New homogeneous and alternating Mn(II)-azido 1D systems

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Abstract

Reaction of sodium azide with manganese(II) and 4-amino-1,2,4-triazol or 3-chloropyridine leads to the 1D systems \([\text{Mn}(\text{N}_3)_2(4\text{-amtr})_2]_n\) (1) or \([\text{Mn}(\text{N}_3)_2(3\text{-Clpy})_2]_{1/2}(3\text{-Clpy})_n\) (2), respectively. Compound 1 crystallises in the \(C2/m\) (monoclinic) group and consists of chains of Mn(II) cations bridged by double \(\mu_1,3\)-azido bridges in trans arrangement. Compound 2 crystallises in the \(P2_1/a\) (monoclinic) group and in this case the 1D system shows alternating double \(\mu_{1,1}\) and \(\mu_{1,3}\) bridges. Magnetic properties follow the expected antiferromagnetic (compound 1) and alternating ferro-antiferromagnetic (compound 2) behaviour.

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1. Introduction

Compounds with general formula \([\text{Mn}(\text{N}_3)_2(\text{R-py})_2]_n\), in which R-py is a pyridinic ligand with a R group in meta or para-position, provides a series of 1D derivatives in which the alternance of end-to-end (\(\mu_{1,3\text{-N}_3}\), EE mode) and end-on (\(\mu_{1,1\text{-N}_3}\), EO mode) azide bridges results in a complete graduation of magnetic responses [1].

This series of compounds, Scheme 1, goes from compounds containing only EE bridges [2,3a] to compounds containing only EO bridges [3] with antiferromagnetic or ferromagnetic response, respectively (I, II), trough systems in which the ratio of EE:EO bridges is 2:1 (V), [4] 1:1 (III, IV) [1,2a,5] or 1:4 (VI) [4a]. This gradual change of AF/F interactions provides an interesting material to study unusual magnetic properties as the topological ferrimagnetic response of compounds type V, [4] the EPR of chains with a gradual change of the superexchange and dipolar interactions [2a] or to develop theoretical studies to explain the new properties [2a,3b,4b].

As a consequence, study of the coordination chemistry and magnetic properties of azido-bridged systems has deserved the attention of magnetochemists in recent years due to the large number of the well characterised uncommon topologies and magnetic responses. The ability of the azido bridge to give different coordination modes as the EE, generally associated to antiferromagnetic coupling, or EO, generally associated to ferromagnetic coupling, [1] is the key of the versatility of this ligand. Moreover, in some limited cases, more exotic coordination modes as the \(\mu_{1,1,1}\), \(\mu_{1,1,3}\) or even \(\mu_{1,1,1,1}\) and \(\mu_{1,1,1,3}\) have been obtained with several cations [6]. In addition to molecular compounds with a wide range
of nuclearity, [1,7] azido ligand easily tends to give extended systems up to 3D dimensionality, containing in the most of the cases EE and EO azido bridges simultaneously, which often gives long range order at moderately low temperatures [1,8].

Following our research on the Mn II/azide/pyridine systems, we have structurally characterized two new systems, using L = 4-amino-1,2,4-triazol (4-amtr) and 3-chloropyridine (3-Clpy) to obtain the 1D systems \([\text{Mn(N}_3\text{)}_2(4\text{-amtr})_2]_n\) (1) and \([\text{Mn(N}_3\text{)}_2(3\text{-Clpy})_2 \cdot 1/2(3\text{-Clpy})]_n\) (2). The two compounds consist of chains in which the manganese atoms are bridged by two azido ligands. For 1 the bridges are exclusively end-to-end, type I, showing the expected antiferromagnetic coupling whereas for 2 there are a regular alternance between the end-to-end and end-on coordination modes, type IV, giving an alternating ferro-antiferromagnetic system. The antiferromagnetic interactions have been correlated with the bond parameters of the bridging fragment on basis on the previously reported coupling model.

2. Experimental

2.1. General and physical measurements

Infrared spectra were recorded on a Bruker IFS-125 model FT-IR spectrophotometer as KBr pellets. Magnetic susceptibility measurements were carried out on polycrystalline samples at the Servei de Magnetoqüimica of the University of Barcelona, with a DSM8 pendulum susceptometer working in the range 4–300 K under magnetic fields of approximately 1 T. Diamagnetic corrections were estimated from Pascal Tables.

2.2. Compounds preparation

WARNING! The reported azido complexes are potentially explosive. Only a small amount of material should be prepared and it should be handled with care.

2.2.1. \([\text{Mn(N}_3\text{)}_2(4\text{-amtr})_2]_n\) (1)

Irregular shaped crystals of 1 were separated from a clear aqueous solution (15 mL) containing Mn(NO$_3$)$_2 \cdot 4$H$_2$O (0.50 g, 2 mmol), NaN$_3$ (0.32 g, 5 mmol) and 4-amino-1,2,4-triazol (0.67 g, 8 mmol) after one day at room temperature. Yield: 0.18 g, 60%.

Anal. calc. for C$_4$H$_8$MnN$_{14}$: C, 15.6; H, 2.6; N, 63.8; Mn, 17.9. Found: C, 15.4; H, 2.5; N, 64.0; Mn, 18.1%.

2.2.2. \([\text{Mn(N}_3\text{)}_2(3\text{-Clpy})_2 \cdot 1/2(3\text{-Clpy})]_n\) (2)

An aqueous solution (5 mL) of NaN$_3$ (0.32 g, 5 mmol) was added drop by drop to a methanolic solution (40 mL) of Mn(NO$_3$)$_2 \cdot 4$H$_2$O (0.50 g, 2 mmol) and 3-chloropyridine (0.68 g, 6 mmol). The resulting solution was filtered off and the filtrate was allowed to stand for several days at room temperature to deposit yellow-green crystals. Yield: 0.55 g, 65%.

Anal. calc. for C$_{50}$H$_{40}$Cl$_{10}$Mn$_4$N$_{34}$: C, 35.5; H, 2.4; N, 28.2; Mn, 13.0. Found: C, 35.3; H, 2.2; N, 28.4; Mn, 13.2%.

2.2.3. X-ray data collection for compounds 1 and 2

The X-ray single-crystal data for 1 and 2 were collected on a modified STOE four circle diffractometer at 90(2)[88(2)] K. Crystal size: 0.40 × 0.22 × 0.14 mm[0.26 × 0.23 × 0.18 mm]. The crystallographic data, conditions retained for the intensity data collection, and

| Crystal data and structure refinement for (1) and (2) |
|------------------------|------------------------|
| Formula                | C$_{4}$H$_{8}$MnN$_{14}$ | C$_{50}$H$_{40}$Cl$_{10}$Mn$_{4}$N$_{34}$ |
| Fw                     | 307.18                 | 1691.42                  |
| Space group            | C$^{2}$m               | I$^{2}$a                 |
| Unit cell dimensions   |                        |                         |
| a (Å)                  | 15.030(5)              | 14.118(4)                |
| b (Å)                  | 6.872(3)               | 14.124(4)                |
| c (Å)                  | 5.362(2)               | 17.308(7)                |
| α (°)                  | 90                     | 90                      |
| β (°)                  | 93.67(3)               | 108.84(3)                |
| γ (°)                  | 90                     | 90                      |
| V (Å$^3$)              | 552.7(4)               | 3266(2)                  |
| Z                       | 2                      | 2                       |
| T (K)                  | 90                     | 88                      |
| χ(Mo Kα) (Å)           | 0.71069                | 0.71069                  |
| $\rho_{\text{calc}}$ (g cm$^{-3}$) | 1.846               | 1.720                    |
| $\mu$ (Mo Kα) (mm$^{-1}$) | 1.211               | 1.232                    |
| $R^2(I > 2\sigma(I))$  | 0.0421                 | 0.0362                   |
| $wR^2$ (all data)      | 0.1157                 | 0.0864                   |

\[ a = \sum(F_0 - F_{e})/\sum F_0, \]
\[ b = \sum w(F_0 - F_{e})^2/\sum w(F_0)^2, \]
\[ c = (\sum w(F_0 - F_{e})^2/\sum w(F_0)^2)_{1/2}. \]
some features of the structure refinement are listed in Table 1.

Graphite-monochromatized MoKα radiation (λ = 0.71069 Å) with the ω-scan technique was used to collect the data sets. The accurate unit cell parameters were determined from automatic centring of 28 [35] reflections (10.2° < θ < 15.4°) [8.8° < θ < 15.4°] and refined by least-squares methods. 1262 [4746] reflections, 872 [4053] independent reflections, and 872 [4053] reflections were determined from automatic centring of 28 reflections [35]. Absorption in case of reflection intensity decay and for Lorentz-polarization effects, intensity decay and for absorption in case of 1, using the DIFABS [9] computer program. The structures were solved by direct methods using the SHELXS-86 [10] program and refined by full-matrix least-squares methods on F2, using the SHELXL-93 [11] program incorporated in the SHELXL/PC V 5.03 [12] program library and the PLATON [13] program. Anisotropic displacement parameters were applied to all non-hydrogen atoms. The hydrogen atoms were assigned with isotropic displacement factors and included in the final refinement cycles by use of geometrical restraints. In case of 2, split occupancy of 0.5 and geometrical restraints were applied to atoms of disordered 3-Clpy lattice molecule located on the special position with site symmetry 2 (diad). Final R[I > 2σ(I)] and wR factor for all observed reflections: 0.0421 and 0.1157 [0.0362 and 0.0864]; number of refined parameters: 65 [247]. Maximum and minimum peaks in the final difference Fourier synthesis: 0.79 and −1.03 e Å−3 [0.48 and −0.37 e Å−3]. Selected bond parameters are given in Tables 2 and 3, respectively.

### 3. Results and discussion

#### 3.1. Crystal structure of [Mn(N3)2(4-amtr)2]n (1)

The labelled diagram for 1 is shown in Fig. 1. The basic structure consist of octahedrically coordinated manganese atoms in which the coordination sites are occupied by two 4-amino-1,2,4-triazol ligands in trans arrangement and four azido ligands. The azido ligands link the manganese atoms in the μ1,3 (EE) coordination mode, giving a 1D system with double azido bridges along the [0 0 1] direction. Bond parameters around MnII atoms are quite regular with all the bond lengths practically equal, around 2.222 Å and all the Mn–N–N bond angles of 129.6(2)°. Intrachain Mn⋯Mn distance is 5.362(2) Å.

#### Table 2

<table>
<thead>
<tr>
<th>Bond lengths</th>
<th>A</th>
<th>angles [°] for compound [Mn(N3)2(4-amtr)2]n (1)</th>
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<tr>
<td>Mn(1)–N(1)</td>
<td>2.222(3)</td>
<td>Mn(1)–N(2)</td>
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<tr>
<td>Mn(1)–N(11)</td>
<td>2.223(2)</td>
<td>N(11)–N(12)</td>
</tr>
<tr>
<td>N(11)–N(12)</td>
<td>1.172(2)</td>
<td>N(2)–C(5)</td>
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<tr>
<td>Mn(1)–N(1)</td>
<td>2.222(3)</td>
<td>N(4)–N(6)</td>
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<tr>
<td>N(11)–N(11A)</td>
<td>90.8(1)</td>
<td>N(4)–C(3)</td>
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<tr>
<td>Mn(1)–N(11A)</td>
<td>89.2(1)</td>
<td>N(4)–C(5)</td>
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#### Table 3

<table>
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<th>Bond lengths</th>
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<td>Mn(1)–N(21)</td>
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</tr>
<tr>
<td>Mn(1)–N(11B)</td>
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<td>Mn(1)–N(1)</td>
</tr>
</tbody>
</table>

#### Bond angles

- N(1)–Mn(1)–N(11) 180°
- N(1)–Mn(1)–N(11A) 89.2(1)°
- N(1)–Mn(1)–N(1) 100.48(7)°
- N(1)–Mn(1)–N(23) 2.193(2) Å
- N(1)–Mn(1)–N(2) 172.43(6)°
- N(1)–Mn(1)–N(11) 90.096(6)°
- N(1)–Mn(1)–N(21) 86.81(7)°
- N(1)–Mn(1)–N(23) 86.81(7)°

#### Fig. 1. ORTEP view (50% ellipsoids) of [Mn(N3)2(4-amtr)2]n (1). The chains are oriented along the c-axis of the unit cell. Symmetry codes: (A) −x, −y, −z; (B) −x, y, −z − 1; (C) −x, y, −z; (D) x, −y, z.
The Mn–($\mu_{1,3}$)$_2$–Mn unit shows a chair distortion with a dihedral angle of 22.6(1)$^\circ$ between the azido plane and the plane determined by N(11)–Mn(1)–N(11D), Fig. 2(a).

The H-atoms of the –NH$_2$ group promote a 3D network on basis of the N(6)–H···N(11) interactions, Fig. 3. N(6)···N(11) distances, 3.098(3) Å corresponds to a strong H-bond.

3.2. Crystal structure of $\{[\text{Mn(N}_3)_2(3\text{-Clpy})_2]\cdot 1/2(3\text{-Clpy})\}_n (2)$

The labelled diagram for 2 is shown in Fig. 4. The basic structure consists of manganese atoms in octahedral environment with the coordination sites occupied by two trans 3-chloropyridines and four azido ligands. The manganese atoms are linked by double azido bridges, giving a 1D system along [0 0 1] direction, in which the azido ligands show a regular alternance between the $\mu_{1,1}$ and the $\mu_{1,3}$ coordination modes resulting an alternating system.

Mn–N bond lengths to pyridinic ligands (2.267–2.274 Å) are slightly larger than the Mn–N bond lengths to azido ligands (around 2.200 Å). The Mn–($\mu_{1,3}$)$_2$–Mn unit forms a planar centrosymmetric Mn$_2$N$_2$ ring with a Mn(1)–N(11)–Mn(1A) bond angle of 100.48(7)$^\circ$ and a Mn···Mn distance of 3.408(2) Å. The Mn–($\mu_{1,3}$)$_2$–Mn unit is not fully planar, showing a dihedral angle between the mean azido plane and N(21)–Mn(1)–N(23) plane of 9.77(9)$^\circ$, with the Mn atoms 0.240(1) Å out the azido plane. In this case, the free 3-Clpy molecule intercalated between the coordinated 3-Clpy ligands forces to increase asymmetrically the interligand distance and produces a very unusual boat-distortion, Fig. 2(b). Mn···Mn distance of 5.287(2) Å. The intercalated 3-Clpy molecule forms mean dihedral angles of 5.1(1)$^\circ$ and 8.2(1)$^\circ$ with the neighbouring coordinated 3-Clpy ligands. The forces that determine the intercalation of neutral ligands in the structure should be attributed to $\pi$–$\pi$ stacking, from the mean distance between the coordinated and intercalated 3-Clpy ligands (around 3.5 Å).

3.3. Susceptibility measurements and coupling constants evaluation

The $\chi_M T$ product and the molar magnetic susceptibility versus temperature for $[\text{Mn(N}_3)_2(4\text{-amtr})_2]_n$ (1) and $\{[\text{Mn(N}_3)_2(3\text{-Clpy})_2]\cdot 1/2(3\text{-Clpy})\}_n (2)$ in the 300–4 K range are plotted in Fig. 5.

![Fig. 2. Chair and boat conformation for the Mn–($\mu_{1,3}$)$_2$–Mn fragments for compounds 1 (a) and 2 (b).](image)

![Fig. 3. 3D H-bond network built from the N(6)–H(6)···N(11) contacts for compound 1.](image)

![Fig. 4. ORTEP view (50% ellipsoids) with atom labelling scheme of $\{[\text{Mn(N}_3)_2(3\text{-Clpy})_2]\cdot 1/2(3\text{-Clpy})\}_n (2)$. The chains are oriented along the c-axis of the unit cell. Symmetry codes: (A) $-x+1/2, -y+1/2, -z+1/2; (B) -x+1/2, y, -z+1$.](image)
As can be expected from the structural data of 1, this system shows antiferromagnetic response: $\chi M T$ at room temperature takes a 3.06-cm$^3$ K mol$^{-1}$ value, decreasing continuously on cooling and tends to zero at low temperature, showing a maximum of susceptibility around 75 K. Fit for the experimental data was performed with the analytical expression derived by Fisher [14] for an infinite chain of classical spins, based in the Hamiltonian $H = -J S_i \cdot S_{i+1}$ and local spin $S = 5/2$. Best fit parameters for the experimental data in the 50–300 K range were $J = -11.9(6)$ cm$^{-1}$ and $g = 2.00(1)$. Introducing a $gJ'$ parameter in the equation in order to take into account the possible interchain interactions derived from the H-bond network, which involves N(11)-atoms of the azido ligands, the best fit parameters in the 20–300 K range of temperature were $J = -11.1(2)$ cm$^{-1}$, $gJ' = -3.7(1)$ cm$^{-1}$ and $g = 1.98(1)$. This second fit confirms that main $J$ value is slightly greater than $-11$ cm$^{-1}$.

Magnetic response for 2 shows an overall antiferromagnetic behaviour. $\chi M T$ at room temperature takes a 3.52-cm$^3$ K mol$^{-1}$ value and decreases continuously on cooling and tends to zero at low temperature, showing a broad maximum of susceptibility at 50 K. Fit for the experimental data was performed with the analytical expression for an alternating system proposed by Drillon and co-workers [15] on basis on the Hamiltonian $H = -J_1 S_{2i} \cdot S_{2i+1} - J_2 S_{2i} \cdot S_{2i+2}$. Best fit calculated parameters for the experimental data in the 25–300 K range were $J_1 = -16.7(4)$ cm$^{-1}$, $J_2 = 6.0(2)$ cm$^{-1}$ and $g = 1.992(4)$.

### 3.4. Coupling constants correlation

End-to-end coordination mode for the azido ligand has been studied previously from the structure-magnetic behaviour point of view for different electronic configurations [1,3b]. In the Mn$^{II}$ case (d5), it was shown that the antiferromagnetic components of the interaction should decrease for larger dihedral angles ($\delta$ between the main azido plane and the N–Mn–N plane), indicating that the loss of overlap due to the increase in the torsion angles becomes the driving force that controls the antiferromagnetic coupling. Due to the residual overlap of the $t_2g$ orbitals with the non-bonding $\pi$ MOs of the azido mediator, even for large dihedral $\delta$ angles there is always an AF dominant interaction. In the case of double EE azido bridges, the AF coupling was related directly with the degree of chair/boat distortion of the Mn($\mu_1,\mu_3$-N$_3$)$_2$–Mn fragment.

In our case, compound 1 is clearly chair distorted with a $\delta$ angle of 22.6° whereas 2 exhibits a more planar Mn($\mu_1,\mu_3$-N$_3$)$_2$–Mn boat-distorted unit ($\delta$ is only 9.77°). These structural parameters are in good qualitative agreement with the lower $J_1$ value of $-11.9$ cm$^{-1}$ for 1 in comparison with the $J$ value found of $-16.7$ cm$^{-1}$ calculated for 2. On the other hand, the coupling due to the EO bridges for 2, give the normal ferromagnetic behaviour characteristic of Mn–N–Mn bond angles slightly greater than 100°.

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## Appendix A. Supplementary material

Crystallographic data in CIF format have been deposited with the Cambridge Structural Data Centre as CCDC-252920 and CCDC-252921 for 1 and 2, respectively. Copies of the data can be obtained free of charge, on application to CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44 1223 336033, e-mail: deposit@ccdc.cam.ac.uk, http://www.ccdc.cam.ac.uk). Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.poly.2005.01.003.

## References