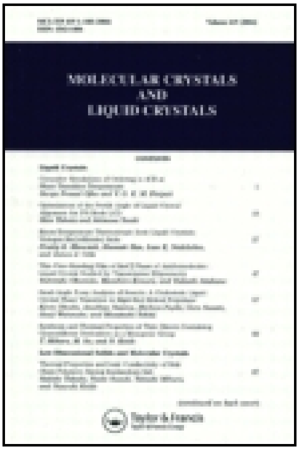

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Temperature-, Pressure- and Light-Induced Electronic Spin Conversions in Transition Metal Complexes

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TEMPERATURE-, PRESSURE- AND LIGHT-INDUCED ELECTRONIC SPIN CONVERSIONS IN TRANSITION METAL COMPLEXES.

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Abstract High spin ↔ low spin electronic spin crossovers may be observed in a number of transition metal complexes when the ligand-field and electron-pairing energies happen to be comparable in magnitude. They are obtained under the effect of an external perturbation such as a variation of temperature, a variation of pressure or an irradiation with light. These three ways of inducing spin conversions are presented.

INTRODUCTION

In a number of transition metal molecular compounds, the metal ion may exhibit an electronic high-spin state (HS) ↔ low-spin state (LS) inter-conversion under the effect of an electronic perturbation. This occurs when the ligand field splitting and the mean spin-pairing energies are comparable in magnitude. Most of the studies reported hitherto on this phenomenon concern iron(II), iron(III), and cobalt(II) complexes[1-8]. As an example, for an iron(II) ion in octahedral environment , the HS ↔ LS crossover can be represented as:

$$(t_{2g})^4(e_g)^2 \leftrightarrow (t_{2g})^6 \quad \text{or} \quad {}^5T_{2g} \leftrightarrow {}^1A_{1g}$$

In that case, the potential energy curves of the two electronic isomers present the following relative characteristics (see Figure 1): with regard to the LS form well, the HS form well is i) shifted horizontally by ΔR, the metal-ligand bond-length variation associated with the spin change and ii) shifted vertically by $\Delta E \approx \Delta H = H_{HS} - H_{LS} > 0$ (H denoting molar enthalpy), which is weak, of the order of RT.

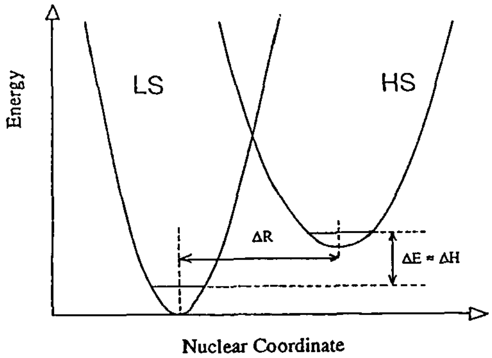

FIGURE 1 Potential energy curves.

Most of the spin crossovers reported to date were obtained by varying temperature. However, the phenomenon can also be induced by a variation of pressure or an irradiation with light . We shall now elaborate on these three ways of getting a spin change.

THERMALLY-INDUCED SPIN CROSSOVERS

It is clear that the spin change is accompagnied by a noticeable entropy variation $\Delta S = S_{HS} - S_{LS}$ which is positive, as a consequence of the higher spin degeneracy and density of vibrational states in the HS form than in the LS form; for iron(II) complexes, ΔS lies generally in the range 40 - 70 J mol^{-1} K^{-1}. Therefore, the relative stability of the two spin isomers is determined by the difference in Gibbs free energy $\Delta G = G_{HS} - G_{LS} = \Delta H - T\Delta S$. At low temperatures, the term TΔS is low, compared to ΔH; ΔG is positive; the stable form is LS. At sufficiently high temperatures, TΔS overbalances ΔH; ΔG is negative; the stable form is HS. This shows that thermally-induced spin crossovers are entropy driven.

Thus, when molecules do not interact significantly, in solutions for instance, the LS fraction / HS fraction ratio can be obtained from:

$$\mathrm{Ln}(n_{LS} / n_{HS}) = \Delta G / RT \qquad (1)$$

Spin crossovers develop then smoothly as a function of temperature.

In the solid state, the existence of intermolecular interactions imparts a cooperative character to the phenomenon. The stronger these interactions, the more pronounced the cooperativity and the sharpness of the transition are. The spin change may occur within a few Kelvin or extend over a wide temperature range (up to more than 100 K). It can be accounted for on the basis of a thermodynamical model derived from the theory of regular solutions[9]. The n_{LS} / n_{HS} ratio is then expressed as:

$$\mathrm{Ln}(n_{LS} / n_{HS}) = [\Delta H + \Gamma(1-2n_{HS})]/RT - \Delta S/R \qquad (2)$$

where Γ is an interaction parameter. For weak interactions, $\Gamma \approx 0$ and equation (2) is restricted to equation (1). For strong interactions, evidence is provided for a discontinuity of the transition and the existence of a hysteresis effect.

A number of abrupt spin conversions occurring with a thermal hysteresis were reported. The corresponding molecular systems have a bistable character in the temperature range of the hysteresis loop and, consequently, may present a memory effect[10]. As an example, Figure 2 shows the transition relative to the iron(II) compound $\mathrm{Fe(py)_2(bpym)(NCS)_2}$, where py = pyridine and bpym = 2,2'-bipyrimidine[11] : 80 % of the spin change takes place within 1 K and the hysteresis width is 3 K. Some transitions of this type were found to occur in the vicinity of room temperature or even above (for instance see ref. 12).

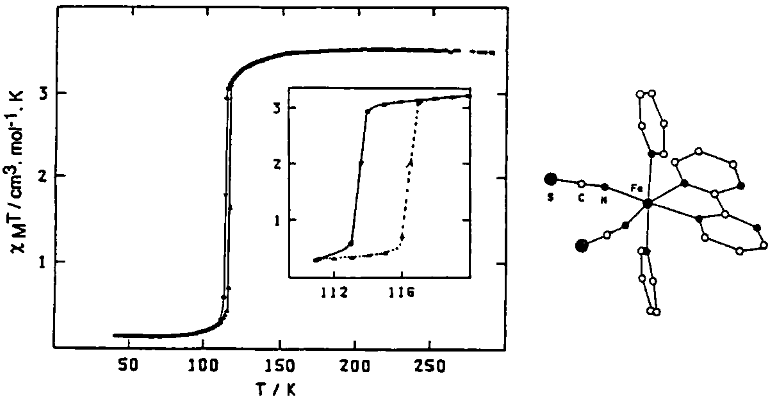

FIGURE 2 Temperature dependence of $\chi_M T$ for the above compound (χ_M = molar magnetic susceptibility)

Presently, few experimental investigations have been devoted to the molecular and crystalline parameters which may govern the cooperativity of spin crossovers. Nevertheless, it seems now established that transitions are all the more abrupt as ΔR values are higher (thus iron(II) complexes are good candidates for presenting discontinuous transitions, since ΔR can be of the order of 0.2 Å) and bulk moduli are larger. However these conditions seem not to be sufficient. Significant interactions between molecules or metal centers are also required. We have shown, for instance, that strong van der Waals contacts, intermolecular hydrogen bonds and bridging ligands highly favour spin-conversion cooperativity. Moreover crystal quality is also expected to play a role, since the presence of crystal defects is known to smoothen the development of the spin change by disturbing the formation of domain of like-spin molecules associated with the phenomenon.

PRESSURE-INDUCED SPIN CROSSOVERS

Since HS↔LS transformations are generally accompanied by a decrease in metal-ligand distances and hence in crystal unit-cell volume, pressure may also act as the external perturbation leading to the spin change.

Applying pressure to a HS complex is expected first to reduce the unit-cell volume, which results in a shortening of intermolecular spacing and, consequently, to an increase of the lattice strain. When the strain becomes high enough to force a structural rearrangement to occur, then the low spin form is stabilized, owing to its lower volume, and a HS↔LS conversion takes place.

We induced spin crossovers with pressure, at room temperature, in a number of six-coordinate cobalt(II) and iron(II) complexes. The phenomenon was followed by near-edge X-ray absorption (XANES) spectrometry, samples being submitted to pressure in a diamond-anvil cell. The variation of the LS fraction as a function of pressure is represented in Figure 3-left for a cobalt(II) complex of the type $Co(SB)L_2$ (SB beeing a Schiff base with a $[N_2O_2]$ donor set and L an axial ligand, here 4-t-butylpyridine)[13], and in Figure 3-right for the crystalline form II of the iron(II) complex $Fe(phen)_2(NCS)_2$, where phen = 1,10-phenanthroline.

These results led to the following observations and comments:

- Concerning compounds which exhibit thermally-induced spin crossovers, the spin change is over for pressures of 1.0 ± 0.1 GPa in the case of Co(II) complexes and of 1.5 ± 0.5 GPa in the case of Fe(II) complexes, the transition

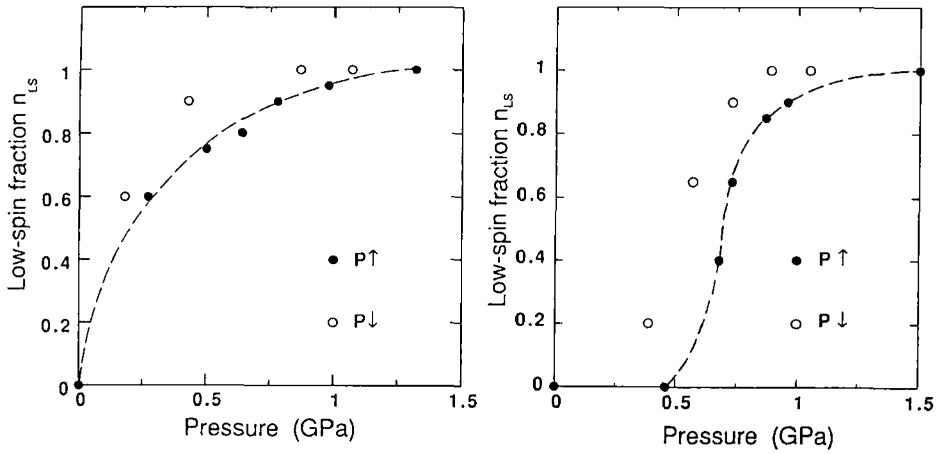

FIGURE 3 Evolution of the low-spin fraction as a function of pressure for one of the cobalt(II) (left) and one of the iron(II) (right) complexes.

extending over a pressure range going from ≈ 0.5 to ≈ 1.0 GPa.

- Spin crossovers were also obtained for compounds which do not present a thermally-driven spin conversion i.e. which retain the HS state at any temperature. Pressures as high as several GPa were then required. Thus, applying pressure proves to be a more efficient way to induce spin changes than varying temperature.

- The HS↔LS transformation was shown to be quasi-complete; moreover, the process is reversible: the spectra obtained before pressure was applied and after pressure was released were found to be quite similar.

- No hysteresis effect was detected. The fact that compounds do not behave in the same way upon the first increase and the first decrease of pressure (see Figure 3) may be mainly accounted for by the sintering of the powdered samples in the former step.

A perspective for pressure-induced spin conversion effect might be to design pressure sensors.

LIGHT-INDUCED SPIN CROSSOVERS

At low temperature (T< ≈ 50 K), the LS state $^1A_1$ of an iron(II) complex known to present a thermally- induced spin crossover can be quantitatively converted into the metastable HS state $^5T_2$ by irradiating the sample into the $^1A_1 \rightarrow {}^1T_1$ d-d absorption band. The relaxation process involves the intermediate spin states $^3T_1$ and $^3T_2$. As the resulting HS state may remain trapped for a very long time, this effect, recently discovered, was termed " Light-induced excited spin state trapping" (LIESST)[14]. The phenomenon being reversible, the system behaves like an optical switch.

We are now developing a new way for inducing durable spin crossovers with light, which should allow one to operate at room temperature in the near future. The method is based on the utilization of ligand photochemical trans↔cis isomerization to vary the ligand-field strength.

The principle is the following (see Figure 4). The first step consists in getting a spin-crossover complex (1) with one of the ligand isomers. A slight modification of this ligand is then expected to modify the metal ion magnetic behavior significantly. Consequently, the complex formed with the other ligand isomer (2) may be in the HS (Cf. Figure 4-left) or the LS (Cf. Figure 4-right) form. In the temperature range where the two complexes present a different spin state, ligand photoisomerization is then capable of inducing metal ion spin change

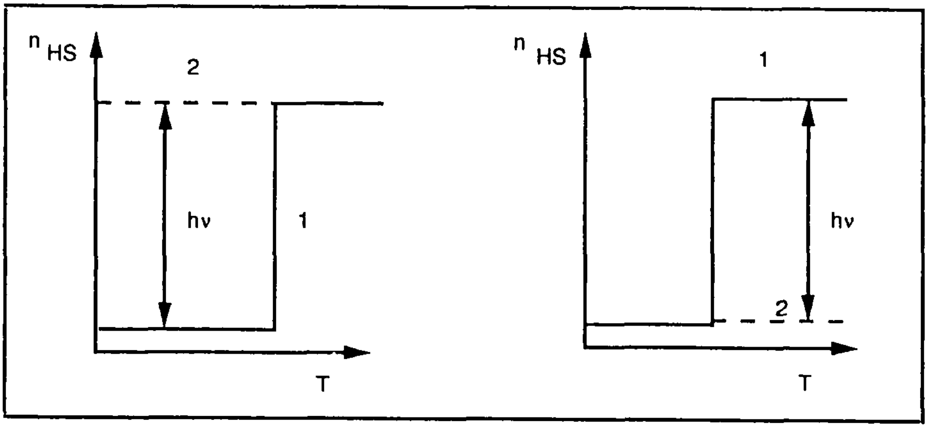

FIGURE 4 Principle scheme for the light-induced spin conversion n_{HS} = high-spin fraction.

The compounds we studied are iron(II) complexes of the type FeL_4X_2, L denoting 4-styrylpyridine and X an anionic ligand. Species formed with L trans-isomer exhibit a thermally-induced spin crossover, the critical temperature of which was increased from 108 K to 185 K, then to 195 K by using NCS^-, $NCB\Phi_3^-$ and $NCBH_3^-$ as X ligands, successively. Compounds formed with the cis-isomer are HS at any temperature. Figure 5 shows the magnetic behavior of the species obtained with X = NCS^- (left) and $NCB\Phi_3^-$ (right).

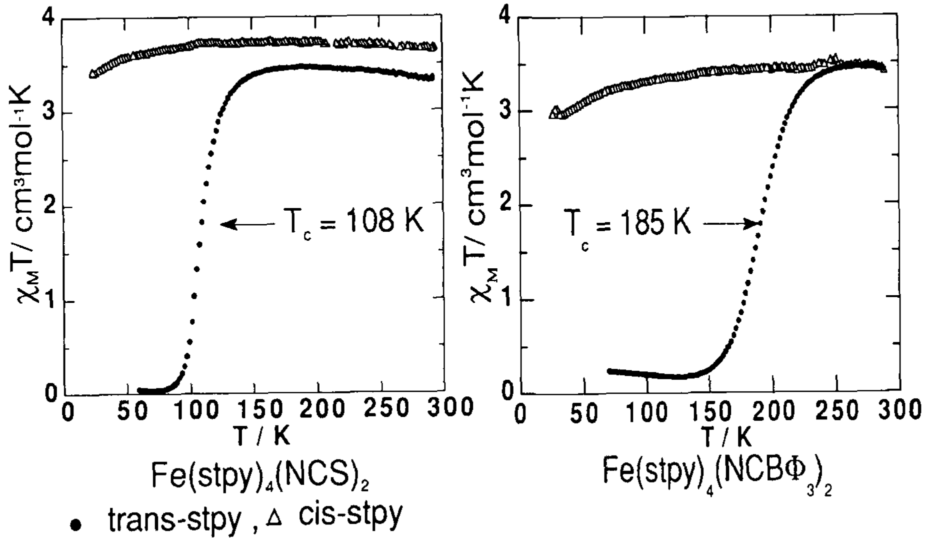

FIGURE 5 Temperature dependence of $\chi_M T$ for FeL_4X_2 complexes with L = 4-styrylpyridine and X = NCS^- (left) and $NCB\Phi_3^-$ (right).

This new way to induce spin crossover with light opens a wide field of investigations, given the fact that trans↔cis photoisomerization is not the only photochemical process that is likely to change the ligand-field strength. Other processes may also be used on the basis of the same approach.

In conclusion, it seems clear now that the spin-crossover phenomenon presents large potentialities for practical applications. This statement is reinforced by the fact that a large number of the physical properties of the systems vary upon the spin conversion, which may allow one to choose among a variety of responses to the external perturbation (colour change, modification of electronic, vibrational, magnetic and structural characteristics).

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