Supplementary Material (ESI) for Chemical Communications

Exploiting the Multifunctionality of Organocations in the Assembly of Hybrid Polyoxometalate Building Blocks and Networks.

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Squid Measurements

The low-field magnetism of compound **1** is defined by weak intramolecular antiferromagnetic coupling that is typical for Mn^{II} dimers. A isotropic Heisenberg-type spin Hamiltonian of the type $\boldsymbol{H} = -J\mathbf{S}_1\mathbf{S}_2$ can be fitted to the χT vs. T data (Figure 1) to yield J/k_B = –0.72 K with g = 1.985 (see Fig.). Analysis of the susceptibility data indicates a paramagnetic background that complies with an impurity of 0.8% isolated (uncoupled) Mn^{II} centers per formula unit.

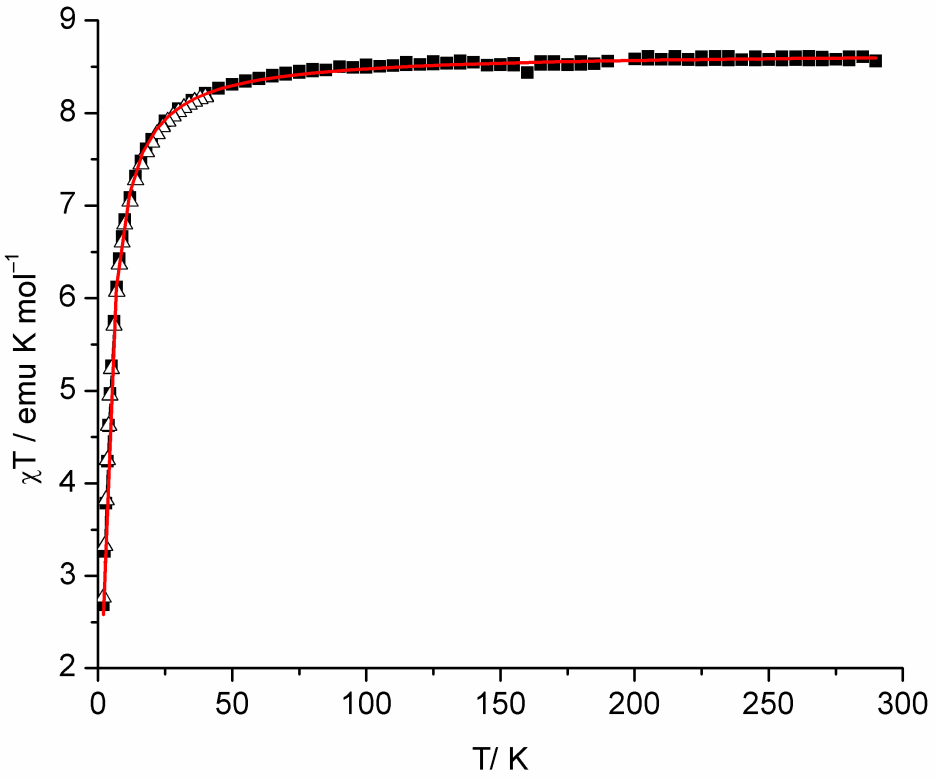


Figure 1: Experimental temperature dependence of χT for compound **1** (squares: 0.1 Tesla, triangles: 1.0 Tesla). The red curve represents the best fit to a isotropic Heisenberg model (see text).

Magnetic susceptibility measurements have been performed at 0.1, 1.0, and 4.0 Tesla between 2 and 290 K using a Quantum Design MPMS-5XL squid magnetometer. All data have been corrected for diamagnetic and temperature-independent paramagnetic (TIP) contributions ($\chi_{dia/TIP}$(**1**) = -1.47×10^{-3} emu mol^{-1}).

Synthesis

1: 1.65 g (5 mmol) $Na_2WO_4.2H_2O$ were dissolved in 20 ml aqueous NaCl solution (1 M) and acidified to pH 3.5 with nitric acid (4 M) followed by the addition of 0.84 g (4.82 mmol) *N*,*N*'-bis(2-hydroxyethyl)piperazine. To this solution 0.446 g phosphoric acid (85 %) were added, resulting in a white precipitate that re-dissolves upon stirring. The solution pH is then adjusted to 6.05 with dilute NaOH. Finally, a solution of 0.1152 g $Mn(NO_3)_2$ in 1 ml H_2O is added. This results in a yellow insoluble precipitate that is removed by centrifugation. Large yellow plates crystallise from the clear yellow solution (pH 6.05) and are isolated by filtration after 3 weeks. Yield: 0.403 g (25 %). Elemental analysis calcd. for **1**: C, 8.25; H, 2.24; N, 2.41 %; Na, 0.66%. Found: C, 8.25; H, 2.22; N, 2.40 %; Na 0.63%. IR bands: 3434(b), 1632(m), 1459(m), 1383(wsh), 1079(msh), 1049(msh), 950(msh), 886(m), 833(s), 805(s), 765(m), 717(m), 591(wk), 512(wk), 408(wk) cm^{-1}.

2: 1.65 g (5 mmol) $Na_2WO_4.2H_2O$ were dissolved in 20 ml NaCl (1 M) and acidified to pH 7.5 with nitric acid (4 M) followed by the addition of 0.84 g (4.82 mmol) *N*,*N*'-bis(2-hydroxyethyl)piperazine. To this solution 0.446 g phosphoric acid (85 %) were added, resulting in a white precipitate that re-dissolves upon stirring. The solution was then acidified further to pH 6.8 using dilute nitric acid. Finally, a solution of 0.1152 g $Mn(NO_3)_2$ in 1 ml H_2O is added. This results in a yellow insoluble precipitate that is removed by centrifugation. The clear yellow solution is then heated to 60 °C for 15 mins. Large yellow plates crystallise from the clear yellow solution (pH 6.80) and are isolated by filtration after 3 weeks. Yield: 0.62 g (39 %). Elemental analysis calcd. for **2**: C, 5.18; H, 1.63; N, 1.51; Na, 1.65 %. Found: C, 5.00; H, 1.55; N, 1.44; Na, 1.62 %. IR bands: 3432(b), 3004(s), 1627(sh), 1441(sh), 1028(sh), 936(sh), 879(sh), 751(m) cm^{-1}.

NMR Measurements:

^{31}P spectra were recorded on a Bruker AV400 spectrometer at 162 MHz in H_2O using a D_2O insert as the internal lock. Chemical shifts are referenced to 85% H_3PO_4. Line broadening parameters were set at 1.00Hz, but increased to 1000Hz in order to observe the broad peak associated with the $(H_2O)_4MnPO_4Mn(H_2O)_4$ species in (**1**).

Expt. (a) Reaction mixture at pH 6.05 and pH 6.8 peaks below 0; -2.211ppm, -10.73ppm, -11.2ppm

Expt. (b) Reaction mixture at pH 6.05 plus Mn^{2+} peaks below 0; -2.211ppm, -11ppm, -20 to 20ppm.

Expt. (c) Reaction mixture at pH 6.8 plus Mn^{2+} peaks below 0; -2.211ppm, -10.73ppm, -11.2ppm

Cold Spray Mass Spectroscopic Measurements:

Cold spray measurements were made at 5° C. The sample, reaction mixture (b), was diluted so that the maximum concentration of ligand and tungsten ions was of the order of 10^{-5} M. Then this aqueous solution was used to make an 95% reaction mixture : 5% isopropyl alcohol solution by volume, and this was infused into the cold spray at 180 μL/h. The mass spectrometer used for the measurements was a Bruker microTOFQ and the data was collected in positive ion mode. The spectrometer was previous calibrated with the standard tune mix to give a precision of *ca.* 1.5 ppm in the region of 500-2000 m/z. The standard parameters for a medium mass data acquisition were used and the end plate voltage was set to -500 V and the capillary to +4500 V. The full range spectrum is shown in Figure 2 (left) and the highest peak observed is shown on the right hand side with the simulated spectrum below for the mono-cation: $[H_{22}Mn_2W_4PO_{28}]$. This can be identified as the phosphate bridged species as shown in Figure 3.

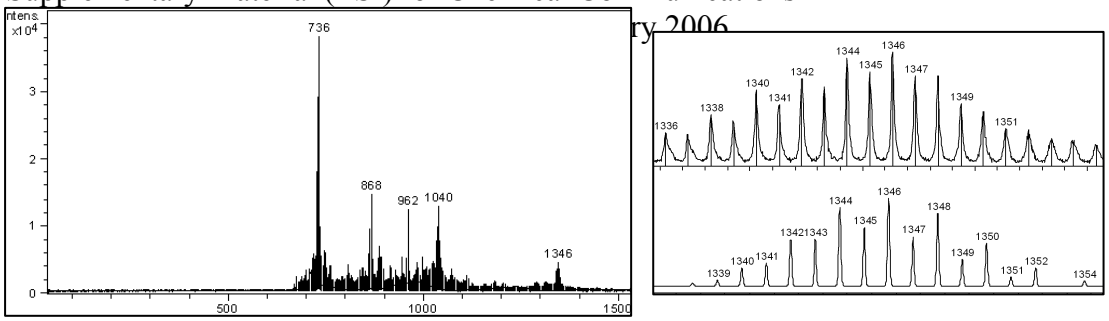
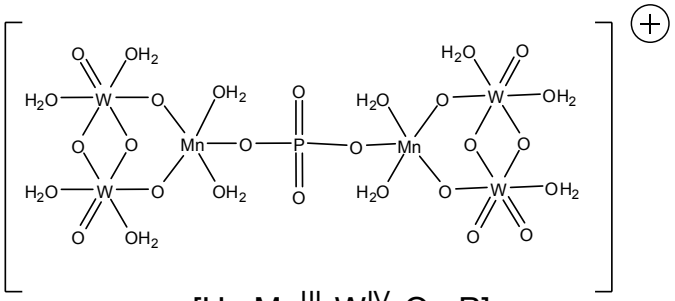


Figure 2. Full range CSI spectrum on the LHS and zoom in on the top RHS with the simulated spectrum below on the RHS.

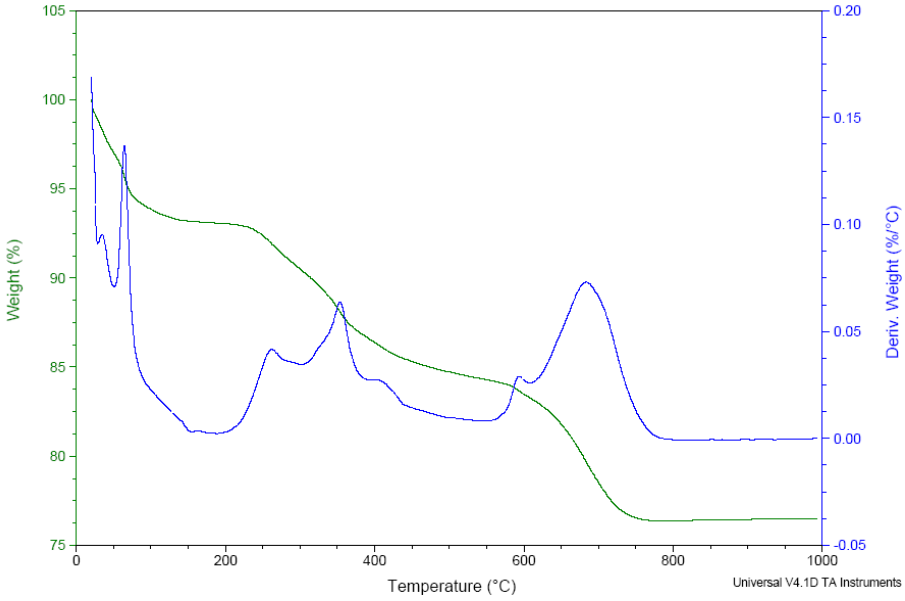


$[H_{22}Mn^{III}_2W^{IV}_4O_{28}P]$

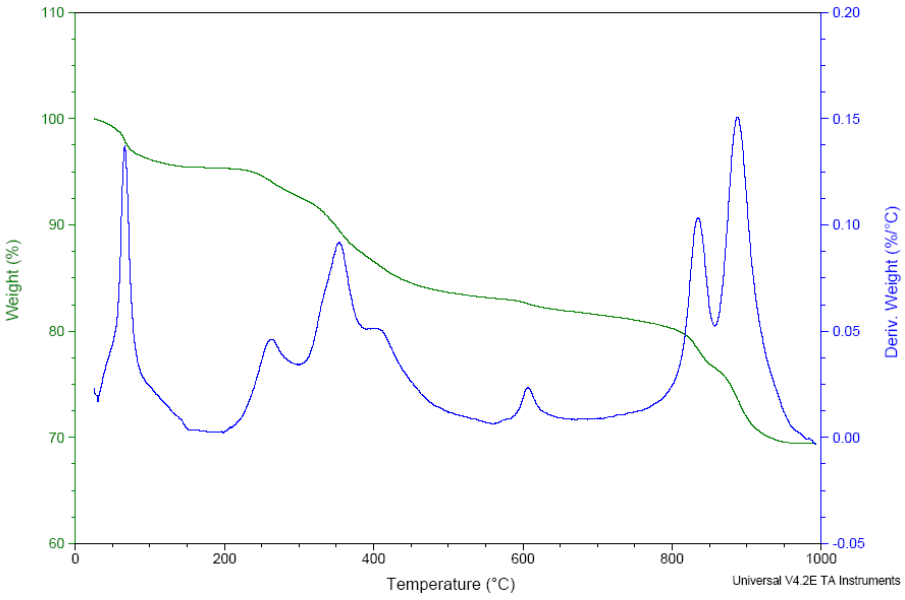
Figure 3. The species centred at m/z = 1346 is assigned as above.

TGA measurements

Compound (1)



(A) Carrier gas = 90ml/min N_2, 30ml/min = Air



(B) Carrier gas = 120ml/min N_2