A two-dimensional azido-based topologic ferrimagnet†

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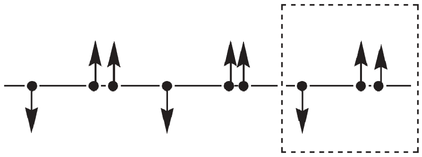
Received (in Cambridge, UK) 7th September 2004, Accepted 25th October 2004
First published as an Advance Article on the web 8th December 2004
DOI: 10.1039/b413665a

The reported Mn^{II}–azide system is the first example of a two-dimensional homometallic ferrimagnet, in which the magnetic properties are due exclusively to topological reasons related with the coordination mode of the bridging ligands; it is also the first case in which a system of this kind exhibits long range order comparable to the classical heterospin ferrimagnets.

Azido ligand chemistry has provided in recent years a large number of compounds, from molecular to 3-D systems.[1] In addition, the versatility of this ligand in being able to coordinate in $\mu_{1,1}$ (end-on, EO) or $\mu_{1,3}$ (end-to-end, EE) modes which typically promote ferromagnetic (F) or antiferromagnetic (AF) interactions[1,2] gives a rich magnetic playing field. One of the most interesting consequences of the co-existence of EE and EO modes in the same compound is the large number of topologies for alternating systems found to date.[3] We have reported three extremely rare examples of 1-D systems in which the unusual alternance of a pair of AF interactions followed by at least one F interaction results in homometallic ferrimagnetic response,[4] Scheme 1. Very recently, a new 1-D azido derivative with similar properties was reported by other authors.[5]

Conventional ferrimagnetic systems (oxalato or cyanide networks are a good example),[6] defined as heterospin systems which interact exclusively by means of AF coupling, are able to exhibit long range ferromagnetic order and the synthetic procedures are well established. In contrast, the increase of dimensionality in heteroligand homometallic systems, yielding ferrimagnetic order, is a synthetic challenge. Azido ligand is one of the candidates for obtaining systems of this kind combining its coordination (EE and EO) and magnetic (AF and F) properties. In this work we present an unprecedented example of a 2-D network with formula $[Mn(4\text{-}N_3py)_2(N_3)_2]_n$ (4-N_3py = 4-azidopyridine) which follows the alternance pattern (EO–EE–EE–EO) in two dimensions and then exhibits ferrimagnetic behaviour. In addition to the formal ferrimagnetic response, this system shows long range order with $Tc = 18$ K with magnetic properties fully comparable to those of conventional heterospin ferrimagnets. Moreover, it is remarkable that in our case, the low T ferrimagnetic network shows an unusual mean S value of 5/3 per paramagnetic center.



Scheme 1 Ferrimagnetic 1-D arrangement of homometallic spins following an EE–EE–EO alternance pattern.

Compound **1** consists of a two-dimensional Mn^{II}–azide arrangement.[7] The Mn^{II} atoms are hexacoordinated, bonded to two *trans* 4-N_3py and four azido bridging ligands. The planes can be properly described as Mn(1)–($\mu_{1,1}$-N_3)$_2$–Mn(1A) dinuclear subunits linked by means of end-to-end azido bridges and an intermediate Mn(2) center (Fig. 1).

The centrosymmetric Mn(1)–($\mu_{1,1}$-N_3)$_2$–Mn(1A) subunit is planar, showing a Mn(1)–N(11)–Mn(1A) bond angle of 99.6(2)°. Mn(1)–N(21)–N(22) and Mn(1)–N(31)–N(32) bond angles are very different with values of 125.2(4)° and 167.5(5)°, respectively. The four azido ligands coordinated to Mn(2) act as EE bridges, showing Mn(2)–N(23)–N(22) and Mn(2)–N(33)–N(32) bond angles of 137.9(4)° and 127.2(4)°. The Mn(1)–N(23)–N(21)–Mn(2) torsion angle is 97.8(5)° whereas Mn(1)–N(31)–N(33)–(Mn2A) is practically planar, with a torsion angle of 0.3(2)°. From these structural data the magnetic properties of this compound can be envisaged as an alternating ferro–antiferromagnetic system: the Mn–N–Mn bond angle related to N(11) (EO mode) lies in the typical ferromagnetic range of interaction[1,8] whereas the two different EE bridges should give AF coupling. The two AF interactions mediated by the EE bridges can be expected to be moderate, because the AF coupling shows a strong dependence on the bond parameters, mainly bond angles: as was previously demonstrated,[9] large bond angles, such as Mn(1)–N(31)–N(32) or torsion angles close to 90° such as Mn(1)–N(23)–N(21)–Mn(2), reduce clearly the AF interaction. Susceptibility measurements on compound **1** are in full agreement with this analysis (Fig. 2).

At room temperature the $\chi_M T$ value (4.10 cm^3 K mol^{-1}) is very close to the value of 4.375 for an isolated Mn^{II} ion. $\chi_M T$ decreases on cooling down to a minimum placed at 55 K, which is the signature of the ferrimagnetic response of this system. Below 50 K, $\chi_M T$ becomes field dependent, reaching a maximum at 15 K, indicative of long range order. In agreement with these data, AC experiments show a frequency-independent maximum at 18 K. Magnetization measurements show a saturation $2S$ value of 1.60 in full agreement with the expected value of 5/3. The hysteresis loop at 2 K has a remnant magnetization of $2S = 0.59$ and a coercive field of 225 G, Fig. 3.

In the light of the above experimental results and the expected interactions for the EE and EO azido bridges, the magnetic properties of compound **1** are the result of the interaction pattern shown in Scheme 2: the high T region is dominated by the AF interactions through the EE azido bridges down to a minimum of susceptibility. Below this point the ferromagnetic interaction

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† Dedicated to Prof. Dr Harald P. Fritzer on the occasion of his 70th birthday.

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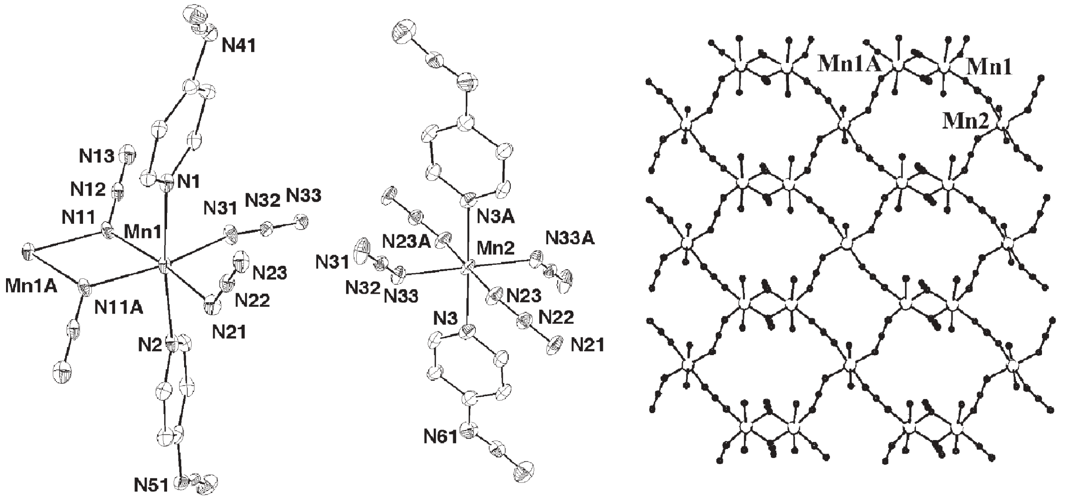


Fig. 1 Left side, ORTEP plot of the manganese environments of **1** (the thermal ellipsoids are set at 30% probability). Right side, a view of a 2-D sheet, showing the bridges between the Mn(1)–Mn(1A) and Mn(2) subunits. Axial pyridinic ligands are not shown in the plot.

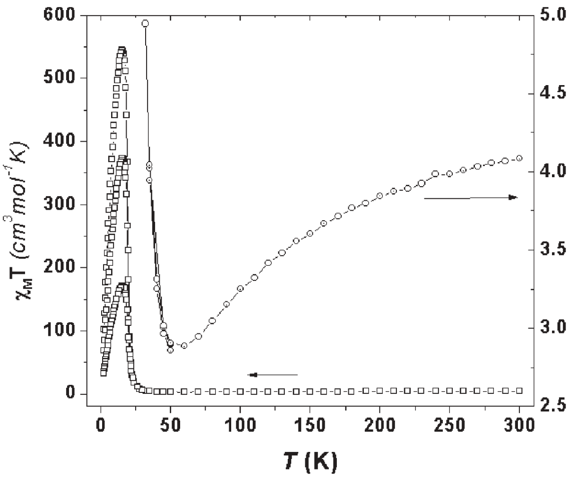


Fig. 2 Susceptibility *versus* T plot for compound **1** (by Mn atom). Open squares (left axis) show the overall magnetic response under external magnetic fields of 300, 100 and 50 G. Open circles (right axis) show in detail the high T paramagnetic region. Solid lines are an eye-guide.

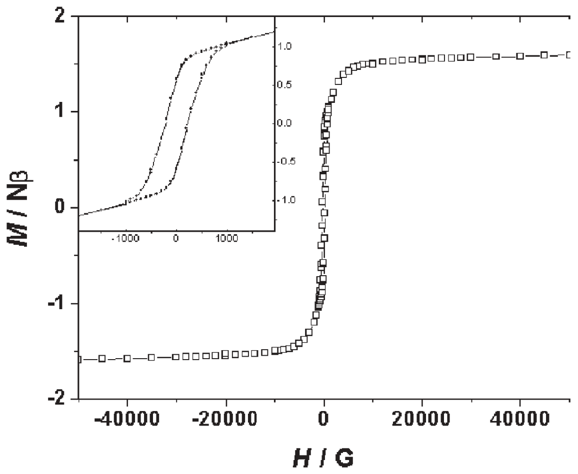
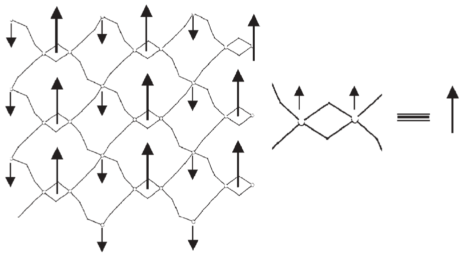


Fig. 3 Magnetization plot at 2 K for compound **1** in the ± 5 T range (by Mn atom). Inset, detail of the hysteresis cycle. Solid line is a guide for the eye.

promoted by the EO azido bridges becomes operative. Calculation of J coupling constants is not possible by conventional methods. At lower T, the ferrimagnetic system shows long range order as a system of local spins S = 5/2 and 10/2 coupled antiferromagnetically.

The above studied compound shows the ability of heteroligand systems to reach ferrimagnetic response even for homometallic compounds, in contrast with the common ferrimagnetic systems based on heterometallic and homoligand systems.

Experimental section: The title complex was synthesized by mixing a methanolic solution (10 mL) of $Mn(NO_3)_2{\cdot}4H_2O$ (0.25 g, 1.0 mmol) and 0.4 g (2.0 mmol) of 4-bromopyridine dissolved in 5 mL of methanol, followed by dropwise addition of a concentrated aqueous solution of sodium azide (0.13 g, 2.0 mmol). The final colorless solution was left to stand in the dark at room temperature for some weeks until crystallisation, yield 30%. Characteristic IR bands (KBr pellet): 2456, 2271 (4-N_3py), 2132, 2097, 2072 (shoulders in a broad band, N_3^-). Reaction of sodium azide with halopyridines is a general method for the syntheses of azidopyridines,[10] but in this case, may be enhanced by the presence of the Mn^{2+} ions, the reaction takes place in mild conditions at room temperature. It should be noted that the 4-N_3py ligand was not produced if the above solution was kept in a cold place.



Scheme 2 Low T spin arrangement for $[Mn(4\text{-}N_3py)_2(N_3)_2]_n$.

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7 X-ray structural analysis: Bruker-AXS SMART APEX CCD diffractometer, graphite monochromator, MoKα radiation (λ = 0.71073 Å), ω-scans, SHELXTL/PC program set for structure solution (direct methods) and refinement (full-matrix least-squares on F^2). Positions of hydrogen atoms were calculated (riding model). **1**: [Mn(4-azidopyridine)$_2$(N$_3$)$_2$]$_n$, $C_{15}H_{12}Mn_{1.5}N_{21}$, M_r = 568.87, 0.30 × 0.20 × 0.15 mm, triclinic, space group *P*-1, a = 8.341(2), b = 11.540(2), c = 11.685(2) Å, α = 90.63(3), β = 91.84(3), γ = 98.94(3)°, V = 1110.4(4) Å^3, Z = 2, D_c = 1.701 g cm^{-3}, T = 100(2) K, μ(MoKα) = 0.922 mm^{-1}, θ_{max} = 25°, 8005 reflections collected, 3858 unique (R_{int} = 0.0610), 2817 observed [$I > 2\sigma(I)$]. 340 parameters refined, with R = 0.0761 [$I > 2\sigma(I)$], wR_2 = 0.2137 (all data), GOF = 1.089, residual electron density: 0.982, −0.963 eÅ^{-3}. CCDC 239517. See http://www.rsc.org/suppdata/cc/b4/b413665a/ for crystallographic data in .cif or other electronic format. These data can be obtained free of charge *via* www.ccdc.cam.ac.uk/conts/retrieving.html.

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