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Magnetic Properties of Some Spin-Crossover, High-Spin, and Low-Spin Cobalt(II) Complexes with Schiff Bases Derived from 3-Formylsalicylic Acid

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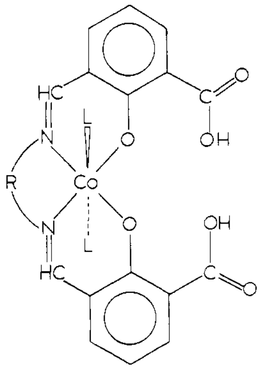
The high-spin–low-spin behavior of cobalt(II) was investigated by variable-temperature magnetic susceptibility measurements and also by EPR spectroscopy in a series of $Co(H_2(fsa)_2R)L_n$ complexes, $H_4(fsa)_2R$ denoting 3-formylsalicylic acid–$R(NH_2)_2$ Schiff bases. The sharp high-spin ($S = {}^3/_2$) $\rightleftharpoons$ low-spin ($S = {}^1/_2$) conversion observed in $Co(H_2(fsa)_2en)(py)_2$ (en = $(CH_2)_2$, py = pyridine) exhibits a pronounced hysteresis of 12 K, being centered at $T_c\downarrow = 115$ K and $T_c\uparrow = 127$ K for lowering and rising temperatures, respectively. About 6% of the molecules persist in the high-spin form at very low temperature. The sensitivity of the transition parameters (T_c, hysteresis, abruptness, completion) to the mean size of crystallites and/or to the number of crystal defects is demonstrated. This is consistent with the coexistence of high-spin and low-spin domains within the spin conversion and hence with a cooperative nature of the phenomenon. In the pseudooctahedral compounds $Co(H_2(fsa)_2en)(\beta\text{-pic})_2$, $Co(H_2(fsa)_2(1,3\text{-pn}))(py)_2$, and $Co(H_2(fsa)_2(1,3\text{-pn}))(tbpy)_2$ (1,3-pn = $(CH_2)_3$, β-pic = 3-methylpyridine, and tbpy = 4-*tert*-butylpyridine), Co(II) remains totally high spin down to 4.2 K. On the contrary, only the low-spin form exists in the square-pyramidal complexes $Co(H_2(fsa)_2en)tbpy$ and $Co(H_2(fsa)_2en)EtOH$. The condition for a spin-crossover transition to occur in the sixfold-coordinated Co(II) ions is that the metal lies in a (4+2) environment, with a strong equatorial ligand field and a large axial distortion. Indeed, low-temperature EPR spectra of $Co(H_2(fsa)_2en)(py)_2$ give evidence of a quasi-tetragonal structure for the low-spin phase ($g_1 = 2.289$, $g_2 = 2.206$, $g_3 = 2.046$), and the magnetic properties of the high-spin phase are effectively those expected for a spin quartet with a very weak orbital contribution. The conditions for Co(II) to remain either in the high-spin or in the low-spin form over the whole temperature range are discussed.

Introduction

Most of the thermally induced spin transitions previously mentioned have been observed in Fe(II)[1] and Fe(III) complexes. Examples concerning Co(II) compounds are much less numerous. In these compounds the cobalt ion (d^7), which exhibits an $S = {}^3/_2 \rightleftharpoons S = {}^1/_2$ spin equilibrium, is either sixfold-coordinated (e.g. see ref 2–6) or fivefold-coordinated (e.g. see ref 7–9). In only a few cases it lies in an oxygen–nitrogen closest environment, as in Co(salen)L_n and Co(salphen)L_n (salen and salphen denote the dianions *N*,*N*′-ethylenebis(salicylideneaminate) and *N*,*N*′-*o*-phenylenebis(salicylideneaminate), respectively; L is a N-heterocycle; n = 1 or 2);[10,11] however, all these complexes are five-coordinate. To our knowledge, the only spin-crossover cobalt(II) compounds with the metal in a pseudooctahedral O_nN_{6-n} environment are those recently obtained in our laboratory.[12] Their formula is $Co(H_2(fsa)_2en)L_2$, $H_4(fsa)_2en$ being the Schiff base resulting from the 2:1 condensation of 3-formylsalicylic acid with ethylenediamine and L denoting pyridine or water. The cobalt atom is located in the N_2O_2 site of the dichelating ligand, as indicated by the IR spectra, which show that the C=N bond is directly involved in the coordination process ($\nu_{C=N}$ is identified at 1640 cm^{-1}, instead of 1652 cm^{-1} in the Schiff base spectrum).

By varying the organic radical R, the ligand L, and the n value in the formula $Co(H_2(fsa)_2R)L_n$ (see **1**, drawn with n = 2), we have prepared a series of compounds and have investigated them by magnetic susceptibility measurements and EPR spectroscopy.



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The purpose of this work was to specify the role of some definite chemical factors in the spin state of the metal ion. In the longer term, our goal in the spin-crossover field is to establish a molecular engineering of the compounds of this kind, i.e. to define what type of environment around the metal ion we have to design in order to obtain a spin transition in a given temperature range.

The studied complexes correspond to R = $(CH_2)_2$ (en) with n = 2, L = pyridine (py) or 3-methylpyridine (β-pic) and n = 1, L = 4-*tert*-butylpyridine (tbpy) and to R = $(CH_2)_3$ (1,3-pn) with n = 2, L = pyridine or 4-*tert*-butylpyridine. Moreover, a detailed magnetic investigation was performed on the spin-crossover compound $Co(H_2(fsa)_2en)(py)_2$ so as to possibly obtain some additional information that might be of some interest to clarify the mechanism of spin transitions.

Experimental Section

Syntheses. 3-Formylsalicylic acid was prepared according to the method of Duff and Bills.[13] The Schiff bases $H_4(fsa)_2en$ and $H_4(fsa)_2(1,3\text{-pn})$ were obtained by reacting this acid with ethylenediamine and 1,3-propylenediamine, respectively, in a 2:1 ratio, with ethanol

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as a solvent. Anal. Calcd for $C_{18}H_{16}N_2O_6$: C, 60.97; H, 4.53; N, 7.86; O, 26.94. Found: C, 60.82; H, 4.58; N, 7.92; O, 26.89. Calcd for $C_{19}H_{18}N_2O_6$: C, 61.62; H, 4.90; N, 7.56; O, 25.92. Found: C, 61.35; H, 5.03; N, 7.60; O, 25.67.

All the syntheses described hereafter were entirely carried out under a nitrogen atmosphere.

$Co(H_2(fsa)_2en)(py)_2$ and $Co(H_2(fsa)_2(1,3\text{-}pn))(py)_2$. These compounds were prepared according to the methods previously reported by Torihara et al.[14] Anal. Calcd for $C_{28}H_{24}N_4O_6Co$: C, 58.85; H, 4.23; N, 9.80; O, 16.80. Found: C, 58.50; H, 4.22; N, 9.79; O, 16.83. Calcd for $C_{29}H_{26}N_4O_6Co$: C, 59.49; H, 4.48; N, 9.57; O, 16.40. Found: C, 59.10; H, 4.55; N, 9.75; O, 16.10.

$Co(H_2(fsa)_2en)(\beta\text{-}pic)_2$. A solution of $Co(CH_3COO)_2 \cdot 4H_2O$ (140 mg) in 3-methylpyridine (20 mL) was added dropwise to a suspension of $H_4(fsa)_2en$ (200 mg) in 3-methylpyridine (25 mL) heated under reflux. Refluxing was continued for 3 h. The dark red limpid solution was then cooled, and diethyl ether (30 mL) was added. The brown precipitate that formed was filtered and dried under reduced pressure. Anal. Calcd for $C_{30}H_{28}N_4O_6Co$: C, 60.10; H, 4.71; N, 9.35; O, 16.01. Found: C, 59.09; H, 4.91; N, 9.34; O, 15.86.

$Co(H_2(fsa)_2en)tbpy$ and $Co(H_2(fsa)_2(1,3\text{-}pn))(tbpy)_2$. To a mixture of $H_4(fsa)_2en$ (or $H_4(fsa)_2(1,3\text{-}pn)$) (200 mg) and 4-*tert*-butylpyridine (2 mL) in isobutyl alcohol (25 mL), heated at 100 °C, was added dropwise a solution of $Co(CH_3COO)_2 \cdot 4H_2O$ (140 or 135 mg, respectively) in ethanol (80 mL). The dark red (or orange) limpid solution thus obtained was kept at 100 °C for about 3 h, so as to evaporate ethanol and part of the isobutyl alcohol. After cooling, diethyl ether (5 mL) was added. The dark red (or yellowish brown) precipitate that forms was filtered and dried under reduced pressure. Anal. Calcd for $C_{27}H_{27}N_3O_6Co$: C, 59.13; H, 4.96; N, 7.66; O, 17.50. Found: C, 59.01; H, 5.00; N, 7.60; O, 17.36. Calcd for $C_{37}H_{42}N_4O_6Co$: C, 63.70; H, 6.07; N, 8.03; O, 13.76. Found: C, 63.47; H, 6.14; N, 8.01; O, 13.75.

Magnetic Susceptibility Measurements. These were performed on polycrystalline samples weighing about 5 mg, in the temperature range 300–4.2 K, by using a Faraday type magnetometer equipped with an Oxford Instruments continuous-flow cryostat. The independence of susceptibility with regard to magnetic field was checked for each compound at room temperature. The data were corrected for the diamagnetism of all constituents, estimated at -291×10^{-6}, -314×10^{-6}, -303×10^{-6}, -397×10^{-6}, and -288×10^{-6} $cm^3 \cdot mol^{-1}$ for $Co(H_2(fsa)_2en)(py)_2$, $Co(H_2(fsa)_2en)(\beta\text{-}pic)_2$, $Co(H_2(fsa)_2(1,3\text{-}pn))(py)_2$, $Co(H_2(fsa)_2(1,3\text{-}pn))(tbpy)_2$, and $Co(H_2(fsa)_2en)tbpy$, respectively. $HgCo(SCN)_4$ was used as a susceptibility standard. The uncertainty in the susceptibility is about 100×10^{-6} $cm^3 \cdot mol^{-1}$. Temperature was determined with an accuracy of about ±0.1 K.

EPR Measurements. EPR spectra were carried out on powdered samples, between 300 and 4.2 K, with a Bruker Model ER 200D X-band spectrometer equipped with an Oxford Instruments continuous-flow cryostat. The klystron frequency was determined with a Hewlett-Packard frequency meter. For poorly resolved spectra, the *g* values were determined by means of a computer program allowing EPR parameters to be refined on the basis of a least-squares fitting procedure.

Results

Magnetic Susceptibility Data. Spin-Crossover Compound. Figure 1 gives the temperature dependence of the product $\chi_M T$ (χ_M denoting the molar magnetic susceptibility) for the $Co(H_2(fsa)_2en)(py)_2$ sample, the analysis of which is reported above. Starting at 295 K, the temperature has been gradually lowered to 20 K as indicated by the falling arrow and then increased up to 295 K as indicated by the rising arrow. Both curves exhibit two plateaus, which correspond to $\chi_M T = 2.61$ $cm^3 \cdot mol^{-1} \cdot K$ ($\mu_{eff} = 4.57$ μ_B) and 0.57 $cm^3 \cdot mol^{-1} \cdot K$ ($\mu_{eff} = 2.13$ μ_B). These values are consistent with high-spin ($S = {}^3/_2$) and low-spin ($S = {}^1/_2$) ground states, respectively.[15] So, $Co(H_2(fsa)_2en)(py)_2$ apparently undergoes a complete spin conversion. However, evidence will be given hereafter, by comparison of magnetic and EPR data, for some incompleteness of the transition. It is worth noting that the high-spin species exhibits a Curie behavior that is not in keeping with an octahedral ${}^4T_{1g}$ ground state perturbed by extensive spin–orbit coupling. This indicates that the orbital momentum for the ground term is largely quenched, owing to degeneracy removal, and hence that the coordination octahedron must be strongly axially distorted.

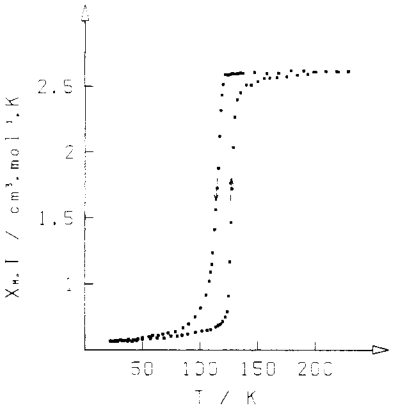

Figure 1. Temperature dependence of $\chi_M T$ for $Co(H_2(fsa)_2en)(py)_2$. Rising and falling arrows indicate increasing and lowering of temperature, respectively. $T_c\!\downarrow = 115$ K and $T_c\!\uparrow = 127$ K.

The transition is fairly abrupt, most of it occurring within ca. 10 K for decreasing temperature ($T\!\downarrow$) and ca. 5 K for increasing temperature ($T\!\uparrow$), which shows the cooperative character of the phenomenon. The critical points, for which there exist equal amounts of high-spin (HS) and low-spin (LS) species, are defined by $T_c\!\downarrow = 115$ K and $T_c\!\uparrow = 127$ K, the hysteresis effect thus obtained ($\Delta T_c = 12$ K) being indicative of the first-order nature of the transition. To our knowledge, this thermal hysteresis is the first one reported for a cobalt(II) spin transition. However, it is worth noting that such an effect has already been observed and/or discussed before in the case of several spin-crossover iron(II) complexes.[16-25]

It clearly appears that the shapes of the $T\!\downarrow$ and $T\!\uparrow$ curves are somewhat different. The former is more asymmetrical than the latter: the $T\!\downarrow$ transition begins abruptly and ends smoothly; on the other hand, both the bottom and the top of the transition, when the system is heated up, are rather smooth. Furthermore, the slope of the rising branch around the critical point is twice as steep as that of the falling branch (vide supra); it should be noted that differences between the slopes of the $T\!\uparrow$ and $T\!\downarrow$ curves have already been pointed out by König et al. for some iron(II) complexes.[17,20]

These remarks concerning the shape of the curves apply for all the samples studied. For a given sample, measurements performed under similar experimental conditions were quite reproducible. However, appreciable deviations of the results have been observed when the monitored temperature variation had suffered some fluctuations. The magnetic data reported

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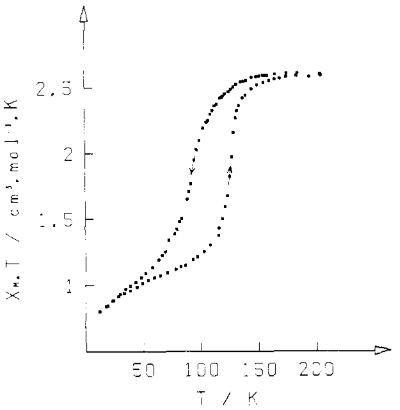

Figure 2. Temperature dependence of $\chi_M T$ for a sample of Co(H_2(fsa)$_2$en)(py)$_2$ previously pressed under 10 kbar. For an explanation of the arrows, see the legend to Figure 1.

in Figure 1 correspond to measurements carried out in about 16 h: the rate of heating and cooling has been carefully maintained at 1 K/min in the temperature range of the plateaus and slowed down to 1 K/30 min during the spin crossover so that the HS $\rightleftharpoons$ LS equilibrium was completely or very closely achieved.

Moreover, when we were operating in the same way, some divergences in the T_c values, the slopes of the curves near the transition, and the hysteresis effect were observed for samples arising from separate preparations, though the compounds exhibit similar chemical analyses, identical IR spectra, and the same appearance when examined under a binocular lens.

The sensitivity of the spin-crossover phenomenon with regard to sample preparation has already been reported by several authors (e.g. see ref 17–24). If we consider that the transition is a cooperative process involving the formation and growth, from nucleation sites, of domains of minority-spin molecules in crystallites of the majority-spin form,[26-28] then we can attribute the deviations observed upon the study of various samples to slight differences in the mean size of the crystallites and/or in the number of crystal defects (which are preferred sites for nucleation). The smaller the mean size and the greater the number of defects, the more difficult the development of the minority-spin domains (which have to attain a critical size to persist) should be, since the activation barrier for the growth process of these domains is then higher;[28] it ensues that T_c tends to decrease and the transition to become more gradual.

To substantiate this explanation, we subjected ca. 100 mg of the sample of Co(H_2(fsa)$_2$en)(py)$_2$ exhibiting the magnetic behavior of Figure 1 to a pressure of 10 kbar for 5 min. This treatment considerably multiplies the grain boundaries and the crystal defects. Magnetic measurements were carried out on a fragment of the disk so obtained. The curve $\chi_M T$ vs. T is given in Figure 2. Comparison with Figure 1 shows that, unlike Haddad et al.,[28] who performed the same operation with an iron(III) compound, we do not observe the formation of low-spin species in the temperature range corresponding to the highest plateau ($\chi_M T$ = 2.60 cm³·mol⁻¹·K). On the other hand, evidence is given for the three other effects reported by these authors, viz., the transition is more gradual than for the unperturbed sample, the temperature at which 50% of the molecules are high spin is lowered, and the HS → LS conversion is incomplete. Concerning this last point, the magnetic data obtained for $T\uparrow$ indicate the persistence of ca. 25% of high-spin molecules at low temperature; the relevant plateau does not form completely because of the curve dropping below ca. 70 K, due to the intermolecular interactions, which are much stronger than in the unperturbed compound. Finally, a large broadening of the hysteresis loop (~33 K instead of 12 K) is observed. All these results clearly support the coexistence of domains of high-spin and low-spin species during the spin conversion and hence the cooperative nature of the transition.

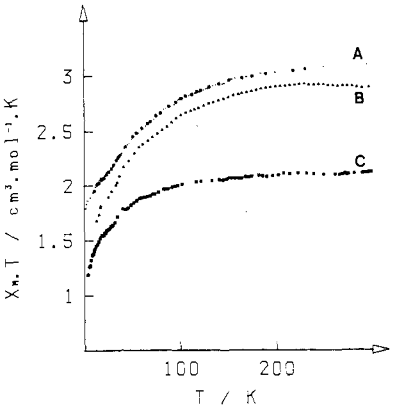

Figure 3. Temperature dependence of $\chi_M T$ for Co(H_2(fsa)$_2$(1,3-pn))(py)$_2$ (A: ·, $T\downarrow$; ●, $T\uparrow$), Co(H_2(fsa)$_2$(1,3-pn))(tbpy)$_2$ (B), and Co(H_2(fsa)$_2$en)(β-pic)$_2$(C).

Consequently, the rounded parts shown by the $\chi_M T$ vs. T curves for the unperturbed compound (Figure 1) at the end of the transition for $T\downarrow$ and at both the beginning and the end of the transition for $T\uparrow$ have a clear origin: they appear when one of the spin states becomes very minor, thus showing that the less numerous and large the domains are, the more difficult the transition propagation is.

High-Spin and Low-Spin Compounds. Plots of $\chi_M T$ vs. T for the pseudooctahedral complexes Co(H_2(fsa)$_2$en)(β-pic)$_2$, Co(H_2(fsa)$_2$(1,3-pn))(py)$_2$, and Co(H_2(fsa)$_2$(1,3-pn))(tbpy)$_2$ are given in Figure 3. Measurements carried out at $T\downarrow$ and $T\uparrow$ are in excellent agreement, as can be noticed on the upper curve. These results show that the compounds do not exhibit spin transition. They are typical of the cobalt(II) high-spin form.

The curves related to Co(H_2(fsa)$_2$(1,3-pn))(py)$_2$ and Co(H_2(fsa)$_2$(1,3-pn))(tbpy)$_2$ have very similar shapes. The continuous decrease of $\chi_M T$ upon cooling down and the high values obtained for this product at room temperature (3.10 and 2.90 cm³·mol⁻¹·K, respectively, compared with 2.61 cm³·mol⁻¹·K for the spin-crossover complex Co(H_2(fsa)$_2$en)(py)$_2$ can be accounted for by strong orbital contribution.[29] The field around the cobalt(II) is predominantly octahedral with a ground state close to $^4T_{1g}$.

On the other hand, the $\chi_M T$ values obtained at 295 K for several samples of Co(H_2(fsa)$_2$en)(β-pic)$_2$ seem abnormally low (2.12 ± 0.04 cm³·mol⁻¹·K). This result may not be completely accounted for by the strong axial distortion of the cobalt(II) octahedral environment, evidenced by the slight variation of $\chi_M T$ vs. T in the temperature range 295–120 K (Figure 3). Other causes have to be considered, e.g. the presence of some diamagnetic impurity or of a low-spin species in small amounts. We shall see hereafter that the latter hypothesis is supported by EPR spectra.

Concerning the complex Co(H_2(fsa)$_2$en)tbpy, $\chi_M T$ slightly decreases from 0.64 to 0.58 cm³·mol⁻¹·K upon cooling down from 300 to 250 K, then exhibits a constant value from 250 to ~30 K, and finally decreases again below ~30 K due to intermolecular interactions. A similar behavior has already

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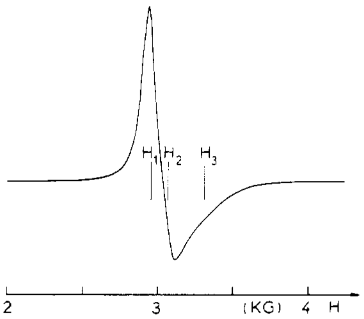

Figure 4. Polycrystalline powder EPR spectrum of $Co(H_2fsa)_2en)(py)_2$ at 9.0 K.

been reported for the compound $Co(H_2(fsa)_2en)EtOH$.[12] The Curie law observed between 250 and ~30 K for $Co(H_2(fsa)_2en)tbpy$ indicates that, in this temperature range, only one energy level without first-order orbital momentum is thermally populated and that this level is a spin doublet. Owing to the fact that the equatorial ligand generally adopts a planar configuration upon coordination,[30-33] it is likely that the environment of cobalt(II) in $Co(H_2(fsa)_2en)tbpy$ and $Co(H_2(fsa)_2en)EtOH$ is square pyramidal.

EPR Spectra. Spin-Crossover Compound. Variable-temperature EPR spectra of $Co(H_2(fsa)_2en)(py)_2$ microcrystalline samples have been recorded for $T\downarrow$ and $T\uparrow$. In both cases, signals were obtained only below a temperature slightly higher than T_c, namely about 120 and 150 K for $T\downarrow$ and $T\uparrow$, respectively. Comparison of this result with the temperature dependence of magnetic susceptibility (Figure 1) clearly indicates that the observed EPR features are connected with the complex low-spin form.

In spite of the fact that each spectrum only consists of one broad asymmetrical peak (see Figure 4), the g values could be accurately determined with the computer program by assuming the lines to have Lorentzian shapes. It was possible to resolve $g_\perp$ (~2.25) into $g_1 = 2.289$ and $g_2 = 2.206$ and to calculate $g_\parallel = g_3 = 2.046$, with a reliability factor $R = \sum|y_{obsd} - y_{calcd}|/\sum|y_{obsd}|$ equal to 4.13×10^{-2} (y denoting the ordinate values). The g values thus obtained are effectively typical of a cobalt(II) spin-doublet ground state. They are indicative of a tetragonally elongated environment of the metal ion, to which is superimposed a weak rhombic distortion. Indeed, due to the Jahn–Teller effect, a sixfold coordination of cobalt(II) in the low-spin form is always accompanied by some deviation from octahedral symmetry.[34]

Calculation of the $\chi_M T$ product in terms of the g values, according to the expression

$$\chi_M T = N\overline{g^2}S(S+1)/3k$$

with $S = {}^1/_2$ and $\overline{g^2} = (g_1{}^2 + g_2{}^2 + g_3{}^2)/3$, yields a result (0.45 $cm^3 \cdot mol^{-1} \cdot K$) that is somewhat lower than the experimental one (0.57 $cm^3 \cdot mol^{-1} \cdot K$). Such a difference has already been observed by Gatteschi et al.[9] in the case of a five-coordinated spin-crossover cobalt(II) complex. Concerning $Co(H_2(fsa)_2en)(py)_2$, this fact is most likely due to the presence of a small amount of a high-spin cobalt(II) compound, owing to the weak feature observed for $g \sim 5$ in the EPR spectra (when strongly amplified). The high-spin species may be either $Co(H_2(fsa)_2en)(py)_2$ or $Co_2((fsa)_2en)(py)_3$. Two facts support the former hypothesis: the $\chi_M T$ value corresponding to the lower plateau of the curves $\chi_M T$ vs. T strongly depends, for a given sample, on cooling or heating conditions; moreover, no dark red crystals of the binuclear complex were observed in the examined samples. The high-spin fraction x at low temperature, calculated by the relation

$$x(\chi_M T)_{HS} + (1 - x)(\chi_M T)_{LS} = 0.57\ cm^3 \cdot mol^{-1} \cdot K$$

was found to be ~6%. The much lower EPR sensitivity for cobalt(II) high-spin complexes than for low-spin species can account for the weakness of the additional observed feature.

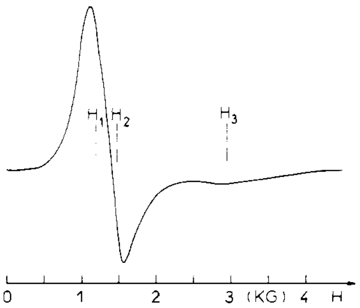

Figure 5. Polycrystalline powder EPR spectrum of $Co(H_2(fsa)_2(1,3\text{-}pn))(py)_2$ at 8.7 K.

Table I. g Values for the High-Spin Complexes

	$g_\perp$		$g_\parallel$
	g_1	g_2	g_3
$Co(H_2(fsa)_2en)(\beta\text{-pic})_2$	5.35^b	5.06^b	2.26^c
$Co(H_2(fsa)_2(1,3\text{-pn}))(py)_2$	5.75^a	4.54^a	2.22^b
$Co(H_2(fsa)_2(1,3\text{-pn}))(tbpy)_2$	4.97^a	3.99^a	2.04^c

[a] ±0.05. [b] ±0.10. [c] ±0.20.

It is worth noting that the g values obtained for $Co(H_4(fsa)_2en)(py)_2$ are comparable with those previously reported for other six-coordinated low-spin cobalt(II) complexes,[35-37] in particular for the related compound $Co(salphen)(py)_2$ ($g_1 = 2.305$, $g_2 = 2.191$, $g_3 = 2.035$).[34]

High-Spin Compounds. The EPR spectra of $Co(H_2(fsa)_2en)(\beta\text{-pic})_2$, $Co(H_2(fsa)_2(1,3\text{-pn}))(py)_2$ and $Co(H_2(fsa)_2(1,3\text{-pn}))(tbpy)_2$ have very similar shapes. The second one is depicted in Figure 5 as an example. As a consequence of the fast spin–lattice relaxation times of high-spin cobalt(II), signals were observed only below ~30 K. Because of the broadness and overlapping of the bands, the g values (specially those of $g_\parallel$) could not be determined with a good accuracy. The best results (see Table I), obtained by assuming the lines to have Gaussian shapes, correspond to $R = 2.22 \times 10^{-1}$, 1.05×10^{-1}, and 1.27×10^{-1}, respectively, for the above compounds. They are typical of high-spin cobalt(II) complexes[29] and can be interpreted by using an $S = {}^1/_2$ effective spin Hamiltonian. Indeed, the ${}^4T_{1g}$ ground state splits into ${}^4A_{2g}$ and ${}^4E_g$ in axial symmetry; then the lower lying state splits by spin–orbit coupling into two Kramers doublets, whose separation in zero magnetic field is larger than the energy of the microwave source used for EPR measurements. Consequently, only transitions within the lowest Kramers doublet can be detected.[38]

The observed anisotropy is clearly indicative of a rhombic distortion.[29,39] The relative values of $g_\parallel$ and $g_\perp$ ($g_\parallel < g_\perp$) show

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that the axial deformation is an elongation. From magnetic susceptibility measurements, the distortion was found to be small for $Co(H_2(fsa)_2(1,3\text{-pn}))(py)_2$ and $Co(H_2(fsa)_2(1,3\text{-pn}))(tbpy)_2$ and large for $Co(H_2(fsa)_2en)(\beta\text{-pic})_2$; the *g*-value patterns obtained for these compounds may be accounted for if one considers that, when the $^4A_{2g}$ state lies lower, the *g* values do not exhibit significant variations with geometrical deformations (except for the very small ones).[29] Moreover, the fact that the rhombicity $g_1 - g_2$ is smaller for $Co(H_2(fsa)_2en)(\beta\text{-pic})_2$ than for both other compounds may be partly due to some structural differences in the cobalt(II) equatorial environment, which is expected to be more distorted with the ligand $H_2(fsa)_2(1,3\text{-pn})^{2-}$ than with $H_2(fsa)_2en^{2-}$.

It can be mentioned that the results obtained for $Co(H_2(fsa)_2en)(\beta\text{-pic})_2$ cannot be readily interpreted, as already noted for the magnetic susceptibility data relevant to this complex. EPR spectra exhibit several additional bands in the $g = 1.8$–2.5 range, which suggests the presence of some amount of a low-spin species in the high-spin compound and can contribute to the low accuracy obtained in the calculation of the *g* values reported in Table I.

Discussion

Two compounds of the type $Co(H_2(fsa)_2R)L_2$ exhibit a spin crossover, viz. $Co(H_2(fsa)_2en)(py)_2$ and $Co(H_2(fsa)_2en)(H_2O)_2$. The $T\downarrow$ transition was found to be centered at 115 K for the former (this work) and 80 K for the latter.[12] A feature common to both species is a strong tetragonal elongation of the coordination octahedron, along the axis perpendicular to the Schiff base (N_2O_2) site. This property is evidenced by the magnetic susceptibility data. Indeed, for the water adduct, $\chi_M T$ is also temperature independent when Co(II) is in the high-spin state, with a value (2.10 $cm^3 \cdot mol^{-1} \cdot K$)[12] still lower than for the pyridine adduct (2.61 $cm^3 \cdot mol^{-1} \cdot K$); moreover the water molecules can be easily removed (at about 70 °C).

So, the condition required for axial ligands L to give spin-crossover compounds seems to be that these ligands complete the cobalt(II) coordination environment so as to form an elongated octahedron. Such a structure can be considered as intermediate between an essentially octahedral stereochemistry, which would stabilize the high-spin form, and a planar surrounding[12] in which cobalt(II) is in the low-spin configuration in the whole temperature range.

Two high-spin compounds were obtained with the anion $H_2(fsa)_2(1,3\text{-pn})^{2-}$. Compared to $H_2(fsa)_2en^{2-}$, this ligand is expected to induce a weaker equatorial field, due to a less favorable chelate effect with a six-membered ring than with a five-membered ring. This allows the axial molecule L to approach the cobalt atom more closely and consequently to favor the high-spin form. This explanation is corroborated by the magnetic data (see above) and also by the results reported by Tanaka et al. for binuclear nickel(II) complexes:[40] in $Ni_2((fsa)_2en)\cdot 3H_2O$, the nickel atom located in the N_2O_2 inside site is four-coordinated, hence diamagnetic, whereas it is six-coordinated and paramagnetic in $Ni_2((fsa)_2(1,3\text{-pn}))\cdot 5H_2O$.

In contrast, the high-spin configuration of cobalt(II) in $Co(H_2(fsa)_2en)(\beta\text{-pic})_2$ cannot be so easily explained, inasmuch as the closely related compound $Co(H_2(fsa)_2en)(py)_2$ exhibits a spin crossover. Probably, the tetragonal elongation of the coordination octahedron is shorter with β-picoline than with pyridine (though it has been shown to be large in both cases), in spite of the bulkiness of the 3-methylpyridine as compared with the size of the nonsubstituted pyridine; the difference between the basicities of these ligands ($pK_a = 5.68$ and 5.25, respectively) may play a prominent part. It is obvious that this point is worth being further investigated.

In the square-pyramidal compounds $Co(H_2(fsa)_2en)tbpy$ and $Co(H_2(fsa)_2en)EtOH$, cobalt(II) is of the low-spin form. A similar result has been reported by Torihara et al.[41] for the binuclear complex $CoMg((fsa)_2en)(py)_3$, in which the cobalt atom lying in the N_2O_2 site is undoubtedly five-coordinated as shown by its EPR spectrum[34] ($g_1 = 2.40$, $g_2 = 2.25$, $g_3 = 2.00$). The stabilization of the doublet ground state ($^2A_1$) relative to the spin-quartet states in these compounds can be ascribed to the existence of a strong ligand field in the basal plane and, to a lesser extent, to the small raising of the cobalt ion out of the plane of the Schiff base ligand, the metal–axial ligand interaction having only a minor *direct* influence.[42] It is worthwhile to note that, in the case of complexes related to those in this study, namely Co(salen)py (low spin), Co(salbn(+))py (low spin) (salbn(+) denoting the dianion *N*,*N'*-butylenebis(salicylideneaminate), optically active form), and $Co(3\text{-MeOsalen})H_2O$ (high spin), the cobalt ion is effectively less displaced from the basal plane in both low-spin species (0.20[43] and 0.21 Å,[44] respectively) than in the high-spin species (0.43 Å[45]).

Conclusion

At the end of this work, we would like to emphasize one of the obtained results, which singularizes Co(II) with regard to the other ions in the field of spin transitions. Fe(II) and Fe(III) ions may exist in an octahedral environment either in a high-spin or in a low-spin state in the whole temperature range, or with a HS ⇌ LS crossover. In contrast, Co(II) in an essentially octahedral environment, with a ground state close to $^4T_1$, cannot apparently exhibit a spin conversion. The magnetic properties are then typical of an ion with an unquenched orbital momentum. On the other hand, a spin transition can be observed when the cobalt(II) ion is in a (4+2) environment. In the range of the high-spin phase, the magnetic properties are then much closer to those expected for a spin quartet with a very weak orbital contribution. In terms of molecular engineering, the question at hand is then how to favor a (4+2) with regard to a 6 environment. This work suggests a strategy consisting of creating a strong field in the equatorial plane by using the chelate effect of five-membered rings. It is obvious that this condition of large equatorial field is necessary but not sufficient. Such a field being obtained, the new question is as follows: "What type of apical ligands do actually lead to new spin-crossover compounds?" We intend now to focus on this problem.

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Registry No. $Co(H_2(fsa)_2en)(py)_2$, 70995-74-3; $Co(H_2(fsa)_2(1,3\text{-pn}))(py)_2$, 88296-37-1; $Co(H_2(fsa)_2en)(\beta\text{-pic})_2$, 88296-38-2; $Co(H_2(fsa)_2en)tbpy$, 88296-39-3; $Co(H_2(fsa)_2(1,3\text{-pn}))(tbpy)_2$, 88296-40-6.

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