

Room-Temperature Magnetic Bistability in Organic Crystals: A Comparison with Spin Crossover Transitions

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Received March 20, 2001; accepted March 21, 2001

IN DEDICATION TO THE LATE PROFESSOR OLIVIER KAHN FOR HIS PIONEERING CONTRIBUTIONS TO THE FIELD OF MOLECULAR MAGNETISM

Magnetic bistability is attracting much interest as a useful function of molecule-based magnetic materials. We report room-temperature magnetic bistability in the crystal of an organic radical, 1,3,5-trithia-2,4,6-triazapentalenyl (abbreviated as TTTA). This material exhibits a first-order phase transition between a paramagnetic high-temperature phase and a diamagnetic low-temperature phase, with a surprisingly wide thermal hysteresis loop; $T_{c\downarrow} = 230$ K and $T_{c\uparrow} = 305$ K. The two phases can be easily distinguished by means of EPR. The DSC measurements reveal an exothermic and an endothermic transition upon cooling and heating, respectively, with the hysteresis in agreement with the magnetic measurements. We compare this transition with the recent spin crossover transitions that also bring about room-temperature magnetic bistability. © 2001

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Key Words: magnetic properties; magnetic bistability; organic radical; phase transition.

INTRODUCTION

There has been considerable interest in molecular bistability, which means the property of a molecular assembly to exist under two stable (or metastable) electronic states in a given range of external parameters (temperature, pressure, etc.), for the purpose of its application to electronic devices, such as thermal sensors, switching units, information storage media, and so on (1, 2). The most spectacular examples of molecular bistability include the specific Fe(II) spin crossover complexes, in which the transitions between a low-spin state ($S = 0$) and a high-spin state ($S = 2$) occur with wide thermal hysteresis in the vicinity of room temperature (3).

The heterocyclic thiazyl radicals are materials located on a boarder line between organic and inorganic (4). It is characteristic of this radical family to possess chemical stabilities and strong intermolecular interactions. Their crystals consist of π stacking, as well as side-by-side $S \cdots N$ and $S \cdots S$ contacts, which are similar to those in the inter-

chain arrangements of the inorganic polymer, $(SN)_x$ (5, 6). Various interesting physical properties of the thiazyl radicals have been reported so far (7–10). One of the derivatives, 1,3,5-trithia-2,4,6-triazapentalenyl (abbreviated as TTTA), was prepared by Wolmershäuser and Johann in 1989 (11). Recently we discovered a first-order phase transition in TTTA that occurs with a drastic change in magnetism and with a surprisingly wide thermal hysteresis loop in the vicinity of room temperature (12). In this report we describe the phase transition in TTTA, based on the results of the magnetic measurements and the differential scanning calorimeter (DSC). We compare the magnetic bistabilities in TTTA and in the spin crossover complexes.

EXPERIMENTAL

TTTA was prepared by a modification of the literature method described in Ref. (7). Its single crystals were obtained by vacuum sublimation. The static magnetic measurements were carried out on a Quantum Design MPMS-XL SQUID susceptometer. The diamagnetic correction was performed using a diamagnetic susceptibility that was evaluated by assuming that TTTA was in a non-magnetic state in the range 100–150 K. The EPR were recorded on a JES RE2X spectrometer equipped with an Oxford He-gas-flow cryostat. The DSC measurements were performed on a Mettler Toledo DSC 822e/200 calorimeter.

RESULTS AND DISCUSSION

The temperature dependence of the paramagnetic susceptibilities χ_p for a polycrystalline sample of TTTA was examined in the range 1.8–330 K. The results in the range 170–330 K are depicted in Fig. 1 (open circles). The bold arrow in this figure indicates the value of χ_p for the virgin sample just after the sublimation. As the sample is cooled from room temperature, χ_p shows a slight decrease. At 230 K χ_p begins to quickly decrease, becoming zero at

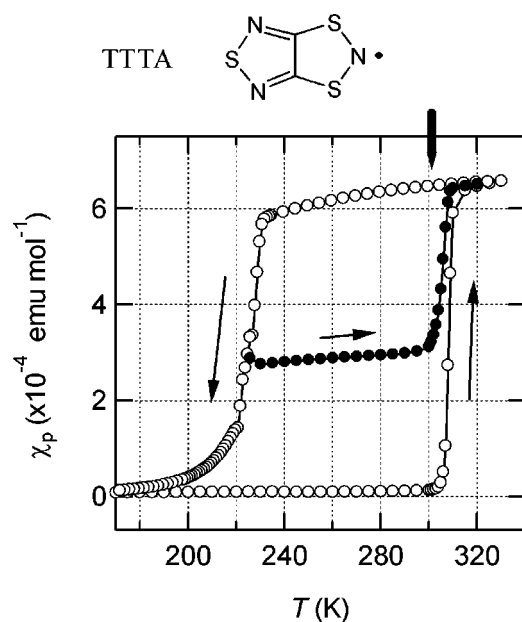


FIG. 1. Temperature dependence of the paramagnetic susceptibility χ_p for a polycrystalline sample of TTTA (open circles). The bold arrow indicates the χ_p value for the virgin sample just after sublimation. The closed circles show the magnetic response to heating of the sample at T_{c1} .

170 K. Below 100 K the plots of χ_p show a gradual increase, caused by the Curie spins on lattice defects. It is considered that TTTA is intrinsically diamagnetic at low temperatures. When the sample is heated from a low temperature below 100 K, χ_p gradually decreases and becomes nearly zero over the range of 80–300 K. Above 120 K χ_p shows a very slight increase, followed by a sudden jump at 305 K to a value that is almost the same as the initial value. The magnetic measurements indicate a first-order phase transition with a wide hysteresis loop; $T_{c1} = 230$ K and $T_{c2} = 305$ K. Since this loop includes the room temperature (290 K), the material exhibits a magnetic bistability at room temperature. We repeated the thermal cycle several times. Although the crystal broke into small pieces at the phase transitions, there was little change in the shape of the loop.

To prove that the hysteresis loop is intrinsic, we performed the following experiment. On the SQUID susceptometer, we slowly cooled the high-temperature (HT) phase and stopped the cooling just during the phase transition to the diamagnetic low-temperature (LT) phase. Then we gradually raised the sample temperature, following the magnetic response. The closed circles in Fig. 1 show the results of this experiment. The plots of χ_p clearly indicate that there is little change in the ratio between the two components in the temperature range within the loop. This means that the two phases can stably coexist in this range. Therefore this is firm evidence that the hysteresis is intrinsic at least in the time scale of the laboratory.

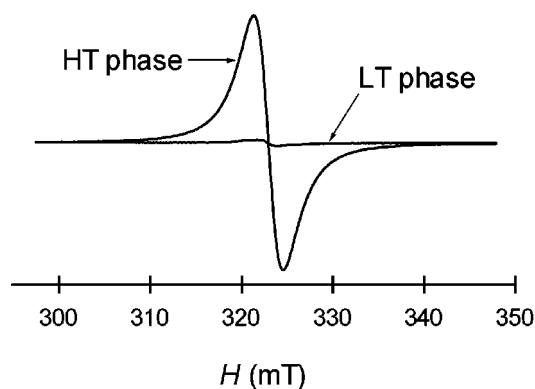


FIG. 2. EPR spectra of the HT and the LT phases of TTTA at room temperature.

Figure 2 shows a comparison between the single-crystal X-band EPR signals of the two phases at 300 K. The spectrum of the HT phase consists of an intense absorption, in contrast to the weak signal of the LT phase. The g -factor of the HT phase signal is $\bar{g} = 2.0043$, which is typical for the thiazyl radicals. Since EPR is a very sensitive tool for the organic radicals, it is easier to distinguish between the two phases by EPR than by SQUID. In the temperature-variable EPR experiments, the phase transition occurs at approx. 200 and 310 K on cooling and heating, respectively. They agree with the corresponding critical temperatures determined in the χ_p measurements.

The phase transition of TTTA was examined by means of DSC. In the cooling and the heating process, we found an exothermic and an endothermic transition at 234 and 315 K (onset temperatures), respectively. They are approximately in agreement with the critical temperature described above. The transition entropy ΔS is estimated to be $7.67 \text{ J K}^{-1} \text{ mol}^{-1}$. The maximum estimation of the magnetic contribution is $R \ln 2 (= 5.76 \text{ J K}^{-1} \text{ mol}^{-1})$. Since the HT phase involves rather strong antiferromagnetic interactions and its paramagnetism is depressed, the real contribution would be much smaller than $R \ln 2$. Despite that $R \ln 2$ is the maximum estimation, the observed ΔS is larger than this value. The presence of such excess entropy is similar to those in the spin crossover transitions (13), and indicates a cooperation of the lattice system in this phase transition.

The phase transition in TTTA is similar to the spin-Peierls transition, which is caused by an instability in the 1D antiferromagnetic chains of the $S = \frac{1}{2}$ Heisenberg spins toward lattice dimerization. The phase transition in TTTA may be explained by this instability to a certain extent. However there is a crucial difference between the two; the spin-Peierls transition is second order in contrast to the first-order phase transition in TTTA. It is natural to consider that the phase transition in TTTA is predominantly structural in character, presumably reflecting electrostatic

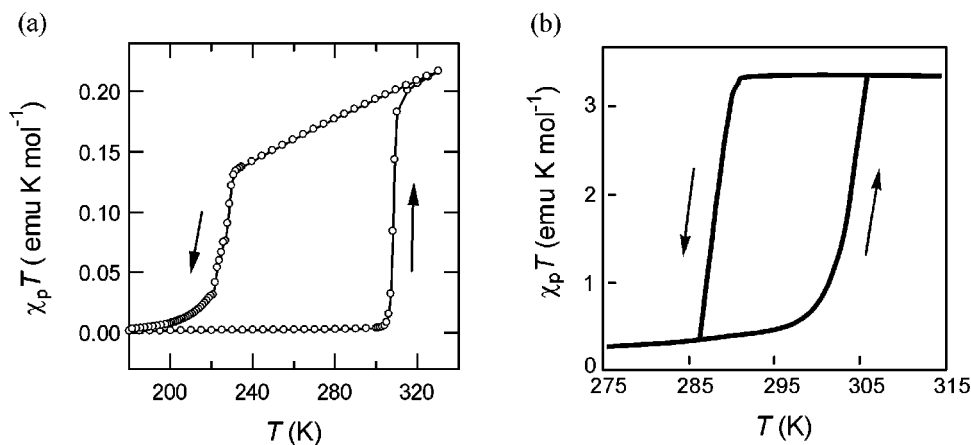


FIG. 3. Comparison between (a) the magnetic data for TTTA and (b) that for $[\text{Fe}(\text{Htrz})_{3-3x}(\text{4-NH}_2\text{trz})_{3x}](\text{ClO}_4)_2$. The curves in (b) were schematically reproduced from the data in Ref. (3).

interactions among the polarized charges mainly on sulfurs and nitrogens, elastic energies, bonding interactions among the unpaired electrons, etc., and the spin-Peierls instability plays a secondary role in assisting the transition.

The spin crossover phenomena have been studied for five decades (14, 15). In this history the discovery of the so-called LIESST (light-induced excited spin-state trapping) effects (16) suggested a possible application of these materials to the molecular devices. Other important findings were specific Fe(II) spin crossover transitions with large thermal hystereses in the vicinity of the room temperature (3). It is interesting to compare the magnetic bistability in TTTA with this type of Fe(II) spin crossover transition. The magnetic data for TTTA in Fig. 1 are replotted as $\chi_p T$ vs T in Fig. 3a in comparison with those of a spin crossover complex, $[\text{Fe}(\text{Htrz})_{3-3x}(\text{4-NH}_2\text{trz})_{3x}](\text{ClO}_4)_2$, whose magnetic behavior is schematically depicted in Fig. 3b. The values of $\chi_p T$ for the HT phase of TTTA are smaller than those for the HT phase of the spin crossover complex by one order of magnitude: the change in $\chi_p T$ at the phase transition of TTTA is much smaller than that at the spin crossover transition. The Fe(II) complex exhibits a change in spin multiplicity between $S=0$ and $S=2$, in contrast with TTTA, which has a change not in molecular spin multiplicity ($S = \frac{1}{2}$) but in intermolecular interaction. While the values of $\chi_p T$ for the HT phase of the Fe(II) complex are temperature independent, those of the HT phase of TTTA show a significant decrease with a decrease in temperature because of its antiferromagnetic intermolecular interactions. The LT phase of the Fe(II) spin crossover complex is intrinsically diamagnetic, but it exhibits weak paramagnetism probably caused by lattice defects of high spin. In contrast the LT phase of TTTA is closely diamagnetic: it also includes paramagnetic lattice defects (not shown) but they are very few. The spin states in TTTA can be sensitively

analyzed by EPR, but the Fe(II) spin crossover complexes are usually EPR silent.¹ The loop width of TTTA is more than 70 K, while that of $[\text{Fe}(\text{Htrz})_{3-3x}(\text{4-NH}_2\text{trz})_{3x}](\text{ClO}_4)_2$ is approx. 20 K. It is reported that $[\text{Fe}(\text{4-NH}_2\text{trz})_3](\text{NO}_3)_{1.7}(\text{BF}_4)_{0.3}$ preencapsulated in a polymer exhibits the loop width of approx. 60 K (1). Regarding the loop width, it is hard to conclude the superiority between TTTA and the spin crossover complexes at this stage. Now it is worth noting color changes at the phase transitions. The spin crossover complex exhibits a spectacular color change at the phase transition: the HT phase is colorless, while the LT phase is purple (3). The phase transition of TTTA is also associated with a color change: the HT phase appears dark purple in contrast to the LT phase being dark green, although this color change is less significant than that of the spin crossover complex.

The changes in magnetic and optical quantities at the phase transition of TTTA are smaller than those of the spin crossover complexes. This may indicate that the application of the spin crossover transitions is more practical. However the transition of TTTA is accompanied by a drastic modification in crystal structure (12), suggesting the stabilities of the two phases. TTTA is the first organic radical with room-temperature magnetic bistability, in contrast to the systematic studies of the spin crossover complexes. It is highly possible that the organic radicals with magnetic bistability will be developed in the near future.

SUMMARY

We described the room-temperature magnetic bistability of TTTA and compared it with those of the spin crossover

¹ The Fe(III) spin crossover complexes are EPR active.

complexes. Although the two systems show similarities and dissimilarities, it is certain that magnetic bistability is one of the most characteristic functions of the molecule-based magnetic materials. We believe that the discovery of the phase transition of TTTA will open a new branch in this field.

ACKNOWLEDGMENTS

We thank Michio Sorai and Kazuya Saito for helpful discussion. This work was supported by the Grant-in-Aid for Scientific Research from the Ministry of Education, Science, and Culture, Japanese government.

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