*Inorg. Chem.* **2005**, *44*, 1786–1793

Inorganic Chemistry
Article

# Rare Azido-Bridged Manganese(II) Systems: Syntheses, Crystal Structures, and Magnetic Properties

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Received November 2, 2004

Two new polymeric azido-bridged manganese complexes of formulas $[Mn(N_3)_2(bpee)]_n$ (**1**) and $\{[Mn(N_3)(dpyo)Cl(H_2O)_2](H_2O)\}_n$ (**2**) [bpee, *trans*-1,2-bis(4-pyridyl)ethylene; dpyo, 4,4′-dipyridyl *N,N′*-dioxide] have been synthesized and characterized by single-crystal X-ray diffraction analysis and low-temperature magnetic study. Both the complexes **1** and **2** crystallize in the triclinic system, space group $P\bar{1}$, with $a = 8.877(3)$ Å, $b = 11.036(3)$ Å, $c = 11.584(4)$ Å, $\alpha = 72.62(2)°$, $\beta = 71.06(2)°$, $\gamma = 87.98(3)°$, and $Z = 1$ and $a = 7.060(3)$ Å, $b = 10.345(3)$ Å, $c = 11.697(4)$ Å, $\alpha = 106.86(2)°$, $\beta = 113.33(2)°$, $\gamma = 96.39(3)°$, and $Z = 2$, respectively. Complex **1** exhibits a 2D structure of $[–Mn(N_3)_2–]_n$ chains, connected by bpee ligands, whose pyridine rings undergo $\pi$–$\pi$ and C–H$\cdots\pi$ interactions. This facilitates the rare arrangement of doubly bridged azide ligands with one end-on and two end-to-end (EO-EE-EE) sequence. Complex **2** is a neutral 1D polymer built up by $[Mn(N_3)(dpyo)Cl(H_2O)_2]$ units and lattice water molecules. The metals are connected by single EE azide ligands, which are arranged in a cis position to the Mn(II) center. The 1D zipped chains are linked by H-bonds involving lattice water molecules and show $\pi$–$\pi$ stacking of dpyo pyridine rings to form a supramolecular 2D layered structure. The magnetic studies were performed in 2–300 K temperature range, and the data were fitted by considering an alternating chain of exchange interactions with $S = 5/2$ (considered as classical spin) with the spin Hamiltonians $H = -J_i\Sigma(S_{3i}S_{3i+1} + S_{3i+1}S_{3i+2}) - J_2\Sigma S_{3i-1}S_{3i}$ and $H = -J_i\Sigma S_{2i}S_{2i+1} - J_2\Sigma S_{2i+1}S_{2i+2}$ for complexes **1** and **2**, respectively. Complex **2** exhibits small antiferromagnetic coupling between the metal centers, whereas **1** exhibits a new case of topological ferrimagnetism, which is very unusual.

## Introduction

During the last two decades scientists of different horizons made significant contributions in the field of molecular magnetism.[1−6] Coordination chemists initiated to build up polynuclear architecture of paramagnetic metal ions using suitable bridging ligands,[4−6] and pseudohalides were one of the initial choices for this synthetic work.[7] Among the pseudohalides, azide has become an extremely popular bridging ligand due to its versatile bridging modes, which facilitate the assembly of coordination complexes with different topology.[8] To explore the magnetochemistry of a metal−ligand system the knowledge of the structure is very much important[2,9] and helpful to access the correlation between single-crystal structure and magnetic properties.[2] To date, a considerable number of works have been reported concerning the versatility of azide to form extended architectures and obviously to affect their magnetic properties.[8a] But chemists have not paid proper attention to the factors that govern the bridging modes of azide in the formation of polymeric systems. As one of the main goals in molecular magnetism is to design molecular-based magnets and/or single-molecule magnets (SMM),[2,3] to get such systems, the

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10.1021/ic048466w CCC: $30.25

understanding of the factors controlling the topology demands giving equal importance to the choice of metal ion and bridging ligands.[10] Among the first row transition metal−azide systems, a look in the literature of Mn(II)−azide ones showed that a variety of topologies and/or dimensionalities can be achieved by making minor changes around the coordination environment of Mn(II).[11−13] For instance, packing forces are a determinant factor for the coordination mode of azide bridges, such has been reported in the case of complexes with general formula $C^+[Mn(N_3)_3]^-$,[12] where the bulk of the countercation ($C^+$) is found to play a key role in forming $\mu_{1,3}$-$N_3$ (end-to-end, EE), $\mu_{1,1}$-$N_3$ (end-on, EO), or alternating EE-EO coordination.

In this paper we present the syntheses of two new polymeric manganese azide complexes, $[Mn(N_3)_2(bpee)]_n$- (**1**) and $\{[Mn(N_3)(dpyo)Cl(H_2O)_2](H_2O)\}_n$ (**2**) [bpee, *trans*-1,2-bis(4-pyridyl)ethylene; dpyo, 4,4′-dipyridyl *N*,*N*′-dioxide] and their characterization by single-crystal X-ray structure and low-temperature magnetic study. On the basis of the structural results and the appropriate analytical expression deduced for interpreting the magnetic behavior of these chains, we get the relevant exchange constants for **1** and **2**, comparing data with those of analogous systems found in the literature.

## Experimental Section

**Materials.** High-purity (98%) *trans*-1,2-bis(4-pyridyl)ethylene and 4,4′-dipyridyl *N*,*N*′-dioxide hydrate were purchased from the Aldrich Chemical Co. Inc. and were used as received. All others chemicals were of AR grade.

**Physical Measurements.** Elemental analyses (carbon, hydrogen, and nitrogen) were performed using a Perkin-Elmer 240C elemental analyzer. IR spectra were measured from KBr pellets on a Nicolet 520 FTIR spectrometer. The magnetic measurements were carried out on polycrystalline samples using a Quantum Design MPMS SQUID magnetometer (applied field = 0.1 T) working in the temperature region 300−2 K. Diamagnetic corrections were estimated from Pascal's table.[1b]

**Synthesis of $[Mn(N_3)_2(bpee)]_n$ (1).** A methanolic solution (5 mL) of *trans*-1,2-bis(4-pyridyl)ethylene (0.0911 g, 0.5 mmol) was gently poured into an aqueous solution (10 mL) of sodium azide (0.0650 g, 1 mmol). Manganese chloride tetrahydrate (0.0985 g, 0.5 mmol) in methanol (5 mL) was added to this solution dropwise with constant stirring. A deep yellow compound separated out. Single crystals suitable for X-ray analysis were obtained by diffusing the methanolic solution (10 mL) of manganese chloride tetrahydrate on a water−methanol (1:1) layer (10 mL) of sodium azide and bpee (2:1) in a corked tube. The yellow colored single crystals were deposited at the junction of the two solutions after a few weeks. Yield: 68%. Anal. Calcd for $C_{36}H_{30}Mn_3N_{24}$: C, 44.87; H, 3.12; N, 34.89. Found: C, 44.83; H, 3.08; N, 34.69.

**Synthesis of $\{[Mn(N_3)(dpyo)Cl(H_2O)_2](H_2O)\}_n$ (2).** This was synthesized by following a similar procedure adopted for complex **1** using 4,4′-dipyridyl *N*,*N*′-dioxide hydrate (0.094 g, 0.5 mmol), instead of *trans*-1,2-bis(4-pyridyl)ethylene. Deep red single crystals of complex **2** suitable for X-ray diffraction were obtained by the diffusion process as adopted in the case of complex **1**. Yield: 70%. Anal. Calcd for $C_{10}H_{14}ClMnN_5O_5$: C, 32.05; H, 3.74; N, 18.69. Found: C, 31.89; H, 3.68; N, 18.54.

**Crystallographic Data Collection and Refinement.** Crystal data and details of data collections and refinements for the structures reported are summarized in Table 1. Data collection for complex

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**Table 1.** Crystal Data and Refinement Details for Complexes **1** and **2**

| | **1** | **2** |
|---|---|---|
| empirical formula | $C_{36}H_{30}Mn_3N_{24}$ | $C_{10}H_{14}ClMnN_5O_5$ |
| fw | 963.66 | 374.65 |
| cryst system | triclinic | triclinic |
| space group | $P\bar{1}$ | $P\bar{1}$ |
| $a$, Å | 8.877(3) | 7.060(3) |
| $b$, Å | 11.036(3) | 10.345(3) |
| $c$, Å | 11.584(4) | 11.697(4) |
| α, deg | 72.62(2) | 106.86(2) |
| $\beta$, deg | 71.06(2) | 113.33(2) |
| $\gamma$, deg | 87.98(3) | 96.39(3) |
| $V$, Å$^3$ | 1022.0(6) | 725.5(4) |
| Z | 1 | 2 |
| $D_{calcd}$, g cm$^{-3}$ | 1.566 | 1.715 |
| $\mu$(Mo Kα), mm$^{-1}$ | 0.975 | 9.410 |
| $\theta_{max}$, deg | 27.48 | 64.82 |
| collcd data | 11006 | 6538 |
| unique data | 4355 | 1986 |
| $R_{int}$ | 0.0657 | 0.0544 |
| refined params | 286 | 220 |
| R1 ($I > 2\sigma(I)$)[a] | 0.0588 | 0.0617 |
| wR2[a] | 0.1446 | 0.1765 |

[a] $R1(F_o) = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $wR2(F_o^2) = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$.

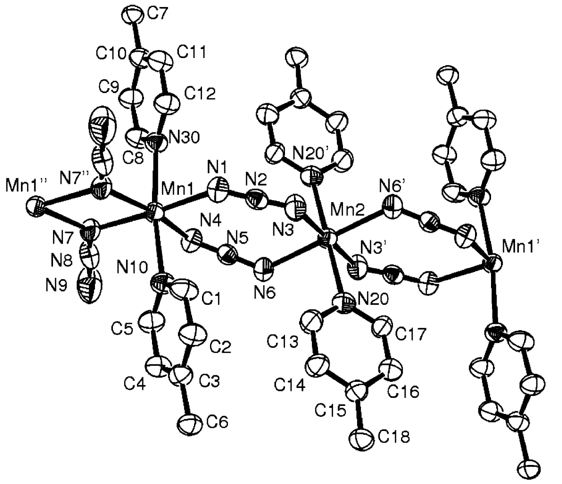

**Figure 1.** ORTEP drawing of a small portion of the 1D polymeric chain of $[Mn(N_3)_2(bpee)]_n$ (**1**).

**1** was carried out at 293(3) K on a Nonius DIP-1030H system with Mo-Kα radiation. A total of 30 frames were collected, each with an exposure time of 15−25 min, with a rotation of 6° about $\varphi$. Intensities of complex **2** were collected on a Bruker-Nonius FR591 rotating anode (Cu-Kα) equipped with a Kappa CCD detector. A total of 60 frames were collected, each with an exposure time of 3 min, with a rotation of 3° about $\varphi$. Cell refinement, indexing, and scaling of the data sets were performed using Mosflm,[14] Scala,[14] and Denzo.[15] The structures were solved by Patterson and Fourier analyses[16] and refined by the full-matrix least-squares method based on $F^2$ with all observed reflections.[16] Hydrogen atoms were included in final cycles of refinement at geometrical positions. A lattice water molecule (full occupancy) was detected in the Δ(Fourier) map of complex **2.** All calculations were carried out using SHELX97,[16] PLATON,[17] ORTEP-3,[18] and the WinGX system, version 1.64.05.[19]

## Results and Discussion

**Synthesis.** The crystalline compounds of both the complexes have been synthesized using same procedure. The suitable single crystals of the complexes are grown using the slow diffusion technique. The chemical reactions of the syntheses are given schematically:

$$MnCl_2 + 2NaN_3 + bpee \xrightarrow[\text{diffusion}]{\text{slow}} [Mn(N_3)_2(bpee)]_n$$

$$MnCl_2 + 2NaN_3 + dpyo \xrightarrow[\text{diffusion}]{\text{slow}} \{[Mn(N_3)(dpyo)Cl(H_2O)_2](H_2O)\}_n$$

**IR Spectroscopy.** Complex **1** shows two strong peaks at 2076 and 2038 cm$^{-1}$ in the IR spectrum, which are assigned to $\nu_{as}(N_3)$ stretching vibrations indicating the presence of two types of the coordination modes of azide.[20] The $\nu_s(N_3)$ stretching vibration also appears at 1331 cm$^{-1}$ with a medium-intensity band. Complex **2** shows one strong peak at 2085 cm$^{-1}$, which corresponds to $\nu_{as}(N_3)$ stretching vibrations of the end-to-end bridging mode of azide. It also shows a pair of strong absorption bands at 1254 and 1211 cm$^{-1}$, which are assigned as the $\nu$(NO) of dpyo.[20] These two sharp peaks indicate that out of the two NO groups only one NO is involved in coordination; in the case of free ligand dpyo, the $\nu$(NO) band is assigned at 1260 cm$^{-1}$.[20] Broad bands appearing in the range 3550−3200 cm$^{-1}$ correspond to the $\nu_s$(OH) and $\nu_{as}$(OH) indicating the presence of a water molecule.[20]

**Structure Description of Complex 1.** The X-ray structure analysis of complex **1** reveals a 2D arrangement of $[-Mn-(N_3)_2-]_n$ chains, connected by bpee ligands. The two crystallographically independent manganese ions are octahedrally coordinated to four azides occupying the equatorial positions and two pyridyl N of bpee in axial positions. The ORTEP drawing (Figure 1) shows the principal structural features of complex **1** with the atom-labeling scheme. The coordination bond lengths and angles shown in Table 2 agree with the values of other Mn−azide systems reported in the literature.[11,13] The $Mn-N_{azide}$ distances vary from 2.204(5) to 2.278(5) Å, and the $Mn-N_{bpee}$ ones, from 2.267(4) to 2.290(4) Å. The azido bridges present doubly end-to-end and end-on modes between the manganese atoms in a (-EO-EE-EE-)$_n$ sequence with intermetallic distances of 3.446(2) Å (along EO bridge) and 5.334(2) Å (along EE). On the other hand, the bidentate bridging bpee spans the metal at 13.917 Å. The Mn(1)−(EO)$_2$−Mn(1′′) fragment shows a planar centrosymmetric ring with a Mn(1′′)−N(7)−Mn(1) bond angle of

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**Table 2.** Selected Bond Lengths (Å) and Angles (deg) of Complex **1**[a]

| | | | |
|---|---|---|---|
| Bond Lengths | | | |
| Mn(1)−N(1) | 2.233(5) | Mn(1)−N(30) | 2.267(4) |
| Mn(1)−N(4) | 2.255(4) | Mn(2)−N(3) | 2.229(5) |
| Mn(1)−N(7) | 2.278(5) | Mn(2)−N(6) | 2.230(5) |
| Mn(1)−N(7″) | 2.204(5) | Mn(2)−N(20) | 2.284(4) |
| Mn(1)−N(10) | 2.290(4) | | |
| Bond Angles | | | |
| Mn(2)−Mn(1)−Mn(1″) | 172.42 | N(3)−Mn(2)−N(3′) | 180.0 |
| N(1)−Mn(1)−N(4) | 95.09(17) | N(6)−Mn(2)−N(6′) | 180.0 |
| N(1)−Mn(1)−N(7) | 176.67(16) | N(20)−Mn(2)−N(20′ ) | 180.0 |
| N(1)−Mn(1)−N(7″) | 98.34(18) | N(3)−Mn(2)−N(6) | 90.78(17) |
| N(1)−Mn(1)−N(10) | 87.11(16) | N(3)−Mn(2)−N(6′) | 89.22(17) |
| N(1)−Mn(1)−N(30) | 85.61(16) | N(3)−Mn(2)−N(20) | 89.55(17) |
| N(4)−Mn(1)−N(7) | 87.03(17) | N(3)−Mn(2)−N(20′) | 90.45(17) |
| N(4)−Mn(1)−N(7″) | 166.55(18) | N(6)−Mn(2)−N(20) | 88.38(16) |
| N(4)−Mn(1)−N(10) | 87.65(16) | N(6)−Mn(2)−N(20′) | 91.62(16) |
| N(4)−Mn(1)−N(30) | 90.37(15) | N(7)−Mn(1)−N(10) | 95.55(16) |
| N(7)−Mn(1)−N(7″) | 79.5(2) | N(7″)−Mn(1)−N(10) | 93.66(16) |
| N(10)−Mn(1)−N(30) | 172.26(16) | N(7″)−Mn(1)−N(30) | 89.99(16) |
| N(30)−Mn(1)−N(7) | 91.83(15) | | |
| Azide Bridge Angles | | | |
| Mn(1″)−N(7)−Mn(1) | 100.5(2) | N(2)−N(3)−Mn(2) | 131.6(4) |
| N(2)−N(1)−Mn(1) | 129.3(4) | N(5)−N(6)−Mn(2) | 128.7(3) |
| N(5)−N(4)−Mn(1) | 124.9(3) | N(3)−N(2)−N(1) | 177.5(5) |
| N(8)−N(7)−Mn(1) | 123.5(4) | N(4)−N(5)−N(6) | 178.2(5) |
| N(8)−N(7)−Mn(1″) | 130.8(4) | N(7)−N(8)−N(9) | 175.8(7) |

[a] Symmetry operations: (′) $-x + 1, -y + 1, -z$; (″) $-x, -y, -z + 1$.

**Table 3.** $\pi-\pi$ and C−H⋯$\pi$ Interactions in Complex **1**[a]

$\pi-\pi$ Interactions (Face-to-Face)

| ring($i$) → ring($j$) | dihedral angle ($i$ ,$j$), deg | slip angle ($i$, $j$), deg | dist of centroid ($i$) from ring ($j$), Å | dist between the ($i$, $j$) ring centroids, Å |
|---|---|---|---|---|
| R(1) → R(2)$^{i}$ | 2.15 | 22.72 | 3.502 | 3.750(7) |
| R(2) → R(1)$^{i}$ | 2.15 | 20.95 | 3.461 | 3.750(7) |

C−H⋯$\pi$ Interactions

| C−H → R(j) | H⋯R, Å | <C−H⋯R, deg | C⋯R, Å |
|---|---|---|---|
| C(13)−H → R(1) | 3.36 | 138.44 | 4.104(7) |
| C(16)−H → R(2)$^{ii}$ | 3.14 | 143.25 | 3.927(6) |
| C(1)−H → R(3)$^{iii}$ | 3.07 | 148.45 | 3.896(6) |
| C(11)−H → R(3)$^{iv}$ | 3.20 | 137.81 | 3.938(6) |

[a] Symmetry code: (i) $-x, -y, 1 - z$; (ii) $1 - x, 1 - y, -z$; (iii) $-x, 1 - y, -z$; (iv) $x, y - 1, z$. R($i$) and R($j$) denote the $i$th/$j$th rings of bpee: R(1) = N(10)/C(1)/C(2)/C(3)/C(4)/C(5); R(2) = N(30)/C(8)/C(9)/C(10)/C(11)/C(12); R(3) = N(20)/C(13)/C(14)/C(15)/C(16)/C(17).

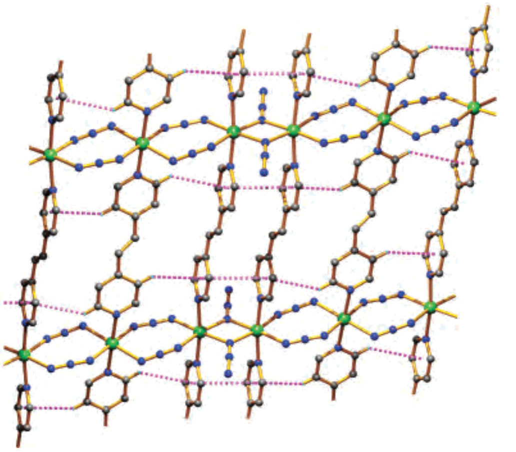

**Figure 2.** 2D layered structure of complex **1** showing both adjacent $\pi-\pi$ and C−H⋯$\pi$ interactions in polymeric chains. Color code: forest green, manganese; blue, nitrogen; cyan, hydrogen; black, carbon; magenta dotted line, $\pi-\pi$ or C−H⋯$\pi$ interaction.

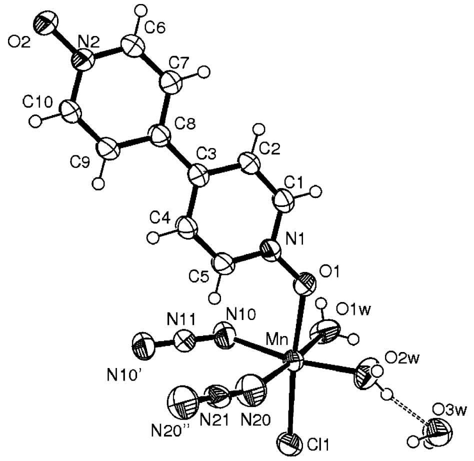

**Figure 3.** ORTEP drawing of a small portion of the 1D polymeric chain of $\{[Mn(N_3)(dpyo)Cl(H_2O)_2](H_2O)\}_n$ (**2**).

100.5(2)°. The Mn−N−N′ angles either for the EE or EO azide fall in a range 123.5(4)−131.6(4)°, while the ideal Mn(1)−N(1)⋯N(3)−Mn(2) and Mn(1)−N(4)⋯N(6)−Mn(2) torsion angles are 14.3 and −54.1° indicating a chair conformation for the EE azide bridges. As usual for the EO bridge the N−N bond lengths are clearly asymmetric, N(8)−N(9) being larger than N(7)−N(8) (1.230(8) and 1.058(6) Å, respectively).

In the 2D layered structure, the pyridine rings of bpee undergo $\pi-\pi$ and C−H⋯$\pi$ interactions (Table 3). It can be judicially conjectured that these weak interactions play an important role in generating such an unusual (-EO-EE-EE-)$_n$ sequence (Figure 2), or conversely, they are facilitated by the alternate double EO and EE bridges of the azide ligands. The present topology is similar to that reported for the 1D systems with 3-methylpyridine or 3,4-dimethylpyridine,[13] which has closely comparable intermetallic distances (mean values of 3.46 (EO) and 5.42 (EE) Å). Strong $\pi-\pi$ and C−H⋯$\pi$ interactions among the pyridine rings are also identified in these systems, although such interactions were not properly mentioned. As a comparison, the related compound $[Mn(N_3)_2(bpa)]_n$ (bpa = 1,2-bis(4-pyridyl)ethane) reveals a 2D structure formed by di-$\mu_{1,3}$-azido-bridged metallic chains connected by bpa ligands.[21]

**Structure Description of Complex 2.** The X-ray diffraction analysis of complex **2** evidences manganese ions in a slightly distorted octahedral environment (Figure 3), being coordinated in the equatorial plane by two water molecules (Mn−O = 2.147(3), 2.175(4) Å) and two azide nitrogen atoms (Mn−N = 2.211(4), 2.222(5) Å), while the axial positions are occupied by a chloride ion (Mn−Cl = 2.493(2) Å) and a dpyo oxygen donor (Mn−O(1) = 2.242(3) Å). The crystal structure consists of neutral 1D polymers built up by $[Mn(N_3)(dpyo)Cl(H_2O)_2]$ units and lattice water molecules. A perspective view of the chain is depicted in Figure 4, and selected bond lengths and angles are shown

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(21) (a) Hernández, M. L.; Barandika, M. G.; Urtiaga, K. K.; Cortés, R.; Lezama, L.; Arriortua, M. I. *J. Chem. Soc., Dalton Trans.* **2000**, 79. (b) Hong, C. S.; Son, S. K.; Lee, Y. S.; Jun, M. J.; Do, Y. *Inorg. Chem.* **1999**, *38*, 5602.

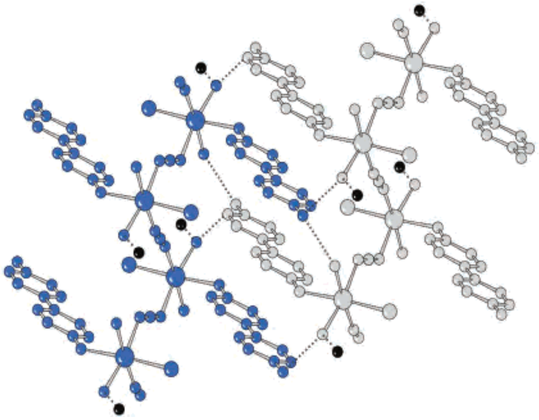


**Figure 4.** Perspective view of 1D polymeric chain of complex **2**: H-bonding (dotted lines) connecting two adjacent chains.

**Table 4.** Selected Bond Lengths (Å) and Angles (deg) of Complex **2**[a]

| | | | |
|---|---|---|---|
| | Bond Lengths | | |
| Mn−O(1) | 2.242(3) | Mn−N(10) | 2.211(4) |
| Mn−O(1w) | 2.175(4) | Mn−N(20) | 2.222(5) |
| Mn−O(2w) | 2.147(3) | Mn−Cl(1) | 2.493(2) |
| | Bond Angles | | |
| O(1)−Mn−O(1w) | 87.45(14) | O(1w)−Mn−Cl(1) | 91.52(11) |
| O(1)−Mn−O(2w) | 81.85(13) | O(2w)−Mn−N(10) | 170.83(15) |
| O(1)−Mn−N(10) | 90.40(14) | O(2w)−Mn−N(20) | 94.47(19) |
| O(1)−Mn−N(20) | 93.22(16) | O(2w)−Mn−Cl(1) | 92.87(11) |
| O(1)−Mn−Cl(1) | 174.59(8) | N(10)−Mn−N(20) | 90.84(19) |
| O(1w)−Mn−O(2w) | 91.53(17) | N(10)−Mn−Cl(1) | 94.76(12) |
| O(1w)−Mn−N(10) | 83.19(17) | N(20)−Mn−Cl(1) | 88.36(14) |
| O(1w)−Mn−N(20) | 174.00(18) | N(1)−O(1)−Mn | 128.6(2) |
| | Azide Bridge Angles | | |
| N(11)−N(10)−Mn | 127.6(3) | N(10)−N(11)−N(10′) | 180.00 |
| N(21)−N(20)−Mn | 159.8(4) | N(20)−N(21)−N(20″) | 180.00 |

[a] Symmetry operations: (′) $-x, -y + 2, -z + 2$; (″) $-x + 1, -y + 2, -z + 2$.

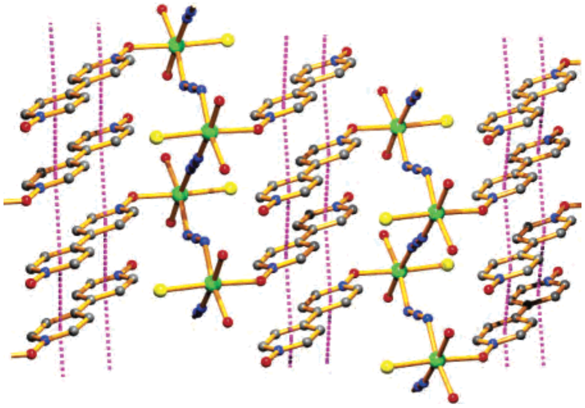


**Figure 5.** 1D chains locked through $\pi-\pi$ interactions between adjacent chains in complex **2**. Color code: forest green, manganese; blue, nitrogen; red, oxygen; black, carbon; magenta dotted line, $\pi-\pi$ interaction.

**Table 5.** Hydrogen Bonding (Å, deg) and $\pi-\pi$ Interactions in Complex **2**[a]

Hydrogen Bonding Interactions

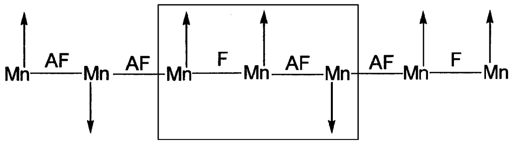
| | D−H···A | H···A | D···A | <D−H···A |
|---|---|---|---|---|
| O(1w)−H1···Cl(1)$^{i}$ | 0.86(5) | 2.29(5) | 3.070(5) | 151(8) |
| O(1w)−H2···O(2)$^{ii}$ | 0.84(7) | 1.88(7) | 2.717(6) | 176(8) |
| O(2w)−H1···O(2)$^{iii}$ | 0.85(8) | 1.89(7) | 2.715(6) | 163(7) |
| O(2w)−H2···O(3w) | 0.84(7) | 1.90(7) | 2.741(6) | 172(8) |
| O(3w)−H1···O(2w) | 0.86(6) | 2.30(5) | 2.741(6) | 112(5) |

$\pi-\pi$ Interactions (Face-to-Face)

| ring(*i*) → ring(*j*) | dihedral angle (*i*, *j*), deg | slip angle (*i* ,*j*), deg | dist of centroid (*i*) from ring (*j*), Å | dist between the (*i*, *j*) ring centroids, Å |
|---|---|---|---|---|
| R(1) → R(2)$^{ii}$ | 2.75 | 26.44 | 3.398 | 3.738(3) |
| R(1) → R(2)$^{iii}$ | 2.75 | 29.92 | 3.395 | 3.863(3) |
| R(2) → R(1)$^{ii}$ | 2.75 | 24.63 | 3.347 | 3.738(3) |
| R(2) → R(1)$^{ii}$ | 2.75 | 28.50 | 3.348 | 3.863(3) |

[a] Symmetry code: (i) $-x, 1 - y, 2 - z$; (ii) $-1 - x, 2 - y, 1 - z$; (iii) $-x, 2 - y, 1 - z$. R(*i*)/R(*j*) denotes the *i*th/*j*th rings of dpyo: R(1) = N(1)/C(1)/C(2)/C(3)/C(4)/C(5); R(2) = N(2)/C(6)/C(7)/C(8)/C(9)/C(10).

**Scheme 1**



in Table 4. The distances between the Mn(II) centers connected by a single EE azide ligand are 6.128 Å (along azide N(10)/N(11)) and 6.634 Å (along N(20)/N(21)). The asymmetry in the Mn−Mn distances for the two crystallographically independent bridging azides accounts for the different Mn−N−N angles of 127.6(3) and 159.8(4)° measured in Mn−N(10)−N(11) and Mn−N(20)−N(21), respectively. It is worth to emphasize that the arrangement of the EE azide ligands in the cis position of each Mn(II) center is unprecedented. The $N_3$ are located on the inversion centers, and thus, both the Mn−N···N−Mn ideal torsion angles are 180.0°.

The crystal packing evidences zipped chains linked through H-bonds and strong $\pi$-stacking (Figures 4 and 5) of dpyo pyridine rings at ca. 3.4 Å (Table 5). The H atom of each coordinated water molecule is hydrogen bonded to the uncoordinated dpyo oxygen of the adjacent chain giving rise to a 2D layered architecture (Figure 4). Both the O(1w)−O(2) (unit at $-x - 1, -y + 2, -z + 1$) and O(2w)−O(2) (at $-x, -y + 2, -z + 1$) distances are 2.72 Å. O(2w) acts also as a H acceptor from the lattice water molecule O(3w) (O(2w)−O(3w) distance of 2.74 Å). Moreover, it is interesting to observe that an electrostatic interaction is evident between O(1w) and the chloride ion at $-x, -y + 1, -z + 2$ with a O−Cl distance of 3.07 Å. Usually the dpyo ligand behaves as a bridging ligand between metal centers as observed in a homometallic complex of manganese.[22] Only a few structures were retrieved from the CSD containing monocoordinated dpyo, and these are often associated with water molecules (as in **2**) that facilitate H-bonds with the pendant dpyo oxygen.[23]

## Magnetic Properties and Magneto−Structural Correlation

**Complex 1.** As described above, the 2D structure encloses hexacoordinated Mn(II) ions bound to four azides with bpee ligands at axial positions. We can assume that the long bpee bridging ligands do not couple the Mn(II) ions or in a quasi

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(23) Allen, F. H.; Kennard, O.; Taylor, R. Cambridge Structural Database. *Acc. Chem. Res.* **1983**, *16*, 146.

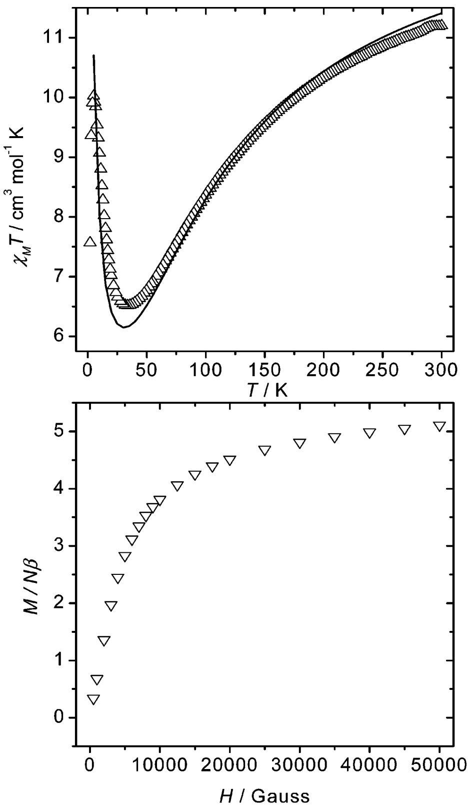

**Figure 6.** Plot of the $\chi_M T$ vs $T$ and $M/N\beta$ vs $H$ for complex **1**. (The solid line represents the curve obtained with the best-fitted parameters.)

negligible strength. Thus, from magnetic point of view, the structure can be considered as a pseudo-one-dimensional structure with Mn(II) ions linked by azide ligands in a very unusual alternating form (-EE-EE-EO-)$_n$, and to date only one similar polymeric arrangement has been reported.[13] Magnetic data, thus, must be treated as derived from an alternating AF-AF-F one-dimensional system, where the magnetic repeated unit can be considered as formed by three Mn(II) ions ($S = 5/2$), as indicated in Scheme 1.

In all Mn(II)−azide complexes, generally EE bridging mode creates antiferromagnetic coupling while EO creates a ferromagnetic one. The temperature dependence of the magnetic susceptibility is shown in Figure 6. The $\chi_M T$ value for three Mn(II) ions at room temperature is 11.20 cm$^3$ mol$^{-1}$ K, a typical value for three quasi-isolated Mn(II) ions of spin $S = 5/2$, with $g$ close to 2.00. When the temperature is decreased, $\chi_M T$ values decrease to 6.52 cm$^3$ mol$^{-1}$ K at 34 K, then there is an abrupt increase to 10.02 cm$^3$ mol$^{-1}$ K at 5 K, and, finally, $\chi_M T$ values again decrease to 7.56 cm$^3$ mol$^{-1}$ K at 2 K. From 5 to 2 K the decreasing experimental $\chi_M T$ may be due to intrachain antiferromagnetic interactions (as the actual structure is 2D). The feature is similar to that reported by Escuer et al.[13] for a similar 1D complex and is the typical signature of the so-called topological ferrimagnetism. The reduced magnetization curve ($M/N\beta$) (for three manganese ions) vs $H$ at 2 K also corroborate this assignment. As indicated in Scheme 1, the ground state must be $S = 5/2$ for each trinuclear Mn$_3$ entity. Thus, the saturation value must tend to 5 $N\beta$, as found experimentally (Figure 6, bottom).

The structural findings demand an alternating chain of exchange interactions with nearest neighbors described by the spin Hamiltonian $H = -J_i\Sigma(S_{3i}S_{3i+1} + S_{3i+1}S_{3i+2}) - J_2\Sigma S_{3i-1}S_{3i}$, where $J_1$ and $J_2$ stand for the alternating exchange constants and "classical" spin operators are expressed by $S$. This approximation is justified for Mn(II) ion, which exhibits a large spin ($S = 5/2$). Thus, the experimental data were fitted according to the reported eq 1 for such 1D system of Mn(II), derived from the above Hamiltonian:[13]

$$\chi = \frac{Ng^2\beta^2}{3kT}\{[3(1 - u_1^{\,4}u_2^{\,2}) + 4u_1(1 - u_1^{\,2}u_2^{\,2}) + 2u_2(1 + u_1)^2(1 - u_2^{\,2}) + 2u_1^{\,2}(1 - u_2^{\,2})]/(1 - u_1^{\,2}u_2)^2\} \quad (1)$$

Here $u_1 = \coth(J_1/kT) - kT/J_1$, $u_2 = \coth(J_2/kT) - kT/J_2$, $J_i = J_iS(S + 1)$, and $g_i = g_i[S(S + 1)]^{1/2}$. The best $J$ parameters obtained are $J_1 = -10.20$ cm$^{-1}$, $J_2 = 0.60$ cm$^{-1}$, and $g = 2.01$ with $R = 2.5 \times 10^{-2}$. These values are comparable to those reported by Escuer et al. for the single analogous complex.[13] This model provides a good fit of $\chi_M T$ variation over the temperature range 5−300 K, with a discrepancy that does not exceed experimental uncertainty. In particular the minimum of $\chi_M T$ and the divergence at low temperature are well reproduced. The AF and F exchange interactions obtained with this model lie in the same range as those reported for azido-bridged complexes. Coupling constant calculations on homogeneous azide chains show that the AF interaction through a double end-to-end azide bridge leads to relatively high $J$ values,[11,13] within the range −7 to −13 cm$^{-1}$. Moreover, the $J$ values reported for the double end-on azide bridges,[11,13] with comparable Mn−N−Mn bond angles (around 100°), are closer to or lower than 2 cm$^{-1}$.

Finally, complex **1** represents a new example of the rare phenomenon of homometallic ferrimagnetism, also named topological ferrimagnetism. Very recently, another topological ferrimagnetic 1D system with Mn(II)−azide (in EE form), containing also diazine bridging ligands, has been reported.[24]

**Complex 2.** The temperature dependence of the magnetic susceptibility is shown in Figure 7. The $\chi_M T$ value at room temperature is 4.18 cm$^3$ mol$^{-1}$ K, a typical value for an isolated ion of $S = 5/2$ with $g$ close to 2.00. When the temperature is decreased, $\chi_M T$ values smoothly decrease to 0.23 cm$^3$ mol$^{-1}$ K at 2 K. The $\chi_M$ value is 0.013 cm$^3$ mol$^{-1}$ at 300 K and increases smoothly with decreasing temperature to a maximum value of 0.098 cm$^3$ mol$^{-1}$ from 7 to 2 K (Figure 7, inset). Both the curves are clearly indicative of small antiferromagnetic coupling between Mn(II) ions.

As illustrated above, the crystal net consists of a one-dimensional polymer with bridging azide ligands (alternating different Mn−N−N angles of 127.6(3) and 159.8(4)°). Thus, magnetic data must be treated as derived from an alternating $S = 5/2$ one-dimensional system. Like complex **1** these structural findings also demand an alternating chain of exchange interactions with nearest neighbors described by the spin Hamiltonian $H = -J_i\Sigma S_{2i}S_{2i+1} - J_2\Sigma S_{2i+1}S_{2i+2}$. Experimental data for such a 1D system of Mn(II) were fitted

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(24) Gao, E.-Q.; Yue, Y.-F.; Bai, S.-Q.; He, Z.; Yan, C.-H. *J. Am. Chem. Soc.* **2004**, *126*, 1419.

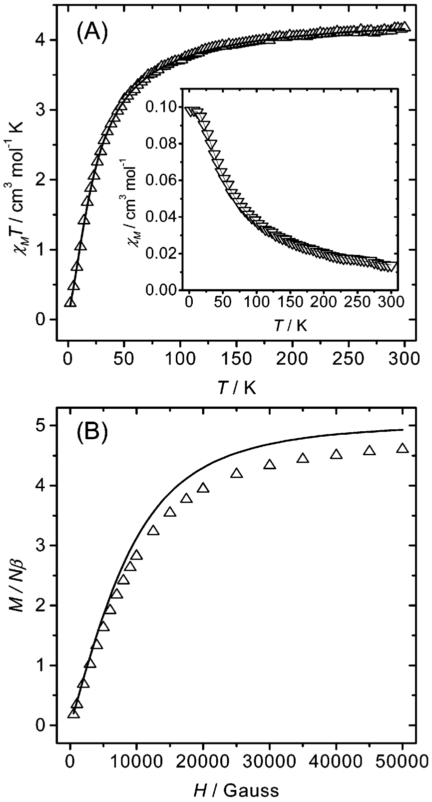

**Figure 7.** (A) Plot of the $\chi_M T$ and $\chi_M$ (inset) vs $T$ and (B) plot of the $M/N\beta$ vs $H$ for complex **2**. (Solid lines represent the curves obtained with the best-fitted parameters.)

according to the reported eq 2 derived from the Hamiltonian:[11c]

$$\chi = \frac{Ng^2\beta^2}{3kT}\left(\frac{1 + u_1 + u_2 + u_1u_2}{(1 - u_1u_2)}\right) \qquad (2)$$

Here $u_1 = \coth(J_1/kT) - kT/J_1$, $u_2 = \coth(J_2/kT) - kT/J_2$, $J_i = J_iS(S + 1)$, and $g_i = g_i[S(S + 1)]^{1/2}$. The best $J$ parameters obtained are $J_1 = -3.5$ cm$^{-1}$, $J_2 = -0.12$ cm$^{-1}$, and $g = 2.00$ with $R = 2.5 \times 10^{-4}$. The small $J$ values can be corroborated by the curve of the reduced magnetization ($M/N\beta$) vs $H$ at 2 K. This curve (Figure 7 bottom) provides a value of 4.5 $N\beta$ at 5 T, and it does not follow the Brillouin formula for an isolated $S = 5/2$ system. Theoretical values are slightly above the experimental ones, in agreement with a weak antiferromagnetic coupling.

To compare these calculated $J$ parameters with those reported in the literature for similar complexes, it must be noticed that a very few Mn(II) complexes with single EE azide bridge have been reported to date. Kahn et al. reported the synthesis and magnetic studies of a trans-coordinated 1D $\mu_{1,3}$-azide−Mn chain compound, namely $[\text{Mn(L)(N}_3\text{)(PF}_6\text{)}]_n$[25] (L = 2,13-dimethyl-3,6,9,12,18-pentaazabicyclo[12.3.1]-octadeca-1,(18)2,12,14,16-pentaene). Other 1D chains of Mn(II) ions linked by a single azide bridge in trans (or cis) position were not reported, contrary to well-known related Ni(II)-based compounds[8a] and to a few Mn(III) systems.[26] On the other hand, only two 2D and one 3D complexes with four single EE azide ligands about the manganese(II) center have been reported, namely $[\text{Mn(minc)}_2\text{(N}_3\text{)}_2]_n$ (minc = methyl isonicotinate),[27] $[\text{Mn(dena)}_2\text{(N}_3\text{)}_2]_n$ (dena = diethylnicotinamide),[28] and $[\text{Mn(4,4'-bpy)(N}_3\text{)}_2]_n$ (4,4′-bpy = 4,4′-bipyridine),[29] respectively.

Assuming that the Mn−N distances do not vary considerably, the most useful structural parameters to correlate with the AF coupling via EE azide bridges are the Mn−N−N angles and the dihedral Mn−NNN−Mn angle.[30] The reported EHMO calculations[30] showed that the AF coupling presents a maximum for a Mn−N−N angle close to 110°, while it would be very small for Mn−N−N angle near to 150°. Here the two alternating Mn−N−N angles are 127.6(3) and 159.8(4)°. Thus, according to these theoretical calculations,[30] it is possible to assign $J_1 = -3.5$ cm$^{-1}$ to the former Mn−N−N angle and $J_2$ value of $-0.12$ cm$^{-1}$ to the larger one, 159.8(4)°. The same calculations demonstrate that the AF coupling diminishes as Mn−N−N−N−Mn torsion angle decreases, but the effect can be neglected in **2** being that the group is coplanar (torsion angles of 180°).

The close comparable complex reported by Kahn,[25] with identical trans-located azide ligands, presents Mn−N−N angles of 118.2 and 125.2°, a Mn−NNN−Mn torsion angle of 53.2°, and a $J$ value of $-4.8$ cm$^{-1}$. Thus, although the M−N−N angles are smaller, favoring the AF coupling, the torsion angle is greater than that of **2**, favoring the ferromagnetic coupling. On the other hand, a subtle difference between Mn(II) Kahn's complex and **2** is that the former was the first coordination polymer with trans-located single EE bridging azide ligands, whereas **2** is the first having a single EE azide in the cis position. This subtlety has already been discussed for Ni(II) analogous complexes.[8a] New similar complexes are necessary to be synthesized to draw magneto−structural correlations for these types of systems.

## Conclusion

From the above study, it is clear that for the generation of new magnetic materials with azide ligands the design of different topologies is very important. For this reason we have to depend on factors which stabilize different topologies or dimensionalities of the azide coordination around the metal center. With pyridine derivatives, such as in complex **1**, it seems documented that the stability of the unusual bridging mode of azide, responsible of the topological ferrimagnetism, is mainly due the directional $\pi-\pi$ and C−H···$\pi$ interactions. In **2** weak interactions also play a key role to generate the

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overall structure. At this juncture, the main challenge is how to control these weak interactions to convert them to be more directional for the generation of complexes with desired structure as well as magnetic properties. We are presently working on this perspective.

**Acknowledgment.** We acknowledge the CSIR (India) and Spanish Government (Grant No. BQU2003/0539) for financial support. The authors gratefully acknowledge Dr. Golam Mostafa of Jadavpur University, Jadavpur, India, for various scientific discussions.

**Note Added after ASAP:** This article was released ASAP on February 12, 2005, with two minor errors in the chemical reactions of the syntheses due to a production error. The corrected version was posted on February 17, 2005.

**Supporting Information Available:** Tables of X-ray crystallographic data in CIF format for the structures reported in this paper. This material is available free of charge via the Internet at http://pubs.acs.org.

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