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Borotungstate Polyoxometalates: Multinuclear NMR Structural Characterization and Conversions in Solutions

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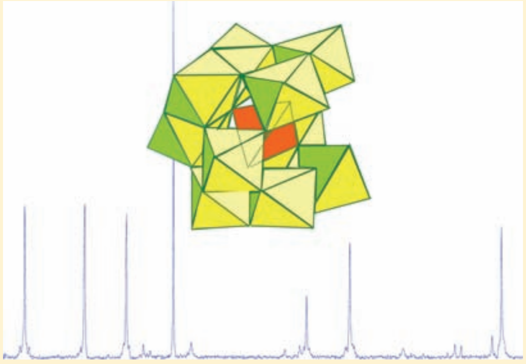
Supporting Information

ABSTRACT: The unique heteropolyanion $[H_3BW_{13}O_{46}]^{8-}$ (**BW_{13}**), previously suggested on the basis of indirect evidence, and protonated lacunary heteropolyanion $[HBW_{11}O_{39}]^{8-}$ (**BW_{11}**) have been identified in aqueous solutions at pH 5−7.5 from NMR spectra. The pattern of tungsten−tungsten connectivities based on the analysis of the $^2J_{W-O-W}$ coupling satellites in the ^{183}W NMR spectrum of BW_{11}, containing six peaks of relative intensities ~2:2:2:1:2:2, indicates that the latter is the α isomer. The ^{17}O NMR spectrum confirms the protonated state of the polyanion with the proton delocalized on two out of four terminal O atoms surrounding the tungsten vacancy. The ^{183}W NMR spectrum of **BW_{13}** contains seven peaks of relative intensities ~2:1:2:2:2:2:2 with additional large couplings due to the connectivity between **BW_{11}** and $[W_2O_7]^{2-}$ fragments. According to the ^{17}O NMR spectrum, two protons of $[BW_{13}O_{46}H_3]^{8-}$ are delocalized on the two terminal trans O atoms of the dimeric fragment while the third one is linked to its bridging O atom. The conversions of **BW_{11}** and **BW_{13}** in solution were followed by using ^{183}W NMR spectra at a "fingerprint" level. In the pH range from ~7.5 to 6, **BW_{11}** transforms to **BW_{13}**, transforming further to $[BW_{12}O_{40}]^{5-}$ (**BW_{12}**) and $[B_3W_{39}O_{132}H_n]^{n-21}$ (**B_3W_{39}**) in different ratios. Conversion of **BW_{13}** to **BW_{12}** proceeds through an intermediate complex of suggested composition $[BW_{11}O_{39}\cdot WO_2]^{7-}$. At high acidity (pH ~ 0), **B_3W_{39}** gradually decomposes into tungstic acid, **BW_{12}** and H_3BO_3. Polyanion **BW_{12}** persists in the pH range ~0−7.5.



INTRODUCTION

Tungsten heteropolyanions are an important class of inorganic metal−oxygen clusters, polyoxometalates, that are widely used in catalysis, analytical chemistry, and medicine.[1−3] Among the non-metal central atoms of tungsten heteropoly compounds, B^{III} has the lowest charge and coordination number and the smallest size, which probably defines some distinctive properties of the borotungstate (BW) system.[4−7] Thus, in addition to a typical heteropolyacid (HPA) $H_5[BW_{12}O_{40}]$ (**BW_{12}**), an unusual HPA $H_{21}[B_3W_{39}O_{132}]$ (**B_3W_{39}**) forms in aqueous BW solutions and can be isolated as a solid. By X-ray crystallography, **B_3W_{39}**, long accepted to be an isomer of **BW_{12}**, has recently been found to consist of three equivalent Keggin derivative subunits **BW_{13}** with C_s symmetry.[5] ^{183}W NMR spectra largely confirmed this structure of the trimer in solution but revealed a deviation from the previously proposed symmetry that gives rise to chirality of the polyanion.[6] This conclusion was confirmed by a re-examination of the acidic sodium salt of **B_3W_{39}** in the solid state, by X-ray structural analysis, and in solution, by ^{183}W NMR spectroscopy.[7] **BW_{12}** and **B_3W_{39}** are ultimate products of a chain of hydrolytic conversions, beginning in weakly acidic BW solutions (pH > 6) with the formation of $[BW_{11}O_{39}H]^{8-}$ (**BW_{11}**), which can be precipitated as a potassium salt. Upon solution acidification, **BW_{11}** is converted into a unique polyanion, $[BW_{13}O_{46}H_3]^{8-}$ (**BW_{13}**), evidenced by polarography and ultracentrifugation, which transforms further to **BW_{12}** or **B_3W_{39}**.[5] Recently, new anions, $[H_3BW_{14}O_{48}]^{6-}$ and $[H_6B_2W_{26}O_{90}]^{12-}$, also derived from **$BW_{13}$**, were isolated as salts, and their crystal structures were determined.[7] Addition of molybdate or organotin moieties acting as linkers to BW solutions results in complex mixed-metal arrangements, including **BW_{11}** or **BW_{13}** as fragments.[8,9] However, the chemistry even of binary BW solutions is not yet completely understood.[5,7] There are doubts that **BW_{11}** has the α structure because it does not interconvert directly with α-**BW_{12}**. Attempts to isolate the key intermediate **BW_{13}** have failed, as well as attempts to characterize it by ^{183}W NMR in solutions, which usually contain mixtures of several species.[7] While examining the acidic and catalytic properties of the HPA **B_3W_{39}**, we used NMR spectroscopy for monitoring its synthesis and identification in solution.[6,10] In studying speciation of polyoxometalates in solutions, NMR spectroscopy is of unique importance, with ^{17}O and ^{183}W NMR spectra being particularly structurally informative.[11−22] In this paper, we present novel findings and for the first time report and interpret the individual ^{183}W and ^{17}O NMR spectra of **BW_{11}** and **BW_{13}**. We have succeeded in obtaining these spectra to a great extent thanks to utilization of the electrochemical method of acidification, which

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allows fine adjustment of the synthesis conditions to be made. The spectra structurally characterize the polyanions and allow their conversions in solution to be followed at a "fingerprint" level. The obtained results clarify the questions concerning the BW system that have been raised by previous studies. It is important for understanding the mechanisms of hydrolytic conversions in borotungstate solutions and the role of the heteroelement in the formation, along with the typical polyanions, of some peculiar structures.

EXPERIMENTAL SECTION

Preparation of $K_8[BW_{11}O_{39}H]\cdot nH_2O$. The salt was synthesized in aqueous solution of $Na_2WO_4\cdot 2H_2O$ and H_3BO_3 (W/B ≈ 2.8) as previously described.[5] Elemental analysis (found/calc) for $K_8[BW_{11}O_{39}H]\cdot 13H_2O$: K, 8.5/9.6; B, 0.32/0.34; W, 61/63; H_2O, 8/7.5. The analyses were done by atomic absorption spectrophotometry and gravimetry. Because of low solubility of the potassium salt corresponding to $[\mathbf{BW_{11}}] \approx 0.01$ mol/L, K^+ was exchanged with Na^+ by reaction with $NaClO_4$ to increase solubility and achieve higher concentration for NMR measurements. To $K_8[BW_{11}O_{39}H]\cdot 13H_2O$ (3.2 g, 1 mmol) were added water (10 mL) and $NaClO_4$ (1.2 g, 9.8 mmol), and the suspension was stirred at room temperature for approximately 20 min. The precipitate of $KClO_4$ and the undissolved residue of K-**BW_{11}** were removed by filtration. The filtrate contained $[\mathbf{BW_{11}}] \approx 0.08$ mol/L. The solution could be further concentrated to about 0.16 mol/L by evaporation at ~40 °C. At higher concentrations, K-salt-based precipitates formed since potassium could not be completely removed from solutions.

Preparation of $H_{21}[B_3W_{39}O_{132}]\cdot 64H_2O$. When HPA **$B_3W_{39}$** was prepared via a procedure of Tézé et al.,[5] the product had composition $H_{17}Na_4[B_3W_{39}O_{132}]\cdot H_2SO_4\cdot xH_2O$.[6] Additional ether extraction and recrystallization afforded the actual heteropolyacid $H_{21}[B_3W_{39}O_{132}]\cdot nH_2O$ with a yield of 10−20%.[6] It did not contain H_2SO_4 (no IR band at ~1200 cm^{-1}), and the molar content of Na^+ was ≤0.1/HPA.

Preparation of BW Solutions. Aqueous BW solutions with [W] > 1 mol/L and W/B ≈ 3.7 and 12, prepared from $Na_2WO_4\cdot 2H_2O$ and H_3BO_3 (of reagent grade) and distilled water, were decationized and acidified by the electrodialysis method, as described in the literature.[23] Solid $Na_2WO_4\cdot 2H_2O$ (20 g, 60.6 mmol) was dissolved in 40 mL of water with stirring, and solid H_3BO_3 (1 g, 16.2 mmol) was added. The BW solutions, placed into the anode compartment of an electrodialyzer to conduct the electrochemical substitution of Na^+ by H^+, were acidified to different pH levels in the range 2−6, at ≤30 °C. Afterward, acidified solutions were boiled for 30−60 min for equilibration and concentration, with the solution pH increasing to 5.5−7.5. The final solution volume was 25 mL, which corresponded to [W] = 2.4 mol/L or to $[\mathbf{BW_{11-13}}] \approx 0.2$ mol/L. The solution kept in a refrigerator overnight gave no precipitates. Acidification by electrodialysis provided minimum content of Na and the absence of foreign anions in solutions, which largely allowed us to avoid precipitation of tungsten at its rather high concentration and to measure the ^{17}O NMR spectra of borotungstates at natural ^{17}O content and the corresponding ^{183}W NMR spectra with good signal/noise ratio.

For preparing several BW solutions, sodium paratungstate, $Na_{10}[H_2W_{12}O_{42}]\cdot 27H_2O$ was used instead of $Na_2WO_4\cdot 2H_2O$. The solution composition was monitored by ^{11}B and ^{183}W NMR spectroscopy.

Instrumentation and Methods. ^{11}B, ^{17}O, and ^{183}W NMR spectra were measured on an MSL-400 Bruker NMR spectrometer at frequencies of 128.37, 54.27, and 16.67 MHz, with 16, 10, and 50 μs pulse widths (flip angle ~70°) and 1, 0.01, and 5 s interpulse delays, respectively. The ^{11}B and ^{183}W NMR measurements were done with a high-resolution multinuclear probe head with 10 mm o.d. (3 mL solution volume) sample tubes. ^{17}O NMR spectra were measured on a more sensitive high-power multinuclear probe head, with cylindrical 8 mm o.d. (1.5 mL) horizontal or inclined sample tubes. NMR measurements were carried out with the magnetic field drift compensation of the spectrometer, without ^2H lock. Chemical shifts (δ) were determined relative to aqueous solutions of H_3BO_3 and Na_2WO_4 and to H_2O as external references. For ^{183}W NMR spectra, saturated aqueous solution of HPA $H_4[SiW_{12}O_{40}]$ was used as a secondary standard (with $\delta = -103.65$ ppm).

RESULTS AND DISCUSSION

Characterization of BW Polyanions. Of all BW polyanions, only **BW_{12}** can be unambiguously identified via ^{11}B NMR by a sharp peak at $\delta = -17.4$ ppm, which corresponds to the BO_4 tetrahedron with high symmetry.[24] Anions **B_3W_{39}**, **BW_{11}**, and **BW_{13}** give ^{11}B NMR signals in the same range, which are broadened by the quadrupolar effect (Figure S1 in Supporting Information). The ^{183}W and ^{17}O NMR spectroscopy is more characteristic and was mainly used for detection of these polyanions.

Multinuclear NMR spectroscopy is often the only and the most accurate method of structural characterization of polyoxometalates in solution. Thus, the ^{183}W NMR spectrum of highly symmetric anions $[XW_{12}O_{40}]^{n-}$ ($X = P^V, Si^{IV}, B^{III}$, ...) is a sharp singlet, while lacunary anions $[XW_{11}O_{39}]^{-n-4}$ of C_s symmetry (Figure 1, top) yield spectra with six peaks (of relative intensities ~2:2:2:1:2:2), each with rather weak (~7% of the main line) $^2J_{W-O-W}$ satellites due to coupling with the neighboring ^{183}W atoms. Analysis of the W−W connectivities allows different isomers to be distinguished.[12] But obtaining the separate spectrum of **BW_{11}** turned out to be problematic. A solution, prepared from the K salt of **BW_{11}** (by exchanging K to Na to increase the salt solubility), instead of the expected six ^{183}W NMR peaks gave a complex spectrum of 15 peaks of comparable intensities. As shown further, the solution contained comparable amounts of **BW_{11}** and **BW_{13}** and an admixture of $[W_7O_{24}]^{6-}$, and its spectrum could not be used for identification purposes. To obtain these BW species separately, we studied a number of different BW solutions of low acidity. We applied gradual acidification of Na_2WO_4/H_3BO_3 solutions at low temperature (<30 °C) with subsequent boiling. For concentrated solutions used in the NMR measurements, acidification by electrodialysis is especially important since it allows one to avoid precipitate formation. The solutions at pH > 6 contained different amounts of **BW_{11}**, **BW_{13}**, **BW_{12}**, and $[W_7O_{24}]^{6-}$. Boiling transforms **BW_{13}** to **BW_{12}** but also decreases the content of **BW_{11}**, which sometimes results in a strong signal of **BW_{12}** (up to 80% of the total intensity). After many attempts, we prepared a solution that, according to the ^{183}W NMR spectrum, contained ~15% of all tungsten as **BW_{12}**, ~70% as **BW_{11}**, ~10% as **BW_{13}**, and <5% as heptatungstate. This particular spectrum, shown in Figure 1a, was used for identification of the **BW_{11}** anion. Sharp signals of **BW_{12}** and $[W_7O_{24}]^{6-}$ do not overlap with the rest of the signals and present no great difficulties for analysis of the spectrum. The obtained set of six signals similar to those of heteropolyanions **XW_{11}** ($X = P^{5+}, Si^{4+}, Ga^{3+}$) confirms that it arises from **BW_{11}**. The **BW_{11}** signals are a little broadened, which is evidently due to the chemical exchange with **BW_{13}**. In this spectrum the $^2J_{W-O-W}$ distant satellites are clearly observable and can be used for the peak assignments (Figure S2 in Supporting Information). The sharpest peak with two different large couplings, which indicates the absence of the edge-sharing neighbors, is from the pair of

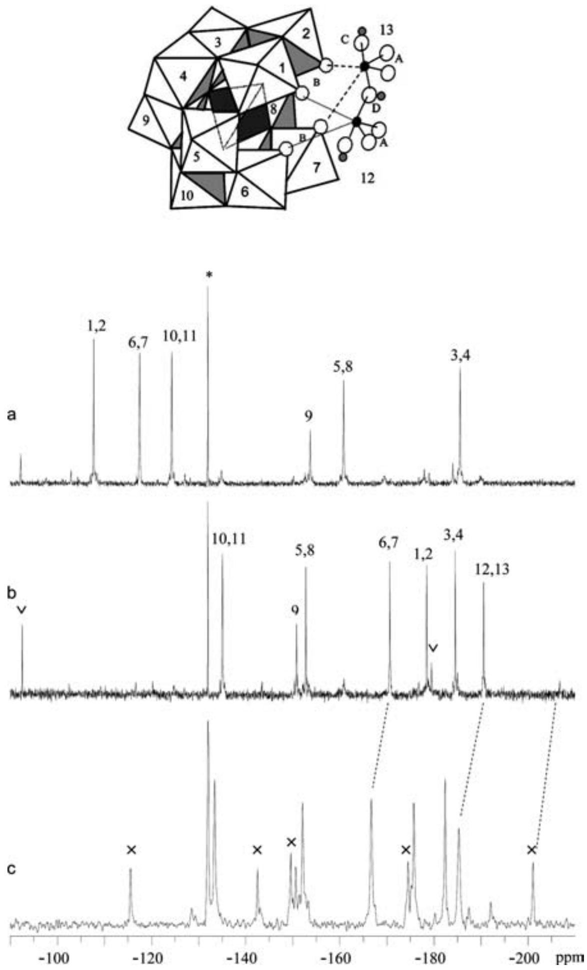

Figure 1. (Top) Polyhedral model of $[BW_{11}O_{39}H]^{8-}$ with attached $\{W_2O_7H_3\}$ fragment (in the ball-and-stick model: white circles, oxygen; black circles, tungsten; gray circles, protons) and ^{183}W NMR spectra of (a) $[BW_{11}O_{39}H]^{8-}$ (electrodialysis, W/B ≈ 4, pH 7), 10 000 scans; (b) $[BW_{13}O_{46}H_3]^{8-}$ (obtained from $\mathbf{B_3W_{39}}$, W/B = 13, pH ~6.5), 13 840 scans; (c) Na_2WO_4/H_3BO_3 (electrodialysis, pH ~4.5, W/B ≈ 4), 14 600 scans. Polyanion concentrations ≈ 0.2 mol/L; (*) signal of $[BW_{12}O_{40}]^{5-}$, (∨) $[W_7O_{24}]^{6-}$, (×) suggested intermediate complex $\mathbf{BW_{11}W}$. Dotted lines show the shift of the signals.

atoms W1,2; the peak that is entirely missing the large couplings is from the pair of atoms W6,7; and the peak having one large coupling coinciding with that of the unique W9 atom is from atoms W10,11. The two remaining peaks having two large couplings are identified from comparing their coupling constants with those of other W atoms as shown in Table 1. The corresponding numbers of unresolved small couplings can be then deduced from the above assignments. The set of large and small couplings thus obtained and the peak assignment correspond to the α-isomer of $\mathbf{BW_{11}}$.[12]

The magnitude of the $^2J_{W-O-W}$ coupling constant depends on the W−O−W bond length and the bridging bond angle. In saturated polyoxoanions, their ranges are ~15−34 Hz for the corner-sharing (bond angle ~150°) W atoms and ~4−7 Hz for the edge-sharing (~120°) W atoms.[12] In lacunary polyoxoanions, much smaller corner couplings (~10 Hz) are observed for W atoms around the vacancy because of the expansion of their trans-bridging bonds. Thus, in $[PW_{11}O_{39}]^{7-}$ the corner couplings for W1,2 are equal to 9.8 and 27.8 Hz.[11e,g] Similarly, in the ^{183}W NMR spectrum of $[BW_{11}O_{39}H]^{8-}$, the corresponding corner couplings are equal to approximately 10.5 and 24.5 Hz (Table 1). Upon filling the vacancy, the normal coupling constants are restored.

Table 1. ^{183}W NMR Parameters for BW Polyanions and Peak Assignments

δ, ppm	large couplings, Hz	corner−edge sharing	tungsten labeling[a]
		$BW_{11}O_{39}H^{8-}$	
−109	24.6, 10.5	2−0	1, 2
−118.8		0−2	6, 7
−125.6	14.8	1−2	10, 11
−155	15	2−2	9
−162.1	24.4, 16.5	2−2	5, 8
−186.9	16.3, 10.5	2−1	3, 4
		$BW_{13}O_{46}H_3^{8-}$	
−135.1	16.4	1−2	10, 11
−150.9	16.1	2−2	9
−152.8	23.2, 17.5	2−2	5, 8
−170.7	12.3	1−2	6, 7
−178.5	22.8, 14.1, 9	3−0	1, 2
−184.5	17.4, 14.2	2−1	3, 4
−190.6	8.7, 12.7	2−0	12, 13
		$BW_{11}O_{39}WO_2^{7-}$[b]	
		−116, −143, −151,3, −176.7, −206 ppm	
		$BW_{12}O_{40}^{5-}$	
		−132 ppm	

[a] Corresponds to Figure 1. [b] Suggested composition.

$\mathbf{BW_{13}}$ can only be obtained in solution. It predominates at pH ~ 4.5−5 in BW solutions prepared by electrodialysis. But the best way for preparing solutions that contain mainly $\mathbf{BW_{13}}$ follows from the scheme of Tézé et al.[5] of hydrolytic conversions of **BW** heteropolyanions. NaOH was added to 0.1 M solution of HPA $\mathbf{B_3W_{39}}$ (pH ~ 0) until the pH reached 5.5−6. Anions $\mathbf{BW_{12}}$ (~20%), $[W_7O_{24}]^{6-}$, and some other species (~10%) were also observed. $\mathbf{BW_{13}}$ was first discovered by polarography, and its composition was determined via pH-metric titration and ultracentrifugation.[5] Also, the structures of three crystalline borotungstates ($\mathbf{B_3W_{39}}$, $\mathbf{BW_{14}}$, and $\mathbf{B_2W_{26}}$), containing $\mathbf{BW_{13}}$ as a fragment, have been investigated by X-ray crystallography.[5,7] The proposed structure of $[H_3BW_{13}O_{46}]^{8-}$ anion, based on the above studies, is presented by Leclerc-Laronze et al.[7] in their Figure 3. Nevertheless, they note that there is a need for more direct structural characterization of $\mathbf{BW_{13}}$, for example, by ^{183}W NMR. Having the individual NMR spectrum of $\mathbf{BW_{13}}$, we checked whether it corresponded to the above model,[7] shown by us schematically in Figure 1. The ^{183}W NMR spectrum, containing seven peaks of relative intensities ~2:1:2:2:2:2:2 (Figure 1 b), confirms the suggestion of $\mathbf{BW_{13}}$ having C_s symmetry. In this spectrum, not only the large but also many small coupling satellites are well observed (Figure S3 in Supporting Information). The peak assignments were made on the basis of the number of corner- and edge-sharing neighbors and the equivalence of the large coupling constants (Table 1). In the spectrum, five peaks of equal intensities and one of half-intensity relate to the $\mathbf{BW_{11}}$ framework. The

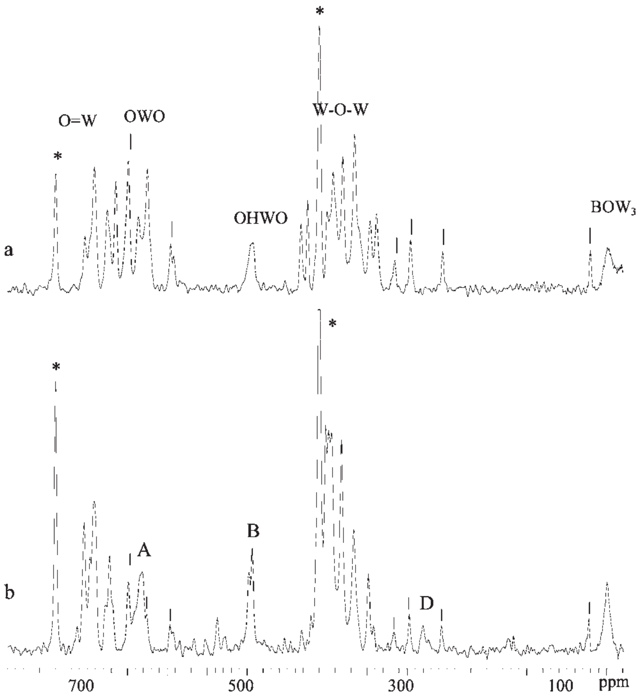

Figure 2. ^{17}O NMR spectra of the same solutions as in Figure 1 a, b: (a) $[BW_{11}O_{39}H]^{8-}$ (pH 7), 240 000 scans; (b) $[BW_{13}O_{46}H_3]^{8-}$ (pH ~6.5), 205 000 scans. Polyanion concentrations ≈ 0.2 mol/L; (*) signal of $BW_{12}O_{40}^{5-}$; (|) signals of $W_7O_{24}^{6-}$. Notations A–D correspond to Figure 1.

seventh peak arises from two W atoms of the attached ditungstic oxo group. As compared with **BW$_{11}$**, additional corner couplings are observed for W1,2 and W6,7 atoms due to the connectivity with W12,13 atoms from the $[W_2O_7]^{2-}$ group. In agreement with the observed splittings, we assigned the signal at −190 ppm to the latter. Small corner coupling values (about 9 and 12 Hz) between W atoms of the **BW$_{11}$** framework and $\{H_3W_2O_7\}$ are due to longer O_B–W12,13 bonds, having terminal O_A atoms in trans position, and consequently longer total bridging bonds (Figure 1).

According to the data of Tézé et al.,[5] the attachment of $[W_2O_7]^{2-}$ to **BW$_{11}$** requires its joining by three protons, $[H_3W_2O_7]^{+}$, which corresponds to the formula of $[BW_{13}O_{46}H_3]^{8-}$. The $\{H_3W_2O_7\}$ group is actually asymmetric, and it would be observed by two separate ^{183}W signals, like similar groups in **B$_3$W$_{39}$**,[6,7] if there was no fast proton exchange. As a result of the exchange, these signals coalesce to a single one that is only a little broader than the rest of the signals.

^{17}O NMR spectroscopy provides important information on polyoxoanion structures.[13–21] Like anions **XW$_{12}$**, anions **XW$_{11}$** are characterized by a typical ^{17}O NMR spectrum determined by the C_s symmetry of the anion. It contains a group of four signals from seven O═W terminal bonds and four signals from eight O_2W *cis*-dioxo terminal bonds, a group of 12 signals from 20 WOW bridges of different types, and a signal from BO_4 tetrahedron, in the corresponding δ ranges.[14] Within the groups, the signals significantly overlap. The observed ^{17}O NMR spectrum of **BW$_{11}$** corresponds to the described type by the set of the signals (Figure 2a, Table 2). The signal from two equivalent *cis*-dioxo terminal O atoms is shifted to lower frequency (δ = 493 ppm). This indicates the lengthening of the corresponding O═W bonds caused by their protonation, which agrees with previously found composition $[BW_{11}O_{39}H]^{8-}$.[5]

According to the ^{183}W NMR spectrum (Figure 1b), the solution of **BW$_{13}$** contains among admixtures a species discussed further as an "intermediate complex". Its content is 7–10 times lower than that of **BW$_{13}$**, and accordingly its ^{17}O NMR spectrum is much weaker and is mostly covered with the groups of stronger signals of **BW$_{13}$** (Figure 2 b), increasing their measured intensity by 10–15%. A weak signal at 167 ppm indicates the impurity SO_4^{2-} (in a trace amount) in **BW$_{13}$**, introduced from **B$_3$W$_{39}$** that had been prepared with H_2SO_4. Assignment of the signals in the spectrum of **BW$_{13}$** follows from intensity considerations and consistency with the composition (Table 2, Figure S4 in Supporting Information), and it is also confirmed by the similarity with spectra of complex polyanions **XW$_{11}$M**.[14] The observed changes as compared to the spectrum of parent **BW$_{11}$** indicate filling the vacancy: the group of signals of terminal O atoms narrows and shifts to high frequency due to the shortening of the O═W bonds, while two overlapping signals of four *cis*-dioxo terminal O_B atoms shift to lower frequencies, which suggests formation of four approximately equivalent $W(n)$–O_B–$W(m)$ bonds between **BW$_{11}$** (n = 1, 2, 6, 7) and $\{W_2O_7H_3\}$ (m = 12, 13) (Figures 1 and 2b). The group of signals of bridging O atoms also becomes narrower upon filling the vacancy, due to the peak shifts to the group center. The intermediate position of signal **B** between the δ ranges of terminal and bridging O atoms indicates asymmetry of the formed bridges with shorter distance O_B–W(1,2,6,7) (<1.85 Å) as compared with a typical length of ~1.9 Å,[25] and accordingly longer bonds O_B–W12,13 having terminal O_A═W bonds in trans position. Signal **A** can be assigned to four *cis*-dioxo terminal O atoms of $\{W_2O_7H_3\}$ on the basis of the ^{17}O NMR chemical shift scale for polyoxometalates (Mo, W) and the relative peak intensities.[15–20] The asymmetry is an inherent characteristics of the $\{W_2O_7H_3\}$ fragment.[5–7] But the asymmetric sequence O═W12–O(H)═W13–O(H$_2$) manifests itself in the ^{17}O and ^{183}W NMR spectra as a symmetric one, HO_C–W12–OH–W13–O_CH (Figure 1), which is due to fast proton exchange in aqueous solutions.[22] According to the averaged HO–W bond length (~1.9 Å), the signal of these two monoprotonated terminal O atoms falls into the range of W–O–W bridges. The signal of atom O_D in bridge $\{W12–O_DH–W13\}$ is expected in the range of 3-fold bridging O atoms. Just in this range we observe a new signal (D) of the appropriate intensity, which can be tentatively assigned to atom O_D. As a whole, the ^{17}O NMR spectrum reflects with full details the oxygen framework of $[BW_{13}O_{46}H_3]^{8-}$ and, together with the seven-line ^{183}W spectrum, confirms both its previously suggested structure and composition.[5] Furthermore, by the line widths, the ^{17}O NMR spectra of **BW$_{11}$** and **BW$_{13}$** correspond to the monomeric forms of these polyanions: dimerization results in the significant line broadening.

Conversions in Solution. We used NMR spectroscopy for monitoring the syntheses and conversions of BW polyanions (Figure 3 and Figure S1 in Supporting Information). In the ^{183}W NMR spectra of solutions containing both **BW$_{11}$** and **BW$_{13}$**, the signals are broadened compared with their individual spectra. More broadened are the signals of atoms W1,2 and W6,7, whose positions in the two spectra differ most of all. This indicates a chemical exchange between the above species, slow-to-intermediate on the NMR time scale.

Solutions of the Na salt of **BW$_{11}$** (pH ~ 7) formed by treatment of $K_8[BW_{11}O_{39}H]$ with $NaClO_4$ contain a mixture

Table 2. ^{17}O NMR Chemical Shifts of Structurally Different O Atoms in BW Polyanions

polyanion	O=W	OWO(H)*	WOW, WOH	W_2OH	W_3OB
$BW_{11}O_{39}H^{8-}$	690(3)[a]	635(2)	431(1), 424(1)		47(4)
	675(2)	624(4)	{400 392 380}(8)		
	663(2)	493*(2)	365(6), 345(2), 338(2)		
$BW_{13}O_{46}H_3{}^{8-}$	704(2)	631(4) A	{497 493}(4) B[b]	280(1) D[c]	49(4)
	692(5)		{402 398 394}(8)		
	672(4)		381(4), 366(4), 348 (2)		
$B_3W_{39}O_{132}H_6{}^{15-}$	770, 752, 739		413, 407[d]		
$BW_{12}O_{40}{}^{5-}$	740(12)		410(24)		49(4)

[a] Number of corresponding O atoms, evaluated from the approximate peak intensities, is given in parentheses. [b] Notations are as in Figures 1 and 2b. [c] Tentative assignment. [d] Reference 6. * Indicates the signal of protonated O atoms.

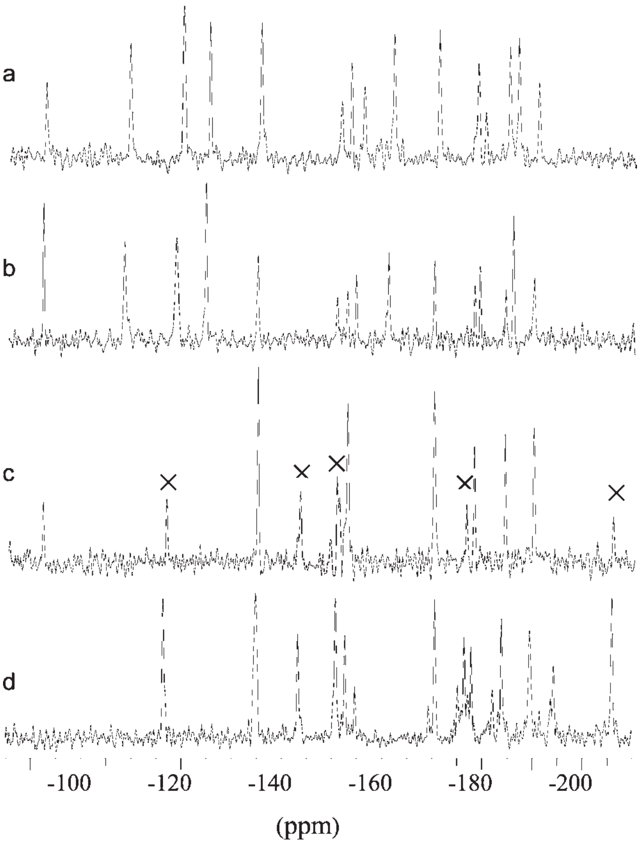

Figure 3. ^{183}W NMR spectra of solutions obtained by exchanging K to Na in $K_8[BW_{11}O_{39}H]$: (a) as prepared, total BW polyanion concentration (C_{BW}) ~ 0.08 mol/L, pH 7, number of scans NS = 16 800; (b) concentrated at 40 °C to ~0.16 mol/L, pH 7.5, NS = 1300; (c) solution acidified with HCl to pH 6, C_{BW} ~ 0.16 mol/L, NS = 680; (d) solution acidified with HCl to pH 5, C_{BW} ~ 0.08 mol/L, NS = 14 300. Solutions contain (a, b) **BW_{11}**, **BW_{13}**, and $[W_7O_{24}]^{6-}$ or (c, d) **BW_{13}** and "**$BW_{11}W$**" (×).

of **BW_{11}**, **BW_{13}**, and $[W_7O_{24}]^{6-}$ (Figure 3a, b). Since these solutions do not contain admixture of **BW_{12}**, they were used for studying the conversion of **BW_{13}** to **BW_{12}** during solution acidification. The set of corresponding ^{183}W NMR spectra is shown in Figure 3. Upon acidification with HCl to pH~ 6, **BW_{11}** disappears completely, and five new weak ^{183}W signals of similar intensities appear. With increasing acidity, the signals of **BW_{13}** shift to higher frequencies and broaden, especially those of atoms W12,13 and then of atoms W1,2 and W6,7 (Figure 1 c). This indicates further protonation of **BW_{13}** and proton exchange processes. At pH ~ 5 the intensities of the two sets of peaks (7 and 5) become comparable. At pH ~ 4, the **BW_{12}** peak appears in the spectrum and gradually increases with time and further acidification. Thus, **BW_{13}** is converted to **BW_{12}** through an intermediate complex. Derived from $[BW_{11}O_{39}W_2O_7H_3]^{8-}$, with its six pairs of equivalent W atoms and corresponding six peaks of equal intensities (and one of half intensity), the intermediate complex has a spectrum of five peaks of equal intensities just as in the $[BW_{11}O_{39}]^{9-}$ framework (and one or two signals of approximately half intensity). The latter is consistent with the presence of a monomeric instead of the dimeric W oxocation in the **BW_{11}** lacuna, but in contrast to the subsequently forming $[BW_{12}O_{40}]^{5-}$ ($\equiv [BW_{11}O_{39}WO]^{5-}$) the 12th W atom is still incompletely incorporated into the polyanion, likely due to an extra O atom linked to it. Most likely, $[H_3W_2O_7]^+$ in **BW_{13}** is at first replaced by $[WO_2]^{2+}$ with formation of a complex $[BW_{11}O_{39}WO_2]^{7-}$ (**$BW_{11}W$**), according to the reaction

$$[BW_{11}O_{39}W_2O_7H_3]^{8-} + 0.5H^+ \rightarrow [BW_{11}O_{39}WO_2]^{7-} + [H_{1.5}WO_4]^{0.5-} + H_2O \quad (1)$$

where $[H_{1.5}WO_4]^{0.5-}$ signifies free tungsten, which further condensates to meta- (or para-) tungstate. For **$BW_{11}W$**, except for five ^{183}W NMR peaks of equal intensity, one or even two peaks of half intensity should be observed. Detection of the two latter peaks might be problematic because of their low intensity and possible overlap with other peaks. However, in the spectrum (Figure 1 c) there are unidentified signals of the appropriate intensity, which might be related to these W atoms. The shift of the peaks of suggested **$BW_{11}W$** with acidity indicates that it is also subject to protonation, which eventually results in removal of the extra O atom and complete conversion into **BW_{12}**:

$$[BW_{11}O_{39}WO_2]^{7-} + 2H^+ \rightarrow [BW_{12}O_{40}]^{5-} + H_2O \quad (2)$$

The two-stage conversion of **BW_{13}** to **BW_{12}**, observed by the ^{183}W spectra, is evidently rather slow, like many other interconversions of polytungstates. Under conditions of slow electrochemical acidification to pH_o 2−3.5 and subsequent boiling, an 80% yield of **BW_{12}** was achieved. Under strong and fast acidification, condensation into **B_3W_{39}** appears to be more favorable.[5]

$\mathbf{B_3W_{39}}$ is unstable in concentrated solutions of the HPA $H_{21}[B_3W_{39}O_{132}]$ (≥ 0.05 M, pH $\sim$ 0). With aging for several days, precipitates of tungstic acid appear, and the NMR signal of $H_5[BW_{12}O_{40}]$ is detected, evidently corresponding to the reaction

$$H_{15}[B_3W_{39}O_{132}H_6] \rightarrow 3H_5[BW_{12}O_{40}] + 3H_2O \cdot WO_3 \quad (3)$$

In essence, this reaction is similar to summary conversion, eqs 1 and 2, leading to the ejection of extra tungsten and to formation of $\mathbf{BW_{12}}$. This conversion, delayed because of faster formation of $\mathbf{B_3W_{39}}$ at strong acidity, is nevertheless completed by decomposition of the latter to the same ingredients, which is accelerated at higher temperatures. Crystalline $H_{21}[B_3W_{39}O_{132}] \cdot nH_2O$, stored for several months, also gave precipitates on dissolving. The acidic sodium salt $H_{17}Na_4[B_3W_{39}O_{132}] \cdot H_2SO_4 \cdot xH_2O$ was more stable.[6] Upon reaction with NaOH, $\mathbf{B_3W_{39}}$ decomposes into $\mathbf{BW_{13}}$, which is converted further to $\mathbf{BW_{12}}$ or $\mathbf{BW_{11}}$, depending on the acidity.

Being more stable than $\mathbf{B_3W_{39}}$ in strongly acidic solutions (pH $\sim$ 0), $[BW_{12}O_{40}]^{5-}$, formed at pH< 5, shows rather high stability to alkaline hydrolysis (pH $\leq$ 7.5 at $[\mathbf{BW_{12}}] \geq 0.1$ M) as compared with $[PW_{12}O_{40}]^{3-}$ (pH $\leq$1.5) and $[SiW_{12}O_{40}]^{4-}$ (pH $\leq$ 4), which is explained by its higher anionic charge.[14,23,26] Similarly, the stability ranges of the corresponding lacunary polyanions shift to higher pH with increase in their charges: $\sim$ 4−7 for $[PW_{11}O_{39}]^{7-}$ and $\sim$5−8 for $[SiW_{11}O_{39}]^{8-}$.[14,27,28] $[BW_{11}O_{39}H]^{8-}$ exists at pH 6−8 and only in the protonated state. Contrary to the PW and SiW systems, polyanions of the 1:9 series ("$\mathbf{BW_9}$") are not formed at all.[5]

On the basis of the observation that $\mathbf{BW_{11}}$, in contrast to $\mathbf{PW_{11}}$, did not convert directly to the Keggin polyanion (α-$\mathbf{BW_{12}}$) upon reaction with WO_4^{2-}, it was suggested that $\mathbf{BW_{11}}$ is not the α-isomer.[5] However, as shown above, the ^{183}W NMR spectrum observed for $\mathbf{BW_{11}}$ is typical of the α-$\mathbf{XW_{11}}$ structure. It should be noted also that the incorporation of tungsten into $\mathbf{PW_{11}}$ to form $\mathbf{PW_{12}}$ (= $\mathbf{PW_{11}} \cdot WO^{4+}$) is not a direct reaction either: it proceeds in the range of pH $\approx$ 1.5−3.5 through intermediate complexes of $\mathbf{PW_{11}}$ with oxocations WO_2^{2+}, giving rise to a wide variety of, mainly unidentified, PW species observed by ^{31}P NMR spectroscopy.[14] $\mathbf{PW_{12}}$ is produced with almost 100% yield directly from $[W_7O_{24}]^{6-}$ and H_3PO_4 ([W] = 1 M, W/P $\approx$ 12) in the course of electrodialysis from pH 6 to 2, while in the mixture $\mathbf{PW_{11}}$ + W under the same conditions only $\leq$75% of $\mathbf{PW_{11}}$ is converted into $\mathbf{PW_{12}}$, the rest being converted into $[P_2W_{21}O_{71}(H_2O)_3]^{6-}$.[29] In solution, free tungsten occurs in the polymerized forms, mainly as stable metatungstate anion, while the required WO^{4+} is quite unlikely in solution. It can form only after joining to $\mathbf{PW_{11}}$ of at least dioxocation WO_2^{2+} that does not exist as such either but can arise for a short time during different conversions of tungstate polyanions. Like other Keggin polyanions, in which the stoichiometry of the WO framework corresponds to WO_3, $\mathbf{BW_{12}}$ requires for its formation rather high acidity, while $\mathbf{BW_{11}}$ exists at pH > 6. That is why $\mathbf{BW_{11}}$ cannot convert directly into $\mathbf{BW_{12}}$ and forms instead intermediate complex $\mathbf{BW_{11}W_2}$, which accommodates a highly charged polyanion to increasing acidity. This occurs through condensation on $\mathbf{BW_{11}}$ of two WO_4^{2-} ions just in the pH range of their condensation into $[W_7O_{24}]^{6-}$.[5,7] Moderate further acidification results in a stepwise conversion $\mathbf{BW_{11}W_2} \rightarrow \mathbf{BW_{11}W} \rightarrow \mathbf{BW_{12}}$, while strong acidification results in condensation of $\mathbf{BW_{11}}$ and intermediate polyanions into various peculiar structures, especially in the presence of third components.

CONCLUSIONS

The results of our ^{17}O and ^{183}W NMR studies confirm the existence in solution of monomeric polyanions $[BW_{13}O_{46}H_3]^{8-}$ and α-$[BW_{11}O_{39}H]^{8-}$. In addition, an intermediate complex was observed during conversion of $\mathbf{BW_{13}}$ to $\mathbf{BW_{12}}$. A composition of $[BW_{11}O_{39} \cdot WO_2]^{7-}$ for this complex and a likely stepwise mechanism for the conversion $\mathbf{BW_{11}} \rightarrow \mathbf{BW_{12}}$ have been suggested. In our opinion, B^{III} as the central atom gives rise to the peculiarities of the BW interaction, mainly owing to the higher negative charge of the typical polyanions $\mathbf{BW_{12}}$ and $\mathbf{BW_{11}}$, which shifts their stability ranges to lower acidity. Accordingly, the occurrence of the unprotonated $\mathbf{BW_{11}}$ and then $\mathbf{BW_9}$ polyanions could be expected only at pH $\geq$ $\sim$9, which lies beyond the range of the tungstate polycondensation and, consequently, is not possible. Thus, $\mathbf{BW_{11}}$ turns out to be the only lacunary derivative of $\mathbf{BW_{12}}$, and as a result BW complexes produced by acidification of weakly acidic or alkaline solutions, in contrast to PW system, are not so numerous and have a tungsten to central atom ratio $\geq$ 11.

ASSOCIATED CONTENT

S **Supporting Information.** ^{11}B, ^{183}W, and ^{17}O NMR spectra of different borotungstate solutions. This material is available free of charge via the Internet at http://pubs.acs.org.

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