

A One-Dimensional Coordination Polymer, BBDTA·InCl₄: Possible Spin-Peierls Transition with High Critical Temperature of 108 K

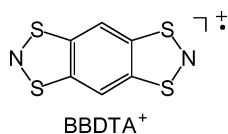
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The spin-Peierls (SP) transition is one of the quantum phenomena which occurs in an $S = 1/2$ antiferromagnetic Heisenberg uniform chain system.¹ Below the SP transition temperature, a lattice dimerization occurs, which increases progressively as the temperature is lowered, together with the concomitant appearance of an energy gap in the spectrum of magnetic excitations. This gap separates a nonmagnetic singlet ground state from a triplet of excited states. The SP transition has been found in several organic compounds.²

Cyclic thiazyl radicals have attracted much interest in view of their potential use as building blocks in the synthesis of organic conductors and magnets.^{3,4} Our target molecule in this paper is the monocationic state ($S = 1/2$) of benzo[1,2-d:4,5-d']bis[1,3,2]-dithiazole (BBDTA).⁵ Recently, we have found a ferromagnetic ordering state below 7.0 K in the salt, γ -BBDTA·GaCl₄, in which GaCl₄⁻ is a nonmagnetic counteranion.⁶ In the present work, we report the crystal structure and magnetic properties of the salt, BBDTA·InCl₄, which has formed a one-dimensional coordination polymer structure and has exhibited the characteristic behavior of the SP transition at 108 K.



BBDTA·InCl₄ was prepared by a reaction of BBDTA·Cl and InCl₃ in CH₃CN under a nitrogen atmosphere.⁵ Dark greenish crystals of this material were obtained by recrystallization from a hot acetonitrile solution.⁷ It crystallizes in the orthorhombic *Cmcm* space group, in which a quarter of the BBDTA·InCl₄ unit is crystallographically asymmetric. Figure 1a depicts the geometry around the indium atom in this material. The radical cation was coordinated to the indium atom as a ligand. The indium atom exhibited a distorted octahedral geometry and was surrounded by four chloride atoms and two nitrogen atoms of BBDTA⁺ radical cations, in contrast to the tetrahedral environment of the gallium atom in BBDTA·GaCl₄.⁶ The In–Cl bond lengths (2.3916(3) and 2.4398(4) Å) in BBDTA·InCl₄ were similar to those in other reported indium chloride complexes.⁸ The two BBDTA⁺ cations occupy a *cis* positions with interatomic In–N distances of 2.586–(5) Å. These coordination bond lengths were longer than those reported for other In–N complexes, on average 2.25 Å.⁸ This indicates that the coordination bond in this material is weaker than those of other analogous complexes. In addition, there were some short interatomic distances which were substantially less than the sum of the van der Waals radii between the ligand species. An interatomic S···Cl short distance of 3.2886(11) Å was observed

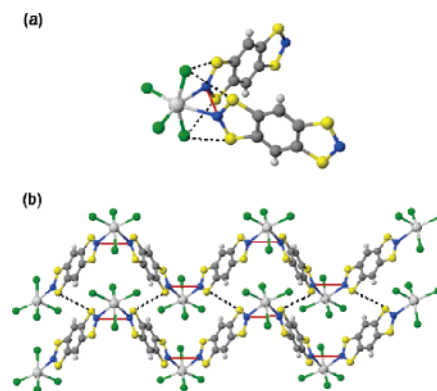


Figure 1. Crystal structure of BBDTA·InCl₄ at room temperature, (a) a coordination environment of an indium atom, and (b) crystal packing in BBDTA·InCl₄.

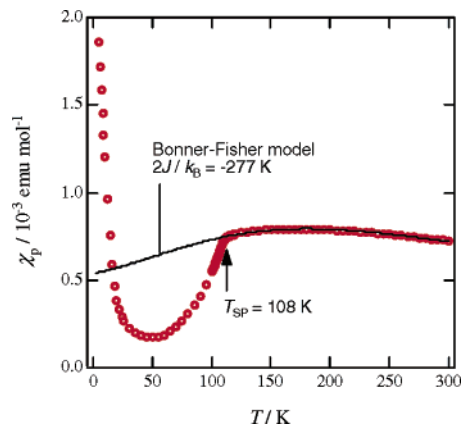


Figure 2. Temperature dependence of the paramagnetic susceptibilities, χ_p , in BBDTA·InCl₄ under 0.5 T.

between BBDTA and Cl, as shown by broken lines in Figure 1a. The S···Cl interatomic contact may be close due to the long In–N coordination bond. Furthermore, there were short interatomic N···N distances of 3.052(8) Å (red solid lines) between the BBDTA⁺ ligands. Figure 1b shows the crystal structure of BBDTA·InCl₄ at room temperature. A BBDTA⁺ radical cation bridged the distance between the InCl₄⁻ anions, resulting in a one-dimensional coordination chain along the *c* axis. In this crystal, a 1D antiferromagnetic network is formed via the nitrogen–nitrogen short contact. In the interchain arrangement, there was a short contact between the sulfur atoms on the dithiazolyl ring (3.559(2) Å), as shown by the broken lines in Figure 1b.

Figure 2 depicts the temperature dependence of the paramagnetic susceptibility, χ_p , for BBDTA·InCl₄ in the temperature range of 2–300 K under 0.5 T. We adopted BBDTA·InCl₄ as the molar unit. The value of the paramagnetic susceptibility, χ_p , was obtained

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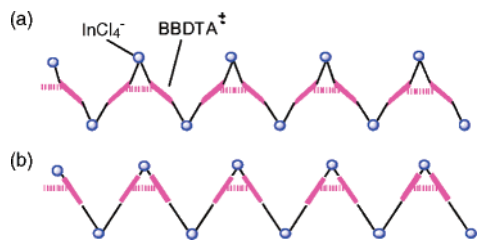


Figure 3. Two structural candidates for the dimeric phase in BBDTA·InCl₄ at 50 K. Based on changes of (a) the N–In–N bond angles or (b) the In–N bond lengths.

from the dc susceptibilities, subtracting a diamagnetic contribution of it. χ_p increased gradually, with decreasing temperature, and showed a broad maximum at ca. 170 K. This magnetic behavior is characteristic of low dimensional magnetic materials. χ_p decreased abruptly at 108 K, suggesting a magnetic phase transition. Below this temperature, this material showed a gap-like magnetic behavior. Below 50 K, χ_p again increased, with decreasing temperature. This behavior is due to magnetic impurities or lattice defects. In the high temperature region above 108 K, the experimental data were reproducible by the Bonner–Fischer equation¹⁰ with the parameters, $C = 0.375 \text{ emu K mol}^{-1}$ (fixed) and $J/k_B = -138.5 \text{ K}$, where C is the Curie constant, J is the intrachain exchange coupling constant, and k_B is the Boltzmann's constant. This indicates that the present material is a typical $S = 1/2$ 1D magnet, as expected from the structure. Below the transition temperature, we estimated that the value of the spin-gap, $-\Delta(0)/k_B$, was 190 K by using a literature method.¹¹ This value is consistent with the value of 191 K, expected from BCS theory.^{2a} This magnetic behavior is characteristic of materials exhibiting the SP distortion.

To estimate lattice deformation in BBDTA·InCl₄ below the transition temperature, we carried out X-ray diffraction measurements of a single crystal in the low temperature region.¹² We did not observe superlattice reflections in the crystal at 50 K, suggesting no significant change in the size of the unit cell below the transition temperature. Lattice dimerization does not always give superlattice reflections because two BBDTA⁺ molecules are included in the c axis of the unit cell in this material. At 50 K, we found several Bragg reflections, (0 5 -7), (3 4 6), (3 -4 0), (-3 4 -6), (3 0 5), and (-3 0 -9), which were not found in the high temperature phase above 108 K because of the extinction rules for a C -centered unit cell and a c -glide plane perpendicular to b .¹³ The appearance of these reflection peaks suggests symmetry changes of the crystal below the transition temperature.

We can propose at least two candidates for the dimerization aspect with no significant change of the unit cell and an absence of the two symmetry operations mentioned above. Since the In–N coordination bond was expected to be weak judging from the room temperature structure, we assume that changes with the N–In–N bond angle, the In–N bond length, or both structural parameters have occurred at low temperature. Figure 3 depicts two dimerization possibilities of the coordination chain structure in BBDTA·InCl₄ at 50 K. As shown in Figure 3a, when only the upper N–In–N bond angles decrease, the corresponding intermolecular N··N

distances may shorten. In this situation, the BBDTA⁺ cations can form a dimeric structure. The other possible structure is shown in Figure 3b. If the BBDTA cations approach the indium atoms in the uppermost part of the chain, that is, if the upper In–N coordination bonds shorten and the lower bonds elongate, it may result in dimerization of the BBDTA cations. It seems that the characteristic behavior of the SP transition in the material correlates with nature of the In–N coordination bond. We believe that this high transition temperature of 108 K is due to the long In–N bond length observed in the structure of our coordination polymer, which brings a certain amount of structural flexibility and therefore may diminish the loss of lattice energy in the phase transition.

In summary, we have reported the SP transition of the organic radical-based magnet, BBDTA·InCl₄, at 108 K, which is higher than those typically observed for the other organic SP materials. More detailed structural studies below the transition temperature on this material are now being carried out.

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Supporting Information Available: Crystallographic data of BBDTA·InCl₄ at 298 K. This material is available free of charge via Internet at <http://pubs.acs.org>.

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- (7) Crystal data for BBDTA·InCl₄: C₆Cl₄H₂In₂N₂S₄, $M = 528.04$, orthorhombic, space group *Cmcm*, $a = 9.0400(4)$, $b = 10.4900(5)$, $c = 13.9240(8)$ Å, $V = 1320.41(11)$ Å³, $Z = 3$, $\rho_{\text{calcd}} = 1.831 \text{ g cm}^{-3}$, $T = 293 \text{ K}$, $R_1(I > 2\sigma(I)) = 0.0433$, $wR_2 = 0.1174$ (all data), $S = 1.191$ (all data).
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