ELSEVIER

Coordination Chemistry Reviews
190–192 (1999) 47–59

COORDINATION CHEMISTRY REVIEWS

www.elsevier.com/locate/ccr

A photomagnetic effect for controlling spin states of Iron(II) complexes in molecular materials

M.-L. Boillot [a,]*, A. Sour [a], P. Delhaès [b], C. Mingotaud [b], H. Soyer [b]

[a] *Laboratoire de Chimie Inorganique, Bâtiment 420, Université Paris-Sud, 91405 Orsay, France*
[b] *Centre de Recherches Paul Pascal (CRPP), Université Bordeaux I, Av A. Schweitzer, 33600 Pessac, France*

Accepted 17 February 1999

Contents

Abstract

The electronic spin-state crossover of an iron(II) complex may be triggered through the *cis/trans* photoisomerization of the ligand. Such a photoinduced spin change has been observed, first at 140 K, then at room temperature, using *cis/trans* photoisomerizable ligands. A photosensitive iron(II) complex exhibiting a thermal spin crossover was stabilized

---

* Corresponding author. Tel.: +33-1-691-54755; fax: +33-1-691-54754.
E-mail address: mboillot@icmo.u-psud.fr (M.-L. Boillot)

PII: S0010-8545(99)00064-8

in a Langmuir monolayer. The thermal spin-crossover process has also been demonstrated on the corresponding Langmuir–Blodgett film.

Keywords: Spin-crossover; Photoisomerization; Light-induced spin change; Molecules; Langmuir–Blodgett; Optical information storage

---

1. Introduction

In a number of transition-metal complexes having high-spin (HS) and low-spin (LS) states in close energy proximity, an electronic spin crossover may be observed under the effect of a very small perturbation. The LS → HS conversion with increasing temperature is entropy-driven. The thermal population of the LS and HS states leads to an almost quantitative conversion to the HS state. In the solid state intermolecular interactions impart a cooperative character to the phenomenon. The attention paid to such systems results from the fact that they may show thermal hysteresis. Bistability and thermochromaticity properties make these materials potential candidates for information storage or display devices. Furthermore, quantitative light-induced spin conversions (according to the light-induced excited spin state trapping effect) may be observed by irradiating iron(II) spin-crossover compounds into d-d transitions or MLCT at temperatures ($T \lessapprox 70$ K) far below the transition temperature of the thermally-induced processes [1–6].

Recently, we reported a new strategy named ligand-driven light-induced spin change (LD-LISC), which for the first time has the potential to obtain light-induced spin changes at any temperature in d^4-to-d^7 transition-metal complexes [7,8]. It allows the electronic spin states of the metal ion to be controlled from the photochemical alteration of the ligands because relatively weak chemical changes of spin crossover complexes may sufficiently change the ligand field such that another spin state becomes the ground state. According to the choice of the molecular components this should enable photoinduced spin conversions between long-lived spin states to be observed at 'high temperature' (of course in the stability range of the compound). The bistable character and hence the optical memory effect exhibited by such compounds at the molecular level may be of importance for practical applications in optical information storage and display devices.

The photochemical reaction, first used, is the *cis*/*trans* photoisomerization. However, any other photoreaction leading to a significant ligand field change might also be appropriate. This method requires the preparation of two complexes (A and B) formed with the ligand photoisomers, which have different magnetic behavior. This first condition is fulfilled if at least one of these compounds (A) shows a thermally-induced spin crossover (Fig. 1). In the temperature range where the metal ion can be either in the LS or HS state depending on the configuration of the ligand in the complex (for example A (LS) and B (HS)), the ligand photoreaction should lead to a reversible spin-state conversion of the metal ion.

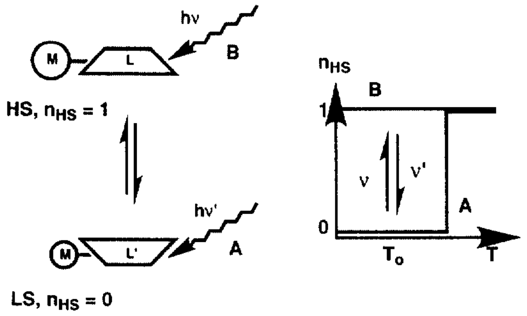

Fig. 1. Principle of the method used to obtain the ligand-driven light-induced spin change: n_{HS} = HS fraction, M metal ion, L and L′ ligand photoisomers, T_0 working temperature for the observation of the LD-LISC effect, ν and ν′ wavelengths for the ligand photoreaction.

In this paper we report on this photomagnetic effect in iron(II) molecular systems [9–11] first observed at 140 K in cellulose acetate films and recently at room temperature (r.t.) in an acetonitrile solution. As a long-range target, we plan to take up the challenge that consists of carrying the photoinduced spin change working at r.t. in organized media of mesoscopic size, such as Langmuir–Blodgett films. An amphiphilic spin-crossover compound was synthesized. The thermal HS↔LS conversion was demonstrated in a well-defined Langmuir–Blodgett film build up from a stable monolayer on a formamide/water mixture used as subphase [11–14].

2. Experimental

Syntheses of $Fe^{II}(Stpy)_4(NCBPh_3)_2$ and $Fe^{II}(t\text{-hsbpy})_2(NCS)_2$ (Stpy = 4-styrylpyridine and *t*-hsbpy = 4-heptadecyl-4′-*trans*-styryl-2,2′-bipyridine) and the related physical measurements were described elsewhere [9,11].

2.1. Syntheses

All compounds were prepared, handled and maintained under inactive light in order to prevent any photoisomerization process. In addition, the syntheses of the iron(II) complexes were carried out under an argon atmosphere, using previously degassed solvents.

Trans-msbpy (*t*-msbpy = 4-methyl-4′-*trans*-styryl-2,2′-bipyridine) was prepared according to the procedures described for some related compounds [15]. It consisted of refluxing, for 40 h, a mixture of 4-4′-dimethyl-2,2′-bipyridine (9.7 mg, 53 mmol), benzaldehyde (8 ml, 72 mmol) and potassium acetate (5.2 mg, 53 mmol) in acetic anhydride (7.4 ml, 67 mmol), in the presence of a small amount (ca. 3 mg) of iodine. Before complete cooling, the resulting viscous solution was poured into chilled water (300 ml) made alkaline (pH 8–9) with triethylamine. The precipitate which formed was isolated by filtration, washed with water, and treated with

CH_2Cl_2 in order to eliminate the insoluble impurity 4,4′-distyryl-2,2′-bipyridine. The solid compound resulting from solvent removal was then sublimated under vacuum at 120°C. ^{1}H-NMR data (ppm) in CD_3CN: 8.62 (d, 1H); 8.54 (d, s, 2H); 8.28 (s, 1H); 7.66 (dd, 2H); 7.54 (d, 16.4 Hz, 1H); 7.54–7.38 (m, 5H); 7.30 (d, 16.4 Hz, 1H). The coupling constant $J = 16.4$ Hz was ascribed to the *trans* ethylenic group.

[Fe(*trans*-msbpy)$_3$](NCS)$_2$, used as the starting material to synthesize Fe(*trans*-msbpy)$_2$(NCS)$_2$, was obtained as follows. A solution of $Fe(SO_4)_2(NH_4)_2 \cdot 6H_2O$ (101 mg, 0.257 mmol) in water (2 ml) was added dropwise to a 206.8 mg (0.767 mmol) sample of *trans*-msbpy dissolved in EtOH (10 ml). The red solution was heated at 65°C for 1 h, then cooled to r.t. After addition of a saturated KNCS aqueous solution (ca. 10 ml), which caused a red precipitate to form, the mixture was stirred for a further 20 min and then decanted. The solid was separated by filtration and dried under vacuum in a desiccator. Anal. Calc. for $C_{59}H_{48}N_8S_2Fe \cdot 3.5H_2O$: C, 67.36; H, 5.27; N, 10.65; S, 6.09. Found: C, 66.56; H, 5.21; N, 10.83; S, 6.91%.

Complete removal of the water molecules was achieved by heating the compound at 60°C for a night under an argon stream.

Fe(*trans*-msbpy)$_2$(NCS)$_2$ was prepared by extracting one msbpy ligand from [Fe(*trans*-msbpy)$_3$](NCS)$_2$. A solution of [Fe(*trans*-msbpy)$_3$](NCS)$_2$ (100 mg, 0.25 mmol) in anhydrous CH_2Cl_2 (10 ml) was stirred for 20 min at r.t. The addition of hexane (25 ml) resulted in the precipitation of a violet compound which was isolated by filtration, washed with ethyl ether and then dried at 80°C for one night under an argon stream. Anal. Calc. for $C_{40}H_{32}N_6S_2Fe$: C, 67.03; H, 4.50; N, 11.73; S, 8.93. Found: C, 66.71; H, 4.62; N, 11.86; S, 8.21%.

2.2. Physical measurements

For the compound Fe(*trans*-msbpy)$_2$(NCS)$_2$ in the solid state, variable-temperature magnetic susceptibility data were determined in both cooling and heating modes, using a Quantum Design SQUID magnetometer Model MPMS5. A sample of palladium was used as the calibrant. The independence of the susceptibility of the applied magnetic field was controlled for the complex at r.t. Diamagnetic corrections were estimated from Pascal's tables at -432×10^{-6} cm^3 mol^{-1}. For the compound in solution magnetic susceptibility measurements were carried out using the technique of Evans, on a Bruker AM 400 (400 MHZ) NMR spectrometer equipped with an Oxford Instruments cryogenic set-up. CD_3CN was utilized as both the solvent and the reference substance.

UV–vis absorption spectra were recorded on a Varian Cary 5E spectrophotometer, the compounds being examined in the form of acetonitrile solutions.

Irradiations were performed with an Oriel equipment including a 200 W mercury (xenon) lamp Model 6292, and a 1/8 m grating monochromator Model 77250 equipped with a 1.56 mm width slit. The solutions were handled under inactive light and stirred during irradiation. The reactors were 10 mm path length quartz cells.

3. Results

3.1. First evidence of the photomagnetic effect in $Fe^{II}(Stpy)_4(NCBPh_3)_2$

The first attempts to achieve the photomagnetic effect were carried out using 4-styrylpyridine as the *cis*/*trans* photoisomerizable ligand. The stability of each photoisomer allows the syntheses of each ligand and related complex. Iron(II) complexes of the type $Fe(Stpy)_4(NCBPh_3)_2$ (Stpy = 4-styrylpyridine) have the magnetic and structural properties required for the LD-LISC effect to be observed [8]. The metal ion retains the HS state at any temperature in Fe(*cis*-Stpy)$_4$(NCBPh$_3$)$_2$ (noted C^c) and undergoes a thermally-induced $S = 2 \leftrightarrow S = 0$ spin crossover centered around 190 K in Fe(*trans*-Stpy)$_4$(NCBPh$_3$)$_2$ (noted C^t) [9]. The difference in the magnetic behavior may be accounted for by a stronger π-acceptor character of the *trans*-Stpy than for the *cis*-Stpy, which strongly deviates from planarity.

The effects of light irradiation were examined at the higher working temperature of 140 K [9]. Molecular compounds were embedded in cellulose acetate films. Both configurational changes and electronic spin-state changes are involved in this effect. With the aim of checking the photochemical and magnetic properties of the photosensitive molecules in the working conditions, we have investigated the electronic properties by variable-temperature UV–vis spectrometry.

From the temperature dependence of absorption spectra it was demonstrated that the electronic properties of C^t and C^c embedded in cellulose acetate films are comparable with those of the polycrystalline samples. The variation of the relative absorbance of C^t versus T was monitored at a wavelength which corresponds to a metal-to-ligand charge transfer absorption (Fig. 2). It shows the expected thermal spin equilibrium for C^t centered at 185 K in contrast to the slight linear variation found for C^c indicating that the spin state (known to be HS) does not change.

Photoisomerizations were carried out at 140 K on films of complexes and monitored by UV–vis spectra. The *trans* → *cis* and *cis* → *trans* transformations of the ligand linked to the metal ion were observed, irradiating at $\lambda_{exc} = 322$ and 260 nm, respectively. The irradiated films were perfectly stable in darkness at 140 K and

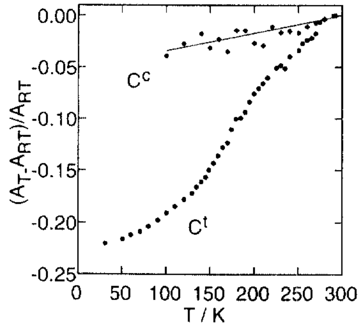

Fig. 2. Temperature dependence of the relative absorbance $(A_T - A_{RT})/A_{RT}$ at 342 nm for the C^c and C^t forms of $Fe(stpy)_4(NCBPh_3)_2$ embedded in cellulose acetate films.

also at r.t. At both wavelengths, the spectra of the samples obtained in the photostationary states are indicative of a prevailing content in the photoisomer, viz. C^c ($\lambda_{exc} = 322$ nm) and C^t ($\lambda_{exc} = 260$ nm).

From the observations above we conclude that, at 140 K, iron(II) ions are at least partly LS in the C^t isomer and HS in the C^c isomer. Consequently isomerizations of the ligand linked to the metal ion are very likely to result in iron(II) spin change. This conclusion was corroborated by analyzing the temperature dependence of the electronic properties of the photoproducts obtained after irradiation at 322 and 260 nm. The relative absorbance versus temperature at 344 nm shows that irradiating C^c in the HS state (Fig. 3 (a)) yields a prevailing C^t compound which undergoes a thermally-induced spin crossover (Fig. 3 (b)) similar to that already characterized. Hence this C^t product is in the LS state at 140 K.

The investigation of the photochemical properties was realized in films at both r.t. and 140 K [10]. Quantum yields and extents of the photoconversion were found to vary significantly according to the temperature and the rigidity of the matrix. The $\Phi_{t \to c}$ quantum yield of thick films drops from 0.40 ± 0.02 (293 K) to 0.06 ± 0.01 (140 K), whereas the $\Phi_{c \to t}$ quantum yield is estimated to be 0.37 ± 0.06 (293 K) and 0.50 ± 0.12 (140 K) for $\lambda_{exc} = 322$ nm. The corresponding extent of the photoconversion *trans* → *cis* is found to be 0.81 ± 0.01 (293 K) and is reduced to 0.35 ± 0.02 (140 K). It appears that the extent of the conversion at 140 K is rather low compared to the results of our previous study [9]. This observation very likely results from an enhancement of the rigidity of the matrix, already high at low temperatures, indeed aged films were used in this study.

3.2. The light-induced spin change at 293 K in $Fe^{II}(t\text{-msbpy})_2(NCS)_2$

A way to increase the working temperature (of 140 K) is to design an appropriate complex with a stronger ligand field than in $Fe^{II}(Stpy)_4(NCBPh_3)_2$. This requirement is expected to be fulfilled with an iron(II) complex containing bidentate ligands of the bipyridine type. The syntheses of a ligand functionalized with a photoisomerizable styryl substituent and that of the iron(II) complex Fe^{II}(*t*-ms-

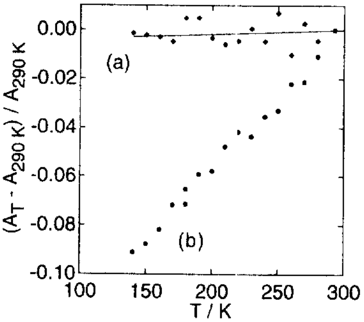

Fig. 3. Temperature dependence of the relative absorbance $(A_T - A_{RT})/A_{RT}$ at 344 nm for the C^c-containing film before (a) and after (b) irradiation at $\lambda_{exc} = 260$ nm at 140 K.

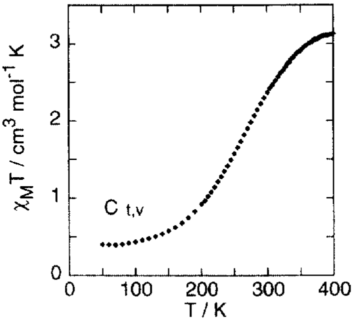

Fig. 4. Temperature dependence of $\chi_M T$ for Fe(t-msbpy)$_2$(NCS)$_2$ in the solid state.

bpy)$_2$(NCS)$_2$ (with t-msbpy = 4-methyl-4′-*trans*-styryl-2,2′-bipyridine) was performed [11]. As shown by the $\chi_M T$ versus T plot (Fig. 4), the microcrystalline violet sample of Fe^{II}(t-msbpy)$_2$(NCS)$_2$ (noted $C_{t,v}$) shows a $S = 2 \leftrightarrow S = 0$ spin equilibrium of the iron(II) ions at 264 K. At r.t. ca. 65% of the molecules are in the HS state. As the observation of the LD-LISC effect requires diluted samples, we have also studied the magnetic behavior of $C_{t,v}$ in acetonitrile solutions, using the NMR Evans method. The complex is almost diamagnetic at 293 K ($\chi_M T = 0.170 \pm 0.006$ cm^3 mol^{-1} K) and probably exhibits the very beginning of a spin conversion on heating from 293 to 333 K. The temperature dependence of the electronic properties of acetonitrile solutions of $C_{t,v}$ was also monitored by UV–vis spectrometry. At r.t. the spectrum (Fig. 6 (a)) is consistent with that of a complex of the type FeL$_2$(NCS)$_2$ (L denoting a bidentate ligand). The most prominent band with a maximum at 331 nm for $C_{t,v}$ and 291 nm for t-msbpy arises from the π–π* transition of the photoisomerizable ligand. The MLCT absorption appears at 550 nm. Isosbestic points and an hypsochromic shift of the MLCT were observed on heating from 295 to 330 K. These reversible changes parallel the trend usually observed with spin-crossover complexes of this type. It can be shown that the difference in absorbance $A_{RT} - A_T$ (RT = room temperature), at a given wavelength, varies with temperature like the HS fraction of the metal ion. The analysis at $\lambda = 345$ nm shows that an LS → HS conversion takes place in solution on heating (Fig. 5 (1)). So it can be stated that a spin-crossover behavior is retained in solution and that this quasi-diamagnetic complex at r.t. is a good candidate for the investigation of the LD-LISC effect.

Trans → *cis* photoisomerizations of the styryl substituent in Fe^{II}(t-msbpy)$_2$(NCS)$_2$ and t-msbpy were carried out on acetonitrile solutions at 293 K. Solutions of $C_{t,v}$ were irradiated at 334 nm until a photostationary state was reached. UV–vis spectra after different times of irradiation are shown in Fig. 6. After each irradiation the solutions are stable in darkness. An isosbestic point can be identified at 273 nm. The evolution of the spectra consists of (i) a blue shift of the electronic transitions assigned to the π–π* transition of t-msbpy and to the MLCT transition and (ii) a reduced absorbance in a wide span of wavelengths (Fig. 6). For comparison, *trans* → *cis* isomerization of uncoordinated t-msbpy was observed with

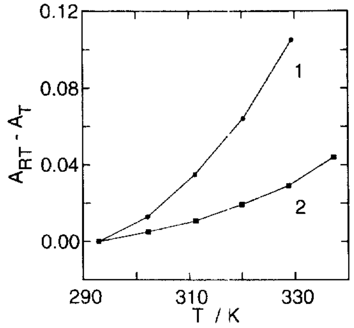

Fig. 5. Temperature dependence of the absorbance $A_{RT} - A_T$ at $\lambda = 345$ nm before irradiation at $\lambda_{exc} = 334$ nm (1) and in the photostationary state (2).

an optical excitation at 312 nm. ^{1}H-NMR spectrometry was used to analyze the solution obtained in the photostationary state. It permits us to confirm the formation of *c*-msbpy (*c* = *cis*) and to estimate a fraction of *c*-msbpy > 70% and of *t*-msbpy < 30%. Similarities in the spectra of $C_{t,v}$ and *t*-msbpy in the absorption range of the ligand indicate the occurrence of a *trans* → *cis* isomerization of the styryl substituent in Fe^{II}(*t*-msbpy)$_2$(NCS)$_2$. Assuming that the absorbance of C_c has a hypothetical zero value at 347 nm, the fraction of Fe^{II}(*c*-msbpy)$_2$(NCS)$_2$ in the photostationary state can be estimated to be higher than ca. 55%.

As mentioned above, iron(II) ions of $C_{t,v}$ in acetonitrile solution are almost in a LS state at r.t. Irradiating this solution a weak band located at ca. 840 nm viz ca. 11 900 cm^{-1} appeared and increased until the photostationary state was reached (Fig. 6, inset). This band has been identified as a spin-allowed d-d transition of a compound of the type Fe(L)$_2$(NCS)$_2$ in a HS state. Thus a significant amount of C_c

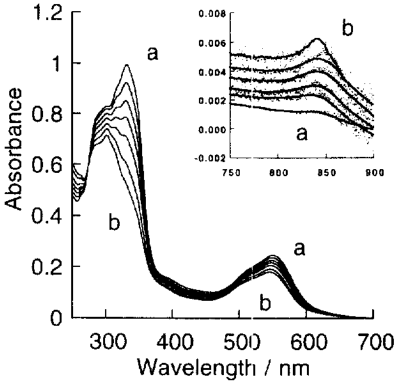

Fig. 6. Evolution of the UV–vis spectrum of 1.9 × 10^{-5} M acetonitrile solution of $C_{t,v}$ upon irradiation at 334 nm. (a) Initial spectrum; (b) spectrum of the photostationary state. Inset: corresponding evolution of the absorbance in the d-d transition area; for clarity, all bands were slightly shifted upwards (except a).

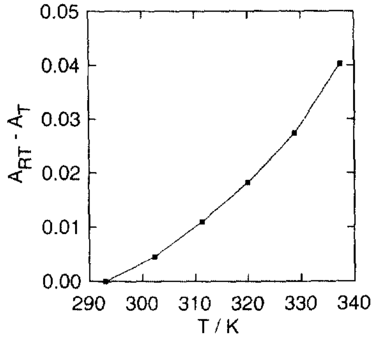

Fig. 7. Temperature dependence of the absorbance $A_{RT} - A_T$ at $\lambda_{isobestic} = 313$ nm in the photostationary state (2).

is in a HS state. In order to support this statement, the UV–vis spectrum of the photostationary state was carefully examined as a function of temperature between 295 and 337 K. The $A_{RT} - A_T$ versus T variation at $\lambda = 345$ nm was found to be flattened compared to the non-irradiated solution (Fig. 5). This results at least partly from the spin equilibrium of the residual fraction of $C_{t,v}$. Therefore, the contribution of C_c is found to be weak or non-existent. It follows that the prevailing C_c complex is either in a HS state at any temperature or exhibits a very gradual thermal spin crossover. Plotting $A_{RT} - A_T$ versus T at $\lambda = 313$ nm (isosbestic point identified in the spectra of $C_{t,v}$ at various temperatures), we find a variation which can be ascribed to an LS↔HS conversion of the single C_c component (Fig. 7). The above data provide evidences for the occurrence of a $C_{t,v}$ (LS) → C_c (HS) photoconversion, and hence for the LD-LISC effect, at r.t.

3.3. Spin crossover of $Fe^{II}(t\text{-hsbpy})_2(NCS)_2$ in a Langmuir–Blodgett film

The influence of the surroundings on spin-crossover molecules has been recognized for a long time. Since the photomagnetic effect is operative on a molecular level we decided to investigate the LD-LISC effect in organized media of mesoscopic size. Taking into account the previous observations (Section 3.2), we chose to synthesize a closely related complex capable of being formed into Langmuir–Blodgett films [12]. The amphiphilic complex $Fe^{II}(t\text{-hsbpy})_2(NCS)_2$ (*t*-hsbpy = 4-heptadecyl-4′-*trans*-styryl-2,2′-bipyridine) was synthesized with a doubly-functionalized bipyridine ligand including both a photoisomerizable group and a long aliphatic chain. The magnetic behavior of a bulk sample of this complex was monitored from direct susceptibility measurements. It is quite similar to the previous one and characterizes a $S = 2 \leftrightarrow S = 0$ spin conversion of the iron(II) ions (requested for the observation of the LD-LISC effect), centered at 295 K. The HS form residue at low temperature can be estimated to be ca. 8%. The conversion is found to be reversible. The next steps are to elaborate a stable monolayer, to prepare LB films by transfer of a monolayer onto a solid substrate and to analyse the electronic and/or vibrational properties of the molecular material. Our first attempts to prepare monolayers of this amphiphilic complex were unsuccessful because of the chemical instability of iron(II) complexes at the gas–water interface [13]. When a toluene solution of $Fe^{II}(t\text{-hsbpy})_2(NCS)_2$ is spread on pure water, a Langmuir film can be obtained. However, it is highly unstable versus time at any surface pressure. This chemical instability is quantified in terms of relative change in area per molecules per unit of time at constant surface pressure (i.e. $(dA/dt)/A$, noted α_π). It can be ascribed to the effect of water which shifts equilibria of HS complexes of the type $Fe(L)_2(NCS)_2$ and causes dissociation. This problem has been solved by using a formamide/10^{-2} M KNCS aqueous solution (v/v 75/25) as the subphase. Then a perfectly stable monolayer is obtained. Under these conditions, α_π reaches a minimum value of ca. 10^{-4} mn^{-1}. The corresponding isotherm starts from ca. 110 $Å^2$ per molecule and shows a collapse point at 17 mN m^{-1} for an area of 65 $Å^2$ per molecule. Examination of the area values shows that they are slightly lower than the ca. 80 $Å^2$ per molecule, evaluated from the crystallographic data of a related compound. This may be indicative of geometric constraints and deformations of the complex induced by the packing at the gas/water interface, which may result in the modification of the ground state of the metal ion.

The Y-type transfer of this monolayer onto a hydrophobic substrate was performed and the transfer ratio was found to be close to 0.90–0.95 [13]. Visible and IR spectra allow one to check the chemical integrity of the iron(II) compound after the monolayer and the LB film elaboration processes. Further details of the characterization are available elsewhere [14].

The spin-crossover behavior was studied by variable temperature IR spectrometry using films of the complex transferred onto a CaF_2 substrate. Focusing on the 2000–2150 cm^{-1} frequency range (Fig. 8) enables one to identify two main peaks (2101 and 2057 cm^{-1} at r.t.). They correspond to the CN stretching vibrations of the thiocyanate ligands in the LS and HS forms of the complex, respectively. Since in all molecular spin-crossover compounds of the type $Fe(L)_2(NCS)_2$, the thio-

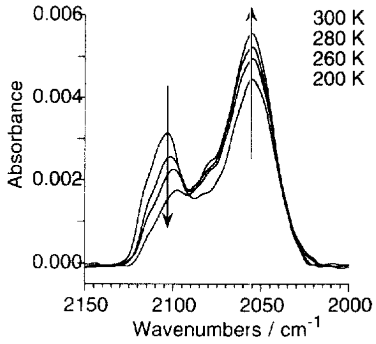

Fig. 8. IR spectrum in the range 2150–2000 cm^{-1} of the $Fe(t\text{-hsbpy})_2(NCS)_2$ complex in the LB film on calcium fluoride for various temperatures ($T = 200$, 260, 280 and 300 K). Arrows indicate the intensity variations for increasing temperature.

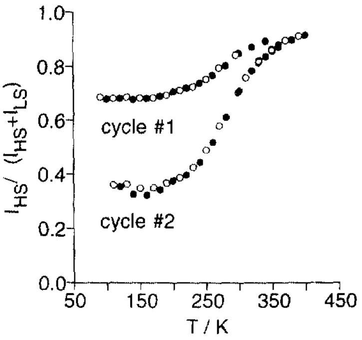

Fig. 9. Ratio $I_{HS}/(I_{HS}+I_{LS})$ of the integrals of the IR peaks between 2090 and 2135 cm^{-1} (I_{LS}) and between 2000–2090 cm^{-1} (I_{HS}) in the LB film versus temperature (see Fig. 8). Open circle: decreasing temperature, full circle: increasing temperature. First thermal cycle: 300 → 100 → 400 K. Second thermal cycle: 400 → 100 → 400 K.

cyanate groups are always in a *cis* configuration, this arrangement is certainly met in this complex. Thus the two shoulders may be ascribed to the corresponding CN stretching vibrations. The temperature dependence of the spectra was recorded in the range of 80–400 K. In the heating mode the intensity of the band located at higher frequency (noted for simplicity I_{LS}) continuously decreases to the benefit of the second one (I_{HS}). This behavior was analyzed by plotting the relative absorbance $(I_{HS}/I_{HS}+I_{BS})(T)$ obtained by integration of these two bands in defined wavenumber ranges. The first thermal cycle (300–80 K) shows a temperature-independent behavior (at $T<150$ K) and a temperature dependent behavior typical of a $S=2\leftrightarrow S=0$ crossover of Fe(II) ions (at $T>150$ K) (Fig. 9 (cycle 1)). The former component (70%) may be ascribed to a fraction of distorted molecules as suggested by the analysis of the compression isotherm (vide supra). Assuming a complete spin conversion at high temperature, we can estimate the temperature $T_{1/2}$ at which half of the conversion is accomplished to be 292 ± 7 K (the value in powder of $T_{1/2}$ is 295 K). The spin change between a HS fraction of 10–90% takes place in the temperature interval $\Delta T^{80}=T^{90}-T^{10}$ ca. 130 ± 20 K (ΔT^{80} ca. 180 K in powder). This behavior was reversibly observed when the temperature was kept below 340 K. These results show unambiguously that a spin-crossover process takes place in the LB film. The sample was then warmed up to 400 K and the second thermal cycle (100–400 K) was recorded. The variation of the ratio $I_{HS}/I_{HS}+I_{BS}$ versus T is quite different (Fig. 9 (cycle 2)). The residue at low temperature was found to be much smaller (30%) and the overall behavior of this sample was not affected by additional thermal cycles. The spin-crossover process compares to that of the bulk sample ($T_{1/2}=291\pm7$ K, ΔT^{80} ca. 169 ± 20 K). The striking alteration of the thermal behavior may be understood in terms of melting of the alkyl chains which should induce the loss of the layer structure of the LB film and the intralayer organization. The study of both the dichroism in the IR spectrum and the thermal variation of the peak associated to the CH stretching confirms that the effect of heating is not reversible for the alkyl chains as expected for a melting process. A close examination of the results obtained with multilayers built from not-so-well defined monolayers was carried out. The main difference consists in the residue at low temperatures which slightly decreases after heating above 340 K. Annealing of more or less well-defined LB films, built up from different subphases, gives similar residues at low temperature (ca. 30%). This value may be ascribed to a fraction of molecules in a same spin state at any temperature.

For the LB film built up from the formamide/water subphase, the residue content drops from 70 to 30% by increasing the temperature above 340 K. The magnetic properties of $Fe^{II}(t\text{-hsbpy})_2(NCS)_2$ in the bulk sample do not exhibit such alteration after heating at 400 K. This thermal behavior seems to be related to the peculiar organization induced by the LB film. This interpretation was also supported by the study of mixed LB films containing the iron(II) complex and behenyl alcohol [14].

These results demonstrate the occurrence of a thermal spin crossover in a LB film and provide evidences of a surroundings effect due to a specific molecular organization induced by the LB film.

4. Conclusion

We have shown in this contribution how the HS↔LS conversion of a metal ion may result from a *cis/trans* photoisomerization of the ligand. One criterion for the application of this phenomenon, the working temperature, can be fine tuned by small chemical changes in the spin-crossover complex. We obtained, for the first time, a light-induced spin conversion at r.t. In order to complete this work the reverse photoconversion $C_c \rightarrow C_{t,v}$ and the photochemical properties of this couple of isomers have to be thoroughly examined. A closely related photosensitive complex has been elaborated to be formed into LB films. The thermal spin crossover phenomenon of this amphiphilic iron(II) has been shown to be retained in a LB film. Efforts are now directed toward the synthesis of new systems that can provide light-induced spin changes in LB films for practical applications.

Acknowledgements

We would like to express our gratitude to Jacqueline Zarembowitch for her pioneering contribution regarding the topic presented here. Financial support from the research fund TMR of the European Community (contract ERB-FMRX-CT 98-0199) and from the CNRS are gratefully acknowledged.

References

[1] P. Gütlich, A. Hauser, H. Spiering, Angew. Chem. Int. Ed. Engl. 33 (1994) 2024.
[2] E. König, G. Ritter, S.K. Kulshreshtha, Chem. Rev. 85 (1985) 219.
[3] E. König, Struct. Bonding 76 (1991) 51.

[4] J.K. Beattie, Adv. Inorg. Chem. 32 (1988) 1.

[5] H. Toftlund, Coord. Chem. Rev. 94 (1989) 67.

[6] A. Hauser, Coord. Chem. Rev. 111 (1991) 275.

[7] J. Zarembowitch, C. Roux, Fr. Patent No. 9205928, 1992.

[8] (a) C. Roux, J. Zarembowitch, B. Gallois, T. Granier, R. Claude, Inorg. Chem. 33 (1994) 2273. (b) C. Roux, Thesis, University of Paris-Sud, 1992.

[9] M.-L. Boillot, C. Roux, J.-P. Audière, A. Dausse, J. Zarembowitch, Inorg. Chem. 35 (1996) 3975.

[10] L. Gueneau, M.-L. Boillot, K. Nakatani, J. Delaire, to be published.

[11] M.-L. Boillot, S. Chantraine, J. Zarembowitch, J.-Y. Lallemand, J. Prunet, New J. Chem. 2 (1999) 179.

[12] M.-L. Boillot, H. Soyer, New J. Chem. 21 (1997) 889.

[13] H. Soyer, C. Mingotaud, M.-L. Boillot, P. Delhaès, Thin Solid Films 327-329 (1998) 435.

[14] H. Soyer, C. Mingotaud, M.-L. Boillot, P. Delhaès, Langmuir 14 (1998) 5890.

[15] J. Stanek, M. Horak, Collect. Czech. Chem. Commun. 15 (1950) 1039.