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$[M(N_3)_2(L)]_n$: building 3-D M^{II}–azido networks with new topologies

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Received (in Cambridge, UK) 1st October 2001, Accepted 21st November 2001
First published as an Advance Article on the web 21st December 2001

Novel 3D topologies combining diazine and azido bridges between Mn^{II} magnetic centres have been obtained and characterised by low-temperature magnetic measurements.

After the successful application of the cyanide ligand to generate high-dimensional systems with magnetic ordering close to room temperature[1] or high nuclearity clusters with large ground spin state,[2] other ligands that are able to build 3-D structures and simultaneously are good superexchange mediators (oxalate,[3] oxamido,[4] dicyanamide[5]), have been widely studied in recent years. The azido ligand is a good candidate to join these already classical bridges due to its ability to transmit moderate or strong magnetic interactions and easily generate 1-D or 2-D systems[6a] or can contribute to generate high-spin clusters.[6b] Design of high-dimensional azido-networks is poorly developed, but recently some 3-D Mn^{II}–azido systems have been characterised, three of them with only azido bridges ($[Mn(N_3)_2(py)_2]$,[7] $Cs[Mn(N_3)_3]$[8] and $(NMe_4)[Mn(N_3)_3]$[9]) and two systems with formula $[Mn(N_3)_2(L)]_n$ (L = 4,4′-bipyridyl[6,10] or bipyrimidine[11]), built from the elegant strategy of mixing aromatic polydentate 4,4′-N-donors with bridging azido ligands. It is interesting to point out that this strategy fails for the donors pyrazine or 4,4′-bipyridylethane, for which only 2-D systems were obtained.[12] In contrast, little attention[13] has been devoted to 3-D azido systems with ions different to Mn^{II} or with 1,2- or 1,3-diazines, in spite of their potential possibilities. In this paper we have successfully explored the strategy to generate new 3-D topologies from these diazines and we present the structural characterisation† and the magnetic properties of these new types of Mn^{II} compounds.

The reaction of $Mn(NO_3)_2$, NaN_3 and pyridazine (pydz) or pyrimidine (pym) in methanolic media yields compounds with formula $[Mn(N_3)_2(L)]_n$ in which L = pydz (**1**) or L = pym (**2**).

For compound **1** the octahedral coordination around the Mn^{II} atoms is achieved by means of two pydz and four azido ligands. The structure consists of dinuclear units triply bridged by two pydz and one end-on (EO) azido, linked to six equivalent units by means of six end-to-end (EE) single azido bridges. The extended 3-D network may be envisaged as quadratic layers of dinuclear units linked to the neighbouring layers by means of axial EE azido ligands, Fig. 1. Bond lengths and angles inside the dimeric unit lies in the normal range reported to date, except for the very large Mn–N–Mn bond angle of 112.6(2)° for the EO-azido bridge. The Mn(1)···Mn(2) distance in these units is 3.613(1) Å. Mn–N–N bond angles between the dimeric units lies between 130.2(4) and 154.2(5)° and the torsion angle Mn–N–N–N–Mn takes values between 79.3(6) and 97.1(8)° for the three non-equivalent EE azido bridges. The Mn(1)···Mn(2) distances through the EE bridges lie between 5.754(2) and 6.062(2) Å.

The structure of **2** consists of a 3-D manganese–azido–pyrimidine network, Fig. 2. The 3-D system can be envisaged as metal–pyrimidine chains, placed in parallel planes. Mn atoms lie on inversion centres, pym ligands lie across mirror planes and azido ligands lie about 2-fold axes. Each metallic atom of one chain is linked by means of four end-to-end azido bridges to two similar chains placed in the upper plane and two similar chains placed in the lower plane. M–N–N bond angles lie around 127° and M–N–N–N–M torsion angles are close to 104° and 132° for the two non-equivalent azido bridges.

The magnetic behaviour of $[Mn(N_3)_2(pydz)]_n$ **1** is indicative of an overall weak antiferromagnetic (AF) coupling, Fig. 3. The

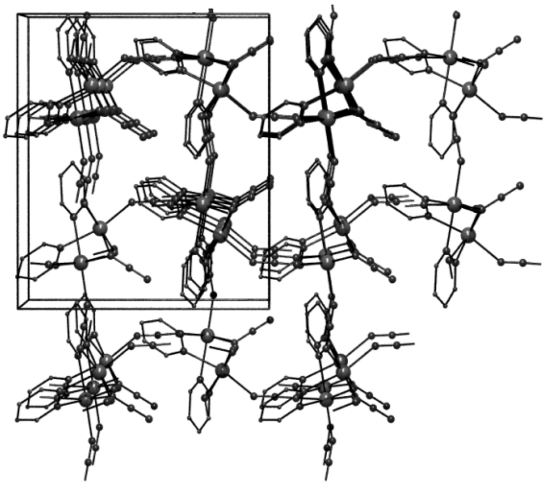

Fig. 1 A view along the (010) direction of $[Mn(N_3)_2(pydz)]_n$ **1**, showing the triply bridged dinuclear units and the connectivity that generates the 3-D network.

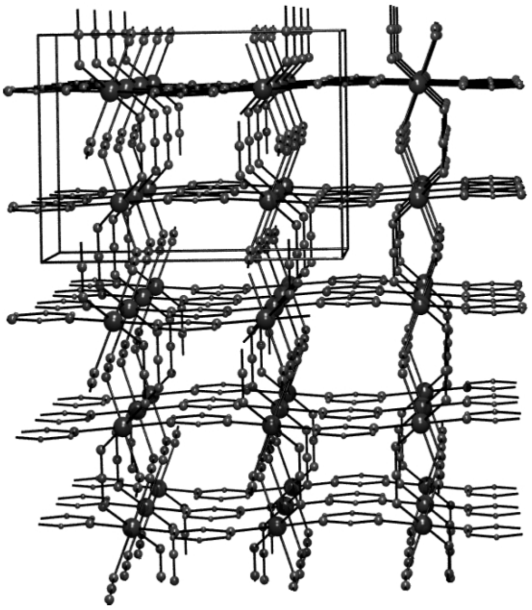

Fig. 2 A view along the (100) direction of $[Mn(N_3)_2(pym)]_n$ **2**, showing the crossed layers of azido and pyrimidine bridges.

DOI: 10.1039/b108812b

value of $\chi_M T$ at room temperature (3.97 cm^{-3} K mol^{-1}) is only slightly lower than that expected for isolated Mn^{II} ions and the χ_M plot shows a maximum of susceptibility at 6 K. Increase of $\chi_M T$ at low T indicates a small amount of paramagnetic impurities (< 1%). This maximum of susceptibility is anomalously shifted to low temperatures compared with other high-dimensional Mn^{II} and EE azide systems with similar bond parameters in the bridging region.[6] The complicated topology of this alternating 3D system makes impossible to calculate the superexchange parameters by conventional methods.

Two main superexchange pathways are present in this 3-D compound: one through the triply bridged manganese ions (pydz/EO azide bridges) and one through the three single EE azido bridges. It is well established that the interaction between Mn^{II} ions through EE azido bridges should always be antiferromagnetic,[14] and all reported comparable manganese–azide 2D and 3D systems show moderate AF coupling with a maximum of susceptibility typically around 30–40 K.[6] On the other hand, Thompson *et al.* have been studied the mixed pydz–EO azide bridges for Cu^{II} systems, concluding that the character of the superexchange interaction is a balance between the opposite characteristics of the pydz (which allows moderate or strong AF coupling) and the EO azide bridge which allows strong or moderate ferromagnetic (FM) coupling (for Cu–N–Cu bond angles lower than 108°).[15] DFT calculations[16] have confirmed the maximum of FM interaction at 84° for a Cu–N–Cu, shifted to 105° for Ni–N–Ni and 114° for Mn–N–Mn bond angles. Recently, a practically non-coupled Ni^{II} system with two pydz and one EO thiocyanate bridge has been reported[17] (Ni–N–Ni bond angle close to 105°). From these previous experimental data, the weaker AF coupling found for $[Mn(N_3)_2(pydz)]_n$ suggest than the interaction through the triply pydz EO azide bridges may be ferromagnetic and then competitive ferro-antiferromagnetic interactions in the 3D network reduces the apparent overall AF coupling.

Compound **2** shows a dominant AF coupling in the paramagnetic region ($\chi_M T$ at room temperature = 3.50 cm^{-3} K mol^{-1}) as may be expected for EE azido and pyridazine bridges, Fig. 3. A χ_M plot measured under an external field of 1 T shows a broad maximum at 50 K and a practically constant value below 40 K. Measurements under variable field and ZFC–FC measurements (100 G) indicates a weak ferromagnetic ordering close to the maximum of susceptibility, T_C = 50 K, due to a canting phenomenon which originates from the large dihedral angle of 65.8° between the Mn–azido planes of neighbouring units, similar to those found in related 2-D systems.[6,18] Magnetic hysteresis with a coercitive field of 350 G but very weak (0.003 $N\beta$) remnant magnetisation was observed at 2 K.

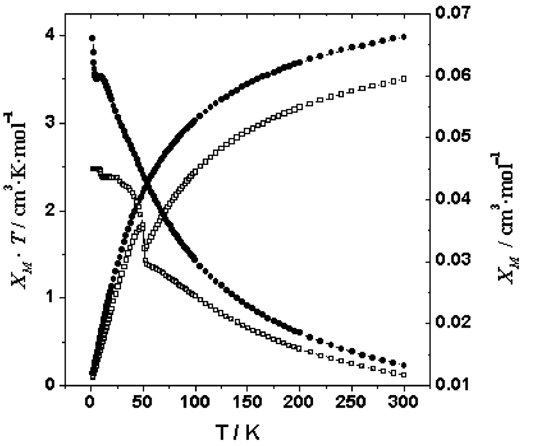

Fig. 3 Plots of $\chi_M T$ (left axis) and χ_M (right axis) *vs.* T for complexes **1** (●) and **2** (□); external field 0.01 T).

The synthetic strategy used for compounds **1** and **2** has been extended to the corresponding isostructural Fe^{II} or Co^{II} derivatives. It should be noted that the characterisation of series of 3-D derivatives for different ions opens, for the first time, the possibility to generate mixed 3-D ferrimagnetic networks based on the azide ligand.

Notes and references

† *Crystal data* for $C_8H_8Mn_2N_{16}$ **1** and $C_4H_4MnN_8$ **2**: M = 438.18 (219.09), orthorhombic, $Pna2_1$ ($I2/m$), a = 14.620(4), b = 8.551(2), c = 13.214(3) Å (a = 7.647(3), b = 12.300(4), c = 8.734(3), β = 91.47(3)°), U = 1652.0(7) (821.2(5)) $Å^3$, Z = 4 (4), D_c = 1.762 (1.772) Mg m^{-3}, μ(Mo-Kα) = 1.56 (1.571) mm^{-1}, T = 88 (298) K. The data were collected on a modified STOE four circle diffractometer. Of 2633 (1169) data, 2.76 < θ < 29.70° (2.9 < θ < 26.5°), 2132 (761) were observed [$I > 2\sigma(I)$]. The structures were solved by direct methods and subsequently refined against F^2. 235 (66) parameters refined, $R(F)$ = 0.0477 (0.050), wR_2 = 0.0995 (0.140). CCDC reference numbers 172083 and 172084. See http://www.rsc.org/suppdata/cc/b1/b108812b/ for crystallographic data in CIF or other electronic format.

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