Magnetic Properties of Iron(II) and Cobalt(II) Complexes of Tetrakis(2-pyridyl)methane. Spin-crossover Behavior in the Cobalt(II) Complex

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Iron(II) and cobalt(II) mononuclear metal complexes with tetrakis(2-pyridyl)methane have been synthesized and characterized. A gradual spin-crossover to the high-spin state above 300 K is observed in the cobalt(II) complex while the iron(II) complex exhibits no spin transition to the high-spin state between 5 and 400 K.

Polypyridine complexes, represented by 2,2′-bipyridine and 2,2′:6′,2″-terpyridine, have attracted considerable attention with respect to their fascinating photo- and electrochemistry.[1] Among numerous polypyridine ligands tris(2-pyridyl)methane, $CH(py)_3$, and its derivatives were synthesized and their metal complexes have been studied because of the presence of tripodal π-acceptor ligands.[2] Previously, we have reported the synthesis of tetrakis(2-pyridyl)methane, $C(py)_4$, as a novel, tetrahedral polypyridine ligand[3] in relation to our studies on pyridine-substituted tetraarylmethanes.[4] This highly symmetric tetradentate ligand $C(py)_4$ would be expected to take three different metal-binding configurations; (i) bidentate, (ii) tripodal, and (iii) twofold bidentate (Chart 1). Indeed, these three metal-binding patterns are observed in Ag$^{\mathrm{I}}$ and Cu$^{\mathrm{II}}$ complexes of $C(py)_4$.[5] Recently we have energetically performed the development of functional coordination compounds using $C(py)_4$ ligand. On the basis of this strategy, we focus on spin-crossover (SCO) compounds.[6] In order to develop this important field, SCO complexes with new ligand systems must be developed. In this communication, structures and magnetic properties of resulting compounds; $[Fe\{C(py)_4\}_2](ClO_4)_2\cdot 2CHCl_3$ (**1**) and $[Co\{C(py)_4\}_2](ClO_4)_2\cdot 2CHCl_3$ (**2**) are described, and **2** exhibits a gradual SCO to the HS state above 300 K. To the best of our knowledge, this is the first SCO behavior among metal complexes of $CH(py)_3$ or its derivatives.

The complexes **1** and **2** were obtained as single crystals by slow contact of a solution of $C(py)_4$ with a solution of the corresponding metal(II) salt in a 1:1 molar ratio in the presence of a small amount of ascorbic acid to prevent air oxidation of M$^{\mathrm{II}}$ to M$^{\mathrm{III}}$ (M = Fe and Co) under an inert atmosphere.[7] The molecular structures of complexes **1** and **2** were determined by X-ray crystallography at 200 K; the crystal structures of **1** and **2** are similar (Figure 1).[8] In the complexes of $CH(py)_3$, $C(py)_4$ acts as a tripodal ligand and one of the four 2-pyridyl groups in the ligand is free from coordination. The coordination geometry around the metal ion is a tetragonally distorted octahedron. It should be noted that the coordination bond lengths in **2** (av. 2.03 Å) are much shorter than those of the $[Co\{CH(py)_3\}_2]^{2+}$ (2.11 Å).[2g] This result suggests that the spin state of Co$^{\mathrm{II}}$ ion in **2** is the LS state, which is in accordance with the magnetic data (see below). In contrast, the spin state of Co$^{\mathrm{II}}$ ion in $[Co\{CH(py)_3\}_2]^{2+}$ is the HS state. This difference of the coordination bond lengths should be attributable to the fourth pyridyl group in $C(py)_4$; the fourth pyridyl group would force the other three pyridyl groups closer each other, by which the adaptability as a tripodal ligand is decreased and shorter coordination bond length is favored.[5] The average coordination bond length in **1** (1.97 Å) is comparable to that in $[Fe\{CH(py)_3\}_2]^{2+}$ (1.949 Å),[2l] suggesting Fe$^{\mathrm{II}}$ configuration takes a LS state in these complexes.

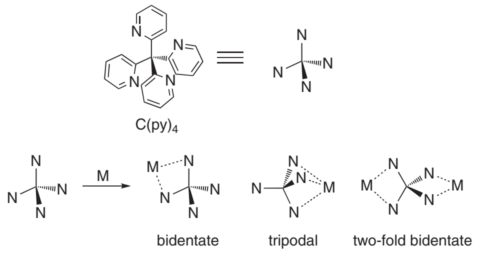

Chart 1.

Temperature dependence of magnetic susceptibilities of **1** and **2** was performed on ground hand-collected crystals in the temperature range of 5–400 K at a 10 kOe field. Temperature dependence of the $\chi_M T$ product of **1** does not change upon repetitive scanning (heating–cooling cycles) in the temperature range 5–400 K (Figure 2), which shows a great tendency to stabilize the LS state with $S = 0$ as seen in the present Fe$^{\mathrm{II}}$ complex with bis-tridentate $C(py)_4$ ligands. The magnetic behavior of **1** is very similar to that observed for related Fe$^{\mathrm{II}}$ complex systems chelat-

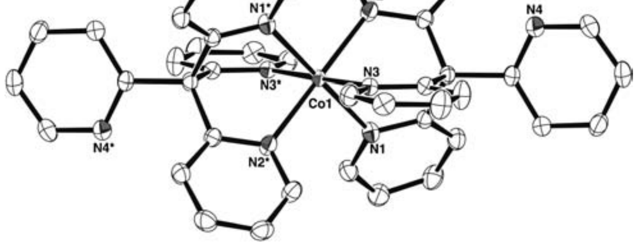

Figure 1. ORTEP drawing of the cationic moiety of **2** (50% probability thermal ellipsoids). Hydrogen atoms are omitted for clarity.

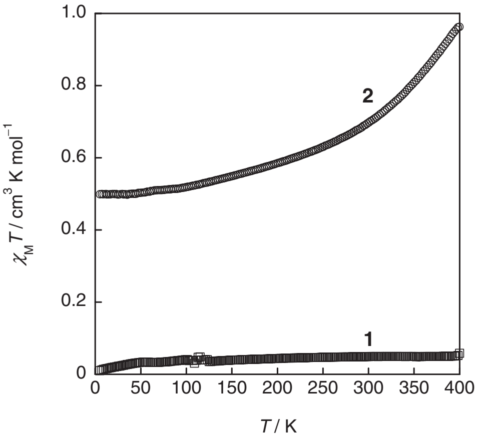

Figure 2. Temperature dependence of the $\chi_M T$ product of **1** and **2**.

ing bis-bidetate tripodal ligands showing no temperature dependence (LS state) in the measuring temperature range. On the other hand, it should be noted that temperature dependence of $\chi_M T$ product of **2** shows gradual SCO behavior (Figure 2). At 5 K, the $\chi_M T$ value is ca. 0.50 cm^3·K·mol^{-1}, the value of which corresponds to the d^7 Co^{II} spin system of the LS state ($S = 1/2, g = 2.24$). Upon heating, the $\chi_M T$ value monotonically increases with increasing temperature constant up to 400 K and finally is ca. 0.96 cm^3·K·mol^{-1} at 400 K. This behavior indicates the occurrence of an incomplete and poorly cooperative $S = 1/2 \leftrightarrow S = 3/2$ conversion at ca. 300 K. Heating–cooling cycles in the temperature range of 5–400 K indicate that no hysteresis occurs in this spin conversion. Additional insight into the magnetic data of **2** was obtained by the temperature dependence of the magnetic moment μ including the spin–orbit coupling-magnetic field interaction from the following equation.[9]

$$\mu^2 = \frac{14.08x + 54.44 + (8.533x - 19.16)\exp(-3x/4) + (9.45x - 35.28)\exp(-2x) + 6x\exp[(E/kT) - 5x/4]}{x\{1 + 2\exp(-3x/4) + 3\exp(-2x) + 2\exp[(E/kT) - 5x/4]\}} \tag{1}$$

in which the energy splitting, E, between the $^4T_1$ and ^2E state, and ζ is the effective spin–orbit coupling coefficient. The best-fitting parameters obtained are $E = 1594.6\,\text{cm}^{-1}$ and $\zeta = 581.2\,\text{cm}^{-1}$. ESR and X-ray analyses at higher temperature of **2** are now under investigation.

In summary, we have synthesized Fe^{II} and Co^{II} complexes of C(py)$_4$ (**1** and **2**, respectively). In the Co^{II} complex **2**, magnetic studies on the solid samples show that thermally induced spin transition occurred in a gradual fashion above ca. 300 K. In order to access both spin states, it will be necessary to finely tune substituent groupings on the pyridine rings. While energetic investigations on such SCO Co^{II} complexes with the tripodal ligand containing polypyridyl moieties have been done previously, one instance was [Co{N(py)$_3$}$_2$][ClO$_4$]$_2$ [N(py)$_3$ = tris(2-pyridyl)amine] which shows abrupt SCO.[10] For Co^{II} complexes, the ratios of the electronic degeneracies and the vibrational densities of state are generally smaller.[11] For this reason, Co^{II} complexes are more sensitive to the local environment, that is, counter ion or solvent molecules, and thus in each compound shows different behaviors. Therefore, further exploration into this series of compounds could give a clue to deeper understanding of spin-crossover phenomena in this system.

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8 Crystal data for **1**: $C_{44}H_{34}Cl_8FeN_8O_8$, MW 1142.27, monoclinic, space group $P2_1/n$ (no. 14), $a = 12.4753(5)$, $b = 13.8140(7)$, $c = 13.2608(5)$ Å, $\beta = 93.4510(5)^\circ$, $V = 2281.14(17)$ Å^3, $Z = 2$, $D_\text{calcd} = 1.663\,\text{g cm}^{-3}$, $T = 200\,\text{K}$, of the 22079 reflections which were collected, 5213 were unique ($R_\text{int} = 0.044$) used in refinement. $R1 = 0.0426$ (5126 data, $I > 2\sigma(I)$), $wR2 = 0.105$ (all data), GOF = 1.08, CCDC-727004. Crystal data for **2**: $C_{44}H_{34}Cl_8CoN_8O_8$, MW 1145.36, monoclinic, space group $P2_1/n$ (no. 14), $a = 12.493(3)$, $b = 13.906(4)$, $c = 13.217(4)$ Å, $\beta = 93.273(3)^\circ$, $V = 2292.4(11)$ Å^3, $Z = 2$, $D_\text{calcd} = 1.659\,\text{g cm}^{-3}$, $T = 200\,\text{K}$, of the 22300 reflections which were collected, 4817 were unique ($R_\text{int} = 0.024$) used in refinement. $R1 = 0.039$ (5242 data, $I > 2\sigma(I)$), $wR2 = 0.094$ (all data), GOF = 1.08, CCDC-727005.

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