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From manganese(II)-azido layers to a novel three-dimensional molecular magnet: spin canting and metamagnetism

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Interlinking 2D azido-bridged and spin-canted antiferromagnetic layers with semi-rigid organic pillars yields a 3D molecular metamagnet.

The design of molecule-based magnetic materials has been of considerable interest in recent years.[1] In this context, azido-bridged complexes have received intense attention, due to the versatility of the azido ion in building extended networks and the diversity of the compounds in magnetic behavior.[2–4] A number of low-dimensional coordination polymers with 1D or 2D metal-azido networks have been reported, some of which exhibit long-range ordering behaviors such as ferromagnetism,[3] metamagnetism,[4,5] and weak ferromagnetism.[5,6] In contrast, the design of 3D metal-azido networks is relatively poorly developed.[7] An interesting strategy toward 3D topologies is to incorporate a second bridging ligand into the metal-azido systems. The incorporation of pyridazine or 4,4′-bipyridyl (bpy) has generated 3D metal-azido networks supported by the organic bridges,[8,9] while the use of pyrimidine (pym) yielded a different 3D topology, in which 2D metal-azido networks are interlinked *via* pym.[9] Weak ferromagnetism due to spin canting has been found for the bpy and pym species. It is interesting to note that the strategy failed to yield 3D networks for pyrazine and the flexible 4,4′-bipyridylethane or 4,4′-bipyridylpropane bridge, for which only 2D or 1D structures were obtained.[10] We are now exploring the strategy by using long semi-rigid organic bridges. Here we present the structural and magnetic characterization of a hybrid inorganic–organic 3D compound (**1**) built by pillaring 2D layers with the semi-rigid 4-pyridylmethylketazine (4-PMK) spacer. To our knowledge, this is the first 3D molecular metamagnet built of spin-canted metal-azido layers.

Slow evaporation of the methanol–aqueous solution containing 4-PMK, $Mn(ClO_4)_2{\cdot}6H_2O$ and NaN_3 in a 1:1:2 ratio yielded crystals with formula $[Mn(4\text{-PMK})(N_3)_2]_n$ (**1**).† X-ray analysis‡ revealed that the structure consists of neutral 2D manganese(II)-azido layers interlinked by the 4-PMK spacers. Each metal atom is placed in a centro-symmetric and axially elongated octahedral environment and linked to four neighboring Mn(II) ions *via* four equatorial azido bridges [Mn–N, 2.191(3) and 2.215(3) Å], yielding a two-dimensional (4,4) square-grid-like layer parallel to the *bc* plane (Figure 1a,b). The azido bridge adopts the end-to-end (EE) mode, the Mn–N–N angles being 146.1(3) and 128.6(3)° and the Mn–N–N–N–Mn torsion angle being 85.3(3)°. The adjacent Mn atoms spanned by the azido bridges are related by 2-fold screw axes and separated by 5.918 Å, and the dihedral angle between the neighboring MnN_4 equatorial planes is 81.6(1)°, defining a systematic alternation of the relative orientation of the metal spheres within the layer. The axial positions around Mn(II) are occupied by the pyridyl nitrogens arising from 4-PMK [Mn–N, 2.281(2) Å] and the ligand resides on inversion centers and serves as spacers between neighboring layers. Consequently, a hybrid 3D architecture built of inorganic layers and organic pillars is generated (Fig. 1c and d). The shortest interlayer Mn···Mn distance is 12.561 Å, and the Mn atoms linked by 4-PMK are separated by 15.624 Å.

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Magnetic susceptibilities of compound **1** were measured at a field of 500 G in the 2–300 K range (Fig. 2). The temperature dependence of $1/\chi_M$ above 50 K obeys the Curie–Weiss law with a negative Weiss constant ($\theta = -67.4$ K), indicating an intralayer antiferromagnetic interaction, as expected for the azido bridges in the end-to-end mode.[2] The room-temperature $\chi_M T$ value is *ca*. 3.92 emu K mol^{-1} per Mn(II), lower than the spin-only value (4.38 emu K mol^{-1}) for a high-spin Mn(II) ion. Upon cooling, $\chi_M T$ decreases smoothly to a rounded minimum about 42 K, confirming the intralayer antiferromagnetic inter-

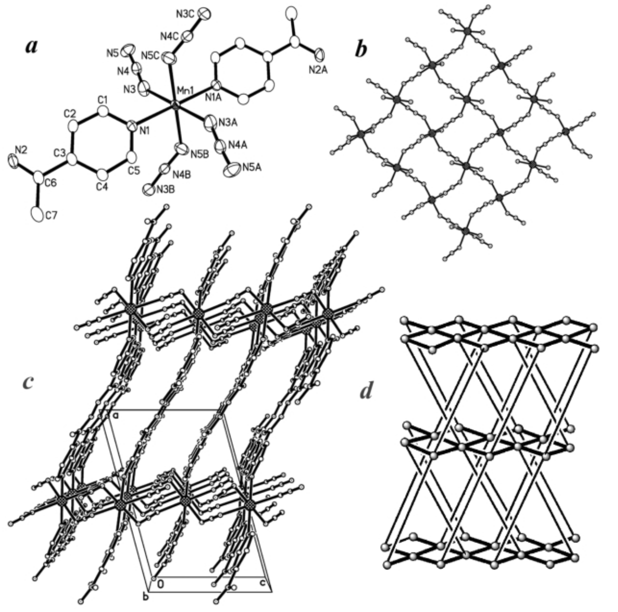

Fig. 1 Views showing the building unit (a), the Mn-azido layer along the *bc* plane (b), the 3D structure (c) and the 3D topology (d, the bold and thin lines stand for the azido and 4-PMK bridges, respectively).

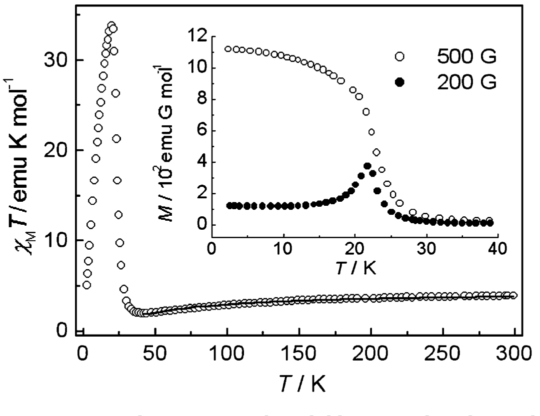

Fig. 2 $\chi_M T$ *versus* *T* plot at 500 G. The solid line was plotted according to the fit parameters given in the text. Inset: field-cooled magnetization curves at 200 and 500 G.

action. To evaluate the antiferromagnetic interactions, the susceptibility data above 42 K were fitted using Lines' expression for an $S = 5/2$ antiferromagnetic quadratic layer.[11] The best-fit parameters are $J = -2.5$ cm^{-1} and $g = 2.0$, comparable with those for related 2D Mn(II) compounds reported elsewhere.[6,12]

Upon cooling further below 42 K, $\chi_M T$ increases first gradually and then rapidly below *ca.* 30 K to a very high and sharp maximum of 33.8 emu K mol^{-1} at 20 K and finally decreases rapidly to 5.08 emu K mol^{-1} at 2 K. The increase in $\chi_M T$ indicates that a mechanism of ferromagnetic correlations is operative within the layer and the final decrease may be due to saturation effects and/or antiferromagnetic interactions between layers. The ferromagnetic correlations can be attributed to spin canting, *i.e.*, perfect antiparallel alignment of the spins on neighboring metal ions within the antiferromagnetic layer is not achieved so that residual spins are generated.[1] The canting of spins is consistent with the structural features of the complex, *i.e.*, the lack of inversion center between neighboring Mn(II) ions and the systematic alternation of the relative orientation of metal chromophores within the layer (*vide supra*).[13] The very high value of the $\chi_M T$ maximum, far above the value expected for a Mn(II) ion, suggests the occurrence of ferromagnetic-like ordering of the residual spins within the layer. To further characterize the weak ferromagnetism, field-cooled magnetizations at different fields are also given in Fig. 2 (inset). At 200 G, the magnetization presents a maximum at 22 K, indicating the onset of 3D antiferromagnetic ordering between the spin-canted layers. However, the magnetization at 500 G shows no maximum and tends to saturate at lower temperatures, indicating that the interlayer antiferromagnetic interaction is overcome by the external field. These features are indicative of a metamagnet built of spin-canted antiferromagnetic layers.

The metamagnetic behavior is confirmed by the sigmoidal shape of the magnetization *vs.* field plot at 1.8 K (Fig. 3): the magnetization first increases slowly with H, as for a typical antiferromagnet, and then increases abruptly above 200 G, indicating the field-induced transition from the antiferromagnetic to a weak ferromagnetic state. The critical field at 1.8 K is *ca.* 300 G, estimated as the field at which a maximum $\partial M/\partial H$ value is reached. Upon further increasing the field, the magnetization increases more and more slowly as the weak ferromagnetic phase tends to saturate, and finally a linear M *vs.* H relationship is achieved above 9 kG. At the highest field measured (70 kG), the magnetization is 0.84 Nβ, far below the saturation value (5 Nβ) expected for an $S = 5/2$ system. This is consistent with weak ferromagnetism due to spin canting. Extrapolating the high-field linear part of the magnetization curve to zero field gives a magnetization value of 0.40 Nβ. Assuming this to be the uncompensated magnetization, the spin canting angle is estimated to be about 4.6°,[14] which is the largest of the values reported for weak ferromagnets with azido bridges. Finally, cycling the field between +10 and −10 kG at 1.8 K generates a hysteresis loop with a remnant magnetization of 0.011 Nβ and a coercive field of 90 G. The metamagnetic character is evident from the shape of the central portion of the loop (Fig. 3, inset b).

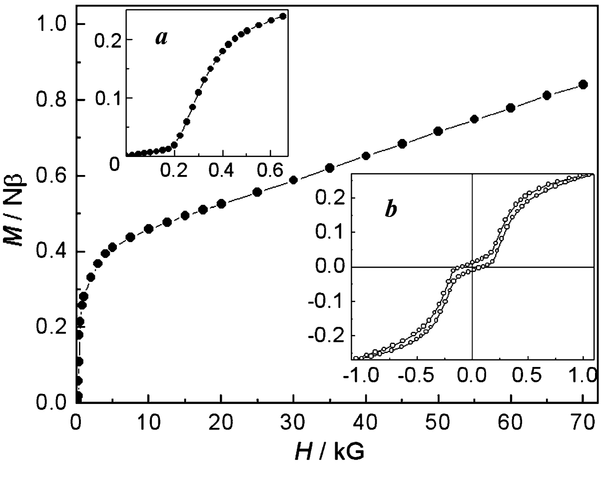

Fig. 3 Field dependence of magnetization at 1.8 K. Inset: a blow-up of the *M–H* plot in the lower field region (a) and the hysteresis loop (b).

Weak ferromagnetism due to spin canting, which is also termed "canted antiferromagnetism", has been recognized for a few 2D azido-bridged systems,[5,6] including a Mn(II) species with only single EE-azido bridges.[6] In this communication, we successfully obtained a 3D hybrid framework, in which 2D Mn(II)-azido inorganic layers are pillared by long and semi-rigid organic spacers. This compound represents the first 3D molecular metamagnet built of spin-canted antiferromagnetic metal-azido layers and demonstrates the great potential for tuning magnetic properties by the selection of organic spacers.§ Further investigations are under way, including more detailed magnetic characterization of the present complex and an extension of the strategy into related organic spacers.

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Notes and references

† **Caution!** Perchlorate salts in the presence of organic ligands are potentially explosive. Only a small amount of the materials should be prepared and handled with care. Anal. Calcd for $C_{14}H_{14}MnN_{10}$ (**1**): C, 44.6; H, 3.7; N, 37.1%. Found: C, 44.7; H, 3.6; N, 37.5%.

‡ Crystal data for **1**: $C_{14}H_{14}N_{10}Mn$, $Mr = 377.29$, monoclinic, $P2_1/c$, $a = 12.5610(7)$, $b = 8.5159(4)$, $c = 8.2206(4)$ Å, $\beta = 105.093(2)°$, $U = 849.01(7)$ Å^3, $T = 293$ K, $Z = 2$, $\rho_{calcd} = 1.476$ Mg m^{-3}, μ(Mo–Kα) = 0.798 mm^{-1}, $S = 1.041$, 13835 reflections measured, 1890 unique ($R_{int} = 0.0719$), $R_1 = 0.0728$, $wR_2 = 0.1240$ (all data). CCDC reference number 205051. See http://www.rsc.org/suppdata/cc/b3/b304536f/ for crystallographic data in CIF or other electronic format.

§ Recently, a 3D compound with similar structure has been reported to exhibit a weak ferromagnetic behavior, but it contains a rigid and much shorter spacer (pym) and does not exhibit metamagnetic behaviors.[9]

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