

## Supplementary Information

Coordination chemistry of the hexavacant tungstophosphate  $[\text{H}_2\text{P}_2\text{W}_{12}\text{O}_{48}]^{12-}$ : synthesis and characterization of iron(III) complexes derived from the unprecedented  $\{\text{P}_2\text{W}_{14}\text{O}_{54}\}$  fragment

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### 1. Magnetic data

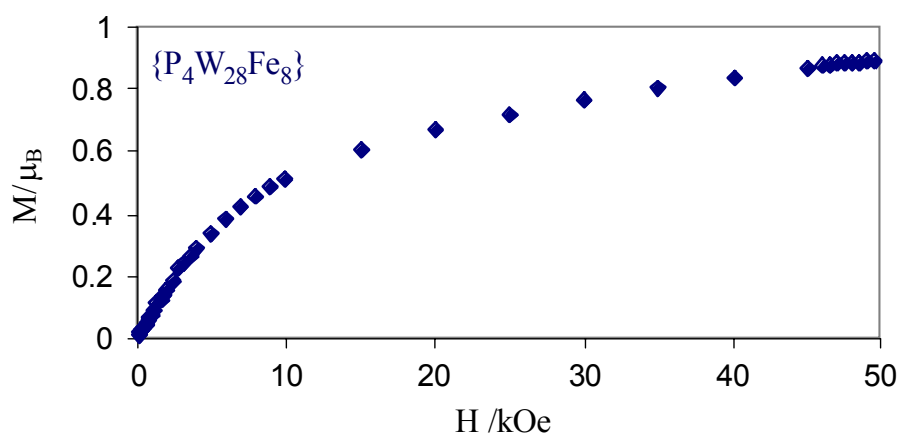


Figure S1. Field dependence of the magnetization of  $\text{Na}_{10}\text{K}_6\mathbf{3a}\cdot 28\text{H}_2\text{O}$  at 2 K

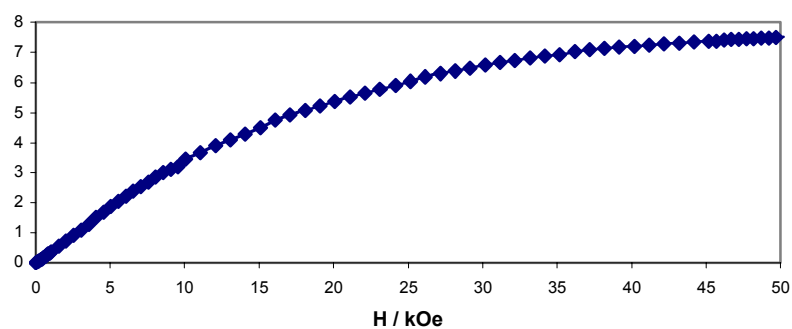


Figure S2. Field dependence of the magnetization of  $\text{K}_{12}\mathbf{4a}\cdot 30\text{H}_2\text{O}$  at 2 K

## 2. Electrochemical data

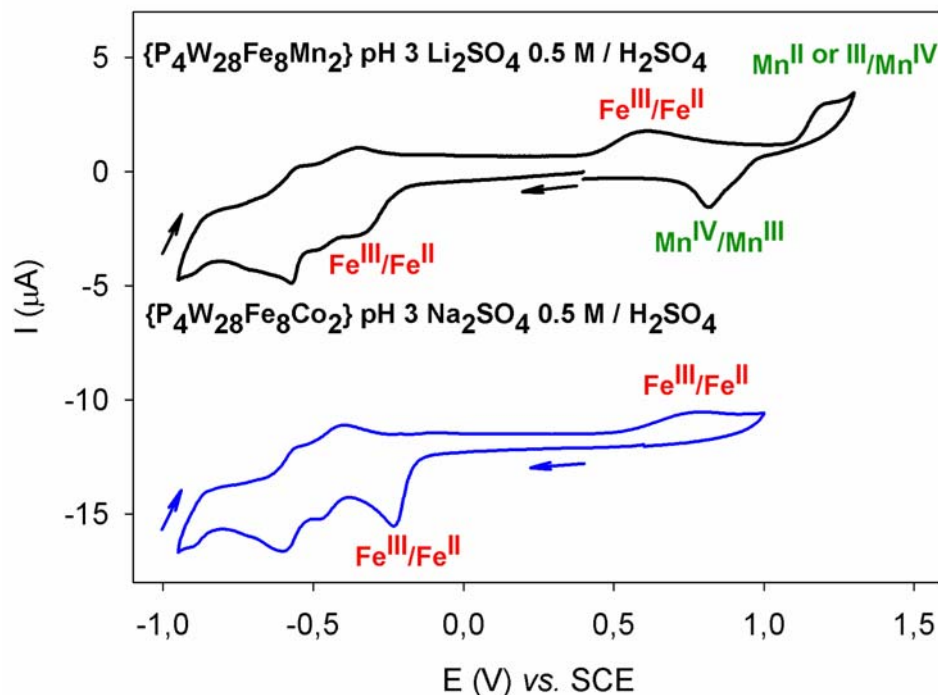


Figure S3. Cyclic voltammograms of **4a** and **4b** at a glassy carbon electrode. Scan rate: 20 mVs<sup>-1</sup>.

## 3. Raman spectra

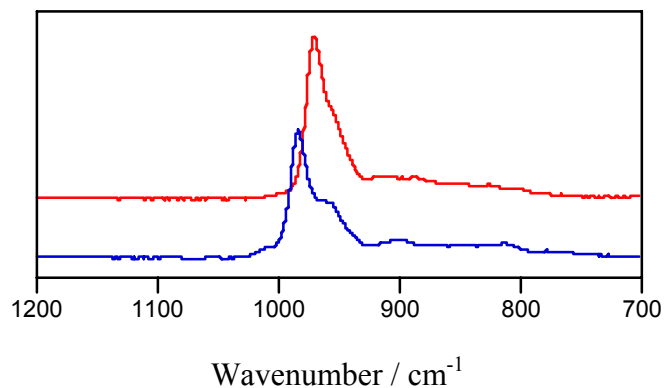


Figure S4. Raman spectra of Na<sub>10</sub>K<sub>6</sub>**3a**·28H<sub>2</sub>O (red) and **3b** (blue)

## 5. Crystal data for **3b**

Only a small amount of crystals (10 mg) was obtained and analytical data are not available. Li<sup>+</sup>, Na<sup>+</sup> and K<sup>+</sup> are possible cations.

Crystal data:  $a = 12.789(3)$ ,  $b = 15.130(3)$ ,  $c = 19.828(1)$  Å,  $\alpha = 72.94(1)$ ,  $\beta = 85.46(1)$ ,  $\gamma = 67.35(1)^\circ$ ,  $V = 3382(1)$  Å<sup>3</sup>, space group  $P-1$ ,  $Z = 1$ ,  $T = 298$  K, 36223 measured reflections, 15451 independent, 6361 with  $I > 3\sigma(I)$ , 450 parameters,  $R = 0.060$ ,  $wR = 0.068$ .