Lacunary Wells−Dawson Sandwich Complexes − Synthesis, Characterization, and Stability Studies of Multi-Iron Species

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Reaction of α-$Na_{12}(As_2W_{15}O_{56})$ with Fe^{II} in 1 M NaCl solution followed by air oxidation yields αααα-$H_2Na_{14}[(NaOH_2)_2Fe^{III}_2(As_2W_{15}O_{56})_2]$ (Na**2**), the arsenic analogue of the divacant lacunary sandwich, αααα-$H_2Na_{14}[(NaOH_2)_2Fe^{III}_2(P_2W_{15}O_{56})_2]$ (Na**1**). This complex (Na**2**) consists of a Na_2Fe_2 central unit sandwiched between two B-α-$As_2W_{15}O_{56}^{12-}$ moieties. Both Na**1** and Na**2** react with one equivalent of Fe^{III} to give ααβα-$Na_{14}[(NaOH_2)(Fe^{III}OH_2)(Fe^{III})_2(X_2W_{15}O_{56})_2]$, where X = P (Na**3**) or As (Na**4**), or two equivalents of Mn^{II} to give αββα-$Na_{14}[(Mn^{II}OH_2)_2(Fe^{III})_2(X_2W_{15}O_{56})_2]$, where X = P (Na**5**) or As (Na**6**). A single-crystal X-ray diffraction analysis of Na**5** has been carried out [a = 13.5387(8) Å, b = 13.9327(9) Å, c = 21.3347(13) Å, α = 92.921(1) °, β = 94.367(1) °, γ = 118.154(1) °, triclinic, $P\bar{1}$, $R1$ = 5.49%, based on 24662 independent reflections], which revealed a Mn_2Fe_2 central unit sandwiched between two B-α-$P_2W_{15}O_{56}^{12-}$ units. All of the new complexes have been characterized by FTIR spectroscopy, UV/Visible spectroscopy, elemental analyses, and cyclic voltammetry, and they are all stable for at least 24 h over a wide pH range (0–7), except for Na**4**, which is unstable below pH 2.

Introduction

Polyoxometalates (POMs for convenience) and their transition metal substituted derivatives (TMSPs) are a versatile and robust group of metal−oxygen anionic clusters with applications in catalysis, medicine, and materials science.[1−3] Among known POM structural types, sandwich complexes are the largest class of TMSPs. There are five major families of sandwich POMs (Figure 1), four of which are derived from trivacant Keggin structures ($XW_9O_{34}^{n-}$ or $XW_9O_{33}^{n-}$, where X = Fe^{III}, Co^{II}, Cu^{II}, Zn^{II}, Si^{IV}, P^{V}, As^{III}, As^{V}, Sb^{III}, Bi^{III}, Se^{IV}, or Te^{IV}),[4−8] and the fifth consists of the Wells−Dawson-derived structures.[8−21] These complexes are composed of a central M_4O_{16} unit encapsulated by two B-α-$X_2W_{15}O_{56}^{12-}$ (X = P^{V} or As^{V}) trivacant POMs. The structural properties of sandwich compounds derived from B-α-$P_2W_{15}O_{56}^{12-}$ are among the most well known because they are more amenable to NMR studies (such as ^{31}P NMR) than are the analogous Keggin (i.e. B-α-$XW_9O_{34}^{n-}$) and arsenic-containing Wells−Dawson species (i.e. B-α-$As_2W_{15}O_{56}^{12-}$).[8,16,18]

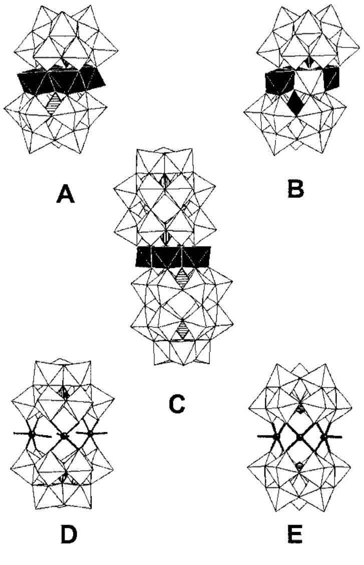

Figure 1. Polyhedral representations of the five major families of sandwich-type polyoxometalates. **A:** Conventional B-type Keggin sandwich **B:** Tourné B-type Keggin sandwich (transition metal heteroatoms) **C:** Wells−Dawson sandwich **D:** Conventional A-type Keggin Sandwich **E:** B-type Keggin sandwich with pyramidal heteroatoms

Recently we reported the new sandwich complex αααα-$H_2Na_{14}[(NaOH_2)_2(Fe^{III})_2(P_2W_{15}O_{56})_2]$ (Na**1**), which differs from conventional B-type Keggin and Wells−Dawson species;[14] X-ray structure analysis reveals only two d-electron metals reside in the central unit,[22] and the other positions are occupied by two weakly bound and labile seven-coordinate Na^+ ions that can readily exchange with a number

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of d-electron-containing metals, including Fe^{III}, Co^{II}, Cu^{II}, and Ni^{II}.[23]

We now report the first arsenic analogue of Na**1**, αααα-$Na_{16}[(NaOH_2)_2(Fe^{III})_2(As_2W_{15}O_{56})_2]$ (Na**2**), which is of considerable interest because the replacement of P with As in other sandwich-type complexes can greatly enhance catalytic activity for the H_2O_2-based epoxidation of alkenes without adversely affecting selectivity.[21,24] Both Na**1** and Na**2** react with a single equivalent of Fe^{III} to produce ααβα-$Na_{14}[(NaOH_2)(Fe^{III}OH_2)(Fe^{III})_2(X_2W_{15}O_{56})_2]$, where X = P (Na**3**)[16] or As (Na**4**), respectively.[25] Na**1** and Na**2** also react with two equivalents of Mn^{II} to yield new mixed-metal sandwich complexes, αββα-$Na_{14}[(Mn^{II}OH_2)_2(Fe^{III})_2(X_2W_{15}O_{56})_2]$, where X = P (Na**5**) or As (Na**6**). The four new complexes reported here (Na**2**, Na**4**, Na**5**, and Na**6**) have all been characterized by FTIR spectroscopy, UV/Visible spectroscopy, elemental analyses, and cyclic voltammetry. Complexes Na**2**, Na**4**, and Na**5** have also been characterized by X-ray crystallography.

Results and Discussion

Syntheses: The reaction of α-$Na_{12}(As_2W_{15}O_{56})$ with Fe^{II} in 1 M NaCl solution followed by air oxidation yields αααα-$H_2Na_{14}[(NaOH_2)_2Fe^{III}_2(As_2W_{15}O_{56})_2]$ (Na**2**), the arsenic analogue of the divacant lacunary sandwich, αααα-$H_2Na_{14}[(NaOH_2)_2Fe^{III}_2(P_2W_{15}O_{56})_2]$ (Na**1**). The synthesis of Na**2** is similar to Na**1** with two important exceptions.[14] First, the trivacant precursor α-$Na_{12}(As_2W_{15}O_{56})$ was used instead of α-$Na_{12}(P_2W_{15}O_{56})$. Second, the metastable dark green complex $Na_{16}[(Fe^{II}OH_2)_2Fe^{II}_2(As_2W_{15}O_{56})_2]$ was crystallized at 4 °C rather than at 10 °C.

Both Na**1** and Na**2** react with a single equivalent of Fe^{III} in water or in dilute NaCl to produce ααβα-$Na_{14}[(NaOH_2)(Fe^{III}OH_2)(Fe^{III})_2(X_2W_{15}O_{56})_2]$, where X = P (Na**3**)[16] or As (Na**4**), respectively.[26] Complexes Na**3** and Na**4** may also be isolated via fractional crystallization (≈ 48−70% yield for Na**4** and Na**3**, respectively) as byproducts in the synthesis of Na**1** and Na**2** {via the air-sensitive $Na_{16}[(Fe^{II}OH_2)_2Fe^{II}_2(X_2W_{15}O_{56})_2]$, where X = P^V or As^V, precursor}. Na**1** and Na**2** may also react with other d-electron-containing metals to yield mixed-metal sandwich complexes. Specifically, Na**1** and Na**2** react with 2.0 equivalents of Mn^{II} to yield αββα-$Na_{14}[(Mn^{II}OH_2)_2(Fe^{III})_2(X_2W_{15}O_{56})_2]$, where X = P (Na**5**) or As (Na**6**). ^{31}P NMR analysis of Na**5** suggests the reaction proceeds to 100% product (one peak for the symmetry-equivalent distal P atoms at δ = −11.9 ppm), although isolated yields of the arsenic analogue, Na**6**, were significantly higher than for the phosphorus analogue, Na**5** (84% versus 10% for Na**6** and Na**5**, respectively).

Crystallographic Studies: The X-ray structure of Na**2** reveals that only two Fe^{III} atoms are present in the innermost positions of the central tetrameric unit (Figure 2, A). The other two positions are occupied by two weakly-bound six-coordinate Na atoms. Each Na atom is coordinated to three oxygen atoms from one B-α-$As_2W_{15}O_{56}{}^{12-}$ moiety, two oxygen atoms from the other B-α-$As_2W_{15}O_{56}{}^{12-}$ moiety, and by a weakly-bound terminal water molecule. This complex is nearly isostructural to Na**1**, except that the As−O bond lengths in Na**2** are slightly longer than the analogous P−O bond lengths in Na**1**.[14] Disorder in the W_3O_{13} triad containing W1, W2, and W3 (rotation by 60 °) and of the Na counter cations and solvent water molecules prevented anisotropic refinement of all atoms (for details see data deposited in the crystal data base).

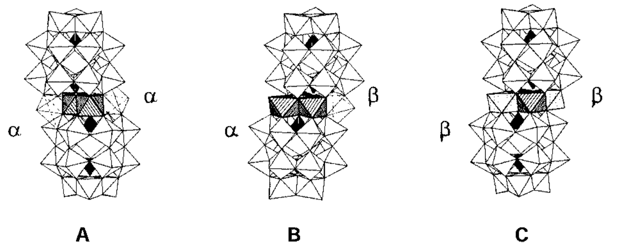

Figure 2. Polyhedral representations of the new Wells−Dawson sandwich complexes. **A:** Na**1** or Na**2** (W atoms are white, P or As atoms are black, Fe atoms are striped) **B:** Na**3** or Na**4** **C:** Na**5** or Na**6** (Mn atoms are gray). The central junctions are labeled α or β, and the central hexacoordinate Na atoms are shown for clarity.

An X-ray crystallographic analysis was also performed on the triferric arsenic complex, Na**4** (Figure 2, B). However, the crystals of this complex were of poorer quality than the analogous phosphorus complex, Na**3**.[16] While the structure of Na**4** was well determined and isostructural with the phosphorus complex, Na**3**, a poor refinement arose from the significant disorder of both a 60 ° rotation of the two W_3O_{13} triads containing W1, W2, and W3 and W28, W29, and W30 and the external Na1 and Fe1 positions in the $NaFe_3$ central unit (see crystal data base for additional details).[27]

An X-ray crystallographic analysis of the new mixed-metal sandwich POM, Na**5** (Table 1, Figure 2, C) shows that two Mn^{II} atoms have replaced the two Na^+ atoms of the

Table 1. Crystal Data and Structure Refinement for Na**5**

Empirical formula	$H_{66}Fe_2Mn_2Na_{14}O_{145}P_4W_{30}$
Formula mass	8569.35
Crystal system	triclinic
Space group	$P\bar{1}$
Unit cell	a = 13.5387(8) Å
	b = 13.9327(9) Å
	c = 21.3347(13) Å
	α = 92.921(1)°
	β = 94.367(1)°
	γ = 118.154(1)°
V	3520.6(4) Å^3
Z/density (calcd.)	1/4.042 Mg/m^3
Absorption coefficient	24.968 mm^{-1}
Reflns. collected	62359
Independent reflns.	24662 [R(int) = 0.0608]
GOF on F^2	1.025
Final R indices [$I > 2\sigma(I)$]	$R1$[a] = 0.0549
	$wR2$[b] = 0.1325

[a] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $wR2 = \{\Sigma[w(F_o{}^2 - F_c{}^2)^2/\Sigma[w(F_o{}^2)^2]\}^{0.5}$

central unit of Na**1**. Each Mn^{II} atom is ligated by three oxygen atoms from one B-α-$P_2W_{15}O_{56}{}^{12-}$ unit, two oxygen atoms from the other B-α-$P_2W_{15}O_{56}{}^{12-}$ unit, and a terminal water ligand. Bond valence sum calculations from the X-ray crystal structure of Na**5** give an average oxidation state of 2.07 ± 0.02 for the two Mn atoms and 2.94 ± 0.02 for the two Fe atoms.[28] Crystals suitable for a complete X-ray crystallographic analysis could not be grown for the arsenic analogue (Na**6**).[29]

Stability Measurements: Unlike the Keggin-derived complexes which show a well-defined peak in their spectra, the UV/Visible spectra of the Wells−Dawson-derived species are usually more complex (with several broad absorptions). The complexes studied here exhibit spectra with different extinction coefficients and different peak wavelengths. Specifically, for a given pH, the spectra for Na**1**, Na**3**, and Na**5** show two main absorption bands around 220−250 nm and 340−360 nm, respectively. The same trends were observed for the As derivatives, Na**2**, Na**4**, and Na**6**. Thus, the stability of the oxidized forms of the complexes (Na**2**, Na**4**, Na**5**, and Na**6**), as a function of pH (0−7) and time (1 to 24 h), can be monitored by their UV/Visible spectra. Each experiment lasted 24 h, which is longer than necessary for complete electrochemical characterization of the complexes, but is relevant for long-lasting or preparative scale catalytic and electrocatalytic processes. All of the reported complexes (Na**2**, Na**4**, Na**5**, and Na**6**) are stable from pH 0 to 7 over a 24 hour period except for Na**4**, which is unstable below pH 2.

In additional stability tests on the reduced forms of the complexes, which are of interest for both catalytic and electrocatalytic processes, the Fe^{III} centers were exhaustively reduced to Fe^{II} by controlled potential coulometry and then reoxidized to the ferric state. The stability was monitored by cyclic voltammetry, recorded before and after the forward and backward electrolysis reaction. The data suggest that the Fe^{II} state within the complexes is stabilized by the two Mn^{II} centers (Na**5** and Na**6**). In contrast, electrolyses in pH < 4 media show that the Fe^{II} forms are unstable within Na**1** and Na**2** in the absence of Mn^{II}.

Electrochemistry: Cyclic voltammetry of the sandwich complexes, in a pH 3 sulfate medium (0.5 M Na_2SO_4 and H_2SO_4), afforded voltammograms of the arsenic complexes Na**2** and Na**4** that are similar to their corresponding phosphorus analogues.[15,20] However, the waves of the arsenic-containing species (Na**2** and Na**4**) are at slightly more positive potentials than for phosphorus-containing complexes (Na**1** and Na**3**).[24] Table 2 compares specifically the peak potential locations for the Fe waves and for the Mn waves (the Fe centers are arbitrarily numbered 1, 2, and 3 for clarity). The representative cyclic voltammograms in Figure 3 show in superposition the patterns for Na**1** and Na**5** (Figure 3, A) as well as Na**2** and Na**6** (Figure 3, B). As expected, only Na**5** and Na**6** show an oxidation process attributable to the overall four-electron oxidation of the Mn centers. The associated reduction patterns are composite and partially feature the characteristic shape of surface adsorbed species.

Table 2. Peak potential (V vs. SCE) for Fe waves E_{pc} (reduction) and the Mn wave (oxidation) determined by cyclic voltammetry at pH 3.00 (0.5 M Na_2SO_4 + H_2SO_4) for the new complexes. Scan rate: 10 mV·s^{-1}, working electrode: glassy carbon

Compound	E_{pa} (V vs. SCE) **Mn**	$-E_{pc}$ (V vs. SCE) **Fe1**	**Fe2**	**Fe3**
Na1	–	0.132	0.238	
Na5	1.156	0.116	0.228	
Na2	–	0.118	0.208	
Na6	1.152	0.106	0.208	
Na4	–	−0.056	0.106	0.202

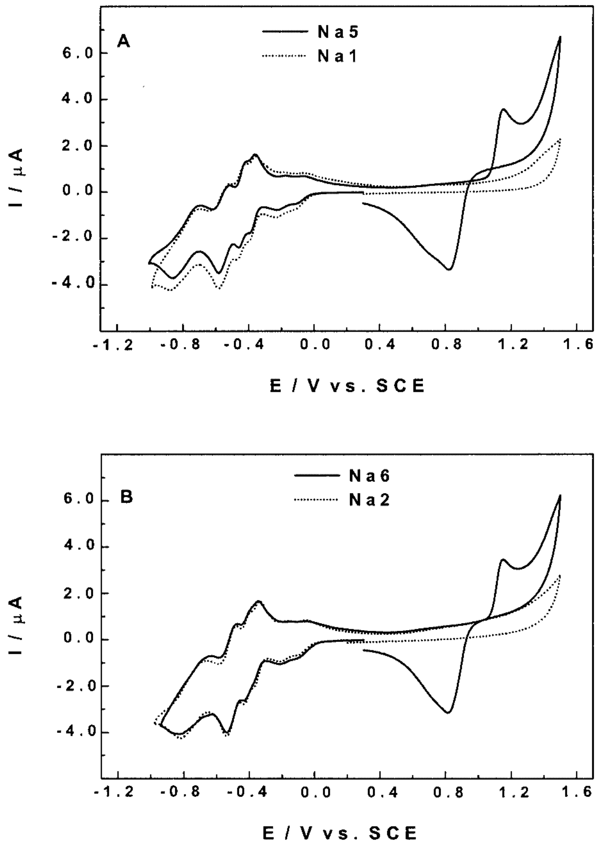

Figure 3. Cyclic voltammograms of Na**1**, Na**2**, Na**5**, and Na**6** in a pH 3 media (0.5 M Na_2SO_4 + H_2SO_4). Heteropolyanion concentration: 2×10^{-4} M; scan rate: 10 mV·s^{-1}; working electrode: glassy carbon; reference electrode: SCE **A:** Comparison of the cyclic voltammograms of Na**1** and Na**5** **B:** Comparison of the cyclic voltammograms of Na**2** and Na**6**

The Fe and W waves are well separated in all of these complexes and the number of Fe waves observed for each complex corresponds exactly to that known from the stoichiometry of the relevant molecules.[15] Similar behavior has been observed for αββα-$Na_{12}[(Fe^{III}OH_2)_2(Fe^{III})_2(As_2W_{15}O_{56})_2]$.[20] Here again, controlled potential coulometry confirms that the exhaustive reduction of each Fe center consumes one electron per molecule. Also noteworthy is the observation that the first Fe wave of Na**4** is at a more positive potential than all other Fe waves present in the series (Table 2). The Mn^{II} in Na**5** and Na**6** also modifies the characteristics of the Fe waves, which are at slightly more positive potentials than for the divacant lacunary precursors Na**1** and Na**2**. Tentatively, and with the assumption of minimal variation in other electronic properties between the two complexes, this change might be attributable to differences in the overall negative charge of the complexes, which decreases from 16 (in Na**1** and Na**2**) to 14 (in Na**5** and Na**6**), thus rendering the Mn-containing complexes easier to reduce than their precursors. The magnitude of this difference, however, might be modulated by the acid−base properties of the reduced forms of these complexes. In short, as expected, Na**5** and Na**6** behave much like saturated sandwich-type derivatives while Na**1** and Na**2** are more lacunary. These observations are similar to those described by Pope and Chorghade for Sn-substituted monovacant POM complexes.[30] Sn^{II} is too large for the octahedral vacancy and the corresponding substituted derivatives behave much like the lacunary precursor complexes. In contrast, Sn^{IV} fits in the vacancy much better, and its derivatives behave very similarly to the saturated complexes.

Conclusions

The new divacant, lacunary arsenic-containing sandwich-type complex, Na**2**, synthesized here is isostructural with its phosphorus analogue, Na**1**. Both complexes react with one equivalent of Fe^{III} to yield triferric sandwich-type complexes, $\alpha\alpha\beta\alpha\text{-}Na_{14}[(NaOH_2)(Fe^{III}OH_2)(Fe^{III})_2(X_2W_{15}O_{56})_2]$, where X = P (Na**3**) or As (Na**4**). Na**1** and Na**2** also react with two equivalents of Mn^{II} to produce new mixed-metal sandwich-type complexes. All of the new complexes are stable for at least 24 h over the wide pH range 0−7, except for Na**4**, which is not stable below pH 2. This stability is remarkable and in sharp contrast with many other TMSPs. Typically within the Wells−Dawson family, the saturated compounds (formula $X_2W_{18}O_{62}{}^{6-}$, where X = P^V or As^V) are stable in mostly acidic media while their monosubstituted derivatives (formula $X_2MW_{17}O_{61}{}^{n-}$, where X = P^V or As^V and M = first row transition metal cation) require a higher pH. The wide stability seen here is an important prerequisite for substantial catalytic and electrocatalytic processes and may be a key parameter in preparing new effective catalysts.

Experimental Section

General Methods and Materials: $\alpha\text{-}Na_{12}(As_2W_{15}O_{56})$, $\alpha\text{-}Na_{12}(P_2W_{15}O_{56})$, Na**1**, and Na**3** were obtained by published procedures, and their purity was confirmed by IR, cyclic voltammetry, and ^{31}P NMR [except $\alpha\text{-}Na_{12}(As_2W_{15}O_{56})$].[14,16−18,31] Elemental analyses of As, Fe, Mn, Na, P, and W were performed by Kanti Labs (Mississauga, Canada). Infrared spectra were recorded with a Perkin−Elmer Spectrum One and Nicolet 510 FT-IR instruments. All electrochemical measurements were performed with an EG and G 273A apparatus under computer control (M270 software). Potentials are quoted against a saturated calomel electrode (SCE). ^{31}P NMR measurements were made with a Varian INOVA 400 MHz spectrometer, and peaks were referenced to 85% H_3PO_4. Thermal analyses were performed with an ISI TGA 1000 and used to confirm the number of water molecules per POM.

X-ray Crystallography: Suitable crystals of Na**2**, Na**4**, and Na**5** were coated with Paratone N oil, suspended on a small fiber loop and placed in a cooled nitrogen stream at 100 K on a Bruker D8 SMART APEX CCD sealed tube diffractometer with graphite-monochromated Mo-K_α (0.71073 Å) radiation. A sphere of data was measured using a series of combinations of φ and ω scans with 10 s frame exposures and 0.3° frame widths. Data collection, indexing, and initial cell refinements were handled using SMART software.[32] Frame integration and final cell refinements were carried out using SAINT software.[33] The final cell parameters were determined from least-squares refinement. The SADABS program was used for absorption corrections.[34] The structures were solved by Direct Methods and difference Fourier techniques.[35] All atoms were refined anisotropically, except where noted (see data deposited in the crystal structure data base). The scattering factors and anomalous dispersion corrections were taken from the International Tables for X-ray Crystallography.[36] Additional details for Na**5** (Table 1) and polyhedral representations of Na**2**, Na**4**, and Na**5** (Figure 2) are given here (see crystallographic details for Na**2** and Na**4** and additional refinement information for Na**2**, Na**4**, and Na**5** deposited in the data base). Further details of the crystal structure investigations may be obtained from the Fachinformationzentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany on quoting depository numbers CSD-380223 (Na**2**), -380224 (Na**4**), and -380225 (Na**5**).

Synthesis of $\alpha\alpha\alpha\alpha\text{-}H_2Na_{14}[(NaOH_2)_2Fe_2^{III}(As_2W_{15}O_{56})_2]\cdot 54H_2O$ (Na2) and $\alpha\alpha\beta\alpha\text{-}Na_{14}(NaOH_2)(Fe^{III}OH_2)Fe_2^{III}(As_2W_{15}O_{56})_2]\cdot 55H_2O$ (Na4): $\alpha\text{-}Na_{12}(As_2W_{15}O_{56})$ (22.3 g, 5 mmol) was slowly added, with stirring, to a solution of $FeCl_2\cdot 4H_2O$ (1.96 g, 9.86 mmol) dissolved in NaCl solution (120 mL, 1 M). The resulting dark green solution was heated to 65 °C for 15 min, filtered hot, and cooled to 4 °C overnight. The crystals that formed were redissolved in deionized water (120 mL) and oxidized in air for one week at ambient temperature. A yellow-brown precipitate of Fe_2O_3 (determined by elemental analysis) was removed daily by filtration. NaCl (6 g) was then added, and the resultant additional yellow-brown precipitate was again filtered off. After 2−3 days, 2.56 g (yield 11%) of large, light-yellow crystals were collected and recrystallized from 0.5 M NaCl. IR (2% KBr pellet, 1000−400 cm^{-1}): $\tilde{\nu}$ = 947 (s), 871 (s), 831 (m), 724 (s), 519 (m), and 494 (w). $H_{114}As_4Fe_2Na_{16}O_{168}W_{30}$ (9097.5): calcd. Na 4.04, As 3.29, Fe 1.23, W 60.63; found Na 4.23, As 3.36, Fe 1.31, W 60.00. The filtrate was concentrated to approximately 70% of its original volume, and, after 2 days, 11 g (yield 48%) of a light yellow precipitate was collected by filtration. The precipitate was redissolved in 0.5 M NaCl to give diffraction-quality crystals. IR (2% KBr pellet, 1000−400 cm^{-1}): $\tilde{\nu}$ = 953 (s), 871 (s), 836 (m), 730 (s), 523 (m), and 494 (w). $H_{114}As_4Fe_3Na_{14}W_{30}O_{169}$ (9123.4): calcd. As 3.28, Fe 1.84, Na 3.53, W 60.45; found As 3.34, Fe 2.10, Na 3.85, W 59.60.

Synthesis of $\alpha\beta\beta\alpha\text{-}Na_{14}[(Mn^{II}OH_2)_2Fe_2^{III}(P_2W_{15}O_{56})_2]\cdot 8H_2O$ (Na5): $MnCl_2\cdot 4H_2O$ (1.38 g, 7 mmol) was slowly added to Na**1** (6.4 g, 0.7 mmol)[18] dissolved in a minimal amount of 0.5 M NaCl (pH adjusted to about 2 by 1 M NaOH). The initial light yellow-green solution turned dark red, and was then heated to 60 °C for 10 min. After 7−8 days, brown crystals formed (0.56 g, yield 10%). IR (2% KBr pellet, 1300−400 cm^{-1}): $\tilde{\nu}$ = 1085 (s), 1060 (w, sh), 1014 (w, sh), 941 (s), 918 (w), 890 (m), 816 (m), 776 (m), 734 (w) and 522 (m). ^{31}P NMR (in D_2O): $\delta = -11.96$ ppm, $\Delta\nu_{1/2} = 100$ Hz. $H_{20}Fe_2Mn_2Na_{14}O_{122}P_4W_{30}$ (8154.9): calcd. Fe 1.37, Mn 1.35, Na 3.95, P 1.52, W 67.63; found Fe 1.47, Mn 1.62, Na 4.10, P 1.43, W 67.6.

Synthesis of αββα-$Na_{14}[(Mn^{II}OH_2)_2Fe_2^{III}(As_2W_{15}O_{56})_2]\cdot 29H_2O$ (Na6): Na**2** (1.9 g, 0.207 mmol) was added, with stirring and heating to 65 °C for about 5 min, to $MnCl_2\cdot 4H_2O$ (0.1 g, 0.5 mmol) dissolved in 1 M NaCl solution (10 mL). The resultant dark brown solution was filtered hot and, after approximately 7 days, 1.5 g (yield 84%) of a brown precipitate formed that was recrystallized from 0.5 M NaCl. IR (2% KBr pellet, 1000−400 cm^{-1}): $\tilde{\nu} = 949$ (s), 871 (s), 823 (m), 712 (s), 523 (m), and 492 (m). $H_{62}As_4Fe_2Mn_2Na_{14}W_{30}O_{143}$ (8709.0): calcd. As 3.44, Fe 1.28, Mn 1.26, Na 3.70, W 63.33; found As 3.30, Fe 1.30, Mn 1.26, Na 3.58, W 62.3.

Acknowledgments

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[23] In addition, the junctions between each trivacant POM and the central tetrameric unit in Na**1** (and Na**2**) differ from those in all previously known sandwich-type POMs derived from Wells−Dawson and B-Keggin units. For more information on α- and β-junctions in Wells−Dawson sandwich-type structures, see ref.[16]

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[26] Complexes Na**3** and Na**4** may be isolated during the synthesis of Na**1** and Na**2** via metastable tetraferrous intermediates and separated via fractional crystallization. Na**3** and Na**4** are also formed by adding one equivalent of Fe^{III} to a solution of Na**1** or Na**2**, respectively [$FeCl_3\cdot 6H_2O$ (0.049 g) was dissolved in water (10 mL) and added dropwise to Na**1** or Na**2** (20 mL 9 mM) with stirring and heating to 55 °C for about 15 min]. The former method is preferable due to higher yields.

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