

## Polyoxometalates

# Fe<sup>III</sup><sub>48</sub>-Containing 96-Tungsto-16-Phosphate: Synthesis, Structure, Magnetism and Electrochemistry

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Dedicated to Professor Imre Tóth on the occasion of his 70th birthday

**Abstract:** The 48-Fe<sup>III</sup>-containing 96-tungsto-16-phosphate, [Fe<sup>III</sup><sub>48</sub>(OH)<sub>76</sub>(H<sub>2</sub>O)<sub>16</sub>(HP<sub>2</sub>W<sub>12</sub>O<sub>48</sub>)<sub>8</sub>]<sup>36-</sup> (**Fe**<sub>48</sub>), has been synthesized and structurally characterized. This polyanion comprises eight equivalent {Fe<sup>III</sup><sub>6</sub>P<sub>2</sub>W<sub>12</sub>} units that are linked in an end-on fashion forming a macrocyclic assembly that contains more iron centers than any other polyoxometalate (POM) known to date. The novel **Fe**<sub>48</sub> was synthesized by a simple one-pot reaction of an {Fe<sub>22</sub>} coordination complex with the hexalacunary {P<sub>2</sub>W<sub>12</sub>} POM precursor in water. The title polyanion was characterized by single-crystal XRD, FTIR, TGA, magnetic and electrochemical studies.

Polyoxometalates (POMs) are discrete, anionic metal oxides of early *d*-block elements in high oxidation states with edge- or corner-shared MO<sub>6</sub> octahedra (M = V<sup>VI</sup>, Mo<sup>VI</sup>, V<sup>V</sup>, Nb<sup>V</sup> and Ta<sup>V</sup>) as building blocks.<sup>[1]</sup> Classical POMs such as the Keggin (e.g. [PW<sub>12</sub>O<sub>40</sub>]<sup>3-</sup>) or Well-Dawson (e.g. [P<sub>2</sub>W<sub>18</sub>O<sub>62</sub>]<sup>6-</sup>) ions allow to remove one or more MO<sub>6</sub> octahedra by controlled base hydrolysis, resulting in vacant (lacunary) derivatives, which can be considered as inorganic polydentate ligands. Such lacunary

POMs can incorporate one or more transition-metal, lanthanide, and actinide ions, resulting in a large variety of metal-oxo clusters of various shape, size and composition, leading to a multitude of interesting physicochemical properties, which are of interest in catalysis, magnetism, biomedicine and material science.<sup>[2,3]</sup>

The number of 3*d* metal-containing POMs is large and includes some Fe<sup>III</sup>-containing species.<sup>[4]</sup> The multilacunary Well-Dawson ion [H<sub>2</sub>P<sub>2</sub>W<sub>12</sub>O<sub>48</sub>]<sup>12-</sup> ({P<sub>2</sub>W<sub>12</sub>}) is a promising POM ligand for the incorporation of several metal ions, due to the six vacant sites in the polyanion. In 2005 Gouzerh's group reported that {P<sub>2</sub>W<sub>12</sub>} can incorporate 9 Fe<sup>3+</sup> ions ([H<sub>4</sub>P<sub>2</sub>W<sub>12</sub>Fe<sub>9</sub>O<sub>56</sub>(OAc)<sub>7</sub>]<sup>6-</sup>) and the same group also made a tetrameric derivative containing 28 Fe<sup>3+</sup> ions ([H<sub>56</sub>P<sub>8</sub>W<sub>48</sub>Fe<sub>28</sub>O<sub>248</sub>]<sup>28-</sup>).<sup>[5]</sup> In 2010 our group reported the cyclic, mixed-valent 8-vanadium-substituted [Rb<sub>3</sub>{V<sup>IV</sup>V<sup>III</sup>O<sub>7</sub>(H<sub>2</sub>O)<sub>6</sub>]<sub>2</sub><sup>-</sup> {H<sub>6</sub>P<sub>6</sub>W<sub>39</sub>O<sub>147</sub>(H<sub>2</sub>O)<sub>3</sub>}]<sup>15-</sup>.<sup>[6a]</sup> In 2011 Kögerler's group reported the 40-manganese(III)-containing polyanion [{(Mn<sup>III</sup><sub>4</sub>P<sub>2</sub>W<sub>14</sub>O<sub>60</sub>)-(Mn<sup>III</sup><sub>3</sub>P<sub>2</sub>W<sub>15</sub>O<sub>58</sub>)<sub>2</sub>]<sub>4</sub>(P<sub>8</sub>W<sub>48</sub>O<sub>184</sub>)]<sup>144-</sup>, using the well-known mixed-valence 'Mn<sub>12</sub>-acetate' [Mn<sup>IV</sup><sub>4</sub>Mn<sup>III</sup><sub>8</sub>O<sub>12</sub>(O<sub>2</sub>CMe)<sub>16</sub>(H<sub>2</sub>O)<sub>4</sub>] as precursor.<sup>[6b]</sup> In 2014 our group reported the 4-oxalato-6-titanium-containing [Ti<sub>6</sub>(C<sub>2</sub>O<sub>4</sub>)<sub>4</sub>P<sub>4</sub>W<sub>32</sub>O<sub>124</sub>]<sup>20-</sup>.<sup>[6c]</sup> In 2016 Mizuno's group reported the 24-manganese(III)-containing species [{P<sub>2</sub>W<sub>12</sub>O<sub>48</sub>Mn<sup>III</sup><sub>4</sub>(C<sub>5</sub>H<sub>7</sub>O<sub>2</sub>)<sub>2</sub>(CH<sub>3</sub>CO<sub>2</sub>)<sub>6</sub>]<sup>42-</sup> (using Mn<sup>III</sup>(acac)<sub>3</sub> as precursor).<sup>[6d]</sup>

All these compounds are based on {P<sub>2</sub>W<sub>12</sub>} as POM precursor, which confirms that multilacunary POM ligands can stabilize high-nuclearity 3*d* metal-oxo clusters. However, the solution chemistry of {P<sub>2</sub>W<sub>12</sub>} is complicated as it tends to transform easily to Wells-Dawson derivatives with fewer lacunarity sites. This is probably the main reason why the total number of known 3*d* transition metal derivatives containing the {P<sub>2</sub>W<sub>12</sub>} fragment is rather small.

Most iron-containing polyoxotungstates are based on high-spin Fe<sup>III</sup> ions (*d*<sup>5</sup>, *s* = 5/2) with five unpaired electrons and if two or more of these ions are present being linked by two bonds then antiferromagnetic exchange interactions are usually dominant.<sup>[7]</sup> On the other hand, if polynuclear iron-oxo clusters inside POMs do have a large spin ground state (*S*) and uniaxial magnetic anisotropy (*D*) then they may behave as single molecule magnets (SMM). Mialane's group demonstrated SMM behavior for [Fe<sub>4</sub>(H<sub>2</sub>O)<sub>2</sub>(FeW<sub>9</sub>O<sub>34</sub>)<sub>2</sub>]<sup>10-</sup>,<sup>[8a]</sup> which had originally been prepared by Krebs' group.<sup>[8b]</sup>

As part of our ongoing research on transition metal-containing POMs, we decided to study further the interaction of the

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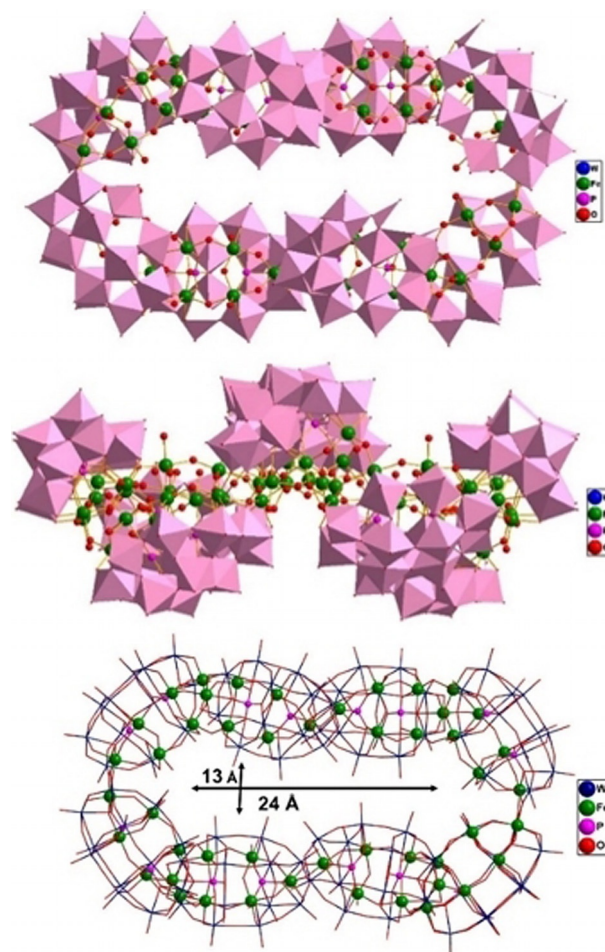
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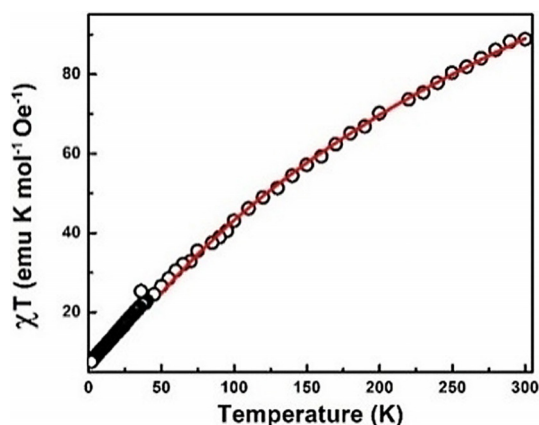
hexalacunary POM precursor  $\{P_2W_{12}\}$  with preformed multinuclear and water-soluble coordination complexes, with the goal to replace the organic ligands by inorganic POM units. Following such strategy, we report herein on the synthesis of the gigantic, macrocyclic 48-Fe<sup>III</sup>-containing 96-tungsto-16-phosphate,  $[Fe_{48}(OH)_7(H_2O)_{16}(HP_2W_{12}O_{48})_8]^{36-}$  (**Fe<sub>48</sub>**), which was isolated as the hydrated potassium salt  $K_{36}[Fe_{48}(OH)_7(H_2O)_{16}(HP_2W_{12}O_{48})_8] \cdot 400H_2O$  (**K-Fe<sub>48</sub>**). Reaction of the formally hexavacant 12-tungsto-2-phosphate POM precursor  $[H_2P_2W_{12}O_{48}]^{12-}$  ( $\{P_2W_{12}\}$ ) with the 22-iron(III)-containing coordination complex  $[Fe_{22}O_{14}(OH)_3(O_2CMe)_{21}(mda)_6](ClO_4)_2$  ( $mdaH_2 = N$ -methyldiethanolamine)<sup>[9]</sup> ( $\{Fe_{22}\}$ , see also Figure S1) in water (pH 5.4) resulted in the formation of **Fe<sub>48</sub>**, which was characterized in the solid state by single-crystal XRD, IR, TGA, elemental analysis, as well as both solid- and solution-state electrochemical studies. Single-crystal X-ray analysis revealed that **K-Fe<sub>48</sub>** crystallizes in the triclinic system with space group  $P\bar{1}$ . The crystallographic parameters are shown in the Supporting Information (Table S1).

Polyanion **Fe<sub>48</sub>** consists of eight equivalent  $\{Fe_6P_2W_{12}\}$  Dawson-type subunits which are linked to each other via Fe–O–Fe/W bonds, forming a cyclic assembly with an inner dimension of ca. 24 Å × 13 Å (Figure 1, upper). The ring is not flat with the Dawson units pointing alternately up and down, resembling a chair conformation of cyclooctane with an idealized  $D_2$  point group symmetry, where both enantiomers are present in the crystal lattice due to the centrosymmetric space group. The inter-Dawson linkage modes at the two caps of each  $\{Fe_6P_2W_{12}\}$  unit are entirely different. At one end there are two equivalent Fe– $\mu_3$ O–Fe/W bonds, whereas at the other end the linkage is accomplished by three Fe–OH–Fe bonds, resulting in the formation of a  $Fe_3(OH)_9$  trigonal prism (see Figure S2). This alternating connectivity mode is preserved throughout the entire macrocycle of **Fe<sub>48</sub>**. The oxidation state of +3 for iron and monoprotonation of the bridging Fe–OH–Fe oxygens were confirmed by bond valence sum (BVS) calculations (see Tables S2–S3).<sup>[10]</sup> Interestingly, the  $Fe_3(OH)_9$  trigonal-prismatic motif has been observed before in Keggin dimers of the type  $[Fe_6(OH)_3(GeW_9O_{34}(OH)_3)_2]^{11-}$ .<sup>[11]</sup>

The **Fe<sub>48</sub>** core is of interest for its magnetic properties, as this structure presents an intermediate between an infinite, 2-dimensional, spin-frustrated, triangular lattice and a molecular complex with a well-defined spin ground state. Spin-frustrated triangular lattices show a variety of phase transitions and magnetic structures.<sup>[12,13,2e]</sup> Detailed magnetic susceptibility measurements over a range of 1.8–300 K and magnetization measurements in an applied field of 0–7 T were performed. Figure 1 (lower) shows the spin topology of the **Fe<sub>48</sub>** core. The 48 exchange-coupled Fe<sup>III</sup> ions ( $S = 5/2$ ) form a two-dimensional ellipsoidal lattice comprising eight spin triangles and four trigonal-prismatic lattice units with 30 slightly different exchange interactions. The magnetism of the **Fe<sub>48</sub>** core unit is approximated by competing exchange interactions of localized magnetic moments in a quasi-continuum limit.<sup>[2e]</sup> Figure 2 shows the temperature dependence of the magnetic susceptibility. At 300 K, the  $\chi_m T$  product is 85.79 emu K mol<sup>-1</sup>. The contribution of temperature-independent paramagnetism (TIP) is consid-



**Figure 1.** Polyhedral/ball-and-stick representation of **Fe<sub>48</sub>**, showing a top view (upper), a side-view (middle) and a combined wireframe/ball-and-stick representation highlighting the 48 Fe<sup>III</sup> centers (lower). The pink octahedra represent  $WO_6$ .



**Figure 2.** Plot of  $\chi_m T$  for a polycrystalline sample of **K-Fe<sub>48</sub>** measured in an applied magnetic field of 0.01 T. The solid line is a fit to Eqn. (2).

ered and discussed below. The  $\chi_m T$  value shows a gradual decrease to a value of 7.59 emu K mol<sup>-1</sup> at 1.8 K. This large decrease in  $\chi_m T$  with decreasing temperature is indicative of the presence of antiferromagnetic exchange interactions. Because

of the exchange coupling between the Fe centers, one can treat the  $\text{Fe}_{48}$  polyanion in the high temperature range ( $>50$  K) as a system of exchange coupled  $\text{Fe}^{\text{III}}$  ions with an averaged small coupling constant. It is shown in Figure 2 that the  $\chi_m T$  above 50 K can be well fitted by the following equation [Eq. (1)]:

$$\chi_m T = \left( \frac{g^2 S(S+1)}{(T-\theta)} + \chi_{\text{TI}P} \right) T \quad (1)$$

in which  $\theta$  is the antiferromagnetic coupling parameter and  $\chi_{\text{TI}P}$  is the temperature independent susceptibility. Taking  $g=2$  and  $S=5/2$ , the fitting gives a  $\theta$  of  $-232$  K and a  $\chi_{\text{TI}P}$  of  $0.071 \text{ emu mol}^{-1}$ . As the 48  $\text{Fe}^{\text{III}}$  centers share a total of 60 exchange pathways (Figure 2), the averaged exchange coupling constant is estimated to be  $J_{\text{av}} = -7.07$  K considering [Eq. (2)]:

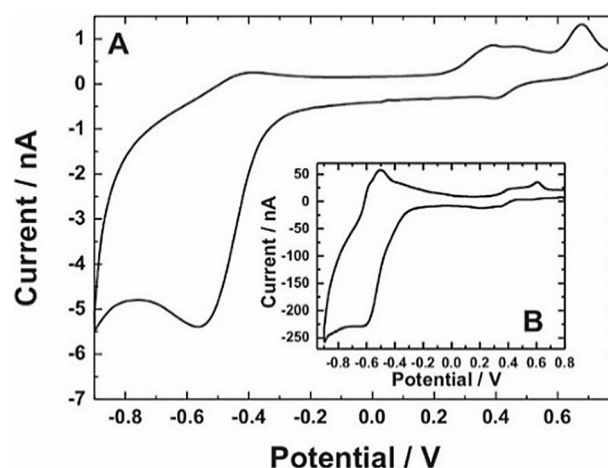
$$\theta = \frac{(zJS(S+1))}{3k_B} \quad (2)$$

in which  $z$  is the number of nearest neighbors of a given Fe center and is  $60/48$  on average for the  $\text{Fe}_{48}$  spin cluster.

The title polyanion  $\text{Fe}_{48}$  contains two types of redox-active metals allowing for electron transfer, namely  $\text{W}^{\text{VI}}/\text{W}^{\text{V}}$  and  $\text{Fe}^{\text{III}}/\text{Fe}^{\text{II}}$ , which renders electrochemical experiments attractive. The electrochemical diagnostic experiments described here include both (i) conventional voltammetry of  $\text{K-Fe}_{48}$  dissolved in aqueous medium (see Supporting Information) and (ii) microelectrode based solid-state-type methodology,<sup>[14–16]</sup> to account for possible hydrolytic decomposition of the polyanion.

Due to a possible decomposition of  $\text{Fe}_{48}$  in aqueous medium we decided to also perform microelectrode-based solid-state electrochemistry on  $\text{K-Fe}_{48}$ . The diagnostic experiments were aimed at verifying the feasibility of fast and reversible electroreduction of  $\text{W}^{\text{VI}}$  to  $\text{W}^{\text{V}}$ , in addition to probing the redox transitions of the  $\text{Fe}^{\text{III}}$  ions in  $\text{Fe}_{48}$ .

Obviously, electron transfer between  $\text{W}^{\text{VI}}$  and  $\text{W}^{\text{V}}$  or  $\text{Fe}^{\text{III}}$  and  $\text{Fe}^{\text{II}}$  could be operative in  $\text{Fe}_{48}$ . It is apparent from the voltammetric characteristics shown in Figure 3A that the reduction of the  $\text{W}^{\text{VI}}$  ionic sites (to  $\text{W}^{\text{V}}$ ) occurs at potentials more negative than  $-0.2$  V, whereas the  $\text{Fe}^{\text{III}}/\text{Fe}^{\text{II}}$  redox transitions become operative at potentials higher than  $0.2$  V. The appearance of two peaks at potentials of ca.  $0.3$  and  $0.7$  V, respectively, may reflect the existence of two types of iron sites, possibly those bridged by oxo ( $\text{Fe-O-W}$ ) or hydroxo ( $\text{Fe-OH-Fe}$ ) ligands. It is noteworthy that, despite the scan rate being as low as  $10 \text{ mVs}^{-1}$ , the voltammetric pattern of Figure 3A does not show plateau currents typically observed when microelectrodes are used to study species dissolved in solution. Simply, under the present solid-state-type conditions, the effective diffusion (charge transport) coefficients are lower than for solution species; consequently, mixed linear/spherical, rather than typical spherical diffusional patterns are produced here. When the experiment of Figure 3A was repeated at a faster scan rate such as  $800 \text{ mVs}^{-1}$ , the overall charge propagation mechanism involved linear diffusion, and the voltammetric behavior of polyanion  $\text{Fe}_{48}$  started to develop voltammetric peaks both during reduction and oxidation (Figure 3B). The fact that (at a scan



**Figure 3.** Microelectrode-based cyclic voltammetry of  $\text{Fe}_{48}$  recorded at (A)  $10 \text{ mVs}^{-1}$  and (B)  $800 \text{ mVs}^{-1}$ . The experiment was performed using a solid-state cell with a planar three-electrode configuration under nitrogen atmosphere. Microdisk diameter,  $30 \mu\text{m}$ .

rate as high as  $800 \text{ mVs}^{-1}$ ) the  $\text{Fe}^{\text{III}}/\text{Fe}^{\text{II}}$  peaks are retained and both the cathodic and anodic peaks for  $\text{W}^{\text{VI}}/\text{W}^{\text{V}}$  redox transitions can be observed, implies fast electron transfers between tungsten ionic sites and the presence of electrochemically well-behaved iron ionic sites, respectively.

In summary, we have synthesized and structurally characterized the polyanion  $\text{Fe}_{48}$ , which contains 48  $\text{Fe}^{\text{III}}$  centers and hence the largest number of iron centers incorporated in any POM known to date. The title polyanion  $\text{Fe}_{48}$  was prepared by a simple one-pot reaction of the polynuclear coordination complex  $\{\text{Fe}_{22}\}$  with the hexalacunary  $\{\text{P}_2\text{W}_{12}\}$  polyoxometalate (POM) precursor in water. The title compound was characterized by standard analytical techniques in the solid state and in solution. Magnetic studies indicate that the 48  $\text{Fe}^{\text{III}}$  centers in  $\text{Fe}_{48}$  share a total of 60 exchange pathways and the averaged exchange coupling constant is estimated to be  $J_{\text{av}} = -7.07$  K. No long-range ferro or antiferromagnetic ordering is observed from 300 K down to 1.2 K. The title polyanion  $\text{Fe}_{48}$  is electrochemically well-behaved, particularly during microelectrode-based solid-state-type voltammetric experiments. The system exhibits redox transitions implying electroactivity of  $\text{Fe}^{\text{III}}$  and  $\text{W}^{\text{VI}}$  ionic sites. It is noteworthy that the  $\text{W}^{\text{VI}}/\text{W}^{\text{V}}$  redox transitions are fast and reversible even at fast scan rates ( $800 \text{ mVs}^{-1}$ ). Under such conditions, the existence of two different structural types of electroactive iron sites can also be postulated.

## Experimental Section

### Synthesis of $\text{K}_{36}[\text{Fe}_{48}(\text{OH})_{76}(\text{H}_2\text{O})_{16}(\text{HP}_2\text{W}_{12}\text{O}_{48})_8] \cdot 400\text{H}_2\text{O}$ ( $\text{K-Fe}_{48}$ )

The known coordination complex  $[\text{Fe}_{22}\text{O}_{14}(\text{OH})_3(\text{O}_2\text{CMe})_2(\text{mda})_6] \cdot (\text{ClO}_4)_2$  ( $\{\text{Fe}_{22}\}$ ) ( $\text{mdaH}_2 = N$ -methyldiethanolamine)<sup>[9]</sup> ( $0.319 \text{ g}$ ,  $0.076 \text{ mmol}$ ) was dissolved in  $\text{H}_2\text{O}$  ( $40 \text{ mL}$ ) and then  $\text{K}_{12}[\text{H}_2\text{P}_2\text{W}_{12}\text{O}_{48}] \cdot 24\text{H}_2\text{O}$  ( $0.200 \text{ g}$ ,  $0.051 \text{ mmol}$ )<sup>[17]</sup> was added. To this reaction mixture solid  $\text{KCl}$  ( $0.055 \text{ g}$ ,  $0.737 \text{ mmol}$ ) was added and the resulting turbid solution was stirred for 1 h at  $70^\circ\text{C}$  and the pH was 5.4. Then the solution was allowed to stand at room tempera-

ture until the brown solid had settled at the bottom of the beaker, which was then removed by centrifugation and filtration. The solution (pH 5.4) was kept in an open vial at room temperature to allow for slow evaporation. After ca two months a yellow crystalline product started to appear. Evaporation was allowed to continue until about half the solvent had evaporated. The solid product was then collected by filtration and air dried. Yield 26 mg (11%, based on W).

IR (2% KBr pellet):  $\tilde{\nu}$  = 3415 (s), 1617 (s), 1462 (m), 1384 (m) 1086 (s), 1063 (s), 999 (w), 943 (s), 909 (s), 827 (sh), 777 (m), 705 (m), 616 (w), 556 (w), 485 (w), 418 (w)  $\text{cm}^{-1}$ . Elemental analysis (%) for  $\text{K}_{36}[\text{Fe}_{48}(\text{OH})_{76}(\text{H}_2\text{O})_{16}(\text{HP}_2\text{W}_{12}\text{O}_{48})_8] \cdot 400\text{H}_2\text{O}$  (K-Fe<sub>48</sub>), calcd: K 3.79, P 1.33, Fe 7.21, W 47.48; found K 3.48, P 1.44, Fe 7.76, W 46.84. Elemental analysis was performed at CREALINS (Villeurbanne, France).

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## Conflict of interest

The authors declare no conflict of interest.

**Keywords:** electrochemistry · iron · macrocycle · magnetism · polyoxometalates

- [1] a) M. T. Pope, *Heteropoly and Isopoly Oxometalates*, Springer: Berlin, **1983**; b) N. V. Izarova, M. T. Pope, U. Kortz, *Angew. Chem. Int. Ed.* **2012**, *51*, 9492–9510; *Angew. Chem.* **2012**, *124*, 9630–9649.
- [2] a) S. S. Mal, U. Kortz, *Angew. Chem. Int. Ed.* **2005**, *44*, 3777–3780; *Angew. Chem.* **2005**, *117*, 3843–3846; b) B. S. Bassil, M. H. Dickman, I. Römer, B. von der Kammer, U. Kortz, *Angew. Chem. Int. Ed.* **2007**, *46*, 6192–6195; *Angew. Chem.* **2007**, *119*, 6305–6308; c) C. Ritchie, A. Ferguson, H. Nojiri, H. N. Miras, Y.-F. Song, D.-L. Long, E. Burkholder, M. Murrie, P. Kögerler, E. K. Brechin, L. Cronin, *Angew. Chem. Int. Ed.* **2008**, *47*, 5609–5612; *Angew. Chem.* **2008**, *120*, 5691–5694; d) M. Ibrahim, Y. Lan, B. S. Bassil, Y. Xiang, A. Suchopar, A. K. Powell, U. Kortz, *Angew. Chem. Int. Ed.* **2011**, *50*, 4708–4711; *Angew. Chem.* **2011**, *123*, 4805–4808; e) B. S. Bassil, M. Ibrahim, R. Al-Oweini, M. Asano, Z. Wang, J. van Tol, N. S. Dalal, K.-Y. Choi, R. N. Biboum, B. Keita, L. Nadjo, U. Kortz, *Angew. Chem. Int. Ed.* **2011**, *50*, 5961–5964; *Angew. Chem.* **2011**, *123*, 6083–6087; f) L. Huang, S.-S. Wang, J.-W. Zhao, L. Cheng, G.-Y. Yang, *J. Am. Chem. Soc.* **2014**, *136*, 7637–7642; g) X.-B. Han, Y.-G. Li, Z.-M. Zhang, H.-Q. Tan, Y. Lu, E.-B. Wang, *J. Am. Chem. Soc.* **2015**, *137*, 5486–5493; h) C. Zhang, M. Zhang, H. Shi, Q. Zeng, D. Zhang, Y. Zhao, Y. Wang, P. Ma, J. Wang, J. Niu, *Chem. Commun.* **2018**, *54*, 5458–5461.
- [3] a) M. T. Pope, *Inorg. Chem.* **1972**, *11*, 1973–1974; b) S. G. Sarafianos, U. Kortz, M. T. Pope, M. J. Modak, *Biochem. J.* **1996**, *319*, 619–626; c) E. Coronado, P. Day, *Chem. Rev.* **2004**, *104*, 5419–5448; d) T. A. Steitz, *Angew. Chem. Int. Ed.* **2010**, *49*, 4381–4398; *Angew. Chem.* **2010**, *122*, 4482–4500.
- [4] a) M. Ibrahim, A. Haider, Y. Xiang, B. S. Bassil, A. M. Carey, L. Rullik, G. B. Jameson, F. Doungmene, I. M. Mbomekallé, P. de Oliveira, V. Mereacre, G. E. Kostakis, A. K. Powell, U. Kortz, *Inorg. Chem.* **2015**, *54*, 6136–6146; b) R. S. Winter, J. M. Cameron, L. Cronin, *J. Am. Chem. Soc.* **2014**, *136*, 12753–12761; c) S. S. Mal, M. H. Dickman, U. Kortz, A. M. Todea, A. Merca, H. Bögge, T. Glaser, A. Müller, S. Nellutla, N. Kaur, J. van Tol, N. S. Dalal, B. Keita, L. Nadjo, *Chem. Eur. J.* **2008**, *14*, 1186–1195; d) A. Müller, S. Sarkar, S. Qaiser, N. Shah, H. Bögge, M. Schmidtman, S. Sarkar, P. Kögerler, B. Hauptfleisch, A. X. Trautwein, V. Schünemann, *Angew. Chem. Int. Ed.* **1999**, *38*, 3238–3241; *Angew. Chem.* **1999**, *111*, 3435–3439.
- [5] a) B. Godin, Y.-G. Chen, J. Vaissermann, L. Ruhlmann, M. Verdaguier, P. Gouzerh, *Angew. Chem. Int. Ed.* **2005**, *44*, 3072–3075; *Angew. Chem.* **2005**, *117*, 3132–3135; b) B. Godin, J. Vaissermann, P. Herson, L. Ruhlmann, M. Verdaguier, P. Gouzerh, *Chem. Commun.* **2005**, 5624–5626.
- [6] a) A. S. Assran, N. V. Izarova, U. Kortz, *CrystEngComm* **2010**, *12*, 2684–2686; b) X. Fang, P. Kögerler, Y. Furukawa, M. Speldrich, M. Luban, *Angew. Chem. Int. Ed.* **2011**, *50*, 5212–5216; *Angew. Chem.* **2011**, *123*, 5318–5322; c) G. Al-Kadamany, B. S. Bassil, F. Raad, U. Kortz, *J. Cluster Sci. J. Clust. Sci.* **2014**, *25*, 867–878; d) T. Minato, K. Suzuki, K. Yamaguchi, N. Mizuno, *Angew. Chem. Int. Ed.* **2016**, *55*, 9630–9633; *Angew. Chem.* **2016**, *128*, 9782–9785.
- [7] a) G. Christou, D. Gatteschi, D. N. Hendrickson, R. Sessoli, *MRS Bull.* **2000**, *25*, 66–71; b) D. Gatteschi, R. Sessoli, *Angew. Chem. Int. Ed.* **2003**, *42*, 268–297; *Angew. Chem.* **2003**, *115*, 278–309; c) B. Botar, Y. V. Geletii, P. Kögerler, D. G. Musaev, K. Morokuma, I. A. Weinstock, C. L. Hill, *J. Am. Chem. Soc.* **2006**, *128*, 11268–11277; d) U. Kortz, A. Müller, J. van Slagere, J. Schnack, N. S. Dalal, M. Dressel, *Coord. Chem. Rev.* **2009**, *253*, 2315–2327.
- [8] a) J.-D. Compain, P. Mialane, A. Dolbecq, I. M. Mbomekallé, J. Marrot, F. Sécheresse, E. Rivière, G. Rogez, W. Wernsdorfer, *Angew. Chem. Int. Ed.* **2009**, *48*, 3077–3081; *Angew. Chem.* **2009**, *121*, 3123–3127; b) E. M. Limanski, M. Piepenbrink, E. Droste, K. Burgemeister, B. Krebs, *J. Cluster Sci.* **2002**, *13*, 369–379.
- [9] D. Foguet-Albiol, K. A. Abboud, G. Christou, *Chem. Commun.* **2005**, 4282–4284.
- [10] I. D. Brown, D. Altermatt, *Acta Crystallogr. Sect. B* **1985**, *41*, 244–247.
- [11] L.-H. Bi, U. Kortz, S. Nellutla, A. C. Stowe, J. van Tol, N. S. Dalal, B. Keita, L. Nadjo, *Inorg. Chem.* **2005**, *44*, 896–903.
- [12] M. F. Collins, O. A. Petrenko, *Can. J. Phys.* **1997**, *75*, 605.
- [13] H. Kawamura, *J. Phys.: Condens. Matter* **1998**, *10*, 4707–4754.
- [14] P. J. Kulesza, M. A. Malik, *Interfacial Electrochemistry: Theory Experiment and Applications Solid-State Voltammetry*, Ed.: A. Wieckowski, Marcel Dekker, New York, **1999**, pp. 673.
- [15] P. J. Kulesza, J. A. Cox, *Electroanalysis* **1998**, *10*, 73–80.
- [16] I. A. Rutkowska, M. Marszalek, J. Orłowska, W. Ozimek, S. M. Zakeeruddin, P. J. Kulesza, M. Grätzel, *ChemSusChem* **2015**, *8*, 2560.
- [17] R. Contant, *Inorg. Synth.* **1990**, *27*, 108–109.
- [18] Crystal Data for  $\text{Fe}_{48}\text{H}_{916}\text{K}_{36}\text{O}_{876}\text{P}_{16}\text{W}_{96}$  ( $M = 37172.79 \text{ g mol}^{-1}$ ): triclinic, space group  $P\bar{1}$ ,  $a = 25.654(3) \text{ \AA}$ ,  $b = 38.137(4) \text{ \AA}$ ,  $c = 41.590(4) \text{ \AA}$ ,  $\alpha = 113.739(3)^\circ$ ,  $\beta = 90.052(3)^\circ$ ,  $\gamma = 105.991(3)^\circ$ ,  $V = 35516(6) \text{ \AA}^3$ ,  $Z = 2$ ,  $T = 100 \text{ K}$ ,  $\mu(\text{MoK}\alpha) = 16.818 \text{ mm}^{-1}$ ,  $D_{\text{calcd}} = 3.476 \text{ g cm}^{-3}$ , 74012 reflections measured ( $6.79^\circ \leq 2\theta \leq 41.63^\circ$ ), 51075 unique ( $R_{\text{int}} = 0.172$ ,  $R_{\text{sigma}} = 0.1076$ ) which were used in all calculations. The final  $R_1$  was 0.1169 ( $I > 2\sigma(I)$ ) and  $wR_2$  was 0.2851 (all data) (CSD-1895635).

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