

Electronic Supplementary Information for:

**Acetate-Controlled Demetalation in Multiiron Polyoxometalates: A
Triiron Cluster Trapped Between β - and γ -Keggin Isomers**

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Additional data on $\text{K}_{10}[(\text{CH}_3)_2(\text{NH}_2)]_2[\{\text{Fe}_3(\text{OH})_2(\text{H}_2\text{O})(\text{OAc})\}(\beta\text{-SiW}_{10}\text{O}_{37})(\gamma\text{-SiW}_{10}\text{O}_{36})\cdot 20\text{H}_2\text{O}$ ($\text{K}_{10}[(\text{CH}_3)_2(\text{NH}_2)]_2\mathbf{4}\cdot 20\text{H}_2\text{O}$)

All elemental analyses (C/H/N and ICP-OES) were performed by Zentralabteilung für Chemische Analysen (ZCH), Forschungszentrum Jülich GmbH, D-52525 Jülich, Germany.

The goodness of the least-squares fitting procedure for the magnetochemical analysis is assessed using the parameter SQ, defined as

$$SQ = \sqrt{\frac{FQ}{n}}; FQ = \sum_{i=1}^n \left(\frac{\chi_{\text{exp}}(i) - \chi_{\text{calc}}(i)}{\chi_{\text{exp}}(i)} \right)^2.$$

Fig. S1 UV-VIS spectrum

Fig. S2 IR spectrum

Fig. S3 TGA/DTA data

Fig. S4 Comparison of simulated susceptibility curves

Fig. S5 Magnetization measurements

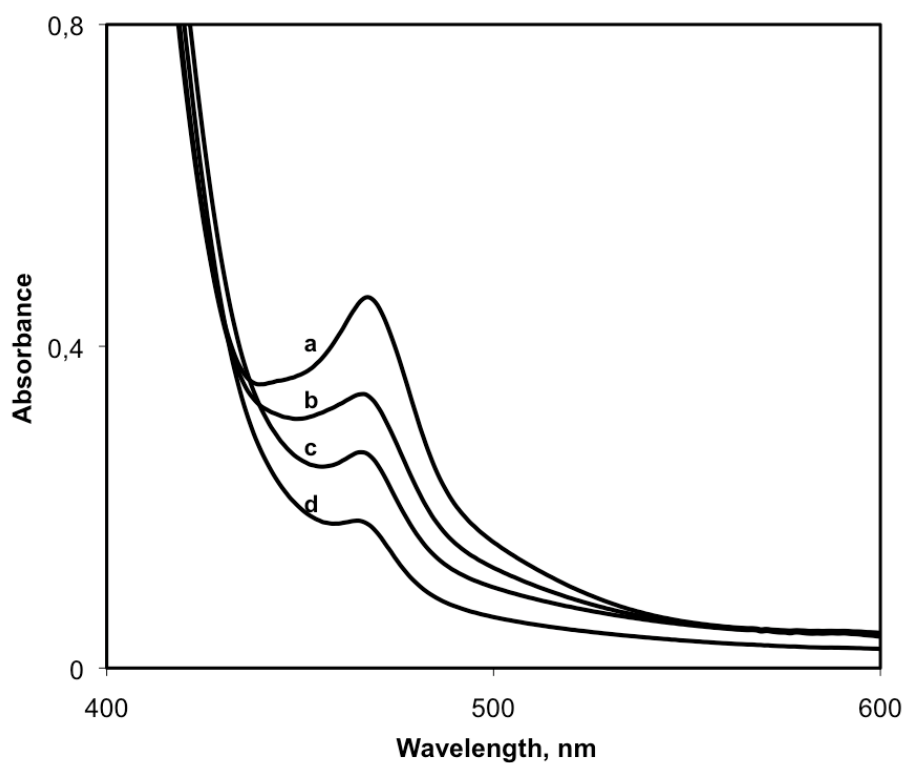


Fig. S1. Time dependence of the electronic absorption spectrum of a 40 mM aqueous solution (1 mm cell path length) of $K_{10}[(CH_3)_2(NH_2)]_2 \cdot 20H_2O$: (a) fresh solution; and after: (b) 2 hours; (c) 24 hours; (d) 6 days.

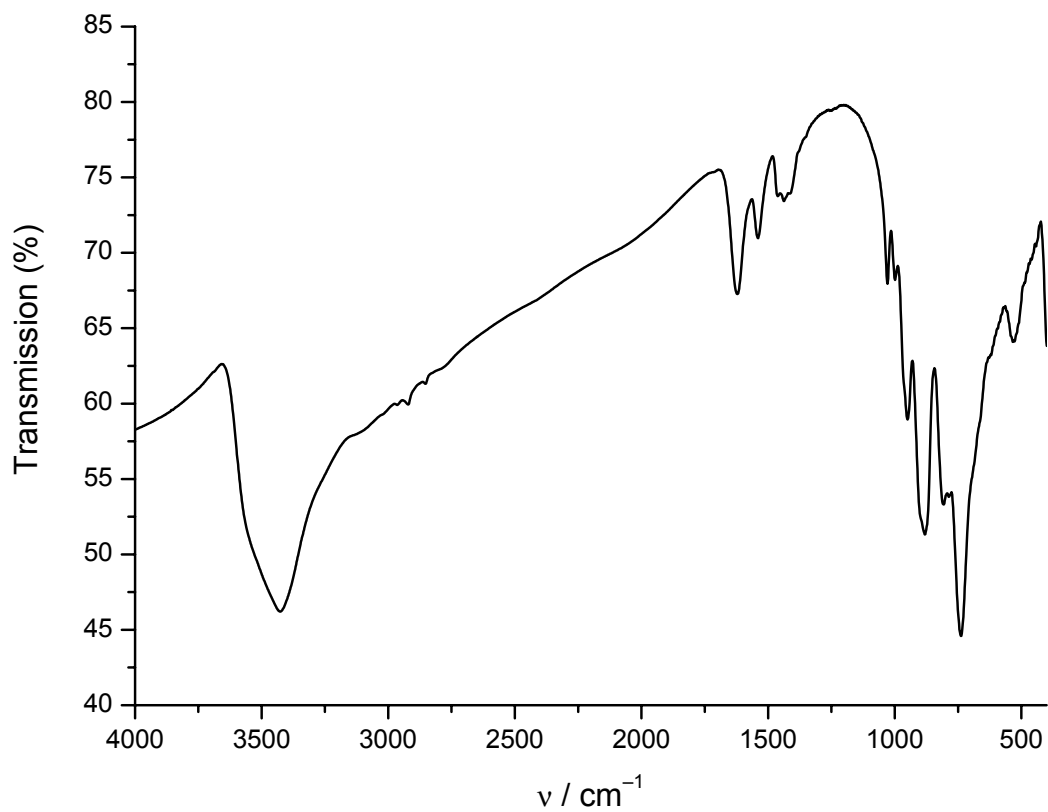


Fig. S2. FT-IR (KBr pellet) spectrum of $\text{K}_{10}[(\text{CH}_3)_2(\text{NH}_2)]_{24} \cdot 20\text{H}_2\text{O}$.

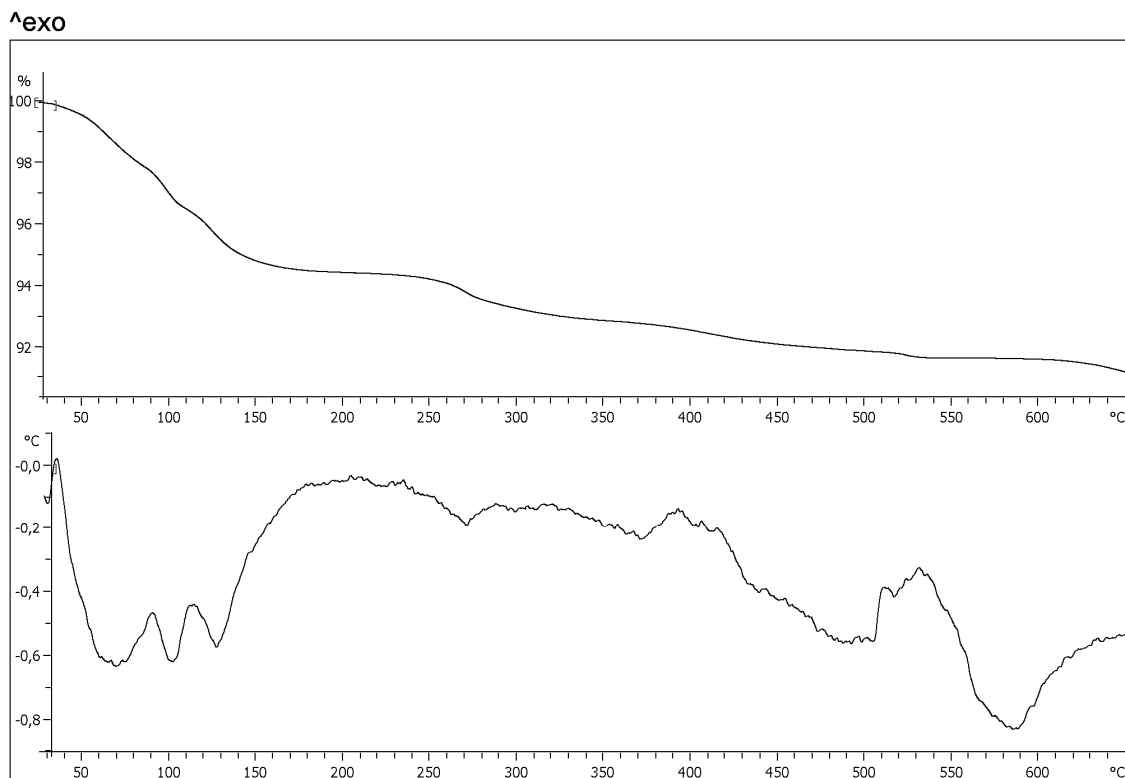


Fig. S3. TGA (top) and DTA (bottom) data of $K_{10}[(CH_3)_2(NH_2)]_2 \cdot 4 \cdot 20H_2O$ (heating rate: $5\text{ }^\circ\text{C}/\text{min}$, N_2 atmosphere with a $60\text{ ml}/\text{min}$ flow rate). Note that the first mass loss of 5.5% up to $200\text{ }^\circ\text{C}$ corresponds to the loss 20 crystal water molecules.

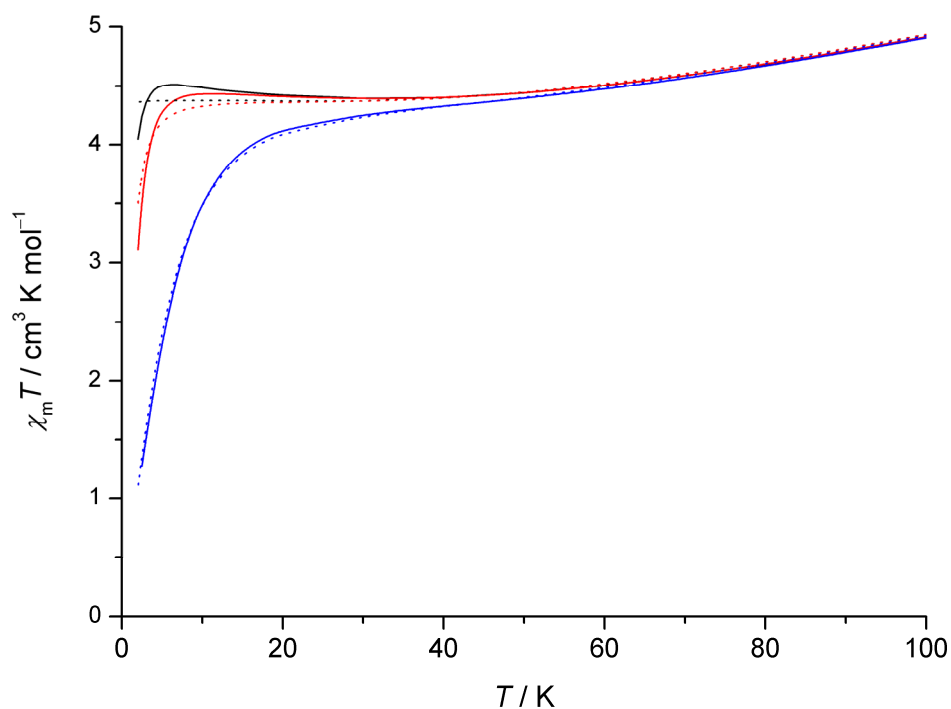


Fig. S4. Comparison of the simulated susceptibility data for $\text{K}_{10}[(\text{CH}_3)_2(\text{NH}_2)]_{24} \cdot 20\text{H}_2\text{O}$ for the temperature interval 2 – 100 K. Solid lines represent least-squares fits to the experimental susceptibility for 0.1 (black), 1.0 (red) and 5.0 Tesla (blue) for the full model described in the text. Dotted curves represent the corresponding simulated curves for a pure spin Heisenberg system (without ligand field contributions).

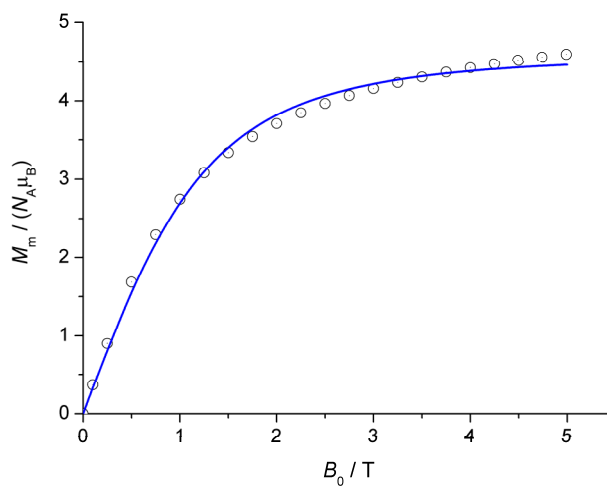


Fig. S5. Field-dependent magnetization measurements of $K_{10}[(CH_3)_2(NH_2)]_{24} \cdot 20H_2O$ at 2.0 K and best least-squares fit to Brillouin function.