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Synthesis and characterization of a new chiral nanomagnet

Neus Domingo [a,*], Philippe Gerbier [b], Jordi Gómez [b], Daniel Ruiz-Molina [b], David B. Amabilino [b], Javier Tejada [a], Jaume Veciana [b]

[a] *Facultat de Física, Universitat de Barcelona, Avinguda Diagonal 647, 08028 Barcelona, Catalonia, Spain*
[b] *Institut de Ciència de Materials de Barcelona (CSIC), Campus Universitari, 08193 Bellaterra, Catalonia, Spain*

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Abstract

The dodecanuclear complexes formed between manganese ions and carboxylate anionic ligands are the single molecule magnets (SMMs) with greatest synthetic accessibility and richness of magnetic properties. In this work, we describe a recently synthesized chiral SMM which presents both spontaneous magnetization and optical activity. This objective has been targeted because of the possibility of observing new phenomena related with the synergy between structural chirality, optical activity, and magnetic ordering.

Keywords: Single molecule magnet; Susceptibility; Chirality; Manganese; Magnetic clusters

1. Introduction

In 1993 it was discovered for the first time that the acetate-coated dodecamanganese cluster $[Mn_{12}O_{12}(O_2CCH_3)_{16}(H_2O)_4]\cdot 4H_2O\cdot 2CH_3CO_2H$ ($[Mn_{12}Ac]$) functions as a nanoscale molecular magnet and for this reason the term of single molecule magnet (SMM) was coined. Since then, a few more families of complexes that function as SMMs have been obtained. There are basically two different synthetic procedures available for making new $[Mn_{12}O_{12}(O_2CR)_{16}(H_2O)_4]$ complexes: the original method used by Lis [1] to synthesize the acetate Mn_{12} complex and a second synthetic approach, based on ligand-substitution reactions, which are driven by the greater acidity of the added carboxylic acids RCO_2H and/or the removal by distillation of an azeotrope of acetic acid and toluene (see Eq. (1)).

$$[Mn_{12}Ac] + 16RCO_2H \rightarrow [Mn_{12}O_{12}(O_2CR)_{16}(H_2O)_4] + 16MeCO_2H \qquad (1)$$

The advantage of this second method is that reaction yields are generally larger than those obtained in the first approach. More recently, a new functionalization of Mn_{12} SMM with ligands other than carboxylate or site-specific modifications to yield mixed carboxylate $[Mn_{12}O_{12}(O_2CR)_8\cdot(O_2CR')_8(H_2O)_4]$ complexes have been achieved [2,3]. The interest for the development of these new synthetic methodologies lies in the variety of reactivity studies and applications that can be achieved with an intrinsic SMM behavior.

Optically active molecular magnetic materials are interesting from various perspectives, but not least from the viewpoint of combining optical and magnetic effects [4,5]. During the last few years, increasing interest about new phenomena of magnetochirality has appeared, particularly after its first experimental observation by Rikken and Raupach [6] in 1997, and due to its possible contributions to the answer of the origin of homochirality of life [7–10]. In this context, we report here the magnetic characterization and natural circular dichroism (CD) properties of enantiomeric SMMs of the $[Mn_{12}O_{12}(OOCR)_{16}]S_x$ (S = solvent) family [11]. The synthesis of the (*R*)-, (*S*)-, and (*RS*)-chloropropionate

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* Corresponding author.
E-mail address: neus@ubxlab.com (N. Domingo).

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Mn_{12} clusters was achieved, and the optical activity of the chiral compounds was confirmed by CD spectroscopy.

2. Experimental

2.1. Synthesis of chiral SMM

The synthesis of the clusters (*R*)- and (*S*)-[$Mn_{12}O_{12}$-($O_2CCHClMe)_{16}(H_2O)_4$]·$CHClMeCO_2H$ ((*R*)- and (*S*)-**1**) described here was achieved using a modification of the synthetic route shown in Eq. (1) using the pivaloate leaving anion strategy reported recently [12]. The synthesis will be detailed elsewhere [13].

2.2. Physical measurements

Magnetic characterization was performed in a commercial Quantum Design MPMS2 SQUID (rf) magnetometer equipped with a 5 T magnet and placed in a cryostat with a working temperature ranging from 1.8 to 300 K. Microcrystals were first oriented and restrained in Eicosan to prevent torquing. Alignment in Eicosan was performed while keeping the samples in a 5 T field at a temperature above the melting point (312 K) of Eicosane for 15 min and then decreasing the temperature gradually to constrain the sample.

3. Results and discussion

The optical activity of the chiral compounds (*R*)- and (*S*)-[$Mn_{12}O_{12}(O_2CCHClMe)_{16}(H_2O)_4$]·$CHClMeCO_2H$ ((*R*)- and (*S*)-**1**) in solution was confirmed by natural circular dichroism (NCD) spectra shown in Fig. 1. Three different contributions can be distinguished: a weak Cotton effect in the region of 520 nm and a more intense one at 345 nm of opposite sign, and a further weak signal at 260 nm. On the other hand, UV–Vis absorption spectrum is characterized by a featureless rise in the extinction coefficient from approximately 800–200 nm, with a plateau between 260 and 240 nm, as in the acetate cluster [14]. Thus, the optical activity arising from the manganese ions in the visible region has a high *g*-value, a prerequisite for the observation of magnetochiral effects.

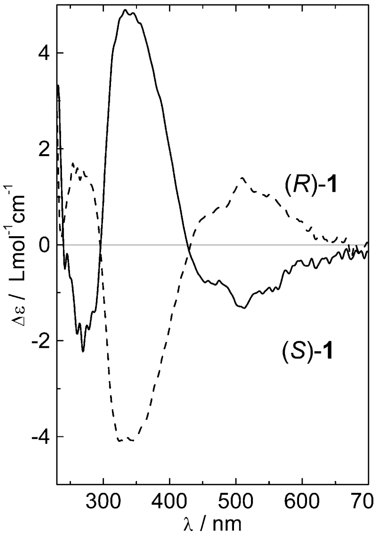

Fig. 1. The CD spectrum of the chiral manganese clusters in dichloromethane at room temperature.

For magnetic characterization in the solid state, polycrystalline samples were oriented in an Eicosan matrix. a.c. magnetic susceptibility was measured in the temperature range from 1.8 to 10 K and at six different frequencies between 3 and 1000 Hz. The in-phase component of the a.c. susceptibility shows two different frequency-dependent peaks, one in the low-temperature region of 2.5–4 K and another in the high-temperature region of 4–7 K, followed by a Curie decrease as temperature is raised (Fig. 2). The out-of-phase component is shown in Fig. 3. It also exhibits two frequency-dependent peaks, the one in the low-temperature region being almost one order of magnitude lower than the one in the high-temperature region. This result has already been observed for other Mn_{12} complexes [15–17] and indicates the presence of two different relaxation mechanisms in the compounds governed by two different effective energy barriers and characteristic relaxation times.

Magnetization relaxation times (τ) are obtained from the relationship $\varpi\tau = 1$ at the maxima of the χ''_M vs. temperature curves, the position of which is defined to be the blocking temperature. Least-square fit of data pairs (w, T_B) for the two peaks obtained for the χ''_M data to the Arrhenius law (Eq. (1))

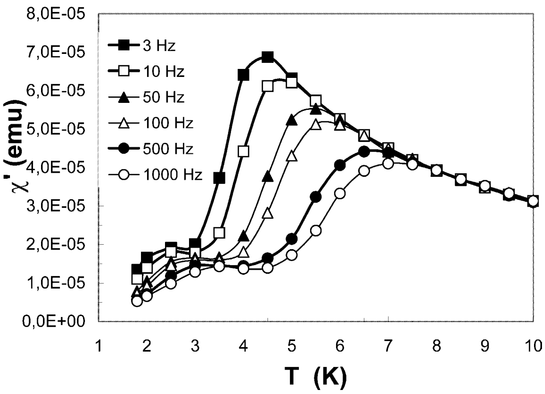

Fig. 2. In-phase component of the a.c. magnetic susceptibility for (*R*)-**1** isomer as a function of the temperature at six different frequencies, measured with applied magnetic fields of $H_{a.c.} = 3.5$ Oe and $H_{d.c.} = 0$ Oe.

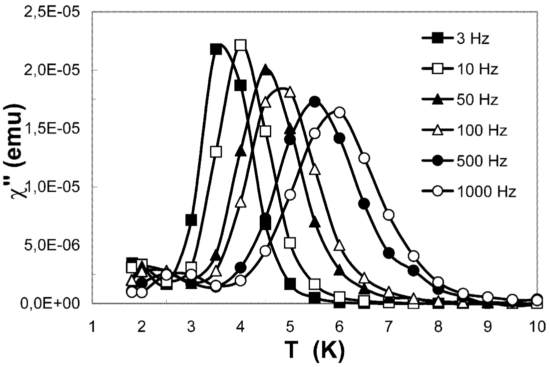

Fig. 3. Out-of-phase component of the a.c. magnetic susceptibility for (*R*)-**1** isomer as a function of the temperature at six different frequencies, measured with applied magnetic fields of $H_{\mathrm{a.c.}} = 3.5$ Oe and $H_{\mathrm{d.c.}} = 0$ Oe.

$$\frac{1}{\tau} = \frac{1}{\tau_0} \exp\left(\frac{-U_{\mathrm{eff}}}{kT_{\mathrm{B}}}\right)$$

where U_{eff} is the effective anisotropy energy barrier, k the Boltzmann constant, and T the temperature, leads to values for the energy barrier of 21.7 and 50.7 K, for the low-temperature peak and the high-temperature peak, respectively, with an attempt frequency of τ_0 of 10^{-6} s for the former and 3×10^{-7} s for the latter. The contribution of each mechanism to the overall signal can be obtained from the adjustment of Curie tail of the in-phase component for high temperatures. It is found that almost a 15% of the molecules follow the fast relaxation mechanism governed by the low energy barrier, while the other 85% behave under the highest energy barrier, more typical for these Mn_{12} clusters.

Field dependence of magnetization at 1.8 K is shown in Fig. 4(b). Typical step hysteresis behavior is observed at regular applied fields of $H = nH_{\mathrm{r}}$, where H_{r} is the resonant field for Mn_{12} clusters taken as 0.46 T. These steps, clearly seen as peaks in the field derivative of the signal shown in Fig. 4(a), correspond to an increase of relaxation of magnetization due to resonant field tunneling of magnetic moment through the anisotropy energy barrier, between two levels with the same energy, one on each side of the barrier. The steps in this case are not very sharp and well defined as it is the case for monocrystalline samples because of a certain lack of orientation of some microcrystals. The big decay of the signal for zero applied field corresponds to the influence of the fast relaxation particles that still behave superparamagnetic at the lowest working temperature of 1.8 K. No difference is observed between the two enantiomers.

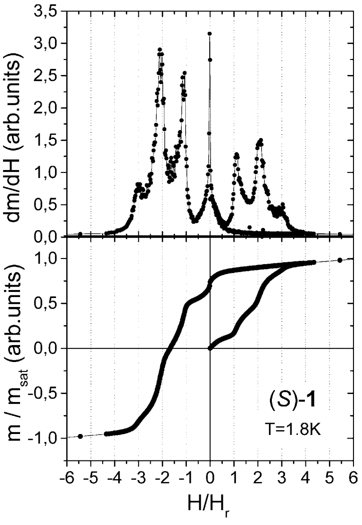

Fig. 4. Field dependence of magnetization (b) and its derivative (a) for oriented microcrystalline sample of the (*S*)-**1** enantiomer in Eicosan matrix, measured at 1.8 K.

4. Conclusions

We have prepared and characterized enantiomeric SMMs which present magnetic ordering and tunneling behavior typical of these dodecamanganese clusters. From the a.c. magnetic susceptibility measurements we have determined the presence of two relaxation barriers in a proportion of 15:85 for the fast and slow, respectively, indicative of the presence of two different clusters in the microcrystalline solid. The presence of significant optical activity in the visible part of the electromagnetic spectrum with a relatively high g-value bodes well for the observation of magnetochiral dichroism in these SMMs.

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