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Synthesis and Characterization of Iron(III)-Substituted, Dimeric Polyoxotungstates, $[Fe_4(H_2O)_{10}(\beta\text{-}XW_9O_{33})_2]^{n-}$ (n = 6, X = As^{III}, Sb^{III}; n = 4, X = Se^{IV}, Te^{IV})

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Interaction of the lacunary $[\alpha\text{-}XW_9O_{33}]^{9-}$ (X = As^{III}, Sb^{III}) with Fe^{3+} ions in acidic, aqueous medium leads to the formation of dimeric polyoxoanions, $[Fe_4(H_2O)_{10}(\beta\text{-}XW_9O_{33})_2]^{6-}$ (X = As^{III}, Sb^{III}) in high yield. X-ray single-crystal analyses were carried out on $Na_6[Fe_4(H_2O)_{10}(\beta\text{-}AsW_9O_{33})_2]\cdot 32H_2O$, which crystallizes in the monoclinic system, space group $C2/m$, with a = 20.2493(18) Å, b = 15.2678(13) Å, c = 16.0689(14) Å, β = 95.766(2)°, and Z = 2; $Na_6[Fe_4(H_2O)_{10}(\beta\text{-}SbW_9O_{33})_2]\cdot 32H_2O$ is isomorphous with a = 20.1542(18) Å, b = 15.2204(13) Å, c = 16.1469(14) Å, and β = 95.795(2)°. The selenium and tellurium analogues are also reported, $[Fe_4(H_2O)_{10}(\beta\text{-}XW_9O_{33})_2]^{4-}$ (X = Se^{IV}, Te^{IV}). They are synthesized from sodium tungstate and a source of the heteroatom as precursors. X-ray single-crystal analysis was carried out on $Cs_4[Fe_4(H_2O)_{10}(\beta\text{-}SeW_9O_{33})_2]\cdot 21H_2O$, which crystallizes in the triclinic system, space group $P\bar{1}$, with a = 12.6648(10) Å, b = 12.8247(10) Å, c = 16.1588(13) Å, α = 75.6540(10)°, β = 87.9550(10)°, γ = 64.3610(10)°, and Z = 1. All title polyanions consist of two ($\beta\text{-}XW_9O_{33}$) units joined by a central pair and a peripheral pair of Fe^{3+} ions leading to a structure with idealized C_{2h} symmetry. It was also possible to synthesize the Cr(III) derivatives $[Cr_4(H_2O)_{10}(\beta\text{-}XW_9O_{33})_2]^{6-}$ (X = As^{III}, Sb^{III}), the tungstoselenates(IV) $[M_4(H_2O)_{10}(\beta\text{-}SeW_9O_{33})_2]^{(16-4n)-}$ (M^{n+} = Cr^{3+}, Mn^{2+}, Co^{2+}, Ni^{2+}, Zn^{2+}, Cd^{2+}, and Hg^{2+}), and the tungstotellurates(IV) $[M_4(H_2O)_{10}(\beta\text{-}TeW_9O_{33})_2]^{(16-4n)-}$ (M^{n+} = Cr^{3+}, Mn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, and Hg^{2+}), as determined by FTIR. The electrochemical properties of the iron-containing species were also studied. Cyclic voltammetry and controlled potential coulometry aided in distinguishing between Fe^{3+} and W^{6+} waves. By variation of pH and scan rate, it was possible to observe the stepwise reduction of the Fe^{3+} centers.

Introduction

The class of polyoxometalates has generated substantial interest in recent years because of a unique structural variety and exciting properties including catalysis, medicine, and materials science.[1−5] Polyoxoanions are usually synthesized in aqueous, acidic medium through condensation reactions. However, the mechanism of formation of polyoxometalates is not well understood and is commonly described as self-assembly. Therefore, the design of novel polyoxometalates remains a challenge for synthetic chemists.

To synthesize novel polyoxoanions, a widely used approach has been to interact lacunary heteropolyanion precursors with transition metal ions. This approach usually leads to monomeric or dimeric polyoxoanions with expected structures, for example, $[A\text{-}\alpha\text{-}SiW_9O_{34}]^{10-} + 3Cu^{2+} \rightarrow [Cu_3(H_2O)_3(A\text{-}\alpha\text{-}SiW_9O_{37})]^{10-}$ and $2[B\text{-}\alpha\text{-}PW_9O_{34}]^{9-} + 4Co^{2+} \rightarrow [Co_4(H_2O)_2(B\text{-}\alpha\text{-}PW_9O_{34})_2]^{10-}$. However, Kortz et al. reported

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recently that using a metastable, lacunary precursor (e.g., $[\gamma\text{-SiW}_{10}O_{36}]^{8-}$) can lead to products with completely unexpected geometries.[6]

Of particular interest are polyoxoanions containing a hetero group with a lone pair of electrons (e.g., As^{III}, Sb^{III}), because this feature does not allow the closed Keggin unit to form.[7] Some polyoxotungstates of this type have been structurally characterized, and most of them consist of dimeric adducts of incomplete Keggin units joined together by extra W or X(III) (X = As, Sb) atoms, for example, $[AsW_8O_{30}AsOH]^{7-}$, $[H_2AsW_{18}O_{60}]^{7-}$, $[As_4W_{20}O_{72}(H_2O)_2]^{12-}$, $[As_2W_{21}O_{69}(H_2O)]^{6-}$, $[NH_4As_4W_{40}O_{140}Co_2(H_2O)_2]^{23-}$, $[NaW_{21}Sb_9O_{86}]^{18-}$, $[Sb_2W_{22}O_{74}(OH)_2]^{12-}$, and $[Na_2Sb_8W_{36}O_{132}(H_2O)_4]^{22-}$.[8] A few years ago, Pope et al. reported the largest compound of this class, $[As^{III}_{12}Ce_{16}(H_2O)_{36}W_{148}O_{524}]^{76-}$.[9] This gigantic structure is composed of 12 $[\alpha\text{-}As^{III}W_9O_{33}]^{9-}$ and 4 $[W_5O_{18}]^{6-}$ units. Very recently, Kortz et al. reported the largest arsenotungstate known to date, $[As^{III}_6W_{65}O_{217}(H_2O)_7]^{26-}$.[10] This polyanion consists of 4 inner ($\beta\text{-}As^{III}W_9O_{33}$) and 2 outer ($\alpha\text{-}As^{III}W_9O_{33}$) fragments that are linked together by a total of 11 corner-sharing WO_6 octahedra.

The first examples of polyoxoanions containing selenium(IV) and tellurium(IV) were reported many years ago.[11] However, only during the last 15 years were some species structurally characterized, for example, $[Se_2MoO_8]_n^{2n-}$, $[PhSeMo_4O_{15}H]^{3-}$, $[Se_2Mo_5O_{21}]^{4-}$, $[Se_2Mo_2V_6O_{28}]^{6-}$, $[SeX_3Mo_6O_{33}]^{8-}$ (X = S^{VI}, Se^{VI}), $[Se^{IV}Se_2^{VI}Mo_6O_{29}(OH)_2]^{8-}$, $[TeMo_6O_{22}]^{4-}$, $[Te_2Mo_6O_{24}]^{4-}$, $[Cu_3(H_2O)_3(\alpha\text{-}XW_9O_{33})_2]^{10-}$ (X = Se^{IV}, Te^{IV}), $[Fe_3(H_2O)_3(\alpha\text{-}XW_9O_{33})_2]^{10-}$ (X = Se^{IV}, Te^{IV}), $[X_2W_{21}O_{69}(H_2O)]^{4-}$ (X = Se^{IV}, Te^{IV}), $[Mn_4(H_2O)_{10}(\beta\text{-}Te^{IV}W_9O_{33})_2]^{8-}$, $[Se_2V_2O_{10}]^{2-}$, $[SeV_3O_{11}]^{3-}$, and $[HSe_4V_{10}O_{37}]^{7-}$.[12] At a recent polyoxometalate symposium, Prof. Krebs presented some novel structures of Se(IV) and Te(IV) substituted heteropolytungstates.[13]

The dimeric structural type $[(WO_2)_4(OH)_2(\beta\text{-}XW_9O_{33})_2]^{12-}$ (X = Sb^{III}, Bi^{III}) was first reported by Krebs et al.[8g,h] The authors were also able to substitute the two equivalent, external tungsten atoms (with three terminal oxygen ligands) by low-valent, first-row transition metals. This study has led to a large family of compounds, $[(WO_2)_2M_2(H_2O)_6(\beta\text{-}XW_9O_{33})_2]^{(14-2n)-}$ (X = Sb^{III}, M^{n+} = Mn^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+}; X = Bi^{III}, M^{n+} = Fe^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}).[8g,h] Recently, Krebs et al. also reported on a Sn(II) derivative with the same structure, $[(WO_2)_2(WO_2(OH))_{0.5}Sn_{1.5}(\beta\text{-}XW_9O_{33})_2]^{10.5-}$ (X = Sb^{III}, Bi^{III}).[14]

Roşu et al. reported on some arsenic(III) derivatives of the Krebs structure, $[As_2W_{22}O_{74}(OH)_2]^{12-}$ and $[As_2M_2W_{20}O_{68}(OH)_2(H_2O)_6]^{8-}$ (M = Mn^{2+}, Co^{2+}, Cu^{2+}).[15] However, very recently, we have shown that their proposed structures are wrong.[12j] Therefore, we were interested to see if we could actually synthesize and structurally characterize some transition metal substituted tungstoarsenates(III) with the Krebs structure.

Experimental Section

Synthesis. $Na_9[\alpha\text{-}AsW_9O_{33}]$ and $Na_9[\alpha\text{-}SbW_9O_{33}]$ were synthesized according to published procedures, and their purity was confirmed by infrared spectroscopy.[8g,16] All other reagents were used as purchased without further purification.

$Na_6[Fe_4(H_2O)_{10}(\beta\text{-}AsW_9O_{33})_2]\cdot 32H_2O$. A 0.97 g (3.6 mmol) sample of $FeCl_3\cdot 6H_2O$ was dissolved in 40 mL of H_2O, and then 4.0 g (1.6 mmol) of $Na_9[\alpha\text{-}AsW_9O_{33}]$ was added. The pH of the solution was adjusted to 3.0 by addition of 4 M HCl. Then, the solution was heated to 90 °C for 1 h and filtered after cooling. Slow evaporation at room temperature led to yellow crystals suitable for X-ray diffraction within 1−2 weeks. The bulk mixed cesium/sodium salt of the polyanion was isolated by precipitation of the

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solution with solid CsCl (4 g). This resulted in a light yellow product, which was isolated and dried in an oven at 60 °C overnight (yield 4.4 g, 92%). IR: 959, 901, 823, 782, 723, 694, 642, 504, 474, 429 $\mathrm{cm^{-1}}$. Anal. Calcd (Found) for $\mathrm{Cs_5Na[Fe_4(H_2O)_{10}(\beta\text{-}AsW_9O_{33})_2]\cdot 19H_2O}$: Cs 11.2 (11.9), Na 0.4 (0.3), W 55.6 (55.5), Fe 3.8 (4.2), As 2.5 (2.5). On the basis of IR data, we were also able to synthesize the $\mathrm{Cr^{3+}}$ substituted derivative, $\mathrm{[Cr_4(H_2O)_{10}(\beta\text{-}AsW_9O_{33})_2]^{6-}}$. The preceding procedure was followed, but 0.96 g (3.6 mmol) of $\mathrm{CrCl_3\cdot 6H_2O}$ was used instead of $\mathrm{FeCl_3\cdot 6H_2O}$, and the pH was adjusted to 1.0. The IR spectrum of $\mathrm{Cs_6[Cr_4(H_2O)_{10}(\beta\text{-}AsW_9O_{33})_2]}$ is shown in Figure S1 (Supporting Information).

$\mathrm{Na_6[Fe_4(H_2O)_{10}(\beta\text{-}SbW_9O_{33})_2]\cdot 32H_2O}$. A 0.97 g (3.6 mmol) sample of $\mathrm{FeCl_3\cdot 6H_2O}$ was dissolved in 40 mL of $\mathrm{H_2O}$, and then 4 g (1.6 mmol) of $\mathrm{Na_9[\alpha\text{-}SbW_9O_{33}]}$ was added. The pH of the solution was adjusted to 3.0 by addition of 4 M HCl. Then, the solution was heated to 90 °C for 1 h and filtered after cooling. Slow evaporation at room temperature led to yellow crystals suitable for X-ray diffraction within 1−2 weeks. The bulk mixed cesium/sodium salt of the polyanion was isolated by precipitation of the solution with solid CsCl (4 g). This resulted in a light yellow product, which was isolated and dried in an oven at 60 °C overnight (yield 4.1 g, 87%). IR: 948, 883, 807, 773, 678, 628, 512, 473, 425 $\mathrm{cm^{-1}}$. Anal. Calcd (Found) for $\mathrm{Cs_5Na[Fe_4(H_2O)_{10}(\beta\text{-}SbW_9O_{33})_2]\cdot 9H_2O}$: Cs 11.3 (12.7), Na 0.4 (0.5), W 56.5 (55.8), Fe 3.8 (3.9), Sb 4.2 (4.1). On the basis of IR data, we were also able to synthesize the $\mathrm{Cr^{3+}}$ substituted derivative, $\mathrm{[Cr_4(H_2O)_{10}(\beta\text{-}SbW_9O_{33})_2]^{6-}}$. The preceding procedure was followed, but 0.96 g (3.6 mmol) of $\mathrm{CrCl_3\cdot 6H_2O}$ were used instead of $\mathrm{FeCl_3\cdot 6H_2O}$, and the pH was adjusted to 1.0. The IR spectrum of $\mathrm{Cs_6[Cr_4(H_2O)_{10}(\beta\text{-}SbW_9O_{33})_2]}$ is shown in Figure S2 (Supporting Information).

$\mathrm{Cs_4[Fe_4(H_2O)_{10}(\beta\text{-}SeW_9O_{33})_2]\cdot 21H_2O}$. A 4.4 g (13.4 mmol) sample of $\mathrm{Na_2WO_4\cdot 2H_2O}$ was dissolved in 40 mL of $\mathrm{H_2O}$ and heated to about 50 °C. Then, 0.82 g (3.0 mmol) of $\mathrm{FeCl_3\cdot 6H_2O}$ and 0.17 g (1.34 mmol) of $\mathrm{H_2SeO_3}$ were added. The pH of the solution was adjusted to 1.0 by addition of 4 M HCl. Then, the solution was heated to 90 °C for 1 h and filtered after cooling. Addition of a dilute CsCl solution and slow evaporation at room temperature led to yellow crystals suitable for X-ray diffraction within 1−2 weeks. The bulk mixed cesium/sodium salt of the polyanion was isolated by precipitation of the solution with solid CsCl (4 g). This resulted in a light yellow product, which was isolated and dried in an oven at 60 °C overnight (yield 2.5 g, 68%). IR: 970, 895, 819, 779, 717, 659, 493, 430 $\mathrm{cm^{-1}}$. Anal. Calcd (Found) for $\mathrm{Cs_{3.5}Na_{0.5}[Fe_4(H_2O)_{10}(\beta\text{-}SeW_9O_{33})_2]\cdot 4H_2O}$: Na 0.2 (0.2), Cs 8.5 (8.9), W 60.4 (60.1), Fe 4.1 (4.2), Se 2.9 (2.9). Following the preceding procedure, we were also able to synthesize derivatives incorporating $\mathrm{Cr^{III}}$, $\mathrm{Mn^{II}}$, $\mathrm{Co^{II}}$, $\mathrm{Ni^{II}}$, $\mathrm{Zn^{II}}$, $\mathrm{Cd^{II}}$, and $\mathrm{Hg^{II}}$ as shown by IR. The IR spectra of $\mathrm{Cs_4[Cr_4(H_2O)_{10}(\beta\text{-}SeW_9O_{33})_2]}$, $\mathrm{Cs_8[Mn_4(H_2O)_{10}(\beta\text{-}SeW_9O_{33})_2]}$, $\mathrm{Cs_8[Co_4(H_2O)_{10}(\beta\text{-}SeW_9O_{33})_2]}$, $\mathrm{Cs_8[Ni_4(H_2O)_{10}(\beta\text{-}SeW_9O_{33})_2]}$, $\mathrm{Cs_8[Zn_4(H_2O)_{10}(\beta\text{-}SeW_9O_{33})_2]}$, $\mathrm{Cs_8[Cd_4(H_2O)_{10}(\beta\text{-}SeW_9O_{33})_2]}$, and $\mathrm{Cs_8[Hg_4(H_2O)_{10}(\beta\text{-}SeW_9O_{33})_2]}$ are shown in Figures S3−S9 (Supporting Information). Instead of $\mathrm{FeCl_3\cdot 6H_2O}$, we used $\mathrm{CrCl_3\cdot 6H_2O}$, $\mathrm{MnCl_2\cdot 4H_2O}$, $\mathrm{CoCl_2\cdot 6H_2O}$, $\mathrm{NiCl_2\cdot 6H_2O}$, $\mathrm{ZnCl_2}$, $\mathrm{CdCl_2}$, and $\mathrm{HgCl_2}$, respectively.

$\mathrm{Cs_{3.8}K_{0.2}[Fe_4(H_2O)_{10}(\beta\text{-}TeW_9O_{33})_2]}$. A 4.4 g (13.4 mmol) sample of $\mathrm{Na_2WO_4\cdot 2H_2O}$ was dissolved in 40 mL of $\mathrm{H_2O}$ and heated to about 50 °C. Then, 0.82 g (3.0 mmol) of $\mathrm{FeCl_3\cdot 6H_2O}$ and 0.41 g (1.34 mmol) of $\mathrm{K_2TeO_3}$ were added. The pH of the solution was adjusted to 1.0 by addition of 4 M HCl. Then, the solution was heated to 90 °C for 1 h and filtered after cooling. The bulk mixed cesium/potassium salt of the polyanion was isolated by precipitation of the solution with solid CsCl (4 g). This resulted in a light yellow product, which was isolated and dried in an oven at 60 °C overnight (yield 2.1 g, 57%). IR: 967, 883, 817, 783, 741, 694, 656, 565 $\mathrm{cm^{-1}}$. Anal. Calcd (Found) for $\mathrm{Cs_{3.8}K_{0.2}[Fe_4(H_2O)_{10}(\beta\text{-}TeW_9O_{33})_2]}$: K 0.1 (0.6), Cs 9.1 (9.7), W 59.8 (61.0), Fe 4.0 (4.1), Te 4.6 (4.7). Following the preceding procedure, we were also able to synthesize derivatives incorporating $\mathrm{Cr^{III}}$, $\mathrm{Mn^{II}}$, $\mathrm{Co^{II}}$, $\mathrm{Ni^{II}}$, $\mathrm{Cu^{II}}$, $\mathrm{Zn^{II}}$, $\mathrm{Cd^{II}}$, and $\mathrm{Hg^{II}}$ as shown by IR. The IR spectra of $\mathrm{Cs_4[Cr_4(H_2O)_{10}(\beta\text{-}TeW_9O_{33})_2]}$, $\mathrm{Cs_8[Mn_4(H_2O)_{10}(\beta\text{-}TeW_9O_{33})_2]}$, $\mathrm{Cs_8[Co_4(H_2O)_{10}(\beta\text{-}TeW_9O_{33})_2]}$, $\mathrm{Cs_8[Ni_4(H_2O)_{10}(\beta\text{-}TeW_9O_{33})_2]}$, $\mathrm{Cs_8[Cu_4(H_2O)_{10}(\beta\text{-}TeW_9O_{33})_2]}$, $\mathrm{Cs_8[Zn_4(H_2O)_{10}(\beta\text{-}TeW_9O_{33})_2]}$, $\mathrm{Cs_8[Cd_4(H_2O)_{10}(\beta\text{-}TeW_9O_{33})_2]}$, and $\mathrm{Cs_8[Hg_4(H_2O)_{10}(\beta\text{-}TeW_9O_{33})_2]}$ are shown in Figures S10−S17 (Supporting Information). Instead of $\mathrm{FeCl_3\cdot 6H_2O}$, we used $\mathrm{CrCl_3\cdot 6H_2O}$, $\mathrm{MnCl_2\cdot 4H_2O}$, $\mathrm{CoCl_2\cdot 6H_2O}$, $\mathrm{NiCl_2\cdot 6H_2O}$, $\mathrm{CuCl_2\cdot 2H_2O}$, $\mathrm{ZnCl_2}$, $\mathrm{CdCl_2}$, and $\mathrm{HgCl_2}$, respectively.

Elemental analyses were performed by Kanti Technologies, Inc., Tonawanda, NY. Infrared spectra were recorded on KBr pellets using a Nicolet Avatar spectrophotometer.

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 (λ = 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.[17] Crystallographic data are summarized in Table 1.

All the sodium counterions in $\mathrm{Na_6[Fe_4(H_2O)_{10}(\beta\text{-}XW_9O_{33})_2]\cdot 32H_2O}$ ($\mathrm{X = As^{III}, Sb^{III}}$) are associated with terminal (Na1, Na2) and bridging (Na3) oxygens of the polyoxoanion as well as with water molecules of the lattice. It was not unexpected that two (Na2, Na3) of the three sodium ions in the asymmetric unit as well as almost all water molecules are disordered requiring partial occupancies. Nevertheless, chemical sense allowed unequivocal assignment of all cations. The cesium ions of $\mathrm{Cs_4[Fe_4(H_2O)_{10}(\beta\text{-}SeW_9O_{33})_2]\cdot 21H_2O}$ are coordinated to bridging and terminal oxygens of the polyoxoanion as well as to water molecules of the lattice. Some cesium ions (Cs2, Cs3, Cs4) as well as the majority of water molecules are disordered, but all required cations for charge balance could be accounted for.

Electrochemistry. Pure water from a Milli-$\mathrm{RO_4}$ unit followed by a Millipore Q purification set was used throughout. All the chemicals were of high-purity grade and were used as received. $\mathrm{H_2SO_4}$, $\mathrm{Na_2SO_4}$, $\mathrm{CH_3COONa}$, and $\mathrm{CH_3COOH}$ were commercial products (Prolabo Normapur). The pH 3 medium was made up with 0.2 M $\mathrm{Na_2SO_4 + H_2SO_4}$, and the pH 5 medium, with 0.4 M $\mathrm{CH_3COONa + CH_3COOH}$. The solutions were deaereated thoroughly for a least 30 min with pure argon and kept under a positive pressure of this gas during the experiments.

Equipment and Apparatus. The source, mounting, and polishing of the glassy carbon (GC, Le Carbone Lorraine, France, 3 mm diameter) have been described.[18] The electrochemical setup was an EG&G 273 A driven by a PC with the 270 software. Potentials are quoted against a saturated calomel electrode (SCE), in a compartment separated from the test solution by a fine porosity glass frit. The counter electrode was a platinum gauze of large surface area in a separated compartment with a medium porosity glass frit. The UV−vis spectra were recorded with a Perkin-Elmer Lambda 19 spectrophotometer. Experiments were performed at

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

(18) Keita, B.; Lu, Y. W.; Nadjo, L.; Contant, R.; Abbessi, M.; Canny, J.; Richet, M. *J. Electroanal. Chem.* **1999**, *477*, 146.

Table 1. Crystal Data and Structure Refinement for $Na_6[Fe_4(H_2O)_{10}(\beta\text{-}AsW_9O_{33})_2]\cdot 32H_2O$, $Na_6[Fe_4(H_2O)_{10}(\beta\text{-}SbW_9O_{33})_2]\cdot 32H_2O$, and $Cs_4[Fe_4(H_2O)_{10}(\beta\text{-}SeW_9O_{33})_2]\cdot 21H_2O$

emp formula:	$AsFe_2H_{42}Na_3O_{54}W_9$	$Fe_2H_{42}Na_3O_{54}SbW_9$	$Cs_2Fe_2H_{31}O_{48.5}SeW_9$
fw	2816.7	2863.5	2918.4
space group (No.)	$C2/m$ (12)	$C2/m$ (12)	$P\bar{1}$ (2)
a (Å)	20.2493(18)	20.1542(18)	12.6648(10)
b (Å)	15.2678(13)	15.2204(13)	12.8247(10)
c (Å)	16.0689(14)	16.1469(14)	16.1588(13)
α (deg)			75.6540(10)
β (deg)	95.766(2)	95.795(2)	87.9550(10)
γ (deg)			64.3610(10)
V (Å^3)	4942.8(7)	4927.8(7)	2284.6(3)
Z	2	2	1
T (°C)	−106	−106	−106
wavelength (Å)	0.710 73	0.710 73	0.710 73
d_{calcd} (Mg m^{-3})	3.728	3.802	4.197
abs coeff (mm^{-1})	22.231	22.168	25.652
R [$I > 2\sigma(I)$][a]	0.058	0.046	0.049
R_w (all data)[b]	0.144	0.116	0.111

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

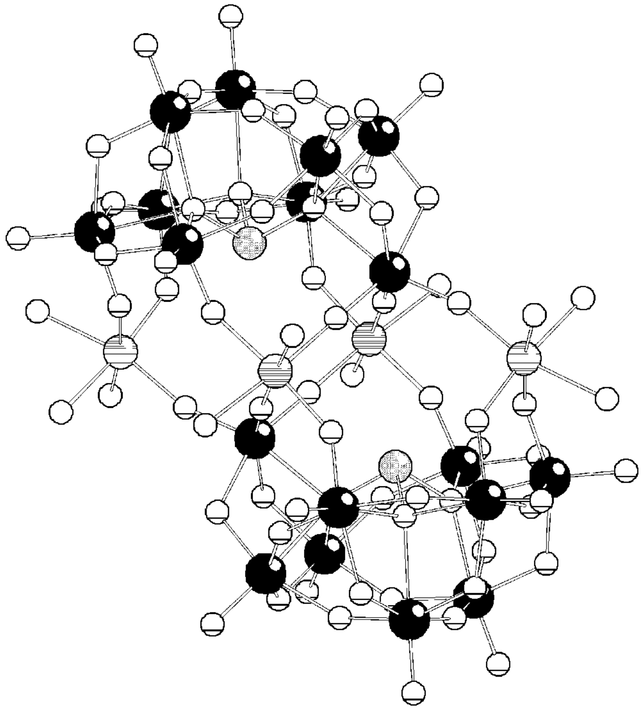

Figure 1. Ball and stick representation of $[Fe_4(H_2O)_{10}(\beta\text{-}AsW_9O_{33})_2]^{6-}$ (**1**). The shading code of the spheres is as follows: W (black), Fe (horizontally hatched), As (crosshatched), O (empty with shadow), and H_2O (empty).

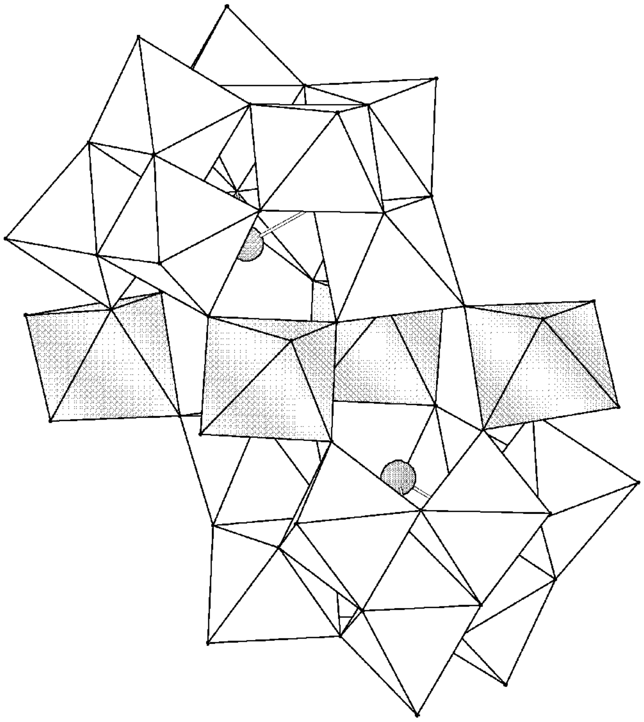

Figure 2. Polyhedral representation of $[Fe_4(H_2O)_{10}(\beta\text{-}AsW_9O_{33})_2]^{6-}$ (**1**).

room temperature. The numbers of electrons consumed per molecule were obtained usually by controlled potential coulometry.

Results and Discussion

Structural Characterization. The four polyoxoanions $[Fe_4(H_2O)_{10}(\beta\text{-}AsW_9O_{33})_2]^{6-}$ (**1**), $[Fe_4(H_2O)_{10}(\beta\text{-}SbW_9O_{33})_2]^{6-}$ (**2**), $[Fe_4(H_2O)_{10}(\beta\text{-}SeW_9O_{33})_2]^{4-}$ (**3**), and $[Fe_4(H_2O)_{10}(\beta\text{-}TeW_9O_{33})_2]^{4-}$ (**4**) have the same molecular structure. They consist of two $[\beta\text{-}XW_9O_{33}]^{n-}$ ($n = 9$, X = As^{III}, Sb^{III}; $n = 8$, X = Se^{IV}, Te^{IV}) moieties linked by four Fe^{3+} ions resulting in a structure with idealized C_{2h} symmetry (see Figures 1 and 2). The four Fe^{3+} ions consist of two inequivalent pairs, the inner two Fe^{3+} ions have two terminal H_2O ligands, and the outer two Fe^{3+} ions have three terminal H_2O ligands. These features seem to justify a detailed study of the catalytic redox properties of the title compounds. The paramagnetic iron centers are separated by four bonds (Fe−O−W−O−Fe) so that their magnetic exchange interaction is expected to be weak.

Polyanions **1** and **2** were synthesized in aqueous acidic medium (pH 3) from an interaction of Fe^{3+} ions with the lacunary Keggin precursors $[\alpha\text{-}AsW_9O_{33}]^{9-}$ and $[\alpha\text{-}SbW_9O_{33}]^{9-}$, respectively. Therefore, the mechanism of formation of **1** and **2** involves insertion, isomerization ($\alpha \rightarrow \beta$), and dimerization. This is of particular interest because interaction of Cu^{2+} and Zn^{2+} ions with $[\alpha\text{-}AsW_9O_{33}]^{9-}$ and $[\alpha\text{-}SbW_9O_{33}]^{9-}$ in neutral aqueous medium resulted in trisubstituted, sandwich-type polyoxoanions, $[M_3(H_2O)_3(\alpha\text{-}XW_9O_{33})_2]^{12-}$ (X = As^{III}, Sb^{III}; M = Cu^{2+}, Zn^{2+}).[12j] It was shown by Krebs et al. that $[\alpha\text{-}SbW_9O_{33}]^{9-}$ and $[\beta\text{-}SbW_9O_{33}]^{9-}$ are in equi-

Table 2. Selected Bond Distances (Å) for $[Fe_4(H_2O)_{10}(\beta\text{-}AsW_9O_{33})_2]^{6-}$ (**1**), $[Fe_4(H_2O)_{10}(\beta\text{-}SbW_9O_{33})_2]^{6-}$ (**2**), and $[Fe_4(H_2O)_{10}(\beta\text{-}SeW_9O_{33})_2]^{4-}$ (**3**)

	1	**2**	**3**
Fe1−O	1.929−1.931(10)	1.943−1.945(9)	1.943−1.965(10)
Fe2−O	1.931−1.971(12)	1.975−2.017(11)	1.926−2.011(10)
Fe1−OH_2	2.146(13)	2.131(10)	2.091−2.096(12)
Fe2−OH_2	2.045−2.161(14)	2.072−2.195(15)	2.018−2.098(11)
X−O (X = As, Sb, Se)	1.797−1.804(11)	1.995−2.003(10)	1.707−1.719(10)
W−$O_{terminal}$	1.696−1.718 (14)	1.699−1.728 (11)	1.692−1.723 (11)
W−O(Fe)	1.787−1.827 (11)	1.763−1.813 (10)	1.763−1.840 (10)
W−O(W)	1.879−2.046 (11)	1.880−2.039 (9)	1.863−2.050 (10)
W−O(X)	2.307−2.383 (11)	2.223−2.349 (10)	2.373−2.508 (10)
X⋯X	6.03(3)	5.68(3)	6.09(3)
X⋯Fe1	4.03(2)	3.90(2)	4.04−4.08(2)
X⋯Fe2	4.10(2)	3.98(2)	4.17(2)
X⋯W1′	4.42(2)	4.20(2)	4.39(2)
Fe1⋯Fe1′	5.36(3)	5.34(3)	5.37(3)
Fe1⋯Fe2	5.60(3)	5.64(3)	5.69−5.70(3)
Fe2⋯Fe2′	9.84(4)	9.93(4)	10.04(4)

librium in aqueous solution.[8g] The former dominates in neutral medium whereas the latter is present in acidic solution. Our observations are in full agreement with this, and we propose that the behavior of $[\alpha\text{-}AsW_9O_{33}]^{9-}$ and $[\beta\text{-}AsW_9O_{33}]^{9-}$ is very similar to that of their antimony analogues.

We were unable to synthesize the Cu^{2+} and Zn^{2+} derivatives of **1** and **2** in acidic medium, but we were also unable to synthesize the Fe^{3+} derivative of the trisubstituted sandwich structure in neutral medium. These observations suggest that the coordination requirements of the transition metal ions play an important role in the formation of the two structural types. The coordination geometry of the Fe^{3+} ions in **1** and **2** is octahedral, whereas the structure of $[M_3(H_2O)_3(\alpha\text{-}XW_9O_{33})_2]^{12-}$ (X = As^{III}, Sb^{III}; M = Cu^{2+}, Zn^{2+}) requires a square pyramidal coordination geometry for Cu^{2+} and Zn^{2+}. Out of all first-row transition metals, we were only able to synthesize the Cr^{3+} derivatives of **1** and **2** as shown by FTIR. Attempts to crystallize these compounds were unsuccessful.

To prepare the Se(IV) and Te(IV) derivatives of **1** and **2**, the synthetic procedure had to be modified, because the selenium and tellurium analogues of $[\alpha\text{-}XW_9O_{33}]^{9-}$ (X = As^{III}, Sb^{III}) are not known yet. Reaction of $FeCl_3$, Na_2WO_4, and H_2SeO_3 in very acidic medium (pH 1) resulted in the formation of **3**. The same approach and using K_2TeO_3 instead of H_2SeO_3 resulted in **4** as shown by FTIR and elemental analysis. A few years ago, Krebs et al. reported on the synthesis (reaction of TeO_2, Na_2WO_4, and $MnCl_2$), structure, and catalytic activity of $[Mn_4(H_2O)_{10}(\beta\text{-}Te^{IV}W_9O_{33})_2]^{8-}$.[12m] This was the first example of a tetrasubstituted derivative of the Krebs structure.

It is of interest to find out what impact the different hetero groups X (X = As^{III}, Sb^{III}, Se^{IV}) have on the structures of **1**, **2**, and **3**. This is of particular importance considering that the sodium salts of **1** and **2** are isomorphous. As expected, the X−O (X = As^{III}, Sb^{III}, Se^{IV}) bond lengths increase in the sequence Se−O < As−O < Sb−O. The observed heteroatom separations X⋯X within **1**, **2**, and **3** are fully consistent with this (see Table 2). On the other hand, the type of hetero group has very little effect on the W−O and Fe−O bond lengths in **1**, **2**, and **3**. These observations allow the conclusion that in **1**, **2**, and **3** there is no significant lone-pair/lone-pair repulsion involving the lone pairs of the two heteroatoms. This is not unexpected considering that the distance between heteroatoms in **1**, **2**, and **3** (6.03, 5.68, 6.09 Å) is significantly larger than in the related sandwich-type polyoxoanions $[Cu_3(H_2O)_3(\alpha\text{-}AsW_9O_{33})_2]^{12-}$ (As⋯As = 5.34 Å), $[Cu_3(H_2O)_3(\alpha\text{-}SbW_9O_{33})_2]^{12-}$ (Sb⋯Sb = 4.85 Å), and $[Cu_3(H_2O)_3(\alpha\text{-}SeW_9O_{33})_2]^{10-}$ (Se⋯Se = 5.38 Å).[12j] For these polyanions with D_{3h} symmetry, no significant lone-pair/lone-pair interaction was observed.

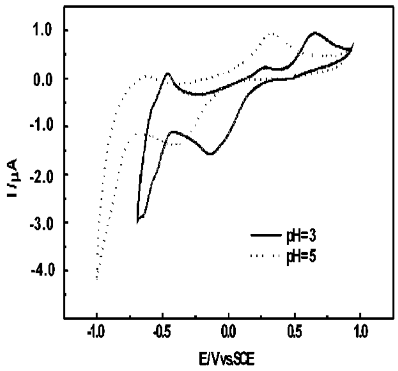

Figure 3. Cyclic voltammogram of $[Fe_4(H_2O)_{10}(\beta\text{-}AsW_9O_{33})_2]^{6-}$ (**1**) in aqueous solution at pH 3 and pH 5.

Electrochemical Characterization. It was decided to first check the stability of the title polyanions **1**−**4** between pH 3 and 5, which is the domain usually explored for electrochemical characterization and studies of electrocatalytic processes. The analytical tool used for these experiments was UV−vis spectroscopy. The spectra of all title compounds were completely reproducible with respect to absorbances and wavelengths over a period of at least 24 h.

The electrochemical studies were performed by cyclic voltammetry. The evolution of the cyclic voltammogram of **1** at pH 3 and pH 5 is presented in Figure 3. The pattern at pH 3 shows a large current for the first reduction wave, which represents the combined series of one-electron reduction processes of the four Fe^{3+} centers. At the scan rate of 10 mV s^{-1} used to run this voltammogram, the cathodic wave appears clearly composite. Controlled potential coulometry confirmed the uptake of four electrons per molecule. Such electrolysis gave a pale pink solution, which constitutes good evidence that the tungsten−oxo framework was not reduced. Reversal of the potential scan (scheme not shown) just before the beginning of the second wave system (see Figure 3) indicates unambiguously two oxidation waves corresponding to the four-electron reduction wave, thus reinforcing the idea that discrete but very close reduction potentials should exist for the Fe^{3+} centers.

The behavior of the iron centers in the title polyanions is very different from that of the iron-monosubstituted Dawson species $[\alpha_1\text{-}Fe(H_2O)(P_2W_{17}O_{61})]^{7-}$ and $[\alpha_2\text{-}Fe(H_2O)(P_2W_{17}O_{61})]^{7-}$.[19] Hill et al. observed, at least partially, stepwise reduction of the Fe^{3+} centers in the sandwich-type tungstophosphates $[Fe_4(H_2O)_2(PW_9O_{34})_2]^{6-}$ and $[Fe_4(H_2O)_2(P_2W_{15}\text{-}$

$O_{56})_2]^{12-}$.[20] This structural family is closer to **1**−**4** with respect to stoichiometry and shape than the monosubstituted Dawson species.

Following the four-electron reduction wave for **1** at pH 3 is a system of two closely spaced two-electron waves, featuring the first redox processes of the W centers (see Figure 3). Upon potential reversal, a single oxidation wave is obtained. At pH 5, the entire voltammetric pattern is shifted in the negative potential direction, and the composite aspect of the four-electron iron wave is no longer visible. The single peak potential at pH 5 is −0.406 V versus SCE, and at pH 3, the well-behaved peak is at −0.126 V versus SCE, indicating a shift of about 0.140 V/pH. More modest potential shifts versus pH have been observed for the Fe^{3+} waves of the above-mentioned monosubstituted Dawson ions.[19a,b] At pH 5, the W waves also mix up, and the system of two two-electron waves is replaced by a single four-electron wave. The aforementioned behavior is roughly valid for all title compounds **1**−**4**.

Small differences in the electrochemical properties of the title polyanions must be attributed to the different heteroatoms X (X = As^{III}, Sb^{III}, Se^{IV}, Te^{IV}), and this will be described in detail elsewhere. However, it is worth noting that it is possible to group the four species in two classes: **1**, **2** and **3**, **4** (see Figure S18 of Supporting Information). This reflects the main groups of the periodic table to which the heteroatoms belong, and it means that the charge of the title polyanions (6− for **1**, **2**; 4− for **3**, **4**) has more influence than structural parameters on their electrochemical properties.

More specifically, the cyclic voltammograms of **1** and **2** show a merging of the Fe^{3+} waves at pH 3 and a scan rate of 10 mV s^{-1}. On the other hand, for **3** and **4**, the four-electron iron wave is clearly composite whatever the scan rate. At pH 5 and a scan rate of 2 mV s^{-1}, it was even possible to distinguish the four steps of Fe^{3+} reduction. For **3**, the approximate reduction peak potentials measured are (in V vs SCE): −0.150, −0.310, −0.415, and −0.550. Tentatively, the separation of the reduction potentials might be attributed to electronic interactions involving the central heteroatoms. Apparently, this interaction generates or reinforces inequivalence among the Fe^{3+} centers.

Polyanion **4** exhibits a special feature: when the potential excursion is extended to include the first W redox processes, a small reduction wave is observed. This wave is located just positive of these W waves, and upon potential reversal, it has associated with it a characteristic pattern of stripping oxidation waves (see Figure S19 of Supporting Information). This deposition process was observed at both pH values studied. Its actual nature and properties are currently under investigation.

Conclusions

A family of four dimeric, iron(III)-substituted heteropolyanions, $[Fe_4(H_2O)_{10}(\beta\text{-}XW_9O_{33})_2]^{n-}$ ($n = 6$, X = As^{III}, Sb^{III}; $n = 4$, X = Se^{IV}, Te^{IV}) with the Krebs structure has been synthesized and characterized. The two arsenic and antimony derivatives, $[Fe_4(H_2O)_{10}(\beta\text{-}XW_9O_{33})_2]^{6-}$ (X = As^{III}, Sb^{III}), were synthesized by interaction of Fe^{3+} ions with the lacunary $[\alpha\text{-}XW_9O_{33}]^{9-}$ (X = As^{III}, Sb^{III}). Therefore, the reaction mechanism must involve metal insertion, isomerization ($\alpha \rightarrow \beta$), and dimerization. The selenium and tellurium derivatives $[Fe_4(H_2O)_{10}(\beta\text{-}XW_9O_{33})_2]^{4-}$ (X = Se^{IV}, Te^{IV}) were synthesized from sodium tungstate and a source of the heteroatom as precursors.

The fact that in all four cases the same structural type is obtained, no matter what the precursors are, indicates that the boundary conditions present during the reaction determine which product is formed. Apparently, the steric impact of the central hetero group with respect to the resulting heteropolyanion structure is very limited. On the other hand, the acidity of the reaction medium and the preferred coordination geometry of the incorporated transition metal seem to be significantly more important.

The same observations apply to the recently reported family of copper-substituted heteropolyanions $[Cu_3(H_2O)_3(\alpha\text{-}XW_9O_{33})_2]^{n-}$ ($n = 12$, X = As^{III}, Sb^{III}; $n = 10$, X = Se^{IV}, Te^{IV}). Interestingly, this structural type ($\alpha\alpha$) was not formed with Fe^{3+} ions, whereas the structural type of the title polyanions ($\beta\beta$) was not formed with Cu^{2+} ions (except for X = Te^{IV}).

In addition to the iron-containing title compounds, we also report on a large number of isostructural derivatives containing first-, second-, and third-row transition metals. Most derivatives were synthesized at exactly the same experimental conditions as the corresponding iron-containing species. Our results show that substitution of the four iron centers by other transition metal ions is significantly easier for **3** and **4** than for **1** and **2**. This means that the polyanion charge must play an important role. Interestingly, the results of our electrochemical studies lead to the same conclusion.

Cyclic voltammetry and controlled potential coulometry aided in distinguishing between Fe^{3+} and W^{6+} waves. By variation of pH and scan rate, it was possible to observe the stepwise reduction of the Fe^{3+} centers. Small differences in the electrochemical properties of **1**−**4** were observed, and on the basis of our preliminary results, the four species can be grouped in two classes (**1**, **2** and **3**, **4**), which reflect the respective polyanion charges.

The 4 title compounds and their 17 isostructural derivatives compose one of the largest polyoxometalate families known to date. This together with some interesting structural features warrants a detailed investigation of the catalytic properties (electrocatalysis and redox catalysis) of all compounds reported here. This work is in progress and will be reported elsewhere.

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Supporting Information Available: Three X-ray crystallographic files in CIF format, seventeen figures of IR spectra, and two figures of cyclic voltammograms. This material is available free of charge via the Internet at http://pubs.acs.org.

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