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Spin Transition and Structural Transformation in a Mononuclear Cobalt(II) Complex

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Supporting Information

ABSTRACT: A mononuclear compound, $[Co^{II}(pyterpy)_2](PF_6)_2{\cdot}2CH_3OH$ [**2**; pyterpy = 4′-(4‴-pyridyl)-2,2′:6′,2″-terpyridine], shows a phase-transition-coupled, abrupt spin transition with a 9 K wide hysteresis that can transform to a spin-crossover compound, $[Co^{II}(pyterpy)_2](PF_6)_2{\cdot}2CH_2Cl_2{\cdot}CH_3OH$ (**3**).

Spin-crossover (SCO) compounds capable of reversibly switching the spin states of metal ions, i.e., low spin (LS) versus high spin (HS), by external stimuli may serve as bistable molecule-based materials, which have attracted much attention because of their promising applications in molecule-based memory, sensing, and switching.[1−3] A prerequisite of the cooperative and memory effect—a hysteretic spin conversion implying spin transition (ST) rather than SCO—to real applications has directed the syntheses of many Fe^{II} SCO compounds[4] because the $3d^6$ electronic configuration of a Fe^{II} ion allows significant shrinkage or expansion of the coordination bonds (about 0.20 Å)[5] so that the elastic interactions can be strong enough to bring about cooperativity during SCO. In contrast, the occurrence of SCO in Co^{II} compounds features a small variation in the coordination bonds (about 0.10 Å)[6] due to the partial occupancy of the antibonding e_g orbitals during SCO ($3d^7$, HS-$t_{2g}{}^5e_g{}^2$ ↔ LS-$t_{2g}{}^6e_g{}^1$); thus, it is less cooperative in nature for Co^{II} compounds, which usually exhibit gradual and nonhysteretic SCO.[7]

However, there were still a handful of mononuclear Co^{II} compounds that displayed abrupt, hysteretic ST behaviors, of which the organic ligands were mainly derivatives of 2,2′:6′,2″-terpyridine (terpy)[8] and a Schiff base.[9] It has been revealed that the cooperativity in these mononuclear Co^{II} compounds depends exclusively on the intermolecular interactions,[10] which include hydrogen-bonding, van de Waals, and $\pi-\pi$ interactions.[11] Particularly, we notice that the Co^{II}-terpy compounds with long alkyl chains on the 4 position of terpy exhibited reverse, abrupt ST phenomena with wide hysteresis loops arising because of order−disorder phase transition (PT),[8a−c,e] while the one-dimensional (1D) Co^{II}-terpy compound with a pyridyl group on the 4 position of terpy, i.e., $[Co^{II}(pyterpy)Cl_2]{\cdot}2H_2O$ [**1**; pyterpy = 4′-(4‴-pyridyl)-2,2′:6′,2″-terpyridine],[12] showed ST behavior with only a 1 K wide hysteresis loop, even though strong interchain interactions were observed. We speculate that coordination of the 4-position pyridyl group (along with two Cl ions), leading to a slightly constrained Co^{II} coordination sphere in the 1D structure, cannot efficiently transmit the small local lattice distortions. Instead, a mononuclear $[Co^{II}(pyterpy)_2]^{2+}$ compound with a pendant 4-position pyridyl group might undergo more cooperative ST because many more intermolecular interactions can be introduced and the monomeric structural unit might more easily move to accommodate PT. Here, we report such a mononuclear compound, $[Co^{II}(pyterpy)_2](PF_6)_2{\cdot}2MeOH$ (**2**), which shows abrupt ST with a hysteresis of 9 K width happened with a symmetry-breaking structural PT. To date, only one mononuclear Co^{II} compound shows symmetry-breaking structural PT during SCO.[8d,13] In addition, this compound can further transform to $[Co^{II}(pyterpy)_2](PF_6)_2{\cdot}2CH_2Cl_2{\cdot}CH_3OH$ (**3**) in the mother liquor, which shows incomplete, gradual SCO behavior.

Compound **2** was synthesized by mixing a methanol solution of $CoCl_2{\cdot}6H_2O$ and KPF_6 with a dichloromethane solution of pyterpy at room temperature (see the Supporting Information, SI). Red block crystals of **2** concomitant with a small amount of black block crystals of **3** were collected by filtration and separated mechanically. If the crystals of **2** were left undisturbed in the mother liquor, all could transform to crystals of **3**. During this process, both a direct transformation mechanism[14] through absorption of CH_2Cl_2 molecules and a dissolve−reassembly mechanism[15] had been observed.

Magnetic susceptibilities of compound **2** were measured in the 100−300 K temperature range in both warming and cooling modes (Figure S9, SI) and shown in the form of $\chi_M T$ between 160 and 210 K, where χ_M is the molar magnetic susceptibility and T the temperature (Figure 1, left). Upon warming, the $\chi_M T$ value remains constant at ~0.40 $cm^3\ K\ mol^{-1}$ from 100 to 150 K, then increases slightly until 189 K (0.62 $cm^3\ K\ mol^{-1}$), and rises

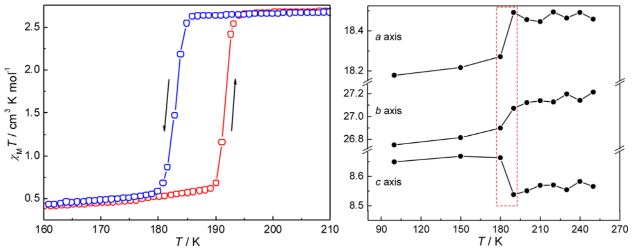

Figure 1. Left: $\chi_M T$ versus T plot for compound **2**. Applied field: 5000 Oe. Sweeping rate: 1 K min^{-1}. Right: Temperature dependence of the unit cell parameters.

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abruptly to reach a value of 2.65 cm^3 K mol^{-1} at 195 K, which remains practically steady until room temperature (Figure S9, SI). This profile clearly indicates a ST from LS Co^{II} ($S = {}^1/_2$) to HS Co^{II} ($S = {}^3/_2$) with $T_{1/2\uparrow}$ = 191 K and a large orbital angular momentum contribution to the Co^{II} magnetic moment (at the HS state), while upon cooling, the $\chi_M T$ value does not change until 186 K, where it drops suddenly to attain a value of 0.59 cm^3 K mol^{-1} at 180 K, giving a $T_{1/2\downarrow}$ value of 182 K. Thus, the ST occurs reversibly with a hysteresis loop of 9 K width, which suggests an efficient cooperative effect between adjacent Co^{II} centers and a possibility of crystallographic PT.

To probe the origin of the cooperative effect in compound **2**, a crystal of compound **2** was used to collect crystallographic data sets to determine the space group and unit cell parameters at temperatures between 100 and 250 K (Figure 1, right). The compound exhibited space groups $P2_1/c$ and $C2/c$ at low and high temperature, respectively, and the crystallographic PT took place between 180 and 190 K along with remarkable changes in the *a* and *c* cell lengths, synchronized with the ST process. Single-crystal structures were resolved at 250 K (**2**$^{\mathbf{HT}}$) and 100 K (**2**$^{\mathbf{LT}}$); see Figures S1 and S2, SI. At 250 K, the asymmetric unit of **2**$^{\mathbf{HT}}$ contains half of the [Co(pyterpy)$_2$]$^{2+}$ molecule, a PF$_6^-$ ion, and a CH$_3$OH molecule, while at 100 K, the symmetry is lost and the two pyterpy ligands become unrelated by symmetry, so the asymmetry unit of **2**$^{\mathbf{LT}}$ contains the whole [Co(pyterpy)$_2$]$^{2+}$ molecule, two PF$_6^-$ ions, and two CH$_3$OH molecules. At both temperatures, the two pyterpy ligands coordinate to the Co^{II} ion in a bis-meridional fashion, equatorially via four terminal pyridyl groups and axially via two central pyridyl groups, giving tetragonally distorted compressed octahedra. The Co−N distances are 2.008(6)−2.132(4) Å in **2**$^{\mathbf{HT}}$ and 1.877(5)−2.153(4) Å in **2**$^{\mathbf{LT}}$. The coordination sphere shows a significant elongation along the N4−Co−N4a direction upon decreasing temperature [Co−N4 = 2.123(4) Å at 250 K and Co−N1/N3 = 2.146(5)/2.153(5) Å at 100 K], which arises from the Jahn−Teller effect of a LS Co^{II} ion with a single e$_g$ electron.[7a,e] The N$_{central}$−Co−N$_{central}$ angle is absolutely linear in **2**$^{\mathbf{HT}}$ (N2−Co−N5), whereas that in **2**$^{\mathbf{LT}}$ (N2−Co−N6) is 178.6(2)°, reflecting a stronger steric effect of the constrained terpy ligands coordinated to the LS Co^{II} ion. This distortion results in the loss of symmetry of the [Co(pyterpy)$_2$]$^{2+}$ molecule and pronounced changes in the intermolecular interactions (see below). All terpy units in **2**$^{\mathbf{HT}}$ and **2**$^{\mathbf{LT}}$ are approximately coplanar, but the pendant pyridyl groups are twisted appreciably with respect to the terpy units. The dihedral angles are 22.1° and 38.3° in **2**$^{\mathbf{HT}}$ and 28.1° and 35.6° in **2**$^{\mathbf{LT}}$.

The average Co−N distances are 2.09 and 2.02 Å in **2**$^{\mathbf{HT}}$ and **2**$^{\mathbf{LT}}$, respectively, obviously not sensitive to ST. Alternatively, the distortion parameter, Σ, defined as the sum of the deviation from the 12 *cis*-N−Co−N angles, is sensitive to the distortion of coordination spheres at HS and LS states. The value of Σ would be larger in HS metal compounds than in LS ones because HS metal compounds allow for more distorted coordination spheres. In compound **2**, the values of Σ increase from 91.71° at 100 K to 116.14° at 250 K, corresponding to LS and HS states, respectively, in a Co-terpy SCO compound.[7e]

Besides structural changes within [Co(pyterpy)$_2$]$^{2+}$ molecules, the PT is accompanied by subtle alterations in the intermolecular interactions. As shown in Figure 2 and Table S5 (SI), four types of intermolecular interactions operate concomitantly in **2**$^{\mathbf{HT}}$ in the *ab* plane, namely, (I) hydrogen bonds between CH$_3$OH molecules and PF$_6^-$ ions [O1···F2 = 3.163(1) Å and O1···F3 = 3.131(1) Å], (II) hydrogen bonds between terpy units and PF$_6^-$ ions [C···F1 = 3.389(1) Å], (III) hydrogen bonds between pendant pyridyl groups and PF$_6^-$ ions [C···F3 = 3.377(1) Å], and (IV) edge-to-face C−H···π interactions between terpy units [C···π = 3.873(1) Å], while in **2**$^{\mathbf{LT}}$, the distorted [Co(pyterpy)$_2$]$^{2+}$ molecules arose from spin-state change stacking in corrugated form along the *b* axis, leading to a displacive motion of partial CH$_3$OH molecules and their hydrogen-bond-associated PF$_6^-$ ions. As a result, more complicated intermolecular interactions are observed in the *ab* plane: (I) hydrogen bonds between intact CH$_3$OH molecules and PF$_6^-$ ions [O2···F3 = 2.966(1) Å and O2···F6 = 3.046(1) Å], (II) hydrogen bonds between terpy units and PF$_6^-$ ions [C···F4 = 3.255(1) Å and C···F12 = 3.291(1) Å], (III) hydrogen bonds between displacive CH$_3$OH molecules and PF$_6^-$ ions [O1···F7 = 3.020(1) Å and O1···F12 = 3.031(1) Å], (IV) hydrogen bonds between pendant pyridyl groups and PF$_6^-$ ions [C···F3 = 3.256(1) Å and C···F9 = 3.332(1) Å], and (V) edge-to-face C−H···π [C···π = 3.735(1)/3.742(1) Å] and edge-to-edge interactions [C···C = 3.948(1) Å] between terpy units. In the *bc* plane, the [Co(pyterpy)$_2$]$^{2+}$ molecules stack through similarly offset π···π interactions in both **2**$^{\mathbf{HT}}$ and **2**$^{\mathbf{LT}}$ (Figures S7 and S8, SI).

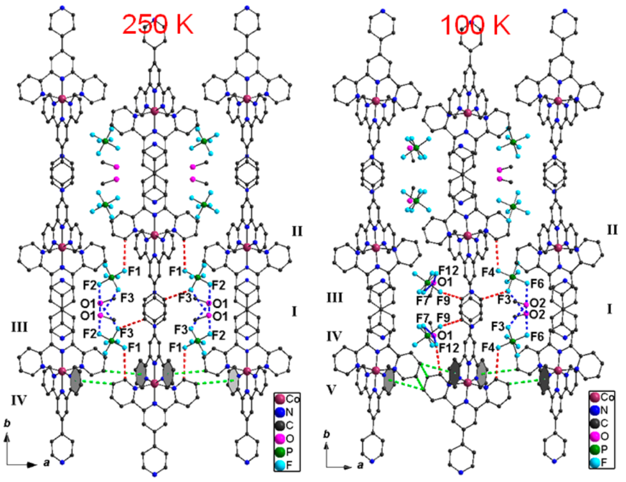

Figure 2. Intermolecular interactions of compound **2** during PT.

Differential scanning calorimetry (DSC) measurements were performed to confirm the PT and ST (Figure S11, SI). Two peaks in cooling and warming modes were observed at 180 and 189 K, respectively, confirming the presence of hysteresis revealed by the magnetic measurements (9 K). The enthalpy and entropy values of the transition calculated from the endothermic process were 4.99 kJ mol^{-1} and 26.38 J K^{-1} mol^{-1}, respectively. Because the entropy change in the electronic transition of a Co^{II} ion is only 5.76 J K^{-1} mol^{-1}, such excess entropy is mainly due to the crystallographic PT involving the displacement of molecules and a change of intermolecular interactions.

When compound **2** was transformed to compound **3**, the cooperative effect between Co^{II} centers vanished. Instead, compound **3** showed an incomplete, gradual SCO behavior in the 2−380 K temperature range (Figure S10, SI). Crystallographic study shows that the [Co(pyterpy)$_2$]$^{2+}$ molecules stack in a different fashion and the CH$_3$OH molecule interacts with the pendant pyridyl group of pyterpy through strong hydrogen bonds (Figure S6, SI), which may prevent the crystal structure from crystallographic phase change.

In summary, mononuclear six-coordinate Co^{II} compound **2** has been revealed to show abrupt ST with a hysteresis loop of 9 K width. The cooperative effect stems from ST-induced PT, as verified by crystallographic and DSC results. This is the first example of synergy between the ST and PT in Co^{II} compounds, where the PT is caused by the concerted displacive motion of both the ST and guest molecules. The transformation from **2** to **3** shows that stacking forms of SCO molecules and SCO behaviors can be easily tuned by guest molecules.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorgchem.5b01344.

Synthesis, figures, and tables (PDF)
X-ray crystallographic data (CIF)

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Notes

The authors declare no competing financial interest.

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