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Magnetic properties of an interlocked molecular magnet

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Abstract

In this work we report the magnetic properties and preliminary structural results of the molecule-based ferrimagnet with formula $[Pr\text{-}Rad]_2[Mn_2\{Cu(opba)\}_3](DMSO)_{3.3}\cdot 5H_2O$, where opba stands for *ortho*-phenylenebis(oxamato) and $Pr\text{-}Rad^+$ is propil–nitronyl nitroxide radical cation, which presents magnetic transition at 24.1 K The single crystal structure was determined using X-ray CPr line from the LNLS synchrotron radiation with $\lambda = 1.2$ Å, at 100 K. The crystal is composed by 2D honeycomb-like M_6Cu_6 hexagons leading to a 3D interlocked network. The low temperature (2 K) magnetization isotherms present a rapid saturation up to about 5 β mol^{-1} with a slow and steady increase up to 6.5 β at 9 T. This feature is common to other molecular magnets of similar structure, and was investigated further with magnetization measurements down to 120 mK and 8 T, which revealed a metamagnetic-like transition at a field of 2.3 T. This is attributed to the weak ferromagnetic coupling of the radical spin to the Cu(II) $S = 1/2$ in the middle of the hexagon edges, the later strongly antiferromagnetically coupled to the Mn(II) $S = 5/2$ spin at the corners of the hexagons. This former interaction is weak and also responsible for the lowering of the decrease of the low field magnetization at low temperature.

Keywords: Molecule-based magnets; Metamagnetism; Interlocked structure

1. Introduction

The synthesis and study of molecule-based materials that exhibit bulk ferromagnetic properties has been a focus of an ever-increasing experimental and theoretical research [1,2]. In contrast to conventional atom-based magnets, molecule-based systems potentially offer the advantages of enhanced processability (many dissolve in common solvents) and low density, in addition to biocompatibility. Furthermore, some materials may have optical properties like transparency at visible frequencies, potentially useful in different technological applications. Implicit or explicit in much of this work has been the idea of self-assembly of specifically designed building blocks. In this way molecular magnetism may be considered as the facet of supramolecular chemistry dealing with open-shell units [3]. The synthesis and the study of new molecular systems with general formula of the type $Rad_2[M_2(CuL)_3]\cdot Sol$ where M is a transition metal (Mn, Co, Ni) or Mg, L is *ortho*-phenylenebis(oxamato), Rad is a cation of the nitronyl nitroxide type and Sol represents the solvent molecules dimethylsulfoxide (DMSO) and H_2O, has been a challenge. These molecule-based magnets present a 3D structure formed by the interlocking of two 2D networks having 15 $K \leq T_c \leq 38$. They attracted much attention since the pioneering work [4], due to its exotic interlocked structure stimulating other studies on a similar interlocked compound [5–7]. In this work we present the preliminary structure of one of the compound of this family and discuss its magnetic properties. In particular we focus attention to the very low temperature approach to magnetic saturation.

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2. Experimental

2.1. Synthesis

The compound was prepared as already described [5]. The synthesis is very sensitive to the purity of the precursor. To obtain a material of stoichiometry Cu/Mn 3/2, the copper building block must be in excess. If the Cu/Mn ratio in the solution is low, the formation of MnCu(opba) chain occurs [8]. The effect of concentration upon the reaction, and on the growth of crystals, is crucial. If the solution is over diluted no product will be obtained, as Mn(II) is slightly base sensitive and will decompose before or during the crystallization, producing an insoluble brown impurity. The use of water as a solvent favors the formation of the chain species.

2.2. X-ray diffraction

Due to the great volume of the unit cell (>8.500 Å^3) and the small size of the available samples (<0.1 mm), single crystal experiments were performed at the CPr line in the National Laboratory of Synchrotron Light (LNLS-Brazil) using a $\lambda = 1.2$ Å radiation, at a temperature of 100 K, using a 35 cm MAR image plate; the samples were frozen immediately after taking them from its mother solution. Crystallographic data: space group Cc; $a = 25.303(5)$ Å; $b = 24.698(5)$ Å; $c = 18.744(4)$ Å; $b = 132.17(3)$; $V = 8682(3)$ Å^3; $Z = 4$. Results of the refinement (in progress) with U isotropic, except the metals: $R_1 = 0.13$, $wR_2 = 0.36$ and $S = 3.043$ for all 4674 reflections.

2.3. Magnetic measurements

The magnetic properties have been studied in two commercial AC susceptometer/DC-magnetometer, Lake Shore model ACS7045 and Quantum Design PPMS system, with magnetic fields up to 9 T. The diamagnetism of the sample and sample holder were taken into account. Very low temperature magnetization measurements were performed using a home made Squid magnetometer with a minidilution refrigerator developed at the CRTBT-CNRS by Dr Carley Paulsen.

3. Results and discussion

The temperature dependence of the AC magnetic susceptibility is shown in Fig. 1. We used a frequency of 140 Hz and a r.m.s. excitation field of 5 Oe. The susceptibility presents an abrupt increase of both χ' and χ'' with an inflexion at $T_c = 24.1$ K. Note that χ' presents a decrease as T is lowered while χ'' an increase. The magnetization measurements as function of temperature are presented in Fig. 2. They are in quantitative

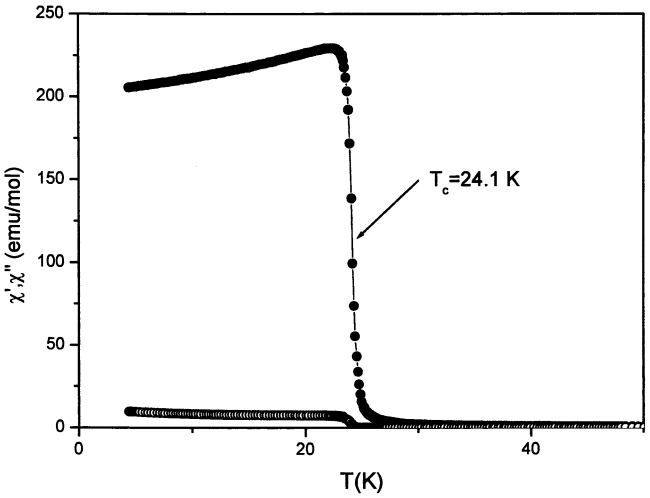

Fig. 1. Ac susceptibility measurements done on powder using 140 Hz and 5 Oe amplitude. T_c was determined at the point where the slope is maximum.

agreement with the AC susceptibility data. Both the zero-field cooled (ZFC) and field cooled (FC) curves (M/H) superpose each other, the apparent shift is due to the rapid time temperature sweep used in the experiment. At low fields both ZFC and FC curves show a downturn suggesting some weak antiferromagnetic interactions. The decrease of the susceptibility with higher fields is due to saturation effects.

The field dependence of the magnetization isotherms for several temperatures is shown in Fig. 3. The magnetization increases steeply up to a field of 500 Oe for temperatures below T_c with roughly the same slope. Above this temperature the initial susceptibility decreases as expected and shown for 25 K. At the lowest

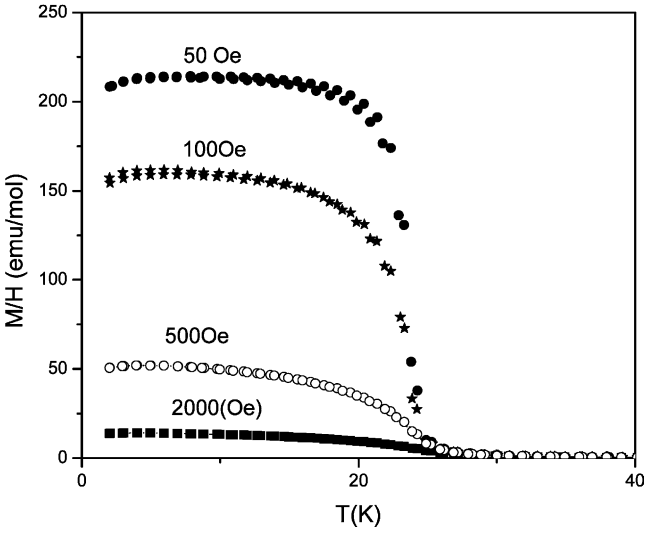

Fig. 2. Magnetization divided by the applied field as function of temperature. Both ZFC and FC data superpose well. The small discrepancy is an artifact due to the fast temperature sweeping. The decrease with field is due to saturation effects.

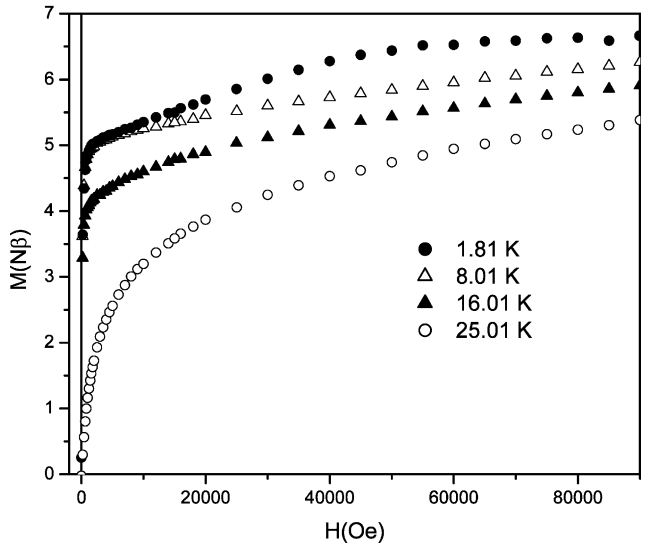

Fig. 3. Typical magnetization isotherms. Below T_c the initial slope is about the same and very large, as expected for a system with spontaneous magnetization. Note that saturation is not reached at the lowest temperature (1.81 K).

temperature (1.8 K) the magnetization increases steadily not reaching saturation even at 90 kOe. The saturation magnetization, M_{sat}, was estimated from this isotherm by extrapolating a plot of M versus 1/H to zero obtaining a value of 6.9 Nβ (Bohr magnetons). Note that for the interlocked compound [4-MeRad]$_2$[Mn$_2${Cu(opba)}$_3$](DMSO)$_2\cdot$2H$_2$O [4], even a magnetic field of 200 kOe, was not sufficient to reach saturation. In order to understand better these features we performed magnetization measurements at very low temperatures, shown in Fig. 4. The first feature to note is that the decrease of both ZFC as FC cooled magnetization continues down to the lowest tempera-

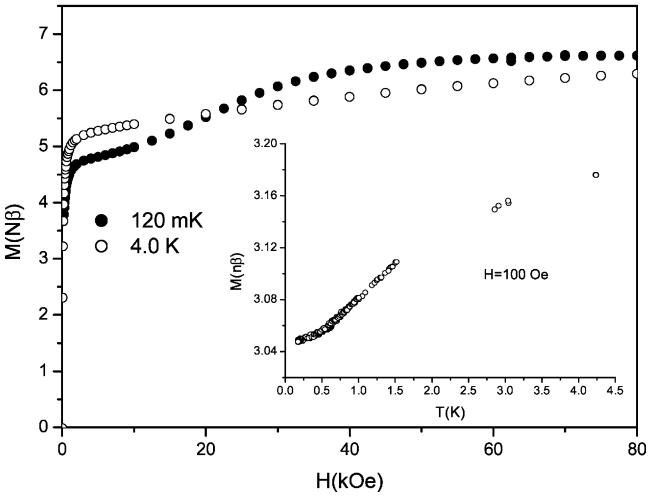

Fig. 4. Very low temperature magnetization (120 mK) in contrast to the 4.0 K isotherm showing a metamagnetic-like transition around 21 kOe. Inset shows that both ZFC and FC (with 100 Oe) magnetization decreases towards low temperatures, also seen in Fig. 2.

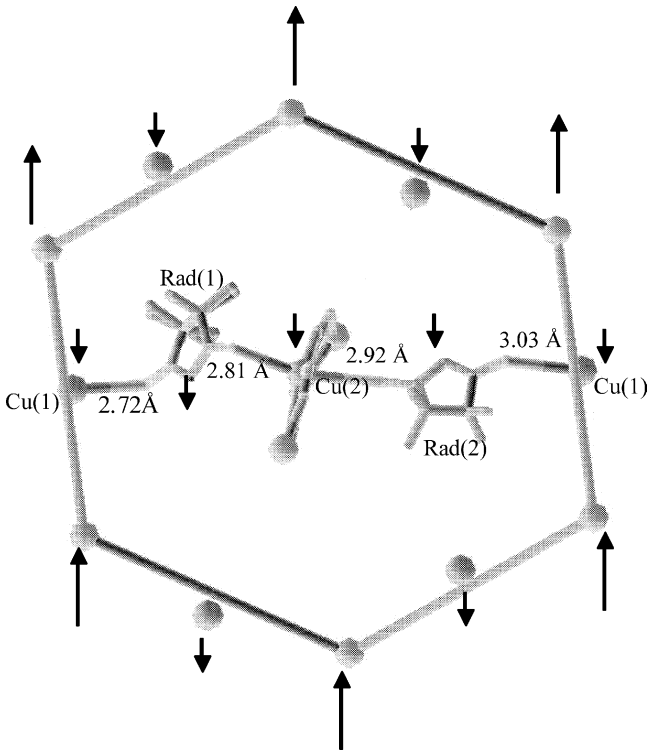

Fig. 5. Proposed magnetic structure. Note the different Cu–O distances and bonding angles.

ture, denoting the existence of weak interactions or some anisotropy that decrease the total moment of the compound. The main feature is that at 120 mK, the increase of the moment with field has a typical shape of a metamagnetic transition. The increase of the magnetic moment is of the order of 2 Bohr magnetons, which may be associated with the flipping of one 1/2 spin. We rule out the possibility of flipping any Cu(II) ion spin as they are strongly antiferromagnetically coupled to the Mn(II) ions by the opba ligand, around 33.1 cm^{-1} in compounds with similar environment [9]. The flipping field is 21 kOe.

In order to explain this magnetic behavior, we propose a model of the magnetic structure where the ferrimagnetic Mn(1)–Cu(1) hexagons of one layer (see Fig. 5) are magnetically coupled to the quasi-perpendicular interlaced hexagon Mn(2)–Cu(2) by 2 Cu–Rad–Cu–Rad ferromagnetic chains. In Fig. 5 we show the proposed magnetic structure with only one of the hexagons and a simplified view of one of the linking chains. Now, from the refinement of the crystallographic data (in progress) the obtained distances between the Cu(II) ions and the oxygens of the Pr-Rad$^+$ are shown. In addition to the different distances, the bonding angles are also different and as a result one of the two free radicals interacts more weakly with the neighboring Cu(II) ions than the other. Due to this, Rad(2) which has a magnetic moment pointing contrary to the applied field will flip its moment to a direction

parallel to the field explaining the increase of the total magnetic moment form by 2 Bohr magnetons.

4. Conclusions

We have presented susceptibility and magnetization results on a new interlocked ferrimagnet with $T_c = 24.1$ K. The approach to saturation at very low temperatures allowed us to associate a metamagnetic-like transition with the flipping of the magnetization of one of the free radical that link the interlocked planar honeycomb networks.

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