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# Thermal Magnetic Hysteresis in a Copper–Gadolinium–Radical Chain Compound

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**Abstract:** Magnetic bistability spanning over a temperature domain of 40 K can result from a small structural deformation of the gadolinium aminoxyl coordination. This is illustrated for a nitronyl nitroxide 3d–4f chain, [Ln(hfac)<sub>3</sub>Cu(hfac)<sub>2</sub>(NIT-Pyrim)<sub>2</sub>] (Ln<sup>III</sup> = Gd, Dy), which is the first example of a bistable lanthanide-based complex.

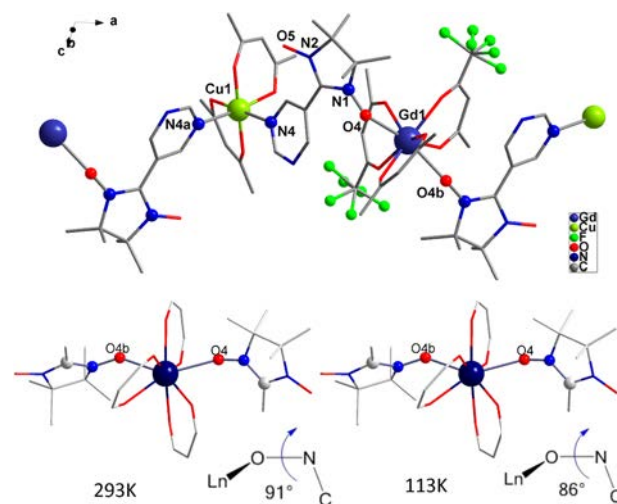
Temperature-triggered bistable molecular materials have received great attention because of their potential applications in switching, sensing, and information storage.<sup>1</sup> The most remarkable examples of such materials are the iron(II) spin-crossover (SCO) compounds taking advantage of conversion of the electronic configuration between high and low spins.<sup>2</sup> Related magnetic bistability has also been observed in valence tautomeric complexes,<sup>3</sup> exchange-coupled systems such as organic radicals,<sup>4</sup> and radical–transition metal complexes,<sup>5</sup> in which a structural phase transition leads to significant modifications of the exchange interactions. Spectacular examples include a dithiadiazolyl radical (i.e., 1,3,5-trithia-2,4,6-triazapentalenyl) found to exhibit bistability over a large temperature domain around room temperature as a result of a dimerization–dissociation process between radical units<sup>4a</sup> and copper nitroxide complexes for which the bistability is associated with an axial-to-equatorial coordination isomerism for the radical ligand.<sup>5a</sup>

The temperature domain for which the bistability exists and the width of thermal hysteresis are two characteristics of special importance in these materials. One of the approaches followed to achieve large hysteresis for the bistability domains is to strengthen the cooperation, i.e., the elastic interactions, between magnetic molecules. A classical way is to increase the intermolecular interactions by hydrogen-bonding,  $\pi$ – $\pi$ , etc., interactions or to extend the dimensions of the molecular system.<sup>7</sup> It has been reported recently that magnetic bistability with a rather wide thermal hysteresis loop may also result from a structural phase transition associated with a disorder–order phenomenon for a molecular fragment.<sup>8</sup>

To date, SCO-like behaviors relying on a disruption of the metal–radical exchange interaction mainly concern copper(II) derivatives.<sup>5a,9</sup> Herein we report a case of spin-transition-like behavior with wide hysteresis resulting from variation of the lanthanide–radical coordination within 2p–3d–4f mixed-spin

compounds. While the amplitude of the magnetic changes is less spectacular than that for the copper–radical complexes, the magnetic transitions are sharp and the domain of bistability spans over about 40 K.

The coordination polymers [Ln(hfac)<sub>3</sub>Cu(hfac)<sub>2</sub>(NIT-Pyrim)<sub>2</sub>] [Ln<sup>III</sup> = Gd (1), Dy (2); NIT-Pyrim = 2-(5-pyrimidinyl)-4,4,5,5-tetramethylimidazoline-1-oxyl-3-oxide] were obtained by reacting Ln(hfac)<sub>3</sub> (Ln<sup>III</sup> = Gd, Dy) with NIT-Pyrim followed by Cu(hfac)<sub>2</sub> in a 1:2:1 ratio. The crystal structures for 1 and 2 (Figure 1) were determined from single-



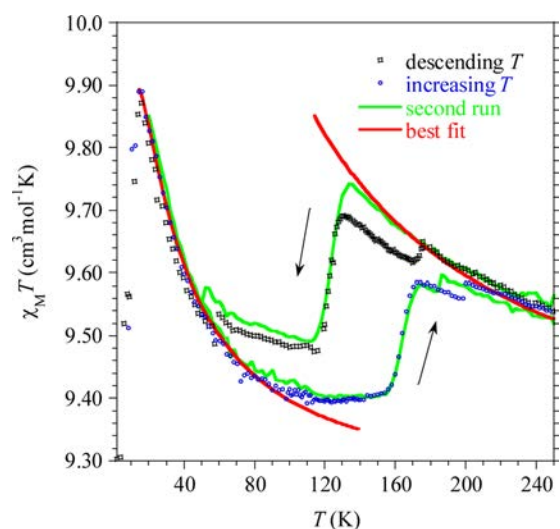
**Figure 1.** Crystal structure of complex 1 (some fluorine and hydrogen atoms are hidden for clarity): (top) view of the 1D coordination polymer at 293 K developing along the *a* axis showing the structurally disordered CF<sub>3</sub> groups; (bottom) detail of the arrangement of the gadolinium surroundings at 293 and 113 K.

crystal X-ray diffraction data collected first at room temperature (HT) and subsequently at 113 K (LT), that is, above and below the magnetic anomaly (vide infra). Because the two compounds are isomorphous, only the structure of 1 will be briefly described. At 293 K, 1 crystallizes in the monoclinic *P2*/*c* space group. It consists of a one-dimensional (1D) array of Gd(hfac)<sub>3</sub> and

Cu(hfac)<sub>2</sub> units bridged by NIT-Pyrim linked to the metal centers respectively through one aminoxy moiety and the pyrimidine group (Figure 1). The copper(II) ion is surrounded by two nitrogen atoms from two pyrimidine groups coordinated in a cis configuration and by four oxygen atoms from two hfac anions. The average equatorial Cu–O/N bond distance is 2.17 Å, and the apical Cu–O bond length is 1.942(7) Å. Accordingly, the coordination polyhedron of the copper(II) ion may be represented as a compressed tetragonal geometry. The gadolinium(III) ion is eight-coordinated with two oxygen atoms from two nitronyl nitroxide moieties and six oxygen atoms of three hfac anions. Continuous-shape-measure analysis indicates that the gadolinium(III) ion is located in a distorted dodecahedral environment ( $D_{2d}$ ; Table S4).<sup>10</sup> The Gd–O<sub>rad</sub> distance with 2.389(8) Å compares well with those of the reported Ln(hfac)<sub>3</sub>–nitronyl nitroxide complexes,<sup>11</sup> the Gd–O–N–C(sp<sup>2</sup>) torsion angle is 91(1)°. The intrachain Gd···Cu distance is 8.202 Å, and the shortest interchain metal–metal separation is found between gadolinium and copper with a distance of 10.945 Å. The shortest distance between two aminoxy moieties belonging to different chains is 4.336 Å (O5···O5<sup>−x,1−y,z</sup>). Finally, it can be pointed out that the fluorine atoms for two CF<sub>3</sub> groups in the surroundings of gadolinium are disordered over two positions (Figure 1).

For the structure collected at 113 K, the space group remains unchanged, and no important modifications are found for the cell parameters (Table S1). These are limited to a shortening of the *a* (the chain growth direction) and *c* parameters by about 0.5 Å (i.e., 3.5%) and 0.1 Å (0.5%) respectively, while *b* is increased by 0.1 Å (0.9%). The overall molecular structure is identical with that found at 293 K with similar bond parameters with the noticeable exception of the Gd–O–N–C(sp<sup>2</sup>) torsion angle, which is reduced from 91(1)° to 86(1)° (Figure 1). Moreover, the CF<sub>3</sub> groups in the Gd(hfac)<sub>3</sub> moieties are no longer found to be disordered. Hence, the structural modifications between the HT and LT phases mainly come down to a disordered-to-ordered location of the CF<sub>3</sub> groups, accompanied by an alteration of the Gd–O–N–C(sp<sup>2</sup>) torsion angles. Interestingly, these rather minor structural alterations have a significant effect on the magnetic feature of the complex.

The  $\chi_M T$  versus *T* behavior for **1** (Figure 2;  $\chi_M$  stands for the molar magnetic susceptibility for a formula unit) is characterized by marked discontinuities that are observed in both the cooling and warming modes (ramp, 1 K min<sup>−1</sup>). Starting from a value of 9.48 cm<sup>3</sup> K mol<sup>−1</sup> (the anticipated spin-only value is 9.0 cm<sup>3</sup> K mol<sup>−1</sup>) at 300 K,  $\chi_M T_{\downarrow}$  ( $\downarrow$  indicates data collected while cooling) gradually increases upon cooling. However, for about 176 K, a slight but clear drop of  $\chi_M T_{\downarrow}$  is observed, followed by a more pronounced decrease below 131 K (from 9.69 to 9.47 cm<sup>3</sup> K mol<sup>−1</sup> for 115 K). Upon further cooling,  $\chi_M T_{\downarrow}$  smoothly increases again, reaching a maximum of 9.87 cm<sup>3</sup> K mol<sup>−1</sup> for 16 K before falling steeply for lower *T*. Upon heating, the sample  $\chi_M T_{\uparrow}$  superposes to the behavior observed during cooling until 55 K; afterward, it runs below (Figure 2). However, between 155 and 172 K, a sudden increase is found, with  $\chi_M T_{\uparrow}$  coming close to that observed in the cooling mode. A second but small hop at 198 K leads to merging of the two curves for the higher temperature domain. The same behavior is found for a subsequent cooling–heating cycle (Figure 2, green plot) apart from the disappearance of the small drop at 176 K seen initially during cooling. It can be noticed that the related small step found while heating is shifted to 185 K. Such an open-S-shaped behavior reveals thermal hysteresis where the magnetic response of **1** depends on its



**Figure 2.**  $\chi_M T$  versus *T* plots for **1** in the cooling and warming modes for two cycles. The red lines represent the calculated behaviors.

thermal history. Considering only the domain for which the difference in  $\chi_M T$  for the two states remains the largest, the bistability temperature range spans from 123 to 163 K, that is, a width of 40 K. The possibility of freezing the HT phase by fast cooling from 298 to 10 K was also considered; however, the subsequent  $\chi_M T_{\uparrow}$  behavior upon warming was characteristic of the LT phase. The field dependence of magnetization for **1** recorded at 2.0 K (Figure S6) shows a rapid increase of *M* for low fields and reaches 9.82 *Nβ* at 70 kOe, a behavior in agreement with ferromagnetic interactions among the spin carriers. In addition, alternating-current (ac) magnetic susceptibility measurements confirmed the absence of magnetic ordering above 2 K (Figure S7).

The steps observed in the  $\chi_M T$  versus *T* behavior are typical for modification of the exchange interactions taking place in **1**. On the basis of the HT and LT crystal structures, the chains are well separated and interchain interactions may be excluded to account for the observed behavior. A structural modification more likely to alter an exchange interaction is the change in the gadolinium–aminoxy coordination. Indeed, experimental observations and theoretical calculation have shown that the strength of the gadolinium–nitroxide interaction depends on the Gd–O–N–C torsion angle: the larger the Gd–O–N–C torsion angle, the stronger should be the Gd–ON magnetic coupling.<sup>12</sup> Analysis of the magnetic behavior for **1** confirms this trend. Bearing in mind that the copper(II) ion is located in a compressed octahedral environment, its magnetic orbital is  $d_{z^2}$ ; hence, the possible magnetic interaction with the nitronyl nitroxide radical through the pyrimidine unit (located in an equatorial position) should be very weak. Thus, from a magnetic point of view, a chain consists of independent Rad–Gd–Rad units plus one noninteracting copper(II) ion. For the Rad–Gd–Rad unit, two kinds of exchange interactions are operative, namely, the direct Gd–ON interaction ( $J_1$ ) and a next-neighbor interaction between two NO groups via the gadolinium(III) ion ( $J_2$ ). The theoretical expression for  $\chi_M T$  derived from the Hamiltonian  $H = -2J_1(S_{\text{Rad}1}S_{\text{Gd}1} + S_{\text{Gd}1}S_{\text{Rad}2}) - 2J_2S_{\text{rad}1}S_{\text{rad}2}$  (see the Supporting Information) was used to model the behaviors between 300 and 136 K and between 14 and 140 K respectively for the HT and LT phases.<sup>13</sup> The best fit to the experimental behaviors yielded  $J_1 = 3.52$  cm<sup>−1</sup>,  $J_2 = -7.14$  cm<sup>−1</sup>,  $g = 2.02$ , and  $g_{\text{Cu}} = 2.10$  for the HT

behavior and  $J_1 = 1.00 \text{ cm}^{-1}$ ,  $J_2 = -6.36 \text{ cm}^{-1}$ ,  $g = 2.02$ , and  $g_{\text{Cu}} = 2.10$  for the LT domain, values consistent with those reported in similar compounds.<sup>14</sup> These  $J_1$  values support the role of the Gd–O–N–C torsion angle in the major transition of the magnetic behavior found in **1**. The different  $\chi_M T$  profiles observed for the HT and LT phases can clearly be ascribed to the marked difference in the strength of the ferromagnetic gadolinium–radical interaction (3.5 versus  $1.0 \text{ cm}^{-1}$ ); the jumps of  $\chi_M T$  result from the temperature-triggered structural transitions, modifying this exchange parameter. Differential scanning calorimetry (DSC) confirmed the coincidence of the magnetic steps and the phase transition (Figure S5). Interestingly, like the two-step transition found in the magnetic behavior, DSC also shows two signals, which suggests that the structural modification involves two steps close in temperatures. While the LT and HT structures are informative on the phase before and after the structural transition, its stepping remains unknown.

As mentioned above, the width of the bistability domain is correlated with the cooperative effect between the molecules. In the absence of obvious chemical interactions between the chains, the observed wide hysteresis in **1** might be associated with the disorder-to-order transformation of  $\text{CF}_3$  on the gadolinium moieties. At room temperature, two  $\text{CF}_3$  per lanthanide are disordered, while they are ordered at low temperature. This transformation couples with the alteration of the gadolinium–radical coordination, which results in thermal magnetic bistability. It is tempting to suggest that ordering–disordering of the  $\text{CF}_3$  groups and structural distortion take place consecutively and contribute respectively to the small and larger steps seen in the  $\chi_M T$  behaviors.

For the dysprosium derivative **2**, the  $\chi_M T$  versus  $T$  behaviors in the cooling and warming modes are almost the same (Figure S8) and do not exhibit the steps found for **1** despite a related structural behavior (the Dy–O–N–C torsion angles are  $92(1)^\circ$  and  $87(1)^\circ$  at 293 and 113 K, respectively). The anticipated change in  $\chi_M T$  with the phase transition might be less marked because of a smaller variation of the ferromagnetic dysprosium–radical interaction and/or be overwhelmed by the contributions of the crystal-field effect of dysprosium(III).<sup>15</sup> The absence of slow magnetization relaxation for **2** was checked by ac susceptibility measurements (Figure S10).

Interestingly, a rather modest change in the Gd–O–N–C torsion angle is sufficient to significantly modify the ferromagnetic gadolinium–radical interaction and, in turn, result in marked differences in the magnetic behavior of the HT and LT phases. Moreover, the dimensionality of the system and the disorder–order transformation of  $\text{CF}_3$  groups may play crucial roles in the wide thermal hysteresis loop characterizing the compound. Exchange-coupled metal–radical compounds exhibiting spin-transition-like behavior with hysteresis are very scarce,<sup>9,16</sup> and to the best of our knowledge, the reported chain is the first example of a lanthanide-based compound with such a desirable feature. This finding may suggest new opportunities to construct bistable systems.

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### Notes

The authors declare no competing financial interest.

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