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$[\mathrm{Tm}^{\mathrm{III}}(\mathrm{hfac})_3(\mathrm{NITPhOPh})]_\infty$: A new member of a lanthanide-based Single Chain Magnets family

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Abstract

The polymeric coordination compound of formula $[\mathrm{Tm}(\mathrm{hfac})_3(\mathrm{NITPhOPh})]_\infty$ (where NITPhOPh is a nitronyl-nitroxide radical) has been synthesized and found to belong to the only reported family of isostructural Single Chain Magnets. Both static and dynamic magnetic measurements have been performed, and a dependence of the out-of-phase signal on the frequency is observed below 3 K. Scaling procedures indicate Ising magnetic anisotropy. Comparison of the extracted parameters with those of the previously reported isostructural compounds confirms a trend along the lanthanide series.

Keywords: Nitronyl-nitroxides; Single chain magnets; Lanthanides; Magnetic anisotropy

1. Introduction

For years the only known class of superparamagnetic molecular materials was that of the zero-dimensional derivatives called single molecule magnets, or SMMs [1]. The observation, a few years ago, of slow relaxation of the magnetization in 1D-materials has opened a new field of great interest for both physicists [2] and chemists [3]. In analogy to SMMs these new compounds have been called Single Chain Magnets (SCMs) [4]. Slow dynamics of the magnetization in anisotropic 1D-systems was originally predicted by Glauber in the 60s [5] and his model has since then been applied to a variety of different systems. The two key requirements of the model, that need to be satisfied in the realization of SCMs, are a strong Ising anisotropy of the magnetic centers and a very low ratio between inter-chain and intra-chain interactions. It is thus interesting to investigate how the variation of both these requirements in a family of related systems affects the magnetic behavior. In this context the use of the chemical tuning offered by nitronyl-nitroxide radicals has provided major advances [5] and, in particular, linear chains based on Cobalt(II) [6,7] and Dysprosium(III) ions [8] have been obtained. In the last case the use of a bulky R substituent on the radical has reduced inter-chain dipolar interactions preventing the onset of three-dimensional magnetic order. In a previous work we showed how lanthanide-based SCMs can be used to investigate the role of anisotropy on the dynamics, by designing a family in which the substitution of the magnetic ion leads to a modulation of the magnetic anisotropy without structural modifications [9]. Our previous study was performed on chains containing the rare earths (REs), Eu, Gd, Tb, Dy, Ho, Er, Yb, for which a non-monotonous trend in the magnetic anisotropy is observed.

The study was performed on chains of formula $[\mathrm{M}(\mathrm{hfac})_3(\mathrm{NITPhOPh})]_\infty$, where M= Eu, Gd, Tb, Dy, Ho, Er, Yb, and NITPhOPh is the nitronyl-nitroxide radical 2,4′-benzoxo-4,4,5,5-tetramethyl-imidazoline-1-oxyl-3-oxide, depicted in. In this family, despite the internal dis-

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position of *f*-electrons, which leads to a weak intra-chain coupling, a very remarkable behavior can be observed. The contribution to the energy barrier of the strong Ising anisotropy significantly compensates the weak exchange interaction that characterizes 4*f*-ions. A very good isolation of the chain, and the huge anisotropy provided by Ln^{III} ions give rise to a SCM behavior for the Tb, Dy and Ho derivatives. Both static and dynamic properties of the system are affected by the change of the magnetic ion. From the static magnetic properties, effects are seen on the intra-chain correlation length at low temperature and on the presence of steps in the magnetization curves. The most interesting feature is displayed by the dynamic behavior of the family. Peaks in χ'' versus T curves appear and shift in temperature as the anisotropy of the ion used changes.

As very little is known about the magnetic anisotropy of Tm^{III} ion in low symmetry environment, in this work we study the Tm-based chain **1**, [Tm(hfac)$_3$(NITPhOPh)]. We thus complete the family of heavy 4*f*-SCMs and give a last evidence of the crucial influence of the anisotropy of Ising ions in SCMs.

2. Synthesis

2.1. General procedures and materials

All chemical and solvents were used in reagent grades. The radical 2,4′-benzoxo-4,4,5,5-tetramethyl-imidazoline-1-oxyl-3-oxide, named NITPhOPh in the following, has been synthesized according to the literature methods [10].

2.2. Synthesis of [Tm(hfac)$_3$(NITPhOPh)]$_\infty$

The reacting salt [Ln(hfac)$_3 \cdot 2H_2O$] was synthesized using the following procedure: 1.78 ml (24 mmol) of a 25% ammonia solution was added drop-wise to 3.39 ml (24 mmol) of hexafluoroacetylacetone (hfac) in 100 ml of ether at 2 °C. Then 8 mmol of [Tm(Cl)$_3 \cdot 5H_2O$] in 10 ml of water were added to the solution. After half an hour of strong stirring, 20 ml of water were added. Then organic and aqueous phases were separated and washed with water and ether, respectively. The organic phase was dried on magnesium sulfate, filtered, and then concentrated to form yellowish oil. Twenty milliliter of hexane was then added and the solution was then heated up to 55 °C for some minutes. After filtration, in order to separate the formed solid, the compound was kept in the freezer at −15 °C, where it crystallized. The mean overall yield was about 50%.

The chain [Tm(hfac)$_3$NITPhOPh]$_\infty$ was synthesized by the following procedure: 1 mmol of [Tm(hfac)$_3 \cdot 2H_2O$] was dissolved in 30 ml of dry boiling *n*-heptane. The solution was left to boil for 20 min and then cooled down to 75°C, when 1 mmol of the crystalline solid radical NITPhOPh was added under stirring together with 3 ml of CH_2Cl_2. The final solution was then cooled down to room temperature and was left still for about 24 h, to give dark needle-like crystals. *Anal.* Calc. for $C_{34}H_{24}O_9N_2F_{18}Tm$: C, 36.61; H, 2.17; O, 12.91. Found: C, 36.58; H, 2.13; O, 12.93%.

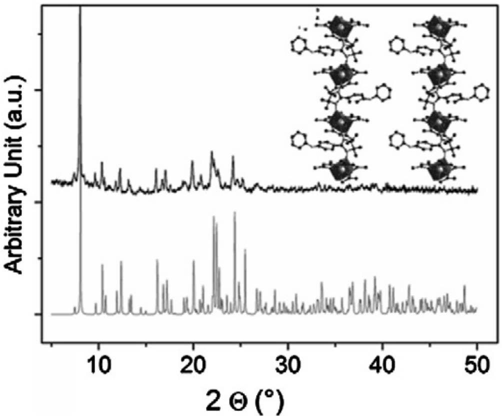

Fig. 1. Powder X-ray spectrum of the chain [Tm(hfac)$_3$NITPhOPh]$_\infty$ compound (upper graph) and simulated spectrum using data from the reported system [8]. In the inset we show the view of the crystal structure of [Dy(hfac)$_3$NITPhOPh]$_\infty$. Fluorine and hydrogen atoms are omitted for clarity.

2.3. Crystallography

A single crystal of [Tm(hfac)$_3$NITPhOPh$_\infty$ was characterized with a cell measurement, revealing that the main crystallographic parameters are: $a = 14.400(4)$, $b = 16.681(2)$, $c = 17.120(8)$, $\alpha = 90.03(7)$, $\beta = 89.96(5)$, $\gamma = 89.95(9)$, at room temperature. As the isostructural Dy-based compound has already been reported by some of us [8], we did not proceed to a full structure determination.

Anyway, as magnetic measurements were performed on microcrystalline powders, a powder X-ray diffraction pattern was recorded at room temperature and superimposed to the simulated powder pattern of the [Dy(hfac)$_3$NITPhOPh]$_\infty$. The two spectra, which match very well, are depicted in Fig. 1, together with the view of the structure of the polymeric compound.

3. Physical measurements

Temperature-dependent *dc* magnetic susceptibility measurements were performed on solid polycrystalline samples with a Cryogenic Ltd. S600 SQUID magnetometer and were corrected for the diamagnetic contribution, as calculated with Pascal's constants, and for the diamagnetism of the sample holder, as independently determined. Magnetization curves were measured with an Oxford VSM system after inclusion in Apiezon grease to prevent orientation of the crystallites in the applied magnetic field. Data were corrected for the magnetism of the grease, which was independently determined at the same temperature and fields. A 12 kOe/min field sweep rate was used, while acquiring continuously. The *ac* magnetic susceptibility was measured