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A F-bridged Mn(II) Molecular Square

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We report on a tetranuclear Mn(II) complex possessing a F-bridged molecular square topology directed by 1,10-phenanthroline ligands.

A significant rise in the use of F⁻ bridging ions in the field of molecular magnetism has been observed over the last 5-10 years. Perhaps the most elegant example is in the synthesis of a vast library of homo- and heterometallic {Cr^{III}₇M^{II}₁} wheels (and their many analogues) reported by Winpenny and co-workers, that have been proposed as qubits in quantum information processing (QIP).¹ The bridging F⁻ ions encircling the inner cavity of the wheels H-bond to templating alkylammonium cations, changes in which allow for modification of both the molecular and supramolecular chemistry; a beautiful example being the formation of inorganic-organic rotaxanes.² Such dipolar H⁺F⁻ interactions have also been used to manipulate the docking of 'guest' molecules (inc. Na⁺, K⁺, NH₄⁺, β-Alanine, MeNH₃⁺) within the double bowl cavities of hexanuclear F-bridged [Cu₆] wheels.³ F-bridged cages of Mn^{II/III} are far rarer in comparison to other 3d metals, perhaps because of the perceived lack of suitable starting materials. MnF₃ was used for the first time very recently for the preparation of a host of polymetallic high spin complexes and Single-Molecule Magnets (SMMs);⁴ its prior lack of use a surprise given the vast majority of SMMs are built using Mn^{III} ions.⁵

In order to further the coordination chemistry of F⁻ with Mn, and with an eye towards investigating Mn-F-Mn magnetic exchange interactions and developing magneto-structural correlations⁶ within various low nuclearity F-bridged complexes, we herein describe an unusual molecular square built from MnF₂. Reaction of anhydrous MnF₂, 1,10-phenanthroline (phen) and NaNO₃ in MeOH[†] for 24 hours produces a yellow solution, which upon filtration and slow evaporation, yields yellow block-like crystals[‡] of [Mn^{II}₄F₄(phen)₈](NO₃)₄·12H₂O (**1**), crystallising in the tetragonal I4₁/a space group in ~20% yield (Figure 1). The structure comprises four symmetry equivalent {Mn(phen)₂}²⁺ units (Mn1) linked into a square by four μ-bridging F⁻ ions (F1 and s.e.). The Mn ions are in distorted octahedral geometries with a {N₄F₂} coordination sphere. The two chelating phen ligands and two fluorides per metal centre are both *cis*, directing the molecular square topology (Fig. 1) - analogous to that observed, for example, in Pd^{II} chemistry.⁷ As can be seen in the lower panel of Figure 1 the [Mn^{II}₄F₄]⁴⁺ core is non-planar, being bent along the body diagonal. Each edge of the square is 3.722 Å (Mn...Mn) in length, with the Mn-F bond distances being Mn1-F1 = 2.061(4) and Mn1-F1' = 2.030(4) Å. The μ-F bridges sit alternately above and below the [Mn₄] "plane" as you

circumnavigate the square. The combination of the non-linear Mn-F-Mn pathways (Mn1-F1-Mn1, 130.9(2)°) and the presence of the bulky phen ligands are presumably the cause of the molecular distortion.

Intra-molecular interactions in the form of π-π stacking of the phen ligands are observed in the lattice with π_{centroid}...π_{centroid} distances in the 3.719 – 3.886 Å range (Fig. 1). The individual [Mn₄F₄(phen)₈]⁴⁺ moieties align in superimposable 1D rows along the *c* axis of the unit cell although they are well separated ([Mn₄] plane-plane distance = 13.231 Å). The NO₃⁻ counter anions (O1, O2 and O3) and the H₂O of crystallisation (O15, O16 and O17) lie in between these 1D columns and H-bonding with each other (O1-O16 = 2.839, O2-O15 = 2.779, O2-O17 = 2.890 Å), and with phen protons of nearby [Mn₄] units (O1-H3(C3) = 2.588, O2-H8(C8) = 2.590, O15-H9(C9) = 2.563 Å). The 1D columns (Fig. 2) interact via numerous π-π stacking interactions (π_{centroid}...π_{centroid} distance = 3.654 Å, Fig. 2).

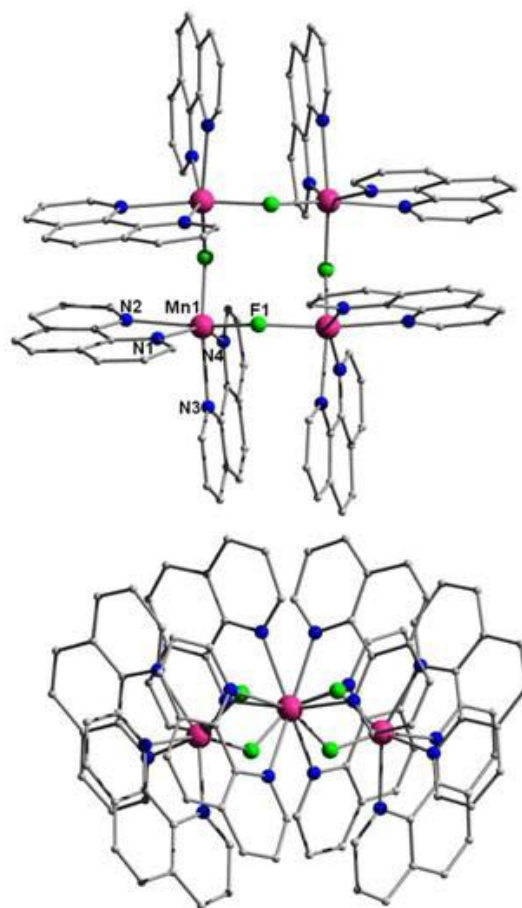


Fig. 1 Molecular structure of the cation of **1** viewed perpendicular (top) and parallel (bottom) to the $[\text{Mn}_4]$ plane. H atoms have been omitted for clarity. Mn = pink; F = green; N = blue, C = grey.

75 Oxidation state assignments and the presence of F^- (versus, for example, OH^-) were made on the basis of bond lengths, BVS calculations (detailed in ESI),⁸ charge balance considerations and Raman spectroscopy (vide infra). Although polymetallic complexes with square topologies are not uncommon,⁹ the
80 synthesis of **1** represents the first reported F-bridged molecular square.

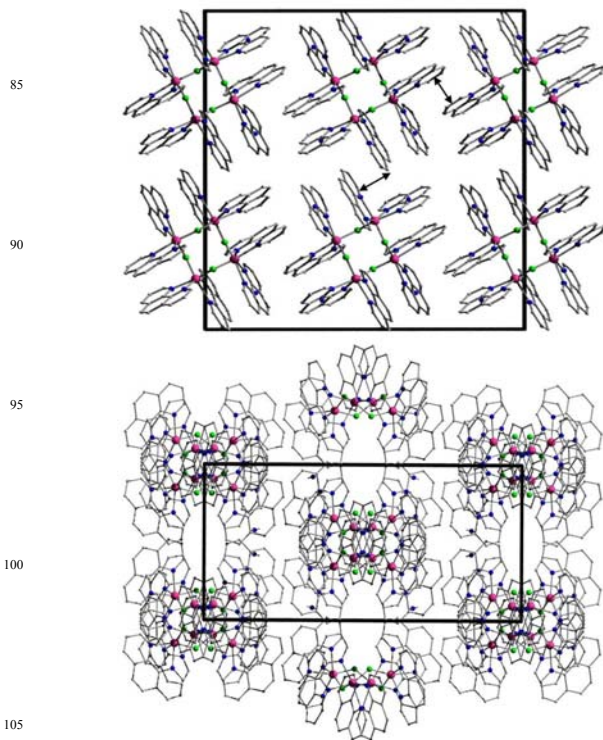


Fig. 2 (Top) Packing of cations of **1** in the crystal (viewed down c axis) highlighting the 1D columnar arrangement of $[\text{Mn}_4]$ units. Arrows represent examples of intermolecular π - π stacking in **1**. (bottom) View along the b axis of the unit cell. In both cases the H-atoms, the NO_3^- counter anions and the H_2O solvent molecules have been removed for clarity.

Variable temperature magnetic susceptibility measurements were carried out on a polycrystalline powder of **1** in the 300 – 5 K
115 temperature range in an applied field of 0.1 T (Fig. 3). The room temperature $\chi_{\text{m}}T$ value of $\sim 12.8 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$ is significantly lower than that expected for four non-interacting Mn^{II} centres ($\sim 17.5 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$ for $g = 2.0$) and is indicative of antiferromagnetic exchange between the four metal centres. The
120 value of $\chi_{\text{m}}T$ drops gradually with decreasing temperature before falling more rapidly below $\sim 125 \text{ K}$ reaching a value of $0.47 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$ at 5 K. Simulation of the magnetic data¹⁰ using the 1- J model of Equation (1) and the scheme of Figure 3 afforded the parameters $J = -3.3 \text{ cm}^{-1}$ and $g = 2.00$; the magnitude of the
125 exchange being in-line with previously reported values for Mn^{II} -F- Mn^{II} interactions.¹¹

$$\mathcal{H} = -2J(\hat{S}_1 \cdot \hat{S}_2 + \hat{S}_1 \cdot \hat{S}_4 + \hat{S}_2 \cdot \hat{S}_3 + \hat{S}_3 \cdot \hat{S}_4) \quad (1)$$

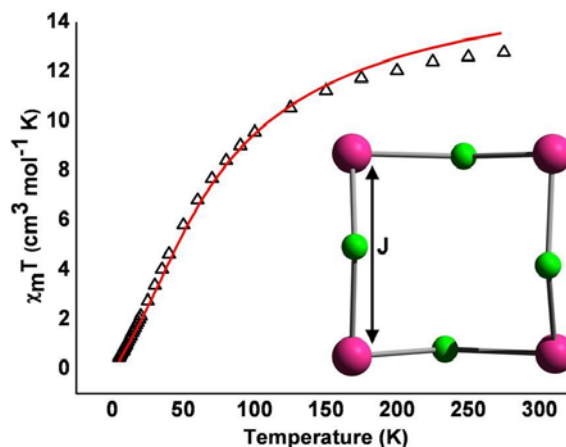


Fig. 3 Plot of $\chi_{\text{m}}T$ vs. T obtained for a powdered polycrystalline sample of **1** in an applied field of 0.1 T. The solid line represents a simulation of the data to the Hamiltonian of equation (1). The inset shows the cartoon describing the 1- J model.

Solid state Raman spectra were collected on a polycrystalline
135 sample of **1** and the MnF_2 starting material (purchased as a powder) in order to confirm the presence of the $\mu_2\text{-F}^-$ bridging ions (Figure 4). Peaks at 242 and 254 cm^{-1} attributed to the $\text{Mn}(\text{II})\text{-F-Mn}(\text{II})$ symmetric stretching modes in **1** were observed.¹² The Raman spectrum of MnF_2 exhibits symmetric
140 stretch peaks at 242 and 245 cm^{-1} (E_g mode)¹³ and a peak at 336 cm^{-1} consistent with terminal Mn-F stretching (A_{1g} mode)¹³ which is corroborated by its absence in the spectrum of **1** (Fig. 3). The band at 273 cm^{-1} is due to the organic ligand.

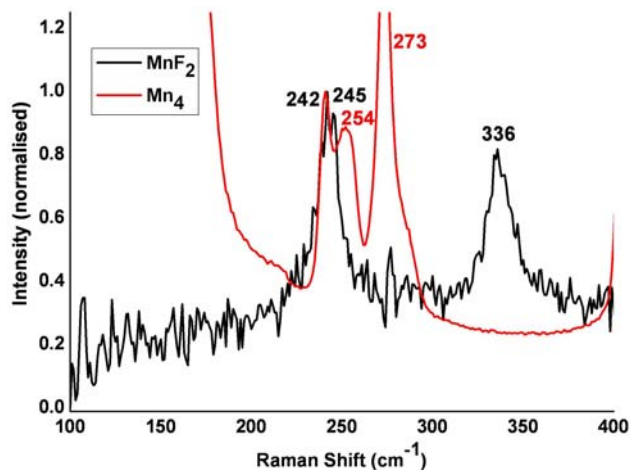


Fig. 4 (top) Raman spectra of **1** (red line) and the MnF_2 precursor material (black line) viewed in the 100-400 cm^{-1} range.

The electrospray mass spectrum gives a prominent parent peak at
150 $m/z = 434$ ($[\text{Mn}_4\text{F}_4(\text{phen})_8]^{4+}$), which suggests that **1** remains intact in solution, although this may also be attributed to the $[\text{Mn}(\text{F})(\text{phen})_2]^+$ fragment species. Other smaller fragments of **1** were also observed as assigned in Fig. SI3. UV/vis studies on **1** in MeCN show two sharp bands (226 and 266 nm respectively),

each associated with $\pi\text{-}\pi^*$ transitions of the 1,10-phenanthroline ligand.¹⁴ A shoulder at 290 nm attributed to 1,10-phen $n\text{-}\pi^*$ transitions was also observed. As expected for isotropic Mn(II) ions no d-d transitions were observed (Fig. S14). In conclusion, [Mn₄($\mu\text{-F}$)₄(1,10-phen)₈](NO₃)₄ (**1**) represents a rare example of a tetranuclear cage linked into a square by bridging F⁻ ions.¹⁵ Work is currently underway to produce siblings of **1** along with other F-bridged dinuclear analogues in order to investigate potential magneto-structural trends.

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Notes and References

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All reagents and solvents were purchased commercially and used as supplied (Anhydrous MnF₂ purchased from Sigma Aldrich). **Caution!** Although we encountered no problems care should be taken when using the potentially explosive nitrate anion.

† Anhydrous MnF₂ (0.5 g, 5.38 mmol), 1,10-phenanthroline (0.96 g, 5.38 mmol) and NaNO₃ (0.22 g, 2.69 mmol) were dissolved in MeOH (35 cm³) and stirred for 24 h before being filtered to give a yellow solution. Yellow block-like crystals of **1** were obtained in 20 % yield upon slow Et₂O diffusion over the period of four days. FT-IR (cm⁻¹): 3423 (w), 3073 (w), 2987(w), 1622 (w), 1589 (w), 1572 (w), 1513 (w), 1494(w), 1420 (m), 1370(m), 1326 (s), 1218 (w), 1141 (w), 1099(w), 1041(w), 841(m), 766(w), 722(s). Raman spectrum (785 nm excitation) (cm⁻¹): 141(w), 250(w), 254(w), 273(m), 404(s), 422(m), 476(m), 513(m), 545(sh), 557(s), 637(w), 726(s), 866(m), 895(m), 954(w), 996(b), 1052(s), 1103(m), 1143(m), 1193(w), 1206(w), 1221(w), 1254(m), 1302(s), 1343(s), 1418(s), 1451(s), 1515(m), 1576(m), 1590(m), 1605(m), 1623(m). Elemental analysis calculated (Found) (%): for C₉₆H₇₀N₂₀O₁₅F₄Mn₄ (1.3H₂O): C: 56.53 (56.98), H: 3.46 (3.81), N: 13.74 (13.43). UV/vis (MeCN): λ_{max} [nm] (ϵ_{max} 10³ dm³ mol⁻¹ cm⁻¹): 229 (90.3), 264 (77), 290(sh).

‡ Crystal data for 1.12H₂O: C₉₆H₈₈N₂₀O₂₄F₄Mn₄: $M = 2201.62$, Tetragonal, space group I4₁/a, $a = b = 26.912(4)$, $c = 13.231(3)$ Å, $\alpha = \beta = \gamma = 90^\circ$, $V = 9583(3)$ Å³, $T = 150(2)$ K, $Z = 4$, $D_c = 1.509$ g cm⁻³, 3928 reflections collected of which 2718 were unique ($R_{\text{int}} = 0.1394$), $R1 [I > 2\sigma(I)] = 0.0848$, $wR2 = 0.2268$ (F^2 , all data). CCDC 743466.

Variable-temperature, solid-state direct current (dc) magnetic susceptibility data down to 1.8 K were collected on a Quantum Design MPMS-XL SQUID magnetometer equipped with a 7 T dc magnet. Diamagnetic corrections were applied to the observed paramagnetic susceptibilities using Pascal's constants. CHN microanalysis was carried out at the School of Chemistry, NUI Galway. Raman measurements were recorded at room temperature using a Raman spectrometer (AVALON Instruments Ltd, UK, now part of Perkin Elmer) equipped with a 785 nm laser diode excitation and a TE cooled (-90°C) back thinned CCD detector. A laser power of ~70 mW (at the sample) with an exposure time of 3 × 5 seconds was used and spectra were collected from 250 to 3311 cm⁻¹ (at a resolution of 1 cm⁻¹).

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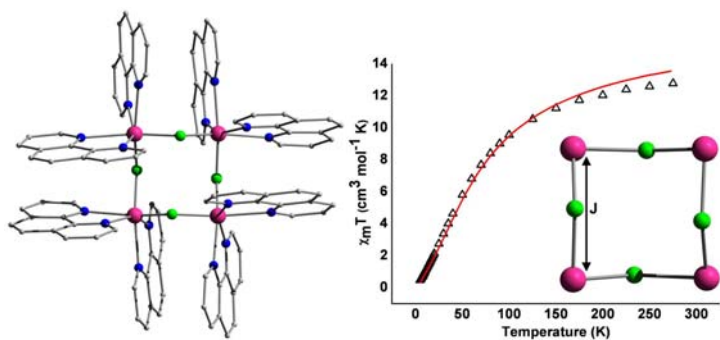
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TOC Entry

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We report on a the solid state and solution characterisation of a tetranuclear Mn(II) cluster possessing a unique F-based '*molecular square*' core.