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Spin Transition at the Mesophase Transition Temperature in a Cobalt(II) Compound with Branched Alkyl Chains

Shinya Hayami,*,[†] Reiko Moriyama,[‡] Aya Shuto,[‡] Yonezo Maeda,[‡] Kazuchika Ohta,[§] and Katsuya Inoue[†]

Department of Chemistry, Graduate School of Science, Hiroshima University, 1-3-1 Kagamiyama, Higashi-hiroshima 739-8526, Japan, Department of Chemistry, Graduate School of Science, Kyushu University, 6-10-1 Hakozaki, Fukuoka 812-8581, Japan, and Smart Materials Science and Technology, Shinshu University, 3-15-1 Tokida, Ueda 386-8567, Japan

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A cobalt(II) compound, $[Co(C5C12C10\text{-}terpy)_2](BF_4)_2$ [C5C12C10-terpy = 4′,5‴-decyl-1‴-(heptadecyloxy)-2,2′:6′,2″-terpyridine] with branched alkyl chains, based on a terpyridine frame, was synthesized. The cobalt(II) compound exhibits a spin transition between low-spin and high-spin with a thermal hysteresis loop ($T_{1/2}\uparrow = 288$ K and $T_{1/2}\downarrow = 284$ K) at the liquid-crystal transition temperature. It is the first example in the cobalt(II) compounds in which the spin transition occurs at the crystal–liquid crystal transition temperature.

Liquid crystals are fascinating functional materials and are important in the field of advanced materials such as electrooptic devices. Organic liquid crystals are diamagnetic and can be easily oriented by an electric field. Liquid crystals of transition-metal complexes, called *metallomesogens*, have attracted a great deal of attention from the point of view of multifunctionality.[1] The development of *metallomesogens* with multifunctions [spin-crossover (SCO), mixed-valence, magnetism, conductivity, etc.] is very important in order to achieve the co-occurrence of various physical properties in the functional molecular-based materials.

The SCO phenomenon occurs when transforming between high-spin (HS) and low-spin (LS) states reversibly, stimulated by external perturbations (e.g., temperature, pressure, magnetic field, or light).[2] Galyametdinov et al. reported such a SCO iron(III) compound ($S = {}^1/_2 \leftrightarrow S = {}^5/_2$) with liquid-crystal properties.[3] This compound consists of an iron(III) ion coordinated to Schiff-base ligands with long alkyl chains and exhibits a rodlike geometry. The SCO behavior was gradual in the temperature range of 50−300 K, and the smectic A mesophase was observed between 380 and 418 K. We have also observed a photoinduced spin transition (LIESST effect) below about 60 K in the SCO iron(II) compounds, which display the mesophase above about 350 K.[4−6] The development of novel compounds exhibiting LIESST is one of the main challenges in this field. It may be possible that both the SCO and mesophase transition can be synchronized. Fujigaya et al. have reported a one-dimensional (1-D) iron(II) compound with triazole derivatives that exhibits SCO and liquid-crystal behavior in the same temperature region.[7,8] However, the supposed mesomorphism of the complexes has not been confirmed. Gaspar et al. have been investigating the possibility of synchronizing both transitions in the iron(II) complexes that are 1-D compounds based on triazole ligands.[9−11] They have reported that thermochromic liquid crystals operating in the room-temperature region exhibited SCO behavior in the temperature range at which the materials show a discotic columnar mesophase. Furthermore, control of the SCO characteristics of 1-D iron(II) compounds by an amphiphilic phase transition has also been reported.[12,13]

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* To whom correspondence should be addressed. E-mail: hayami@hiroshima-u.ac.jp.

[†] Hiroshima University.

[‡] Kyushu University.

[§] Shinshu University.

(1) Serrano, J. L. *Metallomesogens*; VCH: Weinheim, Germany, 1996.

(2) Gütlich, P., Goodwin, H. A., Eds. Spin Crossover in Transition Metal Compounds. *Topics in Current Chemistry*; Springer: Berlin, 2004; Vols. 233−235.

(3) Galyametdinov, Y.; Ksenofontov, V.; Prosvirin, A.; Ovchinnikov, I.; Ivanova, G.; Gütlich, P.; Haase, W. *Angew. Chem., Int. Ed.* **2001**, *40*, 4269.

(4) Hayami, S.; Danjobara, K.; Inoue, K.; Ogawa, Y.; Matsumoto, N.; Maeda, Y. *Adv. Mater.* **2004**, *16*, 869.

(5) Hayami, S.; Danjobara, K.; Miyazaki, S.; Inoue, K.; Ogawa, Y.; Maeda, Y. *Polyhedron* **2005**, *24*, 2821.

(6) Hayami, S.; Motokawa, N.; Shuto, A.; Masuhara, N.; Someya, T.; Ogawa, Y.; Inoue, K.; Maeda, Y. *Inorg. Chem.* **2007**, *46*, 1789.

(7) Fujigaya, T.; Jiang, D.-L.; Aida, T. *J. Am. Chem. Soc.* **2003**, *125*, 14690.

(8) Fujigaya, T.; Jiang, D.-L.; Aida, T. *J. Am. Chem. Soc.* **2005**, *127*, 5484.

(9) Real, J. A.; Gaspar, A. B.; Niel, V. M.; Muñoz, C. *Coord. Chem. Rev.* **2003**, *236*, 121.

(10) Real, J. A.; Gaspar, A. B.; Muñoz, M. C. *Dalton Trans.* **2005**, 2062.

(11) Seredyuk, M.; Gaspar, A. B.; Ksenofontov, V.; Reiman, S.; Galyametdinov, Y.; Haase, W.; Rentschler, E.; Gütlich, P. *Chem. Mater.* **2006**, *18*, 2513.

(12) Bodenthin, Y.; Pietsch, U.; Möhwald, H.; Kurth, D. G. *J. Am. Chem. Soc.* **2005**, *127*, 3110.

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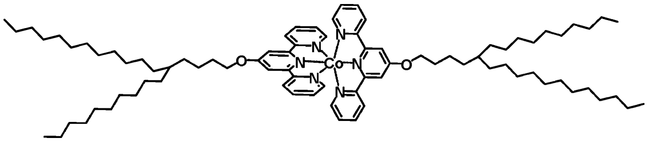

Figure 1. Chemical structure of the cation in **1**.

Hence, in order to develop a variety of switchable molecules that exhibit a spin transition induced by a crystal-to-mesophase transition, we propose the following strategies: (i) the SCO compounds are necessary in order to transform the spin states even by subtle structural changes in the ligands or molecules; (ii) the SCO compounds with $T_{1/2}$ above room temperature are necessary because the liquid-crystal transition temperature is generally higher than room temperature for the *metallomesogens*; (iii) the liquid-crystal transition temperature should be adjusted to $T_{1/2}$ in the SCO compounds by changing the length or type of the alkyl chains. On the basis of strategies i−iii, we aimed at constructing spin-transition compounds that occurred at the liquid-crystal transition temperature. The SCO *metallomesogens* have been investigated for only iron(II) or iron(III) compounds so far. The SCO *metallomesogens* for other metal compounds, cobalt(II) and so on, have also been interesting.

We focused on a cobalt(II) compound, [Co(C5C12C10-terpy)$_2$](BF$_4$)$_2$ [**1**; C5C12C10-terpy = 4′,5‴-decyl-1‴-(heptadecyloxy)-2,2′:6′,2″-terpyridine], with branched alkyl chains. The branched alkyl chains were introduced in order to decrease the mesophase transition temperature and synchronize the liquid-crystal and spin-transition temperatures in compound **1**. Compound **1** was obtained as a brown powder by reacting Co(BF$_4$)$_2$ with C5C12C10-terpy, and the composition for **1** was confirmed by elemental analysis.[14] A rodlike geometry is proposed for the molecular structure of **1** by computer simulation (Figure 1).[15]

Liquid-crystalline properties for **1** were confirmed by powder X-ray diffraction (XRD) and polarizing optical microscopy (POM). Powder XRD measurements for **1** were carried out to confirm this mesophase. Figure 2 shows the XRD pattern of the mesophase state observed at 300 K. The pattern displays a diffuse and broad scattering halo, centered at 4.5 Å ($2\theta = 19.6°$) in the wide-angle region, indicative of the liquidlike order of the aliphatic chains and thus of the fluidlike nature of the phase. In the small-angle region, the XRD pattern displayed four reflections in a ratio of $1:{}^{1}/_{2}:{}^{1}/_{3}:{}^{1}/_{4}$, which could be indexed as the (001), (002), (003), and (004) reflections of a lamellar phase with a periodicity $d = 23.9$ Å ($2\theta = 4.0°$). The natural texture of **1** is shown in Figure S1 in the Supporting Information, and a typical fan-shaped texture was observed at 300 K. The mesophase was identified as a smectic A (S$_A$) mesophase based on the texture observed by POM and the powder XRD pattern.

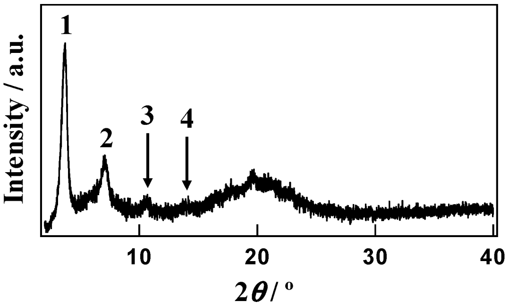

Figure 2. Powder XRD pattern for **1** at 300 K.

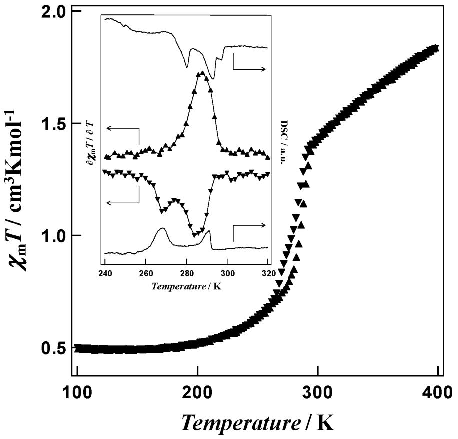

Figure 3. χ_mT vs T plot (▲, heating mode; ▼, cooling mode) for **1**. The inset graph shows the derivative $\partial\chi_mT/\partial T$ plot as a function of the temperature.

Spin transition between the HS and LS states for **1** was followed by measurements of the molar magnetic susceptibility χ_m as a function of the temperature (Figure 3). The χ_mT value for **1** is equal to 0.50 cm^3 K mol^{-1} at 100 K, which is in the range of values expected for LS cobalt(II) ions. As the temperature was increased from 100 K, the χ_mT product remained practically constant from 100 to 200 K and then abruptly increased around $T_{1/2}\uparrow = 288$ K. The χ_mT value at 400 K was 1.73 cm^3 K mol^{-1}, showing that the spin transition from the LS to HS state was induced. The spin transition is directly related to the mesophase transition. On cooling, the χ_mT value for **1** was decreased gradually from 400 to 292 K and then abruptly dropped at around $T_{1/2}\downarrow = 284$ K, showing that the HS moieties were restored to the LS state with a hysteresis loop ($\Delta T = 4$ K). Additional thermal cycles did not modify the thermal hysteresis loop.

Phase transition temperatures for **1** obtained by differential scanning calorimetry (DSC) measurements are summarized in Table 1. The scan-rate-dependent DSC analysis (Figure S2 in the Supporting Information) showed that polymorphism includes three crystal forms, K$_1$, K$_2$, and K$_3$ in compound

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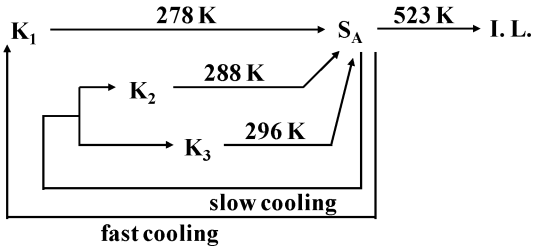
(13) Kuroiwa, K.; Shibata, T.; Sasaki, S.; Ohba, M.; Takahara, A.; Kunitake, T.; Kimizuka, N. *J. Polym. Sci., Part A: Polym. Chem*. **2006**, *44*, 5192.

(14) The ligand C5C12C10-terpy was synthesized by mixing 5-decyl-1-bromoheptadecane (1.57 g, 3.43 mmol), 2,6-bis(2-pyridyl)-4(1*H*)-pyridone (0.57 g, 2.29 mmol), and K$_2$CO$_3$ (0.63 g, 4.58 mmol) in *N*,*N*-dimethylformamide (70 mL) at 80 °C for 12 h. ^{1}H NMR (CDCl$_3$): 0.88 (t, $J = 7.0$ Hz, 3H), 1.25−1.55 (m, 47H), 1.85 (q, $J = 7.3$ Hz, 2H), 4.23 (t, $J = 6.3$ Hz, 2H), 7.32 (td, $J = 6.8$ Hz, 2H), 7.86 (td, $J = 8.5$ Hz, 2H), 8.01 (s, 2H), 8.61 (d, $J = 8.0$ Hz, 2H), 8.68 (d, $J = 6.0$ Hz, 2H). The cobalt(II) compound **1** was synthesized by mixing C5C12C10-terpy (0.44 mmol, 0.28 g) and Co(BF$_4$)$_2$·6H$_2$O (0.23 mmol, 0.078 g) in CHCl$_3$/MeOH (30 mL). The obtained brown powder was collected by filtration and recrystallized from acetone/EtOH (yield: 188 mg, 55%). Anal. Calcd for $C_{84}H_{130}N_6O_2B_2F_8Co_1$: C, 67.78; H, 8.80; N, 5.65. Found: C, 67.83; H, 8.82; N, 5.72.

(15) A geometry optimization for the compounds was performed in the gas phase by using Chem3D Ultra 10.0.

Table 1. Phase Transition Temperatures of **1**[a]



[a] Phase nomenclature: K = crystal, S_A = smectic A mesophase, and I.L. = isotropic liquid.

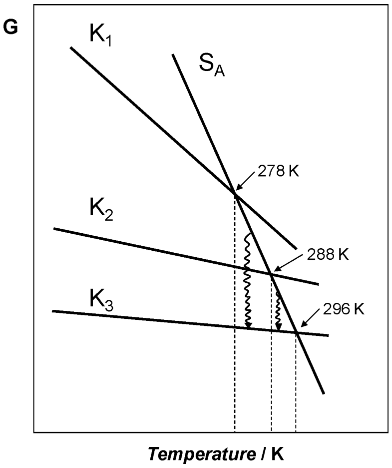


Figure 4. Schematic free energy vs temperature ($G-T$) diagram of **1**. The wavy lines show the relaxation.

1.[16] A virgin sample is almost in the crystal K_2 phase, and the K_2 phase transforms to the mesophase (S_A) at 288 K. After the first heating, the crystal K_1 phase formed by rapid cooling transforms to the mesophase at 278 K. On the other hand, the mixture of crystal K_1 and K_2 phases forms by slow cooling, and the K_2 phase is formed much more in comparison with the K_1 phase. Upon heating of the mixture phases, the relaxation from the mesophase S_A to crystal K_3 phases is observed and the K_3 phase transforms to the mesophase at 296 K. Upon further heating, the mesophase-to-isotropic liquid transition temperature for **1** was observed at 523 K. After the transition to the isotropic liquid, compound **1** decomposed slowly. The complicated phase transition and relaxation behavior can be rationally explained by using the $G-T$ diagram (Figure 4).[17]

The inset of Figure 3 shows the extremes of the derivative $\partial\chi_m T/\partial T$ in the spin-transition behavior and DSC curves measured at the same scan rate as that used in magnetic measurement (2 K min^{-1}) for **1**. The extremes of the derivative $\partial\chi_m T/\partial T$ agree with the peaks in the DSC curves. Upon heating, the spin-transition temperature was observed at 288 K, and the temperature agrees with the crystal-to-mesophase transition temperature from K_2 to S_A phases. The peak of the derivative $\partial\chi_m T/\partial T$ is in the temperature range of 270−300 K; three crystal-to-mesophase transitions, $K_1 \rightarrow S_A$, $K_2 \rightarrow S_A$, and $K_3 \rightarrow S_A$, occur within the temperature range of 270−300 K. On the other hand, the extremes of the derivative $\partial\chi_m T/\partial T$ were observed at 268 and 284 K upon cooling, and the $S_A \rightarrow K_1$ and $S_A \rightarrow K_2$, K_3 mesophase-to-crystal transitions occur in the same temperature range. It has been known that the cobalt(II) compounds with terpy derivative ligands exhibit gradual SCO behavior between $S = {}^1/_2$ and $S = {}^3/_2$.[18−21] Therefore, it has been thought that one part of the LS species (more than 50%) transforms to the HS species induced by a crystal-to-mesophase transition. Upon further heating after the spin transition is induced by a crystal-to-mesophase transition, compound **1** exhibits gradual and thermal SCO behavior.

These results demonstrate that the spin transition for **1** is triggered by a crystal-to-mesophase transition. Below 270 K, the branched alkyl chains in compound **1** do not melt, and the Co−N bond distance in the LS state is held short. Upon heating, the branched alkyl chains melt, and the spin transition from the LS to HS states occurs by permitting elongation of the Co−N bond.

In summary, we have succeeded in synthesizing mesophase and spin transitions for a cobalt(II) compound, [Co(C5C12C10-terpy)$_2$](BF$_4$)$_2$ (**1**), by using branched alkyl chains in the ligand around room temperature. In this way, the phenomenon that one phase transition causes another phase transition is very interesting and will become important in the future in the field of materials science. Furthermore, metallomesogens with multifunctions will play an important role in the field of materials science in the next generation.

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Supporting Information Available: POM and DSC data. This material is available free of charge via the Internet at http://pubs.acs.org.

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[16] Ohta, K.; Takenaka, O.; Hasebe, H.; Morizumi, Y.; Fujimoto, T.; Yamamoto, I. *Mol. Cryst. Liq. Cryst.* **1991**, *195*, 103.

[17] Fox, D., Labes, M. M., Weissberger, A., Eds. *Physics and Chemistry of Organic the Solid State*; Wiley: New York, 1965; p 725.

[18] Judge, J. S.; Baker, W. A., Jr. *Inorg. Chim. Acta* **1967**, *1*, 68.

[19] Kremer, S.; Henke, W.; Reinen, D. *Inorg. Chem.* **1982**, *21*, 3013.

[20] Gaspar, A. B.; Muñoz, M. C.; Niel, V.; Real, J. A. *Inorg. Chem.* **2001**, *40*, 9.

[21] Galet, A.; Gaspar, A. B.; Muñoz, M. C.; Real, J. A. *Inorg. Chem.* **2006**, *45*, 4413.