

Spin Localization in $[\text{Mn}_3(\text{suc})_2(\text{ina})_2]_n$: An Homometallic Molecular 3D Ferrimagnet

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1. Introduction

The research on ferrimagnetic systems of metal complexes (i.e., heterospin systems containing two different magnetic ions with nearest-neighbour antiferromagnetic exchange coupling) in the field of molecular magnetic materials, is well represented by numerous compounds whose metal atoms are bridged through, for example, cyanide, oxalate or carboxylate groups. For such compounds, long-range ferrimagnetic order arises from the non-compensation of the different spin moments. In particular, the number of 3D homometallic complexes with ferrimagnetic behaviours previously reported is scarce due to the requirement for the non-compensation of the individual spin moments,[1] which is difficult to achieve in practice because only one kind of spin is involved. Therefore, a deep structural and magnetic study is required to understand the physical and chemical factors that govern the exchange coupling between homometallic magnetic centres and, as consequence, produces a long-range homometallic molecular ferromagnetic behaviour.

2. Results

The present work is focused on the study of one of these homometallic molecular ferrimagnets: $[\text{Mn}_3(\text{suc})_2(\text{ina})_2]_n$ (*suc* = succinate and *ina* = isonicotinate) compound (**1**). X-ray measurements reveal that there are two crystallographically independent Mn(II) centres, Mn(1) and Mn(2), forming a regular chain along the *b*-axis, involving μ -oxo and *syn-syn* carboxylate bridges. Each chain is linked to two adjacent neighbour chains through *anti-syn* carboxylate bridges giving rise to a rigid layer along the *ab*-plane. The three dimensional structure is reached through the skeleton of the *ina* ligand, resulting in a pillared system with an *AA* packing mode with the interlayer distances of *ca.* 9.47 Å.[2]

The magnetic structure of **1**, indexed with $\mathbf{k} = (0,0,0)$, determined by neutron diffraction measurements at 2 K, indicates that Mn(1) is coupled antiferromagnetically with Mn(2) ($J_1 < 0$), while the coupling between the Mn(2) atoms is ferromagnetic ($J_2 >$

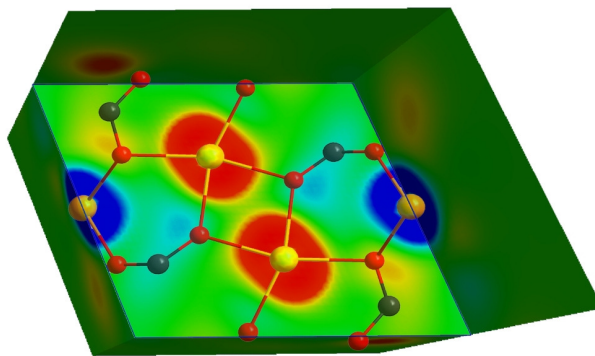


Figure 1. Spin density map resulting from flipping ratios measurements of compound **1**, collected on D3 at 2 K. The antiferromagnetic coupling that promotes the ordering of the different homometallic magnetic moments in a non-compensated way, is observed as a change in the spin density sign of the metallic atoms.

0) (Figure 1). The magnetic coupling between ferrimagnetic chains is also ferromagnetic, as well as the coupling between the layers along the *ab*-plane. The magnetic moment for each Mn(II) site is found to be 3.76 and 4.46 BM/Mn(II), for Mn(1) and Mn(2) respectively, values which are slightly lower than those expected for a magnetically isolated high-spin Mn(II) ($S = 5/2$) ion with $g = 2.00$.^[3] These neutron diffraction results confirm that the ferrimagnetic behavior is caused by the non-compensation of the magnetic moment of the different Mn(II) ions present in the crystal. However, these data give only information about the magnetic moment resident on the Mn(II) sites and not out of them. In order to verify the possible spin delocalisation of **1**, polarized neutron diffraction has been used. With the aim of collecting the flipping ratio data with the highest possible signal, we operated D3 instrument at 9 T and 2 K. The spin density over the different atoms was refined based on the previous magnetic model.

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References

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