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Supplementary Material Available: Thermal parameters for non-hydrogen atoms (Tables S-IV and S-V), calculated atomic coordinates for

H atoms (Table S-VI), bond distances and angles for the cation and BF_4^- anions (Table S-VII), and a packing diagram (5 pages). Ordering information is given on any current masthead page. According to policy instituted Jan 1, 1986, the tables of calculated and observed structure factors (25 pages) are being retained in the editorial office for a period of 1 year following the appearance of this work in print. Inquiries for copies of these materials should be directed to the Editor.

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Spin State of Cobalt(II) in Five- and Six-Coordinate Lewis Base Adducts of (*N,N'*-Ethylenebis(3-carboxysalicylaldiminato))cobalt(II). New Spin-Crossover Complexes

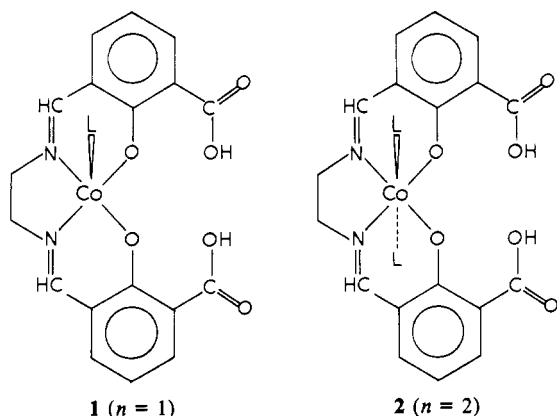
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The spin-state behavior of cobalt(II) was investigated by variable-temperature magnetic susceptibility measurements and EPR spectroscopy in a set of compounds of the type $\text{Co}(\text{H}_2(\text{fsa})_2\text{en})\text{L}_n$, where $\text{H}_2(\text{fsa})_2\text{en}^{2-}$ is the phenolic dianion of the Schiff base *N,N'*-ethylenebis(3-carboxysalicylalimine) and L is a substituted pyridine. These complexes were found to display a wide range of magnetic properties. Concerning the five-coordinate ($n = 1$) species, the L = 2-Mepy adduct admits a spin-quartet ground state, and its magnetic behavior can be described by using a rhombic spin Hamiltonian ($(D^2 + 3E^2)^{1/2} = 16.7 \text{ cm}^{-1}$, $g = 2.04$) with additional temperature-independent paramagnetism ($N\alpha = 211 \times 10^{-6} \text{ cm}^3 \cdot \text{mol}^{-1}$); the L = 3-OHpy adduct is likely to undergo a kinetically controlled $S = 3/2 \leftrightarrow S = 1/2$ crossover, while retaining an essentially high-spin character; finally, the L = 4-Mepy adduct is in the low-spin state, even at room temperature. Concerning the six-coordinate ($n = 2$) species, compounds with L = 3-Mepy, 3-NH₂py, and 3,5-Me₂py present a predominant high-spin behavior. Assuming the existence of a spin admixing between the quartet ground state ($^4A_{2g}$) and the first excited doublet state ($^2A_{1g}$), the energy gaps between these two states (Δ) and between the Kramers doublets arising from $^4A_{2g}$ (δ) could be estimated as $\Delta \sim 550\text{--}600 \text{ cm}^{-1}$ and $\delta \sim 95\text{--}115 \text{ cm}^{-1}$. Compounds with L = 4-Mepy and L = 4-*t*-Bupy exhibit a $S = 3/2 \leftrightarrow S = 1/2$ crossover. In the first case, this transition is of the continuous type and thermodynamic calculations show, as expected, that cooperative effects are negligible; an upper limit of 194 cm^{-1} is calculated for Δ , the ground state being then a spin doublet. By contrast, the spin conversion of the latter complex is one of the most abrupt ever observed in Co(II) complexes and presents a hysteresis of ca. 16 K, being centered at $T_c \downarrow = 138 \text{ K}$ and $T_c \uparrow = 154 \text{ K}$ for decreasing and increasing temperatures, respectively. The effect of the nature of apical ligands on the spin state of Co(II) is discussed in terms of σ -donor ability, orientation of the pyridine ring, and steric requirements.

Introduction

The family of solid cobalt(II) complexes of the type $\text{Co}(\text{H}_2(\text{fsa})_2\text{en})\text{L}_n$ —where $\text{H}_2(\text{fsa})_2\text{en}^{2-}$ is the phenolic dianion of the Schiff base *N,N'*-ethylenebis(3-carboxysalicylalimine) and n the number of axial ligands L—is expected to provide the possibility, through the choice of L, for selecting the metal ion electronic ground state.



Preliminary results^{1,2} have shown that five- (see **1**) or/and six-coordinate (see **2**) adducts could be obtained, according to the nature of L. This property, owing to the fact that the square-planar complex (*N,N'*-ethylenebis(salicylaldiminato))cobalt(II),

or Co(salen), is known to never bind more than one axial Lewis base, may be accounted for by the equatorial ligand field lowering due to the presence of an electron-attracting carboxylic group on each aromatic ring of the Schiff base. The magnetic behavior of $\text{Co}(\text{H}_2(\text{fsa})_2\text{en})\text{L}^{1,2}$ and $\text{Co}(\text{H}_2(\text{fsa})_2\text{en})\text{L}_2^{1-3}$ species clearly suggests that, in both kinds of compounds, the lowest high-spin ($S = 3/2$) and low-spin ($S = 1/2$) states are very close in energy. Indeed, though the $\chi_M T$ products (χ_M = molar magnetic susceptibility) related to $\text{Co}(\text{H}_2(\text{fsa})_2\text{en})(\text{EtOH})^1$ and $\text{Co}(\text{H}_2(\text{fsa})_2\text{en})(4\text{-}t\text{-Bupy})^2$ (EtOH = ethanol, 4-*t*-Bupy = 4-*tert*-butylpyridine) follow, in a wide temperature range, a Curie law characteristic of the low-spin form, the slight increase of $\chi_M T$ with temperature that is observed above $\sim 200 \text{ K}$ for the former compound and $\sim 250 \text{ K}$ for the latter seems to indicate the beginning of an occupation of excited high-spin levels. Likewise, in the sixfold coordinated complexes, the ligand field appears to approximate the conditions suitable for the pairing of electrons: in $\text{Co}(\text{H}_2(\text{fsa})_2\text{en})(3\text{-Mepy})_2^2$, cobalt(II) was found to retain an essentially high-spin state from 300 to 4 K, while in $\text{Co}(\text{H}_2(\text{fsa})_2\text{en})(\text{py})_2^{1,2}$ and $\text{Co}(\text{H}_2(\text{fsa})_2\text{en})(\text{H}_2\text{O})_2^{1,3}$ it exhibits thermally induced quartet \leftrightarrow doublet spin transitions. It is worth noting that these transitions are very abrupt, in contrast with those previously reported for cobalt(II) complexes, which are generally of the continuous type.⁴⁻¹³

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The purpose of this work is to specify the influence of the apical Lewis bases on the spin state of the metal ion, in order to forecast the nature of the L ligands that will likely lead to spin-crossover compounds. In the longer term, the interest of such systematical investigations is to establish relationships between the molecular parameters and the main features of spin transitions (in particular, the critical temperature and possibly the abruptness).

We report here the magnetic susceptibility measurements and the EPR spectra obtained for a series of compounds where L is a substituted (in most cases a monosubstituted) pyridine. The substituents are electron-donating groups (CH₃, NH₂, OH, C-(CH₃)₃) whose position on the pyridine ring is varied. When fivefold coordinated, the metal ion was found either to retain the same spin state ($S = 1/2$ or $S = 3/2$) in the 295–4 K temperature range or to undergo a kinetically controlled spin crossover while admitting a predominant $S = 3/2$ character. It should be noted that very few other genuine examples of complexes in which cobalt(II) exhibits a spin-quartet ground state when lying in a quasi-square-pyramidal environment have been reported as yet.^{6,13–16} Concerning the six-coordinate species, several compounds were shown to keep an essentially high-spin behavior whatever the temperature may be, and evidence was provided for the existence of two doublet–quartet spin transitions, one of these transitions being of the discontinuous type.

Experimental Section

Syntheses. 3-Formylsalicylic acid was prepared according to the method of Duff and Bills.¹⁷ The Schiff base H₄(fsa)₂en was obtained by reacting this acid with ethylenediamine, in a 2:1 ratio, at reflux with ethanol. To prepare the cobalt(II) complexes, three methods have been used; all the syntheses were carried out under an atmosphere of dry argon; solvents and reagents were carefully deoxygenated before use.

Method 1. Co(H₂(fsa)₂en)(3-Mepy)₂. A solution of Co(CH₃COO)₂·4H₂O (70 mg) in 3-methylpyridine (5 mL) was added dropwise to a suspension of H₄(fsa)₂en (100 mg) in 3-methylpyridine (5 mL). The mixture was then stirred at 80 °C for 2 h. The resulting yellow precipitate was isolated, washed with ether, and dried under vacuum.

Methods 2 and 3 include, as a first step, the synthesis of Co(H₂(fsa)₂en)(H₂O)₂ that was carried out according to the method previously described.³ When this complex was heated in the solid state at 90 °C for 3 h, the square-planar complex Co(H₂(fsa)₂en) was then obtained.

Method 2 was used in the case of liquid apical ligands.

Co(H₂(fsa)₂en)(4-Mepy)₂. A 4-mL sample of freshly distilled 4-methylpyridine was stirred with 50 mg of Co(H₂(fsa)₂en). The suspension was then heated at 60 °C for 8 h. The resulting brown-red precipitate was collected and dried under vacuum.

The following complexes were prepared by the same method:

Co(H₂(fsa)₂en)(2-Mepy)₂. The mixture of freshly distilled 2-methylpyridine (3 mL) and Co(H₂(fsa)₂en) (40 mg) was heated at 60 °C for 3 h. The compound that was obtained is light brown.

Co(H₂(fsa)₂en)(4-*t*-Bupy)₂. The mixture of 4-*tert*-butylpyridine (3 mL) and Co(H₂(fsa)₂en) (40 mg) was heated at 100 °C for 5 h. The resulting precipitate is pale yellow.

Co(H₂(fsa)₂en)(3,5-Me₂py)₂. The mixture of 3,5-dimethylpyridine (7 mL) and Co(H₂(fsa)₂en) (120 mg) was heated at 90 °C for 5 h. The compound is brown.

Method 3 was used when the ligand was a solid, or when it was a liquid, with the purpose of fixing only one axial molecule on Co(II).

Co(H₂(fsa)₂en)(3-NH₂py)₂. A solution of 3-aminopyridine (40 mg) in absolute ethanol (2.5 mL) was rapidly dropped on solid Co(H₂(fsa)₂en) (30 mg). After the mixture was heated at 50 °C for 30 min, the light brown precipitate that had formed was collected, washed with absolute ethanol, and dried under vacuum.

The following complexes were prepared likewise:

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- (16) Banci, L.; Bencini, A.; Benelli, C.; Gatteschi, D.; Zanchini, C. *Struct. Bonding (Berlin)* **1982**, *52*, 37 and references therein.
- (17) Duff, J. C.; Bills, E. J. *J. Chem. Soc.* **1932**, 1987.

Table I. Microanalysis Data for Co(H₂(fsa)₂en)L_n Complexes

complex	L	n	(% calcd) % found			
			C	H	N	O
3-Mepy		2	(60.10)	(4.71)	(9.35)	(16.01)
			60.01	4.70	9.64	16.03
4-Mepy		2	(60.10)	(4.71)	(9.35)	(16.01)
			60.24	4.88	9.47	15.77
2-Mepy		1	(57.00)	(4.15)	(8.30)	(18.99)
			56.33	4.18	8.36	18.59
4- <i>t</i> -Bupy		2	(63.24)	(5.91)	(8.20)	(14.03)
			63.10	5.88	8.18	14.09
3,5-Me ₂ py		2	(61.23)	(5.15)	(8.93)	(15.29)
			61.42	5.16	9.17	15.43
3-NH ₂ py		2	(54.37)	(4.51)	(13.49)	(18.02)
			54.51	4.42	13.26	18.11
3-OHpy		1	(54.36)	(3.74)	(8.26)	(22.04)
			54.14	3.89	8.42	22.02
4-Mepy		1	(57.00)	(4.15)	(8.30)	(18.99)
			57.00	4.17	8.19	19.69

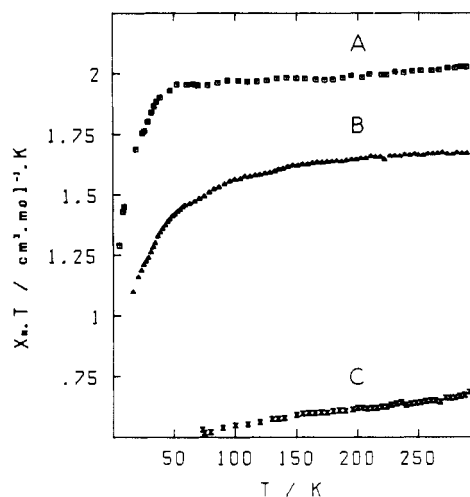


Figure 1. Temperature dependence of $\chi_M T$ for the five-coordinate compounds Co(H₂(fsa)₂en)L, with L = 2-Mepy (A), 3-OHpy (B), and 4-Mepy (C).

Co(H₂(fsa)₂en)(3-OHpy). The suspension of Co(H₂(fsa)₂en) (30 mg) in a solution of 3-hydroxypyridine (60 mg) in absolute ethanol (4 mL) was heated at 60 °C for 2 h. The resulting precipitate had a pinkish light brown color.

Co(H₂(fsa)₂en)(4-Mepy). A solution of freshly distilled 4-methylpyridine (0.2 mL) in absolute ethanol (4 mL) was stirred with a 60-mg amount of Co(H₂(fsa)₂en). The mixture was heated at 60 °C for 15 min, yielding a brown-red precipitate very sensitive to oxygen.

Microanalysis data related to the above complexes are given in Table I.

Physical Measurements. Magnetic susceptibility measurements were performed on polycrystalline samples weighing about 6 mg, over 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 the strength of the applied magnetic field was checked for each compound at room temperature. HgCo(SCN)₄ was used as susceptibility standard. The data were corrected for the diamagnetism of all constituents, estimated at -275×10^{-6} , -275×10^{-6} , -264×10^{-6} , -337×10^{-6} , -340×10^{-6} , -337×10^{-6} , -405×10^{-6} , and $-355 \times 10^{-6} \text{ cm}^3 \text{ mol}^{-1}$ for the monoadducts with L = 2-Mepy, 4-Mepy, and 3-OHpy and for the diadducts with L = 3-Mepy, 3-NH₂py, 4-Mepy, 4-*t*-Bupy, and 3,5-Me₂py, respectively. The temperature resolution was ca. 0.1 K, and the reproducibility of the magnetic susceptibilities for a given compound, between independent runs, was within $\pm 1\%$.

EPR spectra were obtained on polycrystalline samples with a Bruker ER 200D X-band spectrometer equipped with an Oxford Instruments continuous-flow cryostat. A 100-kHz field modulation was used. The magnetic field was measured with a Hall probe and the klystron frequency with a Hewlett-Packard frequency meter.

Analysis of Magnetism and EPR Data

I. Five-Coordinate (CoN₃O₂) Complexes. Co(H₂(fsa)₂en)(2-Mepy) (A). The temperature dependence of the $\chi_M T$ product

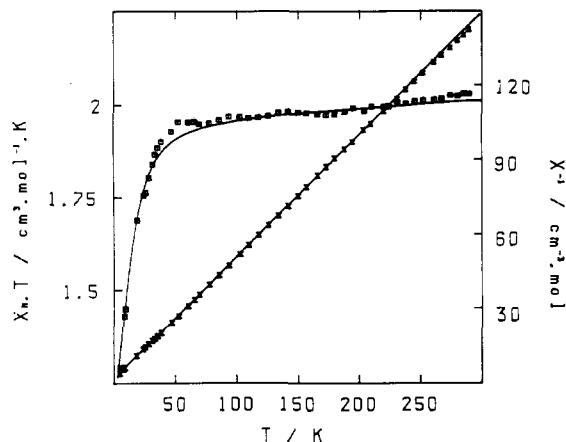


Figure 2. Temperature dependence of $\chi_M T$ (\square) and χ_M^{-1} (\times) for $\text{Co}(\text{H}_2(\text{fsa})_2\text{en})(2\text{-Mepy})$. Solid lines represent the best fits of the data, obtained with $(D^2 + 3E^2)^{1/2} = 16.7 \text{ cm}^{-1}$, $g = 2.04$, and $N\alpha = 211 \times 10^{-6} \text{ cm}^3 \cdot \text{mol}^{-1}$ (see eq 1 in text).

related to this compound is shown in Figure 1A. It is characteristic of a high-spin cobalt(II) ion. $\chi_M T$ decreases very slowly from $2.03 \text{ cm}^3 \cdot \text{mol}^{-1} \cdot \text{K}$ ($\mu_{\text{eff}} = 4.03 \mu_B$) at 290 K to $1.94 \text{ cm}^3 \cdot \text{mol}^{-1} \cdot \text{K}$ ($\mu_{\text{eff}} = 3.94 \mu_B$) at 50 K and then drops more rapidly and reaches $1.29 \text{ cm}^3 \cdot \text{mol}^{-1} \cdot \text{K}$ ($\mu_{\text{eff}} = 3.21 \mu_B$) at 5 K. It should be noted that the room-temperature values of $\chi_M T$ previously reported for some examples of fully high-spin cobalt(II) square-pyramidal complexes lie within a wide range going from $2.19 \text{ cm}^3 \cdot \text{mol}^{-1} \cdot \text{K}$ for $\text{Co}(\text{salphn})(2\text{-MeImd})$ to $3.21 \text{ cm}^3 \cdot \text{mol}^{-1} \cdot \text{K}$ for $[\text{Co}(\text{MePh}_2\text{AsO})_4\text{NO}_3] \cdot \text{NO}_3$ ^{6,13,16} ($\text{H}_2\text{salphn} = N,N'\text{-}o\text{-phenylenebis}(\text{salicylaldehyde})$, $\text{Imd} = \text{imidazole}$, $\text{Ph} = \text{phenyl}$).

The magnetic behavior of $\text{Co}(\text{H}_2(\text{fsa})_2\text{en})(2\text{-Mepy})$ can be explained by the existence of a large zero-field splitting in the 4B_1 ground state and of a temperature-independent paramagnetism, $N\alpha$. This latter parameter was added to account for the slight decrease of $\chi_M T$ when passing from 290 to 50 K. By using, for $S = 3/2$, the rhombic spin Hamiltonian

$$\mathcal{H} = \beta g \hat{H} \cdot \hat{S} + D[\hat{S}_z^2 - \frac{1}{3}S(S+1)] + E[\hat{S}_x^2 - \hat{S}_y^2]$$

in the expression of which all the variables have their usual meaning, and by assuming that $g_{\parallel} = g_{\perp}$, we can express the dependence of $\chi_M T$ on T by the relation¹⁸

$$\chi_M T = \frac{g^2}{8} \left[\frac{9}{4} + \frac{3}{x} \frac{1 - e^{-x}}{1 + e^{-x}} \right] + N\alpha T \quad (1)$$

where $x = (2/kT)(D^2 + 3E^2)^{1/2}$. The best fit parameters were $(D^2 + 3E^2)^{1/2} = 16.7 \text{ cm}^{-1}$, $g = 2.04$ and $N\alpha = 211 \times 10^{-6} \text{ cm}^3 \cdot \text{mol}^{-1}$. Therefore, the D value is somewhat lower than the one reported by Kennedy et al.¹³ for $\text{Co}(\text{salphn})(2\text{-MeImd})$, viz. 22.6 cm^{-1} . As seen in Figure 2, the above parameters satisfactorily reproduce the experimental data.

The powder X-band EPR spectrum, recorded at 11 K (see Figure 3), shows a strong signal at $g = 6.08$ and a very broad feature centered at $g = 2.50$. These anisotropic "effective" g values are associated with an effective spin $S' = 1/2$, the transitions occurring primarily in the lower of the two Kramers doublets into which the 4B_1 state is split. The positions and relative intensities of the corresponding lines are typical¹⁶ of a high-spin Co(II) ion, lying in an axially elongated (associated with a positive D value) and rhombically distorted environment, which is in keeping with the magnetism results.

$\text{Co}(\text{H}_2(\text{fsa})_2\text{en})(3\text{-OHpy})$ (B). The magnetic behavior of this compound is displayed in Figure 1B. The $\chi_M T$ product decreases slightly from 1.67 to $1.56 \text{ cm}^3 \cdot \text{mol}^{-1} \cdot \text{K}$ ($\mu_{\text{eff}} = 3.66\text{--}3.53 \mu_B$) between 290 and 100 K. At lower temperatures, it drops more rapidly, reaching $1.10 \text{ cm}^3 \cdot \text{mol}^{-1} \cdot \text{K}$ ($\mu_{\text{eff}} = 2.97 \mu_B$) at 16 K. The room-temperature value seems rather low as compared with that found for $\text{Co}(\text{H}_2(\text{fsa})_2\text{en})(2\text{-Mepy})$, viz. $2.03 \text{ cm}^3 \cdot \text{mol}^{-1} \cdot \text{K}$, and

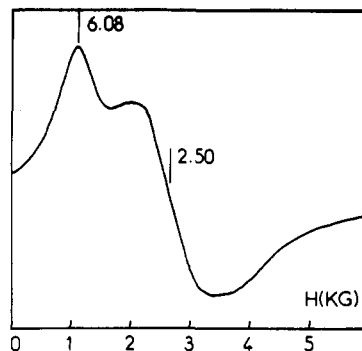


Figure 3. X-Band EPR spectrum at 11 K of a microcrystalline sample of $\text{Co}(\text{H}_2(\text{fsa})_2\text{en})(2\text{-Mepy})$. Effective g values are given.

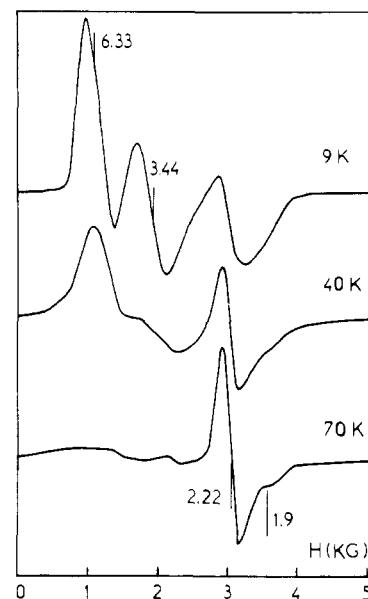


Figure 4. X-Band EPR spectra of a microcrystalline sample of $\text{Co}(\text{H}_2(\text{fsa})_2\text{en})(3\text{-OHpy})$ at 9, 40, and 70 K. The main g values are given. Intensities of the lines cannot be compared between the three spectra, which have been recorded under different experimental conditions.

falls significantly outside the range of values corresponding to square-pyramidal high-spin cobalt (II) complexes (vide supra).

At 9 K, the EPR spectrum exhibits three main features, at $g = 6.33$, 3.44 , and 2.22 . In order to obtain further information on the origin of the signals, the temperature was varied. Figure 4 shows the data obtained at 9, 40, and 70 K. When the temperature is raised, the first two lines broaden and their relative intensity with respect to the third one diminishes; at 70 K, both nearly vanish. In view of these results, we can assign the signals at $g = 6.33$ and 3.44 to a high-spin species, whose relaxation time is expected to be small, and the signal at $g = 2.22$ (and its shoulder at $g \sim 1.9$) to a low-spin species.

Consequently, the compound in this study appears to be a mixture of low-spin and largely predominant high-spin forms. In order to specify whether the ratio of the two forms was temperature-dependent or not, we have plotted the IT product related to the low-spin main EPR signal as a function of T . Here, I is the approximate intensity of the microwave absorption, estimated as $I \propto Y \cdot (\Delta H)^2$, where $2Y$ is the peak-to-peak derivative amplitude and ΔH the peak-to-peak width obtained from EPR spectra.¹⁹ IT values are found to decrease from ~ 3 to ~ 1 (in arbitrary units) when the temperature is raised from 50 to 150 K. Such an effect could be ascribed to relaxation phenomena, as shown in particular by Bertrand et al. in the case of an iron(III) porphyrin.²⁰

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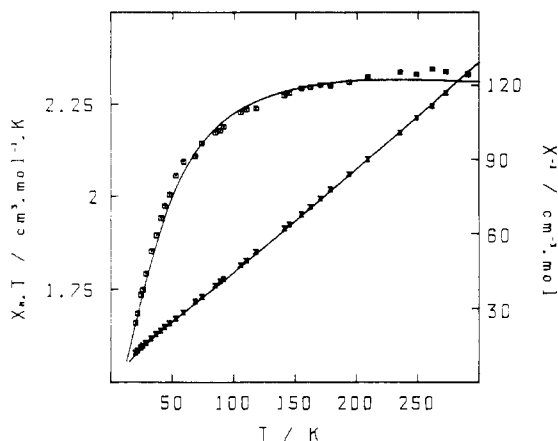


Figure 5. Temperature dependence of $\chi_M T$ (\square) and χ_M^{-1} (X) for $\text{Co}(\text{H}_2(\text{fsa})_2\text{en})(3\text{-Mepy})_2$. Solid lines represent the best fits of the data, calculated on the basis of eq 2 and 3 (see text) with use of the parameters given in Table III.

However, this hypothesis has to be partly ruled out in the present case, for ΔH remains nearly constant in the 50–150 K range, thus evidencing no significant relaxation broadening. So, the variation of IT with T , at least in part, likely reflects a change in the ratio of low-spin molecules to predominant high-spin molecules.

According to this conclusion, it seems that the presence at any temperature of $S = 3/2$ and $S = 1/2$ cobalt(II) ions cannot arise from the coexistence of some different high- and low-spin species, accidentally giving an elemental analysis close to that expected for compound B. The infrared spectrum investigation and the fact that the magnetism and EPR results obtained with samples resulting from different methods of synthesis were found to be closely similar are also in disagreement with such a hypothesis. On the contrary, all the data are consistent with the existence of a $S = 3/2 \leftrightarrow S = 1/2$ spin transition. Both $\chi_M T$ vs. T and IT vs. T curves show that this transition is relatively slow and does not display a Boltzmann behavior. It follows that the equilibrium between the two spin isomers is expected not to be achieved. The spin conversion appears to be kinetically controlled. A possible explanation for this property is the presence, in the powder compound, of crystal defects and/or small-size crystallites that hinder the growth of minority-spin domains.²¹ It should be noted that such a kinetic control in a spin crossover has been recently reported by Gunter et al. in the case of an iron(III) porphyrin axially coordinated with an azido group.²²

Co(H₂(fsa)₂en)(4-Mepy) (C). The plot of $\chi_M T$ vs. T obtained for this compound is given in Figure 1C. It reveals an essentially low-spin behavior. However, a slight decrease in $\chi_M T$ from 0.69 $\text{cm}^3\cdot\text{mol}^{-1}\cdot\text{K}$ ($\mu_{\text{eff}} = 2.35 \mu_B$) at 290 K to 0.52 $\text{cm}^3\cdot\text{mol}^{-1}\cdot\text{K}$ ($\mu_{\text{eff}} = 2.04 \mu_B$) at 80 K can be observed, and the room-temperature value seems rather high for a purely low-spin complex. The EPR spectrum at 4 K shows a strong signal at 2.32 and four additional small features at $g = 5.32, 3.07, 2.17,$ and 1.80 . The $g = 2.32$ line and its shoulder at $g \sim 2.17$ may be identified as being g_{\perp} and g_{\parallel} , respectively, for the low-spin square-pyramidal complex. The signal at $g = 5.32$ can be assigned to a high-spin cobalt(II) species. The values $g = 3.07$ and $g = 1.80$ are in the range of the values expected for low-spin square-planar compounds,²³ so they may be associated with the two components of g_{\perp} for the complex $\text{Co}(\text{H}_2(\text{fsa})_2\text{en})$. Thus, the EPR spectrum indicates that, despite good microanalysis data (see Table I), compound C contains small amounts of the relevant square-planar complex and, presumably, of the six-coordinate $\text{Co}(\text{H}_2(\text{fsa})_2\text{en})(4\text{-Mepy})_2$ species, which undergoes a very smooth spin transition (vide infra).

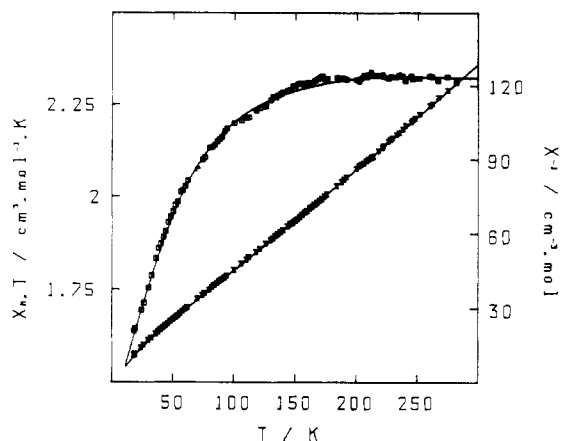


Figure 6. Temperature dependence of $\chi_M T$ (\square) and χ_M^{-1} (X) for $\text{Co}(\text{H}_2(\text{fsa})_2\text{en})(3\text{-NH}_2\text{py})_2$. Solid lines represent the best fits of the data, calculated on the basis of eq 2 and 3 (see text) with use of the parameters given in Table III.

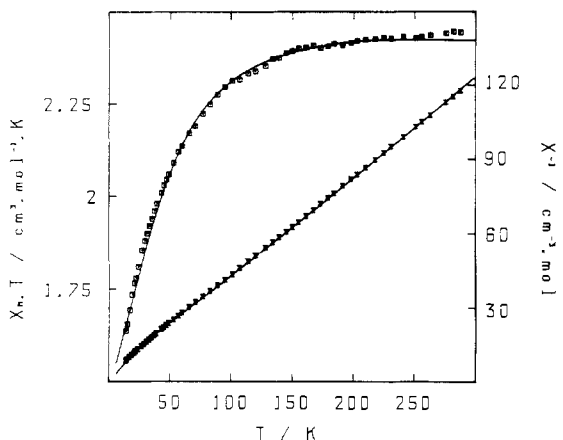


Figure 7. Temperature dependence of $\chi_M T$ (\square) and χ_M^{-1} (X) for $\text{Co}(\text{H}_2(\text{fsa})_2\text{en})(3,5\text{-Me}_2\text{py})_2$. Solid lines represent the best fits of the data, calculated on the basis of eq 2 and 3 (see text) with use of the parameters given in Table III.

It follows that two hypotheses can be proposed to explain the decrease in $\chi_M T$ when the temperature is lowered. The first one attributes this phenomenon to the thermally induced spin conversion in the $\text{Co}(\text{H}_2(\text{fsa})_2\text{en})(4\text{-Mepy})_2$ complex, present as an impurity. The second one postulates the existence of a significant temperature-independent paramagnetism, which would be due to a relative closeness of thermally unpopulated excited levels with respect to the 2A_1 ^{23,24} ground state. The experimental magnetism curve can be fitted by the relation $\chi_M = C/T + N\alpha$, where $C = 0.48 \text{ cm}^3\cdot\text{mol}^{-1}\cdot\text{K}$ and $N\alpha = 720.10^{-6} \text{ cm}^3\cdot\text{mol}^{-1}$. The above two hypotheses do not exclude each other, and the value obtained for $N\alpha$ is certainly overestimated. However, though very few $N\alpha$ data are available up to now for cobalt(II) compounds, it should be noted that similar high values ($600\text{--}790 \times 10^{-6} \text{ cm}^3\cdot\text{mol}^{-1}$) were reported for tetrahedral CoX_4^{2-} complexes, where X is a halogen.²⁵

II. Six-Coordinate (CoN₄O₂) Complexes. **Co(H₂(fsa)₂en)(3-Mepy)₂ (D); Co(H₂(fsa)₂en)(3-NH₂py)₂ (E); Co(H₂(fsa)₂en)(3,5-Me₂py)₂ (F).** $\chi_M T$ and χ_M^{-1} vs. T plots for compounds D, E, and F are given in Figures 5, 6, and 7, respectively. The magnetic behavior of the three compounds appears to be quite similar: $\chi_M T$ remains nearly constant from 290 K (2.29, 2.30, 2.39 $\text{cm}^3\cdot\text{mol}^{-1}\cdot\text{K}$, i.e. $\mu_{\text{eff}} = 4.28, 4.29,$ and $4.37 \mu_B$ for D, E, and F, respectively) to about 150 K and then decreases more and more markedly to reach a value close to 1.7 $\text{cm}^3\cdot\text{mol}^{-1}\cdot\text{K}$ ($\mu_{\text{eff}} \sim 3.7 \mu_B$) at 20 K.

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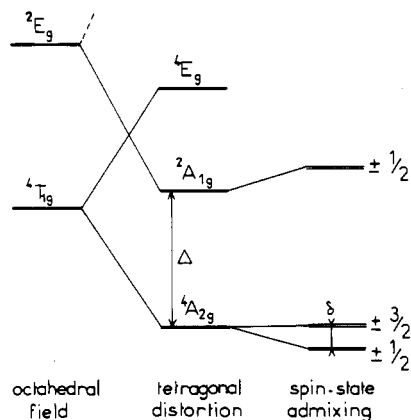


Figure 8. Energy level diagram (not entirely at scale) for a sixfold-coordinated cobalt(II) ion with a quartet ground state, in the presence of a tetragonal distortion and a spin-state admixing. Coupling with the levels arising from the 4E_g excited state is not taken into account.

Several hypotheses may be put forward to account for these $\chi_M T$ values—which are unusually low for high-spin cobalt(II) compounds—and for the shape of the $\chi_M T$ vs. T curves. The more realistic are the existence of (i) a kinetically controlled $S = 3/2 \leftrightarrow S = 1/2$ spin crossover, (ii) a mixture of high-spin and low-spin molecules in a constant ratio, and (iii) a spin-state admixing between the quartet and doublet states of lowest energy. Hypotheses i and ii can be ruled out owing to EPR spectra (vide infra): even at very low temperature (4.2 K), the presence of a low-spin species cannot be detected. Hypothesis iii must be closely examined.

In an octahedral ligand field, the ground level for high-spin cobalt(II) is ${}^4T_{1g}$ and the first excited state is 2E_g . If, in compounds D–F, the metal ion ground state was ${}^4T_{1g}$, the $\chi_M T$ product would decrease significantly from that at room temperature, owing to spin-orbit coupling.²⁶ The fact that this product retains a nearly constant low value from 290 to 250 K provides evidence for a large degeneracy reduction of the ${}^4T_{1g}$ state, which is expected to be mainly due to a tetragonal distortion, the basal ligand being rather rigid. This distortion leads to a splitting of ${}^4T_{1g}$ into ${}^4A_{2g}$ and 4E_g states and of 2E_g into ${}^2A_{1g}$ and ${}^2B_{1g}$ states (see Figure 8). The 4E_g level is supposed to lie at a much higher energy than the ${}^2A_{1g}$ level. This assumption seems authorized if one considers that, in the family of complexes $\text{Co}(\text{H}_2(\text{fsa})_2\text{en})\text{L}_m$, all the compounds studied up to now have been found either to exhibit a spin transition or to be in a situation very close to a spin transition.^{1–3}

We have tried to estimate the energy gap Δ between the quartet ground state ${}^4A_{2g}$ and the doublet first excited state ${}^2A_{1g}$ by assuming that there exists a quantum-mechanical spin admixing of those states. The ${}^4A_{2g}$ level is then split into two Kramers doublets through spin-orbit coupling (see Figure 8). An analogous situation was described by the model of Maltempo²⁷ in the case of Fe(III) porphyrins, where an admixing between $S = 5/2$ and $S = 3/2$ states can occur. In order to reproduce the magnetism curves, we have first diagonalized the matrix describing the action of the spin-orbit operator on the six $|S_z\rangle$ components of the ${}^4A_{2g}$ and ${}^2A_{1g}$ states used as a basis set. This diagonalization led to the energies

$$E_1 = \frac{\Delta}{2} - \left[\left(\frac{\Delta}{2} \right)^2 + 4 \frac{\zeta^2}{3} \right]^{1/2} \quad (2)$$

$$E_2 = \frac{\Delta}{2} + \left[\left(\frac{\Delta}{2} \right)^2 + 4 \frac{\zeta^2}{3} \right]^{1/2}$$

(ζ being the one-electron spin-orbit coupling constant) for the lower and the higher $|\pm 1/2\rangle$ levels, respectively, the zero energy

Table II. Best Fit Parameters Calculated from Magnetism Data for Spin-Admixed $\text{Co}(\text{H}_2(\text{fsa})_2\text{en})\text{L}_2$ Complexes^a

compd	L	Δ , cm^{-1}	ζ , cm^{-1}	g	δ , cm^{-1}
D	3-Mepy	598	223	2.24	96
E	3-NH ₂ py	546	240	2.25	116
F	3,5-Me ₂ py	599	236	2.29	105

^a See text and Figure 8 for meaning of parameters.

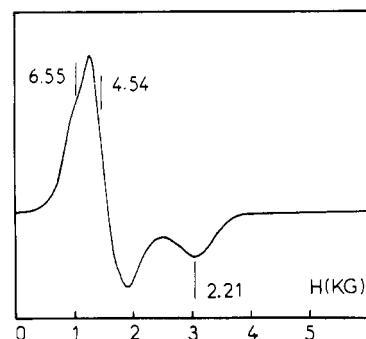


Figure 9. X-Band EPR spectrum at 12 K of a polycrystalline sample of $\text{Co}(\text{H}_2(\text{fsa})_2\text{en})(3\text{-NH}_2\text{py})_2$. Effective g values are given.

corresponding to $|\pm 3/2\rangle$. The magnetic susceptibilities χ_{\parallel} and χ_{\perp} were then calculated by using the Van Vleck formula, and assuming that $g_{\parallel} = g_{\perp} = g$, $\chi_M T$ could be obtained as

$$\chi_M T = \frac{3g^2}{8} \left[\frac{\frac{1}{4}e^{-E_1/kT} + (\frac{3}{4} - kT/E_2)e^{-E_2/kT} + kT/E_2 + \frac{3}{4}}{1 + e^{-E_1/kT} + e^{-E_2/kT}} \right] \quad (3)$$

The Δ , ζ , and g parameters were least-squares fitted. Table II gives the values obtained for the best fits, as also the energy gap δ between the Kramers doublets arising from ${}^4A_{2g}$ ($\delta = |E_1|$). As can be seen in Figures 5–7, the calculated and experimental $\chi_M T$ and χ_M^{-1} vs. T curves are in fairly good agreement.

Since the magnetic and EPR (vide infra) data related to compounds D–F are typical of a mainly high-spin behavior, it can be pointed out that, in such complexes, a Δ/ζ ratio of 2.5 ± 0.2 (calculated from the data given in Table II) is indicative of a weak spin-admixing effect. For the three species, the ζ parameter appears to be rather low as compared with that of the free ion, viz. 535 cm^{-1} . A similar observation has been made by several authors^{20,28} when applying the model of Maltempo to Fe(III) porphyrins: the values obtained for spin-orbit coupling constants were found to be about one-third of the free-ion value, this fact being accounted for by the excessive simplification of the model. The same explanation is likely to apply in the present cases. Moreover, another cause of uncertainty concerning the results reported in Table II is probably that, to a first approximation, the effect of the excited 4E_g level was not taken into account. Indeed, since the splitting of ${}^4T_{1g}$ is expected¹⁶ not to be very far from 1000 cm^{-1} and since Δ is found to be close to 600 cm^{-1} , the 4E_g level may lie only $\sim 400 \text{ cm}^{-1}$ over the ${}^2A_{1g}$ one and its interaction with this doublet level and, hence, with the ground-state level, should not be negligible.

The low-temperature EPR spectra of compounds D–F show rather similar features. Figure 9 gives one of them as a representative example. The patterns of “effective” (vide supra) g values (6.32, 4.37, and 2.22 for D; 6.55, 4.54, and 2.21 for E; 4.52 and 2.19 for F) are similar to those of purely high-spin compounds that present a distorted octahedral coordination geometry,¹⁶ which corroborates the relative weakness of the spin-quartet and -doublet mixing. As can be seen from the g values of the two lowest field signals in the spectra of compounds D and E and from the fact that only one relatively narrow g_{\perp} signal can be observed in the spectrum of F, the rhombicity, which has been neglected in the

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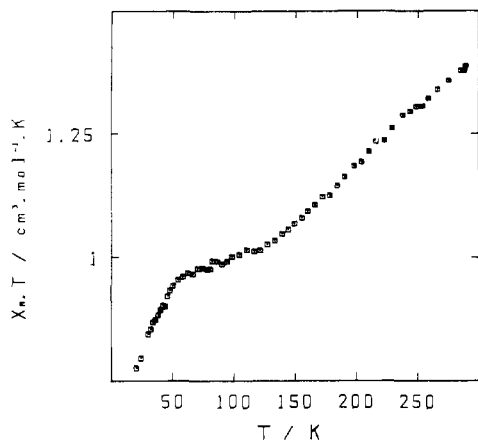


Figure 10. Temperature dependence of $\chi_M T$ for $\text{Co}(\text{H}_2(\text{fsa})_2\text{en})(4\text{-Mepy})_2$.

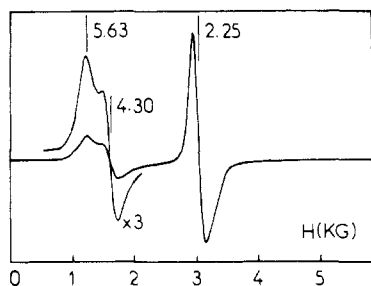


Figure 11. X-Band EPR spectrum at 4.2 K of a polycrystalline sample of $\text{Co}(\text{H}_2(\text{fsa})_2\text{en})(4\text{-Mepy})_2$. g values are given.

above-described calculations, is far from being as pronounced in these compounds as in the high-spin complex $\text{Co}(\text{H}_2(\text{fsa})_2\text{en})(2\text{-Mepy})$ and in the high-spin form of $\text{Co}(\text{H}_2(\text{fsa})_2\text{en})(3\text{-OHpy})$. Moreover, from the patterns of effective g values and the signal intensities, one can deduce that the $\pm 1/2$ doublet lies lower,^{16,29} which agrees with the energy level scheme given in Figure 8.

$\text{Co}(\text{H}_2(\text{fsa})_2\text{en})(4\text{-Mepy})_2$ (G); $\text{Co}(\text{H}_2(\text{fsa})_2\text{en})(4\text{-}t\text{-Bupy})_2$ (H). Both complexes exhibit a thermally induced spin-crossover phenomenon. The G compound gives an example of a very gradual and incomplete transition that can be described in terms of spin equilibrium. The $\chi_M T$ product (see Figure 10) regularly decreases from $1.42 \text{ cm}^3 \cdot \text{mol}^{-1} \cdot \text{K}$ ($\mu_{\text{eff}} = 3.37 \mu_B$) at 290 K to $1.03 \text{ cm}^3 \cdot \text{mol}^{-1} \cdot \text{K}$ ($\mu_{\text{eff}} = 2.87 \mu_B$) at 120 K, hardly varies with temperature between 120 and 55 K, and drops again at lower temperature to reach $0.77 \text{ cm}^3 \cdot \text{mol}^{-1} \cdot \text{K}$ ($\mu_{\text{eff}} = 2.48 \mu_B$) at 20 K. This latter decrease may be due to weak intermolecular exchange coupling between neighboring cobalt atoms. No hysteresis effect was evidenced. The EPR spectrum obtained at 4.2 K (see Figure 11) provides clear evidence for the coexistence of low-spin and high-spin molecules, characterized by the signal at $g = 2.25$ and the signals at $g = 5.63$ and 4.30 , respectively.

We have attempted to estimate the energy gap between the fundamental doublet and the lowest lying quartet state by using a thermodynamical approach. The high-spin mole fraction c was calculated at every temperature according to the relation

$$c = [\chi_M T - (\chi_M T)_{\text{LS}}] / [(\chi_M T)_{\text{HS}} - (\chi_M T)_{\text{LS}}] \quad (4)$$

The low-spin-form $\chi_M T$ product was obtained from the expression

$$(\chi_M T)_{\text{LS}} = N\beta^2 \bar{g}^2 S(S+1)/3k \quad (5)$$

where N , β , and k have their usual meaning, $S = 1/2$, and the mean \bar{g}^2 value was taken as $(2.22)^2$, which led to $(\chi_M T)_{\text{LS}} = 0.46 \text{ cm}^3 \cdot \text{mol}^{-1} \cdot \text{K}$. For the high-spin form, $(\chi_M T)_{\text{HS}}$ was assumed to admit the same value as in the spin-crossover homologous compound $\text{Co}(\text{H}_2(\text{fsa})_2\text{en})(\text{py})_2$, i.e. $2.61 \text{ cm}^3 \cdot \text{mol}^{-1} \cdot \text{K}$. The percentage

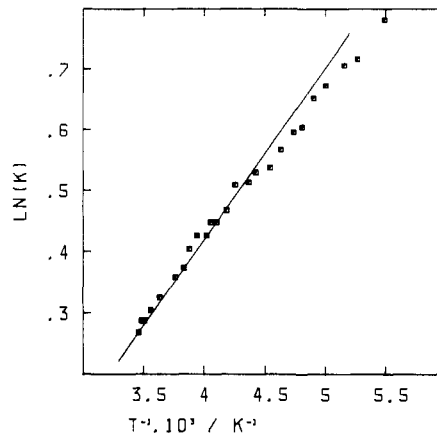


Figure 12. Plot of $\ln K$ vs. T^{-1} for $\text{Co}(\text{H}_2(\text{fsa})_2\text{en})(4\text{-Mepy})_2$.

of high-spin species was then found to be only $\sim 43\%$ at 290 K. Owing to this result and to the shape of the $\chi_M T$ vs. T curve, it clearly appears that the low-spin \leftrightarrow high-spin conversion must proceed above room temperature. Moreover, evidence was provided for the persistence of $\sim 24\%$ of high-spin form in the lower temperature range. Figure 12 shows the plot, as a function of T^{-1} , of $\ln K$, K being the formal constant of the equilibrium $S = 3/2 \leftrightarrow S = 1/2$, defined as $K = (1-c)/c$. The linear portion that is observed between 290 and ~ 200 K can be accounted for by the relation³⁰

$$\ln K = (\Delta H_{\text{eff}}/RT) - (\Delta S_{\text{eff}}/R) \quad (6)$$

where ΔH_{eff} and ΔS_{eff} are the effective (or apparent) enthalpy and entropy changes associated with the spin transition. These two parameters could then be evaluated as

$$\Delta H_{\text{eff}} = 2.3 \text{ kJ} \cdot \text{mol}^{-1} \quad \Delta S_{\text{eff}} = 5.8 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$$

If the spin crossover is assumed to proceed through domain formation from nucleation centers,^{21,31,32} its cooperative character may be expressed in terms of a domain size n .^{30,31} For a smooth transition, n can be determined from the expressions^{30,33}

$$\Delta H_{\text{eff}} = n\Delta H \quad (7a)$$

or

$$\Delta S_{\text{eff}} = n\Delta S \quad (7b)$$

where ΔH and ΔS are the actual values of enthalpy and entropy changes. In the present family of compounds, the existence of a spin-crossover in the six-coordinate species was correlated to a pronounced axial elongation of the complex core.^{2,3} It ensues that, to a first approximation, the entropy-change component of orbital origin can be neglected and ΔS can be written as³

$$\Delta S = \Delta S_{\text{spin}} + \Delta S_{\text{vib}} \quad (8)$$

ΔS_{spin} and ΔS_{vib} denoting spin-only and vibrational entropy changes. In cobalt(II) compounds, the spin contribution, evaluated from $\Delta S_{\text{spin}} = R \ln [(2S+1)_{\text{HS}} - (2S+1)_{\text{LS}}]$, is found to be $5.8 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$. So, in the case of the present complex, ΔS_{eff} and ΔS_{spin} have nearly the same value, which, taking into account relations 7b and 8, indicates a domain size close to unity and thereby negligible cooperative effects; it can be noted that a $n \sim 1$ value has been reported by Stähl³⁴ for an iron(III) compound exhibiting a very smooth spin transition. Consequently, eq 7a gives ΔH_{eff}

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Table III. Summary of Main Features Related to $\text{Co}(\text{H}_2(\text{fsa})_2\text{en})\text{L}_n$ Complexes

compd	L	n	$\chi_{\text{M}}T$, $\text{cm}^3\cdot\text{mol}^{-1}\cdot\text{K}$		spin state ^a	g values ^b (low temp)			$\text{p}K_{\text{a}}(\text{L})^{\text{c}}$
			290 K	100 K					
A	2-Mepy	1	2.03	1.97	HS	6.08	2.50		5.99
B	3-OHpy	1	1.67	1.56	HS ^d	6.33	3.44	2.22	4.79
C	4-Mepy	1	0.69	0.55	LS	5.32	3.07	2.32 2.17 1.80	6.06
D	3-Mepy	2	2.29	2.21	HS ^e	6.32	4.37	2.22	5.75
E	3-NH ₂ py	2	2.30	2.20	HS ^e	6.55	4.54	2.21	6.04
F	3,5-Me ₂ py	2	2.39	2.31	HS ^e	4.52	2.19		6.15
G	4-Mepy	2	1.42	1.00	HS ↔ LS ^f	5.63	4.30	2.25	6.06
H	4- <i>t</i> -Bupy	2	2.56	0.66	HS ↔ LS ^g	4.35	2.23		5.99

^aHS = high spin; LS = low spin. ^bIn italics are values corresponding to low-spin species; other data are effective values associated with high-spin species. ^cValues relevant to the pyridine nitrogen atom. ^dKinetically controlled spin transition with largely predominant HS form. ^eExistence of a spin admixing with predominant $S = 3/2$ character. ^fVery smooth and incomplete spin transition. ^gDiscontinuous spin transition; $T_{\text{c}\downarrow} = 138$ K, $T_{\text{c}\uparrow} = 154$ K.

$\sim \Delta H$. Since the ΔH value can be considered as an upper limit for the energy gap Δ between the lowest lying doublet and quartet states, we obtain $\Delta \lesssim 194$ cm^{-1} .

This result must be compared with that we previously reported for the spin-crossover compound of the same family $\text{Co}(\text{H}_2(\text{fsa})_2\text{en})(\text{H}_2\text{O})_2$,³ viz. $\Delta \lesssim 161$ cm^{-1} . Moreover, it lies within the range of values (0–500 cm^{-1}) calculated for Δ by Kremer et al.¹² in the case of pseudooctahedral $\text{Co}(\text{terpy})_2\text{X}_2\cdot n\text{H}_2\text{O}$ complexes (terpy = terpyridine) on the basis of a Boltzmann distribution of electrons over the lowest lying doublet and quartet states. It can be noted that, for the G compound, the magnetic data cannot be accounted for in terms of a Boltzmann-type behavior, because of the large incompleteness of the transition at low temperatures.

For compound H, the variation of $\chi_{\text{M}}T$ as a function of T was determined between 290 and 70 K, first at decreasing and then at increasing temperatures, as indicated by the falling and rising arrows in Figure 13. The results are typical of a $S = 3/2 \leftrightarrow S = 1/2$ spin transition.

The lower and upper plateaus correspond to $\chi_{\text{M}}T = 0.63$ and 2.56 $\text{cm}^3\cdot\text{mol}^{-1}\cdot\text{K}$ ($\mu_{\text{eff}} = 2.24$ and 4.52 μ_{B}), respectively. The higher value is comparable with that found for the closely related spin-crossover compound $\text{Co}(\text{H}_2(\text{fsa})_2\text{en})(\text{py})_2$, viz. 2.61 $\text{cm}^3\cdot\text{mol}^{-1}\cdot\text{K}$. The existence of the relevant plateau indicates^{2,3} a large quenching of the orbital momentum of the octahedral $^4\text{T}_{1\text{g}}$ state, which is probably mainly induced by a significant axial distortion of the CoN_4O_2 core (vide supra). The lower $\chi_{\text{M}}T$ value is somewhat larger than that expected for a pure low-spin species (~ 0.46 $\text{cm}^3\cdot\text{mol}^{-1}\cdot\text{K}$), which provides evidence for the existence of a residual amount of high-spin molecules in the predominant low-spin isomer at low temperatures. This amount can be estimated at $\sim 8\%$.

The spin transition is of the discontinuous type and is centered around 138 K ($T_{\text{c}\downarrow}$) and 154 K ($T_{\text{c}\uparrow}$) for decreasing and increasing temperatures, respectively. The existence of a hysteresis effect ($\Delta T_{\text{c}} \sim 16$ K) shows the first-order character of the phenomenon. It can be noted that the T_{c} values are higher than those found for the related compounds $\text{Co}(\text{H}_2(\text{fsa})_2\text{en})(\text{py})_2$ ($T_{\text{c}\downarrow} = 115$ K, $T_{\text{c}\uparrow} = 127$ K)² and $\text{Co}(\text{H}_2(\text{fsa})_2\text{en})(\text{H}_2\text{O})_2$ ($T_{\text{c}\downarrow} = 81.5$ K, $T_{\text{c}\uparrow} = 84.6$ K).³

The EPR powder spectrum of compound H, obtained at 6 K, is in keeping with the magnetism data. The predominant low-spin species was identified by its strong component $g_{\perp} = 2.23$, which partially hinders the weak g_{\parallel} component located in the 2.0–2.1 range. This pattern is indicative of a nearly tetragonal axially elongated symmetry. The small feature at $g = 4.35$ was associated with the residual high-spin species.

An additional feature concerning the H complex is worth being pointed out. The magnetic behavior of a sample of the homologous square-pyramidal compound $\text{Co}(\text{H}_2(\text{fsa})_2\text{en})(4\text{-}t\text{-Bupy})$ —which was reported to be low spin²—containing $\sim 4\%$ of the six-coordinate H complex, was investigated. The spin transition of H was detected as an accident in the $\chi_{\text{M}}T$ vs. T curve, but the relevant T_{c} value, at decreasing temperatures, was found to be as low as ~ 120 K. This effect of T_{c} lowering by dilution of the metal ion was previously demonstrated in the case of some mixed-crystal series, viz. $[\text{Fe}_x\text{Zn}_{1-x}(2\text{-pic})_3]\text{Cl}_2\cdot\text{EtOH}$ ^{35,36} and $[\text{Fe}_x\text{Co}_{1-x}(2\text{-pic})_3]\text{Cl}_2\cdot\text{EtOH}$,³⁷ where 2-pic = 2-picolyamine, and $[\text{Fe}_x\text{M}_{1-x}(\text{phen})_2(\text{NCS})_2]$,³⁸ where M = Mn, Co, Ni, and Zn and phen = 1,10-phenanthroline, and was interpreted on the basis of the cooperative-domain model.

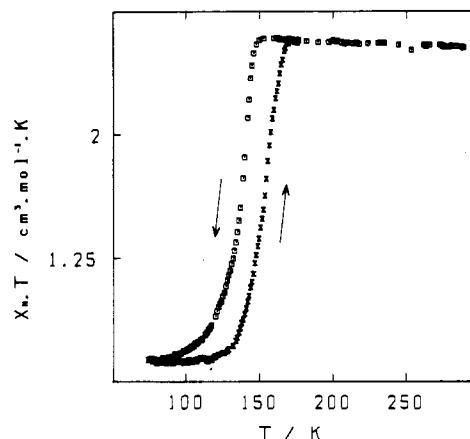


Figure 13. Temperature dependence of $\chi_{\text{M}}T$ for $\text{Co}(\text{H}_2(\text{fsa})_2\text{en})(4\text{-}t\text{-Bupy})_2$. Falling and rising arrows indicate decreasing and increasing temperatures, respectively. The branches of the hysteresis loop are centered at $T_{\text{c}\downarrow} = 138$ K and $T_{\text{c}\uparrow} = 154$ K.

$\text{pic})_3]\text{Cl}_2\cdot\text{EtOH}$,³⁷ where 2-pic = 2-picolyamine, and $[\text{Fe}_x\text{M}_{1-x}(\text{phen})_2(\text{NCS})_2]$,³⁸ where M = Mn, Co, Ni, and Zn and phen = 1,10-phenanthroline, and was interpreted on the basis of the cooperative-domain model.

Discussion

As seen above, the family of compounds of the general type $\text{Co}(\text{H}_2(\text{fsa})_2\text{en})\text{L}_n$ displays an interesting range of structural and magnetic properties: the variation of the axial ligand among a series of closely related substituted pyridines lead to five-coordinate and/or to six-coordinate complexes, in which the cobalt ion can exhibit a fully or an essentially high-spin state, a low-spin state, or a spin-crossover behavior. The main features concerning this study are summarized in Table III.

Let us consider the three compounds with square-pyramidal cores. In the cobalt(II) complexes presenting this geometry, the axial ligand field strength was shown by Hitchman²⁴ to have a small *direct* effect on the energy separation between the lowest lying doublet and quartet spin states, a larger field leading to a relative stabilization of the high-spin state. Moreover, Kennedy et al.¹³ have established that, in complexes of the types $\text{Co}(\text{salen})\text{L}$ and $\text{Co}(\text{salphn})\text{L}$, an increase in the axial ligand σ -donor ability (roughly reflected by the $\text{p}K_{\text{a}}$ value) gives rise to a lowering of the quartet level with respect to the doublet level.

On the basis of these results, the fact that Co(II) has a predominant $S = 3/2$ character in $\text{Co}(\text{H}_2(\text{fsa})_2\text{en})(3\text{-OHpy})$ while it is low-spin in $\text{Co}(\text{H}_2(\text{fsa})_2\text{en})(4\text{-Mepy})$ cannot be accounted for by basicity effects, since the $\text{p}K_{\text{a}}$ value of 3-OHpy (4.79) is significantly lower than that of 4-Mepy (6.06). Steric crowding

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being negligible in both complexes, this spin-state behavior could mainly result from a difference in the pyridine ring orientation around the Co–N axial bond. Likewise, the pK_a value of 2-Mepy (5.99) being very close to that of 4-Mepy, another cause than the σ -donor ability of L has to be considered in order to substantiate the high-spin nature of $\text{Co}(\text{H}_2(\text{fsa})_2\text{en})(2\text{-Mepy})$. In that case, steric hindrance effects are likely to play a prominent part in the phenomenon. The presence of a methyl group near the donor atom in 2-Mepy does not permit this ligand to closely approach the basal one and is therefore expected to cause a raising of the metal ion out of the equatorial plane. It follows that Co(II) is then subjected to a less intense ligand field than in the $L = 4\text{-Mepy}$ complex, which leads to a stabilization of the high-spin state. Moreover, this stabilization may be enhanced by the fact that the axial base, owing to its bulkiness, probably adopts a tilted position that diminishes the Co–L bond orbital overlap. A similar situation was encountered in the case of the related high-spin compound $\text{Co}(\text{salphn})(2\text{-MeImd})$, in which the metal ion was found to lie 0.452 Å out of the (N_2O_2) basal plane and the 2-MeImd moiety was found to be pushed back because of steric requirements.¹³

It is worth noting that, for $L = 4\text{-Mepy}$, both five-coordinate and six-coordinate compounds could be obtained by varying the method of preparation. The same holds true for $L = 4\text{-}t\text{-Bupy}$, the synthesis of the monoadduct having been previously described.² To our knowledge, only one other example of the existence of both homologous species in axial adducts of Co(II)–Schiff base complexes has been reported as yet;²³ it concerns the compounds $\text{Co}(\text{salphn})(\text{py})$ and $\text{Co}(\text{salphn})(\text{py})_2$. By contrast, any attempt to isolate the diadduct corresponding to $L = 3\text{-OHpy}$ and $L = 2\text{-Mepy}$ proved to be unsuccessful. These results can likely be accounted for, at least partly, on the basis of structural considerations. Indeed, in $\text{Co}(\text{H}_2(\text{fsa})_2\text{en})(4\text{-Mepy})$ and $\text{Co}(\text{H}_2(\text{fsa})_2\text{en})(4\text{-}t\text{-Bupy})$, which are low-spin species, the cobalt ion is expected to lie closer to the equatorial plane than in $\text{Co}(\text{H}_2(\text{fsa})_2\text{en})(3\text{-OHpy})$ and $\text{Co}(\text{H}_2(\text{fsa})_2\text{en})(2\text{-Mepy})$, which are essentially or fully high-spin, respectively;^{13,15,24,39,40} consequently, the binding of a second axial base must be easier in the first case.

Concerning the six-coordinate complexes, it is noteworthy that the apical ligands substituted in the 3-position lead to compounds with predominant high-spin character, when 4-substituted pyridines and pyridine itself^{1,2} give spin-crossover species. This can be explained neither by basicity effects (see Table III) nor by steric considerations. Besides, the L moiety symmetry does not seem to be involved, since the complexes obtained with asymmetrically and symmetrically substituted pyridines (e.g., 3-Mepy and 3,5-Me₂py) exhibit the same spin-state behavior. As in the case of the fivefold-coordinated compounds, we suggest this phenomenon to be the result of a difference in the orientation of the apical bases with respect to the equatorial Co–N and Co–O bonds. Indeed, this orientation is expected to affect the π -back-bonding from the metal atom to the substituted-pyridine moiety and hence the axial ligand field strength. A similar hypothesis was recently proposed by Geiger et al.⁴¹ to explain the differing solid- and solution-state magnetic moments in $\text{Fe}(\text{OEP})(2\text{-MeImd})_2\text{ClO}_4$ and by Scheidt et al.,⁴² on the basis of crystal structures, to account for the high-spin and low-spin states of $\text{Fe}(\text{TPP})(\text{py})(\text{NCS})$ and $\text{Fe}(\text{OEP})(\text{py})(\text{NCS})$, respectively (OEP and TPP are the dianions

of octaethylporphyrin and *meso*-tetraphenylporphyrin).

The low values of the doublet–quartet energy gap Δ found for the $L = 3\text{-Mepy}$, 3-NH₂py and 3,5-Me₂py diadducts (see Table III) show that these compounds are very near to presenting spin-crossover behavior. However, the tetragonal elongation of the complex core is likely to be insufficient to cause a lowering of the doublet level below the quartet ground state.

The spin transitions exhibited by $\text{Co}(\text{H}_2(\text{fsa})_2\text{en})(4\text{-}t\text{-Bupy})_2$ and $\text{Co}(\text{H}_2(\text{fsa})_2\text{en})(4\text{-Mepy})_2$ show quite different characteristics. The sharpness of the former (see Figure 13) reflects the cooperative nature of the phenomenon, which implies the formation of domains of like-spin molecules from nucleation centers.^{30,43,44} This cooperativity is known to be mainly induced by the variation in molecular volume (ΔV) that accompanies the spin-state conversion^{44,45} and is expected to be associated with a crystallographic phase change.^{43,44} The strong cooperativity observed in the present case is indicative of a large ΔV value. Moreover, the existence of a hysteresis effect provides evidence for the first-order character of the spin transition. It should be noted that this transition is one of the most abrupt ones ever reported for a cobalt(II) complex, the rare other examples mostly concerning compounds of the same family, namely $\text{Co}(\text{H}_2(\text{fsa})_2\text{en})(\text{py})_2$,^{1,2} $\text{Co}(\text{H}_2(\text{fsa})_2\text{en})(\text{H}_2\text{O})_2$,³ and to a lesser degree, $\text{Co}(\text{H}_2(\text{fsa})_2\text{phn})(\text{H}_2\text{O})_2$.⁴⁶

In the case of $\text{Co}(\text{H}_2(\text{fsa})_2\text{en})(4\text{-Mepy})_2$, the smoothness of the transition (see Figure 10) and the absence of hysteresis effect can be interpreted in terms of a very weak cooperative interaction. Indeed, domains are shown to play an insignificant part since their size is estimated to be $n \sim 1$. The two spin isomers are then assumed to form a solid solution within the same lattice.^{43,44} The phenomenon must not involve a structural phase change, and the ΔV value is certainly very small, as evidenced by the fact that the vibrational entropy term ΔS_{vib} is found to be negligible (for the discontinuous spin crossover of $\text{Co}(\text{H}_2(\text{fsa})_2\text{en})(\text{H}_2\text{O})_2$, ΔS_{vib} was calculated³ as 17.5 J·K⁻¹·mol⁻¹). Furthermore, the large incompleteness of the transition in the low-temperature range—the residual high-spin fraction being about 24%—may be accounted for by the trapping of high-spin molecules at some kind of defects of the low-spin-isomer lattice.^{44,47}

Let us now consider the critical temperatures of both spin transitions. The fact that the values obtained for $\text{Co}(\text{H}_2(\text{fsa})_2\text{en})(4\text{-}t\text{-Bupy})_2$ ($T_c \downarrow = 138$ K, $T_c \uparrow = 154$ K) are higher than those related to $\text{Co}(\text{H}_2(\text{fsa})_2\text{en})(\text{py})_2$ ($T_c \downarrow = 115$ K, $T_c \uparrow = 127$ K)² can be mainly related to the σ -donor ability of apical ligands, estimated from the pK_a values of 5.25 for pyridine and 5.99 for 4-*tert*-butylpyridine. The greater electron-donating capacity of the latter base with respect to the former enhances the stabilization of the doublet ground state and, hence, results in an increase of the critical temperature. In the case of the very gradual and incomplete transition exhibited by $\text{Co}(\text{H}_2(\text{fsa})_2\text{en})(4\text{-Mepy})_2$, it is not possible to estimate T_c , especially as the spin conversion proceeds above room temperature. It can only be inferred that this critical temperature is the highest one ever obtained for a spin transition in this family of compounds,^{1–3,46} which can be related to the high value found for the $\Delta H/\Delta S$ ratio, viz. 396 K.

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