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COMMUNICATION

Spin-Crossover Behaviors in Solvated Cobalt(II) Compounds

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Two solvated cobalt(II) terpyridine complexes, [Co(MeO-terpy)$_2$](BF$_4$)$_2$·H$_2$O (1·H$_2$O) and [Co(MeO-terpy)$_2$](BF$_4$)$_2$·acetone (1·acetone) were prepared. Annealing each of these complexes resulted in the formation of two desolvated species, 1 and 1´, respectively. 1·H$_2$O and 1 exhibited two-step and gradual SCO. The compound 1·acetone is high-spin for all temperatures and 1´ undergoes a reverse spin transition due to a phase change.

Designing molecules that could be used for information processing and storage is a significant challenge in molecular materials science. These molecules must have bistability; they must be stable in two distinct electronic states over a certain range of external perturbation. Typical examples are found in spin-crossover (SCO) compounds.[1] A variety of d^n (n = 4-7) transition metal compounds exhibiting SCO have been reported and the spin transition phenomenon can be induced by a variation of temperature, pressure or illumination.[2] In general, reversible temperature dependent SCO behavior involves a spin transition from LS to HS on heating and from HS to LS on cooling.

Although SCO transitions are due to the electronic structure of the single molecule they can be observed in solutions or polymer matrices.[3,4] Gradual or abrupt spin transitions may be observed in the solid state, depending on cooperativity arising from intermolecular interactions.[5-7] The understanding of cooperative behavior in SCO is important for the design of materials that are useful for information technology. For example, flexibility of ligands can influence the cooperative interactions both directly and indirectly. The former arises from the structural changes of the ligands, and the latter from the random packing structure. Thus the flexibility of molecular assemblies is also a very important factor in achieving synergy of various interesting physical properties in advanced materials.[8,9]

In general, SCO cobalt(II) compounds exhibit a spin change between the LS (S = 1/2) and HS (S = 3/2) states accompanying $\Delta S_{\mathrm{spin}} = R[\ln(2S + 1)_{\mathrm{HS}} - \ln(2S + 1)_{\mathrm{LS}}] = 5.8$ J K^{-1} mol^{-1} which is smaller than those of iron(II) (13.4 J K^{-1} mol^{-1}) or iron(III) (9.1 J K^{-1} mol^{-1}) SCO compounds.[2] Therefore, SCO phenomena for cobalt(II) compounds can be induced by smaller external stimuli than iron complexes. Accordingly, the spin transitions of cobalt(II) complexes can be readily influenced by relatively minor ligand derivatisation. Constable et al. has reported about structure, solvent dependence and some other properties for [Co(MeO-terpy)$_2$](PF$_6$)$_2$ (**2**),[10,11] and Slattery et al. also reported about magnetic behavior for **2** in solution.[12] We therefore measured magnetic behavior for **2** in solid, and discovered that **2** shows gradual SCO.

We have recently demonstrated that the inclusion of long alkyl chains on cobalt(II) terpyridine compounds, [Co(C$_n$-terpy)$_2$](BF$_4$)$_2$ (n = 9 - 16), results in unique spin transitions (HS ↔ LS) triggered by a structural phase transitions.[10-12] We suggested that cooperativity in these soft materials produces novel switching functions, and reported that the long alkylated cobalt(II) compound [Co(C$_{16}$-terpy)$_2$](BF$_4$)$_2$ (C$_{16}$-terpy is 4'-hexadecyloxy-2,2':6',2"-terpyridine) exhibits a 'reverse spin transition' between HS and LS with a thermal hysteresis loop triggered by a structural phase transition.[10]

Here we have focused on a counter anion BF$_4^-$ because it can generate more disorderliness compared with PF$_6^-$. We report variations in magnetic behavior due to different structural phases and solvation in the cobalt(II) complex of 4'-methoxy-2,2':6',2´´-terpyridine (MeO-terpy), [Co(MeO-terpy)$_2$](BF$_4$)$_2$, **1**. Two solvated complexes (**1·H$_2$O** and **1·acetone**) and their corresponding desolvated phases (**1** and **1´**) were prepared and investigated. **1·H$_2$O** and **1·acetone** were obtained by recrystallization from MeOH and acetone, respectively, and the non-solvated compound **1** and **1´** were obtained by annealing **1·H$_2$O** and **1·acetone** under vacuum at 400 K, respectively. **1·H$_2$O** exhibited a two-step SCO and after annealing, the desolvated compound **1**, exhibited gradual SCO behavior. On the other hand, **1·acetone** was found to be HS for all temperatures, and after annealing, the desolvated **1´** exhibited a "reverse spin transition", which can be attributed to a structural change.

A crystal structure of [Co(MeO-terpy)$_2$](BF$_4$)$_2$·MeOH·H$_2$O (**1·MeOH·H$_2$O**) was obtained at 80 K[‡§] (microanalysis of the dried bulk sample of this complex revealed loss of the methanol solvate to yield **1·H$_2$O**). Figure 1 shows the structure of **1·MeOH·H$_2$O**. In the structure, each of the cobalt(II) atoms are octahedrally coordinated by six nitrogen atoms in two MeO-terpy ligands, i.e. an N$_6$ donor set. The Co-N distances are of typical for LS cobalt(II) compounds.[2] One of the tetrafluoroborate anions and the methanol solvent are disordered over two positions. The molecules are tightly packed with a three-dimensional network of interactions including a two-dimensional terpyridine-embrace motif of

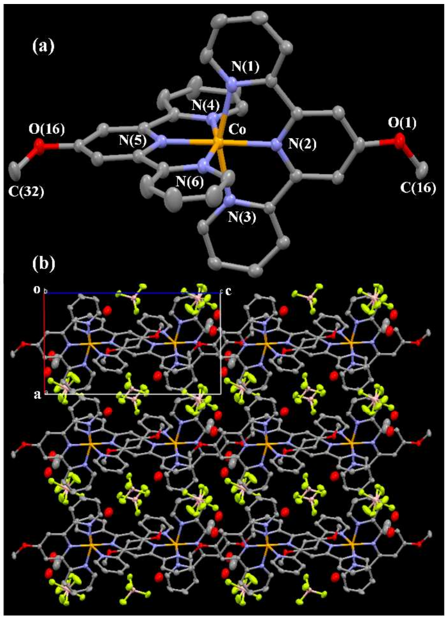

Fig. 1 (a) ORTEP drawing of the compound **1·MeOH·H$_2$O** showing 50% probability displacement ellipsoids. (b) Projection of the crystal structure of **1·MeOH·H$_2$O** along the *ac* plane. H atoms are omitted for clarity.

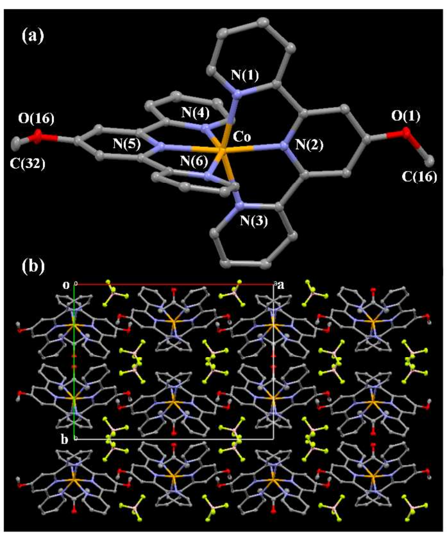

Fig.2 (a) ORTEP drawing of the compound **1·acetone** showing 50% probability displacement ellipsoids. (b) Projection of the crystal structure of **1·acetone** along the *ab* plane. H atoms are omitted for clarity.

aryl-aryl interactions,[13-14] classical hydrogen bonding between solvents and anions and a range of non-classical H$_{pyridyl}$-anion and H$_{pyridyl}$-oxygen hydrogen bonding interactions.

Solvated compound [Co(MeO-terpy)$_2$](BF$_4$)$_2$·acetone (**1·acetone**) was also obtained as brown orange single crystals and single crystal X-ray obtained at 93 K (Figure 2).[‡§] Unlike **1·MeOH·H$_2$O**, which crystallized in a triclinic setting, **1·acetone** crystallized in the monoclinic space group *C2/c*. The molecular structure for **1·acetone** is similar to that for **1·MeOH·H$_2$O**. There is no disorder in the solvent or anions. The Co-N distances are longer in this structure (between 2.0527(8) and 2.1820(12) Å, compared to a range of 1.903(2)-2.142(2) Å for **1·MeOH·H$_2$O**) and are typical for HS cobalt(II) compounds.[2] While in **1·MeOH·H$_2$O**, the two MeO-terpy ligands are arranged almost orthogonally, in **1·acetone** the two ligands deviate significantly with an angle of 85.6° between the ligands' mean planes. The N(3)-containing pyridyl ring also deviates from the mean plane of the ligand.

The crystal packing in **1·acetone** differs significantly to that in **1·MeOH·H$_2$O**. While there are some offset face-to-face π-π interactions present, forming a two-dimensional array that extends in the crystallographic *bc*-plane, they are of poor orientation resulting in a loose packing arrangement; the presence of the acetone solvent essentially disrupts the terpyridine-embrace motif.[15] The anions are located between these layers and are involved in H$_{pyridyl}$-anion interactions.

No suitable single crystals for the annealed compounds **1** and **1´** were obtained in the present study.

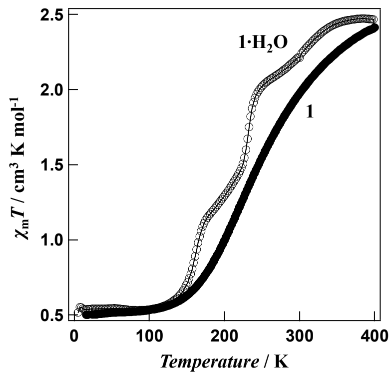

Fig.3 $\chi_m T$ versus T plots for the compounds **1·H$_2$O**(○) and **1** (●).

The temperature dependence of the magnetic susceptibility for **1·H$_2$O** and **1** were measured (Figure 3). **1·H$_2$O** undergoes a two-step SCO with the transitions centred around the temperatures $T_{1/2(S1)}$ = 163K and $T_{1/2(S2)}$ = 231 K, respectively.[16-18] After further heating, a depression of the $\chi_m T$ value was observed at around 300 K, suggesting the solvent water molecule is removed. After annealing, the non-solvated compound **1** exhibited gradual SCO behavior with the $\chi_m T$ value increasing from 0.45 cm^3 K mol^{-1}at 5 K to 2.15 cm^3 K mol^{-1} at 400 K.

In contrast, **1·acetone** was found to exist in the HS state at all temperatures, consistent with the X-ray structure. The $\chi_m T$ value lies within 1.91 - 2.46 cm^3 K mol^{-1}in the temperature range 5 K - 300 K. After further heating, the $\chi_m T$ value again decreases, consistent with the loss of the acetone solvent molecule.

After annealing, however, the desolvated compound **1´** displays markedly different behavior. The $\chi_m T$ value gradually decreases from 1.75 cm^3 K mol^{-1} at 400 K to 1.07 cm^{3}Kmol^{-1} at 270 K, representing normal thermal SCO behavior. Upon further cooling, however, the $\chi_m T$ value increases abruptly at $T_{1/2}\downarrow$ = 256 K to 1.74 cm^3 K mol^{-1} at 220 K. On further cooling, the $\chi_m T$ undulates between 1.41 – 1.85 cm^3 K mol^{-1} in the temperature range 5 K to 190 K. On further heating, the $\chi_m T$ values abruptly dropped ($T_{1/2}\uparrow$ = 309 K), showing the transition from HS to LS. Finally, the $\chi_m T$ value gradually increases from 310 K to 400 K. The wide thermal hysteresis loop (ΔT = 53 K) near room temperature is maintained through successive thermal cycles. Thus **1´** exhibits a "reverse spin transition" which was further confirmed by variable temperature electron spin resonance (ESR) spectra (Figure S1).

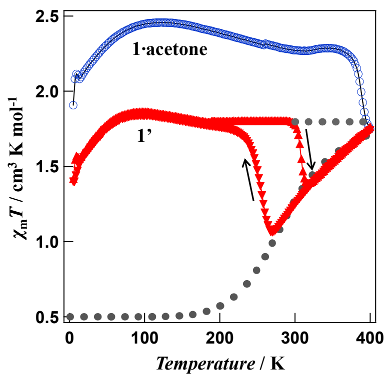

Fig.4 $\chi_m T$ versus T plots for the compounds **1·acetone**(○), and **1´**(▲) on warming (▼) on cooling. (•) represent calculated curves for the two phases of **1´** if no structural transition occurred.

The ESR experiments are consistent with the magnetic results. A variable temperature powder X-ray diffraction (PXRD) study (Figures S2 and S3) suggests that there is a reversible structural change associated with the LS-HS transition in **1´**. This "reverse spin transition" can thus be rationalized in the following way. As prepared, **1´** displays gradual SCO behavior ($T_{1/2}$ = 250 K) with the reduction of temperature (this curve is shown in Fig. 4. as grey dots) until a phase change occurs ($T_2\downarrow$ = 256 K) and **1´** becomes HS. Upon heating the reverse transition occurs at a higher temperature ($T_2\uparrow$ = 309 K) resulting in the magnetic hysteresis. These structural changes are fully reversible and can be cycled through several times.

In conclusion, we have prepared two new cobalt(II) complexes of 4'-methoxy-2,2':6',2´´-terpyridine [Co(MeO-terpy)$_2$](BF$_4$)$_2$·H$_2$O (**1·H$_2$O**) and [Co(MeO-terpy)$_2$](BF$_4$)$_2$·acetone (**1·acetone**) which show distinct magnetic behavior. **1·H$_2$O** exhibits gradual SCO while **1·acetone** is high-spin for all temperatures. After annealing each of these complexes two desolvated forms **1** and **1´** were produced. Solvated **1·H$_2$O** exhibits two-step SCO and non-solvated **1** show gradual SCO, while **1´** shows a "reverse spin transition" which can be attributed to a structural phase transition. Bistable metal complexes of this type may eventually find application in information storage or processing devices.

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‡ The compounds**1·H$_2$O** and **1·acetone** were synthesized by mixing the MeO-terpy ligand (95 mg, 0.36 mmol) and Co(BF$_4$)$_2$·6H$_2$O (60 mg, 0.18 mmol) in MeOH (30 ml). The orange-brown solution was concentrated to approximately 10 ml and micro crystals were filtered and recrystallized slowly from MeOH or acetone, respectively. Anal. Calcd. for C$_{32}$H$_{30}$O$_4$N$_6$B$_2$F$_8$Co$_1$ (**1·H$_2$O**): C, 49.46; H, 3.63; N, 10.81. Found: C, 49.30; H, 3.63; N, 10.82. Anal. Calcd. for C$_{35}$H$_{32}$O$_3$N$_6$B$_2$F$_8$Co$_1$ (**1·acetone**): C, 51.44; H, 3.95; N, 10.28. Found: C, 51.16; H, 3.87; N, 10.38.

§ Crystallographic study. Data collections were carried out on a Rigaku/MSCMercury CCD diffractometer with graphite-monochromated Mo-Kα radiation. The structures were solved by direct methods (Rigaku Crystal Structure crystallographic software package of Molecular Structure Corporation) and refined with a full-matrix least-squares technique using SHELXL-97.[19] One of the anions and the methanol solvent in **1·MeOH·H$_2$O** are disordered over two positions with 0.6 and 0.4 occupancy factors. Each of the disordered components were also modeled with indential thermal parameters. The water hydrogen atoms were first located in the difference Fourier map before refinement with bond length restraints.

Crystallographic data for **1·MeOH·H$_2$O** at 80 K: *F.W.* = 777.15, orange-brown platelet (0.3×0.1×0.1), triclinic, space group *P*–1, a = 8.8542(4), b = 12.5098(7), c = 15.4307(7) Å, α= 88.642(2), β= 89.490(1), γ= 84.725(2)°, V = 1701.42(14) Å^3, Z = 2, $D_{calcd.}$ = 1.580 g cm^{-3}. Full-matrix least-squares refinements gave an R factor of 0.0552 from 7786 reflections with intensity $I > 2\sigma(I)$ for 497 variables. Crystallographic data for **1·acetone** at 93 K: *F.W.* = 817.21, orange-brown platelet (0.6×0.4×0.2), monoclinic, space group *C2/c*, a = 21.5593(8), b = 14.9117(4), c = 12.1365(3) Å,β= 117.426(1)°, V = 3463.2(2) Å^3, Z = 4, $D_{calcd.}$ = 1.567 g cm^{-3}. Full-matrix least-squares refinements gave an R factor of 0.0264 from 3961 reflections with intensity $I > 2\sigma(I)$ for 252 variables.

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Graphic abstract

SCO cobalt(II) compounds with methoxy group have been synthesized, which exhibit unique magnetic behaviors, two-step SCO or reverse spin transition caused by structural transition.