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Spin-Crossover Cobalt(II) Compound with Banana-Shaped Structure

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A banana-shaped spin-crossover (SCO) cobalt(II) complex $[Co(C16\text{-}terpy)_2](BPh_4)_2$ (**1**) with long alkyl chains, based on a terpyridine frame, was synthesized. Compound **1** exhibited very gradual SCO behavior and changes in the dielectric constant. This shows a way in which SCO materials can be used in electronic devices.

There is great interest in the study of the self-assembly of supramolecules. Achievements have included the deliberate design of catenanes and rotaxanes, helices, and so on.[1−3] The applications of such supramolecules have primarily centered around the use of their size and shape, recognition and encapsulation of guest molecules, sensing, extraction, and catalysis.[4] Interesting physical properties may be discovered from compounds with such unique structure, which will be promising in the field of materials science. Banana-shaped molecules have also been extensively studied in the field of liquid crystals because they exhibit ferroelectric or antiferroelectric properties and can be switched between different polar-ordered states by electric fields.[5] Such molecules often form layer structures in which the bent aromatic cores and the flexible terminal chains are segregated. Therefore, the design of molecules that could be utilized for information processing and information storage is one of the main challenges in molecular materials science. Molecules that would be suitable for such applications must exhibit bistability, which may be defined as a property of a molecular system that allows it to exist in two different electronic states over a certain range of external perturbation. A typical example of a molecular species that exhibits molecular bistability is a spin-crossover (SCO) compound.

Since the discovery of the first SCO compound,[6] a variety of d^n ($n = 4-7$) transition-metal compounds exhibiting bistability between the high-spin (HS) and low-spin (LS) states have been reported.[7] Usually, the SCO phenomenon can be induced by a variation in the temperature, pressure, or illumination. Although the SCO transition has a molecular origin and can be observed even in solutions or polymer matrixes, it can be dramatically influenced by interaction of the SCO centers. Gradual or abrupt spin transitions may be observed in the solid state, depending on the absence or presence of cooperativity.[8] Understanding cooperative behavior in an SCO transition can be a key to designing materials that are useful for information technology.

Flexibility in the synthesis of molecular assemblies based on molecular units is also a very important factor in achieving synergy of various interesting and novel physical properties in advanced materials.[9,10] The flexibility of the ligand can be one factor that influences the cooperative interaction, both directly (because the more flexible the ligand, the less probable that it can mediate the effects of structural changes) and indirectly through the packing structure. Therefore, SCO complexes having ligands with long alkyl chains are expected to exhibit not only unique magnetic properties but also various molecular structures because of thermal molecular motions.[11]

SCO cobalt(II) compounds exhibit a $S = {}^1/_2 \leftrightarrow S = {}^3/_2$ spin change. It is known that the cobalt(II) compounds

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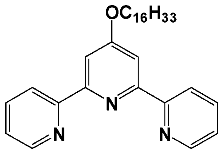
$[Co(terpy)_2]X_2 \cdot nH_2O$ (terpy = 2,2′:6′,2″-terpyridine, X = halide, pseudohalide, NO_3^-, and ClO_4^-, and $n = 0-5$) exhibit incomplete and gradual SCO behavior.[12,13] Unique physical properties are expected for the compounds with long alkyl chains because of the thermal motion of the long alkyl chains. On this basis, we attempted to produce cobalt(II) compounds with long alkyl chains and have succeeded in constructing a banana-shaped structure.



C16-terpy

Here, we focused on the cobalt(II) compound $[Co(C16\text{-}terpy)_2](BPh_4)_2$ (C16-terpy is 4′-(hexadecyloxy)-2,2′:6′,2″-terpyridine),[14] hereafter designated as compound **1**, having 2,2′:6′,2″-terpyridine (terpy) ligands with long alkyl chains. Single crystals of **1**·acetone, suitable for X-ray diffraction (XRD), were isolated as acetone adducts by slow recrystallization from an EtOH/acetone solvent. Nonsolvated compound **1** was obtained as a brownish orange powder by annealing **1**·acetone at 400 K in vacuo.

Single-crystal X-ray analysis was successfully carried out for the compound **1**·acetone at 120 K. Figure 1 shows that when the compound **1**·acetone is in the HS state, it crystallizes in a monoclinic $P2_1/a$ space group.[15] The single-crystal X-ray analysis of **1**·acetone revealed that each of the cobalt(II) atoms is octahedrally coordinated by six nitrogen atoms in two C16-terpy ligands, i.e., an N_6 donor set. The Co−N distances of the central pyridine in the terpyridine unit (2.03 Å) are shorter than the Co−N distances of the side pyridine in the terpyridine unit (2.14 Å), which induces a pronounced distortion of the CoN_6 octahedron. Two tridentate C16-terpy ligands in the complex are found to be nearly perpendicular to each other. The long $C_{16}H_{33}O$ alkyl chains are stuck out of the 4′ position in the terpyridine moiety, and the molecules form a bent-core or banana-shaped structure. The two BPh_4^- counteranions and one acetone molecule are not located in the first coordination sphere. There are $\pi-\pi$ and $\sigma-\pi$ interactions between the BPh_4^- ions and the terpyridine moieties. The dimer structure is formed by hydrogen bonding between two acetone molecules, and there is hydrogen bonding between the acetone dimer and the terpyridine moieties. The BPh_4^- ions and the acetone dimer serve to connect the complexes. The crystal packing for **1**·acetone is shown in Figure 1b. The complex cations form banana structures and are shown in green. Two are lined up in opposition to each other, and the others are face-to-face. The space between the molecules that are in opposition to each other contains BPh_4^- (yellow) and acetone (blue) molecules, and that between the face-to-face molecules contains BPh_4^- (red). It was thought that the dipole moments for the molecules opposed each other. The crystal structure of the nonsolvated compound **1** could not be determined because removal of the acetone molecules induces cracks in the crystal, making a single-crystal X-ray study impossible. However, the powder XRD measurement results suggest that the structure of the nonsolvated **1** is similar to that of the solvated **1**·acetone (Figure S1 of the Supporting Information).

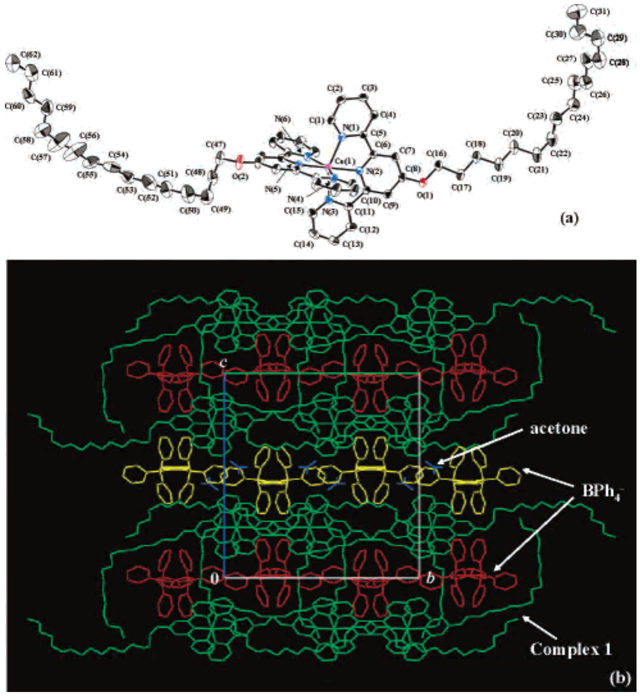


Figure 1. (a) ORTEP drawing of the compound **1**·acetone showing 50% probability displacement ellipsoids. (b) Projection of the crystal structure of **1**·acetone along the *bc* plane. Hydrogen atoms are omitted for clarity.

Phase-transition enthalpies for **1** were measured by carrying out differential scanning calorimetry (DSC) thermal analysis. Two peaks were observed at 401 and 426 K. The DSC peak ($\Delta H = 3.55$ kJ mol^{-1}) at 401 K was assigned to a structural phase transition, and that ($\Delta H = 59.2$ kJ mol^{-1}) at 426 K was assigned to a melting point (Figure S2 of the Supporting Information). Compound **1** did not exhibit a crystal−liquid crystal phase transition, as shown by the small

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(14) The cobalt(II) compound $[Co(C_{16}\text{-}terpy)_2](BPh_4)_2 \cdot$acetone (**1**·acetone) was synthesized as follows: C16-terpy (510 mg, 1.08 mmol) was dissolved in $CHCl_3$/MeOH (30 mL), and the resulting solution was added to a mixed solution of $CoCl_2 \cdot 4H_2O$ (144 mg, 0.60 mmol) and $NaBPh_4$ (513 mg, 1.50 mmol) in MeOH (20 cm^3). The brown solution was concentrated to about 10 mL, and the microcrystals were filtered and recrystallized from acetone/EeOH. Yield: 735 mg (80%); brown prism crystals. Anal. Calcd for $C_{113}H_{132}O_3N_6B_2Co_1$: C, 79.70; H, 7.81; N, 4.94; Co, 3.46. Found: C, 79.74; H, 7.79; N, 4.95; Co, 3.48. The cobalt(II) compound $[Co(C_{16}\text{-}terpy)_2](BPh_4)_2$ (**1**) was obtained by annealing **1**·acetone at 400 K in vacuo. Elemental analysis for **1** after removing acetone molecules was as follows. Calcd for $C_{110}H_{126}O_2N_6B_2Co_1$: C, 80.33; H, 7.72; N, 5.11; Co, 3.58. Found: C, 80.22; H, 7.70; N, 5.10; Co, 3.55.

(15) Crystallographic study of **1**·acetone. X-ray crystallographic data for **1**·acetone at 120 K ($C_{113}H_{132}O_3N_6B_2Co_1$): fw = 1702.88, orange block (0.3 × 0.6 × 0.3), monoclinic, space group $P2_1/a$, $a = 19.011(1)$ Å, $b = 21.985(1)$ Å, $c = 23.380(1)$ Å, $\beta = 98.370(2)°$, $V = 9667.4(9)$ Å^3, $Z = 4$, $D_{calcd} = 1.170$ g cm^{-3}. The structure was solved by direct methods and expanded using Fourier techniques. The refinements by full-matrix least squares gave an R factor of 0.082 from 12 511 reflections with intensity $I > 3\sigma(I)$ for 1126 variables; linear absorption coefficient μ(Mo Kα) = 2.33 cm^{-1}. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined.

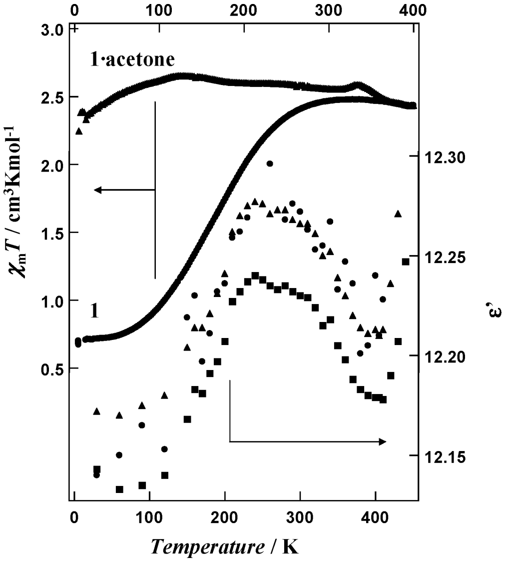

Figure 2. $\chi_m T$ vs T plots for the compounds **1**·acetone and **1** and the temperature dependence of dielectric constant ϵ' of **1** at 1 kHz (●), 10 kHz (▲), and 100 kHz (■).

first DSC peak. The crystal packing was a jumble of banana molecules; the molecules were not lined up. This also suggests that compound **1** does not exhibit a crystal−liquid crystal phase transition.

The temperature dependence of the magnetic susceptibility of the solvated compound **1**·acetone and the nonsolvated compound **1** was measured and is expressed in a $\chi_m T$ vs T curve, where χ_m is the molar magnetic susceptibility and T the temperature (Figure 2). The solvated compound **1**·acetone is in the HS state over the temperature range of 5−400 K. The $\chi_m T$ value for **1**·acetone gradually increases from 2.25 cm^3 K mol^{-1} at 5 K to 2.65 cm^3 K mol^{-1} at 125 K, and then the $\chi_m T$ value is almost constant at 2.56 cm^3 K mol^{-1} up to 320 K. The increase in the $\chi_m T$ value at 336 K corresponds to the removal of the acetone molecules. The nonsolvated compound **1** is obtained by annealing **1**·acetone at 400 K in vacuo. The $\chi_m T$ value for **1** is 2.43 cm^3 K mol^{-1} at 400 K, and the $\chi_m T$ value is constant over the temperature range of 300−400 K. The $\chi_m T$ value decreases very gradually from 2.47 cm^3 K mol^{-1} at 300 K to 0.70 cm^3 K mol^{-1} at 5 K, and the very gradual decrease of the $\chi_m T$ value shows thermal SCO behavior without a thermal hysteresis loop, with a spin-transition temperature $T_{1/2} \approx 160$ K. This gradual transition is as expected because there is no strong intermolecular interaction between the SCO units, as shown by the crystallographic measurement discussed above.

Measurement of the dielectric constant was carried out because compound **1** formed a banana-shaped structure and exhibited SCO behavior. The temperature dependence of the dielectric constant of **1** at 1, 10, and 100 kHz is shown in Figure 2. The gradual thermal SCO behavior between the HS and LS states of **1** is well observed in the temperature dependence of the dielectric constant. Compound **1** exhibited a change in the dielectric constant that was in agreement with the magnetic susceptibility measurement. The SCO phenomenon is accompanied by a spontaneous distortion of the first coordination sphere of the metal ions. Nakano et al. have reported that the SCO manganese(III) compound [Mn(taa)] exhibits a change in its dielectric constant that is in agreement with SCO behavior, by Jahn−Teller distortion.[16] Furthermore, Bousseksou et al. have reported that various SCO iron(II) compounds with a thermal hysteresis loop have exhibited a change in their dielectric constants with the hysteresis.[17] The SCO behavior of **1** is very gradual, and the change in the dielectric constant is also gradual, which is in agreement with the magnetic data.

In summary, we have succeeded in synthesizing a banana-shaped SCO cobalt(II) complex **1** with a long alkyl chain, based on a terpyridine frame. Compound **1** exhibited very gradual SCO behavior and changes in the dielectric constant. This change in the dielectric constant suggests a way in which SCO materials could be used in electronic devices. SCO materials that exhibit changes in their dielectric constants and ferroelectric SCO materials play important roles as molecular materials for electronic-based memories.

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Supporting Information Available: Powder XRD, DSC, and crystal data (CIF format). This material is available free of charge via the Internet at http://pubs.acs.org.

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