Iron Clusters

Coordination Chemistry of the Hexavacant Tungstophosphate $[H_2P_2W_{12}O_{48}]^{12-}$ with Fe^{III} Ions: Towards Original Structures of Increasing Size and Complexity**

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Dedicated to Professor Francis Sécheresse
on the occasion of his 60th birthday

Polyoxometalates (POMs) are known to form original molecular and supramolecular structures of impressive size and complexity. This structural flexibility has been used to synthesize POMs with important chemical, biological, or physical properties.[1–3] Lacunary POMs form magnetic clusters with diverse nuclearities and original topologies.[4] The trivacant Keggin or Wells–Dawson polyoxotungstates have proven the most versatile polyoxoanion synthons for the preparation of magnetic clusters. Magnetic POMs with up to four trivacant POM subunits have been reported to date.[5,6] The largest number of first-row paramagnetic ions encapsulated in a diamagnetic POM matrix is displayed by the copper(II) polyoxotungstates $[\{(SiW_9O_{34})\{SiW_9O_{33}(OH)\}(Cu(OH))_6Cu\}_2X]^{23-}$ (X = Cl, Br) recently reported by Mialane et al.[6]

One of the goals of such studies is the search for single-molecule magnets (SMMs),[7] which are the subject of considerable interest owing to their unique physics and relevance in the development of functional nanosized materials. Their unusual properties derive from the combination of a large spin ground state with a large negative axial-type anisotropy. The current search for new SMMs is largely focused on polynuclear oxo iron[8,9] and manganese complexes.[10] Although interactions between Fe^{III} ions as well as between Mn^{III} ions, mediated by μ-oxo or μ-hydroxo bridges, are often antiferromagnetic, local ion anisotropy and particular topological arrangements can result in reasonably large spin ground states and negative D values. Therefore, original spin topologies and/or new SMMs can be expected from POMs with increasing size and complexity, particularly highly vacant POMs. This led us to explore the coordination chemistry of the hexavacant tungstophosphate $[H_2P_2W_{12}O_{48}]^{12-}$.

Lacunary derivatives of the Wells–Dawson anion α-$[P_2W_{18}O_{62}]^{6-}$ have been thoroughly investigated by Contant and Ciabrini,[11,12] and the related terminology (α, α_1, α_2) can be found in reference [11]. The metastable anion α-$[H_2P_2W_{12}O_{48}]^{12-}$, abbreviated as $\{P_2W_{12}\}$, could not be characterized by X-ray diffraction studies. However, its structure can be inferred from that of the condensed tetramer $[P_8W_{48}O_{184}]^{40-}$.[13] Further evidence for this structure comes from the reactions with tungstate, molybdate, and vanadate in acid media, which provide mixed tungsto-molybdo-vanado-phosphates.[14] Another example of the reactivity of $\{P_2W_{12}\}$ towards d^0-transition metal ions is provided by the polyperoxo polyoxoanion $[P_2W_{12}O_{56}(NbO_2)_6]^{12-}$.[15] The reactions of $\{P_2W_{12}\}$ with lanthanides have led to the isolation of complexes that, instead of $\{P_2W_{12}\}$, contain $[P_2W_{16}O_{59}]^{16-}$ [16] or α_2-$[P_2W_{17}O_{61}]^{10-}$ [17]. In contrast, it was originally reported that $\{P_2W_{12}\}$ does not form complexes with divalent or trivalent transition-metal ions.[13] We have now succeeded in isolating several Fe^{III} and Mn^{III} complexes, and we present here our results on the $\{P_2W_{12}\}/Fe^{III}$ system.

In aqueous mixtures of lithium chloride and lithium acetate at ambient temperature, the reaction of $\{P_2W_{12}\}$ with an excess (8–14 equiv) of iron(III) chloride gives the metastable anion $[H_4P_2W_{12}Fe_9O_{56}(OAc)_7]^{6-}$ (**1**) which crystallizes as Li_2K_4-**1**·34 H_2O.[18] Upon heating in aqueous sodium acetate, **1** transforms into $[H_yP_8W_{48+x}Fe_{28-x}O_{248}]^{(84-y-3x)-}$ (**2**), which has been isolated as different salts that show slight variation in the value of x. A sample formulated as $Na_{16}K_{12}[H_{56}P_8W_{48}Fe_{28}O_{248}]$·ca.90 H_2O ($Na_{16}K_{12}$-**2a**·ca.90 H_2O) based on chemical analysis was obtained by heating $\{P_2W_{12}\}$ with 6 equiv of iron(III) chloride in 0.5 M sodium acetate. It was characterized by electrochemical and magnetic measurements, and by determination of the unit cell parameters. A complete X-ray diffraction study was performed on a crystal from another sample for which the formula $Na_{16}K_{10}[H_{55}P_8W_{49}Fe_{27}O_{248}]$·ca.90 H_2O ($Na_{16}K_{10}$-**2b**·ca.90 H_2O) is proposed on the basis of the structure determination. There is also some evidence of the formation of other representatives of **2** (possibly with x up to 4) when the Fe^{III}:$\{P_2W_{12}\}$ ratio or the pH value is lowered. However, chemical analysis and IR spectroscopy are insufficient to unequivocally determine the composition and purity of these products. When the Fe^{III}:$\{P_2W_{12}\}$ ratio is less than 4, clusters with the generalized formula $[H_yP_4W_{28+x}Fe_{8-x}O_{120}]^{(28-y-3x)-}$ (**3**) are obtained instead of **2**.[19]

The structure of **1** is shown in Figure 1. The cluster has crystallographically imposed C_2 symmetry. It derives from the hexavacant $\{P_2W_{12}\}$ anion by filling up the six vacancies with iron atoms. The substituted Wells–Dawson species $\{P_2W_{12}Fe_6\}$ thus formed supports three additional iron atoms: Two of

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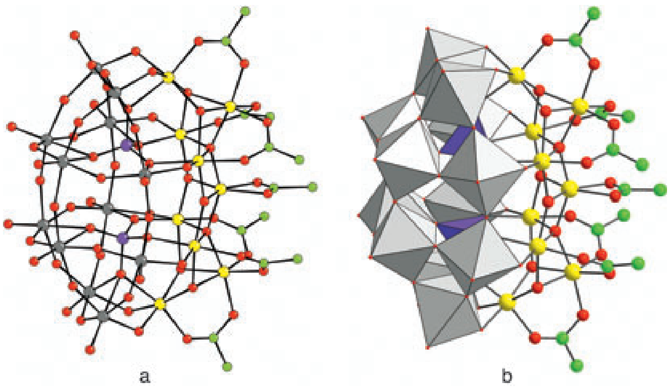

Figure 1. Ball-and-stick (a) and combined polyhedral ball-and-stick representations (b) of **1** in Li_2K_4-**1**·34 H_2O (P violet, O red, Fe yellow, W black, C green).

them are connected to three contiguous bridging oxo ligands of the $\{P_2W_{12}Fe_6\}$ subunit, while the third is connected to four bridging oxo ligands. Sixfold coordination of the Fe^{III} centers is achieved by coordination to acetate ligands. Six of the seven acetate ligands are bridging while the seventh is chelating. The Fe^{III} centers are connected through six μ_3-O and two μ_4-O units. The results of bond valence sum (BVS) calculations[20] indicate that the triply bridging oxygen atoms that do not lie in the equatorial plane are protonated. Thus the anion is formulated as $[H_4P_2W_{12}Fe_9O_{56}(OAc)_7]^{6-}$ in agreement with the results of chemical analysis. Compound **1** can be considered as bridging the gap between transition metal substituted POMs such as $[\alpha\text{-}P_2W_{15}O_{59}(FeCl)_2(FeOH_2)]^{11-}$ [21] and classic coordination clusters such as $[Fe_3O(OAc)_6(H_2O)_3]^{+}$.[22] Apart from the keplerates,[23a] where acetate anions act as bridging ligands for the $\{Mo^{V}_2O_4\}$ linkers, there are only a few complexes of POMs that contain acetate ligands. These include $[\gamma\text{-}SiW_{10}O_{36}(OH)Cr_2(OAc)_2(H_2O)_2]^{5-}$,[24a] $[PW_{11}O_{39}\{Rh_2(OAc)_2\}]^{5-}$,[24b] $[\{\alpha_2\text{-}P_2W_{17}O_{61}La(OAc)(H_2O)_2\}_2]^{16-}$,[17] and $[\{SiW_{11}O_{39}Ln(H_2O)(OAc)\}_2]$.[25]

The structure of **2b** is shown in Figure 2. This cluster can be viewed as a supramolecular Wells–Dawson polyoxotungstate. Each of the four $\{P_2W_{12}Fe_6\}$ subunits is connected by three Fe-O-Fe bridges to an adamantane $\{Fe_4O_6\}$ core. In addition, they are linked into pairs by three Fe-O-Fe bridges involving the three outer iron atoms. These extra bonds differentiate **2b** from the otherwise similar tetra-Keggin anion $[Nb_4O_6(\alpha\text{-}Nb_3SiW_9O_{40})_4]^{20-}$.[26] To our knowledge, there are only a few crystallographically characterized iron(III) clusters that contain an adamantane-like core: These are tetranuclear complexes with ditopic, heptadentate ligands[27] and triazacyclononane.[28]

The inner site α_2 of each Wells–Dawson subunit of **2b** is occupied either by tungsten or iron. Crystallographic refinement resulted in occupancy factors of 0.25 for W and 0.75 for Fe in this site; thus, the composition of the cluster is $\{P_8W_{49}Fe_{27}\}$. According to BVS calculations, all the Fe-O-Fe bridges are protonated, which leads to the composition $[H_{55}P_8W_{49}Fe_{27}O_{248}]^{26-}$. Only a few tetrahedral supramolecular POMs have been characterized so far. Besides the above-mentioned Nb-containing compound,[26] these include the polyoxomolybdo-europate $[Eu_4(MoO_4)(H_2O)_{16}(Mo_7O_{24})_4]^{14-}$,[29] the uranium-containing polyoxotungstate $[(UO_2)_{12}(\mu_3\text{-}O)_4(\mu_2\text{-}H_2O)_{12}(P_2W_{15}O_{56})_4]^{32-}$,[30] the tetrameric titanium(IV)-substituted Wells–Dawson polyoxotungstate $[\{Ti_3P_2W_{15}O_{57.5}(OH)_3\}_4]^{24-}$,[31] and the tetra(polyoxometalate) dendrimers $[\{P_2V_3W_{15}O_{59}(OCH_2)_3CNHCOCH_2CH_2OCH_2\}_4C]^{24-}$ [32a] and $[(SiW_{11}O_{39}GeCH_2CH_2CO_2CH_2)_4C]^{20-}$.[32b]

The cyclic voltammograms of $\{P_2W_{12}\}$, **1**, and **2a** are shown in Figure 3. The electrochemistry of $\{P_2W_{12}\}$ has been described.[33] The first reduction wave of **1** and **2a**, which is attributed to the reduction of Fe^{III} to Fe^{II}, is rather broad, particularly for **1**. However, stepwise reduction of the Fe^{III} centers is not observed, in contrast to the sandwich complexes $\alpha\beta\beta\alpha\text{-}[(Fe^{III}OH_2)_2Fe^{III}_2(X_2W_{15}O_{56})_2]^{12-}$ (X = P,[34a,b] As[34c,d]). Controlled potential coulometry under continuous argon bubbling and stirring consumes 9.3 and 27.8 electrons per molecule, respectively, for **1** at pH 3 and **2a** at pH 2. This is in satisfactory agreement with analytical and structural data. An

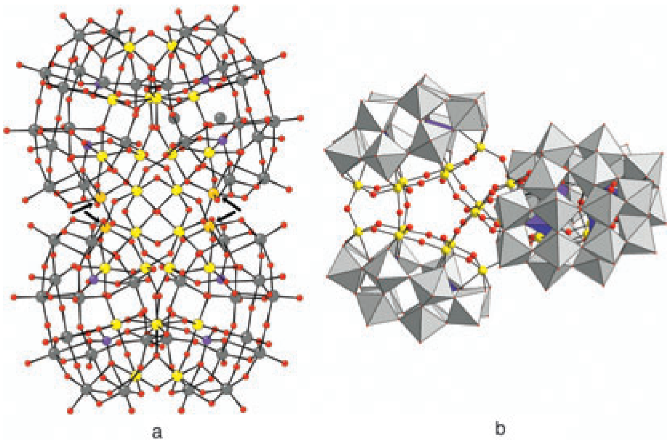

Figure 2. Ball-and-stick (a) and combined polyhedral ball-and-stick representations (b) of **2b** in $Na_{16}K_{10}$-**2b**·90 H_2O (P violet, O red, Fe yellow, W black, C green). The four inner α_2 positions (shown by the arrows) possess 75% Fe and 25% W character.

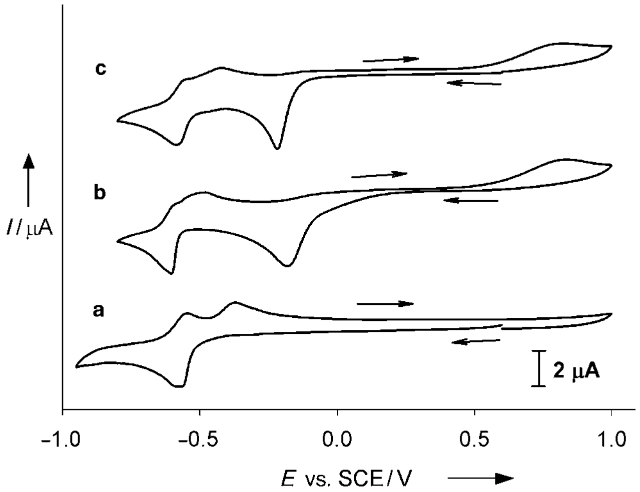

Figure 3. The cyclic voltammograms of 0.1 mM samples of $[H_2P_2W_{12}O_{48}]^{12-}$ (a), **1** (b), and **2a** (c) in 0.5 M $Li_2SO_4 + H_2SO_4$ at pH 3. The scan rate was 20 mV s^{-1}, and a glassy carbon electrode was used.

oxidation wave appears at about +0.8 V, which is attributed to the oxidation of free Fe^{II}. Demetalation of **1** and **2** upon reduction of the Fe^{III} centers parallels the behavior of multi-iron Wells–Dawson sandwich-type polyoxotungstates.[35]

The temperature dependence of the magnetization of Li_2K_4-**1**·34 H_2O was studied down to 2 K. The $\chi_M T$ product at 300 K (20 $cm^3\,mol^{-1}\,K$) is much lower than expected for nine noninteracting Fe^{III} centers (39.4 $cm^3\,mol^{-1}\,K$) and decreases continuously to 1.94 $cm^3\,mol^{-1}\,K$ at 2 K. This indicates strong intramolecular antiferromagnetic coupling between the Fe^{III} centers. The magnetization was studied as a function of the applied magnetic field at 2 K: The magnetization at 50 kOe (4.2 μ_B) is consistent with a paramagnetic ground state, as expected for a cluster with an odd number of Fe^{III} centers. The magnetization data at 2 K, however, do not fit a Brillouin function for a spin $S = 5/2$, which indicates a more complex situation in the ground state. Even if the C_2 symmetry of the cluster results in a reduction in the number of nearest neighbor exchange coupling constants J in **1** to seven, the extraction of very different J values from the magnetic data is far from trivial. Accurate magnetization data, EPR characterization, and computation of the J values by density functional theory methods are in progress.[36] Magnetic studies of **2** also indicate strong antiferromagnetic coupling between the Fe^{III} centers. The residual paramagnetism in the studied sample corresponds to the presence of a species with an odd number of Fe^{III} centers, such as **2b**. Further studies are planned on this family of compounds.

In conclusion, the hexavacant tungstophosphate anion $[H_2P_2W_{12}O_{48}]^{12-}$ can accomodate six Fe^{III} centers. The $\{P_2W_{12}Fe_6\}$ species thus formed is stabilized as either **1** or **2** through further reaction with Fe^{III} centers. In addition, tungsten may substitute a part of the iron in the $\{P_2W_{12}Fe_6\}$ moiety. To our knowledge, cluster **2b**, with 27 Fe^{III} centers, is the second largest iron cluster characterized so far, being only surpassed by the $\{Mo^{VI}_{72}Fe^{III}_{30}\}$ keplerate.[23b] Manganese and nickel derivatives of $\{P_2W_{12}\}$ have been also obtained and will be reported soon.[19]

Experimental Section

1: $FeCl_3\cdot 6\,H_2O$ (1.21 g, 4.48 mmol) was added to a stirred solution of $K_{12}[H_2P_2W_{12}O_{48}]\cdot 24\,H_2O$[12] (1.97 g, 0.50 mmol) in a mixture of 5 M LiCl (25 mL), 4 M LiOAc (9 mL), and H_2O (5 mL). The resulting mixture was stirred for 5 h and then allowed to sit. After 1 day the mixture was filtered. Dark red crystals of Li_2K_4-**1**·34 H_2O deposited from the filtrate (pH 3.7) over 1–2 d. The crystals were collected by filtration through a glass frit and washed with ice-cold water (10 mL). Yield 0.37 g (15 % calculated from $\{P_2W_{12}\}$). Elemental analysis calcd (%) for $C_{14}H_{93}K_4Li_2Fe_9O_{104}P_2W_{12}$: C 3.46, K 3.21, Li 0.29, Fe 10.33, P 1.27, W 45.33; found: C 3.56, K 3.12, Li 0.33, Fe 10.13, P 1.19, W 43.37.

2: $K_{12}[H_2P_2W_{12}O_{48}]\cdot 24\,H_2O$ (1.0 g, 0.25 mmol) and $FeCl_3\cdot 6\,H_2O$ (0.405 g, 1.5 mmol) were added to a mixture of 4 M NaOAc (6 mL) and H_2O (40 mL). The resulting suspension was heated to 95 °C for 3 h and then cooled to 20 °C and filtered. Yellow-green crystals of composition $Na_{16}K_{12}$-**2a**·ca.90 H_2O deposited from the filtrate (pH 5.2) over 5 d. Yield 0.16 g (15 % calculated from $\{P_2W_{12}\}$). Elemental analysis calcd (%) for $H_{238}K_{12}Fe_{28}Na_{16}O_{318}P_8W_{48}$: K 2.79, Fe 9.31, Na 2.17, P 1.47, W 52.53; found: K 2.94, Fe 9.0, Na 2.1, P 1.12, W 50.66.

The crystals thus obtained were of limited quality and only the cell parameters could be determined. Better-quality crystals, used for the crystal structure determination,[18] were obtained as follows: An aqueous solution of $Fe(ClO_4)_3\cdot 6\,H_2O$ (1.39 g, 3 mmol) in H_2O (10 mL) was added to a stirred suspension of $K_{12}[H_2P_2W_{12}O_{48}]\cdot 24\,H_2O$ (2.0 g, 0.51 mmol) in 1 M NaOAc/AcOH (20 mL, pH 6). The mixture was heated at reflux for 1 h, upon which a clear solution was obtained. The sticky solid that deposited on cooling to 20 °C was discarded and the subsequent polycrystalline fraction was recrystallized in 0.5 M NaOAc/AcOH (pH 6) to give yellow-green rods ($Na_{16}K_{10}$-**2b**·ca.90 H_2O). Both sets of crystals display similar cell parameters and IR spectra, despite small differences in the composition.

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refined parameters, $R=0.068$, $wR(F_o^2)=0.077$ [20249 reflections with $I>3\sigma(I)$], GOF = 1.09, $\Delta\rho_{max}=9.92\,e\,Å^{-3}$, $\Delta\rho_{min}=-2.99\,e\,Å^{-3}$. The X-ray crystallographic data were collected at room temperature either on an Enraf-Nonius MACH3 diffractometer (**1**) or on a Bruker SMART three-circle diffractometer equipped with a CCD bidimensional detector (**2b**), both with graphite-monochromated $Mo_{K\alpha}$ radiation ($\lambda=0.71073$ Å). The structures were solved and refined by full-matrix least squares using CRYSTALS. Neutral-atom scattering factors were used with anomalous dispersion corrections applied. Hydrogen atoms were not included in the refinements. Both structures exhibit some disorder in the range of counterions and water molecules, as is often the case with polyoxometalates. Thus, only a limited number of cations and water molecules could be located. This resulted in rather high residual electron densities. CCDC-258626 contains the supplementary crystallographic data for Li_2K_4-**1**·34H_2O. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Further details on the crystal structure investigation on $Na_{16}K_{10}$-**2b**·ca.90H_2O may be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: (+49)7247-808-666; e-mail: crysdata@fiz-karlsruhe.de), on quoting the depository number CSD-391310.

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