

$\{\text{Mn}(\text{OH}_2)_2[\text{Mn}(\text{bpym})(\text{OH}_2)]_2[\text{Fe}(\text{CN})_6]_2\}_\infty$: a two-dimensional ferrimagnet with a partial cubane motif

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$\{\text{Mn}(\text{OH}_2)_2[\text{Mn}(\text{bpym})(\text{OH}_2)]_2[\text{Fe}(\text{CN})_6]_2\}_\infty$, a two-dimensional cyanide-bridged polymer, exhibits canted ferrimagnetism with $T_C = 11$ K.

Molecule-based magnets are the focus of considerable current research effort, from both the fundamental and device-related perspectives. One of the more exciting developments in recent years is the design of magnets from a consideration of the sign and magnitude of superexchange between adjacent paramagnetic metal centers. The family of magnets based on the 3-D Prussian Blue structural motif nicely illustrates this strategy.¹ In these materials, deliberate choices of metal ions at the two ends of the CN^- bridge lead to well established ground states, and the symmetry of the magnetic orbitals allows for a reasonable prediction of the nature of the superexchange (antiferro- versus ferro-magnetic).² For example, $\text{V}[\text{Cr}(\text{CN})_6]_{10.86} \cdot 2.8\text{H}_2\text{O}$ orders ferrimagnetically at 315 K^{1h} (due to direct overlap of t_{2g} magnetic orbitals) whereas $\text{CsNi}[\text{Cr}(\text{CN})_6] \cdot 2\text{H}_2\text{O}$ orders ferromagnetically at 90 K^{1s} (due to orthogonality of the t_{2g} and e_g magnetic orbitals). In addition to the high-symmetry Prussian-Blue architectures, hexacyanometallate building blocks are found in other structural motifs, for example in the 3-D ferrimagnet $[\text{Ni}(\text{tren})_3][\text{Fe}(\text{CN})_6] \cdot 6\text{H}_2\text{O}$ synthesized from $[\text{Fe}(\text{CN})_6]^{3-}$ and $[\text{Ni}(\text{tren})]^{2+}$ [tren is the tetradentate capping ligand tris(2-aminoethyl)amine].^{6e} A number of 1-D chains,⁴ 2-D layered materials⁵ and 3-D networks⁶ have also appeared in the literature, the common theme among all examples being the incorporation of cyanometallates into networks with metal ions that possess a capping ligand(s).

Our involvement in the chemistry of cyanide compounds is directed at the formation of clusters or low-dimensional materials from specifically tailored precursors.⁷ For example, we reasoned that 1:1 reactions between *cis*- $[\text{Mn}(\text{bpym})_2(\text{H}_2\text{O})_2]^{2+}$ and $[\text{Fe}(\text{CN})_6]^{3-}$ would yield a square with *cis*- $[\text{Mn}(\text{bpym})_2]^{2+}$ corners linked by $[\text{Fe}(\text{CN})_6]^{3-}$ edges or a zigzag bimetallic chain. Both of these hypotheses are based on the expectation that the only leaving groups would be the two water molecules on Mn^{II} . Herein, we report an entirely unexpected result, namely that the 2,2'-bipyrimidine chelates are also very good leaving groups in favor of the nitrogen end of a cyanide group in such reactions.

Brown crystalline needles are formed reproducibly by slow diffusion of a solution of $[\text{Mn}(\text{bpym})_2(\text{OH}_2)_2][\text{SO}_4]$ (bpym = 2,2'-bipyrimidine) in MeCN into a solution of $\text{K}_3[\text{Fe}(\text{CN})_6]$ in H_2O .⁸ X-Ray crystallographic studies† revealed that the product is the neutral, 2-D polymer $\{\text{Mn}(\text{OH}_2)_2[\text{Mn}(\text{bpym})(\text{OH}_2)]_2[\text{Fe}(\text{CN})_6]_2\}_\infty$ **1**. The asymmetric unit of the structure consists of one $[\text{Fe}^{\text{III}}(\text{CN})_6]^{3-}$ unit connected to two different types of Mn^{II} centers by cyanide bridges. One Mn atom (Mn2) has retained only one bpym ligand while the other one (Mn1) has lost both of its original bpym ligands. For simplicity in describing the repeat pattern, the building blocks of the layers are defined as $[\text{Fe}(\text{CN})_6]^{3-}$ (Fe1), *trans*- $[\text{Mn}(\text{OH}_2)_2]^{2+}$ (Mn1), and *fac*- $[\text{Mn}(\text{bpym})(\text{OH}_2)]^{2+}$ (Mn2) units. Each Fe^{III} ion forms bridges to three Mn2 and two Mn1 centers, which leaves one terminal CN^- ligand. The *trans*- $[\text{Mn}(\text{OH}_2)_2]^{2+}$ units are linked

to four Fe^{III} ions, and each *fac*- $[\text{Mn}(\text{bpym})(\text{OH}_2)]^{2+}$ building block is connected to three independent $[\text{Fe}(\text{CN})_6]^{3-}$ anions. The resulting polymeric framework can be described as being composed of individual 1-D chains formed by edge-sharing $\{[\text{Mn}(\text{bpym})(\text{OH}_2)]_2[\text{Fe}(\text{CN})_6]_2\}$ squares. These chains, which exhibit a staircase motif, are stitched into layers by *trans*- $[\text{Mn}(\text{OH}_2)_2]^{2+}$ bridges that serve to link Fe atoms of adjacent chains and creates two new $\{[\text{Mn}(\text{bpym})(\text{OH}_2)][\text{Fe}(\text{CN})_6]_2[\text{Mn}(\text{OH}_2)_2]\}$ squares that share a corner (Mn1) [see Fig. 1(a)]. As the simplified diagram in Fig. 1(b) reveals the framework resembles a 2-D array of fused Mn_4Fe_3 cubes that are missing one vertex. It is of further interest to point out that the bpym ligands of adjacent layers are interdigitated to form a stacked column along the *c* axis with a mean spacing of 3.35 Å.

Magnetic studies were performed on a 3.3 mg batch of crystals using a MPMS-XL SQUID magnetometer. Between 50 and 300 K, the molar susceptibility χ_m can be fit to a Curie-Weiss law with $C = 13.8$ emu K mol⁻¹ and $\theta = -12.8$ K (inset in Fig. 2). The Curie constant is in good agreement with the expected spin-only value (13.875 emu K mol⁻¹) for three $S = 5/2$ Mn(II) and two low spin $S = 1/2$ Fe(III) centers. The sign of the Weiss constant indicates that local antiferromagnetic interactions dominate as expected for $\text{Fe}^{\text{III}}\text{-CN-Mn}^{\text{II}}$ bridges where there is direct overlap of the t_{2g} magnetic orbitals. Below 50 K, χ_m deviates from the Curie-Weiss behavior and undergoes an abrupt increase at ca. 11 K which suggests the onset of magnetic ordering (Fig. 3). This state corresponds to a ferrimagnetic ordering, since the Fe^{III} and Mn^{II} spin centers interact antiferromagnetically with non-cancellation of spins. As Fig. 3 shows, the magnetization increases gradually, but saturation is incomplete at 7 T ($M = 11.6 \mu_B$ cf. the expected value of 13 μ_B). This behavior is a signature of a complicated magnetic structure (competing magnetic interactions with possibly some degree of spin canting), which is not unexpected in view of the crystal structure. No hysteresis was observed in the field dependence of the magnetization. Susceptibility

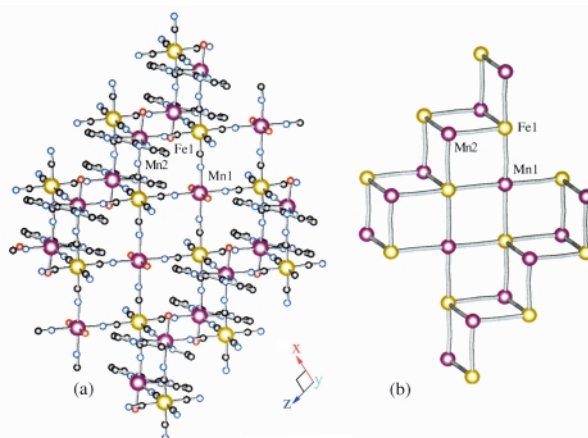


Fig. 1 (a) View of the two-dimensional network down the *b* axis. (b) Scheme emphasizing the partial cubane motif in the 2-D network.

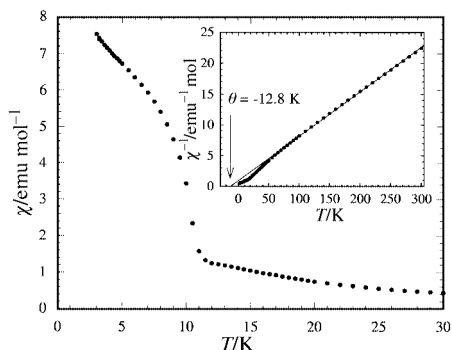


Fig. 2 Thermal dependence below 30 K of χ_m at 100 G for **1**. Inset: temperature dependence of $1/\chi_m$ between 2 and 300 K. The solid line indicates the best fit obtained by the Curie–Weiss law. These measurements were corrected for the sample holder and the diamagnetism contributions estimated from Pascal's constants.

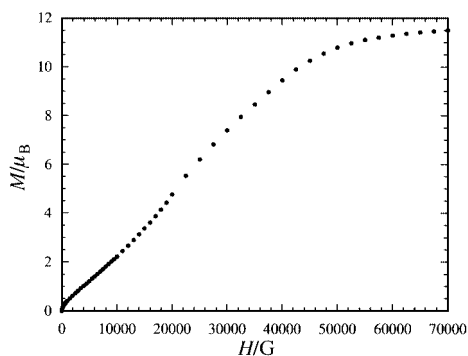


Fig. 3 Field dependence of the magnetization at 2 K.

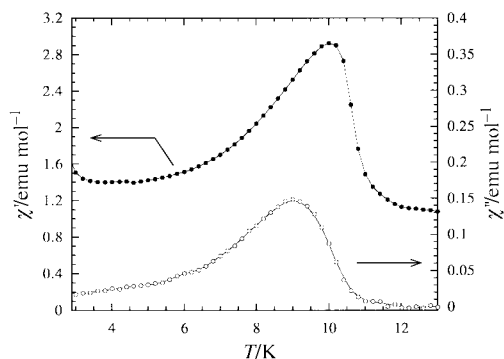


Fig. 4 Temperature dependence of the ac susceptibilities (in-phase, χ' , and out-of-phase, χ'') below 13 K [ac measuring field 1 G (10^{-4} T); frequency of 1 Hz; no external dc field].

measurements of the ac type confirm the ferrimagnetic ordering at 11 K (Fig. 4) and reveal no significant frequency dependence.

The result presented here underscores the structural diversity of materials containing cyanometallate building blocks. The slow loss of 2,2'-bipyrimidine ligands from *cis*-[Mn(bpym)₂(H₂O)₂]²⁺ in H₂O–MeCN contributes to the growth of crystals rather than the rapid deposition of powders which is the outcome of reactions that do not involve capping ligands. We are currently investigating reactions of other ligand-protected cations with hexacyanometallate anions, the results of which are forthcoming.

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Notes and references

† *Crystal data* for Mn(OH)₂[Mn(bpym)(OH)₂]₂[Fe(CN)₆]₂·9H₂O: Independent batches produce crystals with the same unit cell dimensions. C₂₈H₃₈Fe₂Mn₃N₂₀O₁₃, *M_w* = 1139.30, monoclinic, space group *P*2₁/*c*, *a* = 13.209(3), *b* = 26.694(5), *c* = 7.443(2) Å, β = 105.57(3)°, *V* = 2528.1(10) Å³, *T* = 110(2) K, *Z* = 2, *D_c* = 1.497 Mg m⁻³, graphite monochromatized Mo-Kα radiation (λ = 0.71069 Å), Bruker CCD diffractometer, *F*(000) = 1154, μ = 1.361 mm⁻¹, 0.08 × 0.02 × 0.01 mm, 18980 reflections measured, 6134 of which were unique (*R*_{int} = 0.2250). The structure was solved by direct methods (SIR97)⁹ followed by Fourier synthesis, and refined on *F*² (SHELX-97).¹⁰ All non-hydrogen atoms were refined anisotropically, except for the disordered interstitial water molecules. The final refinement gave *R*(*F*²) = 0.0715 and *R*²_w (*F*²) = 0.1630, by using 1490 reflections [*I* > 4σ(*I*)]. H-atoms are in calculated positions as riding atoms.

CCDC 182/1623. See <http://www.rsc.org/suppdata/cc/b0/b001513j/> for crystallographic files in .cif format.

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- Alternative synthesis: three equivalents of [Mn(bpym)₂(H₂O)₂](SO₄) in 25 mL of water were added to 2 equivalents of K₃[Fe(CN)₆] in 25 mL of water to yield a brown precipitate within 12 h. The powder was removed by filtration and the filtrate was slowly evaporated to give a brown crystalline material which was washed with water to remove soluble byproducts (64% yield). IR ν_{CN}/cm⁻¹ = 2145s, 2110br and 2063w, br. Independent batches exhibit the same IR data.
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