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Syntheses and Structures of the Tungstoborate Anions

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A new tungstoboric species, $[BW_{13}O_{46}H_3]^{8-}$, which was identified in solution, is an intermediate between $[BW_{11}O_{39}H]^{8-}$ and the so-called hexagonal acid. This heteropolyacid was obtained in high yield by a new synthetic route. A single-crystal X-ray diffraction study showed that its formula is $H_{21}[B_3W_{39}O_{132}]\cdot 69H_2O$. The heteropolyanion is formed by three $BW_{13}O_{46}$ subunits linked together by sharing vertices leading to C_{3h} symmetry. Each subunit is constituted by a undecatungstic anion derived from the Keggin structure, capped by a μ-oxoditungstic group, W_2O_{11}. The BO_4 tetrahedron is significantly distorted, one of the B−O bonds being longer (1.58 Å) than the three others (1.46 Å). The conversions between the three species $[BW_{11}O_{39}H]^{8-}$, $[BW_{13}O_{46}H_3]^{8-}$ and $[B_3W_{39}O_{132}]^{21-}$ are rapid and reversible. On the contrary, the irreversible formation of the Keggin heteropolyanion, α-$[BW_{12}O_{40}]^{5-}$, is observed by heating of the solution of $[BW_{13}O_{46}H_3]^{8-}$ at pH 1−5.

Introduction

The polycondensation of tungstate ions $[WO_4]^{2-}$ in the presence of oxoanions $[XO_p]^{n-}$ has been studied for a long time.[1] The role of X is to govern the polycondensation around it, so X is generally at the center of the structure of the heteropolyoxotungstate and the overall symmetry of the species corresponds to that of the XO_p polyhedron. The most familiar compounds are obtained with tetrahedral $[XO_4]^{n-}$ assembling anions (X = Si^{IV}, Ge^{IV}, P^{V}, As^{V}) and have the Keggin structure $[XM_{12}O_{40}]^{n-}$, where four trimetallic fragments are arranged around X with a T_d symmetry.[2] Central transition metals with an octahedral coordination sphere lead to compounds with the Anderson structure, $[XO_6M_6O_{18}]^{n-}$.[3] Heteroatoms with lone pairs of electrons (As^{III}, Sb^{III}, Bi^{III}) lead to structures in which several subunits are associated in order to accommodate the unshared electrons.[4]

The chemistry of boron is characterized by its electron deficiency. In the boric oxide and acids, the boron atom is at the center of a triangle of three oxygen atoms, but tetrahedral $[B(OH)_4]^-$ anions exist in alkaline solutions. In between them, several polyborates have been characterized in which trigonal and tetrahedral boron atoms coexist in the same species.[5] It is therefore interesting to study the stereochemistry of boron in compounds resulting from polycondensation reactions with tungstate ions. Several tungstoboric species have been described: in 1883 Klein[6] obtained two tungstoboric acid isomers which crystallized with tetragonal and hexagonal lattices. Later, Copaux[7] gave two different compositions for these compounds, corresponding to W/B ratios of 12 and 14, respectively. But Rosenheim[8] suggested that they had the same composition corresponding to the ratio W/B = 12. Souchay[9] agreed with this conclusion and established the existence of the 11-tungstoborate anion, which was written as $[BW_{11}O_{39}]^{9-}$. It is now well established that the anion corresponding to the quadratic acid has the Keggin structure (noted α) but its route of formation and relations with the other species are not known.

It is tempting to think that the versatility of the trigonal−tetrahedral stereochemistry of the boron atom is responsible for the particular behavior of its reaction with tungstate. The aim of this work was to establish the true composition and the structure of all the species present and to derive their mechanism of formation. In this paper, we show that each species has a different composition or degree of condensation and that its formation can be explained on the basis of the stereochemical properties of the boron atom.

Experimental Section

Preparation of the Compounds. $H_{21}[B_3W_{39}O_{132}]\cdot 69H_2O$. A 200 g sample of sodium tungstate ($Na_2WO_4\cdot 2H_2O$) and a 10 g sample of boric acid were dissolved in 200 mL of boiling water. A solution of 6 M hydrochloric acid was added with vigorous stirring in order to dissolve the local precipitate of tungstic acid until the pH was ∼5.5−6 (∼120 mL in 20 min). The pH was maintained at this value by addition of hydrochloric acid, and the solution was kept boiling for 0.5 h, the final volume being 300 mL. The cooled solution was kept 24 h at 4 °C. The precipitate (mainly the sodium salt of paratungstate $[H_2W_{12}O_{42}]^{10-}$) was eliminated by filtration. The filtrate was quickly acidified by addition of 10 mL of concentrated sulfuric acid. At this point two procedures can be performed: (i) to the cool solution, 180 mL of concentrated perchloric acid was added. The acid precipitated slowly; (ii) or alternatively, in a separatory funnel, 20 mL of diethyl oxide and 50 mL of a chilled mixture, A, made of equal volumes of sulfuric acid and diethyl oxide, were added per 100 mL of the solution. The preparation split into three phases (a small extra amount of diethyl ether might be necessary). The heaviest phase was collected and washed with a mixture made of 100 mL of water and 50 mL of A. The diethyl ether of the heavy layer was removed under vacuum and left the white sodium-free acid. In each case the yield was ∼40%.

The acid was recrystallized at room temperature after dissolution in the minimum amount of water. Anal. Calcd for $H_{21}[B_3W_{39}O_{132}]\cdot 69H_2O$: B, 0.30; W, 67.78. Found: B, 0.30; W, 66.71.

$K_8[BW_{11}O_{39}H]\cdot 13H_2O$. A 300 g sample of sodium tungstate and a 20 g sample of boric acid were dissolved in 500 mL of boiling water. A solution of 6 M hydrochloric acid was added (∼190 mL in 20 min) with vigorous stirring in order to dissolve the local precipitate of tungstic

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Table 1. Crystallographic Data Collection

formula	$H_{21}(B_3W_{39}O_{132})\cdot 69H_2O$
fw	10578.6
cryst color	colorless
cryst habit	needle
calc density (g cm^{-3})	4.04
meas density (g cm^{-3})	4.06
cryst face (distance from center, mm)	100 $\bar{1}00$ (0.078) 010 $0\bar{1}0$ (0.084) 110 $\bar{1}\bar{1}0$ (0.062) 001 $00\bar{1}$ (0.423)
absorptn coeff μ (Mo Kα) cm^{-1}	263.83
cryst syst	hexagonal
space group	$P6_3/m$
$a = b$ (Å)	21.626(9)
c (Å)	21.46(2)
V (Å^3)	8692
Z	2
diffractometer	Philips PW 1100
monochromator	graphite
radiation (λ, Å)	Mo Kα (0.710 69)
temperature (°C)	21
scan type	$\theta - 2\theta$
2θ range (deg)	4−44
scan speed (deg s^{-1})	0.01
scan width (deg)	$0.90 + 0.345$ (tan θ)
background	half of scan time, in two parts, before and after every scan, in fixed position
no. of standard reflections	3 measd every 2 h
no. of reflections collected	4030
no. of reflections kept for refinement	2830
final R $(=\sum\|\|F_o\| - \|F_c\|\|/\|\sum F_o\|)$	0.049
final Rw $(=\sum(w(\|F_o\| - \|F_c\|)^2/\sum wF_o{}^2)^{1/2})$	0.053
GOF	1.36
weight	$1.877/\sigma(F)^2 + 0.00123F^2$

acid until the pH was 6. The solution was kept boiling for 1 h and after cooling to room temperature it was kept 24 h at 4 °C. The precipitate was removed by filtration, and then the potassium salt was precipitated from the solution by addition of potassium chloride (∼100 g). The crude potassium salt was dissolved in 1 L of lukewarm water, the insoluble part eliminated, and the potassium salt precipitated again by addition of KCl (∼100 g). The yield was ∼25%. Anal. Calcd for $K_8[BW_{11}O_{39}H]\cdot 13H_2O$: K, 9.76; B, 0.34; W, 63.10; H_2O, 0.07. Found: K, 9.87; B, 0.31; W, 62.91; H_2O, 0.07.

X-ray Data Collection and Structure Determination. A crystal of $H_{21}[B_3W_{39}O_{132}]\cdot 69H_2O$ was sealed in a thin-walled capillary tube. Preliminary Weissenberg photographs indicated a hexagonal lattice. The systematically absent reflections corresponded to the space groups $P6_3$, $P6_322$, and $P6_3/m$. The choice of the centrosymmetric space group $P6_3/m$ was consistent with the values of various statistical indications using normalized factors and all stages of the subsequent structure determination refinement.

Intensity measurements were carried out with Mo Kα radiation on a Philips PW 1100 instrument (graphite monochromator and scintillation counter) at room temperature. The intensities of three standard reflections were measured every 2 h and showed no significant variation. The data were corrected for Lorentz and polarization effects. The absorption correction was performed by the Gaussian integration method. Information concerning crystal data and conditions of the data collection is summarized in Table 1.

The structure was solved by using a combination of direct methods (MULTAN), which lead to the positions of the tungsten atoms in the asymmetric unit, and alternative difference Fourier syntheses and least-squares refinements for the location of oxygen and boron atoms of the polyanion. Three water molecules have been found. The final cycle of full-matrix least-squares refinements lead to $R = 0.049$ and Rw $= 0.053$ for 2830 reflections with $I > 3\sigma(I)$. All calculations were carried out on a Gould UTX/32 computer using SHELX programs. The atomic coordinates are reported in Table 2 and selected bond distances in Table 3.

Table 2. Fractional Atomic Coordinates and Thermal Parameters

atom	x/a	y/b	z/c	B(eq) (Å^2)^a
W(1)	−0.12420(9)	0.67330(9)	0.7500	3.82(7)
W(2)	−0.12573(5)	0.53926(6)	0.67246(5)	3.24(4)
W(3)	0.17945(5)	0.78208(5)	0.66524(5)	2.49(4)
W(4)	0.03478(6)	0.80095(6)	0.66453(6)	3.72(5)
W(5)	0.03354(6)	0.66777(6)	0.58667(5)	2.96(4)
W(6)	0.03384(5)	0.51995(5)	0.67061(4)	2.31(4)
W(7)	0.22650(6)	0.63981(6)	0.66070(7)	4.64(5)

atom	x/a	y/b	z/c	B(iso) (Å^2)
B	0.027(3)	0.667(3)	0.7500	4.0(10)
O*(77)	0.2726(8)	0.5897(8)	0.6430(7)	2.2(3)
Oa(122)	−0.052(1)	0.621(1)	0.7500	2.5(4)
Oa(345)	0.0562(8)	0.7092(8)	0.6924(7)	2.2(3)
Oa(66)	0.058(1)	0.613(1)	0.7500	1.9(4)
Ob(14)	−0.0619(9)	0.7347(9)	0.6920(8)	3.4(3)
Ob(25)	−0.0631(9)	0.6059(9)	0.6181(8)	3.6(4)
Ob(26)	−0.0567(8)	0.5056(9)	0.6764(7)	2.9(3)
Ob(33)	0.190(1)	0.809(1)	0.7500	3.3(5)
Ob(37)	0.1905(8)	0.7045(8)	0.6812(7)	2.3(3)
Ob(44)	0.051(1)	0.825(1)	0.7500	3.7(5)
Ob(56)	0.0520(8)	0.5955(8)	0.6145(8)	2.9(3)
Ob(66)	0.027(1)	0.476(1)	0.7500	2.4(4)
Ob(67)	0.1376(8)	0.5648(8)	0.6776(7)	2.5(3)
Ob(77)	0.2485(9)	0.6458(9)	0.7500	1.1(3)
Oc(12)	−0.1661(9)	0.5985(9)	0.6885(9)	3.8(4)
Oc(22)	−0.165(1)	0.491(1)	0.7500	3.8(5)
Oc(34)	0.1326(9)	0.8382(9)	0.6535(9)	3.9(4)
Oc(35)	0.1323(9)	0.7352(9)	0.5887(8)	3.6(4)
Oc(45)	0.017(1)	0.746(1)	0.5902(9)	4.1(4)
Od(1)	−0.194(2)	0.694(2)	0.7500	5.4(7)
Od(2)	−0.187(1)	0.478(1)	0.6232(9)	4.3(4)
Od(3)	0.2608(9)	0.8414(9)	0.6352(8)	3.6(4)
Od(4)	0.024(1)	0.868(1)	0.633(1)	5.0(4)
Od(5)	0.0239(9)	0.6502(9)	0.5089(9)	3.9(4)
Od(6)	0.0183(9)	0.4509(9)	0.6218(8)	3.2(3)
Od(7)	0.2021(8)	0.6418(8)	0.5736(7)	2.5(3)
Ow(1)	−0.073(1)	0.468(1)	0.513(1)	8.4(7)
Ow(2)	0.143(2)	0.475(2)	0.523(2)	11.9(10)
Ow(3)	−0.157(2)	0.354(2)	0.595(2)	12.6(11)

[a] $B(\mathrm{eq}) = {}^1/_3\sum_i\sum_j\beta_{ij}\mathbf{a}_i\mathbf{a}_j$.

Table 3. Selected Interatomic Distances (Å)

W(1)−Od(1)	1.74(4)	W(5)−Od(5)	1.70(2)
W(1)−Ob(14)	1.81(2)	W(5)−Oc(35)	1.86(1)
W(1)−Oc(12)	1.91(2)	W(5)−Ob(56)	1.86(2)
W(1)−Oa(122)	2.29(3)	W(5)−Oc(45)	1.87(2)
		W(5)−Ob(25)	1.93(2)
W(2)−Od(2)	1.68(2)	W(5)−Oa(345)	2.39(1)
W(2)−Ob(25)	1.81(2)		
W(2)−Oc(12)	1.88(2)	W(6)−Od(6)	1.70(2)
W(2)−Oc(22)	1.91(1)	W(6)−Ob(26)	1.80(2)
W(2)−Ob(26)	1.93(2)	W(6)−Ob(56)	1.89(2)
W(2)−Oa(122)	2.35(1)	W(6)−Ob(66)	1.92(1)
		W(6)−Ob(67)	1.92(2)
W(3)−Od(3)	1.68(1)	W(6)−Oa(66)	2.46(2)
W(3)−Ob(37)	1.81(2)		
W(3)−Ob(33)	1.88(1)	W(7)−Ob(67)	1.80(1)
W(3)−Oc(34)	1.91(2)	W(7)−O*(77)	1.81(2)
W(3)−Oc(35)	1.92(2)	W(7)−Ob(37)	1.93(2)
W(3)−Oa(345)	2.36(1)	W(7)−O*(77)	1.93(2)
		W(7)−Od(7)	1.95(2)
W(4)−Od(4)	1.69(3)	W(7)−Ob(77)	1.96(1)
W(4)−Oc(34)	1.83(2)		
W(4)−Ob(44)	1.89(1)	B−Oa(122)	1.46(5)
W(4)−Oc(45)	1.90(2)	B−Oa(345)	1.47(3)
W(4)−Ob(14)	1.91(1)	B−Oa(66)	1.58(7)
W(4)−Oa(345)	2.29(2)		

Characterization in Solution. The tungstoborates were characterized in solution by polarography in 1 M CH_3COOH−1 M $NaCH_3COO$ buffer (pH 4.7) on a dropping mercury electrode. ^{11}B NMR spectra were recorded on a Bruker AC 300 spectrometer operating at 96.29 MHz. Concentrated solutions of $[BW_{11}O_{39}H]^{8-}$ were obtained

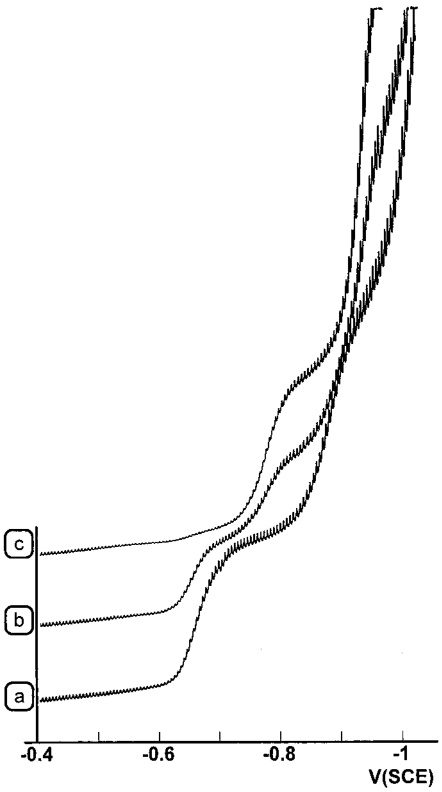

Figure 1. Polarograms of (a) $[BW_{11}O_{39}H]^{8-}$ 3×10^{-4} mol L^{-1} in acetic buffer pH 4.7; (b) and (c) after addition of one and two $[WO_4]^{2-}$ per heteropolyanion, respectively, in the same conditions.

by dissolution of the potassium salt in lithium perchlorate solution and filtration of potassium perchlorate. Solutions of $[BW_{13}O_{46}H_3]^{8-}$ were prepared by addition of tungstate to the solutions of the 11-tungstoborate in acetic buffer (pH 4.7).

Results

The 11-Tungstoborate Anion. Attempts to obtain any tungstoborate species at pH 8−9 failed. This is the first difference between B^{III} and Si^{IV}, P^{V} (tetrahedral atoms), as well as As^{III}, Sb^{III} (pyramidal atoms) which, under these conditions, lead to A- or B-9-tungstoheteropolyanions, respectively.[10] The first species isolated by acidification of mixtures of tungstate and boric acid was the 11-tungstoborate anion at pH 6−7, as previously reported by Souchay.[9] Analysis of its potassium salt gave the composition $[BW_{11}O_{39}H]^{8-}$, which is analogous to the corresponding anions $[XW_{11}O_{39}]^{n-}$ containing tetrahedral central atoms. Because of its high negative charge, owing to the lower oxidation state of the boron atom, the polyanion is protonated. This proton cannot be neutralized at high pH without destruction of the polyanion.

It was expected that boron would have a tetrahedral symmetry in this compound, thereby identifying it as an α-isomer. In favor of this hypothesis is the formation of 1/1 complexes with transition metal cations such as Co^{2+},[11] Mn^{2+}, or Fe^{3+}. These complexes have been shown to be isostructural with the α-isomers of the $[XW_{11}O_{39}M(H_2O)]^{n-}$ complexes which contain tetrahedral central atoms. However, this point of view is not in agreement with another property of the monovacant $[XW_{11}O_{39}]^{n-}$ species: in acid solution, addition of tungstate leads to formation of the complete $[XW_{12}O_{40}]^{m-}$ Keggin anion in a very facile and rapid reaction at room temperature. Since the Keggin anion α-$[BW_{12}O_{40}]^{5-}$ is very stable at pH <6, it should be easily obtained from $[BW_{11}O_{39}H]^{8-}$. Both compounds can be characterized by their electrochemical behavior at pH 4.8: α-$[BW_{12}O_{40}]^{5-}$ shows two monoelectronic waves[12] at $E_{1/2} = -0.48$ and -0.72 V (SCE), respectively and $[BW_{11}O_{39}H]^{8-}$ shows one bielectronic wave[13] at $E_{1/2} = -0.76$ V (SCE). Polarography of mixtures of $[BW_{11}O_{39}H]^{8-}$ and tungstate at pH 4.8 did not show the characteristic waves of α-$[BW_{12}O_{40}]^{5-}$, but instead two new bielectronic waves at $E_{1/2} = -0.63$ and -0.84 V (SCE), respectively, which cannot be assigned to any known tungstoborate anion. Besides, polarographic study of the hydrolysis of α-$[BW_{12}O_{40}]^{5-}$ at pH 7−10 showed that borate and tungstate ions are obtained directly without formation of the 11-tungstoborate anion. This means that there is not pH-dependent, direct interconversion between $[BW_{11}O_{39}H]^{8-}$ and α-$[BW_{12}O_{40}]^{5-}$.

A New Tungstoborate: $[BW_{13}O_{46}H_3]^{8-}$. The composition of the species obtained in acid solution by addition of tungstate to $[BW_{11}O_{39}H]^{8-}$ can be deduced from the polarographic titration curve. Figure 1 shows polarograms of mixtures of tungstate and $[BW_{11}O_{39}H]^{8-}$ in different ratios. At a potential of −0.70 V (SCE), the current intensity increases linearly up to $W/BW_{11} = 2$ and then remains constant. At this potential, the current is only due to the new polyanion. Clearly, the $[BW_{11}O_{39}H]^{8-}$ anion reacts with 2 tungstate ions leading to a compound with 13 tungsten atoms. Its formula was obtained by titration of the mixture $[BW_{11}O_{39}H]^{8-} + 2WO_4^{2-}$ with hydrochloric acid. An equivalence point was observed after addition of four H^+ per polyanion and therefore the formation of the new species can be written as

$$[BW_{11}O_{39}H]^{8-} + 2WO_4^{2-} + 4H^+ \Leftrightarrow [BW_{13}O_{46}H_3]^{8-} + H_2O$$

The number of oxygen atoms (46) was derived from the structure of the parent hexagonal acid (see later). Addition of base to a solution of $[BW_{13}O_{46}H_3]^{8-}$ gave again the 11-tungstoborate anion at pH 7, showing the reversibility of the transformation between $[BW_{11}O_{39}H]^{8-}$ and $[BW_{13}O_{46}H_3]^{8-}$. Attempts to isolate a salt of the new anion (e.g., a potassium salt) failed because of its very high solubility. In fact, the only salt obtained was always that of the sparingly soluble 11-tungstoborate, the equilibrium being shifted by its insolubility.

Strictly speaking, only the formula $([BW_{13}O_{46}H_3]^{8-})_n$ can be derived from the above experiments but it will be proved later that $n = 1$ for this compound.

The Hexagonal Tungstoboric Acid: $H_{21}[B_3W_{39}O_{132}]$. The hexagonal acid had been obtained by Klein[6] and Copaux[7] in low yield, as a byproduct in the synthesis of quadratic tungstoboric acid, α-$H_5[BW_{12}O_{40}]$. It was separated as long needles by fractional crystallization, but the characterization was poor, probably because of small quantities. In the course of the quest for a better method of preparation of the hexagonal acid, it was observed that if a solution of $[BW_{13}O_{46}H_3]^{8-}$ was quickly acidified to a pH close to 0 at room temperature, then the Keggin anion α-$[BW_{12}O_{40}]^{5-}$ was not formed, even if the solution was kept boiling for several hours. If extraction by diethyl ether was performed and the heavy phase was dissolved in water, pure hexagonal acid was obtained in good yields by crystallization. Crystals of good quality were obtained and the structure could be solved by X-ray diffraction.

The anion $[B_3W_{39}O_{132}]^{21-}$ illustrated in Figure 2 has C_{3h} symmetry and is formed by three subunits of 13 WO_6 octahedra

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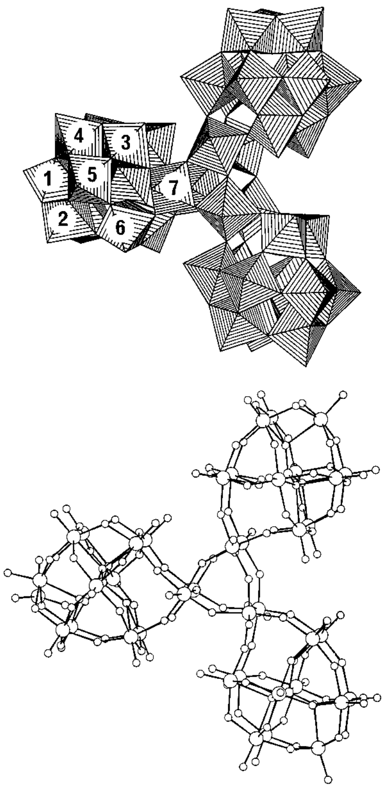

Figure 2. Polyhedral and ball and stick representations of the structure of the tungstoboric acid $H_{21}[B_3W_{39}O_{132}]$.

linked together by sharing vertices. Its formation can be described as a condensation of three $[BW_{13}O_{46}H_3]^{8-}$ units:

$$3[BW_{13}O_{46}H_3]^{8-} + 3H^+ \Leftrightarrow [B_3W_{39}O_{132}]^{21-} + 6H_2O$$

Due to the symmetry of the cell, only one-sixth of the polyanion had to be determined. Different types of oxygen atoms are distinguished in the polyanion as usual. Oa oxygen atoms are linked to the central boron atom, Ob and Oc oxygen atoms link WO_6 octahedra, respectively, by vertices and by edges, and Od are terminal oxygen atoms linked to only one tungsten atom. O* is a particular oxygen atom which is shared by the subunits defined previously. The name given of the oxygen atoms in Table 2 includes both this latter classification and, in parentheses, the numbering of the tungsten atoms they are linked to.

Each $BW_{13}O_{46}$ subunit can be considered as an undecatungstic anion derived from the Keggin structure capped by a μ-oxoditungstic group W_2O_{11} formed by two octahedra (W(7)). An alternative description of the structure is to consider three $BW_{11}O_{39}$ subunits joined together by a W_6O_{27} central group. Each $BW_{11}O_{39}$ subunit has the global geometry observed in the Keggin structure, but some differences in W−W distances can be reported. The distances between the metal atoms of edge-shared octahedra in the triplets are 3.30 Å. This is somewhat shorter than for the Keggin structures of tungstophosphate (3.41 Å) and tungstosilicate (3.42 Å), respectively.[1] The distance between the W(6) atoms in the group of two octahedra is 3.41 Å. The average distance between the W atoms belonging to corner-shared octahedra is 3.62 Å, which is also lower than for 12-tungstophosphate and 12-tungstosilicate anions.

Each $W(7)O_6$ octahedron is sharing corners with the W(6)-O_6, $W(3)O_6$, and three equivalent $W(7)O_6$ octahedra, respectively. The distances between W(7) and W(6), W(3), and C_3 symmetry-related W(7)s are respectively 3.59, 3.63, and 3.55 Å, which are in the usual range of W−O−W bond lengths. On the other hand, the W(7)−W(7) distance between atoms related by the mirror plane is significantly longer (3.83 Å). This difference is due to the relatively large W(7)−Ob(77) bond length (1.96 Å) trans to the Od(7) terminal oxygen (W(7)−Od-(7), 1.60 Å).

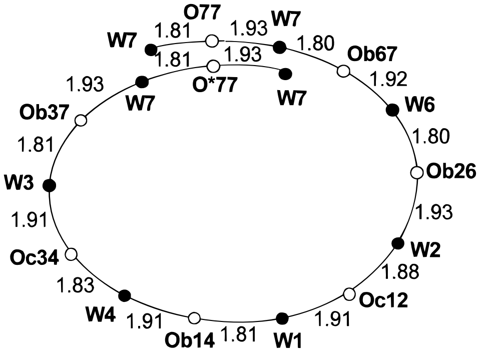

Figure 3. Schematic representation of the successive long and short W−O bonds along the W−O−W chain. Bond lengths are in angstroms.

Table 4. Molecular Weight and Hydrodynamic Radius Determined by Ultracentrifugation and Viscosity Measurements, Respectively

heteropolyanion	mol wt	hydrodynamic radius (Å)
$[BW_{13}O_{46}H_3]^{8-}$	2930	7.5
$[B_3W_{39}O_{132}]^{21-}$	11100	10

As is often observed for molybdic compounds but less for tungtic ones, the distances between tungsten atoms and oxygen atoms Ob or Oc which are bound to them, are alternatively long and short. This is illustrated in Figure 3.

Characterization of the Species in Solution. The molecular weight and the hydrodynamic radius of the three tungstoborates in solution have been determined by ultracentrifugation (Archibal method) and viscosity measurements, respectively (Table 4). The values obtained for $H_{21}[B_3W_{39}O_{132}]$ suggest that the structure of the heteropolyanion is conserved in solution. The hydrodynamic radius matches well with the crystallographic one, which is 10.30 Å. The values obtained for the 13-tungstoborate correspond well to species containing one boron atom.

The environment of the boron atom in the tungstoborates can be characterized by the nuclear magnetic resonance of the most abundant isotope ^{11}B. In particular, this quadrupolar nucleus is sensitive to the arrangement of the oxygen ligands around it. The regular T_d symmetry in α-$[BW_{12}O_{40}]^{5-}$ leads to a very sharp resonance line in the NMR spectrum ($\Delta\nu < 1$ Hz). On the contrary, the very broad signals (between 140 and 250 Hz) for the three other compounds have to be attributed to a less symmetric environment of boron.

Conditions of Formation of α-$[BW_{12}O_{40}]^{5-}$. This heteropolyanion is stable in acid solution up to a pH of ~6 and is obtained by boiling a solution containing tungstate and boric acid at pH 3−5. On the other hand, $[BW_{11}O_{39}H]^{8-}$ is stable at pH 7−8 and transforms into $[BW_{13}O_{46}H_3]^{8-}$ at pH <6. Since the $[B_3W_{39}O_{132}]^{21-}$ anion is stable at pH 0 (even with boiling), the α-$[BW_{12}O_{40}]^{5-}$ anion must be formed at pH 1−5, where $[BW_{13}O_{46}H_3]^{8-}$ is stable at room temperature. Increasing the temperature of such solutions leads effectively to the formation of α-$[BW_{12}O_{40}]^{5-}$, as characterized by its polarographic behavior. A rough polarographic study of the formation of the Keggin type anion showed that the rate was maximal at a pH near 2.

Discussion

The routes of formation of the tungstoborate anions are indicated in Figure 4. This scheme is very different from the

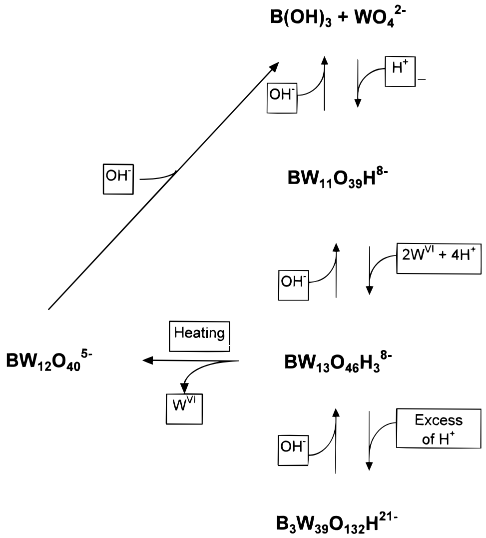

Figure 4. Routes of formation of the tungstoboric heteropolyanions.

scheme previously established for polyanions with tetrahedral or pyramidal central atoms. For tetrahedral heteroatoms, the species obtained at pH 9 is the β-isomer of the trivacant A-$[XW_9O_{34}]^{n-}$ anion. In these compounds, X is in a tetrahedral environment of oxygen atoms and this symmetry is kept in any compound derived from further condensation reactions with tungstate ions even after isomerization.[14] For the pyramidal heteroatoms with three oxygen atoms and a lone pair of electrons, the first species obtained at pH 8−10 is the trivacant B-$[XW_9O_{33}H]^{9-}$ anion and the pyramidal environment of X is kept in all the compounds derived from further reactions.[4]

Differences in the behavior of boric compounds are evidently due to the particular structural chemistry of boron, which shows a great diversity in the binding oxygen atoms and in its acceptance of electrons from donor atoms in order to decrease its electron deficiency. In borates, the B atom can bind to either three oxygen atoms forming a triangle or four oxygen atoms forming a tetrahedron. The very large signals observed in ^{11}B NMR for $[BW_{11}O_{39}H]^{8-}$, $[BW_{13}O_{46}H_3]^{8-}$, and $[B_3W_{39}O_{132}]^{21-}$ can be explained by B being in an environment of low symmetry. The X-ray structure of the hexagonal acid gives more details about this environment: B is 1.46 Å from the three Oa oxygen atoms of the three tritungstic groups and 1.58 Å from the fourth oxygen Oa(66) of the ditungstic group belonging to the $BW_{11}O_{39}$ subunit. The boron atom is ∼0.36 Å above the triangle of the three Oa atoms. If a mean value of 1.48 Å is assumed for the B−O bond length in tetrahedral BO_4,[15] the boron atom would be 0.49 Å above a plane of three oxygen atoms in a regular tetrahedron. It can be concluded, therefore, that the boron atom in $[B_3W_{39}O_{132}]^{21-}$ is intermediate between the trigonal BO_3 and the tetrahedral BO_4 coordination. It can be presumed that the coordination polyhedron of the boron atom is the same for the three compounds $[BW_{11}O_{39}H]^{8-}$, $[BW_{13}O_{46}H_3]^{8-}$, and $[B_3W_{39}O_{132}]^{21-}$, since these species transform reversibly into each other by fast reactions and their ^{11}B NMR signals are also very similar. An important consequence of this geometry is that the reaction of tungstate ions with $[BW_{11}O_{39}]^{9-}$ does not lead to the Keggin ion α-$[BW_{12}O_{40}]^{5-}$ by fixation of one WO^{2+} group in the vacant site. Instead, if the structural features of the hexagonal acid are extended to $[BW_{13}O_{46}H_3]^{8-}$, two tungsten octahedra are symmetrically placed over the vacant site leading to the original $[BW_{13}O_{46}H_3]^{8-}$ species. The $[BW_{11}O_{39}H]^{8-}$ anion acts as a tetradentate ligand for the μ-oxoditungstic W_2O_{11} group, in which two tungsten octahedra share a corner, the Oa(66) atom not being involved in this mode of binding. This feature is clearly connected to the distorted geometry of the BO_4 tetrahedron.

The oxotungstic geometry of the $BW_{11}O_{39}$ subunit in the hexagonal acid is the same as for structure of α-$[SiW_{11}O_{39}]^{8-}$. Isomerism of vacant heteropolyanions has been defined by reference to the complete structure, which is formed in acid solution.[16] For example, α- and β-$[SiW_{11}O_{39}]^{8-}$ react with tungstate in acid solution to form α- and β-$[SiW_{12}O_{40}]^{4-}$, respectively. According to this definition, $[BW_{11}O_{39}H]^{8-}$, which does not lead straight to α-$[BW_{12}O_{40}]^{5-}$ (and conversely alkaline hydrolysis of the latter does not lead to the undecatungtic species), cannot be considered an α-isomer. This could be explained by the difference in the geometry of the central heteroatom. In the structure of $Ba_{3.5}[BCo(H_2O)W_{11}O_{39}]\cdot 26H_2O$ reported by Weakley,[11] the observed regular BO_4 tetrahedron results from the crystallographic treatment and is not in contradiction with our results.

The instability of $[BW_{13}O_{46}H_3]^{8-}$ at high temperature is probably related to the presence of three terminal oxygen atoms on each tungsten atom W(7) of the W_2O_{11} ditungstic group. It can be proposed that the three protons are at least partially localized on this group in order to decrease the π-donor character of the terminal oxygen atoms bound to the W(7) atoms. In contrast, all the tungsten atoms in $[B_3W_{39}O_{132}]^{21-}$ have only one terminal oxygen atom and this anion is very stable in acid solution.

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Supporting Information Available: Listing of anisotropic temperature factors of the tungsten atoms (1 page). Ordering information is given on any current masthead page.

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