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FULL PAPER

Polyoxometalates from heteropoly "brown" precursors. A new structural class of mixed valence heteropolytungstates, $[(XO_4)W^{IV}{}_3W^{VI}{}_{17}O_{62}H_x]^{n-}$

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Reduction of the α-Keggin anion $[X^{n+}O_4W_{12}O_{36}]^{[8-n]-}$ ($X = H_2{}^{2+}$, B^{3+}, Si^{4+}) by six electrons results in the known tungsten "brown" species $[X^{n+}O_4(H_2O)_3W^{IV}{}_3W^{VI}{}_9O_{33}]^{[8-n]-}$ in which three W atoms have been reduced from W^{VI} to W^{IV}, forming a metal–metal bonded triad. The W^{IV} atoms have terminal water coordinated in place of terminal oxo groups. Additional tungstate can condense onto these water molecules in aqueous solution between pH = 4 and 6.5 to form the species reported here, $[(XO_4)W^{IV}{}_3W^{VI}{}_{17}O_{62}H_x]^{y-}$. The boron derivative ($X = B^{3+}$) is more stable than the metatungstate ($X = H_2{}^{2+}$), both of which have been characterized by elemental analysis, ^{183}W NMR and X-ray crystal structure analysis. Eight additional tungstate groups condense in the form of a partial Keggin structure containing two triads and one dyad which is rotated 60° relative to a hypothetical α-isomer.

The extensive redox chemistry of polyoxoanions of vanadium, molybdenum, and tungsten[1] contributes to the applications of such complexes in oxidation- and photochemically-induced catalysis,[2] and in analytical ("molybdenum blue") procedures, and provides an unprecedentedly rich range of mixed valence species with magnetic and electrical properties that have potential for incorporation into novel materials.[3] Reduction of appropriate polytungstates leads to two types of mixed valence anions, the heteropoly "blues" (Robin–Day[4] class II, $W^{V,VI}$), and "browns" (class I, $W^{IV,VI}$). The latter complexes, first recognized by Launay,[5] were proposed to incorporate groups of three edge-shared $W^{IV}O_6$ octahedra. A crystal structure of the rubidium salt of the metatungstate-derived brown, α-$[H_2W^{IV}{}_3W^{VI}{}_9O_{37}(OH_2)_3]^{6-}$, revealed a Keggin anion with metal-atom disorder,[6] although subsequent W-NMR investigation[7] confirmed Launay's structure proposal. Some years ago we attempted to generate the corresponding reduced β isomer of metatungstate ("tungstate-X") in the hope of yielding a non-disordered anion. The targeted synthesis was unsuccessful, but crystals of a new reduced anion were produced in small quantity and the structure solved.[8] Based upon this structure, described below, a rational synthesis of the new anion, starting from α-$[H_2W_{12}O_{40}]^{6-}$, has been devised. We report here that analogous structures can be derived from reduced α-$[BW_{12}O_{40}]^{5-}$ and (probably) α-$[SiW_{12}O_{40}]^{4-}$. The new complexes are hydrolytically stable in aqueous solution according to W-NMR.

Experimental

General

NMR spectra were recorded on a Bruker AM-300 WB spectrometer at 12.505 MHz for ^{183}W using a 20-mm tube. The W^{VI} and W^{IV} regions were scanned separately to minimize acoustic ringing and optimize resolution. About 80,000 scans were taken for each region. Chemical shifts are given relative to saturated Na_2WO_4 solution. Proton chemical shifts are reported relative to sodium 3-(trimethylsilyl)-1-propane sulfonate (TSS). Elemental analyses were performed by Oneida Research Services, Inc., Whitesboro, NY, USA.

Preparations

Crystals of $NaK_{11}[H_6W_{20}O_{66}]\cdot 24H_2O$ (**1**) were isolated adventitiously from a solution that was believed to contain "tungstate-X" (β-$[H_2W_{12}O_{40}]^{6-}$) that had been reduced electrolytically to a "brown" stage. The structure of the anion, revealed by X-ray analysis (see below) led to the following more rational and reproducible syntheses.

$Na_{12}[H_6W_{20}O_{66}]\cdot 24H_2O$ (2). A solution of brown $Na_6H_6[H_2W_{12}O_{40}]$ was prepared by the method of Jeannin *et al.*:[6] 8.0 g (24 mmol) of sodium metatungstate[9] dissolved in 80 mL 0.5 M HCl was electrolytically reduced, by six equivalents per mole, at −0.56 V on a mercury-pool electrode. After allowing the solution to stand for several days followed by membrane filtration to remove any insoluble material, the solution was adjusted to pH 4 by addition of 1 M NaOH drop-wise, with stirring. A second solution of 6.0 g (18 mmol) $Na_2WO_4\cdot 2H_2O$ in 40 mL water was adjusted to pH 6 by slow addition of 0.5 M HCl, with stirring. The two solutions were mixed to produce a yellow-brown solution with a final pH of about 5. The mixture was stirred for several hours. An approximately equal volume of 95% ethanol was then added to precipitate the product. The light brown crystalline solid was filtered off, washed with successive portions of 50% and 95% ethanol to yield the crystalline product; yield 8 g (60%). Recrystallization was accomplished by dissolving the material in 200–300 mL water with stirring, followed by reprecipitation with 200–300 mL 95% ethanol, with filtration and washing as before. Calc. for $Na_{12}[H_6W_{20}O_{66}]\cdot 24H_2O$: Na, 5.06. W, 67.50; Found: Na, 5.05; W 67.67%. ^{183}W NMR spectrum, ppm(intensity): δ 1777.4(1), 1510.2(2), 2.0(2), −77.4(1), −84.1(2), −106.7(2), −124.9(2), −127.7(2), −133.0(2), −148.7(2), −212.2(2).

$NaK_{10}H[H_6W_{20}O_{66}]\cdot 18H_2O$ (3). Dark brown crystals of the

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Table 1 Crystal data for **1**, **3** and **6**

	1	**3**	**6**
Formula	$NaK_{11}[H_6W_{20}O_{66}]\cdot24H_2O$	$NaK_{10}H[H_6W_{20}O_{66}]\cdot18H_2O$	$K_2Rb_9[H_4BW_{20}O_{66}]\cdot12H_2O$
Formula weight	5624.44	5472.26	5811.39
T/K	293(2)	173(2)	173(2)
Space group	Triclinic, $P\bar{1}$	Triclinic, $P\bar{1}$	Monoclinic, $P2_1/m$
a/Å	24.34(2)	12.2390(3)	11.5008(1)
b/Å	12.49(2)	18.0490(4)	21.4528(1)
c/Å	17.33(2)	20.5090(5)	16.9776(2)
α/°	82.57(7)	66.833(1)	
β/°	101.15(7)	85.364(1)	104.903(1)
γ/°	122.96(9)	76.265(1)	
V/Å^3	4336(6)	4045.6(2)	4047.89(6)
Z	2	2	2
μ/mm^{-1}	25.8	28.9	33.9
Reflections collected	22661	43951	33793
Independent reflections	19975 ($R_{int} = 0.049$)	18738 ($R_{int} = 0.134$)	10021 ($R_{int} = 0.103$)
Final R [$I > 2\sigma(I)$]	$R_1 = 8.6$, $R_w = 4.8$	$R_1 = 7.5$, $R_w = 17.4$	$R_1 = 5.5$, $R_w = 14.3$

mixed salt suitable for X-ray analysis were obtained from a solution of the sodium salt by addition of aqueous 0.25 M KCl solution and allowing the resulting mixture to stand for about one day at room temperature.

Salts of $[H_4BW_{20}O_{66}]^{5-}$. A solution[10] of $K_5[BW_{12}O_{40}]$ was converted to the sodium salt by ion exchange and then the above procedure for **2** was followed to produce a red-brown solution of $Na_{11}[H_4BW_{20}O_{66}]$ (**4**). The potassium salt $K_{11}[H_4BW_{20}O_{66}]\cdot20H_2O$ (**5**) was obtained by addition of aqueous KCl to a solution of the sodium salt. Calc. for **5**, $K_{11}[H_4BW_{20}O_{66}]\cdot20H_2O$: K, 7.76; B, 0.20; W, 66.36. Found: K, 7.50; B, 0.14; W, 66.87%. ^{183}W NMR spectrum of **4**, ppm(intensity): δ 1856.8(1), 1541.6(2), −3.6(2), −106.7(1), −109.0(2), −115.4(2), −127.8(2), −132.4(2), −137.6(2), −153.3(2), −209.7(2). Crystals of the mixed potassium–rubidium salt (**6**) suitable for X-ray analysis were grown by addition of dilute aqueous RbCl solution to an aqueous solution of the potassium salt.

X-Ray crystallography

The first structure analysis was performed on a crystal of **1**. Data were collected on a modified Picker automatic diffractometer using Nb filtered Mo-Kα radiation ($\lambda = 0.7107$ Å). Reflections within one-half of the reciprocal lattice sphere within $2\theta = 40°$ were collected and corrected for absorption by the Gaussian quadrature method. Data for **3** and **6** were collected on a Siemens SMART CCD diffractometer. An approximate sphere (97% complete to $\theta = 28°$) was collected. Crystal stability was monitored by re-collection of the first fifty frames after data collection was complete; no decay was found. A semi-empirical absorption correction was applied for each, based on measurement of equivalent reflections.[11]

Except in the early stages, all calculations for **1** were executed using XTAL4[12] on a SUN 4/110 workstation. Calculations for **3** and **6** were carried out with SHELX on the Siemens system.[13] Refinements for **3** and **6** were full-matrix least-squares on F^2 over all data. An extinction correction $(4.7(2) \times 10^{-4})$ was applied to **3**. Oxygen and sodium atoms were refined isotropically in all structures. H atoms were not included in the models. Additional crystal data for **1**, **3** and **6** are given in Table 1.

CCDC reference number 186/1740.

See http://www.rsc.org/suppdata/dt/a9/a905539h/ for crystallographic files in .cif format.

Results and discussion

Synthesis and characterization

The title anion is readily synthesized by addition of acidified Na_2WO_4 solution to an aqueous solution of the reduced complex $Na_6H_6[XO_4W^{IV}_3W^{VI}_9O_{36}]$, X = H_2, B. The resulting sodium salts are very soluble in water and stable in aqueous solution between approximately pH 3.5 and 6.5. Attempts to make the analogous Si-substituted compound resulted in a color change to red-brown characteristic of formation of the W_{20} species. However the resulting solutions were much more air-sensitive than those derived from metatungstate or borotungstate and this compound was not pursued further.

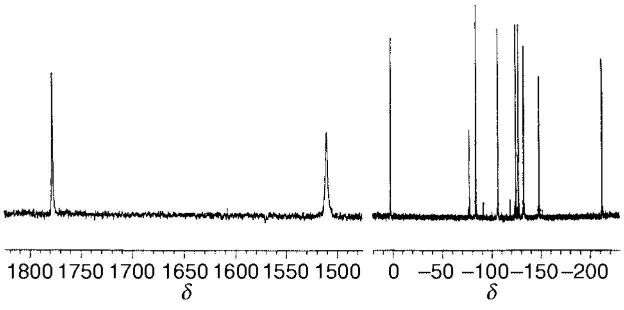

Fig. 1 ^{183}W NMR spectrum of **3**. The spectrum contains eleven lines; a small amount of impurity is evident.

Proton NMR spectroscopy of **2** shows a singlet at δ 7.8 (presumed to be associated with internal H atoms in the Keggin core), to be compared with δ 7.2 for the unreduced $[H_2W_{12}O_{40}]^{6-}$ ion. The ^{183}W NMR spectra of **2** and **4** show eleven peaks: two in the W^{IV} region (intensity ratio 1 : 2), and nine in the W^{VI} region (intensity ratios 2 : 1 : 2 : 2 : 2 : 2 : 2 : 2 : 2) (Fig. 1). This is consistent with the polytungstate structure found (Figs. 2–5) in the mixed salts, in which the molecule has a mirror plane passing through one W^{VI} atom and one W^{IV} atom. Although some W–W couplings are visible in the spectra, most are presumably hidden under other peaks, which are wide (15 Hz or greater) relative to the expected W–W coupling constant values. In the following paragraphs, the structures of **1** and **3** will be compared and discussed and then the structure of **6** will be discussed.

Tungsten valences and protonation. The independent structural determinations of the anions of **1** and **3** are generally in good agreement. The tungsten–tungsten distances among the W(10,12) and W(11) atoms are about 1 Å less than usual for W^{VI} (2.5 *vs.* 3.5 Å), indicating that these are the reduced tungsten atoms. Information about W valence can also be obtained from the structure parameters by examination of bond valences as a function of bond distance. The empirical relationship $\Sigma = \exp[(r_o - r)/B]$ (Σ bond valence, r bond length, r_o unit bond length, B an arbitrary constant), provides a useful approximation, according to Brown and Altermatt,[14] who found $r_o = 1.917$ Å for W^{VI} with $B = 0.37$. Fig. 6 shows Σ plotted for 11

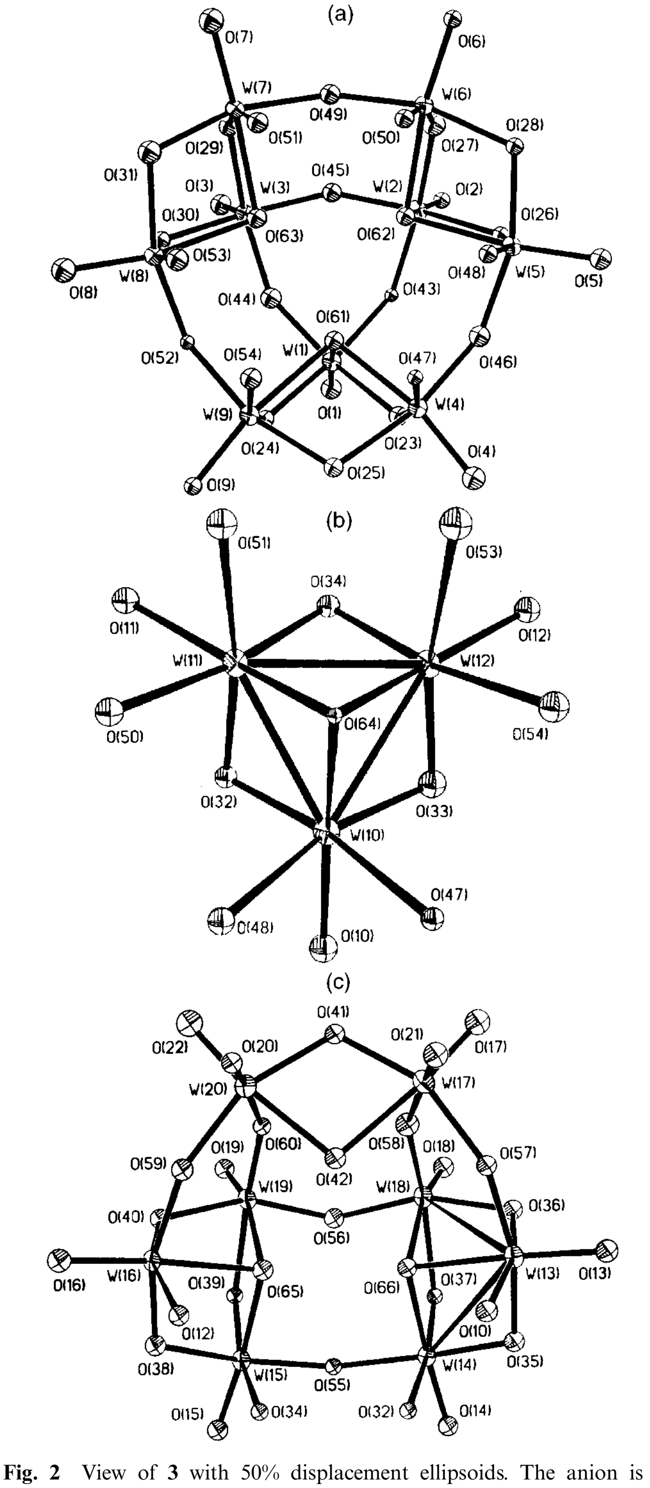

Fig. 2 View of **3** with 50% displacement ellipsoids. The anion is divided into three parts to show the numbering of the oxygen atoms. Part (a) contains the nine W(VI) atoms in the complete Keggin, part (b) the three W(IV) atoms in the middle of the anion, and part (c) the eight W(VI) atoms added in the synthesis.

W atoms averaged from **1** and **3**. The scatter around 6 for 9 W atoms is typical for this type of plot. The values for W(10,12) and W(11) are near 4, and also identify these as the three W^{IV} atoms expected from the electrolysis experiment.

Similar information can be used for the oxygen atoms to find those sufficiently deficient in valency to assign H atoms. The Σ plots for 39 O atoms are also shown in Fig. 6. Again, the scatter around 1.9 is typical for singly and multiply bonded O atoms, but there are striking departures. One, O(11), has a value so low, 0.4, that we may identify this terminal oxygen atom as a water molecule. Six others have values of 1.0 ± 0.25, and are likely carriers of H atoms. Three of these are the central triply bonded oxygen atoms of the W_9O_{31} moiety of the Keggin-like group, which may be compared with the metatungstate molecule $[H_2W_{12}O_{40}]^{6-}$. The disposition of the two H atoms in the center of that molecule is still unknown, but they must be shared in some way with the four oxygen atoms surrounding the central cavity.

In the $W_{20}O_{66}$ molecule [O(61,62,63)] have average valency 1.2, while the fourth, in the $W^{IV}{}_3O_{13}$ group [O(64)] has valence sum 1.8, and is unlikely to be protonated according to this analysis. This is surprising because oxygens bound to W^{IV} should be more basic than those bound to W^{VI}, and ^{183}W NMR results[7] suggested that at least one proton is bound to this oxygen. It should also be noted that the bond valence sums calculated for oxygens bound to W^{IV} have higher errors since we use the W^{VI} parameter to model the W^{IV} bonds (no parameter is available for W^{IV}). Other possible protonation sites are two oxygens [O(65,66)] in the outer W_2O_{10} group of the W_8O_{28} moiety, which have valence sums 1.1. These may each bear a H atom, but the other linking atom O(41) has valence sum 1.5 and is a less likely candidate for OH. Thus we have a probable protonation of the whole molecule of 6: $[H_6W_{20}O_{66}]^{12-}$. The considerable uncertainties of this estimate are apparent ($H_{6\pm1}$).

The cations found in our structures are twelve for **1** and eleven for **3**. The sodium salt **2** was found by chemical analysis to have twelve sodium cations. The remaining charge in **3** may be balanced by a protonated oxygen or water molecule, or possibly an additional unresolved sodium ion. The NMR spectrum showed a single peak representing a single nonlabile type of H atom, which is assumed to correspond to two equivalent atoms associated with O(61–64) in the enclosed W_9O_{31} group. All the other H atoms are exposed to the solution and are therefore labile.

Structure of the polyanion. *Keggin fragment.* The Keggin fragment of the $[H_6W_{20}O_{66}]^{12-}$ polyanion contains nine W^{VI} atoms and three W^{IV} atoms. The metatungstate molecule from which it is derived has been described in a crystal structure determination of $[(CH_3)_4N]_6[H_2W_{12}O_{40}]\cdot 9H_2O$.[15] When metatungstate is reduced by the addition of 6 electrons, they localize in one of the 4 triplet groups, as first suggested by Launay,[5] later confirmed by an incomplete crystal structure analysis,[6] and W-NMR,[7] and finally proved by a full structure analysis of the heteropoly analog compound $K_5[BW_{12}O_{37}(H_2O)_3]\cdot 13.5H_2O$.[16] Table 2 compares average W–O bond lengths of metatungstate, phosphotungstate, and the reduced "brown" complexes. As in the borotungstate complex, in the W_3O_{13} triplet of **1** and **3** the W atoms appear to be strongly attracted to each other, at a distance of 2.54 Å. The bridging oxygen coordination is very regular, with W–O distances of 2.03 ± 0.02 Å.

The reduced triplet group. The $W^{VI}{}_3O_{13}$ unit is one of the main building blocks of extended polyoxotungstate structures. The analogous moiety containing tungsten in lower oxidation states (III–V) is more frequently encountered as a discrete cluster, with ligands containing halogen, nitrogen or sulfur substituting for one or more of the oxygen atoms. The first structural determination of a compound of this type[18] was for $[W_3O_4F_9]^{5-}$. A number of carboxylate derivatives[19] are also known. In these complexes the W–W distances depend strongly on both the nature of the ligands and the oxidation state of the tungsten atoms. Observed W–W distances range from about 2.50 Å for $[W_3O(O_2CCH_3)_5(OCH_3)(H_2O)]^{2+}$ to 2.72 Å in $[W_3OS_3(Hnta)_3]^{2+}$ (H_3nta = nitrilotriacetic acid).[19,20] These discrete trimers are the most closely analogous to the W^{IV} triplet group reported here insofar as each tungsten coordination sphere contains six oxygens. However, the W–W distances in the discrete trimers span a wide range, with an average of 2.70(1) Å in $[W_3O(O_2CCH_3)_6(H_2O)_3]^{2+}$, while the methoxy derivative has two different W–W distances of 2.685(1) Å for carboxylate-bridged W–W bonds and a short methoxy-bridged W–W distance (cited above) of 2.495(1) Å.

Table 2 Comparison of typical bond lengths (Å) with related structures[a]

	$[H_6W_{20}O_{66}]^{12-}$	$[H_2W_{12}O_{40}]^{6-}$	$[H_4BW_{20}O_{66}]^{11-}$	$[BW_{12}O_{37}(H_2O)_3]^{5-}$	$[PW_{12}O_{40}]^{3-}$
W^{VI}–O(a)	1.71	1.71	1.74	1.72	1.704
W^{VI}–O(b)	1.96	1.91	1.94	1.93	1.909
W^{VI}–O(c)	1.90	1.93	1.91	1.89	1.903
W^{VI}–O(d)	2.14	2.21	2.28	2.35	2.435
W^{IV}–O	2.04		2.03	2.04	
Space group	$P\bar{1}$	*Pnma*	$P2_1/m$	$P\bar{1}$	*Pn*3*m*
Ref.	This work	15	This work	16	17

[a] Oxygen types (Evans' notation): O(a) bonded to one W atom (terminal); O(b) bonded to two W atoms within a triplet group; O(c) bonded to two W atoms between two triplet groups; O(d) bonded to three W atoms (enclosing central tetrahedron).

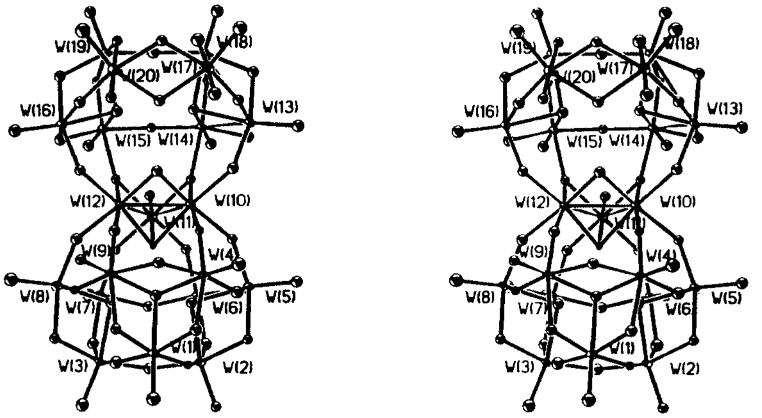

Fig. 3 Stereoview of **3**.

The average W^{IV}–O bond distance in the two determinations of the $[H_6W_{20}O_{66}]^{12-}$ structure is 2.04 Å. The individual W^{IV} environment is more symmetrical than that of W^{VI} in which the tungsten atom is displaced toward the terminal oxygen, away from the center of the Keggin structure. In contrast the W^{IV} atoms are in the center of a more nearly regular octahedron. The range of W^{IV}–O (bridging) distances is 1.98 to 2.08 Å, with a long bond of 2.19 Å to the terminal water molecule, O(11).

The W^{IV}_3 group is attached to the W^{VI}_8 group through four bridging oxygen atoms. Two of these, O(10) and O(12), are oxygens that were coordinated to water molecules in the parent $[H_2W^{IV}_3W^{VI}_9O_{40}]^{12-}$ structure and now bridge one W^{IV} to one W^{VI}. The other two, O(32) and O(34), bridge two edge-sharing W^{IV} atoms in the parent molecule and have now become "external" triply-bridging oxygens in the $[H_6W_{20}O_{66}]^{12-}$ anion, connecting two W^{IV} atoms with one W^{VI} atom. These latter oxygens are nearly coplanar with the tungsten atoms they connect, being slightly displaced toward the outside of the anion. Usually, oxygens which triply bridge tungstens are found on the "inside" of these structures. The existence of external oxygens bridging three W atoms in this structure is presumably due to the decreased charge on W^{IV} and therefore the enhanced basicity of the oxygens connected to W^{IV}.

The octatungstate fragment. The W_8O_{30} fragment, formed from acidified Na_2WO_4 added to the preparative solution, is a unique polytungstate group. Two triplet groups are bonded to four oxygen atoms on the outer surface of the $W^{IV}_3O_{13}$ group of the Keggin fragment, and these are tied together by a further W_2O_8 group extending outward from the main portion of the $[W_{20}O_{66}]$ molecule (Figs. 2–5). Thus, the W_8O_{30} portion can be considered a β-Keggin fragment which is missing one α-triplet and one tungsten from the β triplet. Finally, if W(11) is ignored, the grouping of W(10) and W(12–20) forms a partial γ-Keggin isomer which is missing two WO_6 octahedra, with W(10–12) and W(19,20) representing the two incomplete triplets, both being rotated 60° relative to an α-isomer. The "internal" oxygens of this hypothetical γ-Keggin structure would be O(32), O(42), O(65) and O(66).

The $[H_4BW_{20}O_{66}]^{11-}$ anion. The $[H_4BW_{20}O_{66}]^{11-}$ anion is also readily made, starting from reduced borotungstate instead of metatungstate. It is more stable than the metatungstate derivative, which was found to oxidize, turning colorless, in the solid state in a sealed vial over a period of about six months. A D_2O solution ^1H NMR of the resulting solid showed a peak for metatungstate only. In contrast the solid borotungstate derivative remained brown for over a year under similar conditions.

The reason for the differences in stability is not clear. The order of stability of the browns (and the derived W_{20} species) runs nearly opposite to the ease of adding electrons to the anions. The most easily reduced tungsten Keggin anions are those with less negative charge, *i.e.* those with more positive central atoms. However, attempts to produce a tungsten brown from phosphotungstate have failed, and the brown from silicotungstate is clearly less stable than the borotungstate brown. We speculate that the trend in stability of the browns observed, higher stability with decreasing central atom charge, arises from the requirement in the browns that the W^{IV} triad contracts, due to the metal–metal bonds, and approaches closer to the center of the Keggin anion than the W^{VI} triads. A higher central atom charge would more strongly repel the W^{IV} triad, destabilizing the structure.

The overall pattern of bonds in **6** (Figs. 4, 5) is analogous to **1** and **3**. The W^{IV}–O bond distances in **6** average 2.03 Å and the protonation of the oxygens on the reduced tungstens and in the added W_8O_{30} fragment are like those found in **1** and **3**. A full complement of eleven cations was found for **6**. The main differences from **1** and **3** are that **6** has a crystallographic mirror plane and contains a boron atom. The structural results for the reduced Keggin portion of **6** agree with the results of Yamase and Ishikawa[16] for $BW_{12}(H_2O)_3$ and with the above results for **1** and **3** in that the three W^{IV} atoms form metal–metal bonds, have a more regularly octahedral coordination geometry compared with the W^{VI} atoms, and occupy a position closer to the center of the Keggin unit than the W^{VI} atoms. With regard to the position of the boron atom in the oxidized and reduced borotungstates the situation is less clear. The fully oxidized $[BW_{12}O_{40}]^{5-}$ contains four equal B–O bonds 1.49(6) Å in

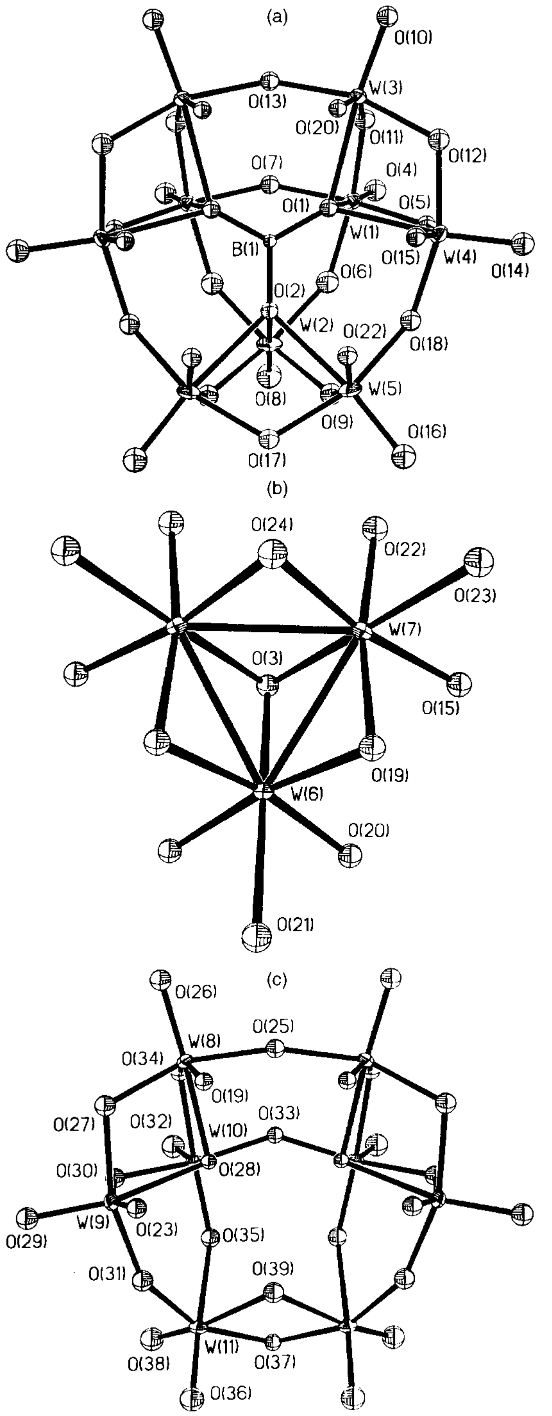

Fig. 4 View of **6** with 50% displacement ellipsoids. The anion is divided into three parts, as in Fig. 2, to show the numbering of the oxygen atoms.

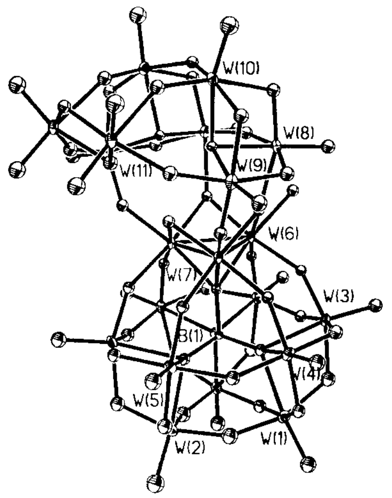

Fig. 5 A view of the complete anion of **6**.

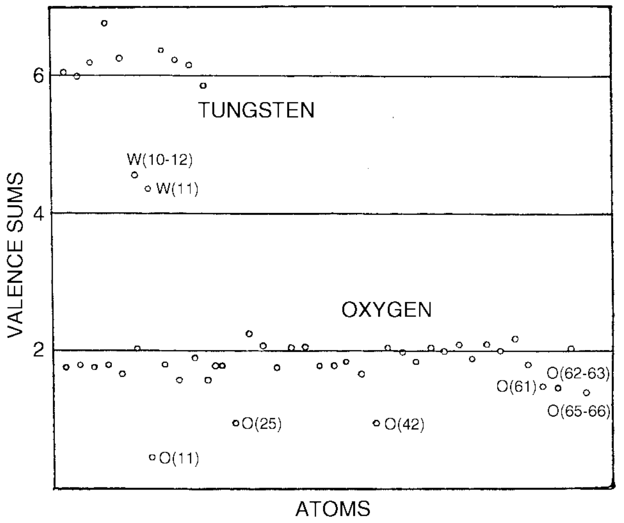

Fig. 6 Plot of valence sums for W and O in averaged $[H_6W_{20}O_{66}]^{12-}$.

length.[16] In **6** there are three short B–O bonds (to the W^{VI} oxygens) each about 1.48(3) Å and one longer (to the W^{IV}_3 oxygen) of 1.56(3) Å. This difference is not quite three esds. In contrast, the $[BW_{12}(H_2O)_3O_{37}]^{5-}$ structure has a corresponding long B–O distance of 1.85(8) Å and three short distances ranging from 1.39(7) to 1.49(7) Å. The work of Yamase *et al.* also included a comparison of the boron position in $[BW_{12}O_{40}]^{5-}$ and $[BW_{12}(H_2O)_3O_{37}]^{5-}$ by examination of the distances from the boron in each structure to three planes of tungsten atoms in the Keggin. These planes correspond to a top set of three W atoms in edge-shared octahedra, a middle band of six W atoms and a bottom set of three W atoms in corner-shared octahedra. The distances found for $[BW_{12}O_{40}]^{5-}$ were 2.9(1), 0.1(1), and 2.8(1) Å respectively; those for $[BW_{12}(H_2O)_3O_{37}]^{5-}$ were 3.3(1), 0.4(1), and 2.3(1) Å respectively. In this last case the top plane contains the three W^{IV} atoms. The corresponding distances in **6** are 3.03(2), 0.18(2), and 2.58(2) Å. Thus, while tending to support the results of Yamase and Ishikawa in finding the B atom displaced from the center and away from the three W^{IV} atoms, the magnitude of the esds in the values of the two previous structures do not allow us to conclude that the position of the B atom found in **6** is significantly different from *either* previous structure. The difficulty in pinning down the B atom presumably comes from the relatively small amount of electron density it possesses compared with the other atoms in the unit cell.

Related polyanions. The 20-tungstate polyanions described here belong to a group of iso- and hetero-polyanions that are formed by condensation of various polytungstate or polymolybdate groups onto a condensed octahedral substrate made from low-valent transition metals (Mn, Fe, Co, Zn, Cu, *etc.*). Such substrates are illustrated in Fig. 7 for M_2O_{10}, M_3O_{13}, and M_4O_{16} $[MO_7(MO_3)_{n-1}]^{8-}$, which shows the triangular layers of oxygen atoms in the upper and lower surfaces of the planar groups.

The firmest bond will be made if an XM_9O_{36} group can form a six- or seven-fold contact with the substrate (dotted lines, Fig. 7b,c); if less than six, a portion of the M_9 group will be left uncoordinated. The six-bonding groups usually retain a Keggin-type structure, but if coordination is incomplete, the M_9 moiety may be somewhat rearranged in the uncoordinated region. These properties are illustrated in Fig. 7 for the various substrates. For M_2O_{10} (Fig. 7a), the polycomplex in the compound[21] $[NH_4]_{12}[Cu_2(Si_2Mo_9O_{33})_2]$ has two 9-molybdosilicate

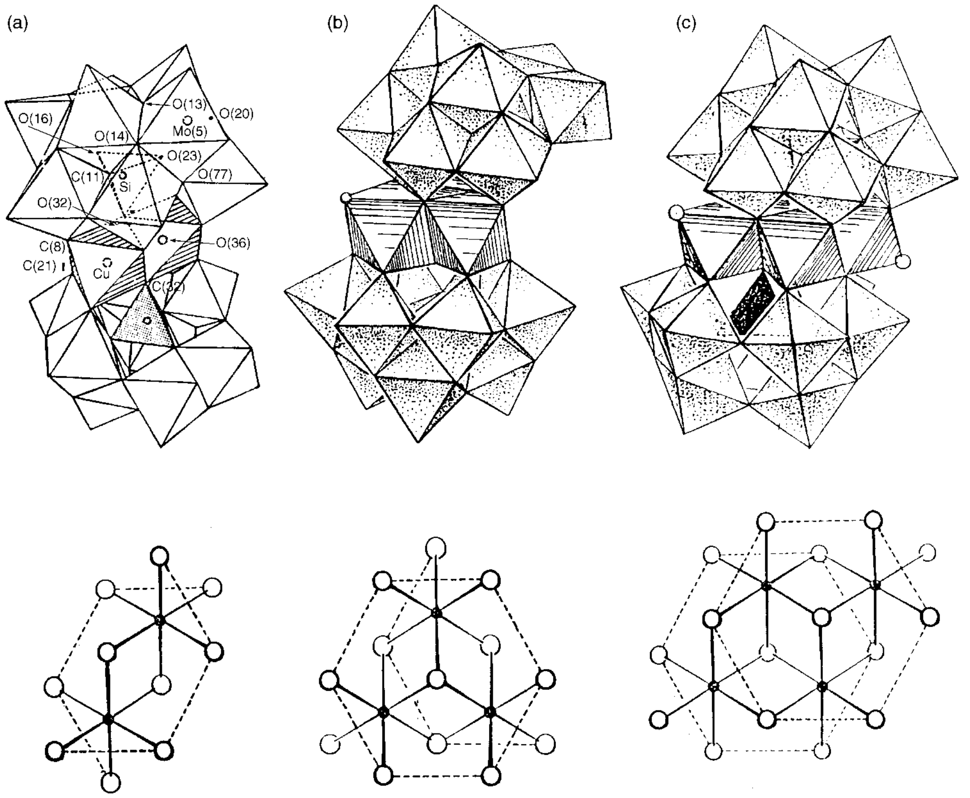

Fig. 7 Substrate structures and typical molecules for three types of related compounds. Dotted lines indicate points of attachment of adducts in each case.

groups coordinated at five points, but one of the MoO_6 octahedra is relocated in the α,β-type group.[22] For M_3O_{13} (Fig. 7b), the complex described here has one such group attached at a full seven points unaltered, while the other with only four points of attachment is rearranged.

For M_4O_{16} (Fig. 7c), the substrate has a complete seven-point base and often attaches two XM_9O_{36} groups, one on each side, as in the polyanion $[Co_4(H_2O)_2(PW_9O_{34})_2]^{10-}$.[23] This configuration appears to be especially stable, and is known in many well defined compounds. The four-fold substrate may be based on other cations such as Cu and Zn, and also attach larger adducts, as in $[Cu_4(H_2O)_2(P_2W_{15}O_{56})_2]^{16-}$.[24]

Conclusion

The $[H_6W_{20}O_{66}]^{12-}$ anion and its borotungstate analog are readily synthesized by addition of acidified tungstate to solutions of the respective polytungstate browns. NMR results suggest that the anions retain the observed solid-state structure in solution. Additional condensation of tungstate appears to have little effect on the coordination sphere geometry of the three reduced tungsten atoms. The attachment of the additional W_8O_{30} group to the Keggin unit is unprecedented for anions containing only tungsten, oxygen, and hydrogen, but close similarities can be seen to anions containing low-valent first-row transition metal ions.

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