Coordination chemistry of the hexavacant tungstophosphate $[H_2P_2W_{12}O_{48}]^{12-}$: synthesis and characterization of iron(III) complexes derived from the unprecedented $\{P_2W_{14}O_{54}\}$ fragment†

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Clusters which display the rare cubic Fe_8 topology have been obtained by reaction of the metastable hexavacant polyoxotungstate $[H_2P_2W_{12}O_{48}]^{12-}$ with basic trinuclear metal acetates.

Lacunary species are key intermediates in polyoxometalate chemistry.[1] In particular, they allow the rational synthesis of mixed heteropolyoxometalates[2] and of magnetic clusters with diverse nuclearities and topologies.[3] For the specific case of the Dawson–Wells family of tungstophosphates,[4] the reactions of the α_1- and α_2-monovacant, and the α-trivacant derivatives with paramagnetic 3d metal ions have been widely studied,[5] while comparatively little attention has been paid to the hexavacant species $[H_2P_2W_{12}O_{48}]^{12-}$, $\{P_2W_{12}\}$ for short, and to the related cyclic $[H_7P_8W_{48}O_{184}]^{33-}$ tetramer until recently.[6,7] In particular, we have shown that the $\{P_2W_{12}Fe_6\}$ unit is formed upon reaction of $\{P_2W_{12}\}$ with Fe^{III} in aqueous mixtures of lithium chloride and lithium acetate at ambient temperature.[6] This unit can be recognized in the clusters $[H_4P_2W_{12}Fe_9O_{56}(OAc)_7]^{6-}$ (**1**) and $[H_{55}P_8W_{49}Fe_{27}O_{248}]^{26-}$ (**2**).[6] The composition of the latter reflects the partial substitution of tungsten for iron in the $\{P_2W_{12}Fe_6\}$ subunits. Substitution is increased by prolonged heating and lowering the $[Fe^{III}]/[\{P_2W_{12}\}]$ ratio and the pH, and leads to the formation of a new series of clusters with the general formula $[H_yP_4W_{28+x}Fe_{8-x}O_{120}]^{(28-y-3x)-}$ (**3**).

The cluster $[H_{12}P_4W_{28}Fe_8O_{120}]^{16-}$ (**3a**, $x = 0$, $y = 12$) is formed in various conditions, *e.g.* in the reaction of $\{P_2W_{12}\}$ with hydrous iron oxide or with the basic iron acetate $[Fe_3O(OAc)_6(H_2O)_3]Cl\cdot 5H_2O$. Although tungstate was added to the reagents when the composition of **3a** was established, it does not appear to be essential for the formation of the cluster. Tungstate arising from the (limited) decomposition of $[H_2P_2W_{12}O_{48}]^{12-}$, or deliberately added, competes with the added metal ions as has been previously observed in the reactions with lanthanide ions.[8,9] The potassium salt of **3a** was recrystallized in sodium acetate to give the crystals $Na_{10}K_6[H_{12}P_4W_{28}Fe_8O_{120}]\cdot 28H_2O$, $Na_{10}K_6$**3a**$\cdot 28H_2O$.‡ Evidence for the formation of other clusters of type **3** has been obtained. Thus, a polyanion with composition $[H_yP_4W_{30}Fe_6O_{120}]^{(22-y)-}$ (**3b**, $x = 2$) was characterized among the products obtained from a 1 : 4 : 2 aqueous mixture of $K_{12}[H_2P_2W_{12}O_{48}]$, sodium tungstate, and Fe(III) chloride at pH 4.2. At pH 2, the complex α_1-$[P_2W_{17}O_{61}\{Fe(H_2O)\}]^{7-}$ forms in the presence of lithium tungstate and crystallizes as the potassium salt which was characterized by ^{31}P NMR by comparison with an authentic sample.[10] When $\{P_2W_{12}\}$ is reacted with the mixed-metal complexes $[Fe^{III}{}_2M^{II}O(OAc)_6(H_2O)_3]$, the clusters $[\{M(H_2O)_4\}_2\{H_{12}P_4W_{28}Fe_8O_{120}\}]^{12-}$ (**4a**: M = Co, **4b**: M = Mn, **4c**: M = Ni) form, together with **3a**, and were isolated as potassium salts.§

Compounds $Na_{10}K_6$**3a**$\cdot 28H_2O$ and K_{12}**4a**$\cdot 30H_2O$ have been characterized by X-ray crystallography.¶ The molecular structure of **3a** is shown in Fig. 1. The cluster has crystallographically-imposed C_i symmetry. It may be viewed as an iron complex of a previously unobserved $\{P_2W_{14}O_{54}\}^{14-}$, $\{P_2W_{14}\}$. The two symmetrically-related halves $\{P_2W_{14}Fe_4\}$ are connected by four Fe–O–Fe bridges. The eight Fe^{III} centers form an almost regular cube, the edges of which range from 3.626(6) to 3.813(6) Å. Such a topology is rare and to our knowledge there are very few examples of cubic $\{Fe_8\}$ clusters.[11] Bond valence sum (BVS) calculations[12] indicate that all the Fe–O–Fe bridges are protonated. Thus the anion must be formulated as $[H_{12}P_4W_{28}Fe_8O_{120}]^{16-}$ in agreement with the results of chemical analysis. Dimerisation through Fe–OH–Fe bridges is rather common in aqueous chemistry of Fe^{III} and has been observed for di-iron-substituted Keggin anions.[13] Different crystals which appeared isostructural with $Na_{10}K_6$**3a**$\cdot 28H_2O$ were obtained during our study. In one case, a distinct shift of the $\nu_s(WO_t)$ Raman band to higher wavenumbers was observed, which led us to complete the X-ray analysis. Although only a few cations and water molecules could be located, the structure of the anion appears reliable. The cluster (**3b**) is similar to **3a** but the vertices of the inner cube are now occupied either by tungsten or by iron, with an occupancy factor of 0.25 for W. Thus the actual formula of the cluster is $[H_yP_4W_{30}Fe_6O_{120}]^{(22-y)-}$. The disorder precludes a reliable determination of y by the BVS method. The change from **3a** to **3b** is accompanied by a small contraction of the inner cube.

The molecular structure of **4a** is shown in Fig. 2. In this cluster, **3a** acts as a ligand for two Co^{II} centers, each of them being linked to one terminal oxo ligand from each $\{P_2W_{14}Fe_4\}$ subunit. The coordination polyhedron of each Co^{II} center is completed by four molecules of water. Bond distances clearly distinguish Co^{II} from Fe^{III}.

The cyclic voltammogram of **3a** displays four reduction waves, the first of which at −0.32 V *vs.* SCE is attributed to the reduction

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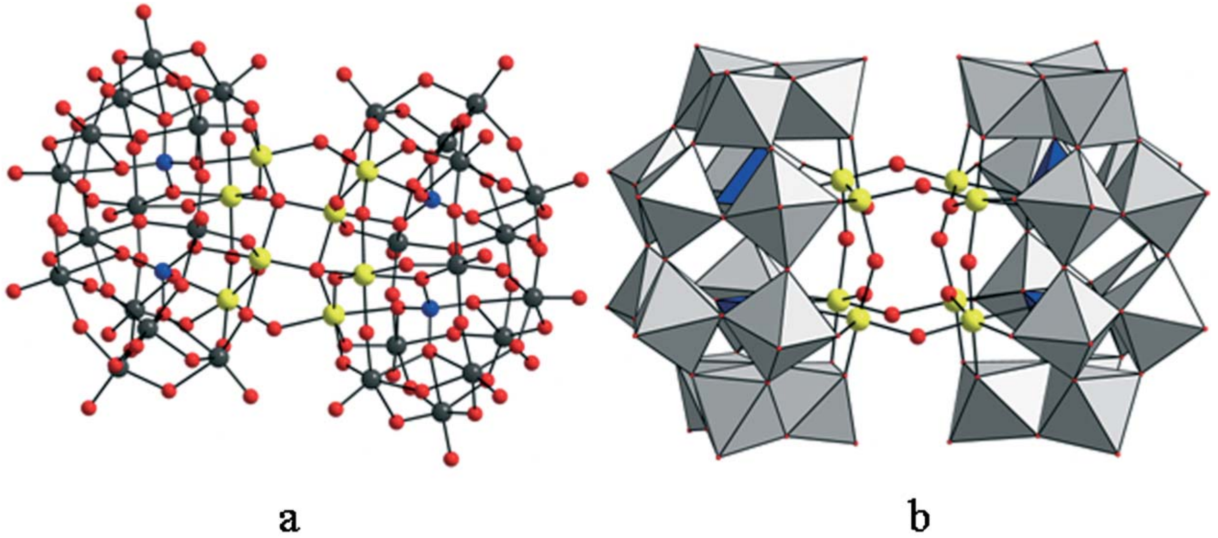

Fig. 1 Ball-and-stick (a) and combined polyhedral ball-and-stick (b) representations of **3a** in $Na_{10}K_6$**3a**$\cdot 28H_2O$. Color code: W: black, O: red, P: blue, Fe: yellow. Fe···Fe distances: from 3.626(6) to 3.813(6) Å; Fe–O–Fe angles: from 133.0(10) to 141.3(11)°.

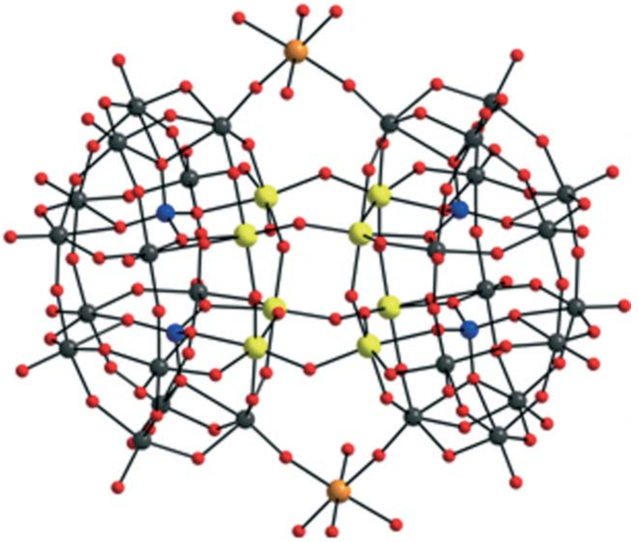

Fig. 2 Ball-and-stick representations of **4a** in K_{12}**4a**$\cdot 30H_2O$. Color code: W: black, O: red, P: blue, Fe: yellow, Co: tan. Fe···Fe distances: from 3.570(6) to 3.707(7) Å. Fe–OH–Fe angles: from 131.5(11) to 144.3(12)°. CoO distances: from 2.03(2) to 2.18(3) Å. Co···Co: 14.931(9) Å.

of Fe^{3+} to Fe^{2+}. The appearance of an oxidation wave at about +0.8 V on potential reversal, which is attributed to the oxidation of free Fe^{2+}, indicates that demetalation of **3a** occurs upon reduction of the Fe^{III} centers as already observed in clusters **1** and **2**[6] and in multi-iron Wells–Dawson sandwich-type polyoxotungstates.[14] The Co^{II} centers are not electrochemically active in the potential range under study and the cyclic voltammogram of **4a** is quite similar to that of **3a**.

The magnetization of K_{12}**4a**$\cdot 30H_2O$ was measured as a function of the applied magnetic field at 2 K. The value at 50 kOe (7.7 μ_B) appears consistent with two non-interacting Co^{II} centres, which suggests that the ground state of **3a** is diamagnetic and indicates strong intramolecular antiferromagnetic coupling of the Fe^{III} centers. The weak magnetization of $Na_{10}K_6$**3a**$\cdot 28H_2O$ (*ca.* 0.9 μ_B at 50 kOe 2 K) could be explained either by the presence of paramagnetic impurities or partial substitution of Fe for W.

In conclusion, reaction of $\{P_2W_{12}\}$ with Fe^{III} leads to clusters with original structures, *e.g.* **1** and **2** with nuclearities 9 and 27,[6] and **3a** which displays the rare cubic Fe_8 topology. Further studies are planned in order to isolate and to characterize the related clusters with a cubic $Fe_{8-x}W_x$ core, as part of our endeavours to obtain strongly coupled highly anisotropic magnetic species. Complexes of the type $[H_yP_4W_{28+x}M_{8-x}O_{120}]^{(28-y-3x)-}$ have also been obtained with Mn^{III} and will be reported soon.

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Notes and references

‡ *Synthesis of K_6Na_{10}**3a**$\cdot 28H_2O$*: $K_{12}[H_2P_2W_{12}O_{48}]\cdot 24H_2O^{4b}$ (10 g, 2.54 mmol) was added to a suspension of hydrous ferric oxide prepared by adding a solution of KOH (2.95 g, 52.58 mmol) in 50 mL of distilled water to a solution of $Fe(NO_3)_3\cdot 9H_2O$ (7.07 g, 17.5 mmol) in 50 mL of distilled water. The resultant mixture was heated at 95 °C for 1 h and then filtered whilst hot. A light yellow powder deposited from the filtrate. Yield: 1 g. Light yellow rods were obtained by recrystallization of the crude product in 1 M sodium acetate (0.2 g in 5 mL). Elemental analysis (%) calc. for $H_{68}Fe_8K_6Na_{10}O_{148}P_4W_{28}$: Fe, 5.18; K, 2.72; Na, 2.67; P, 1.44; W, 59.72; found: Fe, 4.73; K, 2.49; Na, 2.74; P, 1.58; W, 61.10. IR (KBr pellets): ν/cm^{-1} 1074m, 1001w, 940m, 896m, 773s. Raman (crystal): ν/cm^{-1} 970, 957.

§ *Synthesis of K_{12}**4a**$\cdot 30H_2O$*: $[Fe_2CoO(OAc)_6(H_2O)_3]\cdot 3H_2O^{15}$ (0.66 g, 1.02 mmol) was added to a solution of $K_{12}[H_2P_2W_{12}O_{48}]\cdot 24H_2O^{4b}$ (1.5 g, 0.38 mmol) in 60 mL of distilled water and the mixture was heated at 95 °C for 2 h. Then the solution was allowed to cool to room temperature and centrifuged. Thin pink crystals formed from the solution within two days. Yield: 160 mg (10% based on $\{P_2W_{12}\}$). Elemental analysis (%) calc. for $H_{88}Co_2Fe_8K_{12}O_{158}P_4W_{28}$: Co, 1.32; Fe, 5.01; K, 5.26; P, 1.39; W, 57.68; found: Co, 1.37; Fe, 4.90; K, 5.31; P, 1.03; W, 56.87. IR (KBr pellets): ν/cm^{-1} 1078s, 1002w, 944m, 907m, 777s. The analogous manganese and nickel adducts were similarly obtained.

¶ *Crystal data for $Na_{10}K_6$**3a**$\cdot 28H_2O$*: $H_{68}Fe_8K_6Na_{10}O_{148}P_4W_{28}$, $M = 8619.41$, triclinic, $a = 12.643(15)$, $b = 15.390(8)$, $c = 19.218(10)$ Å, $\alpha = 83.49(5)$, $\beta = 82.73(9)$, $\gamma = 79.63(6)°$, $V = 3633(5)$ Å^3, space group *P*-1, $Z = 1$, $T = 298$ K, $\mu(MoK\alpha) = 23.2$ mm^{-1}, 16657 measured reflections, 15820 independent, 9010 with $I > 3\sigma(I)$, 540 parameters, $R = 0.079$, $wR = 0.085$. *Crystal data for* K_{12}***4a***$\cdot 30H_2O$: $H_{88}Co_2Fe_8K_{12}O_{158}P_4W_{28}$, $M = 8922.10$, monoclinic, $a = 17.741(3)$, $b = 18.021(3)$, $c = 24.052(6)$ Å, $\beta = 103.53(1)^\circ$, $V = 7476(3)$ Å^3, space group $P2_1/c$, $Z = 2$, $T = 298$ K, $\mu(\mathrm{MoK}\alpha) = 22.9$ mm^{-1}, 59058 measured reflections, 16788 independent, 5307 with $I > 3\sigma(I)$, 476 parameters, $R = 0.043$, $wR = 0.047$. The X-ray crystallographic data were collected either on an Enraf-Nonius MACH3 diffractometer (**3a**) or on a Nonius Kappa-CCD diffractometer (**4a**) with Mo-Kα ($\lambda = 0.71073$ Å) radiation. Both structures were solved and refined by full-matrix least-squares using CRYSTALS. Absorption effects were empirically corrected. Neutral-atom scattering factors were used with anomalous dispersion corrections applied. All atoms except oxygen atoms in **3a** and only W, Fe and Co atoms in **4a** were refined anisotropically. Hydrogen atoms were not included in the refinements. One of the sodium cations could not be located in $Na_{10}K_6$**3a**$\cdot 28H_2O$. The crystallographic data may be obtained free of charge from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (Fax: (+49)7247-808-666; E-mail: crysdata@fiz-karlsruhe.de), on quoting the depository numbers CSD-415619 and CSD-415620. CCDC 280693–280694. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b510434c

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