Electronic Supplementary Information for Dalton Transactions

Increasing the dimensionality of hybrid vanadium oxyfluorides using ionothermal synthesis

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Supplementary material

Synthesis: The ionic liquid 1-ethyl-3-methylimidazolium bromide (EMIM Br) was synthesised according to the literature procedure[1] by the reaction of *N*-methylimidazole and ethyl bromide. The IL 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (EMIM NTF_2) was synthesised according to the literature procedure[2] by an anion exchange between EMIM Br and lithium bis(trifluoromethylsulfonyl)imide in aqueous solution .

1. P. Wasserscheid and T. Welton, Ionic liquids in synthesis, Wiley-VCH, Weinheim, Germany, 2003, ch.2.1.2, 9.
2. P. Bonhôte, A.-P. Dias, N. Papageorgiou, K. Kalyanasundaram and M. Grätzel, *Inorg. Chem.*, 1996, **35**, 1168.

Figure S1. ORTEP view of the building unit in **1**.

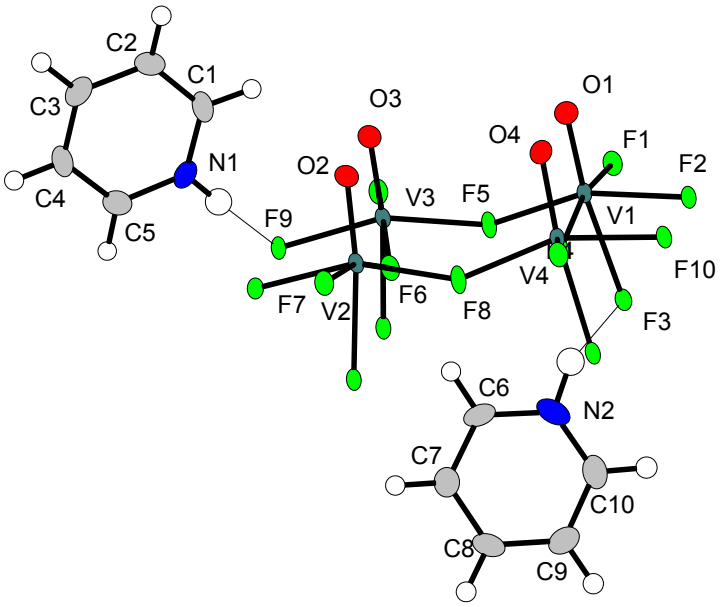


Figure S2. Observed (below) and calculated (above) powder XRD patterns for **1**.

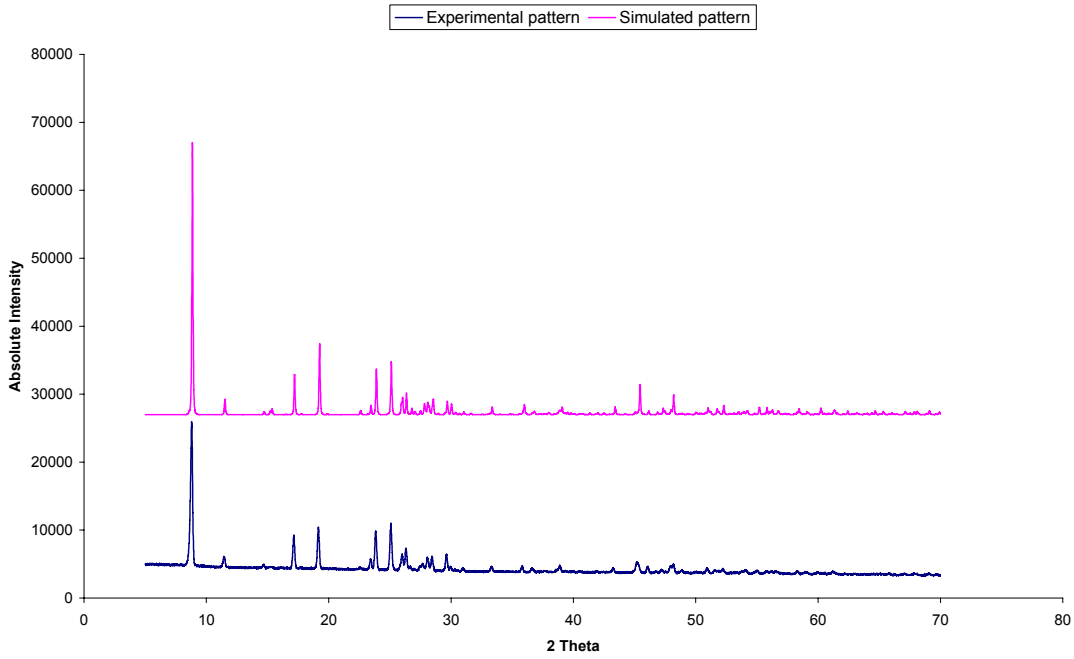
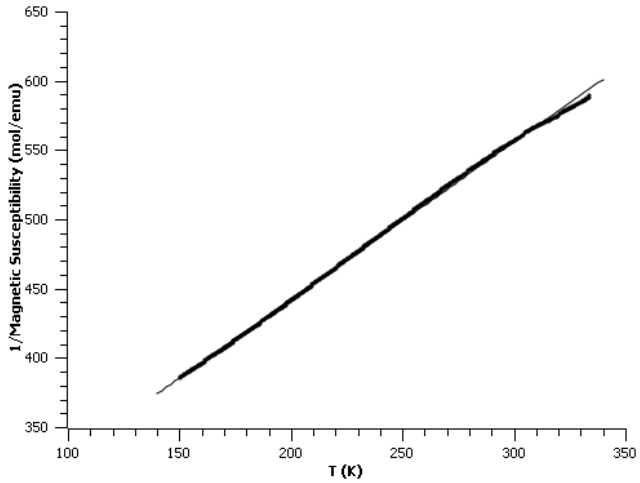


Figure S3. Curie-Weiss fit to χ(T) above 150 K.

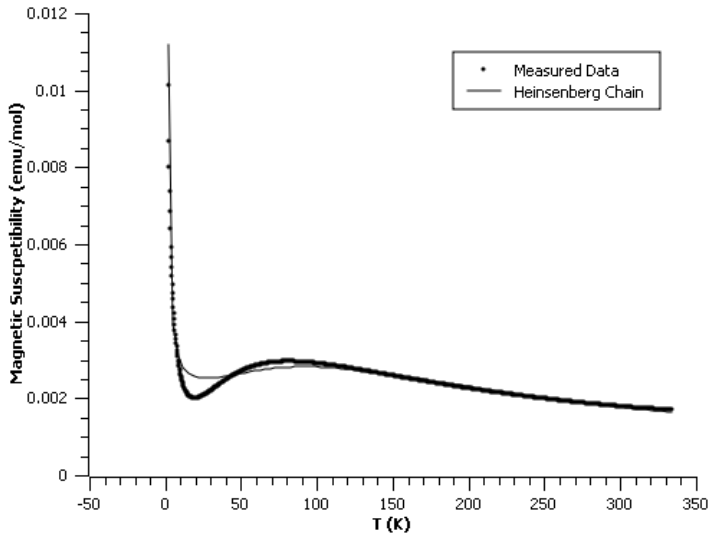


derived μ = 2.65 BM

μ(spin-only) = 2.45 BM

derived θ = -189 K

Figure S4. Fit of the Heisenberg chain model to χ(T).



Note: The difference between Ising and Heisenberg spins is related to their anisotropy; Heisenberg spins are isotropic whereas Ising spins give a differing response to a magnetic field parallel and perpendicular to direction of their magnetic spin. The Ising model was originally proposed for use with ferromagnetic systems, but is equally valid with antiferromagnetic systems, and only considers nearest neighbour interactions.

The Ising fit to the magnetic susceptibility had three components; the parallel component of the Ising model $\chi_{\|}$; the perpendicular component of the Ising model $\chi_{\perp}$; and the low temperature paramagnetic background χ_{LT}. The amounts of each of the components were refined, and a value of J of -56.60(17) K was obtained.

$$\chi(T) = \chi_{\|} + \chi_{\perp} + \chi_{LT}$$

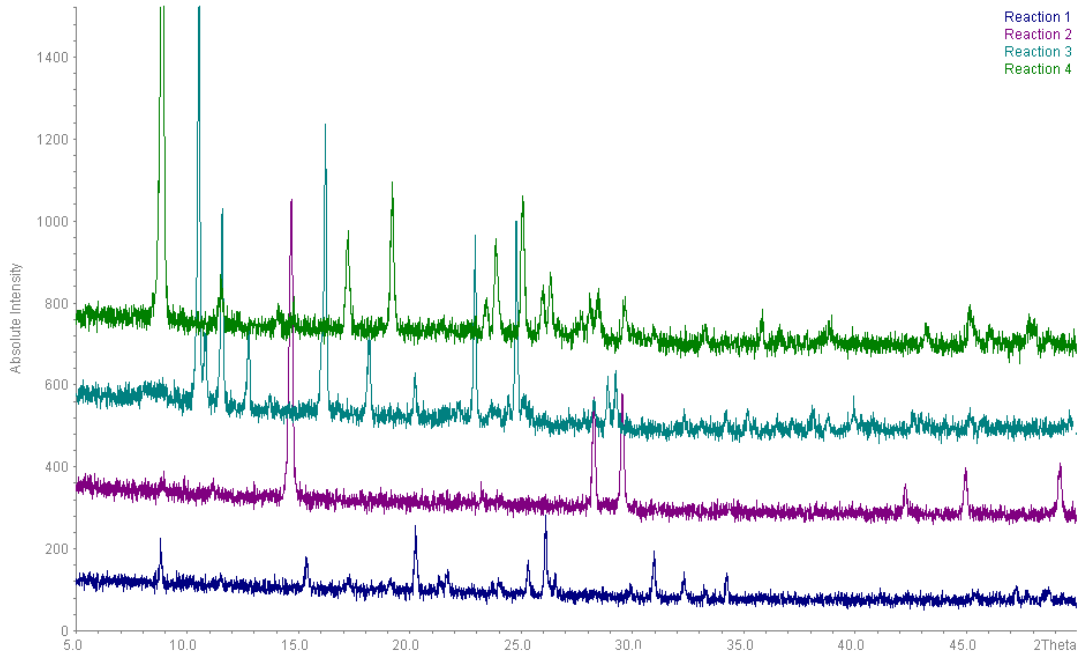
$$\chi_{\|} = \frac{Nm^2}{2J}\left(\tanh\left|\frac{J}{k_B T}\right| + \left|\frac{J}{k_B T}\right|\sec h^2\left(\frac{J}{k_B T}\right)\right)$$

$$\chi_{\perp} = \frac{Nm^2}{|J|}\left(\frac{J}{k_B T}\right)\exp\left(\frac{2J}{k_B T}\right)$$

$$\chi_{LT} = \frac{C}{T}$$

Ising Chain Model: Fisher ME, *J. Math. Phys*., 1963, **4**, 124.
Heisenberg Chain: Kaul, EE et al., *Phys. Rev. B*, 2003, **67**, 174417.

Figure S5. Details of the comparative exploratory syntheses in solvothermal V/py/HF systems, together with the resulting observed powder XRD for the products of these reactions; the synthesis of **1** is not observed under these conditions.



Reaction 1 : 0.182 g (1×10^{-3} mol) V_2O_5 + 0.3 mL (1.15×10^{-2} mol (HF) / 1.25×10^{-3} mol (Pyridine)) of HF.Pyridine.

Reaction 2 : 0.182 g (1×10^{-3} mol) V_2O_5 + 0.3 mL (1.15×10^{-2} mol (HF) / 1.25×10^{-3} mol (Pyridine)) of HF.Pyridine + 5 mL ethylene glycol.

Reaction 3 : 0.182 g (1×10^{-3} mol) V_2O_5 + 0.3 mL (1.15×10^{-2} mol (HF) / 1.25×10^{-3} mol (Pyridine)) of HF.Pyridine + 5 mL pyridine.

Reaction 4 : 0.182 g (1×10^{-3} mol) of V_2O_5 + 1 mL HF (48 % in H_2O) + 5 mL ethylene glycol + 0.098 g (1.25×10^{-3} mol) pyridine