[Co^{II}(4-terpyridone)$_2$]X$_2$: A Novel Cobalt(II) Spin Crossover System [4-Terpyridone = 2,6-Bis(2-pyridyl)-4(1H)-pyridone]

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Six-coordinate transition-metal ions with 3d^n ($n = 4−7$) electronic configurations can adopt either a high-spin (HS) or a low-spin (LS) ground state depending on the ligand field strength relative to the mean spin-pairing energy. A crossover between these states is observed when the difference between the ligand field strength and the mean spin-pairing energy is in the range of the thermal energy. The so-called spin crossover phenomenon can be induced by a change of temperature or pressure or by irradiation with light.[2−6] Examples of spin crossover dealing with cobalt(II) compounds are much less abundant than those concerning iron(II) and iron(III) complexes.[7] In these systems cobalt(II) ion can be five- or six-coordinate and exhibits a $^1/_2 \leftrightarrow {}^3/_2$ spin change.

Two series of compounds [Co(terpy)$_2$]X$_2$·nH$_2$O (terpy = 2,2′: 6′,2′′-terpyridine, X = halide, pseudohalide, NO$_3^-$, ClO$_4^-$, and n = 0−5)[8,9] and [Co(H$_2$-fsa$_2$enL$_2$] (H$_2$-fsa$_2$en = N,N'-o-ethylenebis-(3-carboxysalicylaldiiminate), L = H$_2$O, pyridine, and substituted pyridines)[10−13] have been most studied. The second series of compounds is particularly attractive as it exhibits the most abrupt spin transitions ever observed for cobalt(II) complexes. More recently some new interesting cobalt(II) spin crossover complexes have been reported. Thus, [Co(dmvi)(phen)$_2$] (ClO$_4$)·3H$_2$O (dmvi is the bidentate anion dimethylviolurate, and phen is 1,10-phenanthroline)[14] has been synthesized and characterized by means of temperature variable single-crystal X-ray diffraction, magnetic, and EPR studies. The cationic species [Co(bipy)$_3$]$^{2+}$ (bipy = 2,2′-bipyridine) encapsulated in the super cages of zeolite-Y exhibits thermal spin crossover behavior.[15,16] The spin change is a direct consequence of encapsulation because the chemical pressure induced by the host frame destabilizes the HS respect to the LS state of the [Co(bipy)$_3$]$^{2+}$ guest cation. A similar result has been observed in the oxalate 3D network compound [Co(bipy)$_3$][LiCr(C$_2$O$_4$)$_3$].[17] The synthesis of a binuclear spin

crossover cobalt(II) compound exhibiting intramolecular magnetic exchange has also been recently reported.[18]

Herein we present preliminary results on the new cobalt(II) spin crossover family [Co(4-terpyridone)$_2$]X$_2$·nH$_2$O where 4-terpyridone is the terpy-like ligand 2,6-bis(2-pyridyl)-4(1H)-pyridone, X = SO$_4^{2-}$ ($n = 0$) (**1**), Cl$^-$ ($n = 1$) (**2**), ClO$_4^-$ ($n = 1$) (**3**). The synthesis has been performed by mixing of a methanolic solution of the appropriate cobalt(II) (1 mmol, 10 mL) salt with a methanolic solution of 4-terpyridone (2 mmol, 15 mL). The resulting orange solution was allowed to evaporate in air to give red-brown crystalline samples of **1**, **2**, and **3**. Single crystals of **3** appropriate for crystal analysis were formed in good yield from this solution.
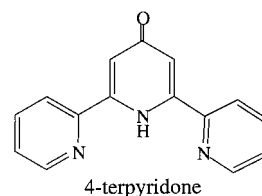
4-terpyridone

The crystal structure of **3** has been solved at 293 K.[19] The structure is composed of discrete [Co(4-terpyridone)$_2$]$^{2+}$ cations, ClO$_4^-$, anions and a H$_2$O molecule. The tridentate N$_3$-4-terpyridone ligand coordinates in a *fac* fashion giving a tetragonally distorted [CoN$_6$] compressed octahedron. Figure 1 shows a perspective view of the structure. The Co−N(2) and Co−N(5) axial bond distances of the pyridone rings [1.992(5) and 1.995-(5) Å, respectively] are considerably shorter than the Co−N(1), N(3), N(4), and N(6) equatorial bond distances to the pyridine rings [2.153(6), 2.144(6), 2.106(5) and 2.122(5) Å, respectively]. The inability of the 4-terpyridone ligand to form a precisely octahedral complex is also reflected in the N−Co−N angles of each 4-terpyridone ligand. They are reduced from the ideal value of 180°, particularly the angles N(6)−Co−N(4) = 154.8(2)° and N(1)−Co−N(3) = 154.4(2)°.

The C(23)−O(2) = 1.356(9) Å and C(8)−O(1) = 1.341(9) Å bond distances indicate that the pyridone ring is present in the enolic form upon coordination. The water molecule, O(3), is hydrogen bonded by two adjacent ClO$_4^-$ [O(3)···O(4) = 2.823(16) Å and O(3)···O(6)^i = 2.886(14) Å] [i = ($-x$, $y + 0.5$, $1 - z$)] defining infinite chains. The cationic species are strongly attached to these chains. The OH group of the central ring interacts with the oxygen atom of the water molecule via hydrogen bonding [O(1)···O(3) = 2.685(12) Å].

The magnetic susceptibility, χ_M, was determined over the 4.5−350 K temperature range in a field of 1 T. The $\chi_M T$ versus T plot

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(19) Crystal structure analysis: C$_{30}$H$_{24}$N$_6$O$_{11}$Cl$_2$Co, M = 774.38 g mol^{-1}, monoclinic, space group $P2_1$ (No. 4), a = 8.7978(9) Å, b = 9.0493(14) Å, c = 20.303(2) Å, β = 98.049(7)°, V = 1600.5(3) Å^3, ρ_{cald} = 1.607 g cm^{-3} for Z = 2.
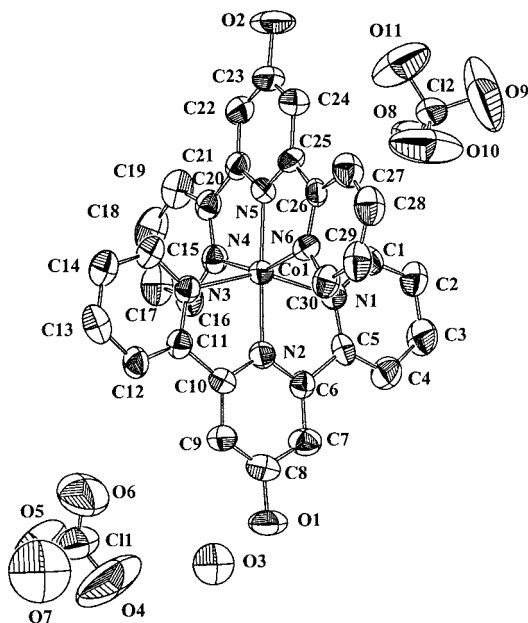
Figure 1. Perspective view of **3** (30% probability ellipsoids). Selected bond lengths (Å): Co−N(1) = 2.153(6), Co−N(2) = 1.992(5), Co−N(3) = 2.144(6), Co−N(4) = 2.106(5), Co−N(5) = 1.995(5), Co−N(6) = 1.122(5); O(1)−C(8) = 1.341(9), O(2)−C(23) = 1.356(9). Selected bond angles (deg): N(22)−Co−N(5) = 177.3(3), N(2)−Co−N(4) = 103.2(2), N(5)−Co−N(4) = 78.0(2), N(2)−Co−N(6) = 102.0(2), N(5)−Co−N(6) = 76.9(2), N(4)−Co−N(6) = 154.8(2), N(2)−Co−N(3) = 77.8(3), N(5)−Co−N(3) = 104.7(2), N(4)−Co−N(3) = 90.9(2), N(6)−Co−N(3) = 93.6(2), N(2)−Co−N(1) = 76.8(3), N(5)−Co−N(1) = 100.8(2), N(4)−Co−N(1) = 93.0(2), N(6)−Co−N(1) = 93.5, N(3)−Co-N(1) = 154.4(2).
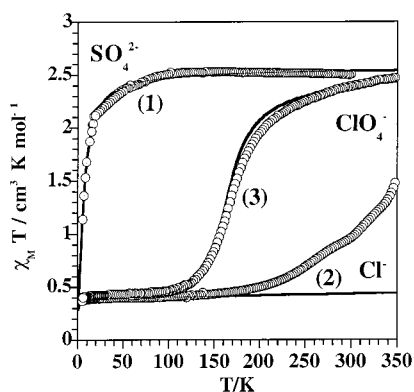
Figure 2. Temperature dependence of the $\chi_M T$ product for compounds **1**−**3**. The solid curves are the fits of the axial zero-field splitting ($S = \frac{3}{2}$) (**1**), the Curie−Weiss (**2**), and the regular solution (**3**) models (see text).

(where T is the absolute temperature) is shown in Figure 2. For **1**, $\chi_M T$ is equal to 2.5 cm^3 K mol^{-1} in the 300−100 K temperature range. Then, $\chi_M T$ decreases upon cooling to 1.1 cm^3 K mol^{-1} at 4.5 K. This behavior indicates a degeneracy reduction of the $^4T_{1g}$ (O_h) ground state (which splits into the ^4E_g and $^4A_{2g}$ levels) resulting from the tetragonal distortion. The low-temperature decrease is most likely due to zero-field splitting in the $^4A_{2g}$ ground state. Taking this into account, we have simulated the magnetic measurements with a Hamiltonian (eq 1) which consid-

$$\hat{H} = D[\hat{S}_z^2 - (1/3)S(S+1) + g\beta H\hat{S}] \qquad (1)$$

ers an axial crystal zero-field splitting D of the ground spin state $S = \frac{3}{2}$. The solid line in Figure 2 has been obtained with the best set of parameters matching the experimental data of $|D| =$

8.8 cm^{-1}, $g = 2.33$. These values are reasonable and agree with those reported for other HS pseudooctahedral cobalt(II) compounds. For **2**, $\chi_M T$ is almost constant in the 4.5−175 K temperature range taking a value around 0.404 cm^3 K mol^{-1}. This value is consistent with a $S = \frac{1}{2}$ ground state that follows the Curie−Weiss law with $g = 2.04$ and $\theta = -0.35$ K (solid line Figure 2). When the sample is warmed, $\chi_M T$ smoothly increases, attaining a value of 1.5 cm^3 K mol^{-1} at 350 K. This behavior clearly indicates the occurrence of a very incomplete (ca. 50%) $\frac{1}{2} \leftrightarrow \frac{3}{2}$ conversion at 350 K.

The magnetic behavior of **3** displays strong temperature dependence in the 350−100 K region, $\chi_M T = 2.48$ cm^3 K mol^{-1} at 350 K and 0.4 cm^3 K mol^{-1} at 100 K indicating the occurrence of an almost complete and relatively cooperative spin conversion. The characteristic temperature of the spin transition for which 50% of HS and LS molecules coexist, $T_{1/2}$, is 172.4 K. The thermodynamic parameters have been deduced from the expression (eq 2) obtained from the regular solution model,[20]

$$\ln[(1 - n_{HS})/n_{HS}] = [\Delta H + \Gamma(1 - 2n_{HS})]/RT - \Delta S/R \quad (2)$$

where ΔH, ΔS, and Γ are the enthalpy and the entropy variations and the parameter accounting for cooperativity associated with the spin conversion, respectively. The HS molar fraction, n_{HS}, has been deduced from the magnetic susceptibility through

$$n_{HS} = [(\chi_M T)_m - (\chi_M T)_{LS}]/[(\chi_M T)_{HS} - (\chi_M T)_{LS}] \quad (3)$$

where $(\chi_M T)_m$ is the value of $\chi_M T$ at intermediate temperatures and $(\chi_M T)_{LS}$ and $(\chi_M T)_{HS}$ correspond to the pure LS and HS states, respectively. In the present case $(\chi_M T)_{HS}$ has been considered an adjustable parameter. Least-squares fitting leads to $\Delta H = 3.45$ kJ mol^{-1}, $\Delta S = 20$ J K^{-1} mol^{-1}, $\Gamma = 2$ kJ mol^{-1}, and $(\chi_M T)_{HS} = 2.8$ cm^3 K mol^{-1}, which corresponds to 11.43% LS molecules at room temperature. These parameters are quite reasonable compared with those previously reported for cobalt(II) spin crossover complexes. The value of ΔS is much greater than the electronic spin change expected for a cobalt(II) ion $\Delta S_{spin} = R \ln[(2S + 1)_{HS}/(2S + 1)_{LS}] = 5.8$ J K^{-1} mol^{-1}. The remainder entropy variation, 14.2 J K^{-1} mol^{-1}, is mainly due to the intramolecular vibrational changes. It should be noted that the value of ΔH (3.45 kJ mol^{-1}, 287 cm^{-1}) corresponds in a first approximation to the upper limit for the difference in energy ΔE_{HL} between HS and LS states. This gap appears to be small compared with the ranges obtained for various [Co(terpy)$_2$]$^{2+}$ complexes, $\Delta E_{HL} = 1110-1700$ cm^{-1} and $\Delta E_{HL} = 300-500$ cm^{-1},[8] but somewhat larger than for [Co(H$_2$-fsa$_2$en) L$_2$] complexes, $\Delta E_{HL} = 158-200$ cm^{-1}.[21] Such a doublet−quartet separation may be accounted for by the lower $T_{1/2}$ and the expected stronger and weaker ligand field associated with 4-terpyridone with respect to (H$_2$-fsa$_2$en)-L and terpy, respectively.

Supporting Information Available: Tables of X-ray crystallographic data in CIF format for **3**. This material is available free of charge via the Internet at http://pubs.acs.org.

IC000788M

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