Coordination Polymers

A Unique 3D Alternating Ferro- and Antiferromagnetic Manganese Azide System with Threefold Interpenetrating (10,3) Nets**

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Azide-containing coordination polymers have received considerable attention for the construction of new molecule-based magnets.[1–4] The versatility of the azido ligand lies not only in its diverse bridging modes but also in it being an efficient magnetic coupler. The azido ligand generally mediates antiferromagnetic interactions when it bridges in an end-to-end (EE) mode, and ferromagnetic interactions in an end-on (EO) mode.[2] The many coordination polymers with azido bridges which have been reported include one-dimensional (1D) chains,[3] two-dimensional (2D) layers,[4] and three-dimensional (3D) networks,[5] and antiferromagnetic, ferromagnetic, alternating, and canted systems have been observed. Because it is believed that increasing dimensionality can enhance bulk magnetic properties,[6] the design of high-dimensionality (especially 3D) transition-metal–azido coordination polymers is attractive, but it still remains a great challenge. One approach to high-dimensionality magnetic coordination polymers is the designed self-assembly of azido bridging ligands with bis(monodentate) or bis(bidentate) ligands by. Several bis(monodentate) ligands such as 4,4-bipyridine, pyrazine, and pyrazine dioxide and the bis(bidentate) ligand bipyrimidine have successfully been utilized to construct 3D azide-containing coordination polymers.[5]

To date most azide-containing magnetic coordination polymers were synthesized by methods of conventional

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coordination chemistry, and there are still few reports on solvothermal synthesis of this type of complexes, although the solvothermal technique, which can not only overcome difficulties arising from differing solubilities of organic and inorganic precursors but can also produce metastable phases, has proved to be a powerful tool for crystallizing many novel transition-metal coordination polymers.[7] The only reported example of a metal coordination polymer with azido bridges prepared by solvothermal reaction is [CdN$_3$(3-ptz)] (3-ptz = 5-(3-pyridyl)tetrazolate),[7e] in which the metal centers are diamagnetic 3d^{10} cadmium ions. We are now exploring the solvothermal chemistry of azide-containing manganese coordination polymers and report herein the isolation of the novel 3D azide-containing magnetic complex [(Mn-$\mu_{1,3}$-N$_3$-$\mu_{1,1}$-N$_3$)$_2$L] (**1**) by using the bis(bidentate) Schiff base ligand 4,5-diazafluoren-9-one azine (L) as the long link and the infinite Mn-$\mu_{1,3}$-N$_3$-$\mu_{1,1}$-N$_3$ chain as the secondary building unit (SBU). This complex exhibits an interesting forbidden catenation framework with triple interpenetrating 3D (10,3) nets.

The 3D coordination polymer **1** was synthesized solvothermally from a mixture of L, Mn(ClO$_4$)$_2$·6H$_2$O, NaN$_3$, H$_2$O, and methanol in a thick Pyrex glass tube. The brown block crystals obtained are insoluble in common solvents. The IR spectrum of **1** shows two sharp bands at 2099 and 2077 cm^{-1}, which suggest the presence of both EO and EE azide bridges.

The crystal structure of **1** shows a 3D network that is composed of the 4,5-diazafluoren-9-one azine links and chains of Mn$^{\mathrm{II}}$ ions alternately connected by two EO and two EE azido bridges (Figure 1).[8] Each manganese atom is octahedrally coordinated to one ligand L (Mn–N1, N2, 2.248(6), 2.376(5) Å), two *cis*-EO (Mn–N6, N6#1, 1.952(6), 2.473(8) Å;#1 $1-x$, y, $-z+1/2$), and two *cis*-EE [Mn–N3, N5#2, 2.522(7), 2.150(5) Å; #2 $-x+1/2$, $-y+1/2$, $-z$) azido ligands. The nearest two Mn$^{\mathrm{II}}$ centers are bonded to each other by two EO azide bridges to generate an asymmetrical planar entity formed by two neighboring manganese ions and two terminal nitrogen atoms from two EO azido ligands (plane 1, defined by Mn1-N6-Mn1A-N6A). These dinuclear entities are further connected to each other through double EE azide bridges to form a manganese–azido chain running along the [101] direction. The double EE azide bridges and the two manganese atoms to which they connected are almost in a plane. The plane formed by Mn1-N3-N4-N5-Mn1B-N3B-N4B-N5B (plane 2) and the plane defined by Mn1A-N3A-N4A-N5A-Mn1D-N3D-N4D-N5D (plane 3) have a dihedral angle of 2.3°. The dihedral angles between planes 1 and 2 and planes 1 and 3 are 88.8 and 91.2°, respectively, that is, the three planes are almost perpendicular to one another.

Unusually, the double EE azide bridges connect the dinuclear entities in a *cis* arrangement (Figure 1 a), and this unique structural feature is quite different from other

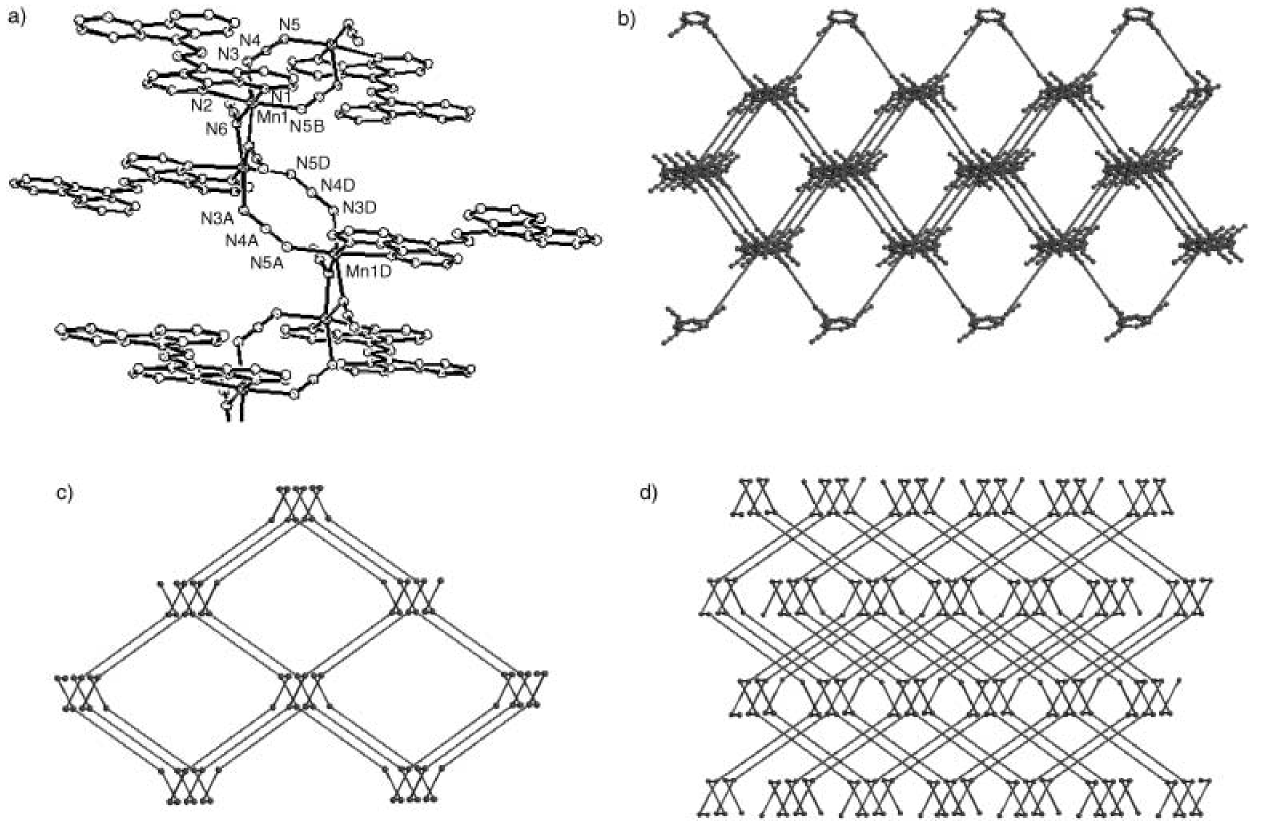

Figure 1. a) Infinite Mn–azido SBU linked by bis(bidentate) ligands L (4,5-diazafluoren-9-one azine). b) A 3D network in **1** along the [101] direction. For clarity, the long link represents the Schiff base ligand L. c) Projection of **1** along the [101] direction showing a 3D (10,3) network based on the topology of Mn–Mn connections. The short, medium, and long links represent the double EO azido, double EE azido, and bis(bidentate) Schiff base ligand L, respectively. d) Three parallel interpenetrating (10,3) nets in the structure of **1**.

reported chains of metal atoms and alternating EO/EE azido ligands, in which only *trans* arrangements of double EE azide bridges are present.[3a,h,e,i,m,q,p] The intrachain Mn···Mn distance through the EO azide bridges is 2.790 Å, much smaller than typical for this type of bridging,[2–5] and that through the EE bridges of 5.794 Å is longer than typical values.[2–5] The Mn-N-Mn bond angle in the EO azide bridges is 77.2(3)°, which is smaller than normal values.[2–5] For the EE azide bridges, the Mn1-N3-N4 and Mn1-N5-N4#2 angles are 134.5(5) and 131.8(5)°, respectively. The Mn-azido-Mn torsion angle τ, defined by the dihedral angle between the mean planes of Mn1-N3-N4-N5 and Mn1B-N5-N4-N3, is 5.5°, and the dihedral angle δ between the (EE-N_3)$_2$ plane and the N3-Mn1-N5B plane is only 2.9°. Both τ and δ values are significantly smaller than those for previously reported Mn^{2+} chains with alternating EE and EO azido bridges ($\tau = 19$–$64°$, $\delta = 10$–$35°$).[3p,r,4]

The structure of **1** consists of three identical interpenetrating nets, one of which is shown in Figure 1 b. The infinite Mn^{II}/alternating EO-EE azido chains are stacked parallel to one another and connected by bis(bidentate) ligands L to generate a 3D framework. The ligands L between the EE azido bridges are mutually parallel, while those between the EO azido bridges form an angle of 106°. 1D rhombic channels would be formed if no interpenetration happened. The threefold interpenetration in **1** increases the calculated filled space to 77.7 %, and the unit cell therefore contains no area accessible to residual solvent. To better illustrate this structure, the topology of Mn–Mn connections is presented in Figure 1 c and Figure 1 d. It exhibits interpenetrating three-connected 3D (10,3) nets, which are reminiscent of nets of the (10,3)-a type.[9] A characteristic feature of the (10,3)-a nets is the presence of parallel fourfold helices, all of the same handedness, and the net as a whole is thus chiral.[9] However, the manganese/alternating EO-EE azido chains in **1** run in a quite different way, similar to a shoelace, running around and crossing two parallel axes in a figure-of-eight fashion. Consequently, such a chain will have no handedness, because it is counteracted automatically by the opposite handedness owing to the double axes. To our knowledge, this type of (10,3) nets had not been reported before.[9]

The variation of the molar magnetic susceptibility χ_M for **1** was investigated in the temperature range 2–300 K (Figure 2). The χ_M value increases on cooling, reaches a rounded maximum at about 60 K, and then tends to zero at low temperature. The $\chi_M T$ value at room temperature is 8.0 cm^3 K mol^{-1}, somewhat smaller than the value expected for two uncoupled spin-only Mn^{II} ions (8.76 cm^3 K mol^{-1}). The $\chi_M T$ value decreases continuously upon cooling. These features indicate a dominant antiferromagnetic interaction. According to the structure, this complex should have alternating ferro (F)- and antiferromagnetic (AF) interactions mediated by double EO and double EE azido bridges, respectively. To evaluate the superexchange coupling constants, we tried to simplify this 3D magnetic system by treating it with the theoretical model for alternating F/AF $S = 5/2$ chains proposed by Cortés et al.[3i] Equation (1). This

$$\chi = [N g^2 \beta^2 S(S+1)/(3kT)][(1+u_1+u_2+u_1u_2)/(1-u_1u_2)] \qquad (1)$$

expression is based on the spin Hamiltonian $\mathcal{H} = -J_1 \Sigma S_{2i} S_{2i+1} - J_1 \Sigma S_{2i} S_{2i+1}$, where J_1 and J_2 are the alternating exchange constants for the EE and EO superexchange pathways, respectively, and the S operators are treated as classical spins where $u_i = \coth[J_i S(S+1)/kT] - kT/[J_i S(S+1)]$ ($i = 1, 2$).

A Weiss constant θ was then introduced by replacing T with $T-\theta$ in Equation (1) because of the possible presence of interchain antiferromagnetic interactions,[3p] mediated by the bis(bidentate) ligand L. By varying all the parameters, the best agreement between theory and experiment was obtained with $J_1 = -8.09$ cm^{-1}, $J_2 = 3.82$ cm^{-1}, $\theta = -2.0$ K, $g = 2.094$, and $R = 5.80 \times 10^{-4}$, which confirms alternating AF and F interactions with domination by the former, and the small negative θ value suggests a weak AF interchain interaction mediated by the bis(bidentate) ligand L. The J_{AF} (J_1) value is smaller than, but the J_F (J_2) and the θ values are comparable to, the corresponding values ($J_{AF} = -11.8$–-15.4 cm^{-1}, $J_F = 3.8$–8.0 cm^{-1}, and $\theta = -1.1$–-2.6 K) for reported Mn^{2+} chains with alternating EE and EO azido bridges and Schiff base ligands.[3p]

Interestingly, weak ferromagnetism, probably arising from spin canting, was observed at temperatures below 2 K. The divergence of the zero-field cooled (ZFC) and the field cooled (FC) magnetization $M(T)$ below 2 K indicates irreversible long-range magnetic order. Alternating-current susceptibility measurements show that both $\chi'\,'_{acac}(T)$ and $\chi''_{ac}(T)$ are frequency-independent, and this excludes any glassy behavior. The $\chi'_{ac}(T)$ curve exhibits a transition temperature at about 2 K, and a nonzero $\chi''_{ac}(T)$ component suggests hysteresis effects and an uncompensated moment. The small magnetization value at 1.8 K suggests the existence of a weakly spin canted moment. Isothermal magnetization experiments performed at 1.8 K showed hysteresis with a coercive field around 20 Oe and a remnant magnetization of 2.95 emu Oe mol^{-1} (Figure 3). The field dependence of the magnetization at 1.9 K shows a pronounced sigmoid shape corresponding to a spin-flop transition[5b,d,f] when the field is large enough (ca. 30 kOe), which happens if the Ising-like anisotropy is small with respect to the weakest antiferromagnetic interaction.[5b] This anisotropy interaction is probably produced by the strong intrachain interaction in the [101] direction through azido bridges in comparison with the weak

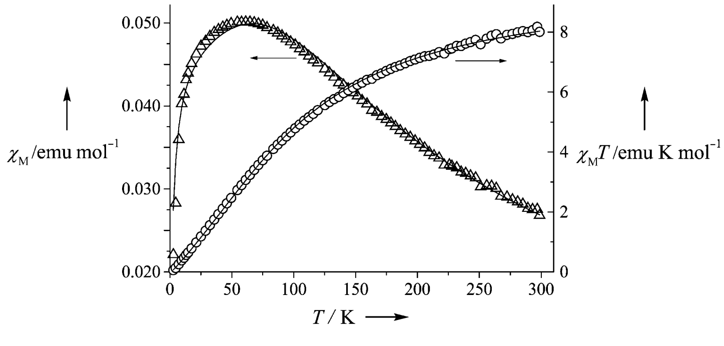

Figure 2. χ_M (△and $\chi_M T$ (●) versus T plots for **1**; the solid lines represent the best fit of the experimental data to Equation (1).

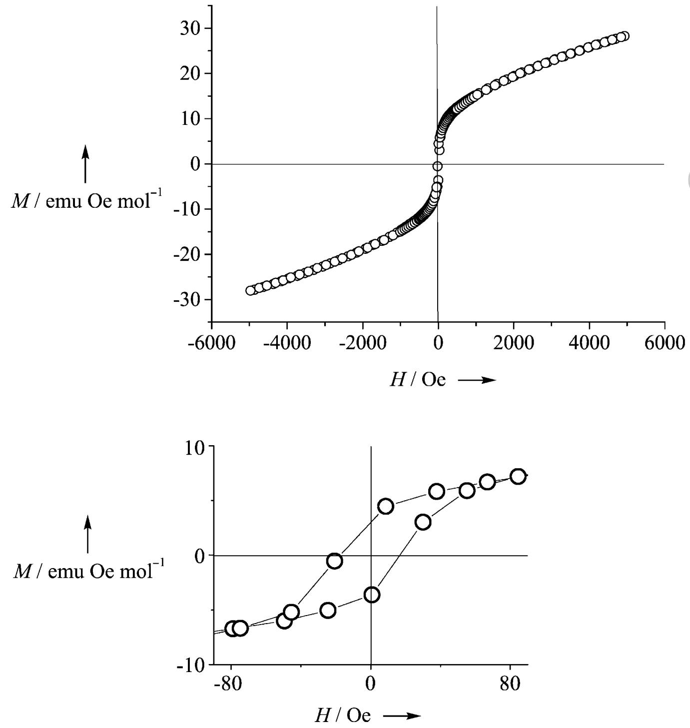

Figure 3. Top: hysteresis loop of **1** recorded at 1.8 K. Bottom: expansion of hysteresis region.

interchain interaction through 4,5-diazafluoren-9-one azine ligands. The magnetization is only 0.11 $N\beta$ at 70 kOe, far from the saturation value of 5 $N\beta$ expected for an $S = 5/2$ system, which is consistent with weak ferromagnetism owing to spin canting.[5f]

Recently, spin-canted ferromagnetism was found in a 1D Ni^{II} complex with single EE azido bridges[3l] and two 3D Mn^{II} complexes with double EE azido bridges.[5d,f] We have now found a 3D manganese coordination polymer with alternating EE azido and EO azido ligands that exhibits spin-canted long-range ferromagnetic ordering, which probably arises from a Dzyaloshinski–Moriya interaction.[11] Furthermore, this work also demonstrates that the solvothermal technique allows the crystallization of novel high-dimensionality azide-containing coordination polymers with magnetic properties.

Experimental Section

The ligand 4,5-diazafluoren-9-one azine was synthesized as described earlier.[10] A mixture of 4,5-diazafluoren-9-one azine (0.4 mmol), $Mn(ClO_4)_2 \cdot 6H_2O$ (0.4 mmol), NaN_3 (0.4 mmol), H_2O (0.2 mL), and methanol (1 mL) was placed in a thick Pyrex tube (ca. 15 cm long), the tube was frozen with liquid N_2, evacuated under vacuum and sealed with a torch. The tube was then heated at 110 °C under autogenous pressure for 2 days to give brown block crystals of **1** in 60 % yield. The elemental analysis of the bulk material was consistent with the formula proposed. IR (KBr pellet): $\tilde{\nu} = 2099$ (vs, $\nu_{as}(\mu_{1,1}\text{-}N_3^-)$), 2077 (vs, $\nu_{as}(\mu_{1,3}\text{-}N_3^-)$), 1330 (w, $\nu_s(\mu_{1,1}\text{-}N_3^-)$), 1631(w, $\nu_s(C{=}N)$), 1577(m, $\nu_s(C{=}C)$), 1476(w), 1404(m), 1280(w), 1165(w), 1091(w), 830(w), 753 cm^{-1} (m).

Caution: $Mn(ClO_4)_2 \cdot 6H_2O$ and NaN_3 are potentially explosive and should be handled with care.

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[8] Crystal data ($C_{22}H_{12}Mn_2N_{18}$): monoclinic, space group $C2/c$; $a = 9.2645(19)$, $b = 23.269(5)$, $c = 11.678(2)$ Å, $\beta = 103.04(3)°$, $V = 2452.5(9)$ Å^3, $Z = 4$, $\rho_{calc} = 1.729\,g\,cm^{-3}$, $\mu = 1.085\,mm^{-1}$, $R_1 = 0.0700$, $wR_2 = 0.1415$; Rigaku RAXIS RAPID IP imaging plate system with $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å), $T = 293(2)$ K; 3822 measured reflections ($5.00 \leq 2\theta \leq 71.54°$; $-15 \leq h \leq 15$, $-29 \leq k \leq 29$, $-11 \leq l \leq 11$), of which 2538 were unique ($R_{int} = 0.0955$) and 828 with $I > 2\sigma(I)$ were used in the refinement. The data were corrected for Lorentzian and polarization effects, and absorption corrections were applied. The structure was solved by direct methods and refined by a full-matrix least-squares technique based on F^2 using the SHELXL97 program. All non-hydrogen atoms were refined anisotropically. The end-on azido ligand was found to be disordered, and the refinement was carried out by considering two positions for each of the two uncoordinated nitrogen atoms with occupation factors fixed at 10.5. All hydrogen atoms were introduced at calculated positions as riding on a bonded atom. CCDC-218191 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).

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