Electronic Supplementary Information for:

Acetate-driven polyoxometalate demetalation: An open-shell di-iron polytungstate comprising two rotational Keggin isomers

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Table of Contents:

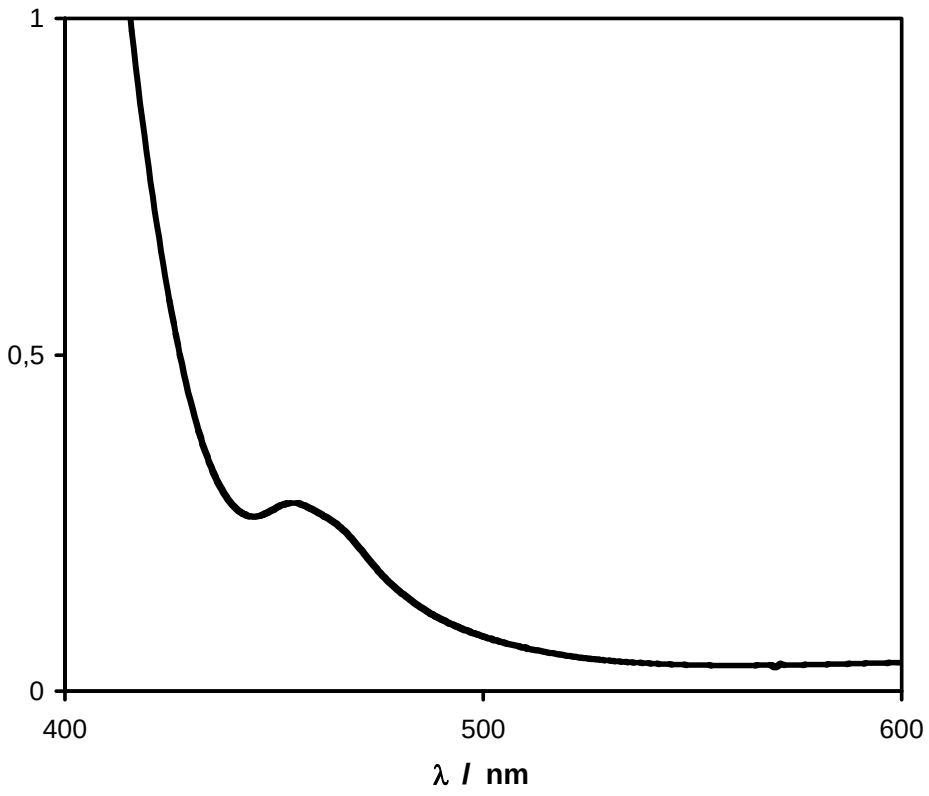

Fig. S1 Electronic absorption spectrum of a 9 mM aqueous solution of $\mathbf{K_8[(CH_3)_2NH_2]_5}$**3** (at natural pH 5.0).

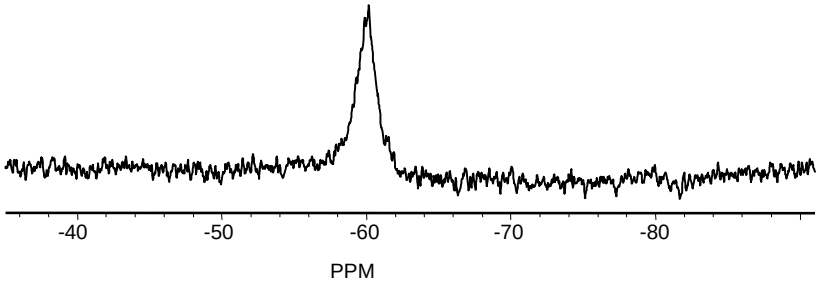

Fig. S2 ^{29}Si NMR spectrum of a 60 mM solution of $\mathbf{K_8[(CH_3)_2NH_2]_5 3}$ in D_2O.

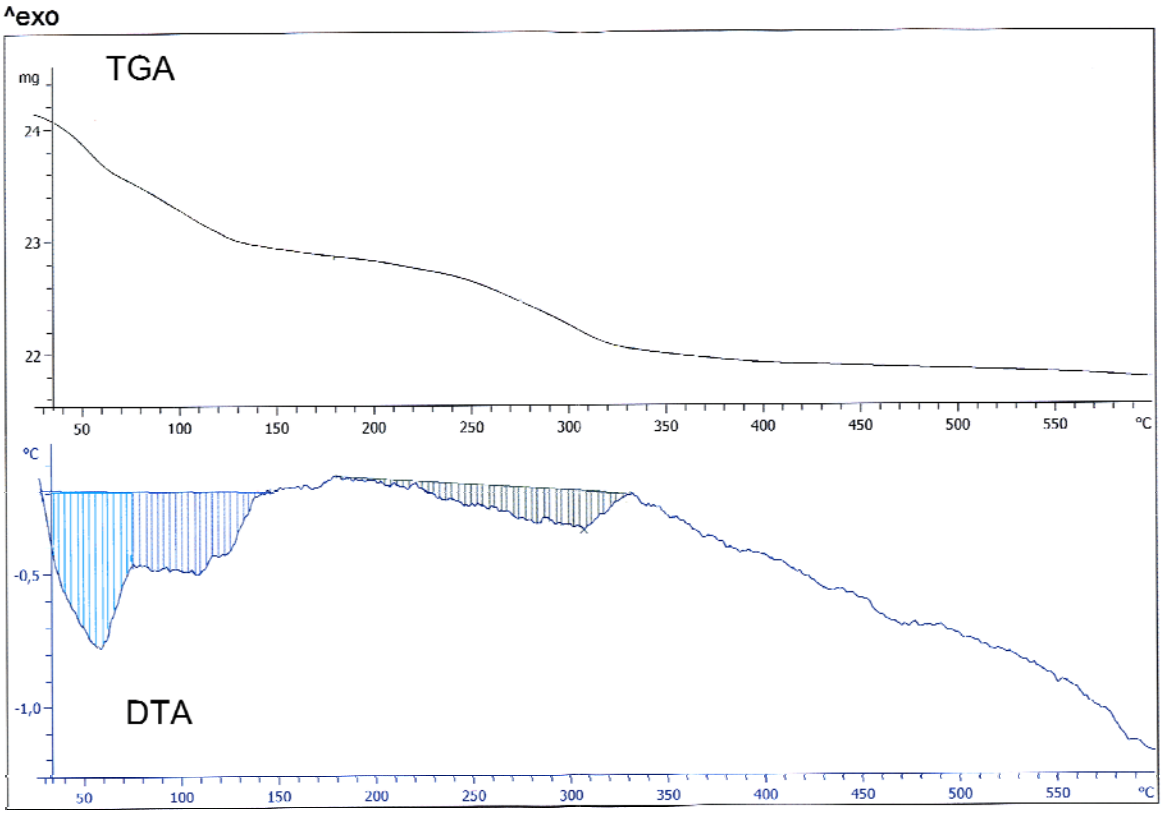

Fig. S3 TGA (top) and DTA (bottom) data of **$K_8[(CH_3)_2(NH_2)]_5$3** (heating rate: 5 °C/min, N_2 atmosphere with a 20 ml/min flow rate). The curves show two endothermic weight-loss steps (marked in the DTA graph). The first step up to *ca*. 180 °C corresponds to a loss of 17 crystal water molecules. The second step, up to *ca*. 350 °C, corresponds to the decomposition of the organic dimethylammonium cations.

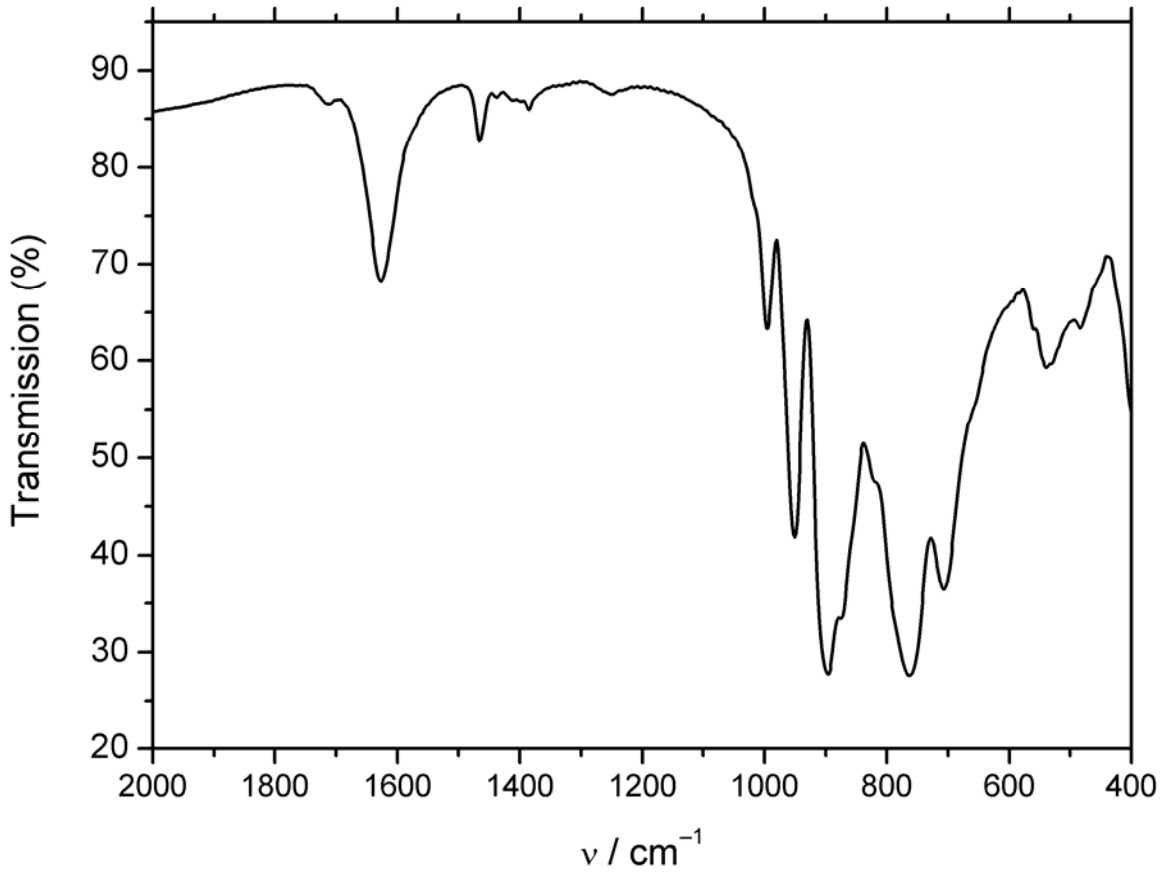

Fig. S4 FT-IR spectrum of **$K_8[(CH_3)_2NH_2]_5$3** (KBr pellet).

Fitting model for magnetic susceptibility data

For the *s* = 5/2 Fe(III) dimer, the following expression was derived from the Heisenberg spin Hamiltonian to fit the temperature dependence of χT:

$$\chi_{\text{dimer}}T = \alpha \frac{55 + 30e^{10x} + 14e^{18x} + 5e^{24x} + e^{28x}}{11 + 9e^{10x} + 7e^{18x} + 5e^{24x} + 3e^{28x} + e^{30x}}$$

with $\alpha = \frac{2Ng^2\mu_B^2}{k_B}$ and $x = -\frac{J}{2k_BT}$.

The least-squares fit included both χ_{dimer} and a Curie term for *s* = 5/2-based paramagnetic impurities.