Spin delocalization in the molecular manganese tetra-helicate cluster: $[Mn_3L_4](ClO_4)_2(H_2O)_2$

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Abstract. The magnetic properties of the compound $[Mn_3L_4](ClO_4)_2(H_2O)_2$ revealed that it is a rare trinuclear Mn^{II} compound showing ferromagnetic interactions and a possible anisotropic behaviour. Here we report preliminary magnetic susceptibility measurements and spin density determinations at the Mn and O atoms to elucidate the magnetic interaction model and the possible anomalous anisotropic magnetic behaviour reported previously for this compound, that it is confirmed to be inexistent.

1. Introduction

The Mn-based magnetic molecular cluster $[Mn_3L_4](ClO_4)_2(H_2O)_2$, with HL=2-methoxy-6-(pyridine-2-ylhydrazonomethyl)phenol, has been described as an almost linear trimer of Mn(II) in a high spin configuration with two isotropic magnetic interactions and an experimental EPR *g* factor of 2.14 which is one striking fact for such an isotropic system[1]. On the other hand, due to its isotropic and not degenerate nature, the system is an ideal benchmark to investigate the magnetic interactions in systems with several magnetic centers and more than one electron per magnetic center.

In this paper we report magnetic susceptibility and polarized neutron diffraction (PND) experiments in the compound, suggesting that it can be used as a case study for the large possibilities of PND technique in providing information on the spin delocalization as a previous step to understand magnetic coupling schemes that are operative in the cluster.

2. Results and Discussion

The reaction of two equivalents of hydrated Mn(II) perchlorate with one equivalent of HL, in methanol produces orange block-shaped crystals $[Mn_3L_4](ClO_4)_2(H_2O)_2$, compound **1**[1]. The structure

of **1** shows a dicationic trinuclear "bent" chain[2] of Mn(II) ions (the angle formed by Mn1–Mn2–Mn3 is 148.2(1)°) assembled by four deprotonated L–ligands. Each L–ligand acts as a tetra-dentate and tris-chelating donor, whereas the pyridyl and imine N atoms and both the methoxy and phenoxide O atoms are used to coordinate.

2.1. Magnetic susceptibility measurements

The magnetic susceptibility data have been collected with a Quantum Design MPMS-5S SQUID magnetometer on polycrystalline **1** in the temperature range from 1.8 to 300 K (Figure 2). The value of the $\chi_M T$ product at RT is 12.59 emu K mol^{-1} Oe^{-1}, which almost corresponds to the spin-only value of 13.12 expected for the magnetic system of three high-spin isolated Mn^{II} ions ($S_i=5/2$) by assuming $g_{Mn}=2.00$. By lowering the temperature, the $\chi_M T$ product increases, reaching a maximum of 13.49 emu K mol^{-1}Oe^{-1} at 9.35 K, then decreases abruptly to 8.99 emu K mol^{-1}Oe^{-1} at 1.8 K. This behavior probably indicates an intra-molecular ferromagnetic coupling between the manganese ions, followed by inter-molecular antiferromagnetic interactions at low temperature.

To fit the magnetic susceptibility data, we used the theoretical expression of the energy levels deduced from diagonalization of the isotropic Heisenberg Hamiltonian:

$$H = -J\left(\mathbf{S}_1 \cdot \mathbf{S}_2 + \mathbf{S}_2 \cdot \mathbf{S}_3\right) - J_{13}\left(\mathbf{S}_1 \cdot \mathbf{S}_3\right) + g\mu_B \sum_{i=1}^{3} S_i^z H^z \tag{1}$$

where the $\mathbf{S}_i$ are spin operators with $S_1=S_2=S_3=5/2$ and the J and J_{13} are the magnetic interaction constants between, respectively, the nearest neighbors Mn$_1$-Mn$_2$ and Mn$_2$-Mn$_3$, and the next nearest neighbors, Mn$_1$-Mn$_3$, as it is schematized in the insert of the figure 1. The energies are given by:

$$E(S_{13},S) = -(J/2)\left[S(S+1) - S_{13}(S_{13}+1)\right] - (J_{13}/2)S_{13}(S_{13}+1) \tag{2}$$

where S is the total spin of the trimmer and S_{13} is the spin quantum number associated with $S_{13} = S_1 + S_3$ of the terminal Mn ions. The conditions $0 \leq S_{13} \leq 5$ and $|S_{13}-5/2| \leq S \leq |S_{13}+5/2|$ are assumed. An inter-molecular interaction given by $-zJ'<S_z>S_z$, has been also included in the determination of the magnetic susceptibility as a perturbation of (1) in mean field approximation [3]. Other effects arising from zero-field splitting as well as anisotropy interaction has not been considered.
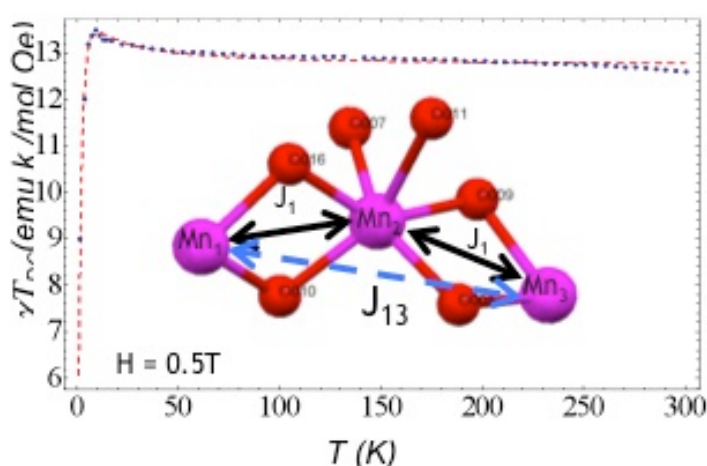

Figure 1. χT vs T; (•) experimental data; (-) fit employing energy levels given by (2). The insert shows a schematic view of the interactions intra-molecule.
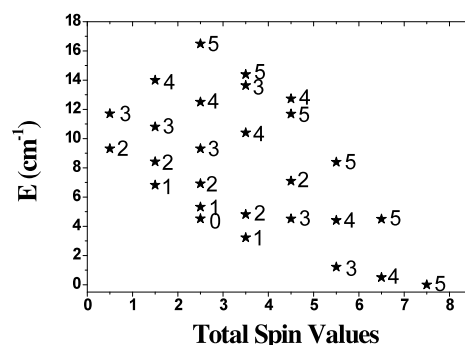
Figure 2. Energy levels for **1** calculated with J=0.59(2) cm^{-1} and J_{13}=-0.19(2) cm^{-1}. The energy is given as function of total spin value S and the S_{13}. The ground state has S=15/2 and S_{13}=5.

The best fit of the magnetic susceptibility data employing the Van Vleck expression for the magnetic susceptibility with the energy values given by (2) and using the molecular field approximation leads to $J=0.59(2)$ cm^{-1}, $J_{13}=-0.19(2)$ cm^{-1}, $zJ'=-0.20(3)$ cm^{-1} and $g=1.97$. There is good agreement between the model and the experimental data as it is observed in the figure 1. The obtained values for the interactions constants lead to an energy levels scheme as showed in figure 2. The ground state is given by $|S_2=5/2, S_{13}=5, S=15/2>$ which corresponds with the three Mn spins aligned ferromagnetically.

2.2. Spin densities determination

The determination of the magnetization density using PND has played a key role during the last fifteen years in the field of molecular magnetism. The observations in a PND experiment are the flipping ratios which are given by $R(\boldsymbol{k})= \Gamma^+/\Gamma^-$ where Γ^+ and Γ^- are the diffracted intensities for the incoming neutron beam polarized parallel (+) or antiparallel (-) to the applied magnetic field on the crystal.

As a previous step, the nuclear structure factors (F_N) at 2K, as well as the absorption coefficients for the compound **1**, have been determined with a non-polarized neutron diffraction experiment carried out at the single crystal thermal diffractometer CRG-D15 at the ILL employing a wavelength $\lambda=1.171$ Å.

The PND experiment was performed on the 2-axis polarized neutron diffractometer 5C1, at the Laboratoire Leon Brillouin (Saclay, France) working with a wavelength of $\lambda=0.84$ Å with a beam polarization equal to 0.920(4). A cryomagnet, which holds the sample at 2K and provides a vertical magnetic field of 6T, was used. After merging, a total of 87 independent flipping ratios were measured with the single crystal of **1** mounted with its a* axis parallel to the vertical applied field. No other orientation was possible to be measured because of the breakdown of the crystal.

The indirect method "Multipole expansion" [4], in which the magnetization density around an atom "*i*" is expanded into the basis of the real spherical harmonics d_{lm} –referred also as multipoles– has been used to analyze the measured flipping ratios. Therefore the magnetization density on atom "*i*" can adopt the expression

$$m_i(r) = \sum_l R_i^{l,dens}\left(|r - r_i|\right)\sum_{m=-l}^{l} P_{ilm}d_{lm}\left(\phi_i,\varphi_i\right) \tag{3}$$

where P_{ilm} are the population coefficients of the real spherical harmonics $d_{lm}(\phi_i,\varphi_i)$, which are normalized according to Coppens, [5] and $R_i^{l,dens}$ are the Slater radial functions. In order to minimize the number of parameters in the fit of $R(K)$, the ζ_i exponent and the n_{il} values of the Slater radial functions were fixed respectively to $\zeta=2\xi$, where ξ is atomic Slater exponent taken from the literature [6] and $n_l=2(n-1)$, where n is the principal quantum number.

The codes MFLOP [6] and FullProf [7] were used to fit the flipping ratios. In both programs the definition of agreement factors, the normalization of the real spherical harmonics, and the way of defining the local axis for non-spherical flipping ratio refinements are identical. The results obtained for the several considered models were independent of the software employed.

Considering the small number of observations, in this case only 87 independent measurements of flipping ratio, models with only a spherical spin distribution on each Mn and O atoms were considered, in order to reduce the number of free parameters.

In a first model (A), where only the Mn ions were independently refined, around +4 μ_B populations were obtained for each Mn ion (see table 1). In a more confident model (B), where the coordination oxygen atoms were allowed to bear some spin density, the Mn populations become into +3.8 μ_B and a spin delocalization of around 11% was observed toward the oxygen atoms. One remarkable fact is the small spin population found at the O(10) (see insert in figure 1) with respect the other O atoms. The magnetization of the sample as function of the magnetic field did not reach saturation at the experimental conditions (2K and 6T) and therefore it is not a surprise that in both models the spin populations were lower than the 5 μ_B expected for each Mn(II).

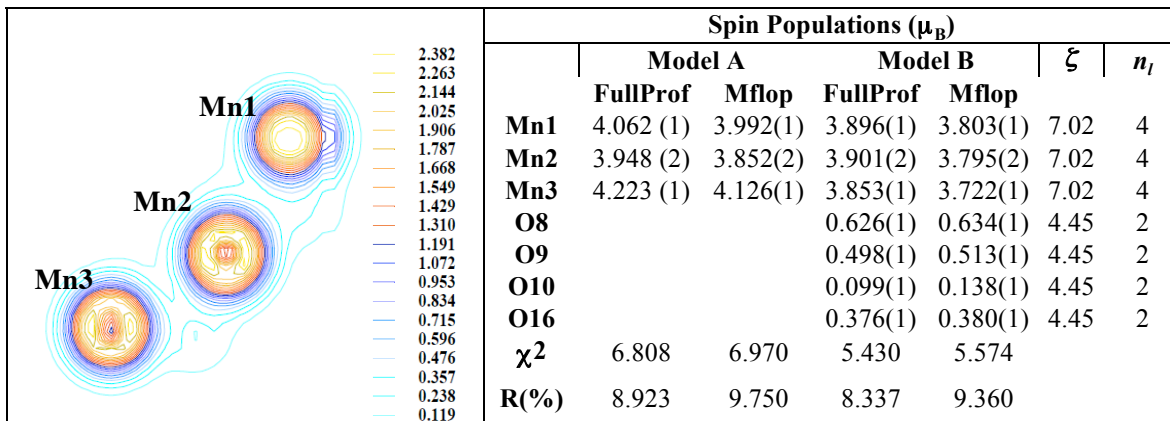**Figure 4.** Spin density projection on the plane containing the 3 Mn(II) atoms

Table 1. Spin populations of **1** determined using MFLOP and FullProf codes. The ζ and n_l exponents for the radial component in the multipolar expansion are listed.

	Spin Populations (μ_B)					
	Model A		Model B		ζ	n_l
	FullProf	Mflop	FullProf	Mflop		
Mn1	4.062 (1)	3.992(1)	3.896(1)	3.803(1)	7.02	4
Mn2	3.948 (2)	3.852(2)	3.901(2)	3.795(2)	7.02	4
Mn3	4.223 (1)	4.126(1)	3.853(1)	3.722(1)	7.02	4
O8			0.626(1)	0.634(1)	4.45	2
O9			0.498(1)	0.513(1)	4.45	2
O10			0.099(1)	0.138(1)	4.45	2
O16			0.376(1)	0.380(1)	4.45	2
χ^2	6.808	6.970	5.430	5.574		
R(%)	8.923	9.750	8.337	9.360		

3. Conclusions

Magnetic susceptibility measurements have been employed to determine the nature of the intra and inter-molecular magnetic interactions, involving energies of less than 1 cm^{-1}. In this case the value obtained for the *g* factor is 1.97 closer to the characteristic value of an isotropic system, g=2.

Spin densities results are compatible with the *S=5/2* model for each Mn^{II} ion, with a small spin delocalization, of about 11%, toward the coordination oxygen atoms. The spin distributions around the Mn atoms are spherical which is indicative of the isotropy of the magnetic system.

The study of the system through the combination of several experimental methods has allowed us to demonstrate the isotropic nature of the system and the ferromagnetic character of the intra-molecular magnetic interactions. This understanding of the delicate magnetic interactions intra- and inter-clusters and the spin delocalization is crucial to permit in future the design of new magnetic interesting compounds.

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