Crystallographic Studies of a Molybdenum-Rich Diarsenotungstate and Reaction of Fe^{III} with Its Isomerically Pure α_1- and α_2-Monolacunary Derivatives

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An isomerically pure form of the molybdenum-rich polytungstate, $[\alpha_1\text{-}As_2Mo_5W_{12}O_{61}]^{10-}$, was prepared by adding 5 equivalents of Mo^{VI} to $[\alpha\text{-}H_2As_2W_{12}O_{48}]^{12-}$, in the presence of Li^+. The α_2-isomer, $[\alpha_2\text{-}As_2Mo_5W_{12}O_{61}]^{10-}$, was prepared by mild alkaline ($KHCO_3$) degradation of $[\alpha\text{-}As_2Mo_6W_{12}O_{62}]^{6-}$. Both $[\alpha_1\text{-}As_2Mo_5W_{12}O_{61}]^{10-}$ and $[\alpha_2\text{-}As_2Mo_5W_{12}O_{61}]^{10-}$ react with Fe^{III} in aqueous solution to give $[\alpha_1\text{-}As_2(FeOH_2)Mo_5W_{12}O_{61}]^{7-}$ (**1**) and $[\alpha_2\text{-}As_2(FeOH_2)Mo_5W_{12}O_{61}]^{7-}$ (**2**), respectively. The parent complex, $[\alpha\text{-}As_2Mo_6W_{12}O_{62}]^{6-}$, was characterized by X-ray crystallography as a mixed potassium-sodium salt [a = 12.8412(17) Å, b = 14.8145(19) Å, c = 19.913(3) Å, α = 70.058°, β = 81.055(5)°, γ = 64,495°, triclinic, $P\bar{1}$, R_1 = 4.99 % based on 9709 reflections]. All of the complexes were characterized by infrared spectroscopy, cyclic voltammetry, and elemental analyses. ^{183}W NMR studies confirm that **1** and **2** are isomerically pure compounds.

Introduction

Polyoxometalates (POMs) are a versatile family of molecular metal oxide clusters with applications in catalysis as well as in medicine and material science.[1–4] Interest in the preparation of isomerically pure polytungstate complexes from lacunary (i.e. tungsten-deficient) precursors continues to be at the center of much of this ongoing research. The first coordination complexes derived from the Wells-Dawson anion, $[\alpha\text{-}P_2W_{18}O_{62}]^{6-}$, were prepared using the monotungsten-vacant derivatives, $[\alpha_1\text{-}P_2W_{17}O_{61}]^{10-}$ and $[\alpha_2\text{-}P_2W_{17}O_{61}]^{10-}$.[5] Later, the tri- and hexatungsten-vacant species ($[\alpha\text{-}P_2W_{15}O_{56}]^{12-}$ and $[\alpha\text{-}H_2P_2W_{12}O_{48}]^{12-}$, respectively) were used.[6,7]

Among the various derivatives prepared by metal incorporation into $[\alpha\text{-}P_2W_{15}O_{56}]^{12-}$ and $[\alpha\text{-}H_2P_2W_{12}O_{48}]^{12-}$, those containing Mo^{VI} or simultaneously Mo^{VI} and a first-row transition metal cation are of particular interest for their electrocatalytic properties.[8,9] It is well established that the presence of one or more molybdenum centers in the polytungstate framework can significantly improve the catalytic properties of the complex. For example, electrocatalysis of NO reduction with $[\alpha_2\text{-}P_2MoW_{17}O_{62}]^{6-}$ was observed at a potential which was 0.270 V more positive than that necessary to carry out the same process with $[\alpha\text{-}P_2W_{18}O_{62}]^{6-}$.[10,11]

Substantial changes in the electrochemical properties of the complexes were also observed upon introducing Fe^{III} centers into a mixed-molybdenum-tungsten framework.[12–14] In a pH 2 medium, the Mo^{VI} centers in $[\alpha\text{-}P_2Mo_3W_{15}O_{62}]^{6-}$ are reduced through three diffusion-controlled one-electron waves. In contrast, $[\alpha_2\text{-}P_2(FeOH_2)Mo_2W_{15}O_{61}]^{7-}$ displays a single three-electron wave in a pH 2 medium as a result of pH-induced merging of the molybdenum and iron waves.

As part of an ongoing program designed to prepare new electrocatalysts for multi-electron transfer reactions,[12,15,16] we now report the isomerically pure preparations of the molybdenum-rich polytungstates, $[\alpha_1\text{-}As_2(FeOH_2)Mo_5W_{12}O_{61}]^{7-}$ (**1**) and $[\alpha_2\text{-}As_2(FeOH_2)Mo_5W_{12}O_{61}]^{7-}$ (**2**). These complexes are formed by the reaction of Fe^{III} with the lacunary precursors, $[\alpha_1\text{-}As_2Mo_5W_{12}O_{61}]^{10-}$ and $[\alpha_2\text{-}As_2Mo_5W_{12}O_{61}]^{10-}$, respectively. Both of these species are structurally derived from $[\alpha\text{-}As_2Mo_6W_{12}O_{62}]^{6-}$ (**3**),[17] which is now characterized by X-ray crystallography. The focus of this manuscript will remain exclusively with the As^V species (rather than the complete isomerically pure P^V series) since $[\alpha_1\text{-}P_2(FeOH_2)Mo_5W_{12}O_{61}]^{7-}$ has not yet been prepared and the first several voltammetric waves of the complexes are driven to more positive potentials by the presence of As^V.[18]

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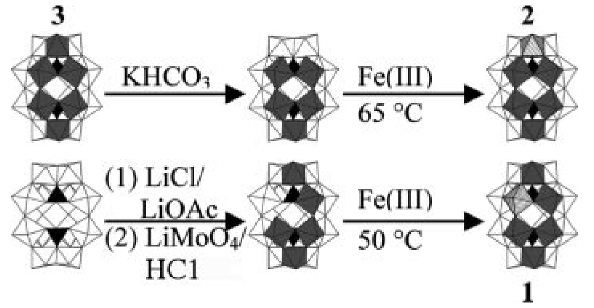
Supporting information for this article is available on the WWW under http://www.eurjic.com or from the author.

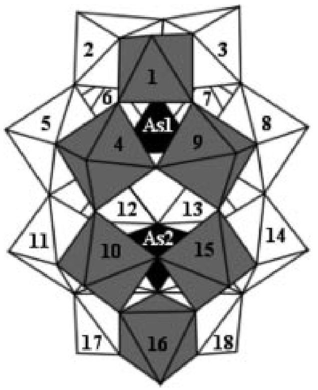
Results and Discussion

Syntheses: Recently we reported the stereospecific synthesis of [α-$As_2Mo_6W_{12}O_{62}]^{6-}$ (**3**).[17] Three parameters were identified in order to achieve high yield and high purity. First, the synthesis must be performed in highly acidic media. Second, a 25% molar excess of molybdate (relative to [α-$H_2As_2W_{12}O_{48}]^{12-}$) must be used in order to prevent the formation of byproducts. Finally, the order of the addition of reactants is important (i.e. solid $K_{12}H_2$[α-$As_2W_{12}O_{48}$] must be slowly added to the molybdate solution in order to keep the Mo concentration as high as possible). Pure complex **3** was the precursor required for the synthesis of [α_2-$As_2Mo_5W_{12}O_{61}]^{10-}$ (Scheme 1). In contrast, the synthesis of [α_1-$As_2Mo_5W_{12}O_{61}]^{10-}$ was achieved by adding 5 equivalents of Mo to [α-$H_2As_2W_{12}O_{48}]^{12-}$, in the presence of Li^+. Syntheses of [α_1-$As_2(FeOH_2)Mo_5W_{12}O_{61}]^{7-}$ (**1**) and [α_2-$As_2(FeOH_2)Mo_5W_{12}O_{61}]^{7-}$ (**2**) were straightforward and involved the gentle heating of aqueous mixtures of Fe^{III} and [α_1-$As_2Mo_5W_{12}O_{61}]^{10-}$ or [α_2-$As_2Mo_5W_{12}O_{61}]^{10-}$, respectively (Scheme 1). In the case of **1**, excessive heating must be avoided in order to prevent the conversion of **1** to **2** (by "hole migration").[19]



Scheme 1. Synthesis of complexes **1** and **2** from [α-$H_2As_2W_{12}O_{48}]^{12-}$ and **3**, respectively.

Crystallographic Studies: X-ray quality crystals of [α-$As_2Mo_6W_{12}O_{62}]^{6-}$ (Scheme 2) were grown by allowing an aqueous solution of the POM (in 1 M NaCl) to slowly evaporate in air over two months. However, over this time period the complex starts to decompose. As a result, the crystals that are obtained are a mixture of 50% [α-$As_2Mo_6W_{12}O_{62}]^{6-}$ and 50% [α-$As_2W_{18}O_{62}]^{6-}$. The data show that a contiguous longitudinal strip of six MO_6 (M = metal) sites (one on each cap position and two on each belt position)[20] are 50% MoO_6 and 50% WO_6 (positions 1, 4, 9, 10, 15, and 16 in Scheme 2). The remaining 12 MO_6 sites are 100% WO_6 (two on each cap position and four on each belt position). This assignment is confirmed by elemental analyses which show that the ratio of As:Mo:W is 2:3:15. A thermal ellipsoid plot with 50% probability surfaces is provided in the Supporting Information.



Scheme 2. Numbering scheme for [α-$As_2Mo_6W_{12}O_{62}]^{6-}$. The MoO_6 octahedra are shown in gray, the WO_6 octahedra are shown in white, and the AsO_4 tetrahedra are shown in black.

Spectroscopic Studies: The infrared spectrum of **3** has a slight shift of the frequencies toward lower wave numbers relative to [α-$As_2W_{18}O_{62}]^{6-}$ as a result of the weakening of bond force constants imposed by the substitution of Mo^{VI} for W^{VI}.[17] A similar trend is observed for the substitution of Fe^{III} for Mo^{VI} in **1** and **2**. In addition, the incorporation of Fe^{III} into the vacant sites of [α_1-$As_2Mo_5W_{12}O_{61}]^{10-}$ and [α_2-$As_2Mo_5W_{12}O_{61}]^{10-}$ partially restores the symmetry in the substituted molecules. The infrared spectra of **1** and **2** are quite similar, but they are clearly distinguishable from their lacunary precursors [α_1-$As_2Mo_5W_{12}O_{61}]^{10-}$ and [α_2-$As_2Mo_5W_{12}O_{61}]^{10-}$ (see Supporting Information).

Table 1 gives the ^{183}W NMR chemical shift values for **1**, **2**, and **3** in aqueous buffer solutions. The substitution of a paramagnetic Fe^{III} center into the mixed-molybdenum-tungsten framework of **1** and **2** results in a substantial broadening of the signals for the two most structurally proximal W^{VI} centers such that they are not observed in the spectrum. Previously it was established (primarily by ^{31}P NMR studies) that the presence of paramagnetic metal centers results in dramatic chemical shift changes and/or substantial broadening of signals.[5b] Low solubility and low stability prevented the acquisition of ^{183}W NMR spectroscopic data on the lacunary precursors [α_1-$As_2Mo_5W_{12}O_{61}]^{10-}$ and [α_2-$As_2Mo_5W_{12}O_{61}]^{10-}$.

Electrochemical Studies: The electrochemical properties of **3** were previously studied in a pH = 0.33 medium suitable for its stability.[17] The observed pattern consists of three chemically reversible waves featuring three quasi-reversible two-electron processes. The cyclic voltammograms of **1**, **2**, [α_1-$As_2Mo_5W_{12}O_{61}]^{10-}$, and [$\alpha_2$-$As_2Mo_5W_{12}O_{61}]^{10-}$ were

Table 1. ^{183}W NMR chemical shift values (vs. 2 M Na_2WO_4 in D_2O) for complexes **1**, **2**, and **3**.

Compound	^{183}W NMR chemical shifts (ppm)	Reference
1	–89.1 (2 W), –115.0 (2 W), –168.1 (2 W), –183.1 (2 W), –191.3 (2 W)	this work
2	–84.3 (2 W), –103.9 (4 W), –150.2 (4 W)	this work
3	–130.2 (4 W), –138.8 (4 W), –156.6 (4 W)	[17]

run at a scan rate of 10 mV s^{-1} in a 1 M CH_3COOLi/CH_3COOH (pH = 5) medium. The electrolyte was chosen to ensure the stability of all four of the compounds. Given the fact that the Mo^{VI} and Fe^{III} waves of $[\alpha_2\text{-}P_2(FeOH_2)Mo_2W_{15}O_{61}]^{7-}$ merge in a pH = 2 medium but become increasingly split at higher pH values,[12,13] similar behavior was anticipated for **1** and **2**. Figure 1 compares the cyclic voltammograms of **1** and **2** with those of their lacunary precursors, $[\alpha_1\text{-}As_2Mo_5W_{12}O_{61}]^{10-}$ and $[\alpha_2\text{-}As_2Mo_5W_{12}O_{61}]^{10-}$, respectively. The patterns were restricted to those waves for which derivatization of the electrode surface is not expected. The superposition of the waves highlights their differences, and in analogy with previous work,[12,13,15b,16,17,21,22] facilitates the assignments of the first several waves. In addition, assignment of the waves is further facilitated by the fact that it is well established that the first electron transfer should occur on one of the "belt" atoms.[9b] With these guidelines in mind, each of the first two waves of **1** and $[\alpha_1\text{-}As_2Mo_5W_{12}O_{61}]^{10-}$ moving toward less positive potentials features a one-electron quasi-reversible process, with Mo^{VI} being more easily reduced than the Fe^{III} center. The apparent redox potential of this first wave, estimated as the average between the cathodic and anodic peak potentials, was +0.134 V vs. SCE. In contrast, the first two one-electron redox processes of $[\alpha_2\text{-}As_2Mo_5W_{12}O_{61}]^{10-}$ are almost completely merged, while those of **2** are well separated with an apparent redox potential of +0.096 V (vs. SCE) for the first wave of the latter. Thus electrochemistry establishes clear differences between all four of the POMs in a pH = 5 medium, at least regarding the location of the potential of the first wave and/or the number of electrons consumed on this first wave. Finally, as anticipated, there is a close similarity observed between the present As^V-based POMs and the corresponding P^V-based complex, $[\alpha_2\text{-}P_2(FeOH_2)Mo_5W_{12}O_{61}]^{7-}$.[16]

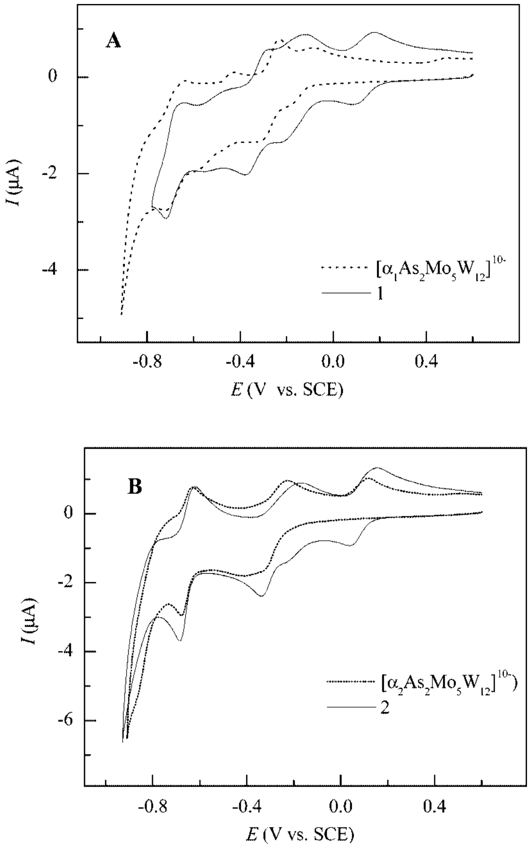


Figure 1. Cyclic voltammograms of 0.2 mM solutions of (**A**) **1** and $[\alpha_1\text{-}As_2Mo_5W_{12}O_{61}]^{10-}$ and (**B**) **2** and $[\alpha_2\text{-}As_2Mo_5W_{12}O_{61}]^{10-}$ in a 1 M CH_3COOLi/CH_3COOH (pH = 5) buffer solution. The working electrode was glassy carbon, the reference electrode was SCE, and the scan rate was 10 mV·s^{-1}.

Conclusions

Molybdenum-rich polytungstates are of proven value in electrocatalysis. However, the preparation of isomerically pure complexes is challenging, in part, due to the high lability of the Mo^{VI} centers. Isomerically pure preparations of $[\alpha_1\text{-}As_2(FeOH_2)Mo_5W_{12}O_{61}]^{7-}$ (**1**) and $[\alpha_2\text{-}As_2(FeOH_2)Mo_5W_{12}O_{61}]^{7-}$ (**2**) were achieved by the reaction of Fe^{III} with the lacunary precursors, $[\alpha_1\text{-}As_2Mo_5W_{12}O_{61}]^{10-}$ and $[\alpha_2\text{-}As_2Mo_5W_{12}O_{61}]^{10-}$, respectively. Both of these species are structurally derived from $[\alpha\text{-}As_2Mo_6W_{12}O_{62}]^{6-}$ (**3**), which is now characterized by X-ray crystallography. The results show that positions 1, 4, 9, 10, 15, and 16 in Scheme 2 are 50% MoO_6 and 50% WO_6. Electrochemical studies reveal that complexes **1** and **2** (and their lacunary precursors) are all clearly distinguishable by cyclic voltammetry.

Experimental Section

General Methods and Materials: $K_6[\alpha\text{-}As_2Mo_6W_{12}O_{62}]\cdot 12H_2O$ and $K_{12}H_2[\alpha\text{-}As_2W_{12}O_{48}]\cdot 23H_2O$ were obtained by published procedures.[17,19,23] Elemental analyses were performed by Kanti Labs (Mississauga, Ontario), and the analysis of W was confirmed by a modified literature method.[24] The water content of the samples was determined by standard methods. Infrared spectra (2% sample in KBr) were recorded with a Perkin–Elmer Spectrum One FT-IR spectrometer. NMR spectra were recorded with a Bruker 400 instrument operating at 16.67 MHz. The ^{183}W chemical shifts were measured with respect to an external 2 M Na_2WO_4 solution in alkaline D_2O.

Synthesis of $K_9Li[\alpha_1\text{-}As_2Mo_5W_{12}O_{61}]\cdot 28H_2O$: A sample of pure α-$K_{12}H_2[As_2W_{12}O_{48}]\cdot 23H_2O$ (12 g; 3 mmol) was dissolved in a solution containing 150 mL of 1 M LiCl and 50 mL of 0.5 M CH_3COOLi (pH ≈ 4.7). This relatively cloudy solution was treated with 15 mL of 1 M $LiMoO_4$ (15 mmol) and 30 mL of 1 M HCl to keep the pH constant (≈ 4.7). The resulting clear, very faintly yellow solution was treated with 60 mL of a saturated KCl solution. The off-white precipitate was filtered (by suction filtration), washed twice with ethyl alcohol and twice with ethyl ether, and dried in air. The amount of pure compound obtained was 13.50 g (yield 96.5% relative to the starting material, α-$K_{12}H_2[As_2W_{12}O_{48}]\cdot 23H_2O$). $K_9Li[\alpha_1\text{-}As_2Mo_5W_{12}O_{61}]\cdot 28H_2O$ (4675): calcd. As 3.19, K 7.45, Mo 9.76, W 46.9; found As 3.21, K 7.52, Mo 10.26, W 47.2. IR (cm^{-1}): $\tilde{\nu}$ = 943.3 (s), 855.3 (w), 823.3 (w), 782.8 (vw), 743.1 (w), 513.7 (vw), 497.9 (w), 419.5 (vw).

Synthesis of $K_{10}[\alpha_2\text{-}As_2Mo_5W_{12}O_{61}]\cdot 21H_2O$: A sample of pure α-$K_6[As_2Mo_6W_{12}O_{62}]\cdot 12H_2O$ (10 g; 2.3 mmol) was dissolved in

25 mL of de-ionized water. A 22 mL aliquot of 1 M $KHCO_3$ (22 mL; 22 mmol) was then added to the clear solution. A yellow precipitate formed progressively and was left to settle for ca. 45 min, after which it was filtered, washed twice successively with ethyl alcohol and ethyl ether, and dried in air. The amount of pure compound was 10.00 g (yield 94.9% relative to the starting material, α-$K_6[As_2Mo_6W_{12}O_{62}]\cdot 12\,H_2O$). $K_{10}[\alpha_2\text{-}As_2Mo_5W_{12}O_{61}]\cdot 21\,H_2O$ (4581): calcd: As 3.31; K 8.61; Mo 10.7, W 48.3; found As 3.27, K 8.54, Mo 10.47, W 48.2. IR (cm^{-1}): $\tilde{\nu}$ = 938.6 (s), 862.5 (s), 818.8 (m), 784.1 (m), 711.0 (s), 519.6 (w), 498.7 (w), 419.1 (w).

Synthesis of $K_7[\alpha_1\text{-}As_2(FeOH_2)Mo_5W_{12}O_{61}]\cdot 22\,H_2O$: A sample of $Fe(NO_3)_3\cdot 9\,H_2O$ (0.30 g; 0.75 mmol) was dissolved in 40 mL of de-ionized water. Then, solid $K_9Li[\alpha_1\text{-}As_2Mo_5W_{12}O_{61}]\cdot 28\,H_2O$ (3.0 g; 0.64 mmol) was added in small portions. The mixture was heated very gently on a water bath (≈ 50 °C) to enhance solubility. After ca. 20 min, the pale yellow solution was filtered and treated with 5 g of solid KCl. The yellow precipitate that formed was filtered off, washed successively (twice with a saturated KCl solution and twice with ethyl alcohol), and dried in air. The amount of pure compound obtained was 1.70 g (yield 58.2% relative to the starting material, $K_9Li[\alpha_1\text{-}As_2Mo_5W_{12}O_{61}]\cdot 28\,H_2O$). $K_7[\alpha_1\text{-}As_2(FeOH_2)Mo_5W_{12}O_{61}]\cdot 22\,H_2O$ (4538): calcd. As 3.26, Fe, 1.25, K 6.12, Mo 10.6, W 48.5, found As 3.29, Fe 1.22, K 6.01, Mo 10.53, W 48.4. IR (cm^{-1}): $\tilde{\nu}$ = 957.0 (s), 882.9 (w), 854.7 (w), 823.3 (w), 762.9 (s), 520.6 (w), 495.7 (w), 420.1 (m).

Synthesis of $K_7[\alpha_2\text{-}As_2(FeOH_2)Mo_5W_{12}O_{61}]\cdot 19\,H_2O$: A sample of $Fe(NO_3)_3\cdot 9\,H_2O$ (0.30 g; 0.75 mmol) was dissolved in 40 mL of de-ionized water. Then, solid $K_{10}[\alpha_2\text{-}As_2Mo_5W_{12}O_{61}]\cdot 21\,H_2O$ (3.0 g; 0.65 mmol) was added in small portions. The mixture was heated gently on a water bath (≈ 65 °C) to enhance solubility. After ca. 20 min, the pale yellow solution was filtered and treated with 5 g of solid KCl. The yellow precipitate that formed was filtered off, washed successively (twice with a saturated KCl solution and twice with ethyl alcohol), and dried in air. The amount of pure compound obtained was 2.60 g (yield 89.3% relative to the starting material, $K_{10}[\alpha_2\text{-}As_2Mo_5W_{12}O_{61}]\cdot 21\,H_2O$). $K_7[\alpha_2\text{-}As_2(FeOH_2)Mo_5W_{12}O_{61}]\cdot 19\,H_2O$ (4484): calcd. K 6.19, As 3.37, Fe 1.32, Mo 10.9, W 50.3, found As 3.37, Fe 1.25; K 6.15, Mo 10.79, W 49.6. IR (cm^{-1}): $\tilde{\nu}$ = 954.1 (s), 882.8 (w), 854.5 (vw), 823.3 (vw), 763.1 (s), 655.3 (w), 522.6 (m), 490.9 (m), 421.7 (s).

Crystallographic Studies of $K_2Na_4[\alpha\text{-}As_2Mo_6W_{12}O_{62}]_{0.5}[\alpha\text{-}As_2W_{18}O_{62}]_{0.5}\cdot 11\,H_2O$: Single-crystal X-ray crystallographic analysis of $[\alpha\text{-}As_2Mo_6W_{12}O_{62}]^{6-}$ was performed at 173 K with a Bruker D8 SMART APEX CCD sealed tube diffractometer with graphite-monochromated Mo-K_α (0.71073 Å) radiation. Data collection, indexing, and initial cell refinements were performed using SMART software.[25] Frame integration and final cell refinements were performed using SAINT software.[26] Final cell parameters were determined from least-squares refinement on 9709 reflections. Absorption corrections were applied using SADABS.[27] The structure was determined using Direct Methods and difference Fourier techniques. No H atoms associated with the eleven water molecules of $[\alpha\text{-}As_2Mo_6W_{12}O_{62}]^{6-}$ were located in the difference Fourier maps. The final R_1 scattering factor and the anomalous dispersion correction were taken from International Tables for X-ray Crystallography.[28] Structure solution, refinement, and generation of publication materials were performed using SHELXTL V6.12 software. Additional details are provided in Table 2, and may also be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany; Fax: +49-7247-808-666, E-mail: crysdata@fiz-karlsruhe.de, on quoting the depository number CSD-414645. Elemental analyses (As, K, Mo, Na and W) on the crystals were performed by Desert Analytics (Tucson, Arizona). $K_2Na_4[\alpha\text{-}As_2Mo_6W_{12}O_{62}]_{0.5}[\alpha\text{-}As_2W_{18}O_{62}]_{0.5}\cdot 11\,H_2O$ (4556): calcd. As 3.29, K 1.72, Mo 6.32, Na 2.02, OH_2 4.3, W 60.5, found As 3.27, K 1.69, Mo 6.34, Na 2.10, OH_2 4.3, W 59.8.

Table 2. Crystallographic data and structure refinement for $K_2Na_4[\alpha\text{-}As_2Mo_6W_{12}O_{62}]_{0.5}[\alpha\text{-}As_2W_{18}O_{62}]_{0.5}\cdot 11\,H_2O$.

Empirical formula	$H_{22}As_2K_2Mo_3Na_4O_{73}W_{15}$
Formula mass	4555.75
Space group	$P\bar{1}$
Unit cell [Å, °]	a = 12.8412(17)
	b = 14.8145(19)
	c = 19.913(3)
	α = 70.058(4)
	β = 81.055(5)
	γ = 64.495(4)
V [Å^3]	3213.8(7)
Z	2
Density (calcd.) [g•cm^{-3}]	4.708
Temperature [K]	173(2)
λ [Å]	0.71073
M [cm^{-1}]	2.8588
GOF	1.066
Final R_1[a] [$I > 2\sigma(I)$]	0.0499
Final wR_2[b] [$I > 2\sigma(I)$]	0.1314

[a] $R_1 = \Sigma||F_o| - |F_c||/|F_o|$. [b] $R_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{0.5}$.

Electrochemical Studies: Cyclic voltammetry studies were performed in a pH 5 acetate (1.0 M CH_3COOLi/CH_3COOH) medium. Solutions were de-aerated with Ar for at least 30 min prior to measurements and kept under positive pressure at all times. The source, mounting, and polishing of the glassy carbon electrodes (GC, Tokai, Japan, 3 mm diameter) have been described in previous work.[21] The electrochemical apparatus was a EG and G 273A under computer control (M270 software). The counter electrode was a platinum gauze of large surface area. All experiments were performed at ambient temperature, and potentials are quoted against a saturated calomel electrode (SCE).

Acknowledgments

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