Synthesis and Characterization of Copper-, Zinc-, Manganese-, and Cobalt-Substituted Dimeric Heteropolyanions, $[(\alpha\text{-}XW_9O_{33})_2M_3(H_2O)_3]^{n-}$ ($n = 12$, X = As^{III}, Sb^{III}, M = Cu^{2+}, Zn^{2+}; $n = 10$, X = Se^{IV}, Te^{IV}, M = Cu^{2+}) and $[(\alpha\text{-}AsW_9O_{33})_2WO(H_2O)M_2(H_2O)_2]^{10-}$ (M = Zn^{2+}, Mn^{2+}, Co^{2+})†

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Received February 5, 2001

Interaction of the lacunary $[\alpha\text{-}XW_9O_{33}]^{9-}$ (X = As^{III}, Sb^{III}) with Cu^{2+} and Zn^{2+} ions in neutral, aqueous medium leads to the formation of dimeric polyoxoanions, $[(\alpha\text{-}XW_9O_{33})_2M_3(H_2O)_3]^{12-}$ (M = Cu^{2+}, Zn^{2+}; X = As^{III}, Sb^{III}), in high yield. The selenium and tellurium analogues of the copper-containing heteropolyanions are also reported: $[(\alpha\text{-}XW_9O_{33})_2Cu_3(H_2O)_3]^{10-}$ (X = Se^{IV}, Te^{IV}). The polyanions consist of two $[\alpha\text{-}XW_9O_{33}]$ units joined by three equivalent Cu^{2+} (X = As, Sb, Se, Te) or Zn^{2+} (X = As, Sb) ions. All copper and zinc ions have one terminal water molecule resulting in square-pyramidal coordination geometry. Therefore, the title anions have idealized D_{3h} symmetry. The space between the three transition metal ions is occupied by three sodium ions (M = Cu^{2+}, Zn^{2+}; X = As^{III}, Sb^{III}) or potassium ions (M = Cu^{2+}; X = Se^{IV}, Te^{IV}) leading to a central belt of six metal atoms alternating in position. Reaction of $[\alpha\text{-}AsW_9O_{33}]^{9-}$ with Zn^{2+}, Co^{2+}, and Mn^{2+} ions in acidic medium (pH = 4−5) results in the same structural type but with a lower degree of transition-metal substitution, $[(\alpha\text{-}AsW_9O_{33})_2WO(H_2O)M_2(H_2O)_2]^{10-}$ (M = Zn^{2+}, Co^{2+}, Mn^{2+}). All nine compounds are characterized by single-crystal X-ray diffraction, IR spectroscopy, and elemental analysis. The solution properties of $[(\alpha\text{-}XW_9O_{33})_2Zn_3(H_2O)_3]^{12-}$ (X = As^{III}, Sb^{III}) were also studied by ^{183}W-NMR spectroscopy.

Introduction

Polyoxometalates are metal−oxygen cluster species that exhibit a fascinating variety of structures and properties including catalysis, materials science, and medicine.[1−4] Usually, polyoxoanions are formed in aqueous, acidic medium through condensation reactions. Although the synthetic conditions can be amazingly simple, the mechanism of formation of polyoxometalates is not well understood and commonly described as self-assembly. Usually, it is not possible to design a multistep synthetic sequence with its associated conditions, unlike in organic chemistry. As a result, novel polyoxometalates are frequently reported as having "unexpected" or "unusual" structures and properties. It can be concluded that design of novel polyoxometalates and derivatization of known polyoxometalates remain a challenge.

The existence of As^{III}-, Sb^{III}-, and Bi^{III}-containing polyoxotungstates has been known for a long time.[5] Because the lone pair of electrons on the heteroatom does not allow the closed Keggin unit to form, the geometries of these products could not be easily predicted. However, the structures of some species have been elucidated, e.g., $[NH_4As_4W_{40}O_{140}Co_2(H_2O)_2]^{23-}$, $[As_2W_{21}O_{69}(H_2O)]^{6-}$, $[As_4W_{20}O_{72}(H_2O)_2]^{12-}$, $[H_2AsW_{18}O_{60}]^{7-}$, $[AsW_8O_{30}AsOH]^{7-}$, $[NaW_{21}Sb_9O_{86}]^{18-}$, $[Na_2Sb_8W_{36}O_{132}(H_2O)_4]^{22-}$, $[Sb_2W_{22}O_{74}(OH)_2]^{12-}$, $[Bi_2W_{22}O_{74}(OH)_2]^{12-}$.[6] Most of these polyoxoanions consist of oligomeric (predominantly di- or tetrameric) adducts of incomplete Keggin units joined together by extra W or X^{III} (X = As, Sb) atoms.

Robert et al. structurally characterized the potassium salt of another example of an As^{III} containing polyoxometalate, $[As_2W_{18}Cu_3O_{66}(H_2O)_2]^{12-}$.[7] They identified a sandwich-type structure with three Cu^{2+} ions linking two $[\alpha\text{-}AsW_9O_{33}]^{9-}$ units. Surprisingly, the three copper ions were not equivalent because

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† This article is dedicated to Professor Yves Jeannin (Université Pierre et Marie Curie, Paris) on the occasion of his retirement.

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10.1021/ic0101477 CCC: $20.00

of a difference in their coordination geometry. The authors identified a glide of one AsW_9 subunit with respect to the other which they explained to be a result of lone-pair/lone-pair repulsion of the two As^{III} atoms.

Because we were interested whether the same structural type could be formed from different heteroatoms and different first-row transition metals, we studied this system in some detail.

Experimental Section

Synthesis. $Na_9[\alpha\text{-}AsW_9O_{33}]\cdot 19.5H_2O$ and $Na_9[\alpha\text{-}SbW_9O_{33}]\cdot 19.5H_2O$ were synthesized according to published procedures, and their purity was confirmed by infrared spectroscopy.[6g,8] All other reagents were used as purchased without further purification.

$Na_{12}[As_2W_{18}Cu_3O_{66}(H_2O)_3]\cdot 32H_2O$ (1). A 1.2 g (6.8 mmol) sample of $CuCl_2\cdot 2H_2O$ was dissolved in 50 mL of H_2O, and then, 10.0 g (4.1 mmol) of $Na_9[\alpha\text{-}AsW_9O_{33}]\cdot 19.5H_2O$ was added. The solution was refluxed for 1 h and filtered after it cooled (pH 6.2). Slow evaporation at room temperature led to large green crystals suitable for X-ray diffraction. The potassium salt of the polyanion can also be isolated in high yield by precipitation of the above solution with solid KCl (15 g). This resulted in 10.1 g of greenish product, which was isolated and air-dried (yield 89%). IR: 956, 904, 873, 785, 750, 735, 503, 472, 405 cm^{-1}. Anal. Calcd (Found) for $Na_{12}[As_2W_{18}Cu_3O_{66}(H_2O)_3]\cdot 32H_2O$: Na 4.92 (4.55), W 58.96 (59.95), Cu 3.40 (3.44), As 2.67 (2.80).

$Na_{12}[Sb_2W_{18}Cu_3O_{66}(H_2O)_3]\cdot 46H_2O$ (2). A 1.0 g (5.8 mmol) sample of $CuCl_2\cdot 2H_2O$ was dissolved in 50 mL of H_2O, and then, 10.0 g (3.5 mmol) of $Na_9[\alpha\text{-}SbW_9O_{33}]\cdot 19.5H_2O$ was added. The solution was refluxed for 1 h and filtered after it cooled (pH 6.2). Slow evaporation at room temperature led to large green crystals. The potassium salt of the polyanion can also be isolated in high yield by precipitation of the above solution with solid KCl (15 g). This resulted in 9.8 g of greenish product, which was isolated and air-dried (yield 97%). IR: 965, 944, 891, 858, 772, 732, 504, 475, 438 cm^{-1}. Anal. Calcd (Found) for $Na_{12}[Sb_2W_{18}Cu_3O_{66}(H_2O)_3]\cdot 41H_2O$: Na 4.7 (5.2), W 56.4 (56.2), Cu 3.3 (3.5), Sb 4.1 (3.7).

$Na_{10}[As_2W_{18}Zn_3O_{66}(H_2O)_3]\cdot 51H_2O$ (3). A 0.92 g (6.7 mmol) sample of $ZnCl_2$ was dissolved in 50 mL of H_2O, and then, 10.0 g (4.1 mmol) of $Na_9[\alpha\text{-}AsW_9O_{33}]\cdot 19.5H_2O$ was added. The solution was refluxed for 1 h and filtered after it cooled (pH 6.6). Slow evaporation at room temperature led to large colorless crystals. The potassium salt of the polyanion can also be isolated in high yield by precipitation of the above solution with solid KCl (15 g). This resulted in 9.5 g of white product, which was isolated and air-dried (yield 83%). IR: 950, 895, 865, 792, 754, 731, 505, 459, 403 cm^{-1}. Anal. Calcd (Found) for $Na_{12}[As_2W_{18}Zn_3O_{66}(H_2O)_3]\cdot 51H_2O$: Na 4.6 (3.9), W 55.5 (55.7), Zn 3.3 (3.4), As 2.5 (2.6). ^{183}W-NMR (293 K) of $Na_{12}[As_2W_{18}Zn_3O_{66}(H_2O)_3]\cdot 51H_2O$ redissolved in D_2O: δ −101.6 (s, 4W), −110.5 (s, 6W), −137.2 (s, 2W), −142.7 (s, 4W), −157.6 (s, 4W), −164.0 (s, 12W), −174.3 (s, 4W).

$Na_{10}[Sb_2W_{18}Zn_3O_{66}(H_2O)_3]\cdot 48H_2O$ (4). A 0.79 g (5.8 mmol) sample of $ZnCl_2$ was dissolved in 50 mL of H_2O, and then, 10.0 g (3.5 mmol) of $Na_9[\alpha\text{-}SbW_9O_{33}]\cdot 19.5H_2O$ was added. The solution was refluxed for 1 h and filtered after it cooled (pH 6.9). Slow evaporation at room temperature led to large colorless crystals. The potassium salt of the polyanion can also be isolated in high yield by precipitation of the above solution with solid KCl (15 g). This resulted in 8.8 g of white product, which was isolated and air-dried (yield 89%). IR: 963, 942, 895, 881, 854, 780, 736, 507, 461, 437 cm^{-1}. Anal. Calcd (Found) for $Na_{12}[Sb_2W_{18}Zn_3O_{66}(H_2O)_3]\cdot 48H_2O$: Na 4.6 (4.3), W 55.2 (55.4), Zn 3.3 (3.5), Sb 4.1 (3.8). ^{183}W-NMR (293 K) of $Na_{12}[Sb_2W_{18}Zn_3O_{66}(H_2O)_3]\cdot 48H_2O$ redissolved in D_2O: δ −85.3 (s, 4W), −97.0 (s, 6W), −127.6 (s, 2W), −131.7 (s, 4W), −138.5 (s, 4W), −148.1 (s, 12W), −159.8 (s, 4W).

$K_9Na[Se_2W_{18}Cu_3O_{66}(H_2O)_3]\cdot 16H_2O$ (5). A 0.19 g (1.1 mmol) sample of $CuCl_2\cdot 2H_2O$ was dissolved in 40 mL of a sodium acetate buffer (0.5 M, pH 4.8), and then, 0.074 g (0.67 mmol) of SeO_2 and 1.98 g (6.0 mmol) of $Na_2WO_4\cdot 2H_2O$ were added. The solution was heated to 90 °C for 1 h and filtered after it cooled. Addition of solid CsCl (4 g) resulted in 2.0 g of a light-greenish precipitate, which was isolated and air-dried (yield 95%). Single-crystals suitable for X-ray diffraction were obtained as follows: KCl (10 g) was used for precipitation instead of CsCl, and the solid product was isolated and then redissolved in water. Slow evaporation of this solution at room temperature led to light-green crystals. IR: 979, 959, 911, 889, 831, 794, 755, 708, 507, 484, 462, 411 cm^{-1}. Anal. Calcd (Found) for $Cs_9Na[Se_2W_{18}Cu_3O_{66}(H_2O)_3]\cdot 13H_2O$: Na 1.2 (1.1), Cs 15.6 (17.3), W 55.4 (55.3), Cu 3.2 (3.3), Se 2.7 (2.6).

$K_9Na[Te_2W_{18}Cu_3O_{66}(H_2O)_3]\cdot 16H_2O$ (6). A 0.19 g (1.1 mmol) sample of $CuCl_2\cdot 2H_2O$ was dissolved in 40 mL of a sodium acetate buffer (0.5 M, pH 4.8), and then 0.25 g (0.67 mmol) of $Te(NO_3)_4$ and 1.98 g (6.0 mmol) of $Na_2WO_4\cdot 2H_2O$ were added. The solution was heated to 90 °C for 1 h and filtered after it cooled. Addition of solid CsCl (4 g) resulted in 0.6 g of a light-greenish precipitate, which was isolated and air-dried (yield 29%). Single-crystals suitable for X-ray diffraction were obtained as follows: a small amount of a dilute KCl solution was added to the above solution after it cooled. Slow evaporation at room temperature led to light-green crystals. IR: 978, 955, 901, 879, 797, 738, 691, 507, 486, 451, 407 cm^{-1}. Anal. Calcd (Found) for $Cs_8Na_2[Te_2W_{18}Cu_3O_{66}(H_2O)_3]$: Na 0.8 (0.7), Cs 17.8 (19.1), W 55.4 (58.7), Cu 3.2 (3.3), Te 4.3 (3.5).

$Cs_2Na_3[As_2W_{18.7}Zn_{2.3}O_{66}(H_2O)_3]\cdot 23H_2O$ (7). A 0.92 g (6.7 mmol) sample of $ZnCl_2$ was dissolved in 50 mL of a sodium acetate buffer (1.0 M, pH 4.8), and then, 10.0 g (4.1 mmol) of $Na_9[\alpha\text{-}AsW_9O_{33}]\cdot 19.5H_2O$ was added. The solution was heated to 90 °C, kept at this temperature for 1 h, cooled to room temperature, and then filtered. Addition of a dilute CsCl solution and slow evaporation at room temperature led to colorless single crystals suitable for X-ray diffraction. IR: 984, 950, 897, 871, 793, 731, 599, 500, 461 cm^{-1}. Anal. Calcd (Found) for $Cs_2Na_8[(\alpha\text{-}AsW_9O_{33})_2WO(H_2O)Zn_2(H_2O)_2]\cdot 23H_2O$: Cs 4.61 (4.67), Na 3.19 (3.39), W 60.60 (58.05), Zn 2.27 (2.77), As 2.60 (2.70).

$Cs_{1.75}Na_3[As_2W_{18.8}Co_{2.2}O_{66}(H_2O)_3]\cdot 22.5H_2O$ (8). The synthesis of this compound and the method of crystallization were identical to that of **7**, but $CoCl_2\cdot 6H_2O$ (1.59 g) was used instead of $ZnCl_2$. The color of the crystals was green. IR: 975, 949, 894, 877, 795, 733, 600, 505, 464 cm^{-1}. Anal. Calcd (Found) for $Cs_2Na_8[(\alpha\text{-}AsW_9O_{33})_2WO(H_2O)Co_2(H_2O)_2]\cdot 22H_2O$: Cs 4.64 (4.33), Na 3.21 (3.40), W 60.93 (58.60), Co 2.06 (2.03), As 2.61 (2.70).

$Cs_{6.25}Na[As_2W_{18.63}Mn_{2.37}O_{66}(H_2O)_3]\cdot 12.5H_2O$ (9). A 1.44 g (6.7 mmol) sample of $MnBr_2$ was dissolved in 50 mL of a sodium formate buffer (1.0 M, pH 3.9), and then, 10.0 g (4.1 mmol) of $Na_9[\alpha\text{-}AsW_9O_{33}]\cdot 19.5H_2O$ was added. The solution was heated to 90 °C and kept at this temperature for 1 h. After cooling to room temperature, the solution was filtered, and then, solid CsCl was added until a precipitate formed. The solid product was filtered off, and the filtrate was kept in an open container. Slow evaporation at room temperature led to orange single crystals suitable for X-ray diffraction. IR: 972, 946, 906, 875, 793, 732, 602, 509, 467 cm^{-1}. Anal. Calcd (Found) for $Cs_6Na_4[(\alpha\text{-}AsW_9O_{33})_2WO(H_2O)Mn_2(H_2O)_2]\cdot 12H_2O$: W 58.37 (59.45), Mn 1.84 (1.71), As 2.50 (2.68).

For compounds **3**, **4**, and **7**−**9** the number of sodium ions detected by X-ray diffraction is smaller than suggested by elemental analysis. This problem is frequently encountered for sodium salts of polyoxoanions, which usually have a large degree of hydration. At least some of the sodium ions and water molecules tend to be disordered so that the presence of the former is masked. Therefore elemental analysis is instrumental for determination of the correct sodium content of a sample. For all compounds elemental analysis was performed on crystalline samples, with the exception of **5** and **6**. We were not able to obtain sufficient amounts of pure, crystalline sample for these two compounds. The mixed cesium/sodium salts obtained by bulk precipitation were analyzed instead.

Elemental analyses for compounds **1** and **7**−**9** were performed by the Service Central d'Analyse of CNRS at 69390 Vernaison, France. Compounds **2**−**6** were analyzed by Kanti Technologies Inc., Tonawanda, NY. Infrared spectra were recorded on KBr pellets using a Nicolet Avatar spectrophotometer. The ^{183}W-NMR experiments were run on a Bruker AM-300WB spectrometer at Georgetown University.

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All NMR spectra were referenced with an external 2 M Na_2WO_4 standard.

X-ray Crystallography. Crystals were mounted on a glass fiber for indexing and intensity data collection on a Siemens SMART-CCD single-crystal diffractometer using Mo Kα radiation ($\lambda = 0.710\ 73$ Å). Direct methods were used to solve the structure and to locate the tungsten atoms (SHELXS86). Then, the remaining atoms were found from successive difference maps (SHELXL93). Routine Lorentz and polarization corrections were applied to all structures, and an absorption correction was performed using the SADABS program.[9] Crystallographic data are summarized in Table 1.

Results and Discussion

Trisubstituted Structures. The six polyoxoanions, $[(\alpha\text{-}AsW_9O_{33})_2Cu_3(H_2O)_3]^{12-}$, $[(\alpha\text{-}SbW_9O_{33})_2Cu_3(H_2O)_3]^{12-}$, $[(\alpha\text{-}SeW_9O_{33})_2Cu_3(H_2O)_3]^{10-}$, $[(\alpha\text{-}TeW_9O_{33})_2Cu_3(H_2O)_3]^{10-}$, $[(\alpha\text{-}AsW_9O_{33})_2Zn_3(H_2O)_3]^{12-}$, and $[(\alpha\text{-}SbW_9O_{33})_2Zn_3(H_2O)_3]^{12-}$, are isostructural. They consist of two $[\alpha\text{-}XW_9O_{33}]^{9-}$ (X = As^{III}, Sb^{III}, Se^{IV}, Te^{IV}) moieties linked by three Cu^{2+} or Zn^{2+} ions resulting in a sandwich-type structure with idealized D_{3h} symmetry (see Figures 1 and 2). This structural type was first reported by Robert et al. for the potassium salt of diaquatricuprooctadecatungstodiarsenate(III)(12−), $K_{12}[As_2W_{18}Cu_3O_{66}(H_2O)_2]\cdot 11H_2O$ (**1a**).[7] Surprisingly, the three copper ions were not equivalent because only two of them had a terminal water molecule resulting in square-pyramidal coordination, whereas the third Cu^{2+} ion exhibited square-planar coordination. The authors identified a glide of one AsW_9 subunit with respect to the other which they explained to be a result of lone-pair/lone-pair repulsion of the two As^{III} atoms. The symmetry of the anion was reduced to C_s. The synthesis of Robert et al. involved reaction of $Na_2WO_4\cdot 2H_2O$, $NaAsO_2$, and $Cu(NO_3)_2$ in aqueous medium, isolation of the sodium salt, and then conversion to the potassium salt through dissolution and precipitation (five times) with KCl.

When we reacted $Na_9[\alpha\text{-}AsW_9O_{33}]$ with Cu^{2+} ions in aqueous solution, we obtained the sodium salt of $[As_2W_{18}Cu_3O_{66}(H_2O)_2]^{12-}$ in crystalline form and high yield. Single-crystal X-ray diffraction of this material showed the expected dimeric polyanion, but careful examination of the structure allowed us to identify significant differences between our sodium salt and the potassium salt of Robert et al. Interestingly, the title compound $Na_{12}[As_2W_{18}Cu_3O_{66}(H_2O)_3]\cdot 32H_2O$ (**1**) exhibits three equivalent Cu^{2+} ions, each with a terminal water molecule resulting in square-pyramidal coordination (see Figures 1 and 2). Furthermore, there was no glide of one AsW_9 subunit with respect to the other, so $[As_2W_{18}Cu_3O_{66}(H_2O)_3]^{12-}$ is a symmetrical polyanion with idealized D_{3h} symmetry. It is of interest to study in detail bond lengths and angles involving Cu and As atoms of **1** (see Table 2). The equatorial Cu−O bond lengths (Cu1−O, 1.909(6)−1.949(6) Å; Cu2−O, 1.912(6)−1.918(6) Å) and the equatorial O−Cu−O bond angles (O−Cu1−O, 88.9(3)°−90.5(3)°; O−Cu2−O, 89.1(3)°−90.4(4)°) are fairly regular, as opposed to those in **1a**. However, the separation of the two arsenic atoms in polyanions of **1** and **1a** is very similar (5.34 vs 5.33 Å).

It seems that for $[As_2W_{18}Cu_3O_{66}(H_2O)_3]^{12-}$, the nature of the counterions has a profound impact on the polyoxoanion structure, at least in the solid state. Apparently, the structure of this polyanion is stabilized by three sodium ions, which are each bound to four μ_3-oxo atoms and two terminal water molecules in cavities separating adjacent copper ions (see Figure 1). The octahedral coordination geometry and the bond lengths (Na1−O, 2.456(7)−2.480(7) Å; Na2−O, 2.339(7)−2.494(7) Å) indicate that the three sodium ions are tightly bound in the central belt. Most likely, exchange of these ions will be slow in solution. The molecular formula of the title polyanion should, therefore, be represented as $[(\alpha\text{-}AsW_9O_{33})_2Cu_3(H_2O)_3Na_3(H_2O)_6]^{9-}$.

Very recently, Mialane et al. reported on the synthesis and characterization of the related anions $[(\alpha\text{-}AsW_9O_{33})_2M_3(H_2O)_3]^{12-}$ (M = Mn, Co, Ni) and $[(\alpha\text{-}AsW_9O_{33})_2(VO)_3]^{11-}$.[10] The authors used the same synthetic approach as we did, and they identified eclipsed polyanions with idealized D_{3h} symmetry. They also found the three vacancies in the central belt to be occupied by sodium or potassium cations.

We were also able to synthesize $Na_{12}[Sb_2W_{18}Cu_3O_{66}(H_2O)_3]\cdot 46H_2O$ (**2**) in analogy to **1** by reacting the preformed, lacunary $[\alpha\text{-}SbW_9O_{33}]^{9-}$ with Cu^{2+} ions. The antimony-containing polyoxoanion is isostructural with the arsenic analogue and is therefore best represented by the formula $[(\alpha\text{-}SbW_9O_{33})_2Cu_3(H_2O)_3Na_3(H_2O)_6]^{9-}$. The central belt is composed of three Cu^{2+} and three Na^+ ions in alternating position leading to a polyanion with idealized D_{3h} symmetry. This is fully consistent with the observed bonds around antimony and copper in **2** (Sb−O, 1.965−1.978(6) Å; Cu−O_{eq}, 1.919−1.948(6) Å; Cu−O_{ax}, 2.203−2.320(9) Å). As expected, the separation of the two heteroatoms is significantly smaller in $[(\alpha\text{-}SbW_9O_{33})_2Cu_3(H_2O)_3Na_3(H_2O)_6]^{9-}$ ($d_{Sb\cdots Sb} = 4.85$ Å) than that in $[(\alpha\text{-}AsW_9O_{33})_2Cu_3(H_2O)_3Na_3(H_2O)_6]^{9-}$ ($d_{As\cdots As} = 5.34$ Å).

On the basis of the lone-pair/lone-pair repulsion arguments by Robert et al., it was not necessarily expected that the antimony analogue is formed at all. However, very recently, Mialane et al. reported on the potassium salt of the same polyanion, $K_{12}[Sb_2W_{18}Cu_3O_{66}(H_2O)_3]\cdot 41H_2O$.[10] Recently, Krebs et al. described the structure and catalytic activity of the mixed sodium/ammonium salt of the manganese-containing analogue, $Na_{11}(NH_4)[Sb_2W_{18}Mn_3O_{66}(H_2O)_3]\cdot 45H_2O$.[11] The belt of both polyanions is composed of three equivalent Cu^{2+} and Mn^{2+} ions with square-pyramidal coordination. The remaining three vacancies are occupied by potassium ions in $K_{12}[Sb_2W_{18}Cu_3O_{66}(H_2O)_3]\cdot 41H_2O$ and by sodium ions in $Na_{11}(NH_4)[Sb_2W_{18}Mn_3O_{66}(H_2O)_3]\cdot 45H_2O$. Sazani et al. reported that in $[(\alpha\text{-}SbW_9O_{33})_2(C_6H_5Sn)_3Na_3(H_2O)_6]^{6-}$, the central belt contains three organotin ions and also three tightly bound sodium ions.[12] Interestingly, in all three polyanions, the distortion observed by Robert et al. for **1a** is not present. This is especially surprising for the polyoxoanions containing the larger Sb^{III} rather than As^{III}, because lone-pair/lone-pair repulsion is expected to be larger for the first. Furthermore, Bösing et al. reported that the solid-state structure of $Na_9[\alpha\text{-}SbW_9O_{33}]$ consists of two eclipsed, lacunary $[\alpha\text{-}SbW_9O_{33}]^{9-}$ units connected via six Na^+ ions.[6g] It becomes apparent that especially sodium ions play a stabilizing role for sandwich-type polyoxoanions of As^{III} and Sb^{III}.

All of our results and those of our colleagues are fully consistent, but there is still no satisfying explanation for the distortion of the copper-substituted arsenotungstate observed by Robert et al. for $K_{12}[As_2W_{18}Cu_3O_{66}(H_2O)_2]\cdot 11H_2O$.[7] We thought it might be helpful to study the solution properties of this class of sandwich-type polyoxoanions. To be able to use

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(9) Sheldrick, G. M. *SADABS*; Siemens Analytical X-ray Instrument Division: Madison, WI, 1995.

(10) Mialane, P.; Marrot, J.; Rivière, E.; Nebout, J.; Hervé, G. *Inorg. Chem.* **2001**, *40*, 44.

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(12) Sazani, G.; Dickman, M. H.; Pope, M. T. *Inorg. Chem.* **2000**, *39*, 939.

Table 1. Crystal Data and Structure Refinement for $Na_{12}[As_2W_{18}Cu_3O_{66}(H_2O)_3]\cdot 32H_2O$ (**1**), $Na_{12}[Sb_2W_{18}Cu_3O_{66}(H_2O)_3]\cdot 46H_2O$ (**2**), $Na_{10}[As_2W_{18}Zn_3O_{66}(H_2O)_3]\cdot 51H_2O$ (**3**), $Na_{10}[Sb_2W_{18}Zn_3O_{66}(H_2O)_3]\cdot 48H_2O$ (**4**), $K_9Na[Se_2W_{18}Cu_3O_{66}(H_2O)_3]\cdot 16H_2O$ (**5**), $K_9Na[Te_2W_{18}Cu_3O_{66}(H_2O)_3]\cdot 16H_2O$ (**6**), $Cs_2Na_3[As_2W_{18.7}Zn_{2.3}O_{66}(H_2O)_3]\cdot 23H_2O$ (**7**), $Cs_{1.75}Na_3[As_2W_{18.8}Co_{2.2}O_{66}(H_2O)_3]\cdot 22.5H_2O$ (**8**), and $Cs_{6.25}Na[As_2W_{18.63}Mn_{2.37}O_{66}(H_2O)_3]\cdot 12.5H_2O$ (**9**)

	1	**2**	**3**
empirical formula	$AsCu_{1.5}H_{35}Na_6O_{50.5}W_9$	$Cu_{1.5}H_{49}Na_6O_{57.5}SbW_9$	$AsH_{54}Na_5O_{60}W_9Zn_{1.5}$
fw	2806.2	2979.2	2957.1
cryst color	green	green	colorless
cryst size (mm^3)	0.20 × 0.16 × 0.14	0.20 × 0.20 × 0.20	0.20 × 0.16 × 0.10
space group (No.)	$P2_1/m$ (11)	$C2/c$ (15)	$C2/c$ (15)
a (Å)	13.4989(9)	13.9956(11)	14.0970(11)
b (Å)	20.7463(14)	23.2361(19)	23.0993(17)
c (Å)	16.7571(11)	32.012(3)	32.149(2)
β (deg)	109.4050(10)	99.2490(10)	98.8680(10)
vol (Å^3)	4426.3(5)	10 275.0(14)	10 343.5(14)
Z	2	4	4
temp (°C)	−100	−106	−106
wavelength (Å)	0.710 73	0.710 73	0.710 73
d_{calcd} (Mg m^{-3})	4.158	3.788	3.757
abs coeff (mm^{-1})	24.917	21.361	21.292
reflns (unique)	11 094	12 550	12 643
reflns (obs)	9914	10 987	10 491
$R(F_o)^a$	0.035	0.032	0.040
$R_w(F_o)^b$	0.088	0.076	0.092
diff peak (e Å^3)	3.595	2.121	2.381
diff hole (e Å^3)	−2.308	−2.390	−2.215

	4	**5**	**6**
empirical formula	$H_{51}Na_5O_{58.5}SbW_9Zn_{1.5}$	$Cu_{1.5}H_{19}K_{4.5}Na_{0.5}O_{42.5}SeW_9$	$Cu_{1.5}H_{19}K_{4.5}Na_{0.5}O_{42.5}TeW_9$
fw	2976.9	2715.6	2764.2
cryst color	colorless	light-green	light-green
cryst size (mm^3)	0.24 × 0.16 × 0.06	0.16 × 0.08 × 0.06	0.18 × 0.10 × 0.10
space group (No.)	$C2/c$ (15)	$P\bar{4}2_1m$ (113)	$P\bar{4}2_1m$ (113)
a (Å)	14.0970(11)	16.7461(8)	16.6529(9)
b (Å)	23.0993(17)	16.7461(8)	16.6529(9)
c (Å)	32.149(2)	13.9075(9)	14.0180(11)
β (deg)	98.8680(10)		
vol (Å^3)	10 343.5(14)	3900.1(4)	3887.5(4)
Z	4	2	2
temp (°C)	−106	−106	−106
wavelength (Å)	0.710 73	0.710 73	0.710 73
d_{calcd} (Mg m^{-3})	3.757	4.592	4.690
abs coeff (mm^{-1})	21.292	28.763	28.656
reflns (unique)	12 621	5004	5051
reflns (obs)	10 376	4517	4707
$R(F_o)^a$	0.040	0.034	0.030
$R_w(F_o)^b$	0.092	0.072	0.082
diff peak (e Å^3)	2.960	1.701	2.800
diff hole (e Å^3)	−2.629	−2.330	−2.110

	7	**8**	**9**
empirical formula	$As_2Cs_2H_{52}Na_3O_{92}W_{18.7}Zn_{2.3}$	$As_2Co_{2.2}Cs_{1.75}H_{51}Na_3O_{91.5}W_{18.8}$	$As_2Cs_{6.25}H_{31}Mn_{2.37}NaO_{81.5}W_{18.63}$
fw	2798.8	2776.5	2947.1
cryst color	colorless	green	orange
cryst size (mm^3)	0.12 × 0.12 × 0.10	0.40 × 0.20 × 0.16	0.44 × 0.20 × 0.16
space group (No.)	$P2_1/m$ (11)	$P2_1/m$ (11)	$P2_1/m$ (11)
a (Å)	13.1939(10)	13.2070(10)	12.5139(11)
b (Å)	19.3214(15)	19.1547(14)	19.1754(17)
c (Å)	18.4524(14)	18.4642(13)	17.2199(16)
β (deg)	99.0840(10)	99.8270(10)	95.838(2)
vol (Å^3)	4645.0(6)	4602.5(6)	4110.6(6)
Z	2	2	2
temp (°C)	−100	−100	−100
wavelength (Å)	0.710 73	0.710 73	0.710 73
d_{calcd} (Mg m^{-3})	3.965	3.970	4.737
abs coeff (mm^{-1})	25.233	25.290	29.937
reflns (unique)	11 729	11 583	10 348
reflns (obs)	8653	9839	8833
$R(F_o)^a$	0.051	0.054	0.105
$R_w(F_o)^b$	0.129	0.145	0.238
diff peak (e Å^3)	6.228	8.873	5.829
diff hole (e Å^3)	−6.903	−7.986	−4.818

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_w = (\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2)^{1/2}$.

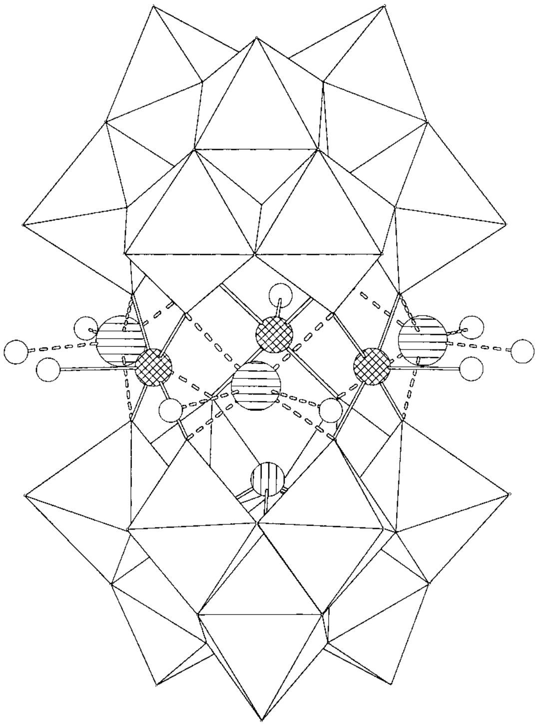

Figure 1. Combined polyhedral/ball-and-stick representation of $[(\alpha\text{-}AsW_9O_{33})_2Cu_3(H_2O)_3Na_3(H_2O)_6]^{9-}$. The coordination geometry of Cu (cross-hatched), Na (horizontally hatched), and As (vertically hatched) is clearly visible. Water molecules are represented as small empty spheres.

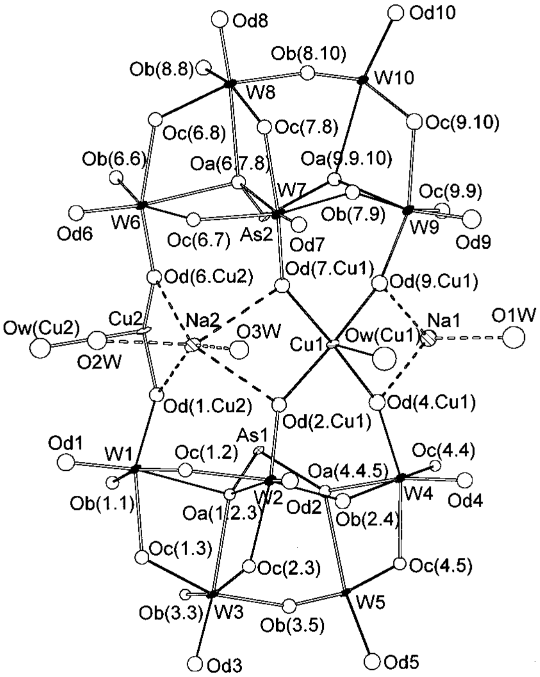

Figure 2. Ball-and-stick representation of the anionic component in the asymmetric unit of $Na_{12}[As_2W_{18}Cu_3O_{66}(H_2O)_3]\cdot 32H_2O$ (**1**) showing 50% probability ellipsoids and the labeling scheme (consistent with Robert et al., 1982).[7]

Table 2. Selected Bond Lengths (Å) and Angles (deg) around As and Cu Atoms in $Na_{12}[As_2W_{18}Cu_3O_{66}(H_2O)_3]\cdot 32H_2O$ (**1**) and $K_{12}[As_2W_{18}Cu_3O_{66}(H_2O)_2]\cdot 11H_2O$ (**1a**)

	1	**1a**
As(1)−O_a(1.2.3)	1.800(5)	1.84(4)
As(1)−O_a(4.4.5)	1.796(8)	1.75(7)
As(2)−O_a(6.7.8)	1.783(6)	1.77(5)
As(2)−O_a(9.9.10)	1.804(8)	1.88(7)
Cu(1)−O_d[2.Cu(1)]	1.911(6)	1.95(5)
Cu(1)−O_d[4.Cu(1)]	1.938(6)	1.88(5)
Cu(1)−O_d[7.Cu(1)]	1.949(6)	1.87(4)
Cu(1)−O_d[9.Cu(1)]	1.909(6)	2.00(4)
Cu(1)−O_w[Cu(1)]	2.390(7)	2.39(8)
Cu(2)−O_d[1.Cu(2)]	1.918(6)	1.92(5)
Cu(2)−O_d[6.Cu(2)]	1.912(6)	1.90(4)
Cu(2)−O_w[Cu(2)]	2.371(10)	
O_a(4.4.5)−As(1)−O_a(1.2.3)	96.8(2)	96(2)
O_a(1.2.3)−As(1)−O_a(1.2.3)′	97.4(3)	95(3)
O_a(9.9.10)−As(2)−O_a(6.7.8)	97.2(3)	94(2)
O_a(6.7.8)−As(2)−O_a(6.7.8)′	97.0(4)	93(3)
O_d[2.Cu(1)]−Cu(1)−O_d[4.Cu(1)]	88.9(3)	89(2)
O_d[2.Cu(1)]−Cu(1)−O_d[7.Cu(1)]	90.3(3)	88(2)
O_d[2.Cu(1)]−Cu(1)−O_d[9.Cu(1)]	171.4(3)	170(2)
O_d[4.Cu(1)]−Cu(1)−O_d[7.Cu(1)]	173.2(3)	174(2)
O_d[4.Cu(1)]−Cu(1)−O_d[9.Cu(1)]	90.5(3)	92(2)
O_d[7.Cu(1)]−Cu(1)−O_d[9.Cu(1)]	89.3(3)	90(2)
O_w[Cu(1)]−Cu(1)−O_d[2.Cu(1)]	88.5(2)	94(2)
O_w[Cu(1)]−Cu(1)−O_d[4.Cu(1)]	95.3(3)	92(2)
O_w[Cu(1)]−Cu(1)−O_d[7.Cu(1)]	91.4(3)	93(2)
O_w[Cu(1)]−Cu(1)−O_d[9.Cu(1)]	100.1(3)	96(2)
O_d[1.Cu(2)]−Cu(2)−O_d[6.Cu(2)]	89.8(2)	93(2)
O_d[1.Cu(2)]−Cu(2)−O_d[1.Cu(2)]′	89.1(3)	88(3)
O_d[1.Cu(2)]−Cu(2)−O_d[6.Cu(2)]′	172.6(3)	177(2)
O_d[6.Cu(2)]−Cu(2)−O_d[6.Cu(2)]′	90.4(4)	86(3)
O_w[Cu(2)]−Cu(2)−O_d[1.Cu(2)]	88.0(2)	
O_w[Cu(2)]−Cu(2)−O_d[6.Cu(2)]	99.2(3)	

^{183}W-NMR spectroscopy, we attempted to synthesize diamagnetic derivatives. Reaction of Zn^{2+} ions with $[\alpha\text{-}AsW_9O_{33}]^{9-}$ and $[\alpha\text{-}SbW_9O_{33}]^{9-}$ under the conditions used to synthesize the copper-containing compounds resulted in the desired species, $[(\alpha\text{-}XW_9O_{33})_2Zn_3(H_2O)_3]^{12-}$ (X = As, Sb). The two compounds, $Na_{10}[As_2W_{18}Zn_3O_{66}(H_2O)_3]\cdot 51H_2O$ (**3**) and $Na_{10}[Sb_2W_{18}Zn_3O_{66}(H_2O)_3]\cdot 48H_2O$ (**4**), are isostructural with **2** (see Table 1). They were isolated in high yield, and it was again the sodium salt that crystallized easily. The belt of the dimeric polyanions included three Na^+ ions in addition to the Zn^{2+} ions, which have a terminal water molecule leading to square-pyramidal coordination. Both polyanions, $[(\alpha\text{-}AsW_9O_{33})_2Zn_3(H_2O)_3Na_3(H_2O)_6]^{9-}$ and $[(\alpha\text{-}SbW_9O_{33})_2Zn_3(H_2O)_3Na_3(H_2O)_6]^{9-}$, have an eclipsed structure of idealized D_{3h} symmetry. The bond lengths around the Zn^{2+} ions and around the heteroatoms in **3** (As−O, 1.794−1.800(6) Å; Zn−O_{eq}, 2.001−2.028(7) Å; Zn−O_{ax}, 2.022−2.048(9) Å) and **4** (Sb−O, 1.980−2.000(6) Å; Zn−O_{eq}, 2.005−2.039(7) Å; Zn−O_{ax}, 2.011−2.028(10) Å) are consistent with this. It is apparent that the terminal Cu−OH_2 bonds in **1** and **2** are significantly longer than the corresponding Zn−OH_2 bonds in **3** and **4** as a result of Jahn−Teller distortion.

To expand the family of compounds further, we also attempted to synthesize and structurally characterize the Se^{IV} and Te^{IV} derivatives of **1**. The synthesis and the IR spectra of the Cu−Se and Cu−Te complexes were first reported by Yurchenko.[13] To synthesize the Se^{IV} derivative, we reacted SeO_2, $Na_2WO_4\cdot 2H_2O$, and $CuCl_2\cdot 2H_2O$ in sodium acetate buffer (0.5 M, pH 4.8), which resulted in the desired product in high yield. Single-crystal X-ray diffraction of $K_9Na[Se_2W_{18}Cu_3O_{66}(H_2O)_3]\cdot 16H_2O$ (**5**) revealed that the expected dimeric polyanion $[(\alpha\text{-}SeW_9O_{33})_2Cu_3(H_2O)_3]^{10-}$ was present and that the structure was eclipsed with idealized D_{3h} symmetry. The bond lengths around selenium and copper (Se−O, 1.694−1.715(11) Å; Cu−O_{eq}, 1.913−1.919(9) Å; Cu−O_{ax}, 2.286(13)−2.357(42) Å) are consistent with this. The terminal H_2O molecule of one of the three Cu^{2+} ions (Cu2) is disordered over two positions with

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(13) Yurchenko, E. N. *Koord. Khim.* **1992**, *18*, 944.

half-occupancy each. An interesting aspect of **5** is that three K^+ ions were located in the central belt together with three Cu^{2+} ions. Therefore, the appropriate molecular formula for the polyanion is $[(\alpha\text{-SeW}_9O_{33})_2Cu_3(H_2O)_3K_3(H_2O)_6]^{7-}$. Experimental results indicate that large single-crystals of the sodium salt of $[(\alpha\text{-SeW}_9O_{33})_2Cu_3(H_2O)_3]^{10-}$ can be obtained but the potassium salt can be isolated in higher yield. Prof. Krebs reported the structure of the sodium salt $Na_{10}[(SeW_9O_{33})_2Cu_3(H_2O)_3]\cdot 15H_2O$ at a recent polyoxometalate symposium.[14]

The tellurium analogue of **5** was obtained by reaction of $Te(NO_3)_4$, $Na_2WO_4\cdot 2H_2O$ and $CuCl_2\cdot 2H_2O$ in sodium acetate buffer (0.5 M, pH 4.8). However, the yield for $K_9Na[Te_2W_{18}Cu_3O_{66}(H_2O)_3]\cdot 16H_2O$ (**6**) was significantly lower than that for **5**. Single-crystal X-ray diffraction revealed that **5** and **6** are isostructural. The bond lengths around tellurium and copper (Te−O, 1.872−1.892(10) Å; $Cu-O_{eq}$, 1.921−1.934(9) Å; $Cu-O_{ax}$, 2.249(14)−2.366(36) Å) are as expected, but in **6**, there is no disorder of terminal H_2O molecules bound to Cu^{2+} ions. The appropriate molecular formula for the tellurium-containing polyanion is $[(\alpha\text{-TeW}_9O_{33})_2Cu_3(H_2O)_3K_3(H_2O)_6]^{7-}$. As expected, the separation of the two heteroatoms is significantly smaller in $[(\alpha\text{-TeW}_9O_{33})_2Cu_3(H_2O)_3K_3(H_2O)_6]^{7-}$ ($d_{Te\cdots Te} = 4.95$ Å) than that in $[(\alpha\text{-SeW}_9O_{33})_2Cu_3(H_2O)_3K_3(H_2O)_6]^{7-}$ ($d_{Se\cdots Se} = 5.38$ Å). However, the separation in the As and Se derivatives (5.34 vs 5.38 Å) as well as in the Sb and Te derivatives (4.85 vs 4.95 Å) is very similar. We were not able to isolate the sodium salt of $[(\alpha\text{-TeW}_9O_{33})_2Cu_3(H_2O)_3]^{10-}$ under the conditions studied. Prof. Krebs reported the structure of $K_9Na[(TeW_9O_{33})_2Cu_3(H_2O)]\cdot 14H_2O$ at a recent polyoxometalate symposium.[14] His molecular formula indicates that only one out of three Cu^{2+} ions has a terminal H_2O molecule. However, it is very likely that his structure is identical to ours and that two H_2O molecules could not be identified crystallographically for one or more of the following reasons: positional disorder, poor crystal quality, poor data set.

Our results indicate that potassium ions seem to stabilize Cu^{2+}-substituted, sandwich-type polyoxotungstates of Se^{IV} and Te^{IV} better than sodium ions. However, sodium ions seem to stabilize Cu^{2+}- and Zn^{2+}-substituted, sandwich-type polyoxotungstates of As^{III} and Sb^{III} better than potassium ions. It would be interesting to find out if these observations are also valid for derivatives incorporating other transition metals.

NMR Spectroscopy. Aqueous solutions of **3** and **4** exhibit seven-line ^{183}W-NMR spectra, but the relative intensities of their peaks are not identical (see Figure 3). This is an indication that the observed signals are not due to one species in solution but to a mixture of two isomers, which are present in different proportions. If the polyanions $[X_2W_{18}Zn_3O_{66}(H_2O)_3]^{12-}$ (X = As, Sb) keep the dimeric, eclipsed D_{3h} conformation also after dissolution in D_2O, two lines with relative intensity of 1:2 should be observed in ^{183}W-NMR. If on the other hand the polyanion is distorted in solution, lowering of its symmetry should lead to an increase in the number of lines in the ^{183}W-NMR spectrum. If the distortion of the polyanion results in C_{2v} symmetry, five peaks with ratios 2:2:2:2:1 are expected. It seems that the observed ^{183}W-NMR spectra for **3** and **4** are a combination of a 2:1 pattern indicating the presence of D_{3h} isomer and a 2:2:2:2:1 pattern indicative of a C_{2v} isomer.

For **4**, the two peaks at −97.0 and −148.1 ppm integrate with a ratio of 1:2 and are therefore assigned to the cap and belt tungsten atoms of a structure with D_{3h} symmetry. The signal for the tungsten atoms in the cap of the polyoxoanion is downfield with respect to the signal for the tungsten atoms in the belt. This is in complete agreement with the observations by Xin et al. for sandwich-type polyoxoanions.[15] The five remaining peaks at −85.3, −127.6, −131.7, −138.5, and −159.8 ppm integrate with ratios of 2:1:2:2:2. They are assigned to the five groups of magnetically inequivalent tungsten atoms in a structure with C_{2v} symmetry. In a saturated, aqueous solution of **4**, the D_{3h} and C_{2v} isomers of $[Sb_2W_{18}Zn_3O_{66}(H_2O)_3]^{12-}$ are present in approximately equal amounts, as based on integration of the ^{183}W-NMR spectrum.

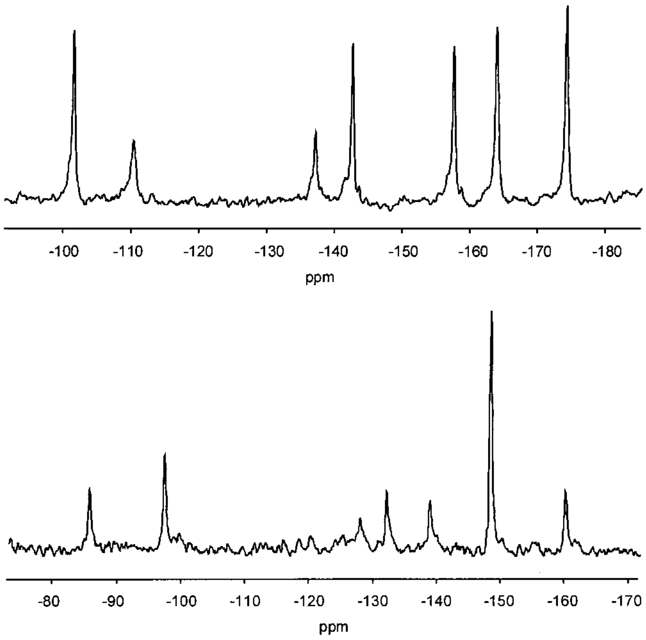

Figure 3. ^{183}W-NMR spectra of $Na_{10}[As_2W_{18}Zn_3O_{66}(H_2O)_3]\cdot 51H_2O$ (**3**), top, and $Na_{10}[Sb_2W_{18}Zn_3O_{66}(H_2O)_3]\cdot 48H_2O$ (**4**), bottom.

The peak assignment in the ^{183}W-NMR spectrum of **3** is more difficult because it is not straightforward to identify the 2:1 signal pair indicative of the D_{3h} isomer of $[As_2W_{18}Zn_3O_{66}(H_2O)_3]^{12-}$. The spectrum consists of two small peaks and five large peaks with almost identical peak areas. Using the ^{183}W-NMR spectrum of **4** and the results of Sazani et al. for $Li_6[(PhSn)_3Na_3(\alpha\text{-SbW}_9O_{33})_2]$ as references, we assigned the peaks at −110.5 and −164.0 ppm to the cap and belt tungsten atoms of a structure with D_{3h} symmetry.[12] We feel fairly confident with the assignment of the smaller peak, but we are not absolutely certain about the corresponding larger peak because the signals at −142.7, −157.6, −164.0, and −174.3 ppm have very similar areas. In a saturated solution of **3**, the D_{3h} and C_{2v} isomers of $[As_2W_{18}Zn_3O_{66}(H_2O)_3]^{12-}$ are present in a ratio of approximately 1:3, as based on integration of the ^{183}W-NMR spectrum. When the solutions of **3** and **4** were measured again after 2 weeks at room temperature, the ^{183}W-NMR spectra were still the same, indicating that the ratios of the two isomers had not changed.

It is useful to remember that Jeannin et al. reported the solid-state structure of the related polyanion $[(As_2W_{21}O_{69}(H_2O)]^{6-}$, which consists of two $[\alpha\text{-AsW}_9O_{33}]^{9-}$ fragments linked by a belt of three inequivalent tungsten atoms.[6b] Two of the central tungsten atoms have square-pyramidal coordination and the unique tungsten atom is octahedrally coordinated with a terminal oxo and a terminal water molecule. By using ^{183}W-NMR spectroscopy, the authors showed that this structure with C_{2v} symmetry was retained in solution. It seems that the solution

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properties of **3** and **4** can be explained on the basis of the observations of Jeannin et al. and the fact that Zn^{2+} ions prefer regular octahedral coordination compared to a square-pyramidal or square-planar geometry. We propose that in solutions of **3** and **4**, one of the three central Zn^{2+} ions coordinates to a second H_2O molecule, which must have entered the central cavity of the polyoxoanion. It is expected that the dimensions of the central cavity allow only one of the three Zn^{2+} ions to become hexacoordinated. This lowers the symmetry of the polyoxoanion to C_{2v} and most likely introduces some distortion in the polyoxoanion framework. However, the degree of distortion cannot be derived from our ^{183}W-NMR spectroscopy data. In solutions of **3** and **4**, the distorted C_{2v} polyoxoanion is in equilibrium with the undistorted D_{3h} anion as indicated above.

Disubstituted Structures. We also investigated the interaction of $[\alpha\text{-AsW}_9O_{33}]^{9-}$ with first-row transition metals in acidic medium. When we reacted $[\alpha\text{-AsW}_9O_{33}]^{9-}$ with Zn^{2+} and Co^{2+} ions in sodium acetate buffer (pH 4.8) and with Mn^{2+} ions in sodium formate buffer (pH 3.9), we obtained products which gave IR spectra very similar to those of compounds **1**−**4**. Single-crystal X-ray diffraction of the samples showed the expected dimeric, eclipsed polyanionic structural type already observed for **1**−**6**. However, it became apparent that there was excess electron density around the transition metal atom positions in the belt region of the polyanions. This was an indication that these positions were not exclusively occupied by Zn^{2+}, Co^{2+}, and Mn^{2+} ions but also by tungsten atoms. Assignment of partial occupancies led to a significant lowering of the *R*-factors in all cases. On the basis of X-ray diffraction, the percentage of first-row transition metal in the three belt positions for the three crystals studied was 77% Zn^{2+}, 73% Co^{2+}, and 79% Mn^{2+}. However, the final conclusions about occupancies are better based on elemental analyses of the bulk crystalline samples. These results indicate that on average two of the three belt positions of the dimeric polyanions are occupied by a first-row transition metal and that the remaining position is occupied by a tungsten atom. The products are therefore best described by the formula $[(\alpha\text{-AsW}_9O_{33})_2WO(H_2O)M_2(H_2O)_2]^{10-}$ (M = Zn^{2+}, Co^{2+}, Mn^{2+}). On the basis of the observations of Jeannin et al. for $[(As_2W_{21}O_{69}(H_2O)]^{6-}$, it is expected that the unique belt tungsten atom is octahedrally coordinated with a terminal oxo and a terminal water molecule.[6b] However, the observed disorder for **7**−**9** did not allow us to verify this.

Although the IR spectra of the trisubstituted compounds **1**−**4** are very similar to those of the disubstituted compounds **7**−**9**, we can distinguish them using this technique because only the disubstituted species show an absorption at 600 cm^{-1}.

Analysis of the synthetic conditions for compounds **1**−**9** and $[As_2W_{21}O_{69}(H_2O)]^{6-}$, which is synthesized in very acidic medium, indicates that the dimeric, sandwich-type structure is stable within the pH range of 0−7.5. At neutral pH, three first-row transition metal ions occupy the belt, but as the pH is lowered, it becomes more and more difficult to isolate this product. We have shown that at around pH = 4−5, only two first-row transition metal ions can be inserted, and we have indications that around pH = 2−3, only one transition metal ion is bound in the belt. It is therefore not unexpected that at pH = 0, the main product is $[As_2W_{21}O_{69}(H_2O)]^{6-}$.

Some time ago, Tourné et al. had reported on the synthesis and interaction of the lacunary arsenotungstate $[As_2W_{19}O_{67}]^{14-}$ with a variety of di-, tri-, and tetravalent cations, and among them were also Zn^{2+}, Co^{2+}, and Mn^{2+}.[16] For these three transition metals, they proposed a product with the formula $[As_2W_{19}M_2O_{67}(H_2O)_2]^{10-}$ (M = Zn^{2+}, Co^{2+}, Mn^{2+}), which they characterized by UV−vis−NIR spectroscopy and elemental analysis. We synthesized $[As_2W_{19}O_{67}]^{14-}$ according to the published procedure by Tourné et al. and reacted it with Zn^{2+}, Co^{2+}, and Mn^{2+} ions in a sodium acetate buffer (pH 5.5) at 50 °C for 30 min. The following precipitation by addition of CsCl or KCl led to solids with IR spectra identical to those of **7**−**9**. We also measured the UV−vis−NIR spectra for aqueous solutions of these solids. These spectra were identical to those described by Tourné et al., which indicates that their conclusions were correct.

Recently, Rosu et al. reported on the synthesis and characterization of novel polyanions with the formulas $[As_2W_{22}O_{74}(OH)_2]^{12-}$ and $[As_2M_2W_{20}O_{68}(OH)_2(H_2O)_6]^{8-}$ (M = Mn^{2+}, Co^{2+}, Cu^{2+}).[17] The results were based on IR and electronic spectroscopy, elemental analysis, and electron spin resonance (ESR). The given formulas imply a dimeric structure composed of two B-$[\beta\text{-AsW}_9O_{33}]^{9-}$ fragments linked either by four tungsten atoms or by two tungsten and two transition metal atoms. This structural type has recently been described by Krebs et al. for the related polyanions $[X_2W_{22}O_{74}(OH)_2]^{12-}$ (X = Sb^{III}, Bi^{III}), $[Sb_2W_{20}M_2O_{70}(H_2O)_6]^{(14-2n)-}$ (M^{n+} = Co^{2+}, Mn^{2+}, Ni^{2+}, Fe^{3+}), and $[Bi_2W_{20}M_2O_{70}(H_2O)_6]^{(14-2n)-}$ (M^{n+} = Co^{2+}, Zn^{2+}, Cu^{2+}, Ni^{2+}, Fe^{3+}).[6g,h] We noticed that the IR spectra of **8** and **9** are identical to those reported by Rosu et al. for $[As_2M_2W_{20}O_{68}(OH)_2(H_2O)_6]^{8-}$ (M = Mn^{2+}, Co^{2+}). We therefore believe that the proposed structures by Rosu et al. are probably wrong. There is strong evidence that their $[As_2M_2W_{20}O_{68}(OH)_2(H_2O)_6]^{8-}$ (M = Co^{2+}, Mn^{2+}) is identical to our $[(\alpha\text{-AsW}_9O_{33})_2WO(H_2O)M_2(H_2O)_2]^{10-}$ (M = Co^{2+}, Mn^{2+}) present in **8** and **9**. Interestingly, the synthetic conditions reported by Rosu et al. (solution containing acetate, pH 4.8, heating at 90 °C for 30 min) are also similar to those for **8** and **9**. The formulas for both types of polyanions are similar and so is their percent composition: $[As_2Co_2W_{20}O_{76}H_{14}]^{8-}$ vs $[As_2Co_2W_{19}O_{70}H_6]^{10-}$; W, 71.1% vs 71.5%; Co, 2.3% vs 2.4%; As, 2.9% vs 3.1%). Therefore, elemental analysis alone does not indicate which of the two structural types is present. Following the original synthetic procedure of Rosu et al., we attempted to reproduce their three transition-metal-substituted arsenotungstates. However, we were not able to isolate the precursor species which Rosu et al. described as $[As_2W_{22}O_{74}(OH)_2]^{12-}$. If it can be reproduced, it seems that single-crystal X-ray diffraction studies are needed to verify the molecular formula and the structure of this polyanion.

Conclusions

A family of nine dimeric, sandwich-type transition-metal-substituted polyoxotungstates has been synthesized and characterized by single-crystal X-ray diffraction, IR and NMR spectroscopy, and elemental analysis. Six of the polyanions are trisubstituted, and three are disubstituted. The trisubstituted polyoxoanions are $[(\alpha\text{-XW}_9O_{33})_2M_3(H_2O)_3]^{12-}$ (M = Cu^{2+}, Zn^{2+}; X = As^{III}, Sb^{III}) and $[(\alpha\text{-XW}_9O_{33})_2Cu_3(H_2O)_3]^{10-}$ (X = Se^{IV}, Te^{IV}). The disubstituted polyoxoanions are $[(\alpha\text{-AsW}_9O_{33})_2WO(H_2O)M_2(H_2O)_2]^{10-}$ (M = Zn^{2+}, Co^{2+}, Mn^{2+}). They have the same structure as the trisubstituted analogues, but only two of the three belt positions are occupied by a first-row transition metal. The trisubstituted derivatives consist of two $[\alpha\text{-XW}_9O_{33}]$ units joined by three equivalent Cu^{2+} (X = As, Sb, Se, Te) or Zn^{2+} (X = As, Sb) ions. All copper and zinc ions have one terminal water molecule resulting in square-pyramidal coordina-

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tion geometry. This leads to idealized D_{3h} symmetry in the solid state. The space between the three transition metal ions is occupied by three sodium ions (M = Cu^{2+}, Zn^{2+}; X = As^{III}, Sb^{III}) or potassium ions (M = Cu^{2+}; X = Se^{IV}, Te^{IV}) leading to a central belt of six metal atoms alternating in position. The solution properties of $[(\alpha\text{-}XW_9O_{33})_2Zn_3(H_2O)_3]^{12-}$ (X = As^{III}, Sb^{III}) were studied by ^{183}W-NMR spectroscopy. The results suggest that in solution, two isomers of the polyanion coexist. One of them has D_{3h} symmetry, indicating that the solid-state structure is maintained in solution. The second isomer has C_{2v} symmetry, indicating a distortion of the polyoxoanion, most likely as a result of inequivalent coordination spheres for the Zn^{2+} ions.

Some time ago, Siedle et al. reported the powder electron paramagnetic resonance (EPR) properties of the sodium salt $Na_{12}[As_2W_{18}Cu_3O_{66}(H_2O)_3]$ and the mixed sodium/potassium salt $Na_{3.2}K_{8.8}[As_2W_{18}Cu_3O_{66}(H_2O)_3]$.[18] Most likely, both compounds contained the polyoxoanion $[(\alpha\text{-}AsW_9O_{33})_2Cu_3(H_2O)_3\text{-}Na_3(H_2O)_6]^{9-}$, since the formula of the mixed salt indicates the presence of three sodium ions per formula unit. Almost certainly, these three sodium ions were bound in the belt of the dimeric polyoxometalate. However, Siedle et al. based the data interpretation for the mixed salt on the structure of the potassium salt **1a**, not being aware of the significant structural differences between the sodium and potassium salts described above. More recently, Cho and So reported that the powder EPR properties of **1a** were identical to those reported by Siedle et al.[19] This would mean that the structural differences between $K_{12}[As_2W_{18}Cu_3O_{66}(H_2O)_2]$ and $Na_{12}[As_2W_{18}Cu_3O_{66}(H_2O)_3]$ have no effect on their EPR properties, which is unexpected. Cho and So also measured single-crystal EPR spectra of $K_{12}[As_2W_{18}Cu_3O_{66}(H_2O)_2]$ and based their interpretation on the structure reported by Robert et al. It seems necessary to do single-crystal EPR studies on $Na_{12}[As_2W_{18}Cu_3O_{66}(H_2O)_3]$ to ascertain that indeed there is no difference between $Na_{12}[As_2W_{18}Cu_3O_{66}(H_2O)_3]$ and $K_{12}[As_2W_{18}Cu_3O_{66}(H_2O)_2]$. Magnetic susceptibility and magnetization measurements may also be useful. These studies are currently underway and will be reported in detail elsewhere.

Acknowledgment. U.K. thanks the University Research Board (URB) of the American University of Beirut for a research grant. X-ray measurements were made during a visit of U.K. in the laboratory of Prof. M. T. Pope at Georgetown University. U.K. thanks the Georgetown University Chemistry Department for allowing use of the X-ray diffractometer. U.K. also thanks Dr. R. Thouvenot (Université Pierre et Marie Curie) for helpful comments regarding interpretation of the NMR data. Figures 1 and 2 were generated by Diamond version 2.1b (copyright Crystal Impact GbR).

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

IC0101477

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