New magnetic behaviour of honeycomb layered compounds. Crystal structures of $[M_2(bipym)(N_3)_4]$ (M = Co^{II}, Fe^{II}; bipym = 2,2′-bipyrimidine)

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A one-pot reaction of $Co(NO_3)_2\cdot6H_2O$ or $FeCl_2$, 2,2′-bipyrimidine (bipym) and NaN_3 affords the two $[M_2(bipym)(N_3)_4]$ (M = Co^{II} 1, Fe^{II} 2) honeycomb sheetlike compounds with alternating double end-on azide and bis(chelating) bipym bridging groups; magnetic susceptibility measurements indicate that they exhibit ferromagnetic (through the end-on azide) and antiferromagnetic (through bipym) magnetic interactions, their magnetization studies revealing the occurrence of metamagnetic like behaviour.

A lot of work has been devoted to the magneto-structural characterization of both homo- and hetero-metallic one-dimensional systems.[1–3] The most significant contribution of 2,2′-bipyrimidine [bipym, a bis(α-diimine)-type ligand] in this field was to afford the first examples of regular alternating ferro- (through a double hydroxo bridge) and antiferromagnetic (through the bipym bridge) interactions in copper(II) chains.[4] However, one of the major challenges in molecular magnetism in the last few years is the design of two- and three-dimensional magnetic systems, and in this respect, the role played by cyanide[5–7] and oxalate-type bis(chelating) ligands as assembling units has been crucial.[8–10] Very recently, taking advantage of the analogy between the coordinating behaviour of bipym and oxalate, we prepared the first honeycomb layered materials of formula $[Cu_2(bipym)(ox)_2]\cdot5H_2O$[11] and $[Mn_2(bipym)(ox)_2]\cdot6H_2O$[12] which behave as alternating magnetic planes with antiferromagnetic interactions through both bipym and oxalate (ox) bridges. The remarkable ability of these bridging ligands to mediate strong antiferromagnetic coupling between magnetic centres separated by more than 5 Å is illustrated by the large singlet–triplet energy gap which can be achieved in their dinuclear copper(II) complexes [up to 380 (ox) and 236 cm^{-1} (bipym)].[13,14] A natural extension of this work would be the design of magnetic planes with alternating ferro- and antiferromagnetic interactions. Given that the azide bridge can mediate ferromagnetic coupling between divalent first-row transition-metal ions when adopting an end-on bridging mode,[15,16] we have tried to polymerize the bipym bridged dinuclear $[M_2(bpym)]^{2+}$ unit through the end-on azide. We describe here our first magneto-structural results concerning the new assembly $[M_2(bipym)(N_3)_4]$ (M = Co^{II} **1**, Fe^{II} **2**) with a two-dimensional network structure.

The sheetlike polymers **1** and **2** were easily obtained in almost quantitative yields as orange (**1**) and brown (**2**) polycrystalline powders by adding an aqueous solution of NaN_3 (2 mmol, 5 ml) to an aqueous solution of $[Fe_2(bipym)Cl_4]$ or $[Co_2(bipym)(NO_3)_4]$ (0.5 mmol, 15 ml). Parallelepiped (**1**) and plate-like (**2**) single crystals were grown by slow diffusion techniques in an H-shaped tube.†

X-Ray crystallography reveals that **1** and **2** are sheetlike isostructural compounds (Fig. 1).‡ The structure is made up of parallel sheets of metal ions (M = Co **1**, Fe **2**) linked by two end-on azide and bipym ligands. Within each sheet chains of azide-bridged metal ions are joined by bis-chelating bipym molecules. The same structure was recently found for the analogous manganese compound **3**.[17] The metal atoms in **1–3** exhibit very distorted octahedral environments, the distortion being mainly due to the small value of the angles subtended at the metal atom by bipym [75.8(2) (**1**), 74.0(1) (**2**) and 71.3(1)° (**3**)] and azido [76.8(2) (**1**), 77.5(1) (**2**) and 78.0(1)° (**3**)] groups. A lengthening of the M–N distances was found in this series, as expected when going from Co to Mn. The metal–metal separations through bipym and bridging azide groups are 5.815(2) (**1**), 5.928(2) (**2**), 6.142(1) Å (**3**), for the former and 3.335(1) (**1**), 3.369(1) (**2**), 3.428(1) Å (**3**), for the latter. The shortest bipym···bipym intralayer distances are 5.693(4), 5.755(3) and 5.876(2) Å for **1**, **2** and **3**, respectively.

The magnetic properties of compounds **1–3** are shown in Fig. 2. The $\chi_M T$ values [insert of Fig. 2(*a*)] at room temperature [7.0 (**1**), 8.4 (**2**) and 9.3 (**3**) $cm^3\ mol^{-1}\ K$] are greater than those

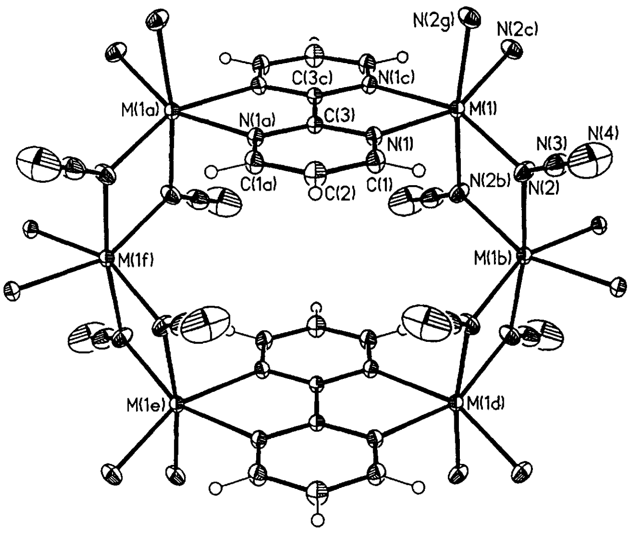

Fig. 1 Hexanuclear repeating unit of the crystal structure of **1** (M = Co) and **2** (M = Fe) showing the atom numbering (ellipsoids are at the 30% probability level). Selected bond distances (Å) and angles (°): compound **1**: Co(1)–N(1) 2.182(3), Co(1)–N(2) 2.082(4), Co(1)–N(2b) 2.175(4); N(1)–Co(1)–N(2) 93.3(1), N(1)–Co(1)–N(1c) 75.8(2), N(2)–Co(1)–N(1c) 157.4(1), N(1)–Co(1)–N(2b) 101.9(1), N(2)–Co(1)–N(2b) 76.8(2), N(2)–Co(1)–N(2c) 103.2(2), N(1)–Co(1)–N(2g) 86.0(1), N(2)–Co(1)–N(2g) 96.9(1), N(2b)–Co(1)–N(2g) 170.1(2), Co(1)–N(2)–Co(1b) 103.2(2), N(2)–N(3)–N(4) 179.0(6). Compound **2**: Fe(1)–N(1) 2.222(2), Fe(1)–N(2) 2.118(2), Fe(1)–N(2b) 2.201(3); N(1)–Fe(1)–N(2) 92.3(1), N(1)–Fe(1)–N(1c) 74.0(1), N(2)–Fe(1)–N(1c) 156.6(1), N(1)–Fe(1)–N(2b) 100.3(1), N(2)–Fe(1)–N(2b) 77.5(1), N(2)–Fe(1)–N(2c) 106.3(1), N(1)–Fe(1)–N(2g) 86.3(1), N(2)–Fe(1)–N(2g) 97.5(1), N(2b)–Fe(1)–N(2g) 171.8(1), Fe(1)–N(2)–Fe(1b) 102.5(1), N(2)–N(3)–N(4) 177.8(3) (symmetry code: b 1.5–*x*, 1.5–*y*, –*z*; c 1 –*x*, *y*, –*z*; g *x* –0.5, 1.5 –*y*, *z*).

expected for the pairs of magnetically uncoupled metal ions. These values increase on cooling, reaching maxima at 80 (**1**), 60 (**2**) and 25 K (**3**), and then rapidly decrease. The susceptibility curves [Fig. 2(*b*)] present maxima at 66 (**1**), 50 (**2**) and 15 K (**3**), but curiously, the susceptibility values remain constant and are very large below 30 (**1**), 25 (**2**) and 10 K (**3**), and therefore, the $\chi_M T$ values decrease linearly with T. In fact, magnetization measurements below these temperatures and in the low-field region show a linear dependence *vs.* the field with the same slope at any temperature [Fig. 2(*a*)]. The magnetization becomes strongly field dependent in the high-field region. This dependence ressembles metamagnetic behaviour[18] but in contrast to a classical metamagnet, the critical fields are extremely temperature dependent and the different isotherms do not present a common crossing point. These features are shown in Fig. 2(*a*) for **3**. Similar behaviour is observed for compounds **1** and **2** but for greater values of critical fields and thus, magnetic measurements at higher fields are required to reach saturation. Anisotropic magnetic susceptibility measurements as a function of the applied field and temperature are in progress in order to obtain further insights into this interesting phenomenon.

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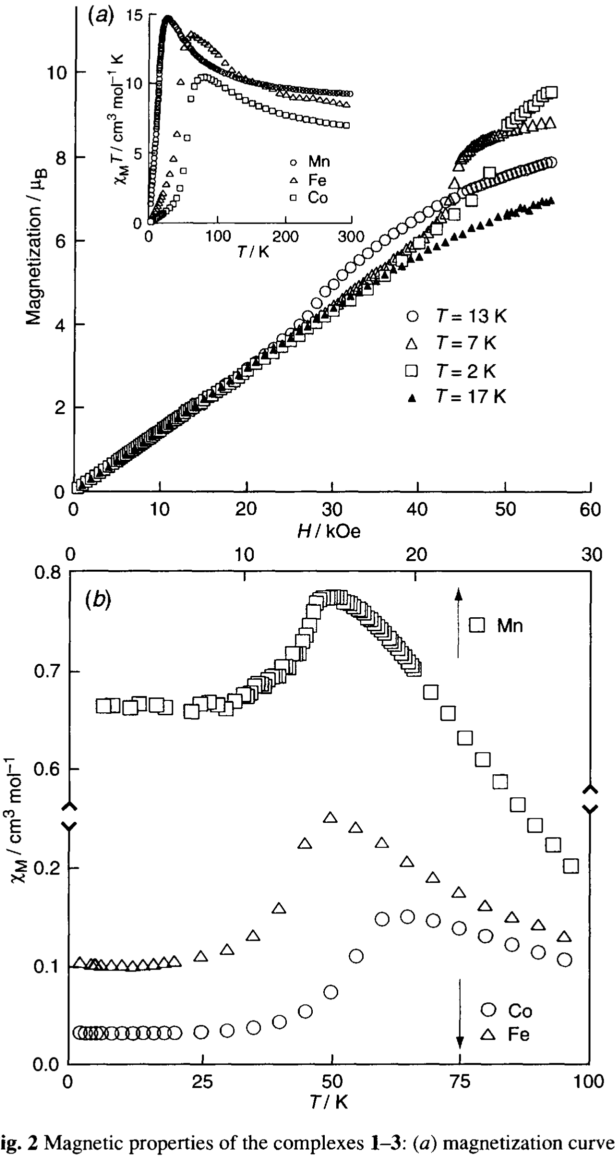

Fig. 2 Magnetic properties of the complexes **1–3**: (*a*) magnetization curves as a function of the applied field at low temperatures for **3** (the insert shows the thermal variation of the $\chi_M T$ product for **1–3**, χ_M being the magnetic susceptibility per two metal ions); (*b*) thermal dependence of the magnetic susceptibility at $T < 100$ K

Footnotes

† Satisfactory elemental analyses (C, H, N) were obtained. Strong absorptions at 1570 (**1**) and 1575 cm^{-1} (**2**) (ring stretching mode of bipym) reveal the presence of bis(chelating) bipym[14] and very strong bands at 2070 (**1**) and 2075 cm^{-1} (**2**) [$\nu_{as}(N_3^-)$ stretching vibration] in the IR spectra are consistent with end-on bridging azide.[16]

‡ *X-Ray crystal structure analyses*: Siemens R3m/V automatic diffractometer, Mo-Kα radiation, $\lambda = 0.710\,73$ Å, graphite monochromator, 295 K. Lorentz polarization and absorption corrections. *Data collection, solution and refinement*: ω–2θ, standard Patterson methods and subsequent Fourier recycling, SHELXTL-PLUS computer program. The two compounds are isostructural, with formula $C_8H_6M_2N_{16}$ (M = Co **1**, Fe **2**), monoclinic, space group *C2/m*. For **1**, $a = 5.978(2)$, $b = 14.591(3)$, $c = 8.971(2)$ Å, $\beta = 96.18(2)°$, $U = 777.9(4)$ Å^3, $Z = 2$, $D_c = 1.896$ g cm^{-3}. Orange laminar crystals, crystal size 0.30 × 0.12 × 0.03 mm. 1005 reflections measured in the range $3 < 2\theta < 54°$, 896 unique, and 779 assumed as observed with $I > 3\sigma(I)$; $R = 0.044$, $R_w = 0.047$. For **2**, $a = 6.104(2)$, $b = 14.711(4)$, $c = 8.931(2)$ Å, $\beta = 95.24(2)°$, $U = 798.6(4)$ Å^3, $Z = 2$, $D_c = 1.821$ g cm^{-3}. Brown parallelepiped crystals, crystal size 0.38 × 0.12 × 0.07 mm. 1026 reflections measured in the range $3 < 2\theta < 54°$, 916 unique, and 807 assumed as observed with $I > 3\sigma(I)$. $R = 0.029$, $R_w = 0.034$. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, Issue No. 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 182/261.

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