

Controlled Assembly & Solution Observation of a 2.6 nm Polyoxometalate ‘Super’ Tetrahedron cluster: $[KFe_{12}(OH)_{18}(\alpha\text{-}1,2,3\text{-}P_2W_{15}O_{56})_4]^{29-}$

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Full Synthesis

Synthesis of $K_{21}Na_8[KFe_{12}(OH)_{18}(\alpha\text{-}1,2,3\text{-}P_2W_{15}O_{56})_4]\cdot70H_2O$ (**1**): A sample of $[Fe_3(\mu_3\text{-}O)(CH_2=CHCOO)_6(H_2O)_3]Cl\cdot7H_2O$ (0.165g, ~0.20 mmol) was dissolved in H_2O (20 mL). Solid $Na_{12}[\alpha\text{-}P_2W_{15}O_{56}]\cdot24H_2O$ (0.8g, ~0.18 mmol) was then added and stirred till a clear brown solution is obtained. Addition of solid KCl (0.16g, 2.14 mmol) to this reaction mixture results in a yellow precipitate. Kept the reaction mixture at 60 °C for 2 h. The clear yellowish brown solution thus obtained was filtered while hot and kept open for slow evaporation in a conical flask. Greenish yellow crystals were collected down the conical flask within one week along with a yellow solid mass. The yellow solid mass is found to be amorphous which might be a mixture of inorganic salts as well as minor side products. Yield of the greenish yellow crystals (**1**) = 0.425 g (52 % calculated from { P_2W_{15} }). Elemental analysis calcd (%) for $H_{158}Fe_{12}K_{22}Na_8O_{312}P_8W_{60}$: H 0.88, Fe 3.69, K 4.74, Na 1.01, W 60.8; found: H 0.72, Fe 2.88, K 4.78, Na 0.99, W 60.7. (Na, K, W and Fe are analyzed using atomic absorption spectroscopy). Characteristic IR bands (KBr): 3432, 1619, 1085, 940, 914, 883, 823, 724, 532, 459, 448, 433, 420, 409 cm^{-1} .

Structural analysis of 1

A single crystal was selected and mounted onto the end of a thin glass fiber using Fomblin oil. X-ray diffraction intensity data were measured at 100(2) K on a Bruker Apex II diffractometer [$\lambda(\text{Mo-K}\alpha) = 0.7107 \text{ \AA}$]. Structure solution and refinement was carried out with SHELXS-97¹ and SHELXL-97² via WinGX.³ Corrections for incident and diffracted beam absorption effects were applied using empirical⁴ methods. The accessible solvent volume in the crystal lattice has been determined by deleting the solvated water molecules from the structure and calculating the resultant void volume using options in PLATON.⁵

- (1) Sheldrick, G. M. *Acta Crystallogr. , Sect. A* **1998**, *A46*, 467.
- (2) Sheldrick, G. M. SHELXL-97. Program for Crystal structure analysis, University of Göttingen, Germany, 1997.
- (3) Farrugia, L. J. *J. Appl. Cryst.* **1999**, *32*, 837.
- (4) Blessing, R. H. *Acta Crstallogr. Sect A* **1995**, *51*, 33.
- (5) Spek, A. L. PLATON, A Multipurpose Crystallographic Tool, Utrecht University, The Netherlands, 2002.

$\text{K}_{21}\text{Na}_8[\text{KFe}_{12}(\text{OH})_{18}(\alpha\text{-1,2,3-P}_2\text{W}_{15}\text{O}_{56})_4]\cdot70\text{H}_2\text{O}$: $\text{H}_{158}\text{Fe}_{12}\text{K}_{22}\text{Na}_8\text{O}_{312}\text{P}_8\text{W}_{60}$, $M_r = 18144.34 \text{ g mol}^{-1}$; block crystal: $0.20 \times 0.16 \times 0.10 \text{ mm}^3$; $T = 100(2) \text{ K}$. Monoclinic, space group $C2/m$, $a = 47.8099(15)$, $b = 30.6240(15)$, $c = 29.8033(11) \text{ \AA}$, $\beta = 122.929(2)$, $V = 36626(3) \text{ \AA}^3$, $Z = 4$, $\rho = 3.291 \text{ g cm}^{-3}$, $\mu(\text{MoK}\alpha) = 19.608 \text{ mm}^{-1}$, $F(000) = 32128$, 254612 reflections measured, of which 34305 are independent ($R_{\text{int}} = 0.113$), 2085 refined parameters, $R1 = 0.0477$, $wR2 = 0.1245$. Structure was finished with high quality as shown by the R values. Half cluster was found in the asymmetrical unit with a number of disordered potassium and sodium sites. Not all potassium and sodium in the formula, which is determined by chemical analysis, are found as they are heavily disordered with solvated water molecules.

TGA and DSC

The TGA (Figure 1) and DSC (Figure 2) studies reveal that the molecular framework of **1** is quite stable up to ~480 °C. The initial water loss of ca. 7% in the TGA profile corresponds to the loss of the 70 solvated water molecules. The loss of ca. 1% molecular weight around 480 °C in the TGA profile is most probably due to loss of 18 bridging OH groups in the molecular structure. The rather stepwise nature of this loss may be attributed to the fact that the OH bridging present in the molecule falls into two category - the 6 Fe–OH–Fe bridges connecting together the four Dawson fragments in the molecule are different from the total 12 Fe–OH–Fe bridges present within each of the Fe₃ capped Dawson units. The loss of these hydroxyl bridges around 480 °C results in the collapse of the molecule as well as the entire framework as revealed by the DSC studies.

Figure 1. TGA profile of the molecule **1**

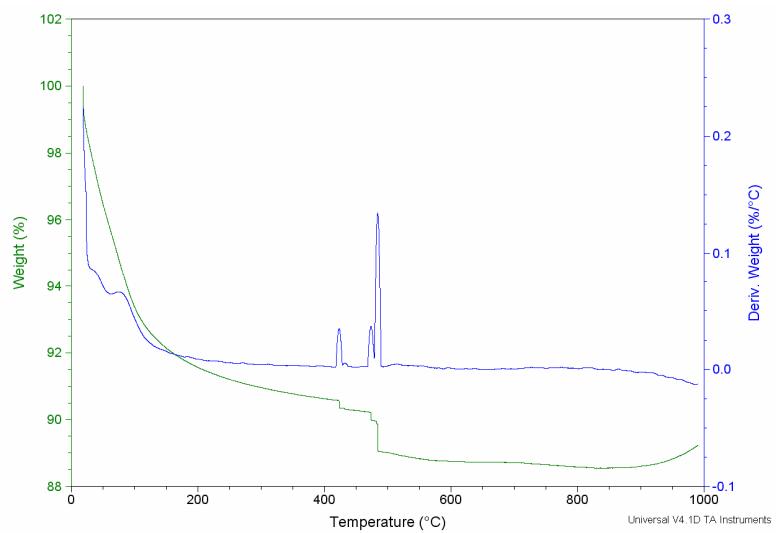
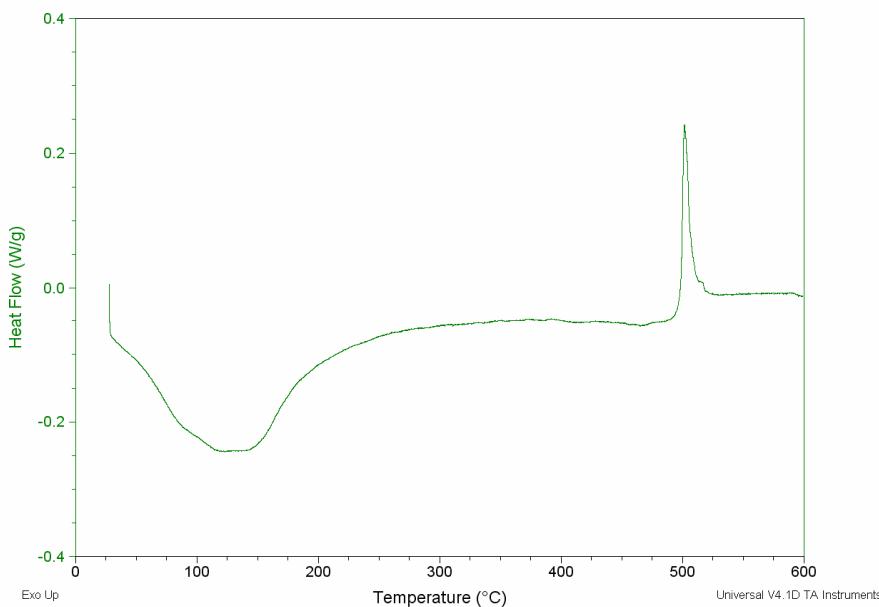


Figure 2. DSC profile of the molecule **1**



Electrospray mass spectroscopic measurements

ESMS measurements were made at 120° C. The aqueous solution of the sample was diluted so that the maximum concentration of ligand and tungsten ions was of the order of 10^{-5} M and this was infused into the electrospray at 180 L/h. The mass spectrometer used for the measurements was a Bruker microTOFQ and the data was collected in negative ion mode. The spectrometer was previously calibrated with the standard tune mix to give a precision of *ca.* 1.5 ppm in the region of 500-5000 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 collision cell was set to a collision energy of -8.0 eV/z with a gas flow rate at 25% of maximum and the cell RF was set at 600 Vpp.

The full range spectrum is shown in Figure 3. The most intense peak is at m/z of 2800 (16800/6) (see Figure 4), represented by a typical species $\{[KFe_{12}(OH)_{18}(\alpha-1,2,3-P_2W_{15}O_{56})_4][K_{14}Na_9](H_2O)_{10}\}^{6-}$ (mw *ca.* 16800 D or 16.8 kD). The spectrum also contained the 4- and 7- ions of the cluster as well as the precursor lacunary $\{W_{15}P_2\}$ species and a Fe adduct.

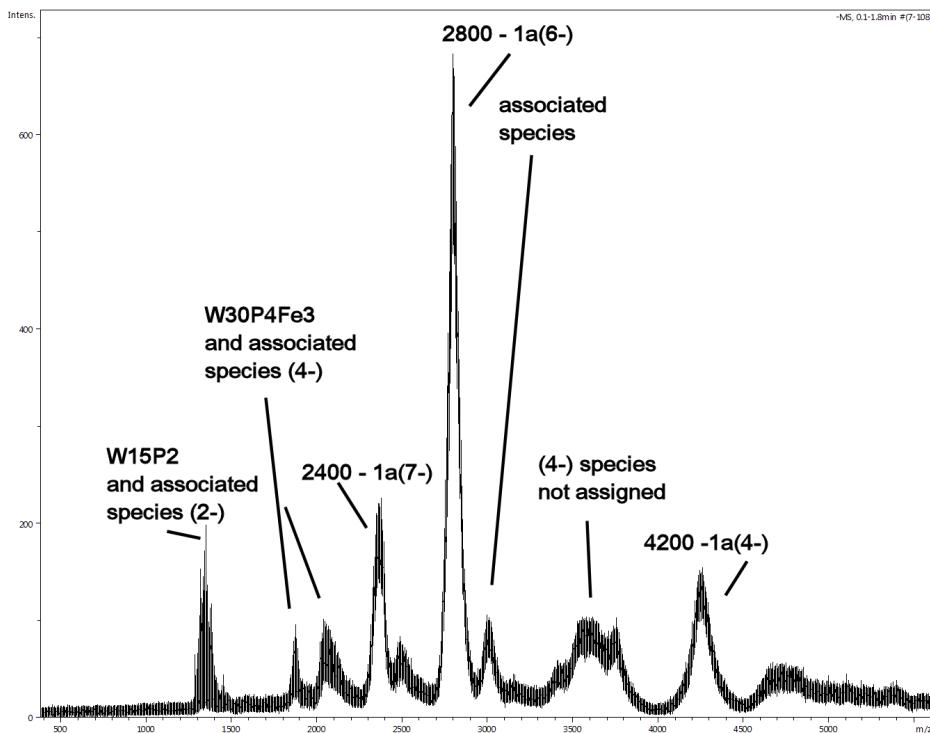


Figure 3. Full range mass spectrum of the aqueous solution containing 1.

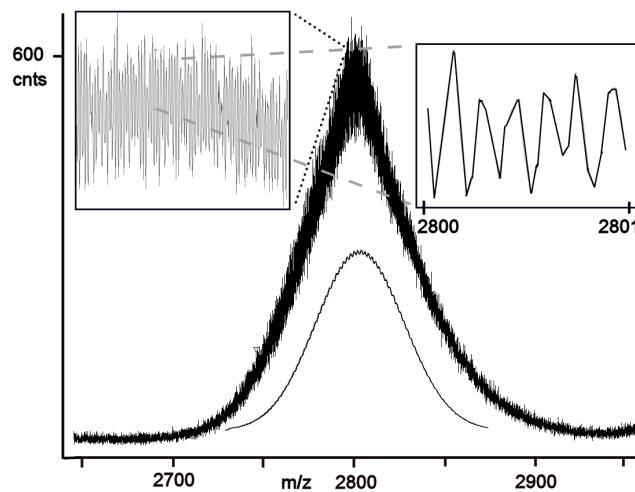


Figure 4. Mass spectrum (black line) showing the $\{[1\text{a}]\}^{6-}$, e.g. $\{[\text{KFe}_{12}(\text{OH})_{18}(\alpha\text{-1,2,3-P}_2\text{W}_{15}\text{O}_{56})_4][\text{K}_4\text{Na}_9](\text{H}_2\text{O})_{10}\}^{6-}$, in aqueous solution at m/z ca. 2800. The simulated spectrum is shown below. The charge state can be deduced from a zoom in (TOP LEFT then TOP RIGHT) demonstrating the six minus charge state of the **1a** (see the full spectrum which shows the presence of the -7, and -4 charge states for **1a** as well as an indication that the $[\alpha\text{-1,2,3-P}_2\text{W}_{15}\text{Fe}_3\text{O}_{62}]^{12-}$ building block is also present).

Magnetic properties:

The magnetic properties of **1** indicate dominating strong antiferromagnetic intramolecular superexchange between the twelve spin-5/2 Fe(III) centers (Fig. 5) which is within the range of expectations for oxo-linked Fe(III) complexes. At room temperature the value of χT is still significantly below the expected high-temperature limit of 52.5 emuK/mol for twelve Fe(III) centers (assuming $g = 2.0$) and decreases steadily with decreasing temperatures to yield a singlet ground state. Below approx. 125 K the susceptibility strongly deviates from a Curie-Weiss form, above 125 K $1/\chi$ increases approximately linear with temperature to yield a Weiss temperature of ca. -1100 K. We are planning additional measurements (low-temperature high-field magnetization measurements, ESR) to establish a full Heisenberg-type model in upcoming work.

Susceptibility measurements were performed at fields ranging from 0.1 to 5 Tesla between 1.8 and 290 K using a Quantum Design MPMS 5 SQUID magnetometer. Susceptibility data were corrected for diamagnetic and temperature-independent paramagnetic terms, $\chi_{\text{dia}}(\mathbf{1}) = -0.0041 \text{ emu/mol}$. Magnetization measurements at 1.8 K did not show paramagnetic impurities.

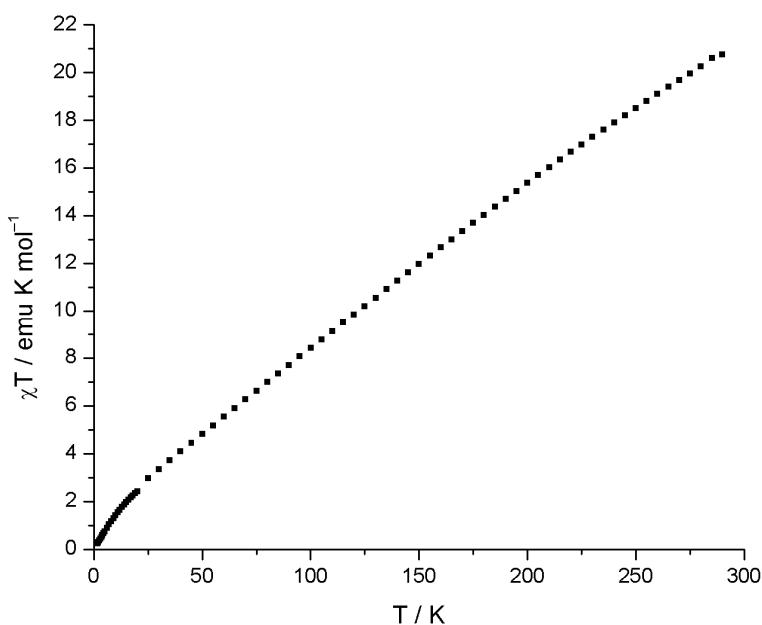


Figure 5: Temperature dependence of χT of **1** at 5.0 Tesla.