Dynamic structural conversion in a spin-crossover cobalt(II) compound with long alkyl chains†

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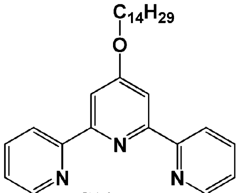
A cobalt(II) compound [Co(C14-terpy)$_2$](BF$_4$)$_2$·MeOH (1) with long alkyl chains was prepared, and exhibited unique SCO at T_1 = 50 K and spin transition at $T_2\uparrow$ = 206 K and $T_2\downarrow$ = 184 K with hysteresis (ΔT = 22 K) accompanying the motion of the long alkyl chains.

Flexible molecules are at the focus of materials research for the construction of molecular devices for polymers, films, gels and liquid crystals.[1–4] Such flexible molecules are very interesting from the point of view in not only functional materials but novel physical properties and has stimulated us for the construction of metal complexes with long alkyl chains to combine such flexibility with central metal complexes. Flexible metal complexes with long alkyl chains may exhibit a synchronicity between the central metal complexes and the long alkyl chains.[5–7] Based on this strategy, we focused on flexible spin-crossover (SCO) cobalt(II) compounds with long alkyl chains. The SCO cobalt(II) compounds exhibit S = 1/2 (LS; low-spin state) ↔ S = 3/2 (HS; high-spin state) spin conversion, and the spin states in the compounds can be controlled by smaller external stimuli than those in SCO iron(II) or iron(III) compounds.[8,9] Furthermore, the cobalt(II) compounds in the HS state show large anisotropy, and can exhibit unique magnetic behaviors. Previously, we reported that cobalt(II) compounds, [Co(Cn-terpy)$_2$](BF$_4$)$_2$ (n = 9–16), with terpyridine derivatives having long alkyl chains exhibited a unique spin transition (LS ↔ HS) triggered by structural phase transition.[7]

Here, we report unique magnetic properties in a cobalt(II) compound with long alkyl chains, [Co(C14-terpy)$_2$](BF$_4$)$_2$·MeOH (**1**) (C14-terpy is 4′-tetradecyloxy-2,2′:6′,2″-terpyridine), which occurs unusual SCO behavior and incomplete spin transition induced by structural phase transition accompanying the motion of the long alkyl chains.



C14-terpy

Single crystals of **1** suitable for X-ray diffraction (XRD) measurement were isolated as MeOH adducts by slow recrystallization from MeOH.‡ Single-crystal X-ray analysis was successfully carried out for samples in HS1 phase at 190 K.§ The sample in the HS1 phase was isolated by heating to 190 K after cooling at 100 K. In the HS1 phase (Fig. 1(b)). Single-crystal X-ray analysis of **1** revealed that each of the cobalt(II) atoms is octahedrally coordinated by six nitrogen atoms in two C14-terpy ligands, *i.e.*, an N$_6$ donor set. The bond lengths are typical of HS cobalt(II) compounds (Table 1).[10–12] The Co–N distance of the central pyridine in the terpyridine unit (2.03 Å) is shorter than the Co–N distance of the side pyridine in the terpyridine unit (2.15 Å), which induces a pronounced distortion of the CoN$_6$ octahedron. The three pyridine rings in the C14-terpy ligand are almost co-planar, and the two tridentate C14-terpy ligands in the compound are found to be nearly perpendicular to one another. The long alkyl chain C$_{14}$H$_{29}$O that forms a rod-like structure sticks out of 4′-position in the terpyridine moiety. Two counteranions BF$_4^-$ and one MeOH molecule are located in the intermolecular space, and there are short contacts among [Co(C14-terpy)$_2$]$^{2+}$ cations, BF$_4^-$ anions, and MeOH molecules. The cations form short contacts (3.43 Å) through the side pyridine and the nearest neighbor pyridine rings in the ligands on the *a* axis, and van der Waals interactions are noted between the alkyl chains, forming a 2-D sheet extended by intermolecular interactions. Furthermore, a fastener effect is noted between chains that face each other in the complexes. That the molecular packing of the compound is extremely tight suggests that there

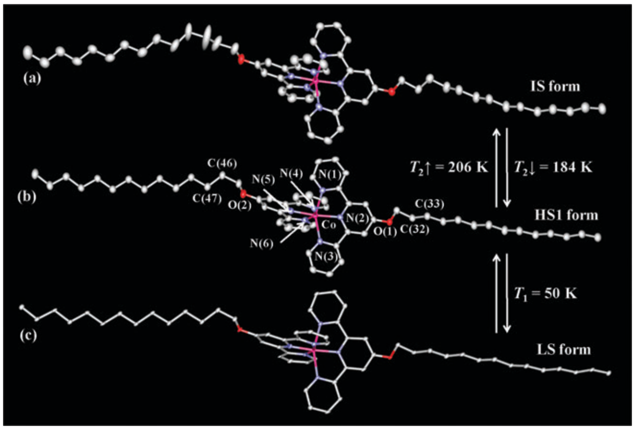


Fig. 1 ORTEP drawing of **1** showing 50% probability displacement ellipsoids: (a) IS phase at 190 K, (b) HS phase at 190 K, and (c) LS phase at 10 K.

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† Electronic supplementary information (ESI) available: Table S1: selected bond angles data in HS, LS and IS phases; Fig. S1: temperature dependence of ESR spectra, Fig. S2: DSC analysis, Fig. S3: temperature dependence of dielectric constants. CCDC 698977–698979. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b814415j

Table 1 Selected bond lengths for **1**

	LS @ 10 K	HS1 @ 190 K	IS @ 190 K
Co–N1	2.137(4)	2.143(4)	2.144(4)
Co–N2	1.910(3)	2.034(4)	1.966(3)
Co–N3	2.114(4)	2.167(4)	2.144(3)
Co–N4	1.977(4)	2.151(4)	2.084(3)
Co–N5	1.8443(3)	2.020(4)	1.945(3)
Co–N6	1.976(4)	2.123(4)	2.079(3)

are strong intermolecular interactions in the molecular assembly (Fig. 2).

The temperature dependence of the magnetic susceptibility for compound **1** was measured in the form of the $\chi_m T$ *vs.* T curve, where χ_m is molar magnetic susceptibility and T is temperature (Fig. 3). Compound **1** exhibited unique magnetic behavior in the temperature range of 5–300 K. Magnetic properties show that the value of $\chi_m T$ for **1** at 5 K is 0.43 cm^3 K mol^{-1}, which corresponds to what is expected for the LS state in cobalt(II) compounds.[8–10] On heating, the $\chi_m T$ value increased steeply around $T_1 = 50$ K. The $\chi_m T$ value at 100 K was equal to 3.62 cm^3 K mol^{-1}, representing the HS state. Further heating led to an abrupt drop in the $\chi_m T$ value around $T_2\uparrow = 206$ K. The $\chi_m T$ value at 210 K was 2.11 cm^3 K mol^{-1}. On cooling, the $\chi_m T$ value increased abruptly around $T_2\downarrow = 184$ K, and the $\chi_m T$ value at 182 K was 3.32 cm^3 K mol^{-1}. In the incomplete spin (IS) transition, a thermal hysteresis loop $\Delta T = 22$ K was observed. The unique magnetic behavior and the thermal hysteresis loop remained unchanged even after successive heating and cooling. The fairly abrupt conversion of $\chi_m T$ with a hysteresis loop is indicative of strong cooperative interaction. On further cooling, the $\chi_m T$ value decreased steeply around $T_1 = 50$ K and returned to the LS state (0.43 cm^3 K mol^{-1}) at 5 K. No hysteresis loop was noted in the SCO at 50 K. Therefore, cobalt(II) compound **1** exhibited SCO at $T_1 = 50$ K without hysteresis, and IS transition at $T_2\uparrow = 206$ K and $T_2\downarrow = 184$ K with hysteresis.

In order to confirm the SCO behavior at $T_1 = 50$ K, variable temperature electron spin resonance (ESR) spectra were measured for compound **1** (Fig. S1, ESI†). The spectrum shows the LS signal for cobalt(II) ions at 10 K, while the LS signal at 100 K disappeared. These indicate that compound **1** exhibits SCO behavior. On warming, the spin transition at $T_{1/2}\uparrow = 206$ K was found to be an endothermic phase transition ($\Delta S = 48.7$ J K^{-1} mol^{-1} at 201 K) in the differential scanning calorimetry (DSC) measurement (Fig. S2, ESI†). On cooling, one peak was also observed at 180 K ($\Delta S = 41.2$ J K^{-1} mol^{-1}), which corresponded to the spin transition temperature ($T_{1/2}\downarrow = 184$ K). It has been reported that the change of entropy is 16–35 J mol^{-1} K^{-1} in SCO cobalt(II) compounds.[8–10] The ΔS values for the spin transition are larger than those previously reported for SCO cobalt(II) compounds. The difference of the entropy variation is mainly due to structural phase transition.

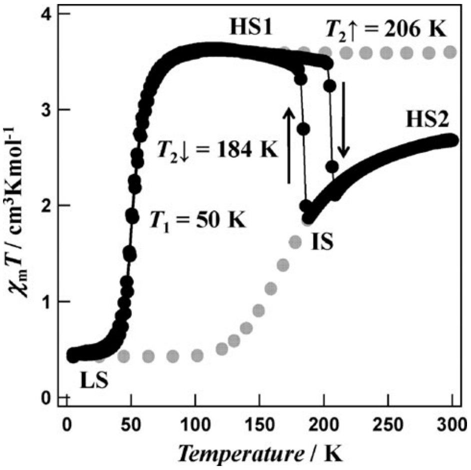

Fig. 3 Magnetic susceptibility measurement displaying spin crossover and incomplete spin transition for **1**.

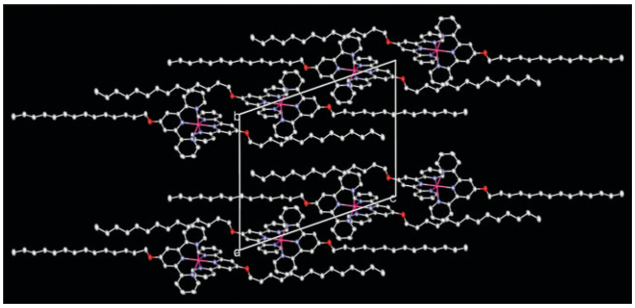

Fig. 2 Projection of the crystal packing of **1** in the HS phase at 190 K along the *a* axis. Displacement ellipsoids are shown at 50% probability. H atoms and BF_4^- anions are omitted for clarity.

The crystal structure was also measured in the LS phase at 10 K (Fig. 1(c)). Although the molecular structures of the samples in LS and HS1 phases are also almost the same, there is a unique difference in bond lengths. The bond lengths for LS are also shown in Table 1. The Co–N distance of the central pyridine in the terpyridine unit is 1.88 Å, and is much shorter than that of HS1 ($\Delta r_{HS1-LS} = 0.15$ Å). For the Co–N distances of the side pyridines in the terpyridine unit, remarkable differences are noted between the N(1)$\cap$N(3) side and the N(4)$\cap$N(6) side. The average Co–N distance of Co–N(1) and Co–N(3) is 2.13 Å ($\Delta r_{HS1-LS} = 0.02$ Å), and that of Co–N(4) and Co–N(6) is 1.98 Å ($\Delta r_{HS1-LS} = 0.16$ Å). The distance shrinks slightly in the N(1)$\cap$N(3) side and considerably in the N(4)$\cap$N(6) side. Generally, SCO compounds show shrinking in the six bond distances. However, it is observed that the distance between cobalt(II) ion and one side ligand mainly shrinks accompanying HS1 ↔ LS SCO behavior because there are interchain interactions between other side ligands.

The sample in the IS phase was also isolated by cooling from room temperature to 190 K, and also measured (Fig. 1(a)). Although the molecular structures of the samples in HS1 and IS phases are almost the same, there is a crucial difference in the alkyl chain form. The chains have extended to form straight lines from their zigzag form in the HS1 phase, whereas the chains curved greatly at C32, C33, C46 and C47 in the IS phase. As a result, the cations in the IS phase form a bent structure. The bond lengths for the IS phase are also shown in Table 1. The Co–N distance of the central pyridine in the terpyridine unit is 1.99 Å, and is shorter than that for HS1 ($\Delta r_{HS1-IS} = 0.04$ Å). For the Co–N distances of the side pyridines in the terpyridine unit, differences are notable between the N(1)∩N(3) side and the N(4)∩N(6) side. The average Co–N distance in Co–N(1) and Co–N(3) is 2.14 Å ($\Delta r_{\mathrm{HS1-HS2}} = 0.01$ Å), and that in Co–N(4) and Co–N(6) is 2.08 Å ($\Delta r_{\mathrm{HS1-HS2}} = 0.07$ Å). The distance in the N(4)∩N(6) side is shorter than that in the N(1)∩N(3) side. Through careful investigation of the crystal structure, we found that compound **1** changes its structure around the cobalt(II) ion during HS1 ↔ IS conversion. The symmetry of the environment around cobalt(II) ion in the IS phase is higher than that in the HS1 phase.

The unique magnetic property can be explained as following. There are two HS states, HS1 and HS2, in the cobalt(II) compound **1** (Fig. 3). One shows steep SCO behavior ($T_{1/2} = 50$ K), and the other shows gradual SCO behavior ($T_{1/2} = 175$ K) as shown by gray plots. When the structural phase transition occurs at $T_2\uparrow = 206$ K and $T_2\downarrow = 184$ K induced by the motion of the long alkyl chains, the magnetic behavior leads to the unique magnetic curve. In the structural transition in SCO and IS transition, the temperature dependence of the dielectric constant was also measured for compound **1** (Fig. S3, ESI†). The changes of the dielectric constant were observed at SCO temperature, $T_1 = 50$ K, and the spin transition temperature, $T_2\uparrow = 206$ K and $T_2\downarrow = 184$ K. It has been thought that the structural transition corresponds to the SCO and the spin transition.

In conclusion, we have succeeded in synthesizing $[\mathrm{Co(C14\text{-}terpy)_2}](\mathrm{BF_4})_2\cdot\mathrm{MeOH}$ (**1**) with long alkyl chains. Compound **1** exhibited unique SCO at $T_1 = 50$ K and incomplete spin transition at $T_2\uparrow = 206$ K and $T_2\downarrow = 184$ K with hysteresis ($\Delta T = 22$ K). In SCO behavior, the change in molecular structure revealed shrinking of Co–N bond lengths in only one side of the C14-terpy ligand. In the spin transition, the change in molecular structure indicated conversion between bending- and rod-like structures. It is thought that the unique magnetic properties are induced by changes of the environments around cobalt(II) ions accompanying the motion of the long alkyl chains. In this regard, flexible compounds can lead to novel and unique function expressions coupled between flexibilities and metal complexes.

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Notes and references

‡ Compound **1** was synthesized by mixing C14-terpy ligand (160 mg, 0.36 mmol) and $\mathrm{Co(BF_4)_2\cdot 6H_2O}$ (60 mg, 0.18 mmol) in $\mathrm{CHCl_3}$–MeOH (30 ml). The orange-brown solution was concentrated to approximately 10 ml and microcrystals were filtered off and recrystallized slowly from MeOH. Anal. Calcd. for $\mathrm{C_{59}H_{82}O_3N_6B_2F_8Co_1}$: C, 61.31; H, 7.15; N, 7.27. Found: C, 61.16; H, 7.30; N, 7.24.

§ Crystallographic study of **1** ($\mathrm{C_{63}H_{90}O_3N_6B_2F_8Co}$). Data were collected on a Bruker SMART APEX three-circle diffractometer equipped with a CCD area detector (graphite-monochromated $\mathrm{Mo_{K\alpha}}$, $\lambda = 0.71073$ Å, ω-scan mode (0.3° steps), semi-empirical absorption correction on Laue equivalents). Crystallographic data for HS phase at 190 K: $M = 1155.86$, orange–brown platelet (0.5 × 0.4 × 0.03), triclinic, space group $P\bar{1}$, $a = 9.009(9)$, $b = 17.065(17)$, $c = 20.96(2)$ Å, $\alpha = 69.400(16)$, $\beta = 77.362(16)$, $\gamma = 79.535(16)^\circ$, $V = 2954(5)$ Å^3, $Z = 2$, $D_c = 1.300$ g cm^{-3}. Full-matrix least-squares refinements gave an R factor of 0.049 from 11 974 reflections with intensity $I > 2\sigma(I)$ for 716 variables. Crystallographic data for IS phase at 190 K: triclinic, space group $P\bar{1}$, $a = 8.933(4)$, $b = 17.784(7)$, $c = 20.520(9)$ Å, $\alpha = 69.596(7)$, $\beta = 79.688(6)$, $\gamma = 85.107(7)^\circ$, $V = 3005(2)$ Å^3, $Z = 2$, $D_c = 1.277$ g cm^{-3}. Full-matrix least-squares refinements gave an R factor of 0.052 from 12 517 reflections with intensity $I > 2\sigma(I)$ for 716 variables. Crystallographic data for LS phase at 10 K: triclinic, space group $P\bar{1}$, $a = 8.897(5)$, $b = 16.527(10)$, $c = 20.591(12)$ Å, $\alpha = 69.685(9)$, $\beta = 76.821(11)$, $\gamma = 78.979(14)^\circ$, $V = 2744(3)$ Å^3, $Z = 2$, $D_c = 1.399$ g cm^{-3}. Full-matrix least-squares refinements gave an R factor of 0.032 from 10 016 reflections with intensity $I > 2\sigma(I)$ for 716 variables. Non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined.

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