

SPIN DENSITY IN A CYANO-BRIDGED MOLECULAR-BASED ORDERED MAGNETIC COMPOUND

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Over the past few years, few molecular-based compounds that display magnetic ordering above room temperature have been reported[1]. These materials, related to Prussian Blue, have a faced-centred cubic structure, with A-NC-B linear linkages, where A and B are both 3d metal ions, A being a high spin ion and B a low spin ion, i. e. V^{II} and Cr^{III} ions. Compounds display either three-dimensional ferro- or ferri-magnetism, depending of the nature of the A-B interactions through the cyano-bridge. However, a major drawback of this class of materials is that no magnetic anisotropy (which is essential for future practical applications) can be expected because of the cubic nature of the structure. In this respect, the recent synthesis of cyano-bridged bimetallic analogues to Prussian Blue but with a lower symmetry, from a 4d ion Mo^{III} -molecular precursor $K_4[Mo^{III}(CN)_7] \cdot 2H_2O$, yielded promising results[2]. A strong magnetic anisotropy in the ordered state has thus been achieved for the compound $(K_2Mn^{II}_3(H_2O)_6[Mo^{III}(CN)_7]_2 \cdot 6H_2O)$, for which a relatively high ferromagnetic ordering temperature T_C (39K) has been reported[3].

In order to investigate the origin of the ferromagnetic coupling between the Mn^{2+} and Mo^{3+} ions through the cyano bridge in this type of compound, we have performed a spin density study on the $(K_2Mn_3(H_2O)_6[Mo(CN)_7]_2 \cdot 6H_2O)$ compound[4]. As a matter of fact, the determination of the spin density provides crucial information about phenomena such as spin delocalization and spin polarization that play a role in magnetic interactions between metallic ions through organic bridges.

This compound presents a two-dimensional structure with double-sheet layers stacked up along the direction of the b-axis. Each sheet, parallel to the (a, b) plane, is built upon cyano-bridged Mn_2Mo_2 lozenges. The nuclear structure at 50K, just above the ordering temperature, has

been determined with help of unpolarised neutron diffraction measurements on the four-circle diffractometer 6T2. The title compound is air sensitive and so the crystal was kept in an inert atmosphere throughout the whole experimental procedure. This material is extensively hydrogen-bonded: three water molecules of crystallisation form small water clusters within the voids between the bi-layers and the three others are H-bonded to coordinated water molecules within the inter-bi-layer regions (Figure 1).

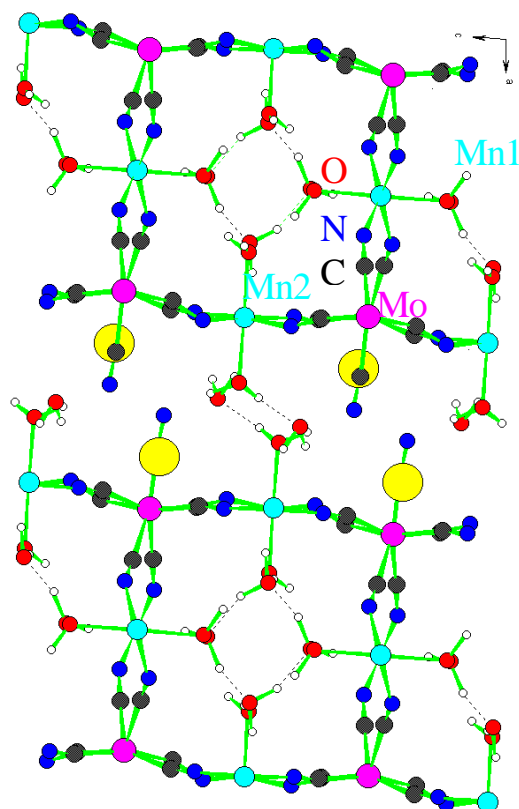


Figure 1: Hydrogen bonding in $K_2Mn_3(H_2O)_6[Mo(CN)_7]_2 \cdot 6H_2O$: projection of the structure at 50K along the b-axis. All interactions shown up to $r_{O...H} < 2 \text{ \AA}$.

The spin density in the ordered magnetic phase was determined from polarised neutron diffraction data at 4K with an applied field of 3 Teslas in order to achieve almost complete magnetic saturation.

The spin density maps displayed in Figure 2 have been reconstructed by a model refinement of the spin density on the set of flipping ratios according to the data treatment for a non-centrosymmetric space group. Surprisingly, opposite signs of the spin densities were observed upon the metal ions, reflecting an antiferromagnetic $\text{Mn}^{\text{II}}\text{--Mo}^{\text{III}}$ interaction through the cyano-bridge.

The spin populations on the manganese (Mn1 and Mn2) and molybdenum sites were determined as being 4.34(16), 4.93(15) and $-0.68(6) \mu_{\text{B}}$, respectively. The spin populations on the Mn sites are close to the spin-only values for the free ions. In contrast, by considering the deviation of the Mo^{III} spin population from $-1 \mu_{\text{B}}$, the degree of spin delocalisation of the Mo^{III} ions is evident. This is manifested by the negative spin density upon the nitrogen atoms of each of the four CN bridging ligands situated in the *bc*-plane. This delocalisation of negative spin density only in the *bc*-plane, is consistent with the occupation of the dx^2-y^2 orbital (that lies in the *bc*-plane) by the unpaired electron of the Mo^{3+} ion. This is consistent with the orbital energy diagram for a Mo^{III} ion in a capped trigonal prism environment, with C_{2n} site symmetry.

The contradiction with the previously reported magnetisation measurements on this material which suggested predominantly ferromagnetic interactions, may be due to the uncertainty on the sample mass due to the special conditioning. The low temperature magnetic measurements are currently being completed in order to clarify this point

Acknowledgments

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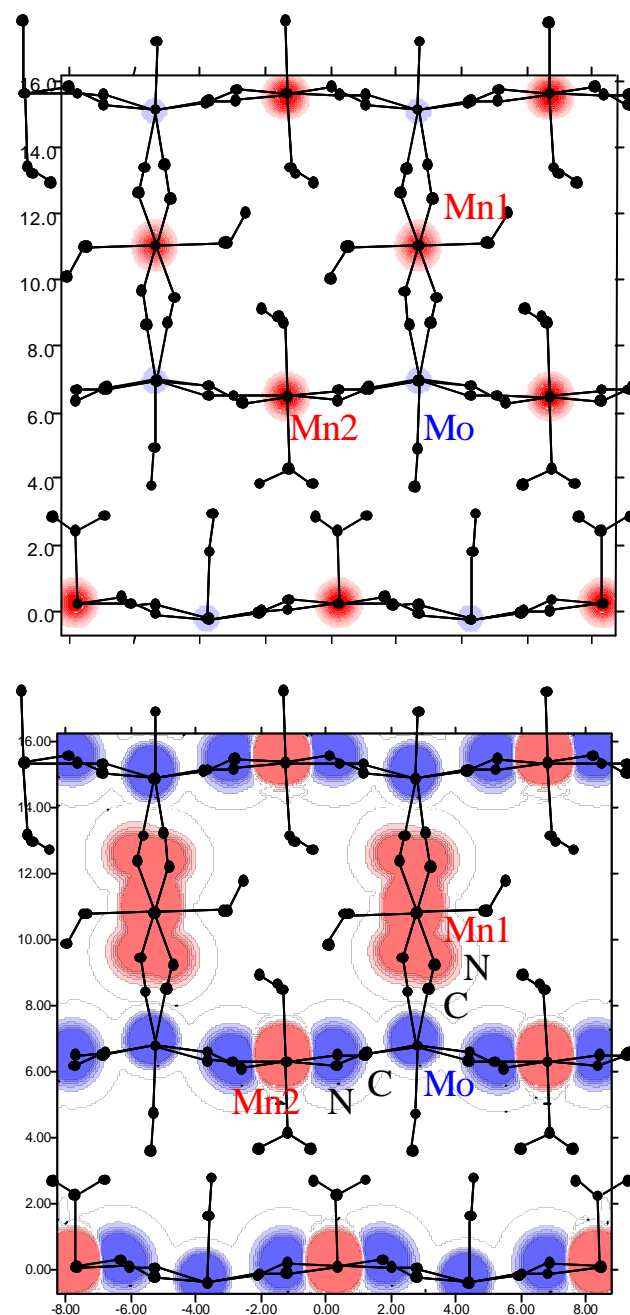


Figure 2: Projection of the spin density in $\text{K}_2\text{Mn}_3(\text{H}_2\text{O})_6[\text{Mo}(\text{CN})_7]_2 \cdot 6\text{H}_2\text{O}$ along the *b*-axis. Positive spin density is in red and negative density in blue.

Top: High levels from $-0.5 \mu_{\text{B}}/\text{\AA}^2$ to $5 \mu_{\text{B}}/\text{\AA}^2$ by step of $0.5 \mu_{\text{B}}/\text{\AA}^2$. Bottom: Low levels from -0.1 to $0.1 \mu_{\text{B}}/\text{\AA}^2$ with intervals of $0.02 \mu_{\text{B}}/\text{\AA}^2$. The zero line is not drawn.

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