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Heteropolymetalate Clusters of the Subvalent Main Group Elements Bi^{III} and Sb^{III} ||

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The heteropolyanions [Bi₂W₂₂O₇₄(OH)₂]¹²⁻ (**1**) and [X₂W₂₀M₂O₇₀(H₂O)₆]⁽¹⁴⁻²ⁿ⁾⁻ (X = Sb³⁺, Bi³⁺; Mⁿ⁺ = Fe³⁺, Co²⁺, Zn²⁺) (**2–7**) have been synthesized as alkali metal and ammonium salts, respectively, and characterized by elemental analysis, infrared spectroscopy, and X-ray crystallography. These tungsto bismutates and antimonates reveal one common feature: the trivacant β -B-XW₉O₃₃ Keggin fragment as the structural building unit. Formally, the unit can be derived from the Keggin structure by removing one trimetalate fragment, W₃O₁₃, and a 60° rotation of one of the remaining W₃O₁₃ subunits around the X–OW_{3X} bond vector (the subscript indicates the element(s) bonded). The unshared pair of electrons of the respective central, pyramidally coordinated heteroatom Sb^{III} or Bi^{III} prevents formation of the complete spherical structure. In the presented heteropolyanions **1–7**, two β -B-XW₉O₃₃ units are connected by two WO₂ groups. Further stabilization of this hitherto unknown bis-decatungsto ion [X₂W₂₀O₇₀]¹⁴⁻ is reached either by addition of two formal *fac*-WO₃ anti-Lipscomb's rule units to give the bis-undecatungsto bismutate [Bi₂W₂₂O₇₄(OH)₂]¹²⁻ (**1**) or by addition of two Mⁿ⁺(H₂O)₃ groups (Mⁿ⁺ = Fe³⁺, Co²⁺, Zn²⁺) forming the large, transition-metal-substituted heteropolyanion clusters [X₂W₂₀M₂O₇₀(H₂O)₆]⁽¹⁴⁻²ⁿ⁾⁻ (X = Sb³⁺, Bi³⁺; Mⁿ⁺ = Fe³⁺, Co²⁺, Zn²⁺) (**2–7**).

Introduction

Early transition metal–oxygen anion clusters are a large and rapidly growing class of compounds.^{1,2} They often have utility in catalysis, medicine, and material science, owing to their unusual properties.^{1,3,4} At present, more than 70 different elements have been reported as constituents of heteropolyanions. Polyoxometalates containing the subvalent main group atoms Sb^{III}, Bi^{III}, and As^{III} as heteroatoms reveal interesting structural properties, and there are a growing number of publications concerning this field. Heteropolymetalates with As^{III} have been extensively investigated, and several compounds, e.g. [KAs₄W₄₀-Co₂O₁₄₀(H₂O)₂]²³⁻ and [As₂W₂₁O₆₉(H₂O)]⁶⁻, have been reported.⁵ In contrast, little is known about the compositions and

structures of heteropolytungstates with Sb^{III} and Bi^{III}.⁶ Formerly, undecatungsto antimonates and bismutates, their electrochemical properties, and their reactions with transition-metal cations have been described.⁷ As a completion of our latest work on the systematic synthesis of large Sb^{III} containing heteropolyanions [SbW₉O₃₃]⁹⁻, [Na₂Sb₈W₃₆O₁₃₂(H₂O)₄]²²⁻, and [Sb₂W₂₂O₇₄(OH)₂]¹²⁻,^{8,9} we herein report the structures of another seven compounds composed of the structural building unit β -B-XW₉O₃₃ (X = Sb^{III}, Bi^{III}) as a common feature. A comparative description of the following fully characterized compounds is given in detail: the bis-undecatungsto bismutate Na₁₂[Bi₂W₂₂O₇₄(OH)₂]¹²⁻·44H₂O (**1**) and the related transition-metal-substituted bis-decatungsto bismutates Na₁₀[Bi₂W₂₀Co₂O₇₀(H₂O)₆]¹⁴⁻·41H₂O (**2**), K₃Na₇[Bi₂W₂₀Zn₂O₇₀(H₂O)₄]¹⁴⁻·23H₂O (**3**), Na₄(NH₄)₆[Bi₂W₂₀Zn₂O₇₀(H₂O)₆]¹⁴⁻·38H₂O (**4**), and [N(CH₃)₄]₅[Bi₂W₂₀Fe₂O₇₀(H₂O)₆]¹⁴⁻·17H₂O (**5**), and antimonates (NH₄)₁₀[Sb₂W₂₀Co₂O₇₀(H₂O)₆]¹⁴⁻·13H₂O (**6**) and K₆NaH[Sb₂W₂₀Fe₂O₇₀(H₂O)₆]¹⁴⁻·29H₂O (**7**). Compound **2** was synthesized independently at Babes-Bolyai University, Romania, and its structure was determined separately at Georgetown University, USA. After realization of the overlap, the decision to publish jointly was made subsequently. The Georgetown determination will be referred to as compound **2a**.

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|| Dedicated to Professor Edgar Niecke on the occasion of his 60th birthday.

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Experimental Section

Synthesis. All chemicals were used without further purification.

Na₁₂[Bi₂W₂₂O₇₄(OH)₂]₂·44H₂O (1). A 15.00 g (45.47 mmol) amount of Na₂WO₄·2H₂O was dissolved in 50 mL water, and 20 mL of 4 M NaOAc/HOAc buffer solution was added. The mixture was heated to 100 °C, and 1.26 g (4.13 mmol) of BiONO₃·H₂O was dissolved in 5 mL of concentrated HNO₃ (65%). After addition of 10 mL of H₂O, the bismuth-containing solution was added dropwise to the tungstate solution. The resulting mixture was heated for 2 h (95 °C). The product crystallized within 48 h as colorless plates. Yield: 4.8 g (0.72 mmol, 35%). Atomic ratios calcd for Na₁₂[Bi₂W₂₂O₇₄(OH)₂]₂·44H₂O: Na, 6; Bi, 1; W, 12. Found: Na, 6.4; Bi, 1; W, 11.8. Elemental anal. (%) calcd: 12.01 H₂O. Found: 12.37 H₂O. IR (cm⁻¹, KBr pellet, polyoxoanion region 1000–700 cm⁻¹): 951 s, 863 s, 796 vs, 645 s.

Na₁₀[Bi₂W₂₀Co₂O₇₀(H₂O)₆]₂·41H₂O (2, 2a). Na₁₂[Bi₂W₂₂O₇₄(OH)₂]₂·44H₂O (1) (2.00 g, 0.29 mmol) was dissolved in 20 mL of H₂O. A solution of 0.138 g (0.58 mmol) of CoCl₂·H₂O in 5 mL of H₂O was added dropwise. The reaction mixture was stirred for 30 min (70 °C). Pink crystals of Na₁₀[Bi₂W₂₀Co₂O₇₀(H₂O)₆]₂·41H₂O (2) were obtained within 2 days. Yield: 1.39 g (0.22 mmol, 73%). Atomic ratios calcd for Na_{8.88}[Co_{1.72}Bi₂W_{20.28}O₇₀(H₂O)₆]₂·41H₂O, i.e. the disordered Bi₂W₂₂ and Bi₂W₂₂Co₂, vide infra: Na, 5.16; Bi, 1.16; W, 11.79; Co, 1. Found: Na, 4.9; Bi, 1; W, 11.9; Co, 1.1. Elemental anal. (%) calcd: 13.19 H₂O. Found: 12.98 H₂O. IR (cm⁻¹, KBr pellet, polyoxoanion region 1000–700 cm⁻¹): 946 s, 822 vs, 797 vs, 748 s, 646 s.

K₃Na₇[Bi₂W₂₀Zn₂O₇₀(H₂O)₄]₂·23H₂O (3). A 4.40 g portion of Na₂WO₄·2H₂O (13.34 mmol) was dissolved in 20 mL of H₂O and 0.7 mL of HNO₃ (concentrated) and heated to 75 °C while stirring. After 5 min, a second solution that was heated to 75 °C and containing 0.485 g (1.63 mmol) of BiONO₃·H₂O in 0.7 mL of HNO₃ (concentrated) and 10 mL of H₂O was added dropwise. The yellow precipitate of tungstic acid that occurred during the addition dissolved quickly. To avoid lowering the pH, 0.3 g of Na₂CO₃ were simultaneously added in individual portions. Then a hot solution (75 °C) of 0.852 g (3.11 mmol) of ZnSO₄·7H₂O in 5 mL of H₂O was slowly added. The colorless reaction mixture was stirred for 1 h at 75 °C allowed to cool, and 0.06 g (0.8 mmol) of KCl was added. After several days, colorless crystals of K₃Na₇[Bi₂W₂₀Zn₂O₇₀(H₂O)₄]₂·23H₂O (3) suitable for X-ray analysis were obtained. Yield: 1.7 g (0.42 mmol, 51%). Atomic ratios calcd for K₃Na₇[Bi₂W₂₀Zn₂O₇₀(H₂O)₄]₂·23H₂O: Na, 3.5; K, 1.5; Zn, 1.0; Bi, 1.0; W, 10.0. Found: Na, 3.9; K, 1.3; Zn, 0.7; Bi, 0.8; W, 10. Elemental anal. (%) calcd: 11.98 H₂O. Found: 12.14 H₂O. IR (cm⁻¹, KBr pellet, polyoxoanion region 1000–700 cm⁻¹): 946 s, 822 s, 758 s, 645 m.

Na₄(NH₄)₆[Bi₂W₂₀Zn₂O₇₀(H₂O)₆]₂·38H₂O (4). Na₁₂[Bi₂W₂₂O₇₄(OH)₂]₂·44H₂O (1) (2.00 g, 0.29 mmol) was dissolved in 20 mL of H₂O. A solution of 0.167 g (0.58 mmol) of ZnSO₄·7H₂O in 5 mL of H₂O was added dropwise. The reaction mixture was stirred for 30 min (70 °C), and 0.06 g (1.1 mmol) of NH₄Cl was added. Colorless needlelike crystals of Na₄(NH₄)₆[Bi₂W₂₀Zn₂O₇₀(H₂O)₆]₂·38H₂O (4) were obtained within 2 days. Yield: 1.16 g (0.18 mmol, 62%). Atomic ratios calcd for Na₄(NH₄)₆[Bi₂W₂₀Zn₂O₇₀(H₂O)₆]₂·38H₂O: Na, 2; Bi, 1; W, 10; Zn, 1. Found: Na, 2.2; Bi, 1; W, 10.2; Zn, 1.3. Elemental anal. (%) calcd: 1.33 N; 10.80 H₂O. Found: 1.40 N; 10.99 H₂O. IR (cm⁻¹, KBr pellet, polyoxoanion region 1000–700 cm⁻¹): 946 s, 825 vs, 759 s, 643 s.

[N(CH₃)₄]₃H₃[Bi₂W₂₀Fe₂O₇₀(H₂O)₆]₂·17H₂O (5). A 5.04 g portion of 1 was suspended in 4.5 mL of H₂O. A solution of 0.59 g (1.7 mmol) of Fe(NO₃)₃·9H₂O in 1.5 mL of water was added dropwise. The resulting pH value of the slightly cloudy mixture was 1.2. The solution was heated to 65 °C for 10 min and allowed to cool, and then 1 g of N(CH₃)₄Cl dissolved in 10 mL water was added. The pale green precipitate obtained was dissolved by adding 90 mL of 0.05 M HCl and heating the solution. The mixture was filtered, and the product crystallized during cooling. Yield: 3.14 g (0.56 mmol, 73%). Atomic ratios calcd for [N(CH₃)₄]₃H₃[Bi₂W₂₀Fe₂O₇₀(H₂O)₆]₂·17H₂O: Bi, 1; W, 10; Fe, 1. Found: Bi, 1.1; W, 10.8; Fe, 1.2. Elemental anal. (%) calcd: 3.94 C; 1.79 H; 1.30 N; 7.71 H₂O. Found: 3.93 C; 1.78 H; 1.15 N; 7.68 H₂O. IR (cm⁻¹, KBr pellet, polyoxoanion region 1000–700 cm⁻¹): 947 s, 870 s, 843 s, 790 vs, 735 vs.

(NH₄)₁₀[Sb₂W₂₀Co₂O₇₀(H₂O)₆]₂·13H₂O (6). One gram (0.159 mmol) of (NH₄)₁₂H₂[Sb₂W₂₂O₇₆]₂·27H₂O prepared according to the literature⁷

was suspended in 20 mL of H₂O. After 2.7 mL of a 0.1 M Co(NO₃)₂·6H₂O solution, was added, the mixture was heated to 60 °C. The pH was adjusted to 7 with aqueous NH₃ (concentrated) solution. Within several hours, a pink precipitate was obtained and recrystallized in 80 mL of water. The crystalline product was obtained as pink plates after several days. Yield: 0.65 g (0.114 mmol, 72%). Atomic ratios calcd for (NH₄)₁₀[Sb₂W₂₀Co₂O₇₀(H₂O)₆]₂·13H₂O: Sb, 1; W, 10; Co, 1. Found: Sb, 1.2; W, 10.3; Co, 1.2. Elemental anal. (%) calcd: 2.38 N; 5.47 H₂O. Found: 2.47 N; 5.73 H₂O. IR (cm⁻¹, KBr pellet, polyoxoanion region 1000–700 cm⁻¹): 940 s, 825 sh vs, 805 vs, 755 s.

K₆NaH[Sb₂W₂₀Fe₂O₇₀(H₂O)₆]₂·29H₂O (7). The sodium salt of [Sb₂W₂₂O₇₆]¹⁴⁻ (5.1 g, 0.80 mmol) prepared according to the literature⁷ was suspended in 5 mL of H₂O. A solution of 0.6 g (1.49 mmol) of Fe(NO₃)₃·9H₂O in H₂O (1.5 mL) was slowly added to the stirred mixture. After the yellow-green colored solution was heated (10 min, 70 °C), it was cooled in an ice bath. The potassium salt was precipitated by adding 0.5 g of KCl dissolved in 2 mL of H₂O. Single crystals suitable for X-ray structural analysis were obtained by adding 40 mL of 0.05 M HCl and heating the reaction mixture to 90 °C. The filtered solution was allowed to cool slowly. The product crystallized within 24 h. Yield: 3.3 g (0.54 mmol, 68%). Atomic ratios calcd for K₆NaH[Sb₂W₂₀Fe₂O₇₀(H₂O)₆]₂·29H₂O: Na, 1; K, 6; Sb, 2; W, 20; Fe, 2. Found: Na, 1.0; K, 5.9 Sb, 2.2; W, 20.0; Fe, 2.6. Elemental anal. (%) calcd: 10.28 H₂O. Found: 10.37 H₂O. IR (cm⁻¹, KBr pellet, polyoxoanion region 1000–700 cm⁻¹): 955 s, 875 sh vs, 805 vs, 745 s.

Instrumentation and Analytical Procedures. IR spectra were performed on a Perkin-Elmer 683 spectrometer as KBr pellets. The atomic ratios of the heavy elements were determined by energy-dispersive X-ray fluorescence analysis (EDAX). The elemental C, H, and N content was determined with an elemental analyzer Hewlett-Packard Scientific model 185. The content of water was determined thermogravimetrically in Mikroanalytisches Labor Pascher, Remagen-Bandorf, Germany.

Crystal Structure Determination. Diffraction experiments were performed on a STOE IPDS (for 1–4), a Syntex P2₁ diffractometer (for 5–7), and a Siemens SMART CCD (for 2a) with MoK α radiation (0.710 73 Å) and with corrections for absorption (numerical for 1 and 2, empirical for 2a and 3–7), Lorentz, and polarization effects. The structures of 1, 2, 2a, and 4 were solved by direct methods with the program SHELXS97 and refined (on *F*²) with SHELXL97 by full-matrix least squares (solution and refinement (on *F*²) of 3 and 5–7 with the programs SHELXS86 and SHELXL93, respectively). Almost all of the eight crystal structures exhibit the appearance, typical for polyoxometalates, of disorder in the range of counterions and water molecules. Especially in the cases of 3–5 and 7, the poor crystal quality, extreme deterioration by easy loss of crystal water, and a pronounced degree of disorder in the cationic part of crystal lattice prevent a more precise structural analysis. This also refers to some rather high residual electron densities. However, it should be stated that none of these deficiencies affects the structural details and reliability of the anionic structures. The exact formulas were determined by elemental analysis. Details of data collection, processing, structure analysis, and refinement of 1–7 are summarized in Table 1.

Results and Discussion

Common Structural Feature: β -B-XW₉. The fundamental common feature of the sandwich-like tungstate clusters 1–7 is represented by the trivacant β -B-XW₉O₃₃ unit (Figure 1). Formally, the unit can be derived from the Keggin structure by removing one W₃O₁₃ fragment. The unshared pair of electrons of the respective heteroatoms Sb^{III} and Bi^{III} prevents formation of the complete spherical structure. The trivacant unit consists of three edge-sharing W₃O₁₃ groups with central Sb^{III} and Bi^{III} and can be derived from the α -form by a 60° rotation of one of the remaining W₃O₁₃ subunits around the X–OW_{3X} bond vector (The subscripted letters indicate the elements bonded.) The X^{III} atom in the center is surrounded pyramidally by three oxygen atoms; the top of the pyramid is formed by the lone pair of the

Table 1. Crystallographic Data for $\text{Na}_{12}[\text{Bi}_2\text{W}_{22}\text{O}_{74}(\text{OH})_2]\cdot 44\text{H}_2\text{O}$ (**1**), $\text{Na}_{10}[\text{Bi}_2\text{W}_{20}\text{Co}_2\text{O}_{70}(\text{H}_2\text{O})_6]\cdot 41\text{H}_2\text{O}$ (**2, 2a**), $\text{K}_3\text{Na}_7[\text{Bi}_2\text{W}_{20}\text{Zn}_2\text{O}_{70}(\text{H}_2\text{O})_4]\cdot 23\text{H}_2\text{O}$ (**3**), $\text{Na}_4(\text{NH}_4)_6[\text{Bi}_2\text{W}_{20}\text{Zn}_2\text{O}_{70}(\text{H}_2\text{O})_6]\cdot 38\text{H}_2\text{O}$ (**4**), $[\text{N}(\text{CH}_3)_4]_5\text{H}_3[\text{Bi}_2\text{W}_{20}\text{Fe}_2\text{O}_{70}(\text{H}_2\text{O})_6]\cdot 17\text{H}_2\text{O}$ (**5**), $(\text{NH}_4)_{10}[\text{Sb}_2\text{W}_{20}\text{Co}_2\text{O}_{70}(\text{H}_2\text{O})_6]\cdot 13\text{H}_2\text{O}$ (**6**), $\text{K}_6\text{NaH}[\text{Sb}_2\text{W}_{20}\text{Fe}_2\text{O}_{70}(\text{H}_2\text{O})_6]\cdot 29\text{H}_2\text{O}$ (**7**)^a

	1	2	2a	3	4	5	6	7
<i>M</i> , g mol ⁻¹	6749.28	6418.48	6417.32	6074.33	6338.62	6114.77	5681.08	6042.37
space group	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 1̄	<i>P</i> 2 ₁ / <i>n</i>	<i>C</i> 2/ <i>c</i>	<i>P</i> 2 ₁ / <i>n</i>
<i>a</i> , Å	12.999(3)	12.903(3)	12.583(1)	12.852(3)	12.757(3)	13.592(5)	20.744(3)	17.995(9)
<i>b</i> , Å	25.389(5)	25.142(5)	26.497(1)	17.512(4)	15.002(3)	19.286(5)	15.474(2)	11.976(5)
<i>c</i> , Å	16.279(3)	16.230(3)	12.811(1)	18.908(4)	16.139(3)	21.237(5)	26.158(5)	22.080(12)
α , deg					68.43(3)			
β , deg	98.36(3)	94.53(3)	93.01(1)	91.99(3)	89.85(3)	93.09(3)	90.60(1)	112.57(3)
γ , deg					66.86(3)			
<i>V</i> , Å ³	5316(2)	5249(2)	4265(1)	4253(2)	2605(2)	5559(3)	8396(2)	4394(4)
<i>Z</i>	2	2	2	2	4	2	4	2
<i>d</i> _{calcd} , Mg m ⁻³	4.22	4.03	4.97	4.72	4.04	3.64	4.49	4.60
μ , mm ⁻¹	27.17	25.89	31.92	31.91	25.94	24.104	28.413	27.405
<i>T</i> , K	213(2)	293(2)	173(2)	293	213(2)	293(2)	293(2)	293(2)
<i>R</i> 1 (>2 σ (<i>I</i>))	0.0596	0.0549	0.0530	0.0855	0.0878	0.0776	0.0504	0.0962
<i>wR</i> 2	0.1665	0.1335	0.1080	0.2087	0.2122	0.1600	0.1209	0.2521
<i>R</i> 1 (all data)	0.0748	0.0639	0.0750	0.1196	0.1245	0.1242	0.0765	0.1109
<i>wR</i> 2	0.1740	0.1389	0.1160	0.2383	0.2465	0.1803	0.1343	0.2644
weighting factors ^b								
<i>g</i>	0.1026	0.0554		0.1110	0.1361	0.0493	0.0724	0.2104
<i>h</i>	287.60	214.27		261.35	0.0	68.38	264.23	0.0

^a $R = \sum ||F_o| - |F_c|| / \sum |F_o|$. $wR2 = \{\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]\}^{1/2}$. $GOF = \{\sum [w(F_o^2 - F_c^2)^2] / (n - p)\}^{1/2}$. ^b Weighting scheme: $1/w = [\sigma^2(F_o^2) + (gP)^2 + hP] / P$ with $P = ((\max(F_o, 0))^2 + 2F_c^2)/3$.

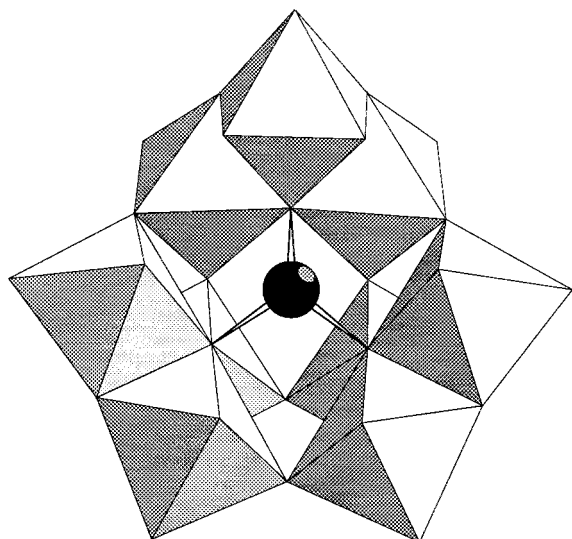


Figure 1. Polyhedral plot of the structural building unit β -B-[XW_9O_{33}].

respective X^{III} atom. The $\text{X}-\text{O}_{\text{W}3\text{X}}$ bond lengths and angles within the Bi and the Sb containing compounds **1–7** are very similar and shown in Table 2. The *fac*- WO_3 group of the β -B- XW_9O_{33} with the three strongly basic oxygen atoms offers sites for further polymerization¹⁰ or direct protonation to obey Lipscomb's rule. In **1–7**, two β -B- XW_9O_{33} units are formally connected by two WO_2 groups to the dimeric structures, resulting in the hitherto unknown bis-decatungstate $[\text{X}_2\text{W}_{20}\text{O}_{70}]^{14-}$. Further stabilization can be reached either by the addition of two *fac*- WO_3 anti-Lipscomb's rule units at pH 4.5 to give the bis-undecatungsto bismutate and antimonate $[\text{Bi}_2\text{W}_{22}\text{O}_{74}(\text{OH})_2]^{12-}$ (**1**) and $[\text{Sb}_2\text{W}_{22}\text{O}_{74}(\text{OH})_2]^{12-}$,⁷ respectively, or by addition of two $\text{M}^{n+}(\text{H}_2\text{O})_3$ groups ($\text{M}^{n+} = \text{Fe}^{3+}$, Co^{2+} , Zn^{2+}) (**2–7**). The octahedral coordination sphere of each transition metal is completed by two oxygen atoms of one and one oxygen atom of the second XW_9O_{33} unit. In comparison with the $[\text{X}_2\text{W}_{22}\text{O}_{74}-$

$(\text{OH})_2]^{12-}$ anion, the *fac*- WO_3 groups have been exchanged for transition-metal ions with three aquo ligands.

$\text{Na}_{12}[\text{Bi}_2\text{W}_{22}\text{O}_{74}(\text{OH})_2]\cdot 44\text{H}_2\text{O}$ (1**)** The sodium bis-undecatungsto bismutate $\text{Na}_{12}[(\text{WO}_2(\text{OH}))_2(\text{WO}_2)_2(\text{BiW}_9\text{O}_{33})_2]\cdot 44\text{H}_2\text{O}$ was obtained by reaction of $\text{Na}_2\text{WO}_4\cdot 2\text{H}_2\text{O}$ and $\text{BiONO}_3\cdot \text{H}_2\text{O}$ in stoichiometric amounts at pH 4.5. Compound **1** crystallizes in the space group *P*2₁/*n* with two formula units per unit cell. For details of structural analysis, refer to the Experimental Section and Table 1.

The $[\text{Bi}_2\text{W}_{22}\text{O}_{74}(\text{OH})_2]^{12-}$ anion consists of two identical β -B- $\text{BiW}_9\text{O}_{33}$ units, which are connected by two WO_2 and two WO_2OH groups. Figure 2 shows a ball-and-stick diagram of the anion; the unit cell is given in Figure 5. During the refinement five of the six Na atoms could be located. The sixth Na atom found in the elemental analysis is probably disordered. For electroneutrality and according to the chemical analysis, there must be another two protons. The bond lengths within the anion do not indicate any hydroxo group, except within the WO_3 groups bridging the dimer, each with three facial terminal oxygen atoms. The $\text{W}-\text{O}_t$ bond lengths are 1.74, 1.81, and 1.92 Å, which are rather long for $\text{W}=\text{O}$ double bonds. Therefore, it is suggested that the bond length of 1.92 Å corresponds to a protonated $\text{W}-\text{OH}$ group with some disorder of the proton between the other two oxygen atoms. Additionally, these results are supported by the analogous $[\text{Sb}_2\text{W}_{22}\text{O}_{74}(\text{OH})_2]^{12-}$ anion that reveals the same bonding conditions.^{7,8} For relevant bond lengths and angles of **1**, see Table 2. Recently, Jeannin and Rodewald published the quite similar compound $\text{Na}_{10}[\text{Bi}_2\text{W}_{22}\text{O}_{70}(\text{OH})_6]\cdot 31\text{H}_2\text{O}$.¹¹ In contrast to **1**, the anion shows two units of each three facial $\text{W}-\text{OH}$ groups. The authors favor this six times

(10) Schreiber, P.; Wieghardt, K.; Nuber, B.; Weiss, J. *Polyhedron* **1989**, *8*, 1675.

(11) Rodewald, D.; Jeannin, Y. *C. R. Acad. Sci., Paris* **1998**, *t.1*; *Série II* c, 175.

(12) In equivalent two-step reactions, we recently have isolated the Bi^{III} -containing anions $[\text{Bi}_2\text{W}_{20}\text{M}_2\text{O}_{70}(\text{H}_2\text{O})_6]^{(14-2n)-}$ ($\text{M}^{2+} = \text{Cu}, \text{Ni}$). ($\text{Na}_3\text{-(NH}_4)_7[\text{Bi}_2\text{W}_{20}\text{Ni}_2\text{O}_{70}(\text{H}_2\text{O})_6]\cdot 31\text{H}_2\text{O}$: $a = 12.787(3)$ Å, $b = 15.050(3)$ Å, $c = 16.155(3)$ Å, $\alpha = 68.42(3)^\circ$, $\beta = 89.40(3)^\circ$, $\gamma = 66.47(3)^\circ$. $\text{K}_2\text{Na}_6\text{H}_2[\text{Bi}_2\text{W}_{20}\text{Cu}_2\text{O}_{70}(\text{H}_2\text{O})_6]\cdot 34\text{H}_2\text{O}$: $a = 12.943(4)$ Å, $b = 13.447(4)$ Å, $c = 16.948(4)$ Å, $\alpha = 83.45(2)^\circ$, $\beta = 72.91(2)^\circ$, $\gamma = 64.25(2)^\circ$.)

(13) Bösing, M.; Nöh, A.; Loose, I.; Krebs, B. *J. Am. Chem. Soc.* **1998**, *120*, 7252.

Table 2. Selected Bond Lengths (Å) and Angles (deg) of $\text{Na}_{12}[\text{Bi}_2\text{W}_{22}\text{O}_{74}(\text{OH})_2] \cdot 44\text{H}_2\text{O}$ (**1**), $\text{Na}_{10}[\text{Bi}_2\text{W}_{20}\text{Co}_2\text{O}_{70}(\text{H}_2\text{O})_6] \cdot 41\text{H}_2\text{O}$ (**2**, **2a**), $\text{K}_3\text{Na}_7[\text{Bi}_2\text{W}_{20}\text{Zn}_2\text{O}_{70}(\text{H}_2\text{O})_4] \cdot 21\text{H}_2\text{O}$ (**3**), $\text{Na}_4(\text{NH}_4)_6[\text{Bi}_2\text{W}_{20}\text{Zn}_2\text{O}_{70}(\text{H}_2\text{O})_6] \cdot 38\text{H}_2\text{O}$ (**4**), $[\text{N}(\text{CH}_3)_4]_3[\text{Bi}_2\text{W}_{20}\text{Fe}_2\text{O}_{70}(\text{H}_2\text{O})_6] \cdot 17\text{H}_2\text{O}$ (**5**), $(\text{NH}_4)_{10}[\text{Sb}_2\text{W}_{20}\text{Co}_2\text{O}_{70}(\text{H}_2\text{O})_6] \cdot 13\text{H}_2\text{O}$ (**6**), $\text{K}_6\text{NaH}[\text{Sb}_2\text{W}_{20}\text{Fe}_2\text{O}_{70}(\text{H}_2\text{O})_6] \cdot 29\text{H}_2\text{O}$ (**7**) with Standard Deviations

	1	2	2a	3	4	5	6	7
W–O ^a	1.67(2)–1.74(2)	1.70(1)–1.74(1)	1.70(1)–1.74(1)	1.65(2)–1.84(3)	1.68(3)–1.76(3)	1.63(3)–1.76(3)	1.70(1)–1.74(2)	1.70(2)–1.74(2)
W–OH	1.81(2)–1.92(2)					1.91(2)		
W–O ^b	1.75(2)–2.22(2)							
W–O ^c		1.80(1)–2.15(1)	1.83(1)–2.14(1)	1.81(2)–2.11(2)	1.74(3)–2.21(3)	1.77(3)–2.19(3)	1.80(1)–2.15(1)	1.76(2)–2.18(2)
W–O ^d		1.76(1)–1.79(1)	1.76(1)–1.80(1)	1.73(2)–1.81(2)	1.75(3)–1.78(3)	1.78(2)–1.94(3)	1.75(1)–1.83(2)	1.78(2)–1.84(2)
W–O ^e		2.19(1)–2.30(1)	2.20(1)–2.31(1)	2.19(2)–2.32(2)	2.18(2)–2.32(2)	2.19(2)–2.34(2)	2.24(1)–2.34(1)	2.20(2)–2.37(2)
X–O ^f		2.13(1)–2.15(1)	2.13(1)–2.17(1)	2.07(2)–2.16(2)	2.13(2)–2.16(2)	2.08(2)–2.12(2)	1.99(2)–2.02(2)	2.00(2)–2.02(3)
M–O ^g		2.06(1)–2.09(1)	2.05(1)–2.15(1)	1.99(3)–2.20(2)	2.05(2)–2.07(2)	1.96(3)–2.00(3)	2.04(1)–2.11(1)	1.92(2)–1.95(2)
M–O ^h		2.04(2)–2.11(1)	1.97(1)–2.10(1)	2.06(3)–2.20(2)	2.06(2)–2.08(2)	2.04(3)–2.08(3)	2.06(2)–2.11(2)	2.04(3)–2.08(2)
O–W–O ^{is}		73(1)–105(1)	72(1)–104(1)	71(1)–104(1)	69(1)–106(1)	72(1)–107(2)	72(1)–105(1)	72(1)–104(1)
O–W–O ^{trans}		155(1)–173(1)	155(1)–173(1)	156(1)–175(1)	153(1)–174(1)	156(2)–179(1)	155(1)–176(1)	153(2)–174(2)
O–X–O		84(1)–88(1)	84(1)–88(1)	83(1)–87(1)	84(1)–88(1)	85(1)–87(2)	85(1)–92(1)	89(1)–92(2)

^a t = terminal. ^b The subscripted letters indicate the element(s) bonded M = Co, Fe; X = Sb, Bi. ^c Ow = water.

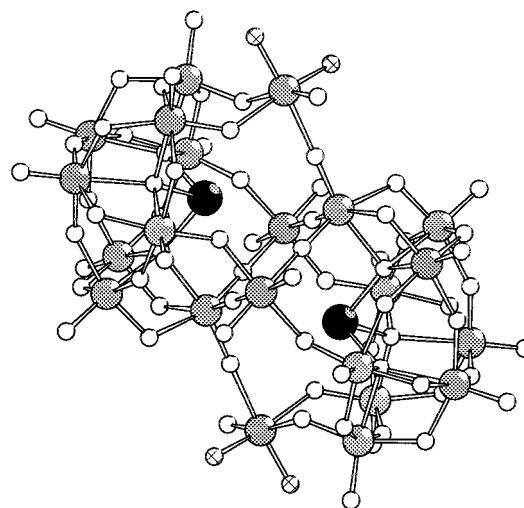


Figure 2. Structure of the bis-undecatungsto bismutate $[\text{Bi}_2\text{W}_{22}\text{O}_{74}(\text{OH})_2]^{12-}$ (W = light gray, Bi = black, O = white, OH = white, stripped).

protonated anion because of the unusual lengths of the relevant terminal W–O bonds (1.93, 1.94, and 1.99 Å). It should be noted that protonation of terminally bonded oxygen atoms is quite unusual, especially the protonation of three facial bonded oxygen atoms. Just as in the structure of **1** the coordination of water molecules and disorder between water and protons cannot be completely excluded as the reason for the rather long W–O_t bonds. In these cases, electroneutrality could also be reached by hydronium ions in the network of crystal water and counterions.

Na₁₀[Bi₂W₂₀Co₂O₇₀(H₂O)₆]·41H₂O (2, 2a). Crystalline cobalt-substituted sodium bis-decatungsto bismutate $\text{Na}_{10}[\text{Bi}_2\text{W}_{20}\text{Co}_2\text{O}_{70}(\text{H}_2\text{O})_6] \cdot 41\text{H}_2\text{O}$ (**2**, **2a**) was obtained by addition of Co^{2+} salts to $[\text{Bi}_2\text{W}_{22}\text{O}_{74}(\text{OH})_2]^{12-}$ solutions. The sodium salt crystallizes in the space group $P2_1/n$ with two formula units per unit cell. Details of the structural analysis are in the Experimental Section and Table 1.

Within the $[\text{Bi}_2\text{W}_{20}\text{Co}_2\text{O}_{70}(\text{H}_2\text{O})_6]^{10-}$ anion, further stabilization of the hypothetical $[\text{X}_2\text{W}_{20}\text{O}_{70}]^{14-}$ is effected by coordination of two $\text{Co}(\text{H}_2\text{O})_3$ groups. As summarized in Table 2, there are no unusual bond lengths in the structure of **2**. The $[\text{Bi}_2\text{W}_{20}\text{M}_2\text{O}_{70}(\text{H}_2\text{O})_6]^{(14-2n)-}$ anion is shown in Figure 3. During refinement, disorder involving the metal atoms became evident. The correct formula of **2** is $\text{Na}_{(10-4x)}[\text{Bi}_2\text{W}_{(20+x)}\text{Co}_{(2-x)}\text{O}_{70}(\text{H}_2\text{O})_6] \cdot 41\text{H}_2\text{O}$ with $x = 0.28$. The original (nondisorder model) displacement parameters U of the Co atom were unusually small apparently from a small amount of W in the Co site. Refinement of a disorder model resulted in occupancies of 86% Co and 14% W. Likewise, the occupation parameters of the Na sites were refined resulting in 4.44 Na per asymmetric unit agreeing with electroneutrality. The structure of **2** consists of disordered $[\text{Bi}_2\text{W}_{20}\text{Co}_2\text{O}_{70}(\text{H}_2\text{O})_6]^{10-}$ and $[\text{Bi}_2\text{W}_{22}\text{O}_{76}]^{12-}$ units. These results were essentially confirmed with only a slight variation in the amount of disorder found by a separate X-ray structural measurement on **2a** at Georgetown University. This type of disorder was not detected in the other structures reported herein.

K₃Na₇[Bi₂W₂₀Zn₂O₇₀(H₂O)₄]·23H₂O (3) and Na₄(NH₄)₆[Bi₂W₂₀Zn₂O₇₀(H₂O)₆]·38H₂O (4). The mixed sodium and potassium salt of the zinc-substituted bis-decatungsto bismutate $[\text{Bi}_2\text{W}_{20}\text{Zn}_2\text{O}_{70}(\text{H}_2\text{O})_4]^{10-}$ was crystallized by reacting $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$, $\text{BiONO}_3 \cdot \text{H}_2\text{O}$, and $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ in an acidified solution. In analogy to the preparation of **2**, the mixed sodium and ammonia salt was synthesized by direct reaction of $[\text{Bi}_2\text{W}_{22}\text{O}_{74}]^{12-}$

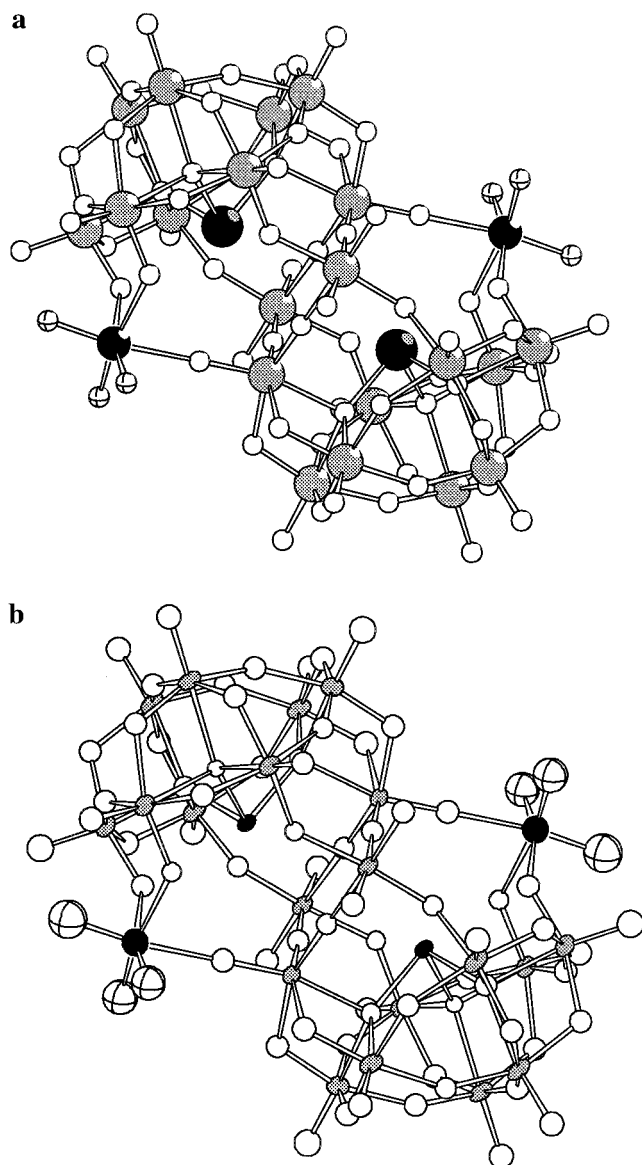


Figure 3. (a) Structure of the transition-metal-substituted bis-decatungsto bismutates and antimonates $[M_2X_2W_{20}O_{76}(H_2O)_6]^{12-}$. (b) Thermal vibrational ellipsoids drawn at 40% probability level (W = light gray, X = black, M = dark gray, O = white, OH₂ = white, stripped).

(OH)₂]¹²⁻ and ZnSO₄·7H₂O. Compound **3** crystallizes in the space group $P2_1/n$; **4** in $P\bar{1}$. The unit cell of **3** is shown in Figure 5. For details of the crystal structure determinations, see the Experimental Section and Table 1. Both anionic structures consist of each two identical β -B-BiW₉O₃₃ units connected by two WO₂ units and two octahedrally coordinated Zn²⁺ ions. The structure of **4** is rather similar to that of the Co-containing compound **2** with two Zn(H₂O)₃ groups stabilizing the monomeric [Bi₂W₂₀O₇₀]¹⁴⁻ fragments. In contrast to this, **3** reveals a two-dimensional polymeric structure in which the monomeric [Bi₂W₂₀Zn₂O₇₀(H₂O)₄]¹⁰⁻ anions are connected to layers by Zn—O—W bridges. The corresponding bond lengths are 2.20(2) Å (Zn—O) and 1.73(2) Å (W—O). The Zn—O—W angle is 138(1)°. The octahedral coordination sphere of both Zn²⁺ ions is completed by each two water molecules, two oxygen of one and one oxygen atom of the other β -B-BiW₉O₃₃ unit. Figure 4 shows a part of one layer lying parallel to the *a*,*c*-plane of the unit cell.

[N(CH₃)₄]₅H₃[Bi₂W₂₀Fe₂O₇₀(H₂O)₆]₁₇H₂O (**5**). Crystalline iron-substituted tetramethyl ammonia bis-decatungsto bismutate

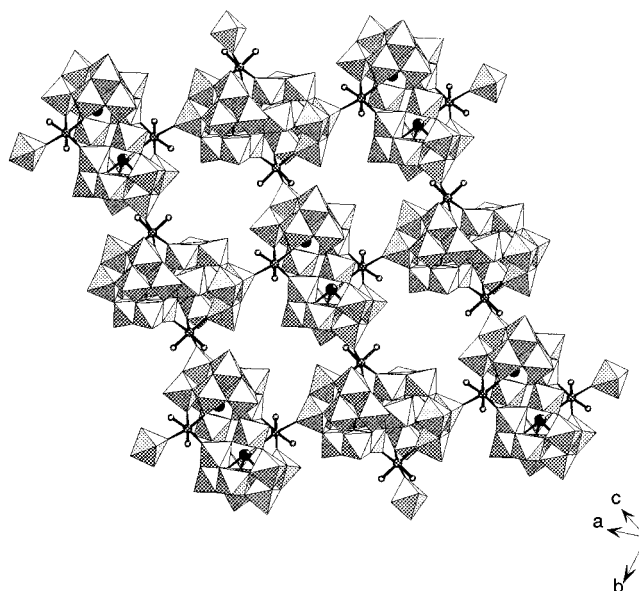


Figure 4. Polyhedral plot of the two-dimensional polymeric [Bi₂W₂₀Zn₂O₇₀(H₂O)₄]¹⁰⁻ anion.

[N(CH₃)₄]₅H₃[Bi₂W₂₀Fe₂O₇₀(H₂O)₆]₁₇H₂O (**5**) may be obtained by reacting stoichiometric amounts of Fe(NO₃)₃·9H₂O and **1** in an acidified aqueous solution (pH 1.3) followed by addition of Me₄NCl. Compound **5** crystallizes in the space group $P2_1/n$. For details of the crystal structure determinations, see the Experimental Section and Table 1. The structure of the [Bi₂W₂₀Fe₂O₆₈(OH)₂(H₂O)₆]⁶⁻ is closely related to the above-described Co- and Zn-containing compounds, except that two of the terminal oxygen atoms are protonated. Apart from the five tetramethyl cations, there is evidence for another three protons. Chemical analysis and potentiometric titrations support this result. Two protons are probably in terminally bonded hydroxo groups localized at the WO₂ group, connecting the two β -B-BiW₉O₃₃ units of the anion. This is suggested by the rather long bond length of the relevant W—O bond (1.92 Å). As in **1**, the presence of terminal hydroxo groups is unusual. The third proton might be disordered or present as a hydronium ion since there are no clear indications in the structure for a third localized hydroxo group. Relevant bond length and angles in the structure of **5** are listed in Table 2.

(NH₄)₁₀[Sb₂W₂₀Co₂O₇₀(H₂O)₆]₁₃H₂O (**6**) and K₆NaH[Sb₂W₂₀Fe₂O₇₀(H₂O)₆]₂₉H₂O (**7**). Single crystals of the cobalt and iron derivatives of the bis-decatungsto antimonates (NH₄)₁₀[Sb₂W₂₀Co₂O₇₀(H₂O)₆]₁₃H₂O (**6**) and K₆NaH[Sb₂W₂₀Fe₂O₇₀(H₂O)₆]₂₉H₂O (**7**) can be obtained by reaction of stoichiometric amounts of [Sb₂W₂₂O₇₄(OH)₂]¹²⁻ with Fe(NO₃)₃·9H₂O and Co(NO₃)₂, respectively. Details of the crystal structural analysis are given in the Experimental Section and Table 1. The unit cell of **6** is shown in Figure 5, omitting crystal water and counterions. Both anionic structures consist of each two identical β -B-SbW₉O₃₃ units with the Sb^{III} atom located in the centers. The two subunits are linked together by corner-sharing WO₆ octahedra. Further stabilization is effected by the two cobalt (iron) atoms bonded to one oxygen atom of one and two oxygen atoms of the other unit. Again, the coordination sphere of the transition metals is completed by three aquo ligands. In analogy to the Bi-containing homologues, the [Sb₂W₂₀O₇₀]¹⁴⁻ anion formally functions as a ligand for W^{VI} in the course of which the latter can be replaced by transition-metal ions due to their similar ionic radii. As expected, there are no significant differences between the antimony- and bismuth-containing

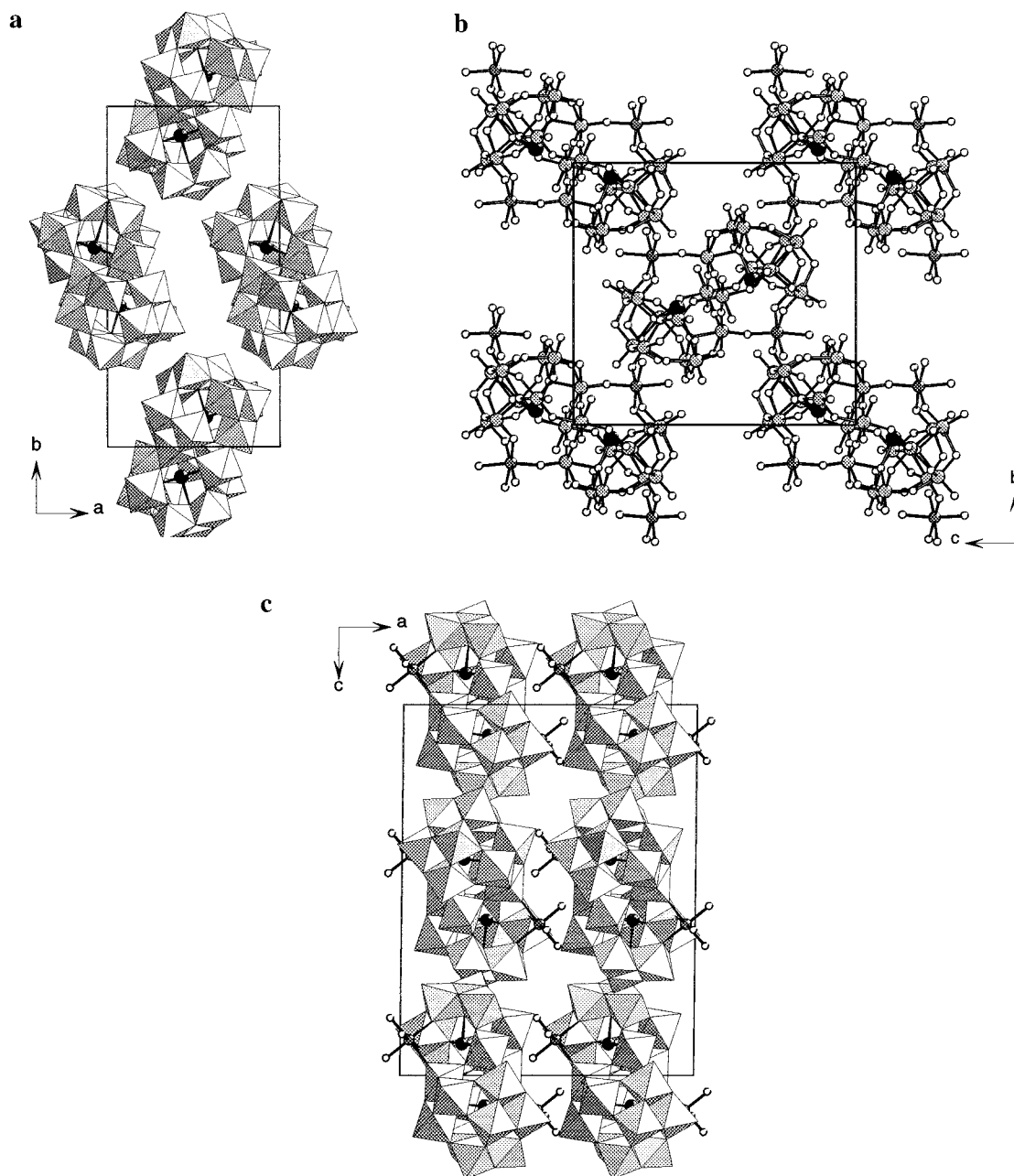


Figure 5. Selected examples of packing diagrams: (a) $\text{Na}_{12}[\text{Bi}_2\text{W}_{22}\text{O}_{72}(\text{OH})_2] \cdot 44\text{H}_2\text{O}$ (**1**); (b) $\text{K}_3\text{Na}_7[\text{Bi}_2\text{W}_{20}\text{Zn}_2\text{O}_{70}(\text{H}_2\text{O})_4] \cdot 23\text{H}_2\text{O}$ (**3**); (c) $(\text{NH}_4)_{10}[\text{Sb}_2\text{W}_{20}\text{Co}_2\text{O}_{70}(\text{H}_2\text{O})_6] \cdot 13\text{H}_2\text{O}$ (**6**). Counterions and water molecules are omitted for better clarity.

$[\text{Sb}_2\text{W}_{20}\text{M}_2\text{O}_{70}(\text{H}_2\text{O})_6]$ and $[\text{Bi}_2\text{W}_{20}\text{M}_2\text{O}_{70}(\text{H}_2\text{O})_6]$ anionic structures. Relevant bond lengths and angles are summarized in Table 2.

Strategy of Preparation. Complex and largely unknown reaction mechanisms make a straightforward reaction route of heteropolyanion syntheses difficult. The present sandwich-like clusters **1–7** were synthesized by means of a strategy based on a general idea described in detail by our group⁸ and can be summarized as follows: The suitable method is founded on production of highly negatively charged intermediates joined to further the stabilization by electrophilic protection groups or polycondensation reactions. The preparation of the bis-undecatungsto antimonate⁸ and bismutate (**1**) succeeded by in situ formation and stabilization of the $\beta\text{-B-XW}_9\text{O}_{33}$ subunit. In aqueous solution, the equilibrium between α - and β -species of the B-XW_9 anion can be shifted toward the β -type in acidic

medium. The resulting *fac*- WO_3 group offers sites for further polymerization because of the more strongly basic oxygen atoms. After direct protonation and condensation reactions with further tungstate, the hypothetical $[\text{X}_2\text{W}_{20}\text{O}_{20}]^{14-}$ intermediate probably stabilizes in situ by addition of two *fac*- WO_3 groups forming the bis-undecatungsto bismutate **1** or by addition of two $\text{Zn}(\text{H}_2\text{O})_3$ fragments to give **3**. In contrast, the remaining transition-metal-substituted clusters **2** and **4–7** reveal examples of a second conceivable route, which consists of two-step reaction containing first the preparation of the bis-undecatungsto bismutate **1** or antimonate, respectively, and afterward the exchange reaction of both outer tungsten atoms by transition-metal centers executed separately. Although different routes of reaction were used, the common goal of dimerization of the $\beta\text{-B-XW}_9\text{O}_{33}$ lacunar fragments by a belt of four metal centers is achieved. Beyond, the polymeric sandwich cluster **3** clearly displays the strong effects of lowering the pH, the way of

establishing the acid intensity, and the order of adding the reactants on the degree of condensation. This structural consequence reveals the sensitiveness of the equilibrium present in aqueous solution of heteropolytungstates. Certainly, one should not forget additional concentration effects. It has to be noted that the herein presented use of the straightforward strategy can of course be applied for incorporation of other 3d transition metals.¹²

Outlook. The Bi-containing heteropolytungstates $[\text{Bi}_2\text{W}_{22}\text{O}_{74}(\text{OH})_2]^{12-}$ and especially the transition-metal-substituted $[\text{X}_2\text{W}_{20}\text{M}_2\text{O}_{70}(\text{H}_2\text{O})_6]^{(14-n)-}$ presented herein not only constitute struc-

turally interesting compounds but also open up possibilities for catalytic oxidation reactions.¹³ At present, the possibilities of these applications are under intensive investigation by our group.

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Supporting Information Available: X-ray crystallographic files, in CIF format, are available. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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