indeed been proposed for the product formed on oxidation of (β-phthalocyaninato)chromium(II) by oxygen.[5]

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Registry No. Cr(TXP)Cl, 84151-96-2; Cr(TCP)Cl, 84151-95-1; Cr(TMP)Cl, 84151-94-0; Cr(TFP)Cl, 94904-25-3; Cr(TPFP)Cl, 94890-04-7; Cr(TFMP)Cl, 94890-05-8; Cr(TTP)Cl, 43145-39-7; Cr(OEP)Cl, 65024-11-5; Cr(TPP), 58344-06-2; CrO(TPP), 78833-34-8; CrO(TMP), 84151-99-5; CrO(TXP), 84151-98-4; CrO(TFP), 94890-06-9; CrO(TCP), 94890-07-0; CrO(TFMP), 94890-08-1; CrO(TPFP), 94890-09-2; (TPP)CrOCr(TPP), 80593-65-3; (TMP)CrOCr(TMP), 94890-10-5; (TCP)CrOCr(TCP), 94890-11-6; (TCP)CrOCr(TPP), 94904-26-4; (TMP)CrOCr(TPP), 94890-12-7; (TXP)CrOCr(TXP), 94904-27-5; (TTP)CrOCr(TTP), 94890-13-8; (TFP)CrOCr(TFP), 94904-28-6; (TPFP)CrOCr(TPFP), 94904-29-7; (OEP)CrOCr(OEP), 94928-85-5; Cr(TMP), 94890-14-9; Cr(TFMP), 94904-30-0; Cr(TXP), 94890-15-0; Cr(TCP), 94890-16-1; Cr(TPFP), 94890-17-2; Cr(TFP), 94904-31-1; Cr(OEP), 67113-83-1; Cr(TTP), 94890-18-3; Cr(TTT)Cl, 28110-70-5; Cr(TPP)(py)$_2$, 67113-84-2; CrO(TPP)(py), 94890-19-4; CrO(TMP)(py), 94890-20-7; Cr(TPP)OH, 33519-59-4; Cr(CO)$_6$, 13007-92-6; O$_2$, 7782-44-7.

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High-Spin ↔ Low-Spin Transition in Solid Co(H_2fsa$_2$en)(H_2O)$_2$ [H_4fsa$_2$en = *N*,*N'*-Ethylenebis(3-carboxysalicylaldimine)]: A Magnetic Investigation

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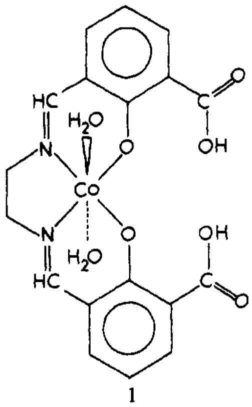
The sharp high-spin ($S = {}^3/_2$) ↔ low-spin ($S = {}^1/_2$) conversion of six-coordinate cobalt(II) in solid Co(H_2fsa$_2$en)(H_2O)$_2$ was investigated by variable-temperature magnetic susceptibility measurements and EPR spectroscopy (H_4fsa$_2$en = *N*,*N'*-ethylenebis(3-carboxysalicylaldimine)). Evidence was given for a small hysteresis effect of ca. 3 K, the transition being centered around 81.5 K ($T_c{\downarrow}$) and 84.6 K ($T_c{\uparrow}$) for decreasing and increasing temperatures, respectively. The temperature dependence of both $\chi_M T$ and $\mathcal{I}T$ products (χ_M = molar magnetic susceptibility, $\mathcal{I}$ = approximate intensity of EPR absorption) are in close agreement. About 9% of the molecules were found to persist in the high-spin form at low temperatures, and a substantial residue of low-spin species, estimated afterward to ca. 6%, was detected in the dominant high-spin form at high temperatures. The magnetic properties indicate a degeneracy removal of the $^4T_{1g}$ term and, hence, a large distortion of the [CoN_2O_4] core in the high-spin phase. The *g* value pattern of the low-spin phase ($g_1 = 2.661$, $g_2 = 2.318$, $g_3 = 2.031$) shows that the core deformation is then constituted by an axial elongation and a rhombic distortion. The thermodynamic model of Slichter and Drickamer was applied to the magnetic data. A simple method was developed so as to enable the calculation of the interaction term ($\Gamma = 1556$ J·mol^{-1}) and of the enthalpy and entropy changes associated with the spin transition ($\Delta H = 1.93$ kJ·mol^{-1} and $\Delta S = 23.3$ J·K^{-1}·mol^{-1}). The domain size was estimated to be $n \sim 25$. These results are discussed. In particular, the relatively high value of *n* is related to a rather strong cooperative effect, which may explain the abruptness of the transition; the large value of ΔS, as compared with the magnetic contribution, is accounted for by the vibrational changes associated with the spin conversion.

Introduction

Investigations concerning thermally induced spin transitions in cobalt(II) (d^7) complexes are still relatively rare,[1-14] as compared with those related to iron(II) (d^6) and iron(III) (d^5) compounds. Most of the reported physical experiments were performed on solid-state samples,[1-12] and the high-spin (HS) ↔ low-spin (LS) conversions ($S = {}^3/_2 \leftrightarrow S = {}^1/_2$) were generally found to be gradual, often extending over more than 100 K.

The present work deals with the magnetic properties of Co(H_2fsa$_2$en)(H_2O)$_2$ (see 1), H_4fsa$_2$en being the Schiff base resulting from the 2:1 condensation of 3-formylsalicylic acid with ethylenediamine. The spin crossover of this compound, previously reported by Kahn et al.,[8] takes place within a temperature range of a few degrees and is, to our knowledge, the most abrupt one ever observed in cobalt complexes. We are aware of only two other Co(II) compounds displaying rather sharp spin changes: Co(H_2fsa$_2$en)(py)$_2$,[11] which is closely related to the title complex, with two pyridine ligands replacing the water molecules in apical positions; Co(saloph)benzimd,[12] a five-coordinate complex that undergoes a very incomplete HS → LS conversion (saloph = dianion of the Schiff base *N*,*N'*-*o*-phenylenebis(salicylaldimine); benzimd = benzimidazole).



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The magnetic behavior of Co(H_2fsa$_2$en)(H_2O)$_2$ polycrystalline samples was investigated by means of variable-temperature

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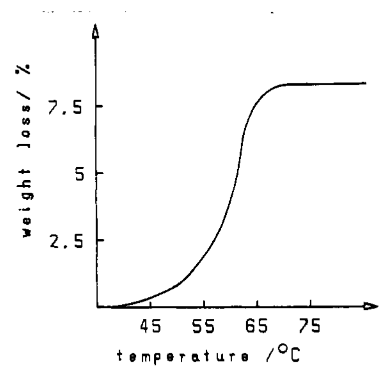

Figure 1. Thermogram of $Co(H_2fsa_2en)(H_2O)_2$. Weight loss for the removal of both water molecules: calcd, 8.01%; found, 8.16%.

magnetic susceptibility measurements and EPR spectra. The enthalpy and entropy changes characterizing the transition, and also the interaction parameter between cobalt centers and the average domain size, were deduced from experimental data.

Experimental Section

Syntheses. 3-Formylsalicylic acid was prepared by the method of Duff and Bills.[15] The Schiff base H_4fsa_2en was obtained by refluxing this acid with ethylenediamine in a 2:1 mole ratio, using absolute ethanol as a solvent. The yellow precipitate that formed was isolated by filtration, washed with absolute ethanol, and dried under vacuum.

The procedure previously described by Kahn et al.[8] to synthesize the complex $Co(H_2fsa_2en)(H_2O)_2$ was slightly modified. A solution of cobalt(II) acetate tetrahydrate (70 mg) in water (4 mL) was added dropwise to a suspension of H_4fsa_2en (100 mg) in ethanol (5 mL) heated at 60 °C. The reaction mixture was stirred for 45 min at 60 °C. $Co(H_2fsa_2en)(H_2O)_2$ was obtained as an orange-red microcrystalline powder that was collected, washed with ethanol, and dried under argon at room temperature. The synthesis was entirely carried out in an argon atmosphere, the solvents having been carefully deaerated before use. Anal. Calcd for $CoC_{18}H_{18}O_8N_2$: C, 48.12; H, 4.04; N, 6.23; O, 28.49. Found: C, 48.12; H, 4.01; N, 6.29; O, 28.29.

Both water molecules of $Co(H_2fsa_2en)(H_2O)_2$ are removed simultaneously when the temperature is raised above $\simeq$70 °C, as shown by the thermogravimetric curve of the complex, depicted in Figure 1. Accordingly, the square-planar compound $Co(H_2fsa_2en)$ was obtained by heating $Co(H_2fsa_2en)(H_2O)_2$ in solid phase at 85 °C for 3 h. Anal. Calcd for $CoC_{18}H_{14}O_6N_2$: C, 52.32; H, 3.41; N, 6.78; O, 23.24. Found: C, 51.85; H, 3.40; N, 6.82; O, 23.60.

Physical Measurements. Magnetic susceptibility measurements in the 4–300 K temperature range were carried out on polycrystalline samples weighing about 6 mg, with a Faraday-type magnetometer equipped with a continuous-flow cryostat. $HgCo(NCS)_4$ was used as calibrant. The molar susceptibilities were corrected for ligand diamagnetism with Pascal's constants.[16] The corrections were estimated at -217×10^{-6} and -191×10^{-6} $cm^3 \cdot mol^{-1}$ for $Co(H_2fsa_2en)(H_2O)_2$ and $Co(H_2fsa_2en)$, respectively. The applied magnetic fields were in the range 0.3–0.6 T. The independence of the susceptibility against the magnetic field was checked for both complexes at room temperature. The uncertainty on the temperature was about 0.1 K and on the molar susceptibility about 10^{-4} $cm^3 \cdot mol^{-1}$.

Variable-temperature EPR spectra were obtained on powdered samples with a Bruker Model ER 200D X-band spectrometer equipped with an Oxford Instruments helium-flow cryostat. The klystron frequency was determined with a Hewlett-Packard frequency meter. The magnetic field was measured with a Hall probe, a 100-kHz field modulation being applied. The samples were sealed under vacuum in quartz tubes.

The thermograms were performed with an Ugine-Eyraud Model B 60 balance, equipped with a Dam Model R.T. 64 temperature controller.

Data Analysis

Magnetic Data. The molar magnetic susceptibility χ_M of $Co(H_2fsa_2en)(H_2O)_2$ was measured between 294 and 15 K, with decreasing ($T\downarrow$) and increasing ($T\uparrow$) temperatures, successively. The $\chi_M T$ vs. T curves (Figure 2) show that the spin transition is of the discontinuous type, taking place for the most part (~80%) over a narrow interval of ca. 4 K, and gives evidence for a hysteresis effect of ca. 3 K, the transition being centered around 81.5 K ($T_c\downarrow$) and 84.6 ($T_c\uparrow$) for decreasing and increasing temperatures, respectively. Both features are indicative of a rather strong cooperative interaction between the individual complexes, with formation of domains in which all cobalt atoms have the same spin;[17] moreover, the existence of a hysteresis effect points out the first-order character of the phase transition. It should be noted that the above results are somewhat different from those previously obtained for the homologous complex $Co(H_2fsa_2en)(py)_2$,[11] which undergoes a slightly more gradual transition (within ca. 10 K for $T\downarrow$ and ca. 5 K for $T\uparrow$) and exhibits a more pronounced hysteresis (ca. 12 K, with $T_c\downarrow \simeq 115$ K and $T_c\uparrow \simeq 127$ K).

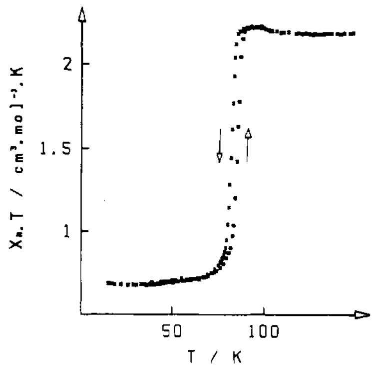

Figure 2. Temperature dependence of $\chi_M T$ for $Co(H_2fsa_2en)(H_2O)_2$. Falling and rising arrows indicate decreasing and increasing temperatures, respectively. The branches of the hysteresis loop are centered at $T_c\downarrow \simeq 81.5$ and $T_c\uparrow \simeq 84.6$ K.

The temperature-independent $\chi_M T$ values obtained for $Co(H_2fsa_2en)(H_2O)_2$, at both high temperatures (2.180 $cm^3 \cdot mol^{-1} \cdot K$ or $\mu_{eff} = 4.18$ μ_B) and low-temperatures (0.680 $cm^3 \cdot mol^{-1} \cdot K$ or $\mu_{eff} = 2.33$ μ_B), lie approximately in the ranges expected for the cobalt(II) HS form—with partially quenched angular momentum—and LS form, respectively. If the coordination around the metal were strictly octahedral, the effect of spin–orbit coupling on the lowest lying quartet state $^4T_{1g}$ would involve a continuous decrease of $\chi_M T$ upon cooling. The observed Curie law indicates a removal of the $^4T_{1g}$ term degeneracy, as in the pyridine diadduct,[11] giving evidence for a large distortion of the octahedron; in particular, both water molecules are probably located relatively far from the cobalt atom, as suggested by their easy elimination when heating (Figure 1). However, the $^4T_{1g}$ term splitting alone does not seem sufficient to account for the low $\chi_M T$ value in the high-temperature range (the corresponding value for $Co(H_2fsa_2en)(py)_2$, which is fully in its high-spin form, is 2.61 $cm^3 \cdot mol^{-1} \cdot K$ or $\mu_{eff} = 4.57$ μ_B). We shall see hereafter, from EPR data, that a substantial proportion of $Co(H_2fsa_2en)(H_2O)_2$ is in the LS form at high temperatures and also that a residual HS fraction subsists at low temperatures. Furthermore, it can be observed in Figure 2 that the upper part of both $\chi_M T$ vs. T curves is not entirely a "plateau". the round feature that exists in the vicinity of 95 K may be due to some instability in the domain formation, just before (for $T\downarrow$) or after (for $T\uparrow$) the transition.

All the above results, in contrast with those previously reported for other spin-crossover systems[18] and in particular for $Co(H_2fsa_2en)(py)_2$,[11] were found to be independent of the sample preparation.

It should be noted that intermolecular bonding between the water hydrogen atoms and the C=O groups probably plays a part in the spin transition of $Co(H_2fsa_2en)(H_2O)_2$ by alterating the ligand field[19,20] and/or by favoring the phenomenon propagation. Evidence for these hydrogen bonds was given by the ν(C=O)

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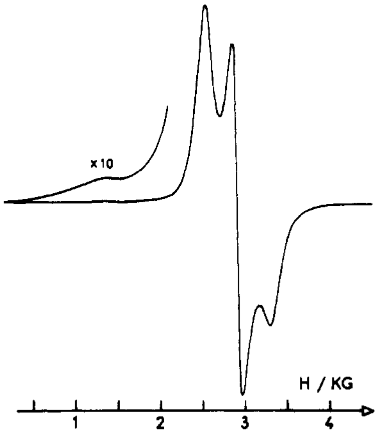

Figure 3. Polycrystalline powder EPR spectrum of $Co(H_2fsa_2en)(H_2O)_2$ at 20 K.

stretching mode frequency, which is lower in the water diadduct (1670 cm^{-1}) than in the pyridine diadduct (1703 cm^{-1}).

EPR Spectra. Polycrystalline powder EPR spectra of $Co(H_2fsa_2en)(H_2O)_2$ were carried out as a function of temperature by cooling the samples from 300 to 4 K. The results are typical of a cobalt(II) spin doublet ground state. The spectrum obtained at 20 K is shown, as an example, in Figure 3; the g value pattern ($g_1 = 2.661$, $g_2 = 2.318$, $g_3 = 2.031$) is indicative not only of an axially elongated environment of the metal ion but also of a pronounced rhombic distortion. So, the rhombicity g_1–g_2 is found to increase drastically on passing from pyridine ($g_1 = 2.289$, $g_2 = 2.206$, $g_3 = 2.046$)[11] to water as axial ligands.

The $\chi_M T$ product, calculated at low temperature according to the expression

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

where N, β, and k have their usual meaning, $S = {}^1/_2$, and $\overline{g^2} = (g_1^2 + g_2^2 + g_3^2)/3$, has a lower value (0.518 cm^3·mol^{-1}·K) than the experimental one (0.680 cm^3·mol^{-1}·K), thus substantiating the presence of some amount of HS species in the dominant LS form. By assuming that 6% of the molecules persist in the HS form at high temperatures—which will be further justified—and that both HS and LS forms obey Curie laws, the fraction of HS species at low temperatures could be estimated at ~9%. It is responsible for the weak signal that can be observed near $g = 5.0$ in Figure 3. The transition being of the discontinuous type, this residual HS fraction may be formed of crystallites that, owing to their too small size, cannot undergo the crystallographic phase change that is supposed to trigger the spin conversion.[21]

All of the spectra recorded between ~8 and 4 K were found to have the same shape. At higher temperatures, EPR signals are still observed, but they are less resolved in consequence of the broadening of lines due to the decrease of spin–lattice relaxation times. In particular, above ~150 K, the spectra only exhibit one broad feature centered at $g \simeq 2.3$. This last result indicates the presence of some amount of LS species in the high-temperature range where $\chi_M T$ has the nearly constant value 2.180 cm^3 mol^{-1}·K (see Figure 2).

Approximate absorption intensities ($\mathcal{J}$) were determined between 55 and 90 K for the well-shaped central signal at $g = 2.318$, and $\mathcal{J}T$ products were plotted against T (Figure 4). Defining ΔH as the peak-to-peak width and $2Y$ as the peak-to-peak derivative amplitude in the recorded EPR spectra, $\mathcal{J}$ values were obtained according to the relation[22]

$$\mathcal{J} \propto Y(\Delta H)^2$$

by taking into account the following parameters: amplifier gain, field modulation amplitude, and incident microwave power.

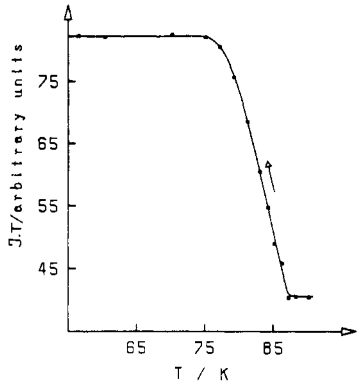

Figure 4. Temperature dependence of $\mathcal{J}T$ for $Co(H_2fsa_2en)(H_2O)_2$. $\mathcal{J}$ is the approximate intensity of EPR absorption, calculated as specified in the text. EPR spectra were recorded for decreasing temperatures.

$\mathcal{J}$ varies as the molar magnetic susceptibility of the LS form.[23,24] So, since $\chi_M T$ has been found to follow the Curie law at low temperature, $\mathcal{J}T$ varies as the LS form concentration. Consequently, outside the spin transition region, this product is expected to be temperature independent. Figure 4 shows that this property is actually checked above ≃87 K and below ≃74 K. The sharp increase in $\mathcal{J}T$ values, observed between ≃87 and ≃80 K, gives further evidence of the spin conversion. The transition is found to be centered at ≃82 K, beginning abruptly at ~87 K and ending smoothly from ~78 K to reach its equilibrium near 74 K. These results are in good agreement with those obtained from magnetic data.

In order to point out a possible alteration of $Co(H_2fsa_2en)(H_2O)_2$ in EPR tubes, magnetic susceptibility measurements were carried out at room temperature on the samples previously utilized to record EPR spectra. The values obtained for $\chi_M T$ (~1.65 cm^3·mol^{-1}·K) show that about one-third of spin-crossover molecules was converted into the square-planar species $Co(H_2fsa_2en)$ by loss of water ligands. However, pure samples of this latter compound, for which $\chi_M T$ values characteristic of Co(II) LS form were obtained (≃0.60 cm^3·mol^{-1}·K), happened surprisingly to be EPR silent, even at 4 K. This point is worth being further investigated. Whatever the origin of this phenomenon may be, the presence of a square-planar complex was found not to significantly modify the EPR spectra of $Co(H_2fsa_2en)(H_2O)_2$.

Phenomenological Interpretation

According to Slichter and Drickamer[25] who developed a thermodynamic description of spin-crossover systems based on the assumption that HS and LS molecules are statistically distributed and form regular solutions, the molar Gibbs free energy of such systems can be expressed as

$$G = cG_{HS}(p,T) + (1-c)G_{LS}(p,T) + \Gamma(p,T)c(1-c) - T\sigma_{mix} \tag{1}$$

Here, c is the HS species fraction, G_{HS} and G_{LS} are the Gibbs free energy terms of one high-spin or low-spin mole, respectively, σ is the mixing entropy contribution, and Γ is an interaction term taking into account the fact that a change in the ligand field at a given ion depends on the spin conversions of neighboring ions. Therefore, Γ reflects the strength of cooperative intermolecular interactions. At equilibrium the condition $(\delta G/\delta c)_{p,T} = 0$ is fulfilled, which yields

$$\ln K = [\Delta G(p,T) + \Gamma(p,T)(1-2c)]/RT \tag{2}$$

with $K = (1-c)/c$ and $\Delta G = G_{HS} - G_{LS}$, R being the perfect gas constant per mole. At fixed pressure, if ΔH, ΔS, and Γ were

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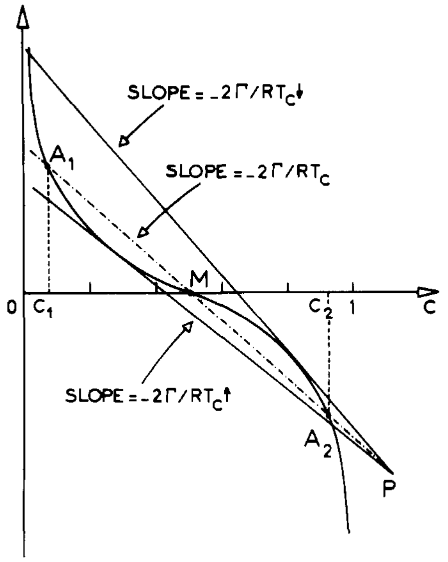

Figure 5. Graphical solution of eq 3, showing the intersection of the curve $\ln [(1 - c)/c] = f(c)$ with the straight lines of slopes $-2\Gamma/RT$ drawn through the point P (c = HS fraction). To make the figure clearer, the curvature of the logarithmic plot was largely amplified.

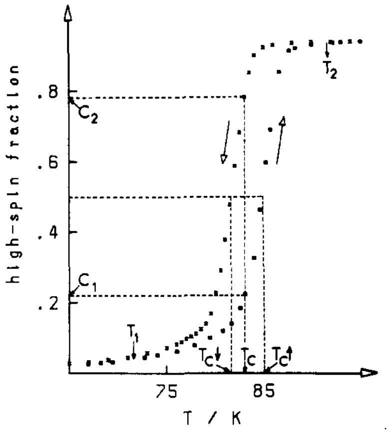

Figure 6. Temperature dependence of the HS fraction c, normalized between 0 and 0.94. T_1 and T_2 correspond to the junction points of the hysteresis branches. T_c↓ (81.6 K) and T_c↑ (85.0 K) are obtained from $c = 0.5$. T_c (82.9_6 K) is determined from c_1 and c_2 such that $c_1 + c_2 = 1$.

assumed to be temperature independent (ΔH and ΔS being the molar enthalpy and entropy changes), eq 2 can be written

$$\ln K = \frac{\Delta H + \Gamma(1 - 2c)}{RT} - \frac{\Delta S}{R} \tag{3}$$

If ΔH, ΔS, and Γ are known, c may be determined for each temperature by intersecting the curve $\ln K = f(c)$ with the straight lines of slope $-2\Gamma/RT$ drawn through the point P ($y = -\Delta S/R$, $x = {}^1/_2 + \Delta H/2\Gamma$). Such a construction is shown in Figure 5. For there to be a jump in the temperature dependence of c, the straight lines must be steeper than the central region (slope -4) of the logarithmic curve, which implies $\Gamma > 2RT_c$↑. Two values of c corresponding to a minimum of G are then found in the range T_c↓–T_c↑, as expected for a hysteresis behavior, the intermediate third value representing a system out of equilibrium.

This model has been applied by König et al.[26] in the case of abrupt spin transitions exhibited by iron(II) complexes.[26] The authors have calculated Γ for several values of ΔS, but the only comparison of the computed c values with the experimental ones could not enable them to choose between the sets of parameters.

Table I. Normalized Values of the High-Spin Fraction c, in the Vicinity of the Spin Transition Critical Temperature

	T, K							
	81.5	82.0	82.5	83.0	83.5	84.0	84.5	85.0
$c(T$↓$)$	0.478	0.588	0.682	0.784	0.852	0.901	0.917	0.924
$c(T$↑$)$	0.136	0.156	0.184	0.224	0.273	0.326	0.395	0.506

We have developed a method allowing the determination of ΔS, ΔH, and Γ from the temperature dependence of c.

Figure 6 shows the plot, as a function of T, of the c values obtained from magnetic susceptibility measurements on $Co(H_2fsa_2en)(H_2O)_2$. Calculation of these values was carried out by smoothing the T↑ and T↓ experimental curves $\chi_M T = f(T)$, by straightening them in the vicinity of ~95 K (see Figure 2) and by normalizing the results so as to obtain $c = 0$ at low temperatures and $c = 0.94$ (i.e., 6% of the HS form in the LS form, percentage that will be justified hereafter) at high temperatures.

It clearly appears that eq 3 is not able to *closely* reproduce the experimental data: this equation implies that the slope of the previous curve is infinite for T_c↓ and T_c↑ and that T_c↓ = T_1 and T_c↑ = T_2, T_1 and T_2 being the border temperatures between the regions where there exist one and two suitable solutions for c (see Figure 6). Moreover, it does not allow one to account for the transition incompleteness at low temperatures. Nevertheless, we shall see further that for satisfying values of ΔH, ΔS, and Γ to be obtained from eq 3 we have to only consider the experimental points located within a narrow temperature range in the vicinity of the transition and to normalize the c values as specified above. It should be noted that the three parameters can then be considered as temperature independent.

For $c = {}^1/_2$, eq 3 leads to the relation

$$\Delta H = T_c \Delta S \tag{4}$$

that enables one to define T_c, the "actual" critical temperature of the spin transition. As shown in Figure 5, the straight line of slope $-2\Gamma/RT_c$ drawn through the point P intersects the curve $\ln K = f(c)$ at points A_1, M, and A_2, giving the three roots $c = c_1$, ${}^1/_2$, and c_2, respectively. It can be easily demonstrated tha the only thermodynamically stable solutions are those arising from A_1 and A_2. Moreover, since M is the inversion center of the logarithmic curve, c_1 and c_2 are related by

$$c_1 + c_2 = 1 \tag{5}$$

Consequently, T_c *can also be defined as the temperature, within the hysteresis loop, for which the c values obtained at* T↓ *and* T↑ *are symmetrical with regard to* ${}^1/_2$.

According to this latter definition, it is possible to deduce T_c, c_1, and c_2 from the dependence in temperature of the normalized c values (Table I). We find (see Figure 6) that $T_c = 82.9_6$ K, $c_1 = 0.222$, and $c_2 = 0.778$. For these values, by taking the eq 4 condition into account, we get the simplified form of eq 3

$$\ln \frac{1 - c_{1,2}}{c_{1,2}} = \frac{\Gamma(1 - 2c_{1,2})}{RT_c} \tag{6}$$

leading to $\Gamma = 1556\ \mathrm{J{\cdot}mol^{-1}}$.

Point P of the graphical method is then obtained by intersecting the tangents of slopes $-2\Gamma/RT_c$↓ and $-2\Gamma/RT_c$↑ to the right-hand side and to the left-hand side of the curve $\ln K = f(c)$, respectively, with the straight line of slope $-2\Gamma/RT_c$ passing through M (see Figure 5). T_c↓ and T_c↑ are the temperatures corresponding to a normalized c value of ${}^1/_2$: T_c↓ = 81.6 K and T_c↑ = 85.0 K (see Figure 6). Coordinates of P are found to be $x = 1.123 \pm 0.010$, $y = 2.80 \pm 0.04$. It ensues that $\Delta S = 23.3\ \mathrm{J{\cdot}K^{-1}\ mol^{-1}}$ and $\Delta H = 1.93\ \mathrm{kJ{\cdot}mol^{-1}}$. The uncertainty due to the graphical method ($\pm 0.3\ \mathrm{J{\cdot}K^{-1}\ mol^{-1}}$ for ΔS and $\pm 0.03\ \mathrm{kJ{\cdot}mol^{-1}}$ for ΔH) is probably much smaller than the effective one.

In Figure 7, $\ln K$ is plotted as a function of $1/T$ for increasing and decreasing temperatures, in the immediate neighborhood of the spin transition (the formal equilibrium constant $K = (1 - c)/c$ being calculated with normalized c values). According to the

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[26] (a) König, E.; Ritter, G. *Solid State Commun.* **1976**, *18*, 279. (b) König, E.; Ritter, G.; Irler, W.; Nelson, S. . *Inorg. Chim. Acta* **1979**, *37*, 169.

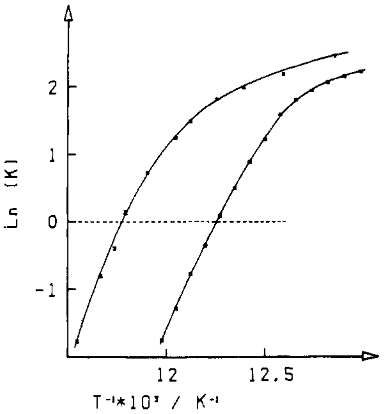

Figure 7. Plot of ln *K* vs. T^{-1} for $Co(H_2fsa_2en)(H_2O)_2$: □, cooling; ×, heating.

thermodynamical model established by Gütlich et al.,[27] the slope of these curves can be expressed as

$$\frac{d \ln K}{d(1/T)} = n\Delta H/R \equiv \Delta H_{eff}/R \qquad (7)$$

In this relation, *n* denotes a domain size that is expected to be correlated with the strength of the cooperative coupling (all domains are assumed to consist of an equal number *n* of like spin molecules). Slope measurements performed on the curves ln *K* = $f(1/T)$ at points $T_c\uparrow$ and $T_c\downarrow$ (ln *K* = 0) yielded $\Delta H_{eff} \simeq 51$ kJ·mol^{-1} at $T_c\uparrow$ and 47 kJ·mol^{-1} at $T_c\downarrow$; hence, the approximate ΔH_{eff} value at T_c is 49 kJ·mol^{-1}, leading to $n \approx 25$.

Discussion

The above results suggest the following comments:

(a) The interaction term value (1556 J·mol^{-1}) is consistent with the condition $\Gamma > 2RT_c\uparrow = 1413$ J·mol^{-1} required in order to obtain a jump on the curve $c = f(T)$. This datum is worth being compared to the Γ value calculated with $\Delta S = 50.0$ J·K^{-1}·mol^{-1} for the iron(II) complex $Fe(4,7\text{-}(CH_3)_2phen)_2(NCS)_2$[26a] (phen = 1,10-phenanthroline): $\Gamma = 2311$ J·mol^{-1} $> 2RT_c\uparrow = 2020$ J·mol^{-1}. Indeed this compound exhibits a spin transition, the abruptness and hysteresis of which are very similar to those observed in the case of $Co(H_2fsa_2en)(H_2O)_2$.

Furthermore, as the domain size may also serve as a measure of the cooperative interaction strength, the value $n \simeq 25$ we obtained at the temperature T_c seems of reasonable magnitude: it is indicative of a rather strong intermolecular coupling, which agrees with the fact that the spin transition is relatively abrupt. As expected, this domain size is found to be smaller than those estimated by Sorai and Seki for $Fe(phen)_2(NCS)_2$ ($n = 95$) and $Fe(phen)_2(NCSe)_2$ ($n = 77$)[28] and larger than those determined by Gütlich et al. for $Fe(2\text{-picolylamine})_3Cl_2\cdot C_2H_5OH$ (average domain size $\bar{n} \simeq 3.5$)[27] and by Stähl for $Fe(4\text{-morpholinecarbodithioato})_3\cdot CH_2Cl_2$ ($n \sim 1$).[29] Indeed, the first two iron compounds are strongly coupling systems, which exhibit almost discontinuous spin transitions taking place within a few Kelvin. On the contrary, the spin transitions of the last two complexes are of the continuous type, the first one occurring over a temperature range as wide as nearly 100 K, the second one being still much smoother.

(b) The value of ΔS (23.3 J·K^{-1}·mol^{-1}) is much greater than that expected for a change in spin only, viz. $\Delta S_{spin} = R \ln [(2S + 1)_{HS}/(2S + 1)_{LS}] = 5.8$ J·K^{-1}·mol^{-1}. As the $[CoN_2O_4]$ core of $Co(H_2fsa_2en)(H_2O)_2$ has lower than octahedral symmetry, the entropy variation of orbital origin can be assumed to be negligible, as a consequence of the orbital degeneracy removal of HS and LS ground states. Accordingly, the additional entropy must be considered as arising from the vibrational changes associated with the spin transition. The ratio of this vibrational contribution (ΔS_{vib}) with regard to the electronic one ($\Delta S_{el} \simeq \Delta S_{spin}$) is found to be $\simeq 3.0$. It is of the same order of magnitude than the one obtained for $Fe(phen)_2(NCS)_2$ ($\simeq 2.6$) or $Fe(phen)_2(NCSe)_2$ ($\simeq 2.8$) from heat capacity measurements.[28] The low value of ΔS_{vib} ($\simeq 17.5$ J·K^{-1}·mol^{-1}) as compared with that related to both iron(II) compounds (~ 36 J·K^{-1}·mol^{-1}) can be accounted for by the fact that the spin conversion involves a single electron in Co(II) and two electrons in Fe(II). Indeed, a large part of ΔS_{vib} is expected to result from changes in the metal–ligand stretching frequencies—the low spin state possessing the higher wavenumbers and the variations in coordinative bond lengths can be assumed to be approximately proportional to the number of electrons implied in the transition.[30]

Moreover, eq 3 shows that, at high temperatures, ln *K* tends toward $-\Delta S/R$, thus yielding a value of 6% for the low-spin residues in the high-spin form. Obviously, we find here the percentage previously used to calculate the normalized *c* values, since this percentage is obtained according to a self-consistent process.

(c) Finally, it should be noted that the value obtained for ΔH (1.93 kJ·mol^{-1}; i.e., $\simeq 161$ cm^{-1}) gives an upper limit for the difference in energy ΔE between HS and LS ground states. This gap appears to be relatively narrow, as compared with the ranges $\Delta E = 1110$–1700 cm^{-1}[2] and $\Delta E = 300$–500 cm^{-1}[9] obtained for various $[Co(terpy)_2]^{2+}$ complexes (terpy = 2,2′,2″-terpyridine). Such a small doublet–quartet separation may be accounted for by the low critical temperature of the phenomenon, one of the lowest ever found for a spin transition.

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Registry No. 1, 95532-62-0.

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