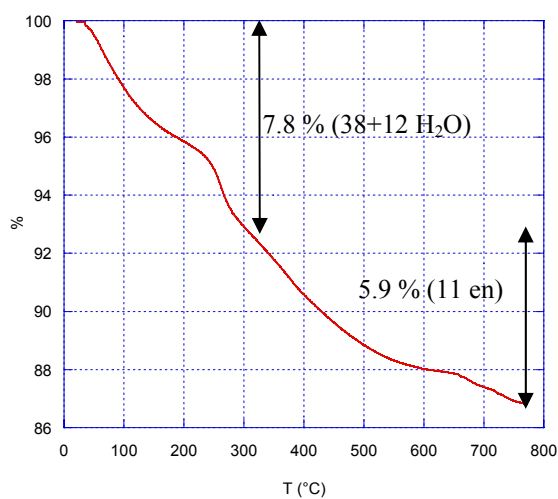


Supporting Information

Square versus tetrahedral iron clusters with polyoxometalates ligands†

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TGA for 1:



TGA for 2:

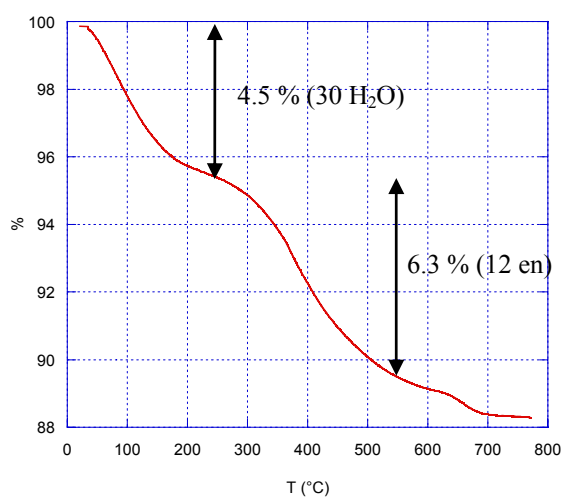


Figure S11. TG curve of 1 and 2 under nitrogen flow.

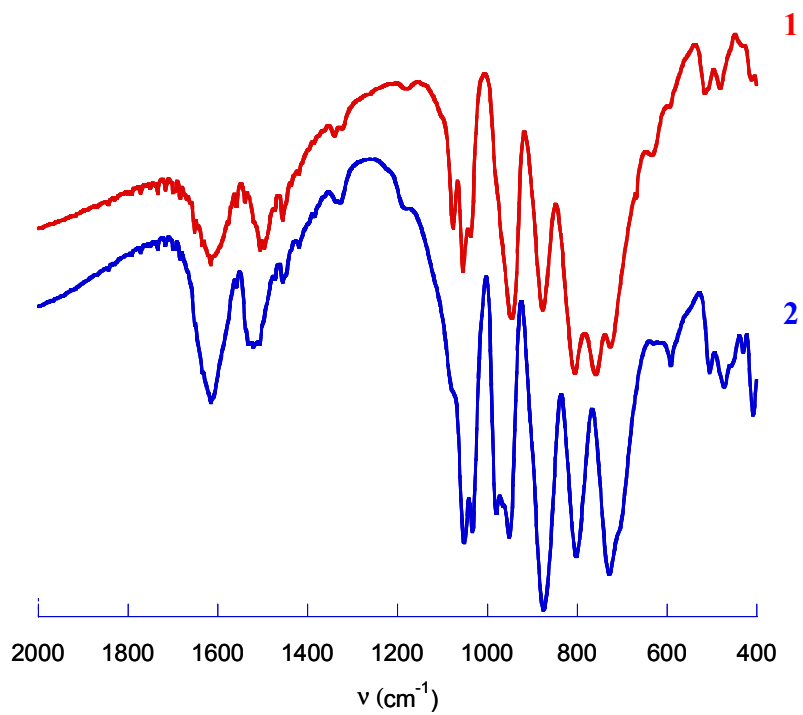
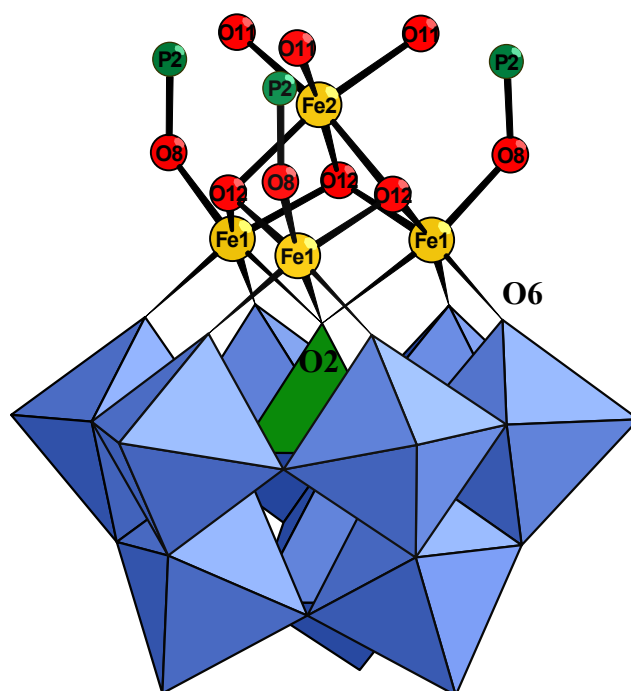


Figure SI2. IR spectra of **1** and **2**.

a)



b)

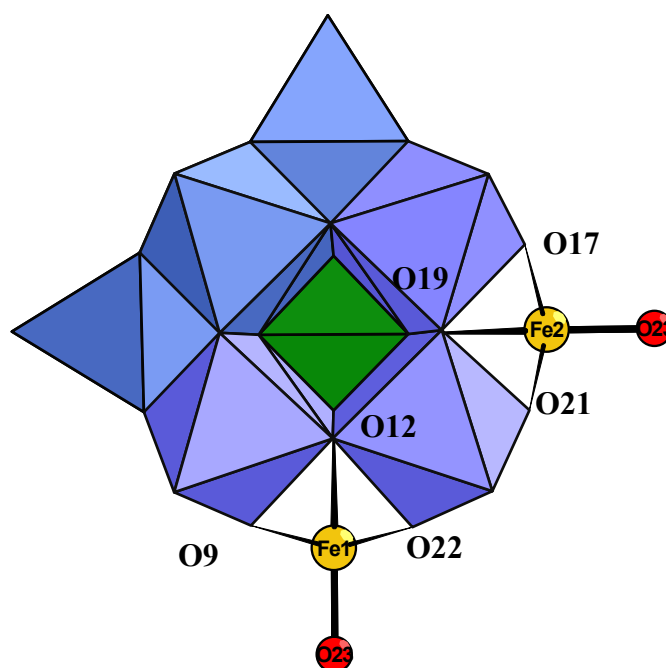


Figure SI3. Mixed ball and stick and polyhedral representation with partial atomic labelling scheme of a) the cubane-type unit capping the $[\text{PW}_9\text{O}_{34}]^{9-}$ lacunary POM in **1**. Fe1-O8 1.916(16), Fe1-O6 1.968(11), Fe1-O12 2.001(9), Fe1-O2 2.315(16), Fe2-O11 2.086(19), Fe2-O12 2.11(2) Å, $\Sigma_8(\text{Fe1}) = 3.0$, $\Sigma_8(\text{Fe2}) = 2.2$, $\Sigma_8(\text{O12}) = 1.1$; b) the $[\text{PW}_{10}\text{Fe}_2\text{O}_{39}]^{7-}$ anion in **2**. Fe1-O23 1.759(18), Fe1-O22 1.938(14), Fe1-O9 1.968(15), Fe1-O12 2.447(18), Fe2-O23 1.786(18), Fe2-O21 1.961(15), Fe2-O17 2.012(14), Fe2-O19 2.486(20), $\Sigma_8(\text{Fe1}) = 3.5$, $\Sigma_8(\text{Fe2}) = 3.2$.

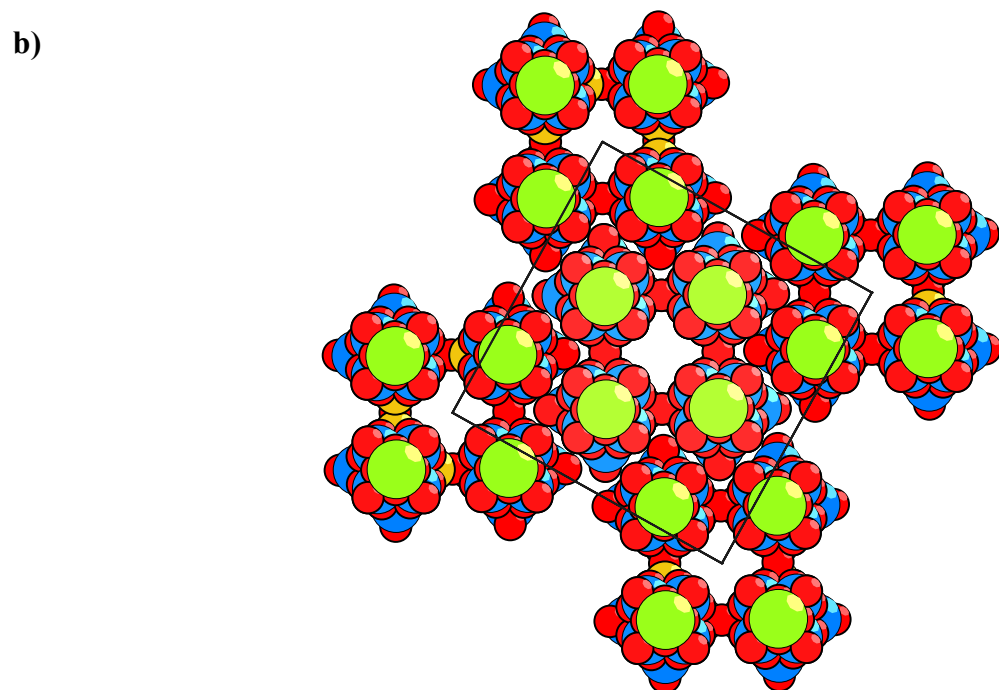
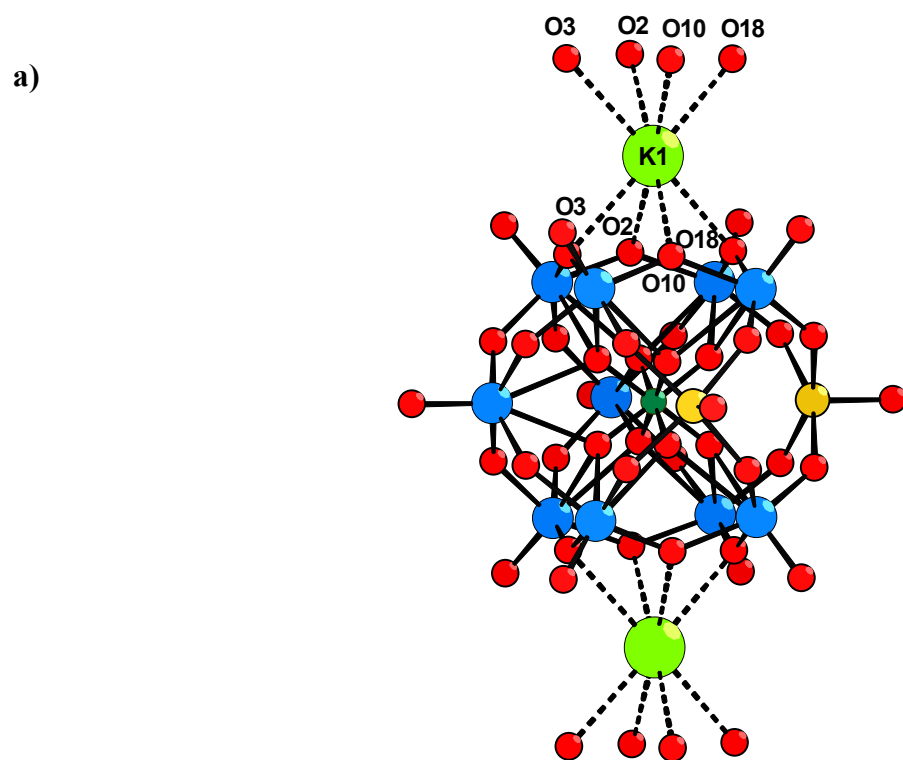


Figure SI4. a) View of the coordination of the potassium ions to one POM, for clarity only the four oxygen atoms of the two adjacent POMs bound to the potassium ions are represented; b) space filling representation of the arrangement of the square tetrameric POMs in the unit-cell of **2**; blue sphere W; dark green sphere, P; light green sphere, K; K1-O2 2.817(14), K1-O3 2.830(13), K1-O10 2.712(12), K1-O18 2.720(13) Å.

Supplementary information for the magnetic part:

The magnetic data of compound **2** have been fitted considering the following equation:

$$\chi_M T = [\chi_{M_{\text{dimer}}} T \times 4] \times \rho + [\chi_{M_{\text{monomer}}} T] \times M_{\text{Fe8}} \times (1-\rho) / M_{\text{impurity}}$$

with :

$\chi_{M_{\text{dimer}}} T = (2N\beta^2 g^2/k) [(x + 5x^3 + 14x^6 + 30x^{10} + 55x^{15}) / (1 + 3x + 5x^3 + 7x^6 + 9x^{10} + 11x^{15})]$ with $x = \exp(J/kT)$ and where ρ is the molar fraction of paramagnetic impurity, M_{Fe8} and M_{impurity} being the molecular weight of the octanuclear Fe^{III} cluster and of the monomeric $(\text{C}_2\text{N}_2\text{H}_{10})_2[\text{PW}_{11}\text{O}_{39}\text{Fe}^{\text{III}}] \cdot 15\text{H}_2\text{O}$ complex postulated as the paramagnetic impurity, respectively.