**Bi-functionalized Polyoxotungstates: Dilacunary Keggin Clusters Incorporating FeIII and Organoarsonate Constituents**

Fabian Faassen,†,§ Natalya V. Izarova,\*†,§ Jan van Leusen† and Paul Kögerler\*†,§

† Institut für Anorganische Chemie, RWTH Aachen University, D-52074 Aachen, Germany.

§ Jülich-Aachen Research Alliance (JARA-FIT) and Peter Grünberg Institute (PGI-6), Forschungszentrum Jülich, D-52425 Jülich, Germany.

**KEYWORDS:** polyoxotungstates, organoarsonates, crystal structure, electrochemistry, magnetic properties.

**ABSTRACT:** Polyanions [{*B-α-*(OH)Fe2(PW10O37)}2{*o*-R−C6H4−AsO3)}2]12− (R = NH2 (**1**) and NO2 (**2**)) represent the first polyoxotungstates functionalized by both organoarsonates and FeIII. **1** and **2** comprise the rare dilacunary Keggin-type phosphotungstate {*B-α*-PW10O37}9− isomer that coordinates FeIII ions to form {*B-α*-FeIII2PW10} complexes linked into dimers via two organoarsonate groups. The title polyanions have been isolated as crystalline materials and fully characterized via single-crystal and powder X-ray diffraction, elemental analysis, IR and UV-vis spectroscopy, including solution stability studies. In addition, their electrochemical and magnetic properties have been characterized.

**INTRODUCTION**

Bi-functionalization of discrete polynuclear WVI oxo complexes known as polyoxotungstates (POTs) with heterometal ions and organic groups offers broad perspectives for the fine-tuning of electronic properties of the polyanions, their solubility, reactivity as well as ability to be controllably deposited on various surfaces relevant to catalysis, magnetism, photophysics, medicine as well as for fabrication of sensors and other molecular devices.1−13

A variety of organic ligands, such as alkoxides, carboxylates, organo(bis)phosphonates and arsonates, siloxanes, boranes, organotin and others have been widely used to functionalize polyanions with organic groups.6−14 Among them, organoarsonates remain severely underrepresented. One of the reasons for that is their close structural analogy with organophosphonates that are less toxic and provide a possibility for 31P NMR studies. At the same time, our recent investigations showed that despite this structural similarity the actual behavior of arsonates and phosphonates in reactions with POTs can show pronounced differences, and in many cases hybrid species that are readily available with organoarsonates cannot be obtained with organophosphonates. The most evident difference concerns the larger size of AsV in comparison to PV and consequently larger size of the whole tetrahedral arsonate R−AsO32− group, giving it the possibility to more conveniently anchor on the POT surface.15−17

Until now only three examples of heterometallic organoarsonate-functionalized POTs have been reported, namely a lanthanum derivative of *p*-arsanilate-decorated Keggin-type polyanion [*A-α-*PW9O34(*p*-H2N–C6H4–AsO)2{La(dmf)3(H2O)2}]2– reported by Villaneau *et al.* in 201318 and two derivatives [CoII9(H2O)6(OH)3(*p*-R–C6H4–AsO3)2(*α-*P2W15O56)3]25– (R = H and NH2) reported by us previously.15 The terminal *p*-aminophenyl (*p*-arsanilate) groups of the latter were used to form monolayers of these polyanions on a Au(111) surface, which allowed further investigation of molecular charge-transport features associated with their molecular frontier orbitals.15

In the course of this work we have isolated two novel discrete dimeric organoarsonate-functionalized POT derivatives based on the rare dilacunary {*B-α-*PW10} Keggin isomer that here incorporates FeIII ions, [{*B-α-*(OH)FeIII2(PW10O37)}2{*o*-H2N−C6H4−AsO3)}2]12− (**1**) and [{*B-α-*(OH)FeIII2(PW10O37)}2{*o*-O2N−C6H4−AsO3)}2]12− (**2**), and herein report on their synthesis, crystal structure, electrochemical and magnetic properties.

**RESULTS AND DISCUSSIONS**

**Synthesis**

The organoarsonates-functionalized FeIII-containing POTs were obtained by stirring and heating of FeIII nitrate with trilacunary Keggin-type polyanions [*A-α-*PW9O34]9− ({*A-α-*PW9})19 and the respective organoarsonic acid in the molar ratio of 1 : 2.8 : 2.8 in 0.66 M sodium acetate buffer with pH 5.2 at 75 °C for 2 h. During the reactions solution-unstable {*A-α-*PW9} polyanions underwent a partial decomposition combined with a rearrangement of the remaining POT units into {*B-α-*PW10O37}9− moieties stabilized by formation of a complex with two FeIII centers. The polyanions **1** and **2** were isolated as crystals of the hydrated dimethylammonium salts [H2N(CH3)2]11(H3O)[{*B-α-*(OH)FeIII2(PW10O37)}2{*o*-H2N−C6H4−AsO3)}2]⋅9H2O (**D-1**) and [H2N(CH3)2]11(H3O)[{*B-α-*(OH)FeIII2(PW10O37)}2{*o-*O2N−C6H4−AsO3)}2]⋅10H2O (**D-2**), which appear after addition of dimethylammonium chloride in the obtained after the heating and the subsequent filtration mother solutions and further slow evaporation of the resulting solutions in air. Different reaction temperatures from 75 to 120 °C have been tested for these reactions. However, the increase of the temperature did not lead to any improvements of the yield of the products. We also observed that if the reaction solution of **D-1** is left for another 2–3 weeks, rectangular plate-shaped crystals that differ from the initially formed **D-1** product (diamond-shaped blocks) start to form in a mixture with an additional portion of **D-1** crystals. Based on single-crystal XRD studies the second product is based on the same polyanion **1** and represents its hydrated mixed sodium/dimethylammonium salt Na1.5[H2N(CH3)2]10.5[{*B-α-*(OH)FeIII2(PW10O37)}2{*o*-H2N−C6H4−AsO3)}2]⋅*x*H2O (**D-1\***).

The exact composition of **D-1** and **D-2** in terms of the amount of countercations and crystal water molecules was established by a combination of single-crystal XRD and elemental analyses. The bulk purity of these crystalline materials was further confirmed by powder X-ray diffraction, which showed a very good match of the obtained powder XRD patterns to the curves simulated from the single-crystal X-ray data (see Figures S2–S5).

**Crystal structures**

The compounds **D-1** and **D-2** are isostructural and crystallize in the monoclinic space group *P*21/*n*. Polyanions **1** and **2** are both based on the {*B-α-*(HO)FeIII2PW10O37} units interconnected into dimers via two organoarsonate moieties (Figure 1, left and right).

The monomeric unit {*B-α-*(HO)FeIII2PW10O37} exhibits a typical *α*-Keggin-type structure containing three {WVI3O13} and one {FeIII2WVIO13} triads assembled in a corner-sharing mode around a central phosphate group (Figure 1, middle). All W−O and P−O bond lengths in **1** and **2** are in line with usual values observed for POTs (see Table S1). Each octahedrally coordinated FeIII center binds to four O atoms of {*B-α-*PW10} POT: a *μ*4-O of the central phosphate group linking together central PV, one WVI and two FeIII ions (Fe−O: 2.302(16)–2.374(15) Å in **1**, 2.347(16)–2.372(15) Å in **2**) and three *μ*2-O connecting the FeIII ion to three WVI centers (Fe−O: 1.910(16)–2.019(14) Å in **1**, 1.917(15)–2.001(15) Å in **2**). The octahedral environment is completed by an oxygen atom of one of the organoarsonate moieties (Fe−O: 1.903(16)–1.910(18) Å in **1**, 1.895(16)–1.902(19) Å in **2**) and a *μ*2-OH group bridging the two FeIII sites (Fe−O: 2.003(17)–2.010(16) Å in **1**, 1.964(17)–2.027(16) Å in **2**). The protonation of this oxygen center is clearly established from the elongation of the respective Fe−O bonds and bond valence sum calculations (see Tables S2–S4).20,21



**Figure 1**. Structure of polyanions **1** (left) and **2** (right) as well as the monomeric {*B-α-*FeIII2PW10} unit (center). Color code: {WO6} blue octahedra (different shades of blue differentiate the {W3O13} triads), {PO4} pink tetrahedra; Fe orange, O red, C black, N blue, H light gray spheres. Internal organoarsonate bonds in gray, Fe–O bonds in yellow/red. The O atoms of the Fe–(μ-OH)–Fe bridges are highlighted as brown spheres.

The AsV center in each organophosphonate group interlinks two {*B-α-*(HO)FeIII2PW10O37} units, binding to each of them by one of the O atoms on FeIII ion (As−O: 1.665(16)–1.678(16) Å in **1**, 1.669(18)–1.730(17) Å in **2**) and bearing one terminal oxygen atom (As−O: 1.666(19) Å in **1**, 1.620(18) Å in **2**) and an *ortho*-aminophenyl (in **1**) or *ortho*-nitrophenyl (in **2**) moiety (As−C: 1.900(19) Å in **1**, 1.955(13) Å in **2**), which is exo-oriented relative to the polyanions.

Alternatively, **1** and **2** could be imagined as {*B-α-*PW10}-stabilized 12-membered {FeIII4AsV2O6} rings, where O atoms alternately link FeIII and AsV centers in such a way that two FeIII ions interchange with one AsV (see Figure 1, left and right). The closest FeIII···FeIII distance within one {*B-α-*(HO)FeIII2PW10O37} subunit is 3.362 Å in **1** and 3.375 Å in **2** and 5.227 Å (**1**) / 5.226 Å (**2**) between the two subunits. The closest FeIII···AsV distance is 3.280 Å (**1**) / 3.317 Å (**2**) Å, while the AsV···AsV separation equals 7.174 Å in **1** and 7.262 Å in **2**.

The structures of **1** and **1\*** are very similar and only differ in the mutual orientation of the arsonate groups and {*B-α-*(HO)FeIII2PW10O37} subunits (Figure S1, Supporting Information).

**1**, **1\*** and **2** are *C*i-symmetric. The *ortho* position of the substituent in the phenyl ring appears to play an important role for formation of **1** and **2** as no similar polyanions could be isolated with bare phenylarsonate groups or with phenylarsonate groups with substituents in *meta* or *para* positions under similar conditions.

**1** and **2** represent the first examples of heterometal complexes of dilacunary Keggin-type POTs comprising organoarsonate moieties. {*B-α-*PW10} units themselves are not unprecedented and although they cannot be isolated without a heterometal, they were observed in complexes with CoII, CuII, ZrIV and HfIV ions: [CoII6(*B*-*α*-PW10O37)2(pyridazine)4(H2O)6]6−,22 {[CuII5(en)2(OH)2(CH3COO)2(H2O)8][CuII10.75(ethylenediamine)6(OH)4(H2O)5(*α*-PW11O39)(*B-α-*PW10.25O37)(*B-α*-PW9O34)]2}6−,23 [{M(H2O)}2{M(H2O)2}2(*µ*-OH)3(*µ*3-OH)2](*B-α-*PW10O37)2]7− (M = ZrIV, HfIV),24 and [ZrIV4(*μ*3-O)2(*L*-/*D-*malate)2(*B-α-*PW10O37)2]8−.25 At the same time, Keggin-type POTs in which two heterometal sites replace W positions belonging to one triad substructure are rare; species comprising {*A-α-*PW10} isomers of dilacunary Keggin-type phosphotungstates, where the heterometals are located in two neighboring {W2MO13} triads, are much more common (see Table S5 in the SI). One representative example is [FeIII4(OH)4(*A-α-*PW10O37)2]10−, where two {*A-α-*(HO)FeIII2PW10O37} subunits are interlinked directly via two OH groups.26,27 Complexes comprising {*α-*PW10} isomer with two separate lacunary sites has been also reported.28

Formation of {*B-α-*PW10} from the trilacunary derivative {*A-α-*PW9} requires partial decomposition and rebuilding of the POT skeleton during the reaction. This not surprising when considering the very limited solution stability of the {*A-α-*PW9} species. In our case, complexation with FeIII ions and organoarsonate units allows for sufficient stabilization of the rare dilacunary {*B-α-*PW10} POT moieties. **1** and **2** also readily form in reactions of {*B-α-*PW9}, but since preparation of this POT precursor requires an additional energy-consuming step in comparison to the synthesis of {*A-α-*PW9}, we did not pursue this possibility further.

Interestingly, the arsonate moieties in **1** and **2** are attached solely to heterometal FeIII centers, as has also been observed for Co9-POTs [CoII9(H2O)6(OH)3(*p*-R–C6H4–AsO3)2(*α-*P2W15O56)3]25– (R = H and NH2).15 This is in contrast to the bi-functionalized trilacunary Keggin type POTs [*A-α-*PW9O34(*p-*H2N–C6H4–AsO)2{La(dmf)3(H2O)2}]2–, where the *p*-arsanilate groups are bound to both {*A-α-*PW9} POT units as well as to the LaIII heterometal.18 The underlying reason appears to be the one-pot self-assembly synthetic pathway for **1**, **2** and Co9-POTs, while the La derivative was prepared by reaction of the LaIII ions with the POT precursor [*A-α-*PW9O34(*p-*H2N–C6H4–AsO)2]5– that was pre-functionalized with arsonate groups. This observation also suggests a slightly higher affinity of arsonate groups to 3d metal ions *vs*. 5d WVI centers.

**IR spectroscopy**

The IR spectra for **D-1** and **D-2** (Figures 2 and S6) are similar to each other. The characteristic P−O vibrations (two bands at 1018 and 1051 cm−1) are complimentary to the P−O vibrations observed for the Na9[*A-α-*PW9O34]·7H2O (Na-PW9) precursor (1014 and 1055 cm−1). A band corresponding to terminal W=O bonds is significantly shifted from 931 cm−1 in Na-PW9 to 949 cm−1 (**D-1**) and 948 cm−1 (**D-2**), reflecting the {*A-α-*PW9} → {*B-α-*PW10} rearrangement as well as the FeIII coordination.

The bands in the region from 900 to 400 cm−1 correspond to W−O−W, W−O−P, W−O−As, W−O−Fe, and Fe−O−As vibrations. Here the characteristic vibration of As−O bonds should appear at *ca*. 870 and 790 cm−1, however, they overlap with the bending vibrations of the bonds in POT skeleton. The broad line width of a band at 790 cm−1 for **D-1** and its partial splitting in the spectrum of **D-2** (two not well-resolved bands at 791 and 740 cm−1) further support this assignment.

The medium and weak bands in the region from 1600 to 1100 cm–1 are attributed to the C−C, C−N, N−H vibrations of aniline (**D-1**) and nitrophenyl (**D-2**) groups and DMA+ countercations (from 1550 to 1400 cm–1) as well as N−O vibrations of nitrophenyl in **D-2** (see also Figures S7 and S8 for a comparison of the spectra of **D-1** and **D-2** with the corresponding organoarsonic acid).

Broad bands at around 1600 and 3510–3100 cm−1 for the both samples belong to bending and stretching, respectively, vibrations of O−H bonds in the co-crystallized water molecules as well as N−H bonds of amino groups in *o*-arsanilate in **D-1** and DMA+ countercations in the both samples. Other broad peaks at around 2790 and 2420–2410 cm−1 (Figures S6−S8) are attributed to C−H and C−C bonds in **D-1** and **D-2**, and they are expectedly absent in the spectrum of Na-PW9.



**Figure 2**. FTIR-ATR spectra of **D-1** (blue) and **D-2** (green) in comparison with that of the POT-precursor Na-PW9.

**Solution stability studies: UV-vis spectroscopy**

UV-vis spectra (Figure S9) of **D-1** and **D-2** solutions in 0.66 M aqueous acetate medium (pH 5.2) exhibit strong absorption in the UV region at 245 nm (*ε* = 76700 M−1 cm−1) for **D-1** and 255 nm (*ε* = 99900 M−1 cm−1) for **D-2**, which are associated with ligand-to-metal charge transfer bands of the POT framework, followed by a much less intense and broad absorption shoulder centered at around 360 nm (*ε* = 2037 M−1 cm−1 for **D-1**, *ε* = 3630 M−1 cm−1 for **D-2**).

The stability tests in the same medium show no change within 1 h (Figures S10 and S11, left) and only a very slight decrease of the absorption intensity over 16 h for the solution of **D-1** (Figure S10, right), while the spectrum of **D-2** remains unchanged over the same period of time (Figure S11, right). This suggest at least a short-term stability (several hours) for the polyanions **1** and **2** in acetate aqueous buffer (pH 5.2), which is sufficient for performing of cyclic voltammetry measurements on solutions of **D-1** and **D-2** in this medium.

**Cyclic voltammetry (CV)**

The cyclic voltammograms for **D-1** and **D-2** were recorded on their 1.00 mM (**D-1**) and 0.77 mM (**D-2**) solutions in 0.66 M CH3COONa buffer (pH 5.2). The electrochemical behavior of polyanions **1** and **2** has both common for the two compounds features, which could be therefore attributed to the redox activity of {*B-α-*FeIII2PW10} units as well as unique characteristics reflecting reduction and oxidation of their organoarsonate moieties (Figures 3, 4 and S12).



**Figure 3.** Room-temperature cyclic voltammograms of 1.00 mM solution of **D-1** (left) and 0.77 mM solution of **D-2** (right) in 0.66 M CH3COONa buffer (pH 5.2) with different negative potential limits (–0.35 V, −0,77V and −0.93 V for **D-1**; −0.33 V, −0.80 V and −0.90 V for **D-2**) at a scan rate of 20 mV/s.

Thus, the pronounced redox couple at −0.109 V for **D-1** and −0.113 V *vs.* Ag/AgCl for **D-2**29 corresponds to the reversible reduction of FeIII centers in polyanions **1** and **2** to FeII. In the cyclic voltammogram of **D-2** it is followed by an intense irreversible reduction wave at −0.470 V that could be attributed to the reduction of a nitro group of *ortho*-nitrophenylarsonate moieties in **2** in agreement with the reports on electrochemical activities of nitro aromatic compounds (Figure 3, right).30 This reduction wave is expectedly absent in the cyclic voltammetry curve for **D-1**. The reversible redox couple centered at −0.709 V for **D-1** and at −0.725 for **D-2** reflects reduction and re-oxidation of the WVI centers of {*B-α-*FeIII2PW10} units. The low intensity of this wave suggests that it might belong to the redox activity of the WVI centers in {Fe2WO13} triads. The next intense redox couple appears at around −0.820 V for **D-1** and at −0.840 for **D-2**.

The cyclic voltammogram for **D-2** does not show any features in the positive potential range. However, a strong oxidation wave at +0.988 V is present in the curve for **D-1**, which corresponds to the irreversible oxidation of amino groups in the *ortho*-aminophenylarsonate fragments in **1** into the corresponding {NH2+}• radical (Figure 4).31



**Figure 4**. Room-temperature cyclic voltammograms of 1.00 mM solution of **D-1** (left) and 0.77 mM solution of **D-2** (right) in 0.66 M CH3COONa buffer (pH 5.2) at a scan rate of 20 mV/s in the positive potential range.

The proportionality of peak currents for the (quasi-)reversible redox processes in the negative potential domain to the square root of the scan rate was checked and observed for **D-1**, which does not show any waves associated with irreversible reduction/oxidation of the organogroups in this potential area (Figures S13, S14 and Table S6). The obtained result indicates diffusion-controlled electrode reactions for scan rates from 10 to 100 mV/s. The Randles-Ševčik equation32 was applied to estimate a diffusion coefficient *D* for **1** assuming transfer of four electrons for the FeIII→FeII reduction wave (one electron per every four FeIII centers in **1**). The obtained value of *D* = 8.37×10−7 cm2/s compares well to the values reported for other POTs.33−36

The CV curves for **D-1** and **D-2** remain unchanged for at least 1.5 − 2 h, which further suggests stability of polyanions **1** and **2** in aqueous acetic medium for at least this period of time.

**SQUID Magnetometry**

The magnetic data of **D-1** are shown in Figure S15 as *χ*m*T* *vs*. *T* and *M*m *vs*. *B* plots. At 290 K, the value of *χ*m*T* is 13.47 cm3 K mol–1 at 0.1 T and 13.37 cm3 K mol–1 at 1.0 T. These values are significantly below the range 16.2–18.0 cm3 K mol–1 expected37 for four non-interacting high spin FeIII centers. Upon cooling the compound, *χ*m*T* continuously decreases to reach 0.22 cm3 K mol–1 0.1 T (0.18 cm3 K mol–1 at 1.0 T) at 2.0 K. A change of the curvature can be observed below 5 K. At 2.0 K, the molar magnetization *M*m remains very small up to an applied field of 5.0 T: *M*m increases from 0 at 0 T to 0.41 *N*A *μ*B at 5.0 T. The latter value is distinctly below the saturation value (20 *N*A *μ*B) of four high-spin FeIII centers. The lower values of *χ*m*T* at 1.0 T *vs*. 0.1 T at lower temperatures are due to the Zeeman effect. The generally low values of *χ*m*T* at 290 K combined with the steady temperature-dependent decrease reveals dominant antiferromagnetic exchange interactions between the four FeIII centers. Such interactions also are in line with the small molar magnetization values as observed at 2.0 K. Considering the structural data of **1**, the exchange interaction pathways via the arsenate groups should be weaker than via the µ2-OH bridge of each {Fe2PW10}. The change of the *χ*m*T* vs *T* curve below 5 K as well as the non-vanishing and non-linear behavior of the *M*m vs *B* curve reveal a small amount of Fe3+ centers in the cationic lattice (0.05 Fe3+ centers per formula unit).

*χ*m*T* *vs*. *T* and *M*m *vs*. *B* plots for **D-2** (Figure S16) show very similar characteristics, including a similar small amount of Fe3+ centers in the cationic lattice (0.06 Fe3+ centers per formula unit).

In order to estimate the exchange coupling between the four Fe3+ sites, representing isotropic spin-5/2 centers, we evaluated the magnetic data using a Heisenberg-Dirac-van Vleck spin Hamiltonian ('–2*J*' notation) in which two different exchange pathways are taken into accounts: the exchange between neighboring Fe3+ sites in each {*B-α*-FeIII2PW10} units, mediated by the polyoxotungstate framework and the µ2-OH bridge and characterized by the exchange energy *J*OH, as well as the coupling between the Fe3+ centers linked by an arsonate group (*J*As). Utilizing the computational framework CONDON 3.0,38 we find *J*As = (–0.6±0.1) cm–1 and *J*OH = (–7.6±0.1) cm–1 for **D-1** (*SQ* = 1.8%), and *J*As = (–0.6±0.2) cm–1 and *J*OH = (–7.4±0.1) cm–1 for **D-2** (SQ = 1.7%). The corresponding least-squares fits are shown as gray solid curves in Figures S15 and S16. As anticipated, the exchange energies are all-antiferromagnetic and virtually identical between **D-1** and **D-2** and result in singlet ground states.

**CONCLUSIONS**

In conclusion, the one-pot reactions of FeIII nitrate with trilacunary Keggin-type phosphotungstates {*A-α-*PW9} and the respective organoarsonic acid in aqueous acetate medium with pH 5.2 yielded discrete solution stable polyanions [{*B-α-*(OH)Fe2(PW10O37)}2{*o*-R−C6H4−AsO3)}2]12− (R = NH2 (**1**) and NO2 (**2**)) representing the first examples of organoarsonate-functionalized FeIII-POTs. **1** and **2** comprise FeIII complexes of rare isomers of dilacunary {*B-α*-PW10}-type phosphotungstates that are joined to dimers via two organoarsonate moieties. The electrochemical behavior of **1** and **2** is associated with reversible FeIII↔FeII and WVI↔WV transitions as well as an oxidation of −NH2 (**1**) and reduction of −NO2 (**2**) groups of organoarsonate ligands. The magnetism of both title compounds exhibits the expected weak-to-moderate antiferromagnetic coupling between the four FeIII sites in **1** and **2**.

**EXPERIMENTAL SECTION**

**General methods and materials**

The reagents were used as purchased without further purification. Na9[*A-α-*PW9O34]·7H2O (Na-PW9) was obtained according to the reported procedure19 and its identity was confirmed by IR spectroscopy. The 0.66 M CH3COONa buffer (pH 5.2) was prepared by dissolving 41.0 g of CH3COONa and 9.14 mL of glacial CH3COOH in 1000 mL of H2O.

Elemental analyses results (ICP-OES and C/H/N) were obtained from Central Institute for Engineering, Electronics and Analytics (ZEA-3), Forschungszentrum Jülich GmbH (D-52425 Jülich, Germany). ATR-FT-IR spectra were recorded on a Bruker VERTEX 70 FT-IR spectrometer on solid materials. UV-Vis spectra were registered in the range of 180–1000 nm on a UV-2600 Shimadzu spectrophotometer. Cyclic voltammograms were recorded on 1.0 mM and 0.77 mM solutions of **D-1** and **D-2**, respectively, in 0.66 M CH3COONa buffer (pH 5.2) at room temperature, using a SP-150 potentiostat (Bio Logic Science Instruments) controlled by EC-Lab software. The conventional three-electrode electrochemical cell included a glassy carbon working electrode with a 3 mm diameter, a platinum wire counter electrode and an aqueous Ag/AgCl (3 M NaCl) reference electrode. The solutions were thoroughly deaerated with pure argon and kept under a positive Ar pressure during the experiments. Alumina nanopowder was used for the cleaning of the working electrode which was then thoroughly rinsed with deionized water. Redox potentials were defined from the average values of the anodic and cathodic peak potentials and reported *vs.* the Ag/AgCl reference electrode.

The magnetic properties of **D-1** and **D-2** were determined using a Quantum Design MPMS-5XL SQUID magnetometer. Microcrystalline samples were packed and immobilized in cylindrical PTFE capsules. Data were taken in the temperature range 2.0–290 K at 0.1 and 1.0 T, and in the magnetic field range 0.1–5.0 T at 2.0 K. All data were corrected for the diamagnetic contributions of the sample holders and the intrinsic diamagnetic contributions of the compounds: *χ*m,dia / 10–3 cm3 mol–1 = –3.19 (**D-1**), –3.24 (**D-2**).

**Synthesis of [H2N(CH3)2]11(H3O)[{*B-α-*(OH)FeIII2(PW10O37)}2{*o-*H2N−C6H4−AsO3)}2]⋅9H2O (D-1)**

Samples of Na-PW9 (0.10 g, 0.039 mmol), Fe(NO3)3·9H2O (0.045 g, 0.111 mmol) and *o*-aminophenylarsonic acid (0.024 g, 0.111 mmol) were reacted in 0.66 M sodium acetate buffer with pH 5.2 (6 mL) in a closed vial at 70−80 °C. The heating and vigorous stirring of the reaction mixture was continued for 2 h, after that it was cooled to room temperature and filtered. 1 M aqueous solution of [H2N(CH3)2]Cl (0.5 mL) was added to the obtained filtrate and it was left for evaporation. Dark-yellow or light-orange block shaped crystals of **D-1** appeared after 2–3 days. They were collected by vacuum filtration and dried in air. Yield: 0.0135 g (12.2 % based on W). Further evaporation of the solution for 2–4 weeks yields dark-orange plate-like crystals of Na1.5[H2N(CH3)2]10.5[{*B-α-*(OH)FeIII2(PW10O37)}2{*o*-H2N−C6H4−AsO3)}2]⋅*x*H2O (**D-1\***) in a mixture with the crystals of **D-1**.

Elemental analysis: calculated for C34H123As2Fe4N13O92P2W20 (found): C, 6.48 (6.48); H, 1.97 (1.95); As, 2.38 (2.38); Fe 3.55 (3.46); N 2.89 (2.93); P 0.98 (1.06); W 58.4 (59.9) mass %.

IR spectrum (ATR), cm–1: 3422 (m, br); 3144 (m, br); 2790 (m, br); 2419 (m, br); 1603 (m); 1570 (m); 1464 (m); 1411 (m); 1379 (w); 1319 (w); 1250 (w); 1232 (w); 1165 (w); 1051 (s); 1018 (m); 949 (s); 872 (s); 790 (s); 731 (s); 690 (s); 655 (s, sh); 590 (s); 501 (s); 476 (s); 455 (s); 432 (s).

UV-Vis (0.66 M CH3COONa buffer solution, pH 5.2): *λ* = 245 nm, *ε* = 76700 M–1 cm–1; *λ* = 360 nm, *ε* = 2037 M–1 cm–1 (shoulder).

**Synthesis of [H2N(CH3)2]11(H3O)[{*B-α-*(OH)Fe2(PW10O37)}2{*o-*O2N−C6H4−AsO3)}2]⋅10H2O (D-2)**

The yellow block-shaped crystals of **D-2** were prepared in a similar to the preparation of **D-1** way using *o*-nitrophenylarsonic acid (0.027 g, 0.110 mmol) instead of *o*-aminophenylarsonic acid. The pale-yellow diamond-shaped crystals of the product appear after 11 days. Yield: 0.0201 g (18.0 % based on W).

Elemental analysis: calculated for C34H121As2Fe4N13O97P2W20 (found): C, 6.40 (6.48); H, 1.91 (1.92); As, 2.35 (2.34); Fe 3.50 (3.51); N 2.86 (2.90); P 0.97 (1.04); W 57.6 (57.2) mass %.

IR spectrum (ATR), cm–1: 3505 (m, br); 3155 (m, br); 2794 (m, br); 2410 (m, br); 1602 (m); 1573 (w); 1537 (m); 1464 (m); 1441 (w); 1415 (w); 1355 (m); 1315 (w); 1250 (w); 1233 (w); 1118 (w); 1051 (s); 1018 (m); 948 (s); 870 (s); 860 (s, sh);791 (s); 740 (s); 727 (s); 690 (s); 630 (s); 590 (s); 501 (s); 474 (s); 430 (s); 409 (s).

UV-Vis (0.66 M CH3COONa buffer solution, pH 5.2): *λ* = 255 nm, *ε* = 99900 M–1 cm–1; *λ* = 360 nm, *ε* = 3630 M–1 cm–1 (shoulder).

**Single-crystal X-ray diffraction analysis**

Single-crystal X-ray diffraction data on **D-1**, **D-2** and **D-1\*** were collected on a STOE STADIVARI diffractometer at 100 K with MoKα radiation (*λ* = 0.71073 Å). The crystals were mounted in a Hampton cryoloop with Paratone-N oil to prevent water loss. Absorption corrections were done by Gaussian integration using STOE X-Red32 software39 and afterwards scaling of reflection intensities was performed within STOE LANA.40

The structures were solved by direct methods and refined by full-matrix least-squares method against |F|2 with anisotropic thermal parameters for all heavy atoms (P, W, Fe, As and Na) as well as for oxygen atoms of the polyoxotungstate part employing the SHELXTL software package.41 ISOR restrictions have to be applied to some oxygen atoms in **D-1\*** structure. Hydrogen atoms of the phenyl rings, amino groups of the *ortho*-arsanilate fragments in **D-1** as well as dimethylammonium countercations were placed in geometrically calculated positions. Hydrogen atoms of co-crystallized water molecules were not located.

The *o*-NH2−C6H4-moiety in the structure of **D-1** exhibits rotational disorder. One of the possible positions for this moiety could be located with the site occupancy factors (s. o. f.) of 0.5, while the other orientations could not be unambiguously found from the electron density map.

The relative s. o. f. for the disordered positions of O atoms of the most water molecules (from the co-crystallized solvent as well as carbon and nitrogen atoms of dimethylammonium and natrium (**D-1\***) counterions were first refined in an isotropic approximation with *U*iso = 0.05 and then fixed at the obtained values and refined without restrictions of the thermal parameters. One of the disordered water molecules in **D-2** (O2W) was refined using a combination of PART and EADP commands.

Due to severe disorder, we were not able to locate part of solvent H2O molecules and some [H2N(CH3)2]+ positions in the **D-1** and **D-2** structures, which is a typical problem in the POT crystallography. Therefore, additional analytical techniques were involved to establish the full composition of the bulk **D-1** and **D-2** materials. An exact number of countercations and co-crystallized water molecules were established using elemental analysis. The obtained formulae were used throughout the manuscript and in the CIF files for overall consistency. The remaining electron density in the voids of the structures was treated by the SQUEEZE procedure.

We could not isolate pure **D-1\*** crystals as they always form only in a small amount and are present in the mixture with **D-1** crystals. Therefore, we did not perform elemental analysis for this salt, also due to the fact it contains exactly the same polyanions **1** as **D-1**. The formula for this salt (**D-1\***) was adjusted based on single-crystal XRD data as well as on a chemical sense. Rather high *R*int factor for **D-1\*** (0.18) reflects apparent twinning issues as the crystals were thin plates and overall, the quality of this structure was not very high. Nevertheless, we decided to report it herein as it provides additional valuable information on the products forming in the FeIII/{*A-α*-PW9}/*o*-arsanilate reaction system.

Additional crystallographic data are summarized in Table 1. Further details on the crystal structures investigation can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK: http://www.ccdc.cam.ac.uk/, e-mail: data\_request@ccdc.cam.ac.uk, or fax: +441223 336033 upon quoting CCDC numbers 2210197 (**D-1**), 2210199 (**D-2**) and 2210203 (**D-1\***). The selected bond lengths in **1** and **2** are shown in Table S1.

**Table 1**. Crystal data and structure refinement for **D-1**, **D-2** and **D-1\***.

|  |  |  |  |
| --- | --- | --- | --- |
| Sample | **D-1** | **D-2** | **D-1\*** |
| Empirical formula | C34H123As2Fe4N13O92-P2W20 | C34H121As2Fe4N13-O97P2W20 | C33H128As2Fe4N12.5-Na1.5O97P2W20 |
| Formula weight / g mol–1 | 6298.63 | 6376.61 | 6399.14 |
| Crystal system | Monoclinic | Monoclinic | Monoclinic |
| Space group | *P*21/*n* | *P*21/*n* | *P*−1 |
| *a* / Å | 12.051(2) | 12.090(2) | 13.284(3) |
| *b* / Å | 20.872(4) | 21.030(4) | 13.683(3) |
| *c* / Å | 22.665(5) | 22.983(5) | 19.932(4) |
| *α* | 90° | 90° | 87.46(3)° |
| *β* | 92.93(3)° | 95.55(3)° | 84.65(3)° |
| *γ* | 90° | 90° | 70.00(3)° |
| Volume / Å3 | 5693(2) | 5816(2) | 3389.3(13) |
| *Z* | 2 | 2 | 1 |
| *D*calc / g cm–3 | 3.674 | 3.641 | 3.135 |
| Absorption coefficient / mm–1 | 21.320 | 20.876 | 17.917 |
| *F*(000) | 5668 | 5744 | 2886 |
| Crystal size / mm3 | 0.03 × 0.09 × 0.13 | 0.12 × 0.21 × 0.26 | 0.045 × 0.08 × 0.20 |
| Theta range for data collection | 2.187° – 25.027° | 1.937° – 25.026° | 2.039° – 25.026° |
| Completeness to **max | 99.7 % | 99.7 % | 99.8 % |
| Index ranges | –14 ≤ *h* ≤ 12,  –24 ≤ *k* ≤ 24,  –26 ≤ *l* ≤ 26 | –14 ≤ *h* ≤ 14,  –25 ≤ *k* ≤ 25,  –27 ≤ *l* ≤ 27 | –13 ≤ *h* ≤ 15,  –16 ≤ *k* ≤ 16,  –23 ≤ *l* ≤ 23 |
| Reflections collected | 54717 | 56145 | 74491 |
| Independent reflections | 10025 | 10230 | 11964 |
| *R*int | 0.1100 | 0.1304 | 0.1830 |
| Observed  (*I* > 2*σ*(*I*)) | 6672 | 6817 | 8907 |
| Absorption correction | Gaussian integration | | |
| *T*min / *T*max | 0.0723 / 0.5110 | 0.0249 / 0.1623 | 0.0414/ 0.4677 |
| Data / restraints / parameters | 10025 / 2 / 592 | 10230 / 0 / 608 | 11964 / 24 / 622 |
| Goodness-of-fit on *F*2 | 1.013 | 1.009 | 1.019 |
| *R*1, *wR*2 (*I* > 2*σ*(*I*)) | *R*1 = 0.0814,  *wR*2 = 0.2140 | *R*1 = 0.0812,  *wR*2 = 0.2076 | *R*1 = 0.0824,  *wR*2 = 0.2156 |
| *R*1, *wR*2 (all data) | *R*1 = 0.1151,  *wR*2 = 0.2380 | *R*1 = 0.1145,  *wR*2 = 0.2327 | *R*1 = 0.0990,  *wR*2 = 0.2284 |
| Largest diff. peak and hole / e Å–3 | 3.712 / –2.678 | 4.124 / –2.686 | 4.004 / –5.362 |

**Powder X-ray diffraction**

PXRD patterns for **D-1** (Figures S2, S3) and **D-2** (Figures S4, S5) were recorded on a STOE STADI P powder diffractometer. The experiments were performed on flat samples in a transmission geometry using a Cu anode (Kα1, *λ* = 1.54059 Å; 40 kV, 30 mA) and a focusing Ge-monochromator (Johann-type) at room temperature. The omega angle was held at 55° and the data were recorded with an image plate detector (140° in 2Θ, stepwidth 0.015°). The exposure times were between 3600 s and 7200 s.

For the measurements the crystals of the respective sample were mortared in a small amount of mother liquor to prevent a removal of co-crystallized solvent molecules and a subsequent crystallinity loss and placed to a sample holder together with a small amount of mother solution.

The observed PXRD patterns show very good fit to the curves simulated form the single crystal X-ray data and, thus, confirm the bulk purity of the **D-1** and **D-2** materials. Sharpness and high intensity of the reflexes observed below 2Θ = 10° indicate a high crystallinity of the measured samples.

**ASSOCIATED CONTENT**

**Supporting Information**.

The Supporting Information is available free of charge on the ACS Publications website at DOI: XXXX. It contains additional structural details, IR and time-dependent UV-Vis spectra, results of rate-dependent cyclic voltammetry studies (curves and tables), a list of reported {*α-*PW10}-based POTs, magnetochemical details, TGA curves as well as crystallographic data in CIF format for all three compounds.

The following files are available free of charge:  
- Electronic Supporting Information (PDF file)  
- CIF files for **D-1**, **D-2** and **D-1\*** (CIF files).

**Accession Codes**

CCDC 2210197 (**D-1**), 2210199 (**D-2**) and 2210203 (**D-1\***) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data\_request/cif, or by emailing data\_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

**AUTHOR INFORMATION**

Corresponding Authors

\* *E-mail:* natalya.izarova@ac.rwth-aachen.de

\* *E-mail:* paul.koegerler@ac.rwth-aachen.de

Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Funding Sources

ERC 308051 - MOLSPINTRON.

DFG − IZ 60/3-1

ORCID numbers

Prof. Dr. Paul Kögerler: https://orcid.org/0000-0001-7831-3953

Dr. Natalya V. Izarova: https://orcid.org/0000-0001-5631-1930

Notes

The authors declare no competing financial interests.

**ACKNOWLEDGMENT**

We gratefully acknowledge financial support by Forschungszentrum Jülich, EU ERC Grant 308051 - MOLSPINTRON and the German Science Foundation (DFG: IZ 60/3-1).

**ABBREVIATIONS**

POT, polyoxotungstate.

**REFERENCES**

(1) Oms, O.; Dolbecq, A.; Mialane, P. Diversity in structures and properties of 3d-incorporating polyoxotungstates. *Chem. Soc. Rev.* **2012**, *41*, 7497−7536.

(2) Zheng, S.-T.; Yang, G.-Y. Recent advances in paramagnetic-TM-substituted polyoxometalates (TM = Mn, Fe, Co, Ni, Cu). *Chem. Soc. Rev.* **2012**, *41*, 7623–7646.

(3) Liu, J.; Han, Q.; Chen L.; Zhao, J. A brief review of the crucial progress on heterometallic polyoxotungstates in the past decade. *CrystEngComm.* **2016**, *18*, 842−862.

(4) Zhao, J.-W.; Li, Y.-Z.; Chen, L.-J.; Yang, G.-Y. *Chem. Commun.* **2016**, *52*, 4418−4445.

(5) Boskovic, C. Rare Earth Polyoxometalates. *Acc. Chem. Res.* **2017**, *50*, 2205–2214.

(6) Dolbecq, A.; Dumas, E.; Mayer, C.R.; Mialane, P. Hybrid Organic−Inorganic Polyoxometalate Compounds: From Structural Diversity to Applications. *Chem. Rev.* **2010**, *110*, 6009–6048.

(7) Proust, A.; Matt, B.; Villanneau, R.; Guillemot, G.; Gouzerh, P.; Izzet, G. Functionalization and post-functionalization: a step towards polyoxometalate-based materials. *Chem. Soc. Rev.* **2012**, *41*, 7605−7622.

(8) Hutin, M.; Rosnes, M. H.; Long, D.-L.; Cronin, L. Polyoxometalates: Synthesis and Structure – From Building Blocks to Emergent Materials. *Compr. Inorg. Chem. II*, **2013**, *2*, 241−269.

(9) Heravi, M. M.; Mirzaei, M.; Heidari, B. Applications of inorganic-organic hybrid architectures based on polyoxometalates in catalyzed and photocatalyzed chemical transformations. *Appl Organometal Chem.* **2019**, *33*, e4808: 1−25.

(10) Anyushin, A. V.; Kondinski, A.; Parac-Vogt, T. N. Hybrid polyoxometalates as post-functionalization platforms: from fundamentals to emerging applications. *Chem. Soc. Rev*. **2020**, *49*, 382−432.

(11) Veríssimo, M. I. S.; Evtuguin, D. V.; Gomes, M. T. S. R. Polyoxometalate Functionalized Sensors: A Review. *Front. Chem.* **2022**, *10*, 840657.

(12) Santoni, M.-P.; Hanan, G. S.; Hasenknopf, B. Covalent multi-component systems of polyoxometalates and metal complexes: Toward multi-functional organic–inorganic hybrids in molecular and material sciences. *Coord. Chem. Rev.* **2014**, *281*, 64−85.

(13) Cameron, J. M.; Guillemot, G.; Galambos, T.; Amin, S. S.; Hampson, E.; Mall Haidaraly, K.; Newton, G. N.; Izzet, G. Supramolecular assemblies of organo-functionalised hybrid polyoxometalates: from functional building blocks to hierarchical nanomaterials. *Chem. Soc. Rev.* **2022**, *51*, 293−328.

(14) Gouzerh, P.; Proust, A. Main-Group Element, Organic, and Organometallic Derivatives of Polyoxometalates*. Chem. Rev.* **1998**, *98*, 77–111.

(15) Yi, X.; Izarova, N. V.; Stuckart, M.; Guérin, D.; Thomas, L.; Lenfant, S.; Vuillaume, D.; van Leusen, J.; Duchoň, T.; Nemšák, S.; Bourone, S. D. M.; Schmitz, S.; Kögerler, P. Probing Frontier Orbital Energies of {Co9(P2W15)3} Polyoxometalate Clusters at Molecule–Metal and Molecule–Water Interfaces. *J. Am. Chem. Soc.* **2017**, *139*, 14501–14510.

(16) Yi, X.; Izarova, N. V.; Kögerler, P. Organoarsonate Functionalization of Heteropolyoxotungstates. *Inorg. Chem.* **2017**, *56*, 13822−13828.

(17) Wang, W.; Izarova, N. V.; van Leusen, J.; Kögerler, P. Polyoxometalates with separate lacuna sites. *Chem. Commun.* **2020**, *56*, 14857−14860.

(18) R. Villanneau, R.; Ben Djamâa, A.; Chamoreau, L.-M.; Gontard, G.; Proust, A. Bisorganophosphonyl and -Organoarsenyl Derivatives of Heteropolytungstates as Hard Ligands for Early-Transition-Metal and Lanthanide Cations. *Eur. J. Inorg. Chem.* **2013**, 1815–1820.

(19) Domaille, P. J.; Hervéa, G.; Téazéa, A. Vanadium(V) Substituted Dodecatungstophosphates. *Inorg. Synth.* **1990**, *27*, 96−104.

(20) Brown, I. D.; Altermatt, D. Bond-valence parameters obtained from a systematic analysis of the Inorganic Crystal Structure Database. *Acta Crystallogr.* **1985**, *B41*, 244−247.

(21) Knížek, K. Kalvados – Software for crystal structure and powder diffraction; see <http://www.fzu.cz/~knizek/kalvados/index.html>.

(22) Guo, L.-Y.; Zeng, S.-Y.; Jagličić, Z.; Hu, Q.-D.; Wang, S.-X.; Wang, Z.; Sun, D. A Pyridazine-Bridged Sandwiched Cluster Incorporating Planar Hexanuclear Cobalt Ring and Bivacant Phosphotungstate. *Inorg. Chem.* **2016**, *55*, 9006–9011.

(23) Fang, W.-H.; Wang, W.-D.; Yang, G.-Y. A novel poly(polyoxometalate) built by {Cu9}/{Cu5} clusters and {PW9}/{PW10}/{PW11} lacunary fragments. *Dalton Trans.* **2015**, *44*, 12546−12549.

(24) Nomiya, K.; Ohta, K.; Sakai, Y.; Hosoya, T.; Ohtake, A.; Takakura, A.; Matsunaga, S. Tetranuclear Hafnium(IV) and Zirconium(IV) Cationic Complexes Sandwiched between Two Di-Lacunary Species of alpha-Keggin Polyoxometalates: Lewis Acid Catalysis of the Mukaiyama-Aldol Reaction. *Bull. Chem. Soc. Japan* **2013**, *86*, 800−812.

(25) Wang, Y.-L.; Zhao, J.-W.; Zhang, Z.; Sun, J.-J.; Li, X.-Y.; Yang, B.-F.; Yang, G.-Y. Enantiomeric Polyoxometalates Based on Malate Chirality-Inducing Tetra-ZrIV–Substituted Keggin Dimeric Clusters. *Inorg. Chem.* **2019**, *58*, 4657–4664.

(26) Li, M.-X.; Jin, S.-L.; Liu, H.-Z.; Xie, G.-Y.; Chen, M.-Q.; Xu, Z.; You, X.-Z. A novel hydroxo-bridged ferric bisubstituted Keggin heteropolytungstate dimer: synthesis and crystal structure of (Me4N)10[Fe4(OH)4(PW10O37)2]⋅15H2O. *Polyhedron* **1998**, *17*, 3721−3725.

(27) Wu, J.-C.; Chen, M.-Q.; Li, M.-X.; Xie, G.-Y.; Jin, S.-L. A novel heteropolymetalate containing Fe4(OH)4 segment: crystal structure of (Me4N)10[Fe4(OH)4(PW10O37)2]⋅15H2O. *Chin. J. Chem.* **1999**, *17*, 350−355.

(28) Pichon, C.; Dolbecq, A.; Mialane, P.; Marrot, J.; Rivière, E.; Sécheresse, F. Square versus tetrahedral iron clusters with polyoxometalate ligands. *Dalton Trans.* **2008**, *37*, 71–76.

(29) All potentials are provided at 20 mV/s *vs*. Ag/AgCl reference electrode.

(30) Laviron, E.; Meunier-Prest, R.; Vallat, A.; Roullier, L.; Lacasse, R. The reduction mechanism of aromatic nitro compounds in aqueous medium. Part II. The reduction of 4-nitropyridine between H0 = −6 and pH 9.6. *J. Electroanal. Chem.* **1992**, *341*, 227−255.

(31) Sharma, L. R.; Manchanda, A. K.; Singh, G.; Verma, R. S. Cyclic voltammetry of aromatic amines in aqueous and non-aqueous media. *Electrochim. Acta* **1982**, *27*, 223−233.

(32) Bard, A. J.; Faulkner, L. R. Electrochemical Methods: Fundamentals and Applications. New York: John Wiley & Sons, **1980**.

(33) Rong, C.; Anson, F. C. Simplified Preparations and Electrochemical Behavior of Two Chromium-Substituted Heteropolytungstate Anions*. Inorg. Chem.* **1994**, *33*, 1064–1070.

(34) Bernardini, G.; Wedd, A. G.; Zhao, C.; Bond, A. M. Electrochemical Probing of the Photoreduction of Molybdenum and Tungsten Dawson-type Polyoxometalates in Molecular and Ionic Liquid Media Using Water as an Electron Donor. *Dalton Trans.* **2012**, *41*, 9944–9954.

(35) Adonin, S. A.; Izarova, N. V.; Besson, C.; Abramov, P. A.; Santiago-Schübel, B.; Kögerler, P.; Fedin, V. P.; Sokolov, M. N. An Ir(IV)-containing Polyoxometalate. *Chem. Commun.* **2015**, *51*, 1222–1225.

(36) Wang, W.; Izarova, N. V.; van Leusen, J.; Kögerler, P. Ce(III)-functionalized Polyoxotungstates: Discrete vs. Extended Architectures. *Cryst. Growth Des.* **2019**, *19*, 4860−4870.

(37) Lueken, H. *Magnetochemie*, Teubner Verlag, Stuttgart, **1999**.

(38) Speldrich, M.; van Leusen, J.; Kögerler, P. CONDON 3.0: An Updated Software Package for Magnetochemical Analysis - All the Way to Polynuclear Actinide Complexes. *J. Comput. Chem.* **2018**, *39*, 2133–2145.

(39) STOE X-Red32, absorption correction by Gaussian integration, analogous to P. Coppens, The Evaluation of Absorption and Extinction in Single-Crystal Structure Analysis. Crystallographic Computing, Ahmed, F. R. (Ed.), Munksgaard Publishers, Copenhagen, **1970**, 255−270.

(40) Koziskova, J.; Hahn, F.; Richter, J.; Kožíšek, J. Comparison of different absorption corrections on the model structure of tetrakis(μ2-acetato)-diaqua-di-copper(II). *Acta Chim. Slov.* **2016**, *9*, 136−140.

(41) Sheldrick, G. M. Crystal structure refinement with SHELXL. *Acta Crystallogr.* **2015**, *C71*, 3−8.

**For Table of Contents Use Only**

**Bi-functionalized Polyoxotungstates: Dilacunary Keggin Clusters Incorporating FeIII and Organoarsonate Constituents**

Fabian Faassen, Natalya V. Izarova, Jan van Leusen and Paul Kögerler



Organoarsonate/FeIII bifunctionalization yield rare derivatives of solution-stable {*B-α*-PW10O37}-type Keggin isomers.