Supplementary Material (ESI) for Chemical Communications

Electronic Supplementary Information for:

Ferrimagnetically ordered nanosized polyoxomolybdate-based cluster spheres

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Potentiometric titrations:

Potentiometric titrations were performed using a Mettler-Toledo DL50 autotitrator with freshly prepared samples. For each compound the results of ten individual measurements (both direct titrations and back titrations) were obtained and averaged. For direct titrations, approximately 150 mg of the sample were dissolved in approximately 60 mL nitrogen-saturated 0.5M sulfuric acid and titrated with 0.1M aqueous cerium(IV) sulfate solution at room temperature. All direct titrations revealed two well-separated equivalence points corresponding to the oxidation of Mo(V) and, subsequently, V(IV). For back titrations, 100-200 mg of sample were dissolved in a solution of 250-350 mg of $Ce(NH_4)_2(NO_3)_6$ in *ca*. 60 ml of 0.5M H_2SO_4 at 60 °C under stirring. The resulting clear solution is titrated with 0.1N $NaNO_2$ (a single equivalence point is observed). Experimental errors are estimated to translate into an error limit of ±1.5 electrons.

Crystallographic data:

The nine crystallographically independent linker sites were refined as a Fe/V/Mo mixture with their respective partial occupancy values of 0.233/0.5/0.267 for **1** and 0.367/0.367/0.266 for **2**, based on the analytical data. Refinement of these sites as V or Fe only resulted in an increase of the *R* value by *ca*. 0.7%. All S atoms were found to be disordered over five sites with the total occupancy adding up to 1.0. Their terminal oxo ligands were refined accordingly. As commonly observed for this type of compounds some Mo atoms show the $O{=}Mo{-}OH_2 \leftrightarrow H_2O{-}Mo{=}O$ type disorder. For both compounds, all Mo (except for Mo41-Mo49 in **1** and Mo41-Mo48 in **2**), V, Fe, K and anionic O atoms were refined anisotropically.
G. Sheldrick, *SADABS*, version 2.10; University of Göttingen, Germany, 2003.
SHELXTL V6.12, 2002, Bruker AXS, Inc., Analytical X-ray Systems, 5465 East Cheryl Parkway, Madison, WI, 53711.

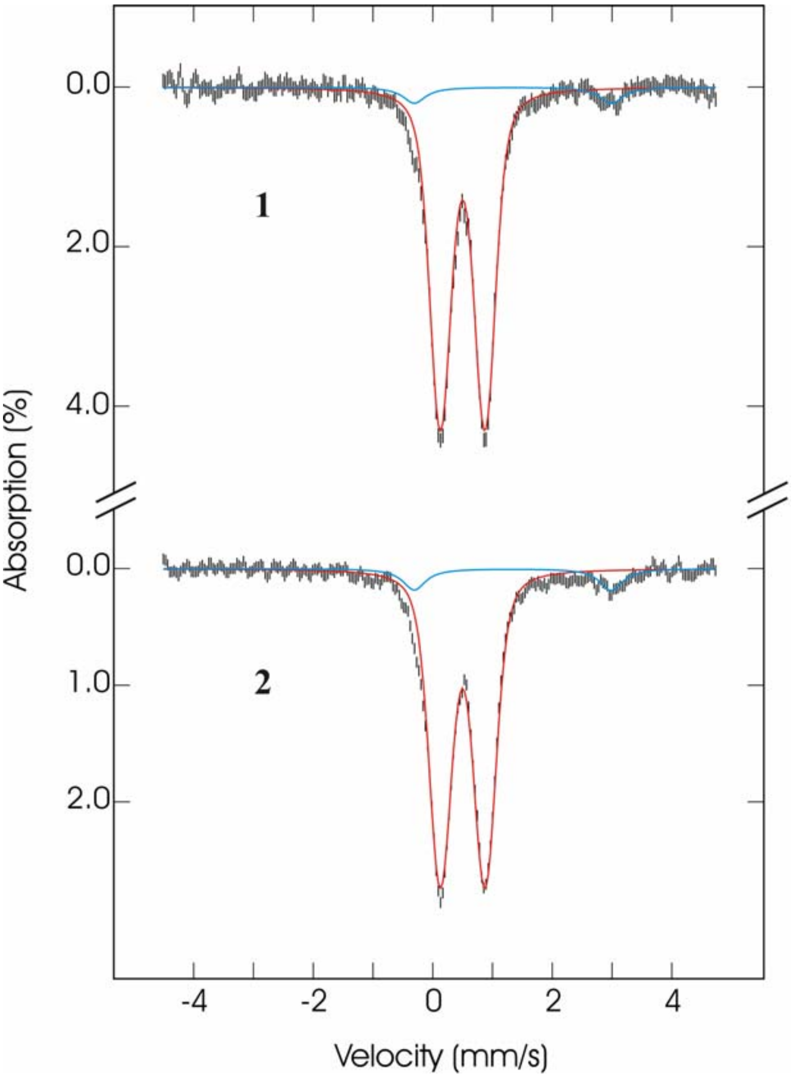

Fig. S1 Mössbauer spectra of **1** and **2** measured at 145 K and 155 K, respectively, with a 500 Gauss magnetic field applied parallel to the γ-beam. The spectra are fitted with two quadrupole doublets: a high-spin Fe^{III} (red line) and a high-spin Fe^{II} (blue line) component. The ferric component accounts for 94% of the iron in **1** and 92% in **2**. It is simulated with a voigt-shape doublet with $\delta = 0.50$ mm/s, $\Delta E_Q = 0.75$ mm/s. The FWHM is 0.37 mm/s for **1** and 0.41 mm/s for **2**. The ferrous component is simulated with a doublet of lorentzians with $\delta = 1.34$ mm/s, $\Delta E_Q = 3.30$ mm/s and $\Gamma = 0.47$ mm/s.

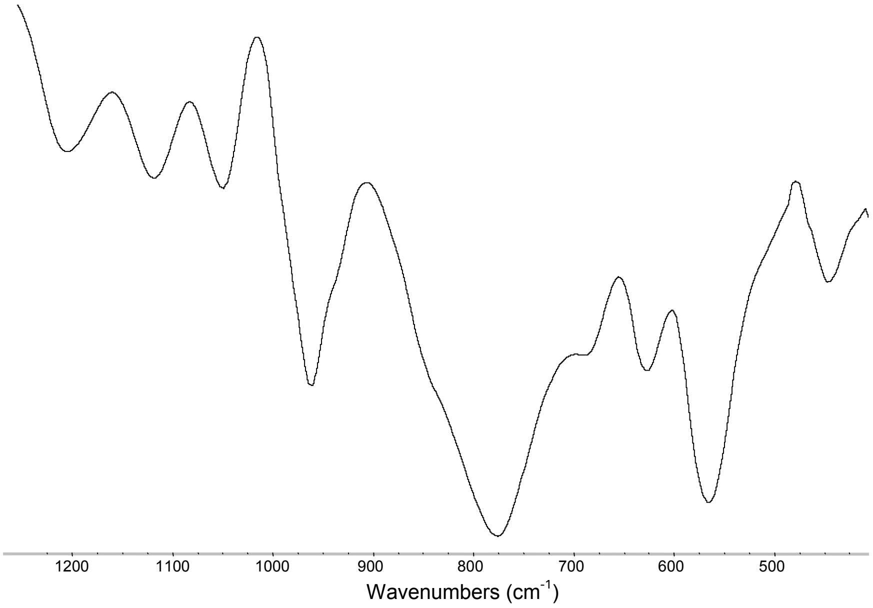

Fig. S2 IR spectrum of **1**. The corresponding spectrum of **2** is virtually identical.

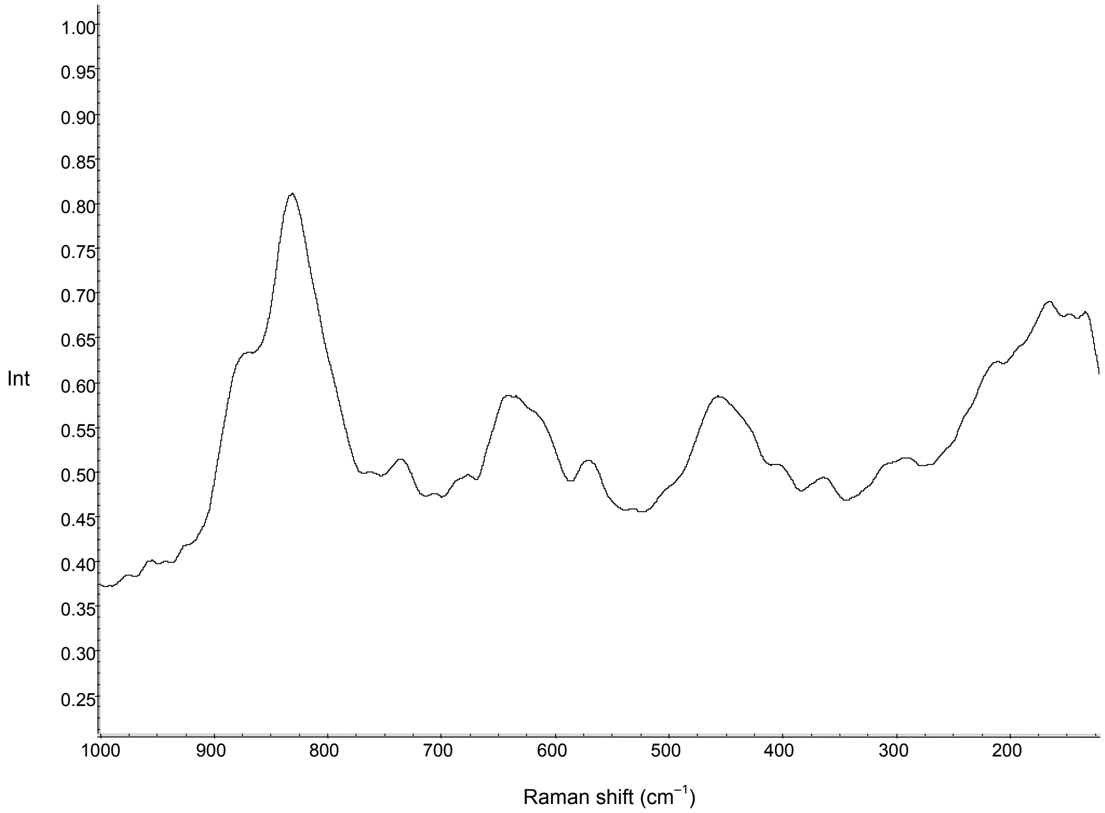

Fig. S3 Resonance Raman spectrum of **1** in H_2O (λ_e = 1064 nm).

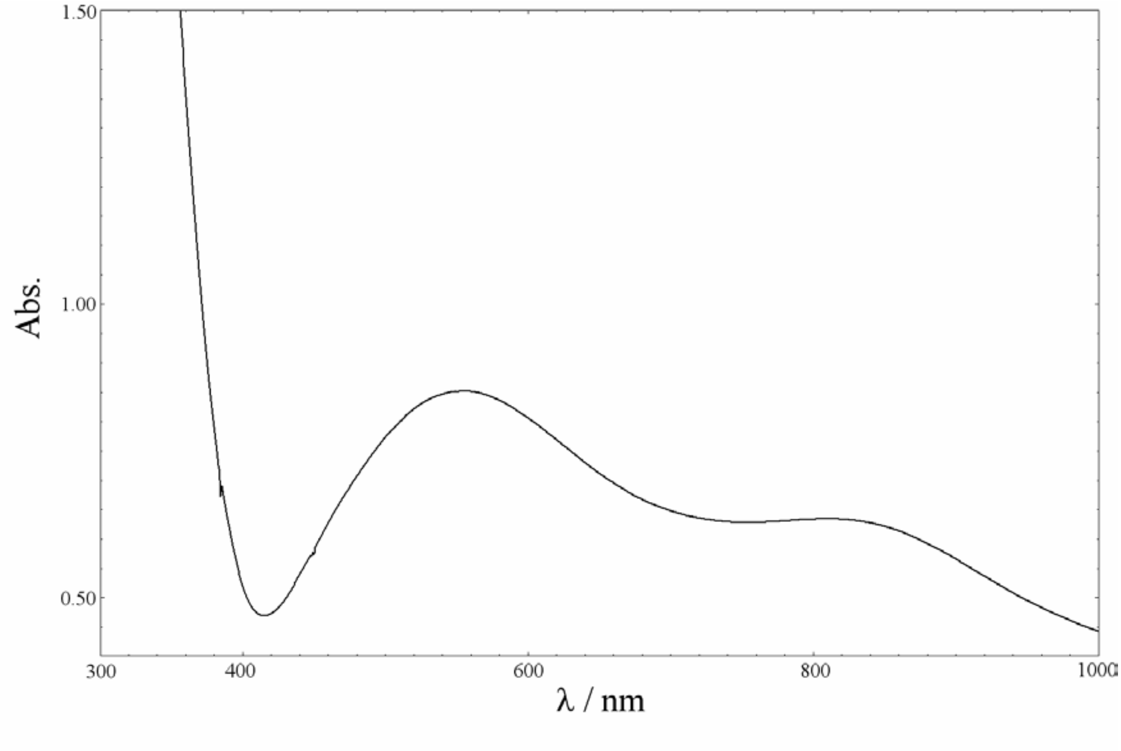

Fig. S4 Electronic absorption spectrum of a 2 x 10^{-5} M solution of **1** in water.

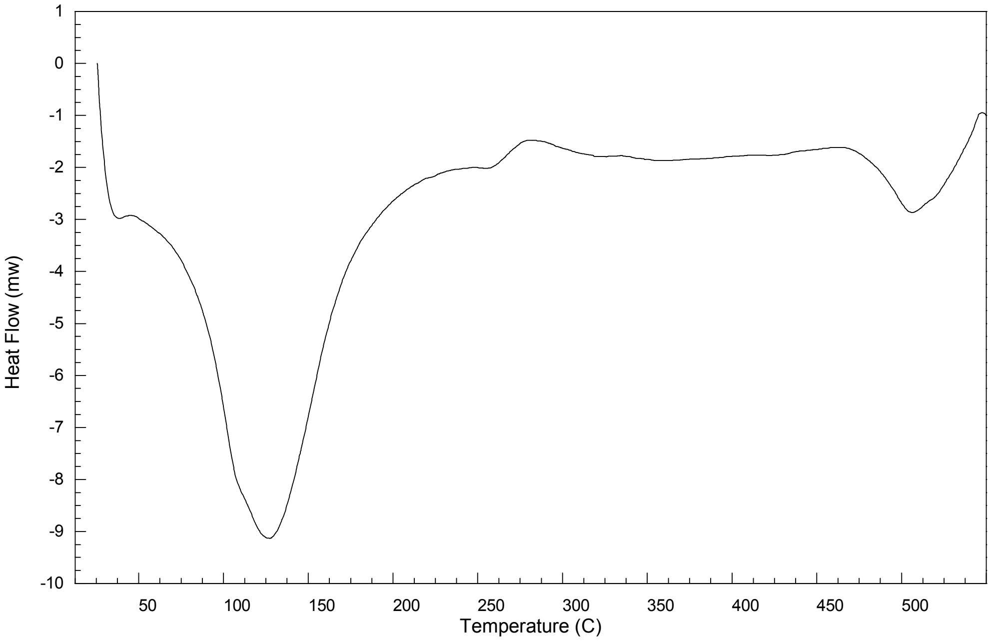

Fig. S5 Differential scanning calorimetry (DSC) data of **1**. Crystalline samples (10 mg) were heated from 25 °C to 550 °C at a rate of 20 °C/min.