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Antiferromagnetic interactions in a distorted cubane-type tetranuclear manganese cluster

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Abstract. We have synthesized a new tetranuclear manganese cluster with a distorted cubane-like $[\text{Mn}_4\text{O}_4]$ -core. High field magnetization experiments reveal an intramolecular antiferromagnetic coupling between the four manganese ions. We explain our results both qualitatively and quantitatively by a simple spin square model in terms of four equal antiferromagnetic exchange interactions in the core with coupling strengths of $J = -1.69$ K.

1. Introduction

Understanding the magnetic interactions in molecules has been a research topic for many years, starting with the discovery of the antiferromagnetic coordination compound dimeric copper acetate [1] and possible control over the magnetic properties of such compounds has been looked for ever since. Anderson was able to supply a quantum mechanical description of the interactions between spins, localized on neighbouring metal ions and bridged by a diamagnetic ligand, and named it superexchange [2]. Since his description was rather elaborate, Goodenough and Kanamori [3,4] translated his ideas into a series of symmetry rules. Further implementation of these rules in molecular magnet design was established by the pioneering work of Kahn. By combining different metal ions in binuclear coordination complexes and changing their ligand environment he was able to control the electronic orbital overlap of these ions and therefore the magnetic exchange interactions between them [5]. The major breakthrough in the field of molecular magnetism was the serendipitous discovery of zero-dimensional single molecule magnets (SMMs) like the well-known Mn_{12} - [6], Fe_8 - [7] and V_{15} -clusters [8]. These molecules have shown very interesting physical behaviour on a molecular scale, like magnetic bistability and quantum tunnelling of magnetization [9].

In this paper we present the full magnetic characterization of a new and interesting magnetic molecular compound, the tetranuclear manganese cluster $[\text{Mn}_4(\text{OAc})_4]$. We have been able to measure the high field magnetic moment up to its saturation, therefore following the complete repopulation of the underlying energy levels. Furthermore, we can fully explain this magnetization behaviour with a basic model for exchange interactions in spin quartets. This leads to an easy understanding of the magnetic character of the manganese cluster and provides a fast access to the size of the intramolecular exchange constants.

2. Experiment

2.1. The molecular structure

We have prepared a manganese cluster based on a penta-dentate pyridine-diimine type ligand and acetate ligands, which both allow further chemical modification. It consists of a distorted cubane-like core containing four manganese ions and four oxygens at the corners with two extra acetate bridges at the top and bottom of the cube (Figures 1 and 2).

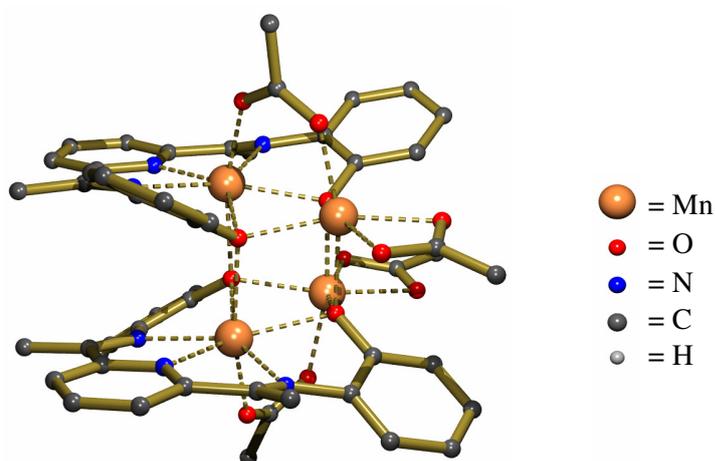


Figure 1. Schematic representation of the X-ray structure of the $[\text{Mn}_4(\text{OAc})_4]$ -cluster (hydrogen atoms are omitted for clarity)

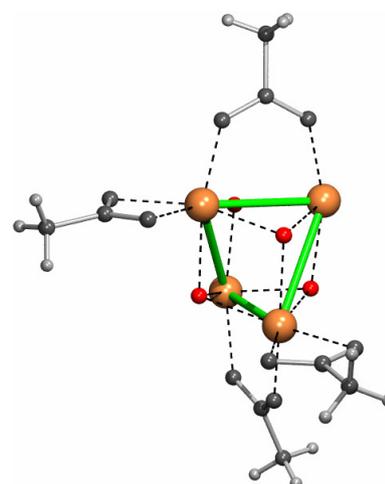


Figure 2. The distorted cubane-like core consisting of four manganese ions, four phenolate oxygens and four acetate ligands. The exchange interactions of the spin square structure are shown in green.

2.2. Magnetization

In order to elucidate the magnetic exchange coupling between the manganese centres of this new structure influenced by the ligand environment and the cubic core structure, we have performed magnetization experiments with an extraction magnetometer [10]. Figure 3 shows the magnetic moment of a powdered sample of Mn_4 -cluster (66.3 mg, 51.4 μmol) in high magnetic fields up to 31 T and a wide temperature range $T = 4 \dots 300$ K. At low temperatures, the magnetic moment increases its slope for magnetic fields up to 5-10 T, followed by linear behaviour at intermediate fields and a slowly decreasing slope on the approach to saturation at the highest magnetic fields. Since all manganese ions are Mn^{II} , with 5 unpaired d-electrons per ion, these curves represent the cluster's magnetic field dependent energy level population starting at a nonmagnetic $S = 0$ state, continuing through all consecutive spin states and ending in the saturated $S = 10$ state, where all twenty unpaired electrons have their spins aligned parallel to the magnetic field. Upon temperature increase these slope changes are spread out over the entire isotherm, resulting in a nearly linearly increasing magnetization over the whole magnetic field regime. For comparison with other typical measurement techniques that directly obtain the magnetic susceptibility, we have taken the derivative of the magnetic moment isotherms to

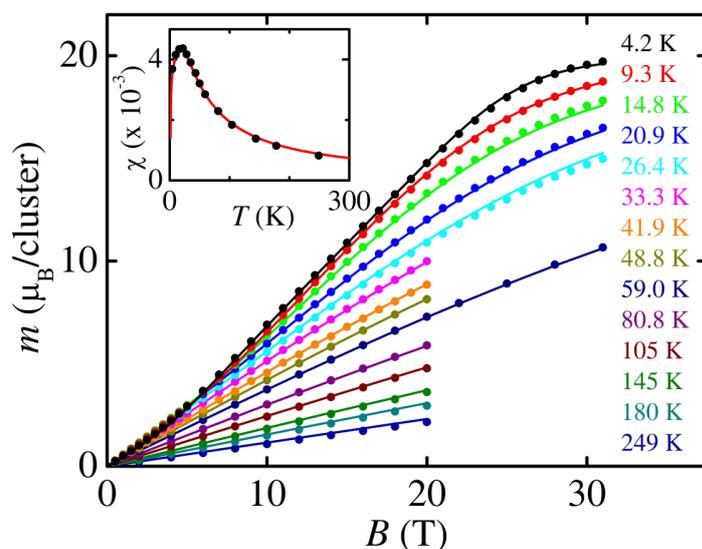


Figure 3. Measured magnetic moment of the Mn₄-cluster (closed circles). The solid lines represent the fits for a square spin quartet with $J = -1.69$ K and $g = 2$ at the measured temperatures.

Inset: Temperature dependence of the volume magnetic susceptibility extracted from the magnetic moment data at low magnetic fields. The red solid line represents the fit for a spin square quartet with $J = -1.69$ K and $g = 2$.

the magnetic field to obtain the volume magnetic susceptibility as a function of temperature for all magnetic fields. At low magnetic fields this susceptibility displays the typical behaviour of a molecular antiferromagnet, as is shown in the inset of Figure 3. It starts with almost zero susceptibility at the lowest temperatures, gradually increases through the Néel point (inflection point) to a maximum susceptibility, continuing in inverse temperature behaviour towards higher temperatures, similar to paramagnetic materials. The Néel temperature provides an indication of the coupling strength between the manganese ions and is approximately 15 K. Thus, the single spin energy exceeds this antiferromagnetic exchange coupling in magnetic fields higher than 25 T, which is indeed observed as a saturation of the magnetization when approaching 31 T.

2.3. Analysis

For a more quantitative analysis of the measured magnetization data in terms of exchange interactions between the manganese ions, we have used a model based on the expressions for the magnetization behaviour of spin quartets determined by Liu and Shapira [11]. The used expressions are valid for describing a system with exclusively antiferromagnetic interactions with one exchange constant J between four identical spins S . Combining their energy level functions with Boltzmann's distribution function yields the net magnetic moment of the system. To see the influence of the number of exchange coupling paths on the magnetization behaviour we have based our fits on three types of spin quartets, that best resemble the cubane-like structure of the [Mn₄O₄]-core (Figure 4): two separated spin dimers with only one magnetic interaction in each pair, a spin tetrahedron with interactions between all magnetic centres and a spin square in which every centre interacts with only two of its neighbouring centres. Our full data set, spanning a large temperature and magnetic field range, allows an accurate discrimination between the different possible scenarios.

Differences between the fits for these spin quartets are best visualized in the residuals, which are shown in Figure 5a for 4.2 K and 59 K. Clearly, the best fits with the smallest residuals are obtained with the spin square model for $J = -1.69$ K, where only a small overestimation at high magnetic fields and low temperatures is visible. The obtained J value is within the range $+0.4 \dots -5.9$ K reported for other [Mn₄O₄]-cubane complexes [12] and we have confirmed this spin structure with four antiferromagnetic exchange interactions by density functional theory calculations (DFT) based on the determined crystallographic structure. The sensitivity of the spin square fits for variation of J is shown in Figure 5b, where the relative residuals for optimized J and for $J \pm 0.10$ K are plotted for 4.2 K and 59 K. The maximum relative residuals increase to 5 % for both higher and lower J , which visualizes the rather high sensitivity of this model to exchange constant variation. The perfect fits to the

experimental data with the spin square model and optimized J are plotted in Figure 3, where the total magnetic moment is shown as a function of the magnetic field at all measured temperatures.

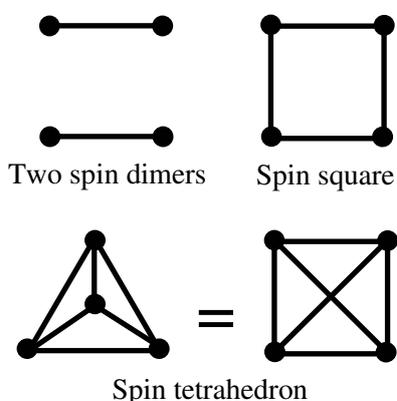


Figure 4. Spin quartet types resembling the $[\text{Mn}_4\text{O}_4]$ -core and its intramolecular magnetic interactions. The closed circles represent the spin centres and the solid lines between them the exchange interactions J .

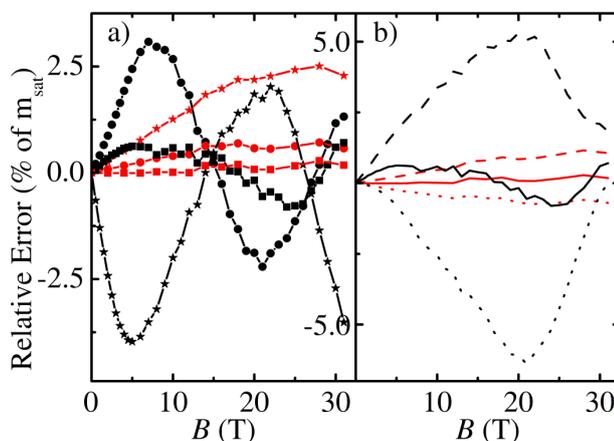


Figure 5. Relative residuals at 4.2 K (black) and 59 K (red) of a) optimal exchange constant per spin quartet type: $J = -3.05$ K for dimer (closed circle), $J = -1.74$ K for tetrahedron (closed star) and $J = -1.69$ K for square (closed square); b) exchange constant variation for spin square: $J = -1.69$ K (solid line), $J = -1.59$ K (dashed line) and $J = -1.79$ K (dotted line).

3. Conclusion

We have synthesized a new manganese cluster with a distorted $[\text{Mn}_4\text{O}_4]$ -cubane structure. The exchange interaction of the manganese ions through the oxygen bonds results in an overall antiferromagnetic behaviour measured in magnetic moment isotherms up to 31 T, which can be described by a spin square model with $J = -1.69$ K. In addition, we would like to mention that preliminary DFT calculations have shown us that electron density withdrawal of the $[\text{Mn}_4\text{O}_4]$ -core will result in stronger and positive intramolecular exchange interactions directed towards ferromagnetic behaviour. We are currently investigating related clusters bearing electron withdrawing substituents on their ligands. Eventually this will result in user-designed magnetic molecules in which we have full control over the magnetic properties via the choice of the ligands and their substituents.

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