

Long-range 3D Magnetic Order in the Layered Molecular Network Compounds $M(\text{NCO})_2(\text{pyz})$, $M = \text{Mn, Fe or Co}$

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Introduction

It has recently been shown that organic ligands are capable of mediating exchange interactions over convoluted pathways, giving rise to long-range magnetic order at quite high temperatures [1]. Much effort has consequently been invested in understanding the nature and origin of these interactions [2], furthering progress towards potential applications of these low-dimensional ‘molecular magnetic’ materials. The design, synthesis and study of further such coordination polymers are fundamental to this effort.

We have been studying a variety of novel molecular magnetic solids comprised of pseudo-halide building blocks and first-row transition metal ions, M . The ensuing structures possess either 1-, 2- or 3D networks where divalent M cations are held together *via* organic anions such as dicyanamide ($\text{N}(\text{CN})_2^-$) [3–5], azide (N_3^-) [6, 7], thiocyanate (NCS^-) [8] or cyanate (NCO^-) plus neutral organic ligands such as pyrazine (pyz) or 4,4-bipyridine (bipy).

Numerous compounds have been reported that contain $\text{N}(\text{CN})_2^-$, N_3^- , or NCS^- anions but very few have been reported with NCO^- . While N_3^- is a well-known super-exchange mediator in molecular magnetic materials, its major drawback is that it is potentially explosive if handled in sizeable quantities. This has hampered neutron scattering studies into the magnetism of these compounds and motivated our interest in NCO^- .

Both NCO^- and N_3^- can coordinate to M ions in a different ways such as $M\text{-N-}M$, $M\text{-NNN-}M$ or $M\text{-N-C-O-}M$, although the latter is rare in the case of NCO^- . Singly-bridging $M\text{-N-}M$ generally gives rise to ferromagnetic interactions although the strength of this coupling is dictated by the bond angle. By combining these anions with other organic bridging ligands we can build a plethora of new structures with interesting magnetic behavior.

We have now synthesised $M(\text{NCO})_2(\text{pyz})$ compounds where M is Mn, Fe or Co. Here, we present the results of a neutron powder diffraction (NPD) investigation into the crystal and magnetic structures of these compounds as a function of temperature. We find that the structures of all three compounds are isomorphic and related to that of $\text{Mn}(\text{N}_3)_2(\text{pyz})$ [6], and yet exhibit two distinct magnetic structures at low temperature. The relationship between these two magnetic structures, and the finely balanced interactions that lead to the adoption of one over the other, are discussed.

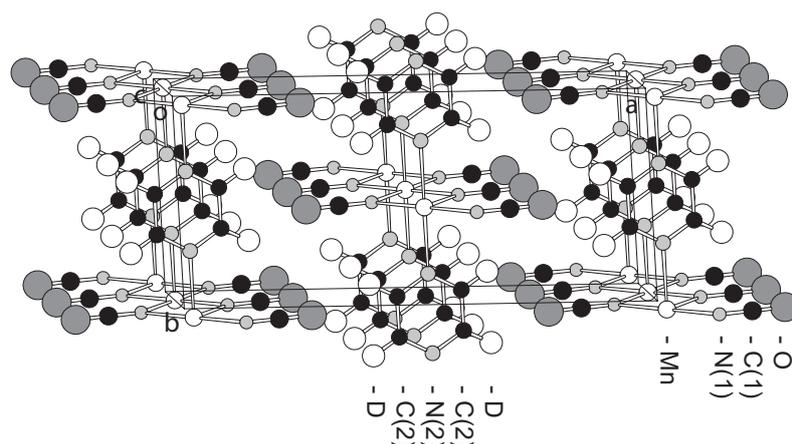


Figure 1: Final Rietveld-refined structure of $\text{Mn}(\text{NCO})_2(\text{pyz})$ at room temperature viewed close to the $[001]$ direction. Unit cell axes a , b and c are indicated with respect to the origin o . Sphere sizes correspond to 50 % probability (isotropic) thermal ellipsoids. Monoclinic space group $C2/m$ (standard setting $b1$).

Technical Details

Temperature-dependent neutron powder diffraction (NPD) data were collected on the instrument D2B at the Institut Laue-Langevin in Grenoble, France. Refinements were carried out using the GSAS program [9]. Room-temperature data were collected at $\lambda = 1.5984 \text{ \AA}$ in high-resolution mode in order to maximize the number of reflections collected, while low-temperature ($T = 1.5 \text{ K}$) data were collected at $\lambda = 2.3925 \text{ \AA}$ in order to maximize resolution in the low-angle region containing magnetic reflections.

Crystal Structures

A C -centered monoclinic unit cell was determined for $\text{Mn}(\text{NCO})_2(\text{pyz})$ by analogy to that of $\text{Mn}(\text{N}_3)_2(\text{pyz})$ [6]. $\text{Mn}(\text{N}_3)_2(\text{pyz})$ consists of linear chains of $\text{Mn}(\text{NCO})_2$ along the z -direction, linked by μ - pyz ligands along the y -direction. The resulting 2-D layers are stacked along the x -direction. A model for $\text{Mn}[\text{NCO}]_2(\text{pyz})$ could therefore be based on this structure, substituting NCO for N_3 ligands, with the Mn still coordinating to the N atom. On closer examination of the unit cell against room temperature NPD data, it was found that all reflections could still be indexed when the c -axis was halved. Looking at the structure of $\text{Mn}[\text{N}_3]_2(\text{pyz})$ (Fig. 1 of Manson *et al.* [6]), this implies that the alternating up-down-up tilts of N_3 ligands along the y -direction do not occur in the present structure, where the NCO ligands presumably remain in the xz -plane. The starting model for $\text{Mn}(\text{NCO})_2(\text{pyz})$ was constructed in this reduced unit cell with space group #12 $C2/m$ (standard setting $b1$), with $Z = 2$.

The structure of $\text{Mn}(\text{NCO})_2(\text{pyz})$ was then Rietveld-refined against room-temperature NPD data. The unit cell, atomic positions and isotropic atomic displacement parameters (ADPs) were refined for each atom, along with the zero-offset of the pattern, a scale factor and background polynomial (total of 49 refined variables). The room-temperature structures of $\text{Fe}(\text{NCO})_2(\text{pyz})$ and $\text{Co}(\text{NCO})_2(\text{pyz})$ were Rietveld-refined in the same manner. The final Rietveld-refined structure of the $M = \text{Mn}$ compound is shown in Fig. 1.

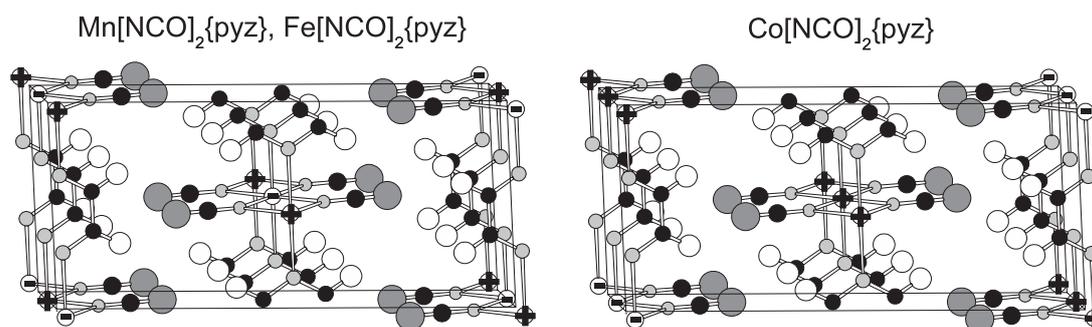


Figure 2: The metal-atom spin-ordering scheme observed at 1.5 K in $\text{Mn}(\text{NCO})_2(\text{pyz})$ and $\text{Fe}(\text{NCO})_2(\text{pyz})$ versus that observed in $\text{Co}(\text{NCO})_2(\text{pyz})$.

Magnetic Structures

The 1.5 K structures of $M(\text{NCO})_2(\text{pyz})$, $M = \text{Mn}, \text{Fe}, \text{Co}$ were Rietveld-refined against NPD data based on the room-temperature structures. No significant structural changes were observed other than the expected contraction of the unit cells. In the low-angle region, all three low-temperature patterns presented magnetic Bragg peaks that could be indexed to an expanded unit cell. In the case of $M = \text{Mn}$ and $M = \text{Fe}$, the magnetic cell was doubled in all three directions x, y and z *i.e.* the magnetic vector is $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$. In the case of $M = \text{Co}$, the magnetic cell was doubled only in the x - and y -directions *i.e.* the magnetic vector is $(\frac{1}{2}, \frac{1}{2}, 0)$. The antiferromagnetic (AFM) structures that these vectors imply are shown in Fig. 2 by the +/- symbols on the M sites. In all compounds, there is an AFM relationship among M atoms linked through μ -pyz ligands along the y -direction, and an AFM relationship among M atoms in next-nearest 2-D layers along the x -direction (the relationship among M atoms in neighbouring 2-D layers is degenerate). The difference between the two magnetic structures is that in the case of $M = \text{Mn}$ and $M = \text{Fe}$, there is an AFM relationship among M atoms in $M(\text{NCO})_2$ chains along the z -direction, whereas for $M = \text{Co}$ these chains are FM. The magnitudes and orientations of the spins for these magnetic structures were successfully refined. For $M = \text{Mn}$ and $M = \text{Fe}$, spins were found to be oriented principally along the y -direction, whereas for $M = \text{Co}$ they clearly lie along the FM z -direction and were fixed as such.

Unit cell parameters and details of the Rietveld-refined magnetic structures at 1.5 K of $M(\text{NCO})_2(\text{pyz})$, $M = \text{Mn}, \text{Fe}, \text{Co}$ are shown in Table 1. Directions of the spins are described by θ (angle to z) and ψ (angle to x in the xy -plane).

Discussion

There are evidently some rather subtle differences between $M(\text{NCO})_2(\text{pyz})$ for $M = \text{Mn}$ and Fe , versus $M = \text{Co}$, that gives rise to AFM along the b -axis in the former and FM along the b -axis in the latter. The crystallographic data presented here does not provide any clear indication of what these differences might be; in particular, bond lengths and angles through the magnetic exchange pathways show no significant variations among different M compounds. These differences are the subject of ongoing investigation at the time of writing. Most importantly, magnetic susceptibility measurements have been made, however, the form of the magnetisation curve is rather complex. It does not appear to fit an Ising, or even

Table 1: Refinement statistics, unit cell parameters and details of the magnetic structures for the final Rietveld-refined 1.5 K structures of $M(\text{NCO})_2(\text{pyz})$, $M = \text{Mn, Fe, Co}$.

	$M = \text{Mn}$	$M = \text{Fe}$	$M = \text{Co}$
T_N (K)	30	23	5.3
a (Å)	15.8108(8)	15.9051(13)	15.8082(13)
b (Å)	7.3390(3)	7.1502(5)	7.0660(5)
c (Å)	3.36114(14)	3.2862(2)	3.2762(2)
β (°)	109.160(3)	109.510(5)	109.449(6)
V (Å ³)	368.41(3)	352.26(5)	345.08(6)
M spin structure	$(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$	$(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$	$(\frac{1}{2}, \frac{1}{2}, 0)$
μ_{sat} (μ_B/M)	3.62(16)	4.9(3)	2.70(7)
θ (°)	70(4)	75(6)	85(9)
ψ (°)	70(7)	0	0
R_p	0.0507	0.0532	0.0498
wR_p	0.0635	0.0710	0.0638
$R(F^2)$	0.0992	0.0730	0.0753
χ^2	2.77	2.91	3.61

Hamiltonian, model of 3D magnetisation, despite the NPD evidence presented here that indicates 3D magnetic ordering. It may be necessary to develop new models of pseudo-2D magnetism to interpret this data. Such complexity is perhaps to be expected in molecular magnetic materials due to the extreme anisotropy of the magnetic exchange interactions, which are mediated by quite different types of organic ligands in different directions. Hence, although they present a difficult problem, they clearly deserve further efforts since these difficulties are a consequence of the unusual ‘soft’ exchange pathways that make them potentially so useful.

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