O(10)	1.93(3)	W(4)–O(17)	1.94(3)
W(1)–O(12)	1.95(3)	W(2)–O(12$^{\text{III}}$)	1.93(3)	W(3)–O(11)	1.92(3)	W(4)–O(19)	1.89(3)
W(1)–O(13)	1.88(3)	W(2)–O(13)	1.94(3)	W(3)–O(14)	1.90(4)	W(4)–O(20$^{\text{VI}}$)	1.90(4)
W(1)–O(14)	1.96(4)	W(2)–O(15)	1.91(4)	W(3)–O(15)	1.86(4)	W(4)–O(21$^{\text{VI}}$)	1.82(3)
W(1)–O(16)	2.38(3)	W(2)–O(16$^{\text{III}}$)	2.43(3)	W(3)–O(16$^{\text{II}}$)	2.38(3)	W(4)–O(29)	2.33(3)
W(5)–O(5)	1.72(3)	W(6)–O(6)	1.74(3)	W(7)–O(7)	1.69(4)	W(8)–O(8)	1.72(3)
W(5)–O(17)	1.92(3)	W(6)–O(18)	1.92(3)	W(7)–O(21)	1.95(3)	W(8)–O(22)	1.89(3)
W(5)–O(18)	1.96(3)	W(6)–O(19)	1.90(3)	W(7)–O(24)	1.89(3)	W(8)–O(25)	1.95(3)
W(5)–O(22)	1.88(3)	W(6)–O(20)	1.92(4)	W(7)–O(25$^{\text{VI}}$)	1.91(3)	W(8)–O(26)	1.90(3)
W(5)–O(23)	1.93(3)	W(6)–O(24)	1.88(3)	W(7)–O(27)	1.91(4)	W(8)–O(28)	1.94(3)
W(5)–O(29)	2.47(3)	W(6)–O(29)	2.38(3)	W(7)–O(30$^{\text{VI}}$)	2.42(3)	W(8)–O(30)	2.34(3)
W(9)–O(9)	1.79(5)	W(9)–O(27)	1.95(3)	B(1)–O(16)	1.46(3)		
W(9)–O(23)	1.88(3)	W(9)–O(28$^{\text{VI}}$)	1.89(3)	B(2)–O(29)	1.25(6)		
W(9)–O(26)	1.90(3)	W(9)–O(30$^{\text{VI}}$)	2.38(3)	B(2)–O(30)	1.79(9)		
O(1)–W(1)–O(10$^{\text{II}}$)	99(2)	O(10$^{\text{II}}$)–W(1)–O(16)	77(1)	O(4)–W(4)–O(17)	96(1)	O(17)–W(4)–O(29)	79(1)
O(1)–W(1)–O(12)	99(2)	O(12)–W(1)–O(16)	78(1)	O(4)–W(4)–O(21$^{\text{VI}}$)	99(1)	O(19)–W(4)–O(29)	75(1)
O(1)–W(1)–O(13)	100(1)	O(13)–W(1)–O(16)	85(1)	O(4)–W(4)–O(19)	101(1)	O(20$^{\text{VI}}$)–W(4)–O(29)	85(1)
O(1)–W(1)–O(14)	100(2)	O(14)–W(1)–O(16)	84(1)	O(4)–W(4)–O(20$^{\text{VI}}$)	101(1)	O(21$^{\text{VI}}$)–W(4)–O(29)	85(1)
O(1)–W(1)–O(16)	174(1)	O(16)–B(1)–O(16$^{\text{III}}$)	110(2)	O(4)–W(4)–O(29)	173(1)		
O(16)–B(1)–O(16$^{\text{II}}$)	107(2)	O(16)–B(1)–O(16$^{\text{IV}}$)	111(2)	O(29)–B(2)–O(29$^{\text{VI}}$)	134(11)	O(29)–B(2)–O(30$^{\text{VI}}$)	108(4)
				O(29)–B(2)–O(30)	106(4)	O(30)–B(2)–O(30$^{\text{VI}}$)	84(6)

Symmetry codes: II $-x, -y, z$; III $x, -y, -z$; IV $-x, y, -z$; VI $\frac{1}{2} - x, \frac{1}{2} - y, z$.

at a general position in space group $P\bar{1}$ and has retained the original α-Keggin structure of the parent oxidized form of **1** with the exception that the every terminal oxo group of the W_3O_{13} moiety in **1** is replaced by three aqua ligands in **2** (as discussed below). To our knowledge, this is the first example of a complete crystallographic study of six-electron-reduced polyoxometalates. Atomic coordinates and selected bond distances and angles for **2** are shown in Tables 4 and 5, respectively. The α-Keggin structure of the approximately C_{3v} symmetrical arrangement of four W_3O_{13} groups of W(1–3), W(4,9,10), W(5,6,11) and W(7,8,12) sites is found, each group resulting from the association of three edge-sharing WO_6 octahedra. The relative values of the tungsten–terminal oxygen bond strengths, $s_{\text{W-O}} = (d_{\text{W-O}}\ 1.904)^{-6.0}$, where *d* is the bond length in Å, were estimated.[15] The valence sums of all the W–O bond strengths for atoms W(1–3) and W(4–12) were 3.9(3)–4.2(4) and 5.7(5)–6.7(7), respectively, consistent with oxidation states of IV and VI. Fig. 3 shows the anion structure and the dimensions of three kinds of W_3O_{13} edge-shared units in **2**. As indicated by the ^{183}W NMR spectrum of **2**,[4,6] three types of metal sites are clear: three W(1–3) sites of type 1, six W(4–9) sites of type 2, and three W(10–12) sites of type 3. Each tungsten for types 1, 2 and 3 would be present as W^{IV}, W^{VI} and W^{VI}, respectively. Six WO_6 octahedra of type 2 are linked by alternate corner and edge sharing, and also share corners and edges with the type 1 and 3 site octahedra, respectively. In type 3 sites the tungsten co-ordination is almost identical with that observed in the parent oxidized anion **1**: the W=O bond lengths

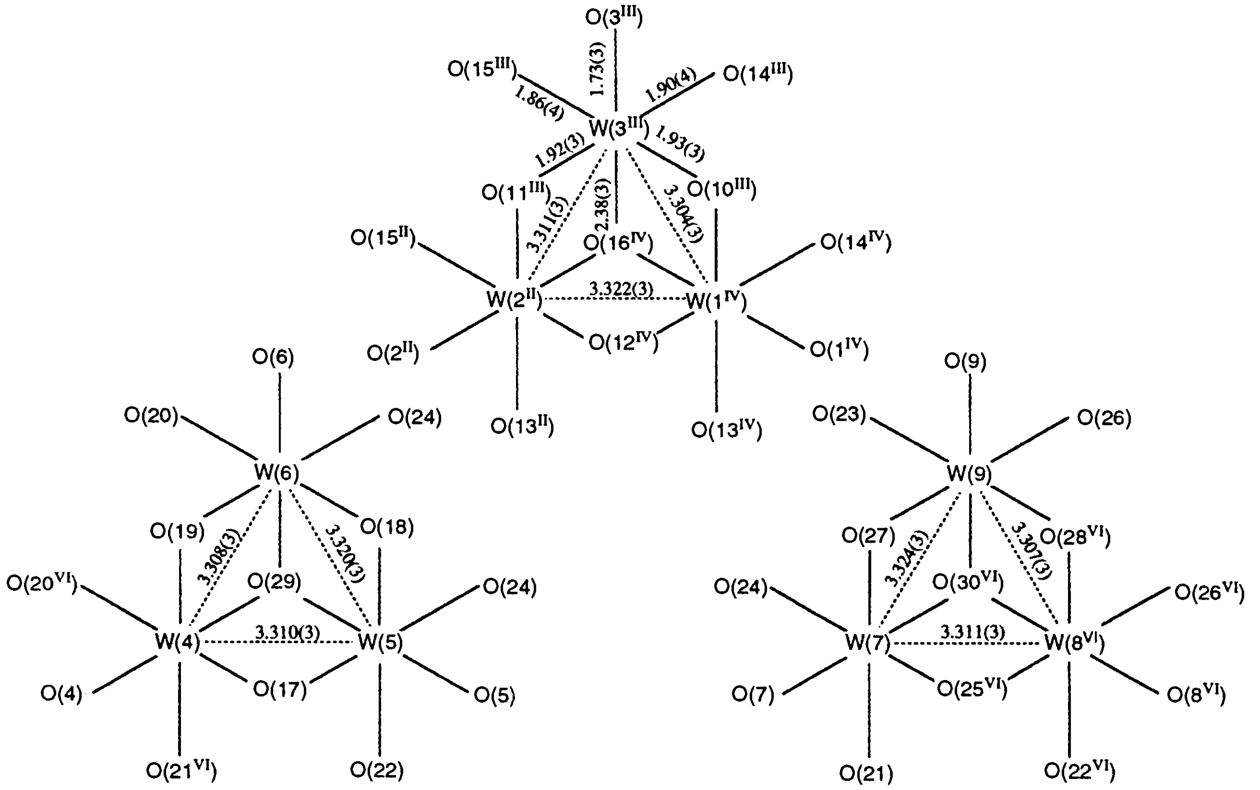

Fig. 2 Schematic views of the edge-shared W_3O_{13} groups in complex **1**. Symmetry codes II, III, IV and VI indicate $(-x, -y, z)$, $(x, -y, -z)$, $(-x, y, -z)$ and $(\frac{1}{2} - x, \frac{1}{2} - y, z)$, respectively

Table 4 Atomic coordinates for complex **2** with e.s.d.s in parentheses

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
W(1)	−0.1751(2)	0.0281(2)	−0.1458(1)	O(20)	−0.423(3)	0.421(3)	−0.119(1)
W(2)	−0.1317(2)	0.1863(2)	−0.0857(1)	O(21)	−0.465(3)	0.267(3)	−0.183(1)
W(3)	−0.3591(2)	0.2347(2)	−0.1011(1)	O(22)	−0.069(3)	−0.008(3)	−0.347(2)
W(4)	−0.2485(2)	0.0441(2)	−0.3299(1)	O(23)	0.191(3)	0.008(3)	−0.260(1)
W(5)	0.0759(2)	−0.0305(2)	−0.3042(1)	O(24)	0.038(3)	0.341(3)	−0.205(1)
W(6)	0.1303(2)	0.1779(2)	−0.2255(1)	O(25)	−0.316(3)	0.576(3)	−0.144(2)
W(7)	−0.1325(2)	0.4733(2)	−0.1641(1)	O(26)	−0.495(3)	0.465(3)	−0.252(2)
W(8)	−0.4302(2)	0.5373(2)	−0.1858(1)	O(27)	−0.429(3)	0.152(3)	−0.307(2)
W(9)	−0.4917(2)	0.3157(2)	−0.2729(1)	O(28)	−0.256(3)	0.136(3)	−0.422(1)
W(10)	−0.2777(2)	0.3025(2)	−0.4178(1)	O(29)	0.120(3)	0.054(3)	−0.392(2)
W(11)	0.0507(2)	0.2275(2)	−0.3911(1)	O(30)	0.166(3)	0.214(3)	−0.328(2)
W(12)	−0.2153(2)	0.5288(2)	−0.3295(1)	O(31)	−0.137(3)	0.558(4)	−0.253(3)
				O(32)	−0.378(3)	0.613(3)	−0.273(2)
K(1)	0.194(1)	−0.143(2)	−0.1269(7)	O(33)	−0.452(3)	0.357(3)	−0.376(1)
K(2)	−0.501(1)	0.037(2)	−0.170(1)	O(34)	−0.094(3)	0.240(3)	−0.429(1)
K(3)	−0.568(1)	0.641(2)	−0.3829(7)	O(35)	−0.047(3)	0.393(3)	−0.365(2)
K(4)	−0.396(1)	0.865(1)	−0.4495(6)	O(36)	−0.288(3)	0.451(3)	−0.387(1)
K(5)	−0.014(2)	0.262(2)	−0.5837(7)	O(37)	−0.201(2)	0.204(3)	−0.182(1)
				O(38)	−0.260(3)	0.241(3)	−0.303(2)
O(1)	−0.141(3)	−0.158(4)	−0.129(2)	O(39)	−0.039(3)	0.186(3)	−0.283(1)
O(2)	−0.041(3)	0.190(3)	0.004(1)	O(40)	−0.223(3)	0.393(3)	−0.243(1)
O(3)	−0.534(3)	0.281(4)	−0.025(2)				
O(4)	−0.249(3)	−0.092(3)	−0.358(2)	O(41)	0.380(5)	−0.092(5)	−0.091(2)
O(5)	0.172(3)	−0.180(3)	−0.325(2)	O(42)	−0.655(4)	0.139(4)	−0.014(2)
O(6)	0.269(3)	0.160(3)	−0.198(2)	O(43)	−0.682(3)	0.518(4)	−0.030(2)
O(7)	−0.095(3)	0.562(3)	−0.113(2)	O(44)	0.093(4)	0.323(4)	−0.012(2)
O(8)	−0.573(3)	0.666(4)	−0.154(2)	O(45)	0.199(4)	0.433(5)	−0.120(2)
O(9)	−0.655(3)	0.367(3)	−0.272(2)	O(46)	−0.303(4)	−0.199(5)	−0.188(2)
O(10)	−0.291(3)	0.335(4)	−0.507(2)	O(47)	0.109(4)	−0.318(4)	−0.172(2)
O(11)	0.135(3)	0.242(4)	−0.470(2)	O(48)	0.115(5)	0.553(6)	−0.304(3)
O(12)	−0.216(3)	0.643(3)	−0.388(1)	O(49)	0.463(5)	−0.134(5)	−0.306(3)
O(13)	−0.080(3)	0.011(3)	−0.066(2)	O(50)	0.417(3)	0.127(4)	−0.404(2)
O(14)	−0.287(3)	0.241(4)	−0.016(2)	O(51)	0.361(4)	−0.082(4)	−0.471(2)
O(15)	−0.343(3)	0.066(2)	−0.085(2)	O(52)	0.592(4)	−0.362(5)	−0.502(2)
O(16)	−0.248(3)	0.014(3)	−0.232(2)	O(53)	0.115(4)	0.502(4)	−0.467(2)
O(17)	−0.007(3)	−0.045(3)	−0.212(1)	O(54)	1.0	0	−0.5
O(18)	0.045(3)	0.143(3)	−0.143(2)				
O(19)	−0.142(3)	0.358(3)	−0.098(1)	B	−0.172(6)	0.273(3)	−0.270(3)

Table 5 Selected bond distances (Å) and angles (°) for complex **2**

W(1)–O(1)	2.11(4)	W(2)–O(2)	2.16(3)	W(6)–O(6)	1.71(3)	W(7)–O(7)	1.72(3)
W(1)–O(13)	1.96(3)	W(2)–O(13)	1.95(4)	W(6)–O(18)	1.83(3)	W(7)–O(19)	1.84(3)
W(1)–O(15)	1.99(3)	W(2)–O(14)	1.94(3)	W(6)–O(23)	1.96(3)	W(7)–O(24)	1.99(3)
W(1)–O(16)	2.01(3)	W(2)–O(18)	2.04(3)	W(6)–O(24)	1.80(3)	W(7)–O(25)	1.94(3)
W(1)–O(17)	2.01(2)	W(2)–O(19)	2.02(3)	W(6)–O(30)	1.97(3)	W(7)–O(31)	1.90(4)
W(1)–O(37)	2.09(3)	W(2)–O(37)	2.06(3)	W(6)–O(39)	2.38(3)	W(7)–O(40)	2.42(3)
W(12)–O(12)	1.71(3)	W(12)–O(35)	1.97(3)	B–O(37)	1.85(8)	B–O(39)	1.44(7)
W(12)–O(31)	1.96(3)	W(12)–O(36)	1.99(3)	B–O(38)	1.49(7)	B–O(40)	1.39(7)
W(12)–O(32)	1.88(3)	W(12)–O(40)	2.26(3)				
O(1)–W(1)–O(13)	88(1)	O(37)–W(1)–O(13)	100(1)	O(4)–W(4)–O(16)	100(2)	O(38)–W(4)–O(16)	86(1)
O(1)–W(1)–O(15)	84(1)	O(37)–W(1)–O(15)	102(1)	O(4)–W(4)–O(22)	99(1)	O(38)–W(4)–O(22)	84(1)
O(1)–W(1)–O(16)	84(1)	O(37)–W(1)–O(16)	88(1)	O(4)–W(4)–O(27)	102(1)	O(38)–W(4)–O(27)	75(1)
O(1)–W(1)–O(17)	85(1)	O(37)–W(1)–O(17)	89(1)	O(4)–W(4)–O(28)	101(1)	O(38)–W(4)–O(28)	72(1)
O(1)–W(1)–O(37)	170(1)	O(39)–W(6)–O(18)	85(1)	O(4)–W(4)–O(38)	173(1)	O(38)–W(10)–O(28)	77(1)
O(6)–W(6)–O(18)	102(2)	O(39)–W(6)–O(23)	76(1)	O(10)–W(10)–O(28)	97(1)	O(38)–W(10)–O(33)	78(1)
O(6)–W(6)–O(23)	98(1)	O(39)–W(6)–O(24)	89(1)	O(10)–W(10)–O(33)	101(1)	O(38)–W(10)–O(34)	84(1)
O(6)–W(6)–O(24)	98(1)	O(39)–W(6)–O(30)	72(1)	O(10)–W(10)–O(34)	96(1)	O(38)–W(10)–O(36)	86(1)
O(6)–W(6)–O(30)	99(1)	O(14)–W(2)–W(1)	94.2(9)	O(10)–W(10)–O(36)	99(2)	O(37)–B–O(38)	94(4)
O(6)–W(6)–O(39)	170(1)	O(14)–W(2)–W(3)	50(1)	O(10)–W(10)–O(38)	174(1)	O(37)–B–O(39)	93(5)
O(13)–W(1)–W(2)	49(1)	O(14)–W(3)–W(1)	94(1)	O(15)–W(1)–W(2)	96.4(9)	O(37)–B–O(40)	95(3)
O(13)–W(1)–W(3)	94.6(9)	O(14)–W(3)–W(2)	49.0(9)	O(15)–W(1)–W(3)	50(1)	O(38)–B–O(39)	115(4)
O(13)–W(2)–W(1)	49.5(9)			O(15)–W(3)–W(1)	50.5(9)	O(38)–B–O(40)	116(5)
O(13)–W(2)–W(3)	94.8(9)			O(15)–W(3)–W(2)	97(1)	O(39)–B–O(40)	127(5)

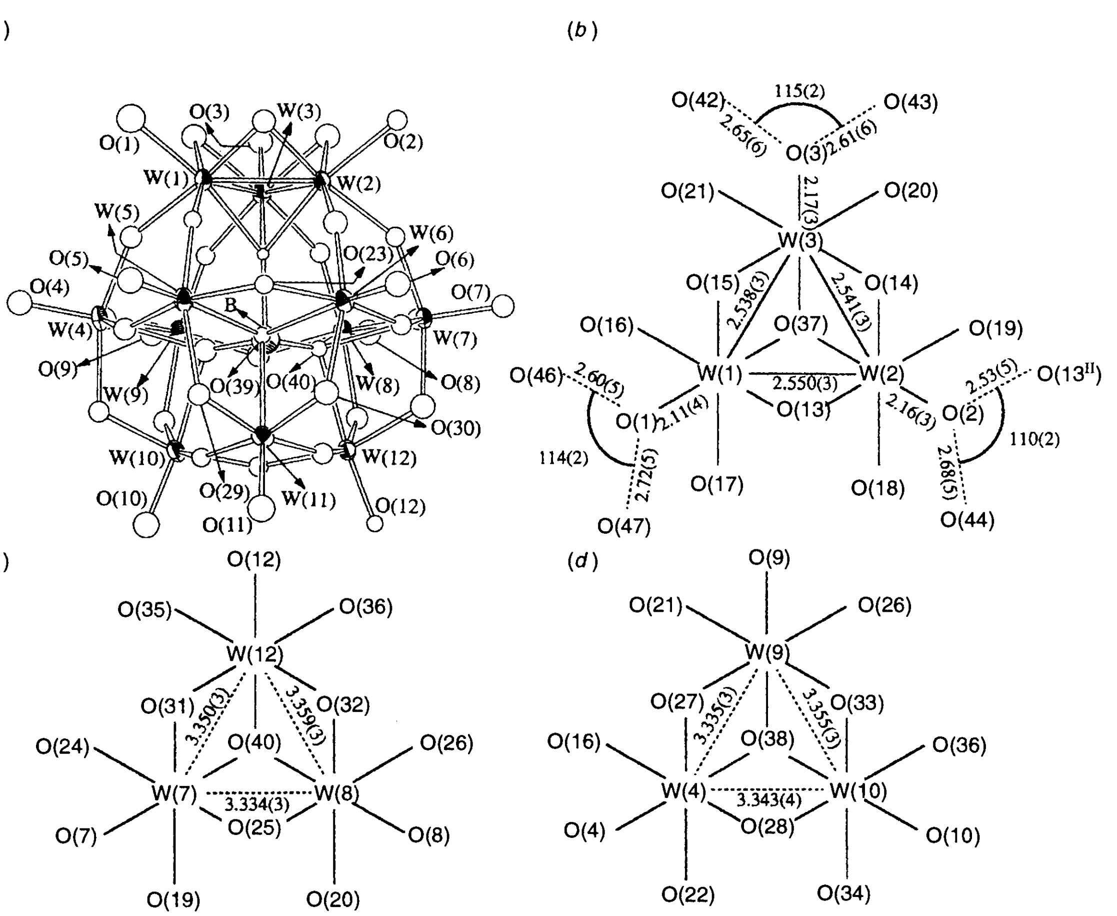

Fig. 3 Schematic representation (*a*) of the structure of the $[BW_{12}O_{37}(H_2O)_3]^{5-}$ anion with atom labelling and views (*b*)–(*d*) of the edge-shared W_3O_{13} groups for complex **2**

1.69(3)–1.70(4) Å [average 1.71(3) Å] reflect the presence of strong W=O π bonds and the W–O(μ_4) bond *trans* to W=O bond is long [2.24(3)–2.27(3), average 2.26(3) Å]. In type 2 sites the former is 1.67(3)–1.76(3) [average 1.73(3)] and the latter 2.36(3)–2.44(3) [average 2.40(3) Å]. By contrast, in type 1 sites the bond lengths [2.11(4)–2.17(3), average 2.15(4) Å] between tungsten and terminal aqua oxygen atoms are lengthened and the W–O(μ_4) bond *trans* to the tungsten–terminal aqua oxygen bond is shortened [2.06(3)–2.11(2), average 2.09(3) Å]. The approximately symmetric feature of the W–O (aqua) and W–O(μ_4) bond lengths at the $W^{IV}O_6$ site leads to the O(aqua)–W–O(μ) bond angles [81(1)–88(1)°] being close to 90° due to the electrostatic repulsive interaction of the equatorial μ-O atoms with two axial O atoms, as indicated by approximately equidistant separations [2.71(5)–2.94(4) and 2.84(4)–3.17(4) Å] of the μ-O atoms from terminal O and μ_4-O atoms. On the other hand, as also indicated for **1**, the asymmetric bond lengths for the W–O(terminal) and W–O(μ_4) bonds at any $W^{VI}O_6$ in type 2 and 3 sites are reflected by the O(terminal)–W–O(μ) bond angles [95(1)–105(1)°] of about 100°, resulting in approximately equidistant separations [2.65(5)–2.92(4) and 2.55(5)–2.96(4) Å] of μ-O atoms from the axial terminal O and μ_4-O atoms, respectively. The tungsten–aqua oxygen bond strengths are 0.45(4)–0.55(6) for O(1–3), while the W=O bond strengths are 1.6(2)–2.2(3) for O(4–12). These imply a considerable negative charge on the aqua O atoms if they are not protonated. Since the bond orders of atoms O(1–3) are close to the value (0.2 × 2 = 0.4) predicted for the three-co-ordinate water O atom in the crystal,[16] two protons can be located with a high degree of confidence on each of these atoms. The separations O(1) ··· O(46), O(1) ··· O(47), O(2) ··· O(44), O(2) ··· O(13^{II}), O(3) ··· O(42) and O(3) ··· O(43) (symmetry code II: $-x$, $-y$, $-z$) of 2.60(5), 2.72(5), 2.68(5), 2.53(5), 2.65(6) and 2.61(6) Å respectively are in the range of O ··· O distances (2.5–2.8 Å) for hydrogen-bonded water molecules.[17] The O(46)–O(1)–O(47), O(44)–O(2)–O(13^{II}) and O(42)–O(3)–O(43) angles are 114(2), 110(2) and 115(2)° which are close to the H–O–H bond angle (118.7°) of the lattice water.[18] Such a structural environment of atoms O(1–3) reveals that each of the aqua ligands is bound either to lattice water oxygen or neighbouring anion oxygen by hydrogen bonding [Fig. 3(*b*)].

If a maximum K ··· O distance of 3.2 Å is assumed, K ··· O distances for the potassium–oxygen polyhedra are 2.58(4)–3.21(3) Å. The K^+ cations occupy positions between the anions in irregular seven- to nine-co-ordination with oxygen: the co-ordination to K(1) and K(4) is nine-fold, eight-fold to K(2) and K(5), and seven-fold to K(3). Cations and water molecules serve to bind the anions together by a complex system of ionic and hydrogen bonds. Of the fourteen lattice water O atoms, O(54) showed a large displacement parameter. Therefore, its site occupancy was fixed at 0.5 and refined until it converged.

Structural comparison between complexes 1 and 2

Fig. 4 compares simplified tungsten-atom frameworks of complexes **1** and **2**. The framework consists of three parallel planes, one central hexagonal plane (with neighbouring W–W–W angles of almost 120°) and two different-sized trianglular planes (neighbouring W–W–W angles almost 60°) above and below at approximately equal distances of about 2.8 Å. The B atom at the centre of the hexagonal plane is located at a mean distance of 0.1(1) Å from this plane toward the large-sized triangle plane for **1**. In **2** it is more distantly located, 0.4(1) Å. toward the large-sized W(10–12) triangle plane. In **2** the edge-sharing octahedra within type 1 sites show short W ··· W distances [2.538(3)–2.550(2), average 2.543(3) Å], within type 2 sites intermediate distances [3.334(3)–3.336(3), average 3.335(3) Å], and between type 2 and 3 sites long distances [3.341(3)–3.359(3), average 3.348(3) Å]. The short W^{IV} ··· W^{IV} distances in type 1 sites reveal the formation of the W–W bonding in the $W^{IV}{}_3O_{13}$ group, as such bond lengths for W_3 clusters with six-electron configurations, in which the co-ordination shell of each W atom is an octahedron, are in the range 2.514–2.609 Å.[19] A similar distance [2.50(2) Å] was reported for Rb_4H_8-$[H_2W_{12}O_{40}]\cdot{\approx}18H_2O$.[5] The W^{VI} ··· W^{VI} distances in the $W^{VI}{}_3O_{13}$ group in **2** are 0.010(3)–0.055(3) Å longer than the 3.304(3)–3.324(3) Å [average 3.313(3) Å] in **1**.

In complex **2** the W ··· W distances for the corner-sharing octahedra within type 2 and 3 sites are 3.606(3)–3.630(3) [average 3.618(3) Å] and 3.673(3)–3.679(3) Å [average 3.676(3) Å], respectively. The W ··· W distances between type 1 and 2 sites are 3.675(3)–3.706(3) Å [average 3.686(3) Å]. Thus, any W ··· W distances between types 1 and 2 and within type 3 for the corner-sharing octahedra in **2** are 0.014(3)–0.073(3) Å longer than the 3.633(3)–3.659(3) Å [average 3.645(3) Å] in **1**, while the W ··· W distances within type 2 are 0.003(3)–0.053(3) Å shorter.

With the assumption that each $W^{VI}O_6$ octahedron has approximately C_{4v} symmetry with the z axis defined by the W=O(terminal) bond, the unpaired electron induced by one-electron reduction occupies a d_{xy} orbital with an accompanying protonation of the terminal oxygen atom. This protonation results in elongation of the W–O(terminal) bond due to the breaking of the W=O π bond. In the $W^{IV}{}_3O_{13}$ group in **2**, the bond angles O(13)–W(1)–W(2), O(13)–W(2)–W(1), O(14)–W(2)–W(3), O(14)–W(3)–W(2), O(15)–W(1)–W(3) and O(15)–W(3)–W(1) [49.0(9)–50.5(9)°] are close to 45°, while O(13)–W(1)–W(3), O(13)–W(2)–W(3), O(14)–W(2)–W(1), O(14)–W(3)–W(1), O(15)–W(3)–W(2) and O(15)–W(1)–W(2) lie in the range 94.2(9)–97.0° (Table 5). Such a structural feature of the $W^{IV}{}_3$ triad reveals that the six electrons for the W^{IV}–W^{IV} bonding will occupy both d_{xz} and d_{yz} orbitals which would

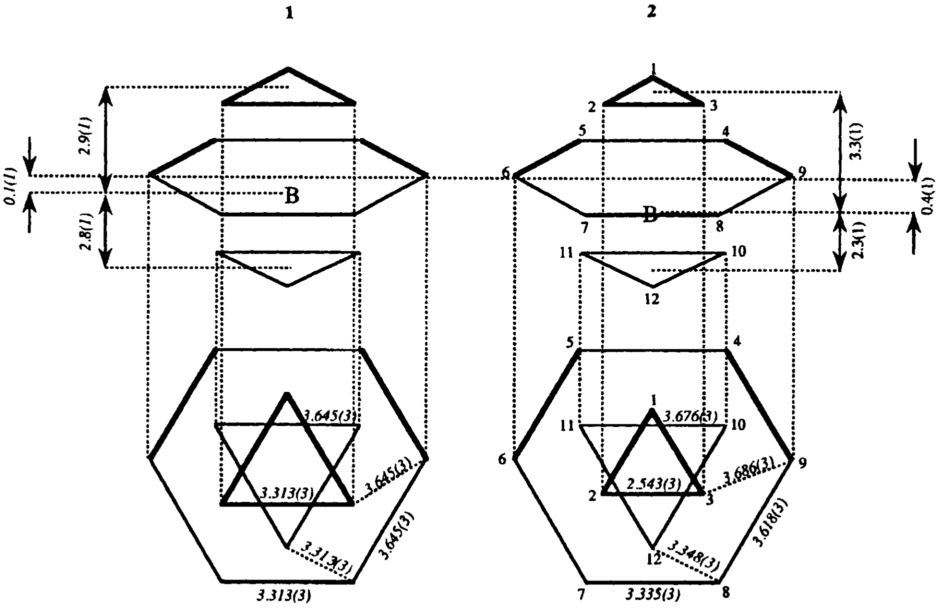

Fig. 4 Tungsten frameworks of the anions in complexes **1** and **2**. Numbers at vertices indicate W atoms, thick lines imply that the WO_6 octahedra share edges, and thin lines that they share corners. Italic distances (Å) indicate mean values

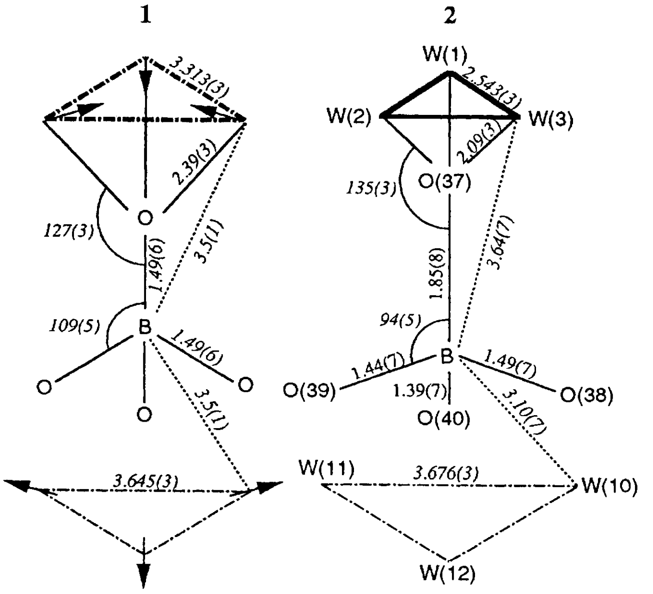

Fig. 5 Environments of the central BO_4 tetrahedra for complexes **1** and **2**. Numbers in italics for distances (Å) and bond angles (°) are mean values. The upper and lower triangles indicate the edge- and corner-shared W_3 triads, respectively

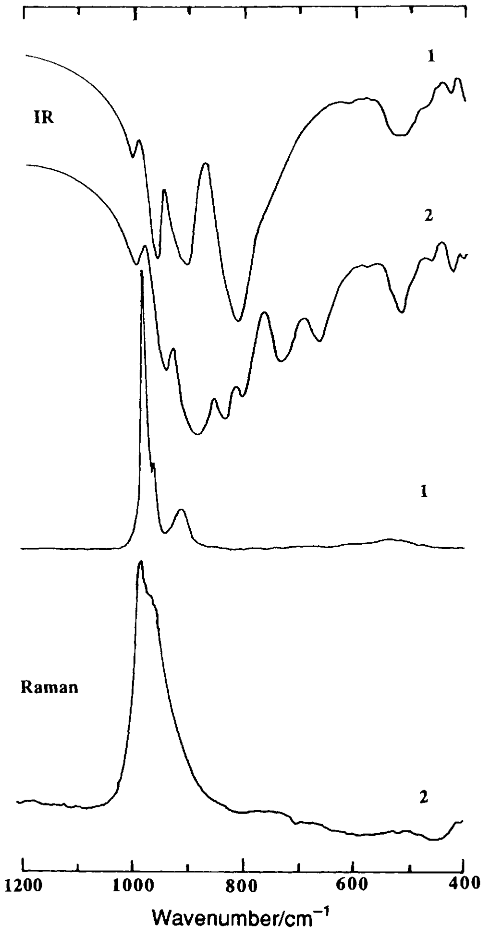

Fig. 6 Selected regions of the IR and Raman spectra of complexes **1** and **2**

constitute the bonding molecular orbitals, probably with the ground-state electronic configuration of $(1a_1)^2(1e)^4$ according to simplified molecular orbital calculations.[19] Thus, it is understandable that this triad should be diamagnetic. The six-electron reduction with simultaneous protonation of the terminal oxo atoms (to give aqua ligands) leads to lengthening of the distances between W(1–3) and the aqua oxygen atoms, resulting in approximately symmetric bond lengths for W^{IV}–O (aqua) and W^{IV}–O(μ_4). The mean distance of 5.7(1) Å between the two triangular planes is not significantly altered upon six-electron reduction [5.6(1) Å], while the B–O(μ_4) distance [1.85(8) Å] associated with the $W^{IV}{}_3O_{13}$ group is longer than the mean distance [1.49(6) Å] in **1**. Fig. 5 shows the change in the environment of the central BO_4 tetrahedron upon six-electron reduction. The mean B–O bond length [1.49(6)Å] and the mean O–B–O bond angle [109(5)°] in **1** change to 1.85(8) Å and 93(5)–95(3)° with an average of 94(5)° in **2**. It should be noted that the B $\cdots$ W(1–3) distances are slightly longer for **2** [3.59(7)–3.68(8), average 3.64(8) Å], the B $\cdots$ W^{VI} distances in **1a** and **1b** being 3.473(2)–3.488(2) [average 3.482(3) Å] and 3.4(1)–3.6(1) Å [average 3.5(1) Å], respectively. In **2** the B $\cdots$ W^{VI} distances are 3.45(6)–3.58(6) Å [average 3.51(7) Å] for the W(4–9) hexagon and 3.05(6)–3.17(7) Å [average 3.10(7) Å] for the W(10–12) triangle. Thus, the formation of the W^{IV}–W^{IV} bonds with an accompanying elongation [0.016(3)–0.073(3) Å] in the corner-shared $W^{IV} \cdots W^{VI}$ distances between types 1 and 2 forces the B $\cdots$ W^{VI} distances for W(10–12) in type 3 sites to be shortened with a resultant lengthening [0.014(3)–0.046(3) Å] of the W $\cdots$ W distances in these sites, as implied by a short distance [2.3(1) Å] between B and the W(10–12) triangle plane (Fig. 4). The contraction [0.754(3)–0.786(3) Å] of the W $\cdots$ W distances due to the W^{IV}–W^{IV} bond formation in the $W^{IV}{}_3$ triad (with a slight lengthening of B $\cdots$ W^{IV} distances) is concerted, pushing B down ($\approx$0.4 Å) toward the corner-shared $W^{VI}{}_3$ triad in which the expansion ($\approx$0.03 Å) in the W $\cdots$ W distances occurs with shortening ($\approx$0.4 Å) of the B $\cdots$ W^{VI} distances. This feature is reflected in both a lengthening ($\approx$0.4 Å) of the B(1)–O(37) bond and a decrease ($\approx$15°) in the O(37)–B(1)–O(38–40) bond angles upon six-electron reduction.

The difference in the molecular structure between complexes **1** and **2** is also reflected in the IR and Raman spectra, as shown in Fig. 6. A systematic vibrational study of the oxidized α-Keggin structural complexes has indicated that 980 (Raman), 961 (Raman) and 959 (IR), 912 (Raman) and 910 (IR), and 812 cm^{-1} (IR) can be assigned to ν_{sym}(W=O), ν_{asym}(W=O), mixing of ν_{asym}(B–O) with W–O(μ)–W corner stretching and W–O(μ)–W edge stretching modes, respectively.[20,21] The formation of W^{IV}–W^{IV} bonds in the C_{3v}-symmetrical $W^{IV}{}_3O_{13}$ group in the anion causes the two broad peaks centred at about 910 and 810 cm^{-1} to split into several lines. The peak around 960 cm^{-1} remains unchanged. The change in the vibrational patterns is consistent with the fact that the six-electron reduction of **1** induces a significant change in both B–O and W $\cdots$ W distances, as mentioned above. It may be noted that the IR spectrum of **2** is similar to that of lacunary derivatives of **1**, such as $[BW_{11}O_{39}]^{9-}$ and $[BW_{11}O_{39}Co(H_2O)]^{6-}$ [22]

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References

1 J. P. Launay, *J. Inorg. Nucl. Chem.*, 1976, **38**, 807; L. P. Kazansky and J. P. Launay, *Chem. Phys. Lett.*, 1977, **51**, 242.
2 J. M. Fruchart and G. Hervé, *Ann. Chim. (Paris)*, 1971, **6**, 337.
3 T. Yamase and R. Watanabe, *J. Chem. Soc., Dalton Trans.*, 1986, 1669.
4 K. Piepgrass and M. T. Pope, *J. Am. Chem. Soc.*, 1987, **109**, 1586; 1989, **111**, 753.
5 Y. Jeannin, J. P. Launay and M. A. Seid Sedjadi, *Inorg. Chem.*, 1980, **19**, 2933.
6 T. Yamase and T. Usami, *J. Chem. Soc., Dalton Trans.*, 1988, 183.
7 G. Hervé and A. Tezé, *Inorg. Chem.*, 1977, **16**, 2115.

8 C. R. Deltcheff, M. Fournier, R. Franck and R. Thouvenot, *Inorg. Chem.*, 1983, **22**, 207.

9 G. J. Gilmore, *J. Appl. Crystallogr.*, 1984, **42**, 46.

10 H.-F. Fan, SAPI 91, Structure Analysis Programs with Intelligent Control, Rigaku Corporation, Tokyo, 1991.

11 N. Walker and D. Stuart, *Acta Crystallogr., Sect. A*, 1983, **158**, 3.

12 A. C. T. North, D. C. Phillips and F. S. Mathews, *Acta Crystallogr., Sect. A*, 1968, **24**, 351.

13 TEXSAN, Single-crystal Sructure Analysis Software, Molecular Structure Corporation, The Woodlands, TX, 1989.

14 M. T. Pope, *Heteropoly and Isopoly Oxometalates*, Springer, New York, 1983.

15 I. D. Brown and K. K. Wu, *Acta Crystallogr., Sect. B*, 1976, **32**, 1957.

16 I. D. Brown, *Structure and Bonding in Crystals*, eds. M. O'Keeffe and A. Navrotsky, Academic Press, New York, 1981, vol. 2.

17 J. Emsley, *Chem. Soc. Rev.*, 1980, **9**, 91.

18 G. M. Brown, M.-R. Noe-Spirlet, W. R. Busing and H. A. Levy, *Acta Crystallogr., Sect. B*, 1977, **33**, 1038.

19 A. Müller, R. Jostes and F. A. Cotton, *Angew. Chem., Int. Ed. Engl.*, 1980, **19**, 875.

20 R. Thouvenot, M. Fournier, R. Franck and C. R. Deltcheff, *Inorg. Chem.*, 1984, **23**, 598.

21 C. R. Deltcheff, R. Thouvenot and R. Franck, *Spectrochim. Acta, Part A*, 1976, **32**, 587.

22 A. R. Couto, C. N. Trovao, J. Rocha, A. M. V. Cavaleiro and J. D. Pedrosa de Jesus, *J. Chem. Soc., Dalton Trans.*, 1994, 2585.

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