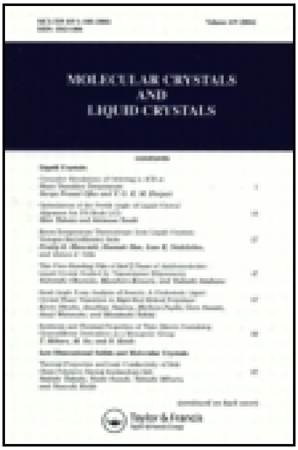

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Magnetic Molecular Bistability in the Crystals of Heterocyclic Thiazyl Radicals

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Magnetic Molecular Bistability in the Crystals of Heterocyclic Thiazyl Radicals

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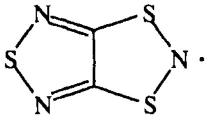
A large first-order magnetic phase transition in an organic radical, 1,3,5-trithia-2,4,6-triazapentalenyl is described, that occurs with a wide thermal hysteresis loop over the temperature range from 230 to 305 K. The high-temperature phase is paramagnetic, while the low-temperature phase is diamagnetic. The results reported here on room-temperature magnetic molecular bistability may have applications in thermal sensors, switching units and information storage media, based on organic radical crystals.

Keywords: Molecular Bistability; Phase Transition; Organic Radical; Low-Dimensional Magnetism

INTRODUCTION

Magnetic properties of organic radical crystals have been studied for a long time. It has been known that such materials provide excellent models of quasi-one-dimensional (1D) magnets, due to 1D stacking of the anisotropic π-orbitals in their crystals. One of the most successful demonstrations of the usefulness of the organic radicals was the discovery of the so-called spin-Peierls transition [1] in the



TTTA

antiferromagnetic spin chain of ionized tetrathiafulvalene, TTF$^+$, in (TTF)[$CuS_4C_4(CF_3)_4$] in 1975 [2]. Uniform antiferromagnetic chains of Heisenberg S-1/2 spins allow a gap-less excitation of a paramagnetic spin wave, resulting in a transition to a dimerized state with a spin-gap, as the temperature is lowered to a point at which the stabilization of the spin system caused by formation of the spin gap overcomes the elastic energy. While the spin-Peierls transition is intrinsically second-order, specific organic-radical insulators with 1D molecular stacking exhibit first-order phase transitions accompanied by lattice dimerization [3-7]. Although their similarity to the spin-Peierls transition has been recognized, there has been no systematic discussion on the difference between the first- and second-order transitions. We report an unusual first-order phase transition in an organic radical, 1,3,5-trithia-2,4,6-triazapentalenyl (abbreviated as **TTTA**), which occurs with a surprisingly wide hysteresis loop and with a drastic change in magnetism.

EXPERIMENTAL

TTTA was prepared by a modification of the literature method described in ref. 8. Its single crystals were obtained by vacuum sublimation. The magnetic measurements were carried out on a Quantum Design MPMS-*XL* SQUID susceptometer. The diamagnetic correction was performed using a diamagnetic susceptibility which was evaluated by assuming that **TTTA** was in a non-magnetic state in the range 100-150 K.

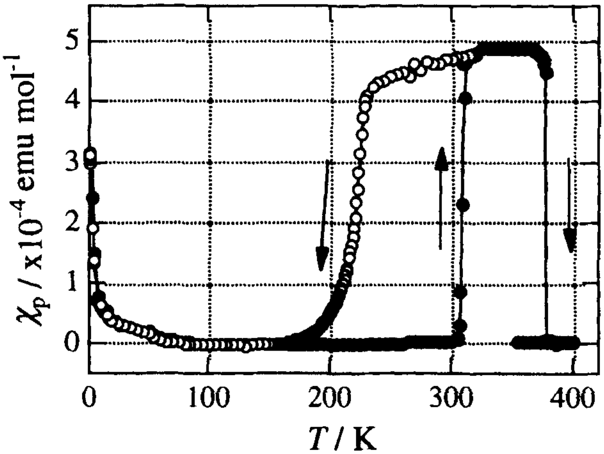


FIGURE 1. Temperature dependence of the paramagnetic susceptibility, χ_p, for a polycrystalline sample of **TTTA** on cooling (open circles) and on heating (closed circles). The behavior clearly indicates a first-order phase transition with wide thermal hysteresis; $T_{c\downarrow}$=230 K and $T_{c\uparrow}$=305 K.

RESULTS AND DISCUSSION

The temperature dependence of the paramagnetic susceptibilities, χ_p, for a polycrystalline sample of **TTTA** was examined. The open circles in Fig. 1 present the dependence on cooling from room temperature. When the temperature is decreased to 230 K, χ_p shows a slight decrease. At this temperature, the value of χ_p begins to quickly decrease and becomes nearly zero at 180 K. After being zero, χ_p shows a slight increase below 100 K, which is probably due to paramagnetic lattice defects. It is considered that this compound is intrinsically diamagnetic at low temperatures. The results of heating are shown as the closed circles in Fig. 1. When the sample is heated from the lowest temperature to 150 K, χ_p decreases without thermal hysteresis. The plots of χ_p exhibit a continuous change even in the range of 150-230 K, where the drastic change appears upon cooling. Above 200 K, χ_p shows a very slight increase followed by a sudden increase at 305 K to a value which is almost the same as the initial value. After this transition, χ_p exhibits reversible temperature dependence in the range of 230-360 K. When the sample is heated above 360 K, χ_p irreversibly decreases to zero. This is caused by the sample decomposition. The magnetic measurements indicated a first-order phase transition with a surprisingly wide hysteresis loop; $T_{c\downarrow}$=230 K and $T_{c\uparrow}$=305 K. Therefore, the material exhibits a room-temperature bistability in its magnetic properties. We repeated the cycles several times, but there was little change in the hysteresis loop.

There has been considerable interest in molecular bistability [9, 10], which means the property of a molecular assembly existing 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. If such bistability can be controlled by illumination, the system can be useful as a photo-memory, as well as an excellent model for the study of photo-induced phase transition [11]. Since the first step to realize the photo-induced phase transitions is to make bistability in the crystals, **TTTA** already satisfies the first requirement. In addition **TTTA** is thermochromic as well: the high-temperature phase is purple, while the low-temperature phase is green. This means that we can photo-excite the high- and low-temperature phases separately. The study of **TTTA** will be developed as not only a new aspect of the low-dimensional magnetism but also a new branch of the molecular bistability.

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