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1-D Cobalt(II) Spin Transition Compound with Strong Interchain Interaction: $[Co(pyterpy)Cl_2]\cdot X$

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Cobalt(II) compounds $[Co(pyterpy)Cl_2]\cdot MeOH$ (**1**·(MeOH)) and $[Co(pyterpy)Cl_2]\cdot 2H_2O$ (**1**·($2H_2O$)) were synthesized. The compound **1**·(MeOH) forms the quasi 3-D networks by making $\pi-\pi$ stacking between the 1-D chains. The methanol molecules from **1**·(MeOH) can be removed by heating, and substituted by absorption of water molecules. The MeOH molecules in **1**·(MeOH) are removed by heating at 410 K, and they are substituted by water molecules to form **1**·($2H_2O$). **1**·($2H_2O$) exhibits a $S = {}^{3}/_{2}$ (HS) $\leftrightarrows$ $S = {}^{1}/_{2}$ (LS) spin transition with a thermal hysteresis. We have succeeded in constructing a guest dependent 1-D spin-crossover cobalt(II) compound.

Self-assembly has been recognized as a most efficient process that organizes individual molecular components into highly ordered supramolecular species.[1] The designed construction of supramolecules from molecular building blocks is noted as one of the most challenging issues facing synthetic chemistry today. During the past few years, many one-, two-, and three-dimensional coordination polymers have been generated from transition metal templates with rigid and flexible pyridyl containing bidentate or multidentate organic spacers.[2] In addition, self-assembly of molecules driven by coordination to transition metal ions has become an important tool to explore the cooperative nature of the spin-crossover phenomenon between the LS (low-spin) and HS (high-spin) states.[3] Particularly, the ligands of the polypyridine type have been proved to be particularly suitable for metallosupramolecular chemistry as well as for the field of the spin-crossover phenomenon. Usually, the spin transition phenomena can be induced by a variation of temperature or of pressure.[4] The spin-crossover phenomenon depends strongly on intermolecular interactions.[5−8] When the magnitude of these intermolecular interactions overcomes a threshold value, the spin-crossover phenomenon proceeds cooperatively. In such a case, the spin transitions not only may be very abrupt but also may occur with a hysteresis effect.[5−8] The molecular compound that exhibits hysteresis can take two different electronic states between $T_{1/2}\uparrow$ and $T_{1/2}\downarrow$ depending on its history. $T_{1/2}\uparrow$ and $T_{1/2}\downarrow$ are defined as the temperatures for which there are 50% high-spin and 50% low-spin states in the warming and cooling modes, respectively.

Recently, the iron(II) spin-crossover coordination polymers, Hofmann-like[3,9−11] or interpenetrated framework[12,13] coordination polymers have been the subject of much research. The spin-crossover compounds with microporous framework can lead to multiple functions such as thermo-, photo-, and piezo-switching.[14] Kepert et al. reported that $[Fe(azpy)_2(NCS)_2]\cdot$(guest), where azpy is *trans*-4,4′-azopyridine, exhibits reversible uptake and release of guest molecules and contains electronic switching centers that are sensitive to the nature of the sorbed guests.[15] Supramolecular

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systems have attracted the attention of many research groups because of their photochemical and magnetic properties that can result from the interaction among their subunits. However, the number of polymeric spin-crossover compounds reported up to now is still small.[3,8−15]

Cobalt(II) spin-crossover compounds exhibit spin conversion between $S = {}^{1}/_{2}$ and $S = {}^{3}/_{2}$. Cobalt(II) compounds $[Co(H_2fsa_2en)(L)_2]$ (L = H_2O or pyridine, and H_2fsa_2en = *N*,*N*′-*o*-ethylenebis(3-carboxysalicylaldiminate)) exhibit spin transition with thermal hysteresis.[16−18] Other cobalt(II) spin-crossover compounds exhibit spin-crossover behavior without thermal hysteresis.[19−22] Furthermore, there are no examples of spin-crossover phenomena for 1-D cobalt(II) compounds.

Here we report the self-assembly of 4′-(4‴-pyridyl)-2,2′:6′,2″-terpyridine (pyterpy) and cobalt(II) ions. The resulting assembly of formulas $[Co(pyterpy)Cl_2]\cdot MeOH$ (**1**·(MeOH)) and $[Co(pyterpy)Cl_2]\cdot 2H_2O$ (**1**·($2H_2O$)) are 1-D compounds with solvent molecules. **1**·($2H_2O$) exhibits a $S = {}^{3}/_{2}$ (HS) $\leftrightarrows$ $S = {}^{1}/_{2}$ (LS) spin transition with a thermal hysteresis.

Ligand pyterpy (4′-(4‴-pyridyl)-2,2′:6′2″-terpyridine) is based on a combination of a pyridine (py) and terpyridine (terpy) units. The ligand was prepared from 2-acetylpyridine and pyridine-4-carbaldehyde according to the method described previously.[23] Single crystals of the solvated cobalt(II) compound $[Co(pyterpy)Cl_2]\cdot MeOH$ (**1**·(MeOH)) were obtained by slow diffusion in MeOH.[24] The solvent molecules in the crystals, MeOH, could be removed by heating **1**·(MeOH) at 410 K, and the water solvated $[Co(pyterpy)Cl_2]\cdot 2H_2O$ (**1**·($2H_2O$)) was obtained under the saturation vapor at room temperature. Thermogravimetry measurements for **1**·(MeOH) and **1**·($2H_2O$) have revealed a continuous loss of mass, starting at room temperature. The decrease in mass proceeds in the temperature ranges 310−410 K and 315−360 K, respectively. The loss of mass is in exact agreement with the removal of a MeOH molecule and two water molecules for **1**·(MeOH) and **1**·($2H_2O$). Elemental analysis also supports the idea for the removal of a MeOH molecule and the incorporation of two water molecules.[24] The transformation from **1**·($2H_2O$) to **1**·(MeOH) is irreversible because the nonsolvated compound **1** absorbs the atmospheric water by heating in the atmosphere.

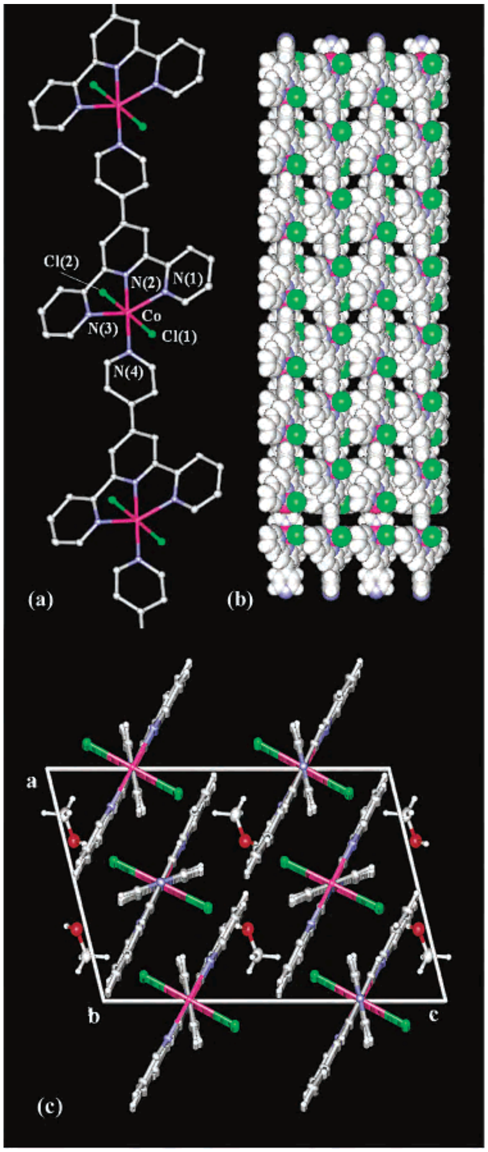

Figure 1. (a) X-ray crystal structure of the directional 1-D network **1**·(MeOH) in "head-to-tail" fashion. Hydrogen atoms and solvent molecules are omitted for clarity. (b) Space-filling view of the compound **1**·(MeOH) omitting solvent molecules. (c) Molecular packing of **1**·(MeOH) along the *b* axis.

The compound $[Co(pyterpy)Cl_2]\cdot MeOH$ (**1**·(MeOH)) crystallizes in the monoclinic $P2/c$ space group at room temperature (Figure 1).[25] The values of the bond lengths for **1**·(MeOH) are consistent with those typical for high-spin cobalt(II) compounds.[26] A moiety of terpy and py in the pyterpy ligand and two chloride anions coordinating to a cobalt(II) ion form a 1-D network. The two Cl^- anions occupy the two axial positions with a Co−Cl distance of

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(24) Ligand pyterpy (0.31 mg, 1 mmol) in MeOH was placed in one sidearm of an H-tube. Cobalt(II) chloride hexahydrate (0.24 g, 1 mmol) was placed in the other side, and MeOH was gently layered over both sides until the H-tube was full. After 2 weeks the orange solution contained brown crystals of **1**·(MeOH). Anal. Calcd for $C_{21}H_{18}O_1N_4Cl_2Co_1$ (**1**·(MeOH)): C, 53.41; H, 3.84; N, 11.86. Found: C, 53.21; H, 3.84; N, 11.85. Anal. Calcd for $C_{20}H_{18}O_2N_4Cl_2Co_1$ (**1**·($2H_2O$)): C, 50.44; H, 3.81; N, 11.76. Found: C, 50.26; H, 3.73; N, 11.74.

(25) Crystal data for **1**·(MeOH) ($C_{21}H_{18}O_1N_4Cl_2Co_1$) at 110 K: fw = 470.22; brown blocks, crystal dimensions 0.10 × 0.08 × 0.16 mm, monoclinic, space group $P2/c$; $a = 11.227(4)$ Å, $b = 11.267(4)$ Å, $c = 16.090(6)$ Å, $\beta = 103.750(5)^\circ$, $V = 1976(1)$ Å^3, $Z = 4$, $D_{calc} = 1.580$ g cm^{-3}, $R1 = 0.033$ for $I > 3\sigma(I)$, $R = 0.049$ and $R_w = 0.100$ for all data with a linear absorption coefficient μ(Mo Kα) = 11.59 cm^{-1}.

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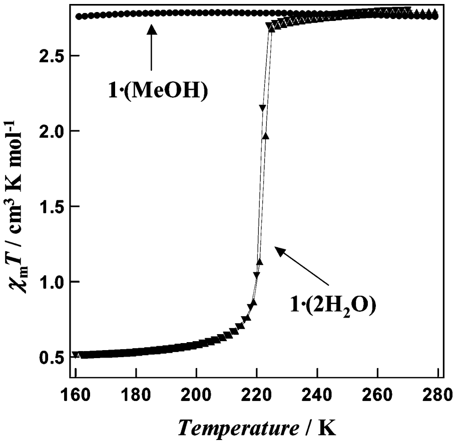

Figure 2. $\chi_m T$ vs T plots for **1**·(MeOH) and **1**·(2H$_2$O).

2.4665(7) Å and Cl(1)−Co−Cl(2) angle of 179.02(3)°. The square base of the octahedron is composed of one py and three py moieties in the terpy unit with a Co−N(4) distance of 2.137(3) Å for the py unit and a Co−N(2) distance of 2.067(3) Å for the central py of the terpy unit. The other two Co−N(1) and Co−N(3) distances are 2.185(2) Å. The N(2)−Co−N(4) angle between the py unit and the central py moiety of the terpy unit is 180.0°, and the N(1)−Co−N(3) angle between the side py in the terpy unit is 152.2(1)°. The py and the terpy units are not coplanar but tilted by 50° (Figure 1c). The 1-D networks align along the *b* axis. Through careful investigation of the intermolecular arrangement in the analyzed crystal structure, it was found that 1-D compounds form $\pi-\pi$ stacking in the pyterpy ligands between the terpy units, forming a quasi 3-D network for **1**·(MeOH) (Figure 1c). The MeOH molecules are located in the interchain position formed by the quasi 3-D networks (Figure 1b). The crystal structures of the water solvated compound [Co(pyterpy)Cl$_2$]·2H$_2$O (**1**·(2H$_2$O)) could not be determined because the removal of the MeOH molecules induces cracks in the crystal, making an X-ray single crystal study impossible. The result of the powder XRD measurement suggested that the structure of the water solvated **1**·(2H$_2$O) is similar to that of the methanol solvated **1**·(MeOH). In spite of the similarity of the two XRD patterns, we were not able to index all the peaks and any attempt to solve the structure by the Rietveld method was not successful.

The temperature dependence of the magnetic susceptibility for the single crystals of **1**·(MeOH) and **1**·(2H$_2$O) was measured in the form of the $\chi_m T$ vs T curve, where χ_m is the molar magnetic susceptibility and T the temperature (Figure 2). The $\chi_m T$ value for **1**·(MeOH) is equal to 2.74 cm^3 K mol^{-1} in the temperature range 150−300 K, which is in the range of values expected for the HS cobalt(II) ion. The $\chi_m T$ value decreases to 1.67 cm^3 K mol^{-1} at 5 K, and the decrease of the value is interpreted by assuming the existence of a tetragonal distortion of the coordination octahedron and that of a spin admixing between the resulting quartet ground state $^4A_{2g}$ and the first excited doublet state $^2A_{1g}$.[19]

The magnetic data for the compound **1**·(2H$_2$O) were also measured. The $\chi_m T$ value for **1**·(2H$_2$O) is equal to 2.80 cm^3 K mol^{-1} at 300 K, which is in the range of values expected for HS cobalt(II) ions. As the temperature is decreased from 300 K, the $\chi_m T$ product remained practically constant from 300 to 225 K, then abruptly dropped around $T_{1/2}\downarrow = 222$ K. The $\chi_m T$ value at 150 K was 0.41 cm^3 K mol^{-1}, showing that the spin transition from the HS to the LS state was induced. The spin transition is directly related to the displacement of solvent molecules.[27,28] On warming, the $\chi_m T$ value for the compound **1**·(2H$_2$O) was almost constant from 5 to 200 K, then abruptly increased at around $T_{1/2}\uparrow = 223$ K, showing that the LS moieties were restored to the HS state with a hysteresis loop ($\Delta T = 1$ K). Additional thermal cycles did not modify the thermal hysteresis loop.

In order to confirm the induction of the spin-crossover, the variable temperature ESR spectra of microcrystalline powder sample **1**·(2H$_2$O) were measured. At 5 K, the spectrum mainly shows the LS form signal ($g = 2.144$).

In summary, the compound **1**·(MeOH) forms quasi 3-D networks by making $\pi-\pi$ stacking between the 1-D chains. The MeOH molecules in **1**·(MeOH) are removed by heating at 410 K, and they are substituted by water molecules to form **1**·(2H$_2$O). The 1-D cobalt(II) compound **1**·(2H$_2$O) displays a hysteresis in the spin transition behavior. We have succeeded in constructing a 1-D cobalt(II) spin transition compound.

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Supporting Information Available: Crystallographic data (CIF) for **1**·(MeOH) and powder XRD patterns for **1**·(MeOH) and **1**·(2H$_2$O). This material is available free of charge via the Internet at http://pubs.acs.org.

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