*Inorg. Chem.* **2004**, *43*, 3257−3263

Inorganic Chemistry
Article

# Multi-Iron Wells–Dawson Heteropolytungstates. Electrochemical Probing of Siderophoric Behavior in Sandwich-Type Complexes

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Received December 30, 2003

The demetalation process of 10 multi-iron Wells–Dawson polyoxometalates is studied by cyclic voltammetry and controlled potential coulometry. Eight sandwich-type complexes ($\alpha\alpha\alpha\alpha$-$Na_{16}[(NaOH_2)_2(Fe^{III})_2(X_2W_{15}O_{56})_2]$, $\alpha\alpha\beta\alpha$-$Na_{14}[(NaOH_2)(Fe^{III}OH_2)(Fe^{III})_2(X_2W_{15}O_{56})_2]$, $\alpha\beta\beta\alpha$-$Na_{12}[(Fe^{III}OH_2)_2(Fe^{III})_2(X_2W_{15}O_{56})_2]$, and $\alpha\beta\beta\alpha$-$Na_{14}[(Mn^{II}OH_2)_2(Fe^{III})_2(X_2W_{15}O_{56})_2]$ (where X = P(V) or As(V))) and two monomeric complexes ($\alpha$-$Na_{11}[(P_2(Fe^{III}Cl)_2(Fe^{III}OH_2)W_{15}O_{59})]$ and $\alpha$-$Na_{11}[(As_2(Fe^{III}Cl)_2Fe^{III}OH_2)W_{15}O_{59})]$) were selected for this study. All 10 complexes show Fe(III) waves which are well-separated from the redox activity of the W(VI) centers. At room temperature and under mild conditions, iron release from the complexes is observed upon reduction of the Fe(III) centers. This release is controlled by the ionic strength of the medium, the nature and concentration of the anions present in the supporting electrolyte, and by the pH of the solution. This behavior parallels those described for most siderophores which depend on the same parameters.

## Introduction

Early transition metal−oxygen anionic clusters, or polyoxometalates (POMs) for short, simultaneously exhibit many properties that make them attractive for applications in catalysis, separations, imaging, materials science, and medicine.[1,2] Among these properties is the ability to undergo reversible multi-electron-transfer reactions, synthetic versatility and accessibility, and thermodynamic stability toward oxidative degradation. Recently, we reported a series of multi-iron sandwich-type complexes that are effective catalysts for the $H_2O_2$-based epoxidation of alkenes and electrocatalysts for the reduction of $H_2O_2$ and $O_2$.[3−12] Sandwich-type POMs are formed by the fusion of two trivacant $\alpha$-$XW_9O_{34}^{n-}$ (X = P(V), As (V), Si(IV), Ge(IV), Fe(III), Co(II), Cu(II), or Zn(II)), $\alpha$-$XW_9O_{33}^{n-}$ (X = As(III), Sb(III), Bi(III), Se(IV), or Te(IV)), or $\alpha$-$X_2W_{15}O_{56}^{n-}$ (X = P(V) or As(V)) units via two or more d-electron centers and now constitute one of the largest classes of transition-metal-substituted heteropolytungstates.[13,14]

The formation of sandwich-type POMs from solutions of metal cations and trivacant heteropolytungstate species may alternatively be viewed as a means to sequester the cations

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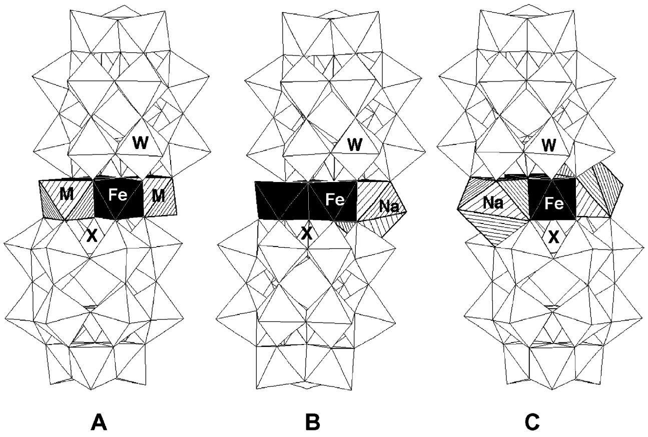

**Figure 1.** Polyhedral representations of (A) $\alpha\beta\beta\alpha$-$[(MOH_2)_2(Fe^{III})_2(X_2W_{15}O_{56})_2]^{n-}$ (M = Fe(III) or Mn(II), $n$ = 12 or 14, and X = P(V) or As(V)), (B) $\alpha\alpha\beta\alpha$-$[(NaOH_2)(Fe^{III}OH_2)(Fe^{III})_2(X_2W_{15}O_{56})_2]^{14-}$ (X = P(V) or As(V)), and (C) $\alpha\alpha\alpha\alpha$-$[(NaOH_2)_2(Fe^{III})_2(X_2W_{15}O_{56})_2]^{16-}$ (X = P(V) or As(V)). Most of the $Na^+$ cations are omitted for clarity.

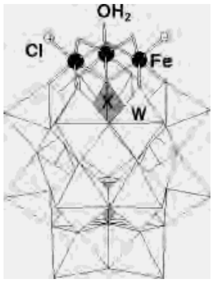

**Figure 2.** Combination polyhedral/ball-and-stick representation of $\alpha$-$[(X_2(Fe^{III}Cl)_2(Fe^{III}OH_2)W_{15}O_{59})]^{11-}$ (X = P(V) or As(V)).

from solution. The question then arises as to whether reversible dissociation of the metal centers from the multidentate ligands is possible as well. The sequestration and subsequent release of metal cations under appropriate conditions is of considerable interest in waste decontamination technology as well as in medicine.[15] Our interest was stimulated by the possibility that reversible metal binding by POM ligands might mimic naturally occurring ion chelators. Specifically, we were interested in investigating how closely our recently reported multi-iron sandwich-type complexes might mimic the behavior of siderophores. Siderophores are powerful and selective low molecular weight iron chelators produced and secreted by bacteria and other organisms to regulate environmental iron concentrations.[16] Chelation is established through hydroxamate or catecholate groups, regardless of the diversity of the overall structures. The catecholate-based siderophores typically bind iron far more tightly than hydroxamates. As a result, the catecholates are generated by the microorganism when iron concentrations are low, whereas the hydroxamates are generated when iron concentrations are high.

This paper focuses on the demetalation process of eight closely related multi-iron Wells–Dawson sandwich-type complexes and two multi-iron Wells–Dawson monomers (Figures 1 and 2). We have chosen cyclic voltammetry and controlled potential coulometry as the primary means of characterization for two reasons. First, the electrochemical properties of the multi-iron heteropolytungstates have been well established, and cyclic voltammetry has been shown to be a powerful and species-specific means of characterization over a wide range of POM concentrations and pH values. Second, electrochemistry provides a means of circumventing the shortcomings of UV–vis spectroscopy (lack of species specific characterization and interference from the intense oxygen-to-tungsten charge-transfer bands). In addition, it avoids the long acquisition times and high concentration requirements associated with $^{183}W$ NMR, the most powerful solution technique for the determination of the structure/symmetry of a POM.

## Experimental Section

**General Methods and Materials.** Samples of $\alpha$-$Na_{12}[(X_2W_{15}O_{56})]\cdot18H_2O$, $\alpha\alpha\alpha\alpha$-$Na_{16}[(NaOH_2)_2(Fe^{III})_2(X_2W_{15}O_{56})_2]\cdot54H_2O$ (**Fe2X4**), $\alpha\alpha\beta\alpha$-$Na_{14}[(NaOH_2)(Fe^{III}OH_2)(Fe^{III})_2(X_2W_{15}O_{56})_2]\cdot20H_2O$ (**Fe3X4**), $\alpha\beta\beta\alpha$-$Na_{12}[(Fe^{III}OH_2)_2(Fe^{III})_2(X_2W_{15}O_{56})_2]\cdot54H_2O$ (**Fe4X4**), $\alpha\beta\beta\alpha$-$Na_{14}[(Mn^{II}OH_2)_2(Fe^{III})_2(X_2W_{15}O_{56})_2]\cdot18H_2O$ (**Mn2-Fe2X4**), and $\alpha$-$Na_{11}[(X_2(Fe^{III}Cl)_2(Fe^{III}OH_2)W_{15}O_{59})]\cdot14H_2O$ (**Fe3X2**) (where X = P(V) or As(V)) were obtained by published procedures,[7,9–11,17,18] and purity was confirmed by IR, elemental analysis, and cyclic voltammetry. Infrared spectra (1 wt % of POM in KBr) were recorded on a Perkin-Elmer Spectrum One FT-IR spectrometer. UV–vis spectra were recorded on a Perkin-Elmer Lambda 19 spectrophotometer. Measurements of pH and p$K_a$ were performed with a Tacussel MVN 83 millivoltmeter–pH meter. The water content of the samples was measured by thermogravimetric analyses (TGA). All chemicals used were high purity grade and were used without further purification.

**Electrochemical Experiments.** For a few series of experiments, the following media were used: $H_2SO_4$ (pH 0), 1 M NaCl + HCl (pH 1), and 0.5 M $Na_2SO_4$ + $H_2SO_4$ (pH 1–3). For a majority of the experiments, however, buffer solutions ranging from pH 2 to 7 were used. Solutions between pH 2 and 3 consist of 2 M NaCl and HCl. Buffers between pH 4 and 5 are composed of 2 M NaCl, 0.1 M $CH_3COONa$, and $CH_3COOH$, and buffers between pH 6 and 7 are made up of 2 M NaCl, 0.05 M $NaH_2PO_4$, and 0.05 M NaOH. Certain experiments required the use of more specialized buffer solutions. These buffer solutions are described in the text of the Results and Discussion section or in the figure captions of their

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respective cyclic voltammograms. Solutions were deaerated with Ar for 30 min prior to measurements and kept under positive pressure at all times. The concentration of the POM in solution was $2 \times 10^{-4}$ M, unless otherwise stated. The source, mounting, and polishing of the glassy carbon electrodes (GC, Tokai, Japan, 3 mm diameter) were described in previous work.[19] The counter electrode was a platinum gauze of large surface area. The electrochemical apparatus was an EG and G 273A under computer control (M270 software). All experiments were performed at ambient temperature, and potentials are quoted against a saturated calomel electrode (SCE). Controlled potential coulometry determinations were performed as described for the cyclic voltammetry experiments except that the working electrode used was a 4 cm$^2$ surface area glassy carbon plate. In addition, after deaeration, Ar was continuously bubbled through the solution to ensure a constant stirring of the mixture.

## Results and Discussion

**Background.** The synthesis and structural characterization of the eight multi-iron Wells−Dawson-derived sandwich POMs has been previously reported.[4,7,10,11,12] All of these compounds are stable in the pH = 5 buffer solution (1 M $CH_3COOLi$ + 1 M $CH_3COOH$) over the time scale of the voltammetric studies. The electrochemistry of the trivacant $\alpha$-$P_2W_{15}O_{56}^{12-}$ and $\alpha$-$As_2W_{15}O_{56}^{12-}$ ligands consists of one four-electron wave followed by a two-electron process.[11,20−22] These waves feature the reduction of W(VI) centers. The positive potential shifts of the first two W(VI) waves of $\alpha$-$As_2W_{15}O_{56}^{12-}$ compared to those of $\alpha$-$P_2W_{15}O_{56}^{12-}$ (20 mV and 54 mV, respectively) are in agreement with the finding that $\alpha$-$As_2W_{18}O_{62}^{6-}$ is easier to reduce than $\alpha$-$P_2W_{18}O_{62}^{6-}$.[23] In contrast to the voltammograms of $\alpha$-$P_2W_{15}O_{56}^{12-}$ and $\alpha$-$As_2W_{15}O_{56}^{12-}$, those of the multi-iron sandwich species **Fe(*n*)X4** (X = P or As; $n$ = 2, 3, 4) show 2−4 new waves in the potential domain +0.2 to −0.5 V. The stepwise reduction of the Fe(III) centers observed in these sandwich-type species indicates there is electronic communication among these metal centers.[11] This interaction generates and/or reinforces inequivalence among the Fe(III) centers, especially in the reduced state. Ion pairing also influences the electrochemistry of the multi-iron sandwich complexes **Fe(*n*)X4** (X = P or As; $n$ = 2, 3, 4) with protonation superseding ion pairing upon decreasing the pH of the supporting electrolyte.[24,25]

**Demetalation Studies.** Samples of $\alpha\beta\beta\alpha$-$Na_{12}[(Fe^{III}OH_2)_2(Fe^{III})_2(P_2W_{15}O_{56})_2]$ (**Fe4P4**) and $\alpha\beta\beta\alpha$-$Na_{12}[(Fe^{III}OH_2)_2(Fe^{III})_2(As_2W_{15}O_{56})_2]$ (**Fe4As4**) were dissolved in a pH 3 medium with 2 M NaCl to study the demetalation process. All of the cyclic voltammograms are restricted to the Fe(III) waves. A demetalation process of the reduced POMs was detected and is shown in Figure 3. Controlled potential coulometry was used to confirm that each of the four Fe(III)-based waves represents the one-electron reduction process of Fe(III) to Fe(II). Here again the As-containing species, **Fe4As4**, is more easily reduced than the P-containing analogue (**Fe4P4**), with the interesting finding that the influence of the heteroatoms appears to be larger on the first two redox couples.[26]

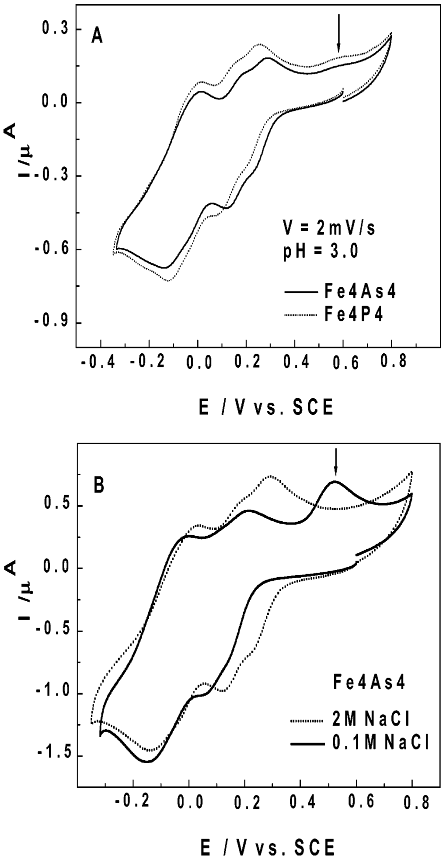

**Figure 3.** Cyclic voltammograms of complexes **Fe4P4** and **Fe4As4** ($2 \times 10^{-4}$ M) in pH 3 solution. The working electrode was glassy carbon, and the reference electrode was SCE. (A) The scan rate was 2 mV s$^{-1}$, and the arrow indicates the oxidation of free Fe(II). (B) Evolution of the cyclic voltammogram of **Fe4As4** as a function of the ionic strength of the solution (solid line (—), 2 M NaCl + HCl; dotted line (···), 0.1 M NaCl + HCl). The scan rate was 10 mV s$^{-1}$, and the arrow indicates free Fe(II) oxidation.

The voltammetric characteristics of the Fe(III)-based centers in the Wells−Dawson-derived sandwich complexes change with scan rate similar to those reported for the Keggin-derived tetra-iron analogues.[14f] Figure 3A shows the main change is the appearance of an oxidation wave located between +0.5 and +0.7 V for scan rates lower than 10 mV

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(26) This observation is consistent with the X-ray crystal structures of **Fe4P4** and **Fe4As4**, that show there are two pairs of symmetry-equivalent Fe(III) centers. The “external” pair of Fe(III) centers have aqua ligands and can thus be considered as less electron rich than the “internal” Fe(III) centers, which contain a sixth oxo ligand. As a result, the “external” Fe(III) centers are likely to be reduced first. Furthermore, **Fe3X4** and **Fe2X4**, which have been shown by X-ray crystallography to lose one or both of their external Fe(III) atoms, also show the loss of one or two of their most positive Fe(III)-based redox potentials, respectively. This is also consistent with the observation that the two most positive redox potentials are more sensitive than the two most negative potentials to changes in pH and ionic strength. For more information, see ref 25.

$s^{-1}$. The potential position of this anodic process with no apparent cathodic counterpart coincides with that of free Fe(II) oxidation. The absence of the reduction branch for free Fe(III) in several experiments indicates the rapid reincorporation of this cation into the sandwich-type complex. The results show that demetalation is slow and is only observed for slow scan rates. Complete reduction of the four Fe(III) centers within **Fe4As4** was performed to enhance the demetalation process, followed by an attempt to regenerate Fe(III) by electrolysis. A new redox couple appeared after electrolysis and was identified as the Fe(III)/Fe(II) redox couple by addition of authentic $FeCl_3$ (see Supporting Information (SI)). Controlled potential coulometry shows this new wave is a one-electron redox process. This result corresponds to the overall balance of the various reactions shortly after the forward and backward electrolysis but might not indicate the stoichiometry of the primary demetalation reaction. The observation is consistent with $^{31}P$ NMR studies which show the tri-iron complex, $\alpha\alpha\beta\alpha$-$Na_{14}[(NaOH_2)(Fe^{III}OH_2)(Fe^{III})_2(P_2W_{15}O_{56})_2]$ (**Fe3P4**), is more stable than the di- and tetra-iron species ($\alpha\alpha\alpha\alpha$-$Na_{16}[(NaOH_2)_2(Fe^{III})_2(P_2W_{15}O_{56})_2]$ (**Fe2P4**) and $\alpha\beta\beta\alpha$-$Na_{12}[(Fe^{III}OH_2)_2(Fe^{III})_2(P_2W_{15}O_{56})_2]$ (**Fe4P4**), respectively).[10] These results show that only one Fe(III) center of **Fe4P4** and **Fe4As4** is involved in the demetalation process. Therefore, the demetalation of **Fe4P4** and **Fe4As4** results in the formation of the tri-iron sandwich complexes, **Fe3P4** and **Fe3As4**, respectively. In addition, the tri-iron complexes **Fe3P4** and **Fe3As4** show better complexation of Fe(III) than Fe(II), since $\mathbf{Fe^{II}Fe^{III}3X}4$ (X = P or As) is not observed in solution and the reoxidation of $\mathbf{Fe^{II}4X4}$ results exclusively in the formation of $\mathbf{Fe^{III}3X4}$. Furthermore, this observation is in agreement with the much lower stability constant of Fe(II) complexation with $OH^-$ (a hard base) than Fe(III) with the same anion ($\log K = 4.3$ versus 11.9 for Fe(II) and Fe(III), respectively).[27] The overall reaction sequence is then given by eqs 1−4 (with X = P or As). Study of the Fe(III) reincorporation rate constant into **Fe3X4** as well as any Baker-Figgis rotational isomerism which may accompany this reaction is beyond the scope of this work. Therefore, eq 4 may be only partially operable on the time scale of cyclic voltammetry.[28,29a]

$$\mathbf{Fe^{III}4X4} + 1e^- \leftrightarrow \mathbf{Fe^{II}Fe^{III}3X4} \tag{1}$$

$$\mathbf{Fe^{II}Fe^{III}3X4} \leftrightarrow Fe^{II} + \mathbf{Fe^{III}3X4} \text{ (slow step)} \tag{2}$$

$$Fe^{II} - 1e^- \leftrightarrow Fe^{III} \tag{3}$$

$$Fe^{III} + \mathbf{Fe^{III}3X4} \leftrightarrow \mathbf{Fe^{III}4X4} \tag{4}$$

**Table 1.** Selected Peak Potentials (mV versus SCE) for Fe(III) Reductions in **Fe4X4** (X = P or As) as a Function of NaCl Concentration ($C°_{NaCl}$) in a pH 3 Medium[a]

| | Fe4P4 | | Fe4As4 | |
|---|---|---|---|---|
| $C°_{NaCl}$ (M) | Fe2 | Fe4 | Fe2 | Fe4 |
| 2.0 | 82 | −120 | 122 | −118 |
| 1.0 | 60 | −118 | 100 | −112 with merging |
| 0.4 | 30 | −128 | 84 | −126 |
| 0.1 | 0 | −212 | 56 | −172 |

[a] The POM concentration was $2 \times 10^{-4}$ M. The cyclic voltammograms were run at a scan rate of 2 mV $s^{-1}$. The Fe waves are numbered from 1 to 4 for the least to the most negatively reduced centers.

**Ionic Strength Effects.** Ionic strength effects were studied at pH 3 in regards to their influence on the demetalation process. The concentration of NaCl in the buffer solution was gradually changed from 2 to 0.1 M (Figure 3B). Using the cyclic voltammogram of the 2 M NaCl solution as a reference, lower ionic strength values are found to shift the Fe(III)-based waves in the negative direction, with the two most positive redox couples remaining more sensitive to ionic strength changes as previously observed in a pH 5 medium.[25] These results are consistent with a decrease in the extent of ion pairing since it was previously proposed that the first two redox couples are assigned to the "external" Fe(III) sites.[26] Demetalation was observed to be more favorable for both **Fe4P4** and **Fe4As4** at low ionic strength values and slower scan rates (see SI). Table 1 summarizes the reduction peak potentials of two of the Fe(III) centers (Fe2 and Fe4) for **Fe4P4** and **Fe4As4** as a function of NaCl concentration in a pH 3 medium.[29b] These values were measured for cyclic voltammograms recorded at a scan rate of 2 mV $s^{-1}$ and were selected because they are the most sharply defined at this scan rate. The formal potential for the free Fe(III)/Fe(II) redox couple is determined to be +0.445 V (versus SCE) in the pH 3, 0.1 M NaCl medium. Noteworthy is the fact that traces of free Fe(II) are detected at scan rates as high as 500 mV $s^{-1}$ in the 0.1 M NaCl medium. As the ionic strength increases, slower scan rates must be used if any Fe loss is to be observed. In summary, there are two main effects of ionic strength on the redox processes of the Fe centers within **Fe4P4** and **Fe4As4**. First, an increase in ionic strength favors ion pairing between the POM and the $Na^+$ cations, thus decreasing the overall negative charge of the polyanion and consequently making its reduction easier.[30] Second, in the presence of high $Na^+$ concentrations, the reduced Fe(II) centers are stabilized within the sandwich complexes by ion pairing.

**Supporting Electrolyte Effects.** The ability of the supporting electrolyte anions to complex to Fe(III) and/or Fe(II) is expected to influence the demetalation process. Therefore, the study with the $Cl^-$ anion is extended to other classical anions ($ClO_4^-$, $SO_4^{2-}$, $H_2PO_4^-$, and $CH_3COO^-$) commonly used for electrochemical studies of POMs in aqueous media. A pH 3 medium with a total concentration of 0.4 M $Na^+$ was selected to facilitate the comparisons. Under these conditions, the stability of the Fe(II) form of

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(29) (a) The analogous ejection of Fe(II) was observed previously upon reduction of the single Fe(III) center within $\alpha_2$-$[P_2(FeOH_2)W_{17}O_{61}]^{7-}$ (see ref 28) and $\alpha$-$[Zn(FeOH_2)W_{11}O_{39}]^{7-}$. See: Cheng, L.; Sun, H.; Liu, B.; Lin, J.; Dong, S. *Electrochem. Commun.* **1999**, *1*, 155−158. (b) The Fe(III) waves are numbered Fe1 through Fe4 for the least negative to the most negative reduction potentials, respectively.

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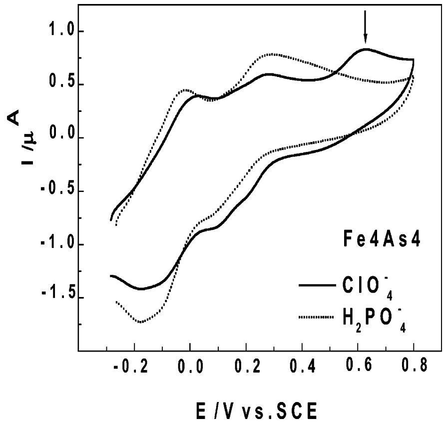

**Figure 4.** Evolution of the cyclic voltammogram observed for $2 \times 10^{-4}$ M **Fe4As4** with the nature of the anion present in the supporting electrolyte. The scan rate was 10 mV $s^{-1}$, the working electrode was glassy carbon, and the reference electrode was SCE. The arrow indicates the free Fe(II) oxidation. The pH 3 buffer solution was composed of 0.4 M $NaClO_4$ + $HClO_4$ (—) or 0.4 M $NaH_2PO_4$ + $H_3PO_4$ (···), and the cyclic voltammograms are run from negative to positive potentials following 60 s of microelectrolysis at −0.266 and −0.284 V for the $ClO_4^-$ and $H_2PO_4^-$ media, respectively.

**Table 2.** Formal Potentials (mV versus SCE) for the Fe(III)/Fe(II) Redox Couples within **Fe4X4** (X = P or As) as a Function of the pH of the Supporting Electrolyte

| | Fe4P4 | | | | Fe4As4 | | | |
|---|---|---|---|---|---|---|---|---|
| pH | Fe1 | Fe2 | Fe3 | Fe4 | Fe1 | Fe2 | Fe3 | Fe4 |
| 2 | 234 | | −19 | −135 | 266 | 178 | −19 | −124 |
| 3 | 227 | 124 | −16 | −93 | 264 | 152 | −13 | |
| 4 | 207 | 105 | −34 | −142 | 231 | 140 | −27 | −149 |
| 5 | 194 | 99 | −46 | −188 | 221 | 127 | −29 | −175 |
| 6 | 147 | 67 | −47 | −188 | 169 | 86 | −25 | −162 |
| 7 | 101 | 32 | −58 | −193 | 123 | 28 | −54 | −172 |

the POM was found to depend strongly on the nature of the anion present in the supporting electrolyte, with the stability decreasing in the following order: $H_2PO_4^-$ > $ClO_4^-$ > $SO_4^{2-}$ > $Cl^-$ > $CH_3COO^-$. The cyclic voltammograms in the presence of the two anions least prone to facilitate demetalation, $H_2PO_4^-$ and $ClO_4^-$, differ only by the fact that partial ejection of Fe(II) is observed in the presence of $ClO_4^-$ (see SI). The reduction characteristics of the Fe(III) centers are not modified from one medium to the next, but the reoxidation waves are modified in two ways. First, there is a decrease in the current intensities of the first two reoxidation waves in the $ClO_4^-$ medium. Second, a new wave attributable to demetalation appears in the $ClO_4^-$ medium between +0.5 and +0.7 V. In contrast, no Fe(II) loss is observed in the presence of $H_2PO_4^-$, even at a scan rate as low as 2 mV $s^{-1}$. In order to enhance the demetalation process, the cyclic voltammograms in Figure 4 were run from the negative to the positive potential direction, following 60 s of microelectrolysis at −0.266 and −0.284 V for the $ClO_4^-$ and $H_2PO_4^-$ media, respectively. Under these conditions, the Fe(II) and Fe(III) centers remain stable within the POM in the $H_2PO_4^-$ medium, but demetalation is clearly enhanced in the $ClO_4^-$ medium. A small reduction wave for free Fe(III) can even be observed between +0.3 and +0.5 V on potential reversal. The order of stabilization of the Fe(II) center within the reduced POMs generally parallels the complexation constants of free Fe(II) with $H_2PO_4^-$, $SO_4^{2-}$, and $Cl^-$, but complementary effects should be invoked for explaining the relative behavior of $ClO_4^-$ and $CH_3COO^-$.[31a]

**pH Effects.** The pH variation effects (pH 2−7) on the demetalation properties of **Fe4P4** and **Fe4As4** were studied by adding the appropriate amount of mineral acid or base to a 2 M NaCl solution.[31b] The large concentration of NaCl used in these experiments is intended to minimize any effect induced by ionic strength variations. There were two main phenomena observed for the Fe-centered reductions as a function of pH changes. First, the change in acidity influences the demetalation process. Second, the potentials for the Fe(III) waves shift with a change in pH. The latter phenomenon has been the subject of a previous investigation.[25] The waves of **Fe4As4** and **Fe4P4** are shifted in the positive potential direction when the pH was changed from 3 to 2 (with the ionic strength kept constant). During the reoxidation process, a new wave is observed in the pH 2 medium between +0.5 and +0.7 V which is consistent with the oxidation of free Fe(II) (see SI). The identity of this species is confirmed by the addition of an authentic sample of Fe(II). These results, along with the observation that an increase of pH from 3 to 4 does not induce demetalation (see SI), suggest that an increase in acidity favors demetalation. This is consistent with the fact that protonation of the POM would decrease its overall negative charge and consequently diminish its ability to complex with Fe(II). Table 2 gathers the formal potentials of the Fe(III)/Fe(II) redox couple within **Fe4As4** and **Fe4P4** as a function of the pH of the supporting electrolyte (from pH 2 to 7). All four sets of waves shift with a change in pH, albeit to different extents.[25] The reduction domains shown in Table 2 for the Fe centers in these sandwich-type structures are in a range accessible to the usual biological reductants, thus reinforcing the idea that these complexes can mimic the behavior of siderophores.[32]

**Comparative Demetalation Studies.** For these experiments, we compare the cyclic voltammograms of the tetrairon species, **Fe4As4** and **Fe4P4**, with those of their di- and tri-iron sandwich-type analogues, αααα-$Na_{16}[(NaOH_2)_2(Fe^{III})_2(X_2W_{15}O_{56})_2]$ (**Fe2X4**) and αα*β*α-$Na_{14}[(NaOH_2)(Fe^{III}OH_2)(Fe^{III})_2(X_2W_{15}O_{56})_2]$ (**Fe3X4**), respectively (X =

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(31) (a) The phenomena of electrolyte anion effects parallel the complexation ability of the anions towards the Fe(II) centers within the reduced sandwich POMs. Literature values are consistent with the order of stabilization found experimentally, except for $ClO_4^-$ and $CH_3COO^-$. For $ClO_4^-$, no literature value is found. The value found for $CH_3COO^-$ is comparable to that of $SO_4^{2-}$, which contrasts somewhat with the clear differences found for these two anions in our experiments. Such erratic correspondence is not unexpected considering that the experimental conditions for determination (or calculation) of these constants were very different from those used in our experiments. In addition, the dissymmetry of charge distribution within the sandwich POMs, on one hand, and in the complexing anions, on the other hand, might be important in the overall observations made in the present work. (b) The behavior of W(VI) waves within POMs as a function of pH has been the subject of several previous investigations. See: (i) Reference 1. (ii) Reference 4. (iii) Reference 14. (iv) Reference 19. (v) References 30−31. (vi) Reference 34. (vii) Keita, B.; Nadjo, L. *Mater. Chem. Phys.* **1989**, *22*, 77−103.

(32) (a) Cooper, S. R.; McArdle, J. V.; Raymond, K. N. *Proc. Natl. Acad. Sci. U.S.A.* **1978**, *75*, 3551−3554. (b) Cheraïti, N.; Brik, M. E.; Bricard, L.; Keita, B.; Nadjo, L.; Gaudemer, A. *Bioorg. Med. Chem. Lett.* **1999**, *9*, 2309−2314.

P or As) (Figure 1). The number of waves corresponds to the number of Fe atoms within each relevant complex.[26] The number of Fe(III) centers was confirmed by controlled potential coulometry, which gives 2.95 ± 0.06 and 1.95 ± 0.07 electrons per molecule for the exhaustive reduction of these centers within **Fe3X4** (at −0.300 V versus SCE) and **Fe2X4** (at −0.360 V versus SCE), respectively.

Electrolysis experiments were performed on **Fe3X4** and **Fe2X4** analogous to those performed on **Fe4As4** and **Fe4P4** (i.e., reduction of the Fe(III) centers is immediately followed by an attempt at their reoxidation). Regardless of the value of *n* in **Fe(*n*)X4** (X = P or As; *n* = 2, 3, 4), combined results of cyclic voltammetry and electrolysis show that one primary step following the reduction process is slow iron loss. However, there are subtle differences in the complexes depending on the number of Fe centers present. With **Fe4X4** (X = P or As), free Fe(II) is detected in solution, accompanied by the formation of **Fe3X4**. In the case of **Fe3X4**, iron loss is followed by its relatively rapid reincorporation, resulting only in the reformation of **Fe3X4**. This particular behavior is interesting in the context of its possible reuse after the initial iron release. Finally, for **Fe2X4** (X = P or As), the cyclic voltammograms become more complex after the forward and backward electrolysis at pH 3. In addition to the presence of redox processes associated with the free $Fe^{III}/Fe^{II}$ couple and **Fe2X4**, there is a new redox couple at +0.069 V for the phosphorus derivative and +0.115 V for the arsenic analogue. These values are those corresponding to the most positively reduced Fe-center within **Fe3X4** (X = P or As) at pH 3. Therefore, electrochemistry has permitted us to detect a mixture of **Fe2X4** and **Fe3X4** as a result of the electrolysis reaction.

There is a shift in the negative potential direction with a decrease in the number of Fe(III) atoms. The formal potentials measured from the cyclic voltammograms of the **Fe(*n*)X4** (X = P or As; *n* = 2, 3, 4) complexes are found to support the previously mentioned distinction between the two groups of Fe(III) centers within **Fe4X4** and the suggestion that the "external" Fe(III) centers, which bear water molecules, are likely to be reduced before the "internal" Fe(III) centers.[26] An alternative reasoning might attribute the negative potential shifts of the Fe(III) waves on going from **Fe4X4** to **Fe3X4** and **Fe2X4** entirely to the increase in the overall negative charge of the POMs, with no particular link to the "internal" or "external" position of the Fe atoms. This idea requires further experiments and/or theoretical calculations before any clear conclusions can be made.

Another interesting aspect of the behaviors of the multi-iron sandwich complexes is illustrated by the electrochemical study of $\alpha\beta\beta\alpha$-$Na_{14}[(Mn^{II}OH_2)_2(Fe^{III})_2(X_2W_{15}O_{56})_2]$ (X = P or As) (**Mn2Fe2X4**). These complexes can be considered as "saturated" species derived from the lacunary precursors **Fe2P4** and **Fe2As4**. These mixed-metal complexes were found to be stable between pH 0 and 7.[12,25] Controlled potential coulometry confirms that exhaustive reduction of the Fe(III) centers consumes 2.00 ± 0.05 electrons per molecule. Unlike their precursors **Fe2P4** and **Fe2As4**, no demetalation was observed, even at low pH. This behavior is interesting in that it is consistent with the Fe centers being less labile as a result of their internal and trapped location.

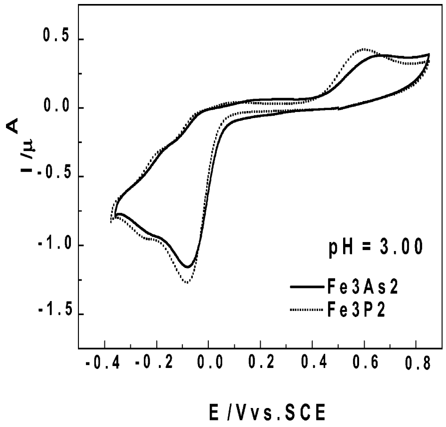

**Figure 5.** Comparison of the cyclic voltammograms of $2 \times 10^{-4}$ M **Fe3X2** (X = P or As) in a pH 3 medium (2 M NaCl + HCl). The scan rate was 10 mV $s^{-1}$, the working electrode was glassy carbon (3 mm diameter), and the reference electrode was SCE.

**Multi-Iron Wells−Dawson Monomers.** To date, there has been no electrochemical characterization reported for the multi-iron Wells−Dawson monomer complexes, $\alpha$-$Na_{11}[(P_2(Fe^{III}Cl)_2(Fe^{III}OH_2)W_{15}O_{59})]$ (**Fe3P2**) and $\alpha$-$Na_{11}[(As_2(Fe^{III}Cl)_2(Fe^{III}OH_2)W_{15}O_{59})]$ (**Fe3As2**) (Figure 2).[33] Figure 5 was recorded with **Fe3X2** (X = P or As) in a pH 3 medium. The main reduction peak has a large current intensity. In addition, it is chemically irreversible and is followed by a small shoulder peak. In contrast to the sandwich-type complexes, the Fe(III) centers are now simultaneously reduced in the pH 3 medium. Free Fe(II) is detected between +0.5 and +0.7 V. Exhaustive reduction of the Fe(III) centers of **Fe3X2** gives three electrons per molecule. Controlled potential electrolyses of **Fe3As2** and **Fe3P2** were performed as described for the sandwich-type complexes (see SI). The Fe(III)/Fe(II) redox couple is unambiguously present after electrolysis and is accompanied by the formation of the sandwich-type complexes **Fe4X4** and **Fe3X4**. This transformation, obtained under mild conditions, is consistent with previous reports showing that prolonged heating of A-$\alpha$-$[X(MOH_2)_3W_9O_{37}]^{n-}$ (X = P or Si; M = d-electron-containing transition metal) or **Fe3P2** results in the formation of sandwich-type structures.[10,34−36] A brief study of electrolyte anion effects was also performed at pH 3. Indeed, demetalation is slowed in $ClO_4^-$ and $H_2PO_4^-$ media. However, unlike **Fe4X4**, even pure phosphate medium could not completely suppress demetalation at slow scan rates in pH 3 buffer solution.

The simultaneous reduction of the Fe(III) centers in these monomeric species is puzzling. X-ray studies of crystals

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(33) The synthesis of **Fe3As2** is identical to that of **Fe3P2** (ref 10) except that $\alpha$-$Na_{12}[(As_2W_{15}O_{56})]$ is used instead of $\alpha$-$Na_{12}[(P_2W_{15}O_{56})]$. The purity of the product was confirmed by elemental analysis and infrared spectroscopy.

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(35) Katsoulis, D. E.; Pope, M. T. *J. Am. Chem. Soc.* **1984**, *106*, 6, 2737−2738.

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grown from aqueous media of comparable pH, ionic strength, and chloride concentration show there are two different groups of iron centers present. Two of the three Fe(III) centers have a chloride terminal ligand while the third Fe(III) site has an aqua ligand (Figure 2). Furthermore, these centers are in adjacent edge-sharing octahedra, which should permit some electronic communication between the Fe centers. Therefore, we wondered whether the apparently simultaneous reduction of the Fe(III) centers could be modified by an appropriate change in the reaction medium. To test this idea, a cyclic voltammogram of **Fe3X2** was recorded in a pH 5 medium (see SI). The main observation is the splitting into two steps of the formerly unique Fe(III) reduction wave. This splitting clearly indicates that the medium does play an important role in the communication between the Fe(III) centers. In addition, the first of these waves appears to become slightly more reversible. In pure phosphate medium (pH 5), no iron loss is observed.

**Conclusions.** In this work, we are interested in factors that control the release of iron from multi-iron polyoxometalates. At room temperature and under mild conditions, iron release from the complexes studied in this work is observed upon reduction of the Fe(III) centers. This release is controlled by the ionic strength of the medium, the nature and concentration of the anions present in the supporting electrolyte, and by the pH of the solution. This behavior parallels and/or mimics that described for many siderophores that largely depend on the same parameters. In particular, it is worth noting that iron release is favored on going from neutral to acidic media, exactly as observed for several siderophores in which an increase in acidity facilitates the activity of biological reductants. In addition, the reduction potentials of the Fe(III) centers in the multi-iron complexes in this work fall in the domain accessible to usual biological reductants. The observation that these multi-iron heteropolytungstate complexes are more stable than their precursor lacunary species, α-$P_2W_{15}O_{56}^{12-}$ and α-$As_2W_{15}O_{56}^{12-}$, suggests that complexation of iron cations in solution by these lacunary complexes is faster than hydrolysis of the heteropolytungstate cages, and that Fe(III) is more strongly bound than Fe(II). The rearrangement of reduced **Fe3X2** into a mixture of **Fe3X4** and **Fe4X4**, that of reduced **Fe2X4** into a mixture of **Fe2X4** and **Fe3X4**, the fast reconstitution of **Fe3X4** upon reduction, and the partial breakdown of **Fe4X4** into **Fe3X4** can all be cited as examples which support this view. Most importantly, these observations point to the possibility that the complex remaining after iron release can be used repeatedly, a feature reminiscent of the behavior encountered in hydroxamate-type siderophores.

**Acknowledgment.** This work was supported in part by the University Paris XI and the CNRS (UMR 8000). We also thank the NSF (Grant CHE-0236686) for the research and Véronique Barra for running several experiments.

**Supporting Information Available:** Cyclic voltammograms for **Fe4As4** and **Fe4P4** showing Fe(III) reduction, ionic strength, supporting electrolyte, and pH effects and cyclic voltammograms for **Fe3As2** and **Fe3P2** showing Fe(III) reduction and pH effects. This material is available free of charge via the Internet at http://pubs.acs.org.

IC035495I