Inorg. Chem. **2007**, *46*, 4114–4119

Inorganic Chemistry

Article

Photomagnetic Properties of an Iron(II) Low-Spin Complex with an Unusually Long-Lived Metastable LIESST State

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Received December 16, 2006

A comprehensive study of the photomagnetic behavior of the $[Fe(L_{222}N_5)(CN)_2]\bullet H_2O$ complex has been carried out. This complex is characterized by a low-spin (LS) iron(II)–metal center up to 400 K and exhibits at 10 K the well-known Light-Induced Excited Spin State Trapping (LIESST) effect. The critical LIESST temperature (*T*(LIESST)) has been measured to be 105 K. The kinetics of the transition from the metastable high-spin (HS) state to the low-spin state have been determined and used for reproducing the experimental *T*(LIESST) curve. This study represents a second example of a fully low-spin iron(II)–metal complex up to 400 K, which can be photoexcited at low temperature with an atypical long-lived metastable HS state. This underlines the preponderant role of the inner coordination sphere for stabilizing the lifetime of the photoinduced HS state.

Introduction

The design of materials able to store information on the single molecule level or on assemblies of molecules is a current challenge in information technology.[1] Among all the investigated systems, an interesting class of molecular switches are those involving the Light-Induced Excited Spin State Trapping (LIESST) phenomenon.[2−5] Materials of this kind combine (i) low addressing power (about 5 mW/cm^2), (ii) short addressing time (nanosecond scale), (iii) perfect reproducibility over successive cycles even in a solid matrix, and (iv) optical reversibility, as the low-spin (LS, $^1A_1$) → high-spin (HS, $^5T_2$) transition in iron(II) molecular materials can be induced with green light and the back conversion to the LS state with red light.[6−8] The main limitation comes, in fact, from the stability of the photoinduced metastable HS state. Below 50 K, the lifetime is almost infinite and optical data storage can be envisaged, while at higher temperatures the relaxation is governed by the activated regime and the photoinduced HS state decays within seconds or less. To overpass this limitation, it has been recently indicated that in some iron(II) molecular materials the light-induced phenomenon can be generated in the center of a thermal hysteresis.[9−11] But the integration into a genuine

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10.1021/ic062418p CCC: $37.00

device will impose to prepare an iron(II) spin crossover (SCO) material with a thermal hysteresis loop of around 100 K in width, a value never reached up to now.[12]

An alternative strategy will be to identify the factors accountable for stabilizing the light-induced metastable state at low temperature, i.e., outside the thermal hysteresis through the LIESST phenomenon. Along with that we have introduced the idea of systematically determining the *T*(LIESST) value, which represents the limiting temperature above which the light-induced magnetic HS information is erased when the temperature in a SQUID magnetometer is increased at a rate of 0.3 K/min.[13] Using this procedure, we have now compared the photomagnetic properties of more than 60 SCO materials,[14−17] and we have evidenced that factors such as cooperativity, nature of the salt, or degree of hydration are relatively negligible. In contrast, the influence of the inner FeN_6 coordination sphere, more precisely the degree of coordination of the metal center, on the stabilization of the photoinduced HS state seems to be one of the key factors. Following this idea, we have decided to investigate the magnetic and photomagnetic properties of a large number of iron(II) complexes involving macrocyclic ligands.

In the present work, we report the photomagnetic properties of the $[Fe(L_{222}N_5)(CN)_2]\bullet H_2O$ complex involving the $L_{222}N_5$ macrocyclic Schiff-base ligand, 2,13-dimethyl-3,6,9,-12,18-pentaazabicyclo[12.3.1]octadeca-1(18),2,12,14,16-pentaene. This complex was originally synthesized by Nelson et al.,[18] and it was indicated to be low-spin at room temperature. We have found that the $[Fe(L_{222}N_5)(CN)_2]\bullet H_2O$ system exhibits at low temperature the well-known LIESST phenomenon with an exceptionally long-lived lifetime. This finding is in contradiction to the inverse energy gap law, which has been proposed by Hauser to govern the relaxation kinetics of the metastable LIESST state.[3]

Experimental Section

The given $[Fe(L_{222}N_5)(CN)_2]\bullet H_2O$ complex was obtained as described by Nelson et al.[18] from the condensation of the 2,6-diacetylpyridine and the 3,6-diazooctane-1,8-diamine. The elemental analysis was consistent with the expected formula $C_{17}H_{25}N_7OFe$ (399.27): Anal. Calcd C 51.1, H 6.3, Fe 14.0, N 24.6. Found C 50.22, H 6.17, Fe 13.85, N 23.65. Attempts to obtain single crystals of the $[Fe(L_{222}N_5)(CN)_2]\bullet H_2O$ complex for solving the structure of the sample in the different spin states were not successful.

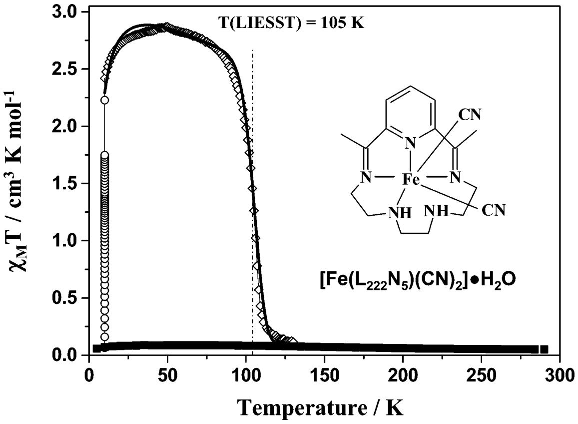

Figure 1. Magnetic and photomagnetic properties recorded of a polycrystalline sample of 0.3 mg of $[Fe(L_{222}N_5)(CN)_2]\bullet H_2O$. ■ = data recorded in the cooling and warming mode without irradiation; ○ = data recorded with irradiation at 10 K; ◆ = *T*(LIESST) measurement, data recorded in the warming mode at a rate of 0.3 K/min with the laser turned off after irradiation for 1 h. The solid line through the *T*(LIESST) measurement shows the fit generated from the deduced experimental thermodynamic parameters (E_a, k_∞, and Γ) and with a zero-field splitting value of 16 cm^{-1} and a *g* factor of 2.1.

The measurement of the diffuse absorption spectra and reflectivity signal were performed by using a custom-built setup equipped with a SM240 spectrometer (Opton Laser International). This equipment allows for recording both the diffuse absorption spectra within the range of 500−900 nm at a given temperature and the temperature dependence (5−290 K) of the reflectivity signal at a selected wavelength (±2.5 nm). The diffuse reflectance spectrum was calibrated with respect to charcoal activated (Merck) as black standard and barium sulfate ($BaSO_4$, Din 5033, Merck) as white standard. The analysis was done by using a thin layer of the powdered sample without any dispersion in a matrix.

The photomagnetic measurements were performed using the light source of a Spectra Physics Series 2025 Kr^+ laser ($\lambda = 530.9$ nm) coupled via an optical fiber to the cavity of a MPMS-55 Quantum Design SQUID magnetometer. Photomagnetic samples consisted of a thin layer of the compound the weight of which was meticulously measured to 0.3 mg. The optical power at the surface was adjusted to 5 mW cm^{-2}, and it was checked that no change in the magnetic response occurs due to heating of the sample. Our previously published standardized method for measuring the *T*(LIESST) temperature was followed;[13,16,17] i.e. the sample was first cooled slowly to 10 K and then irradiated until photosaturation. The laser was then switched off, and the temperature increased at a rate of 0.3 K min^{-1}. The magnetization was measured every 1 K. The *T*(LIESST) value was determined from the minimum of a $d\chi_M T/dT$ vs *T* plot.

Results

Figure 1 shows the magnetic properties as a function of temperature, expressed as the $\chi_M T$ vs *T* plot, with χ_M being the molar magnetic susceptibility and *T* the temperature. From 300 to 5 K, the $[Fe(L_{222}N_5)(CN)_2]\bullet H_2O$ complex is totally diamagnetic with a $\chi_M T$ product lower than 0.25 cm^3 K mol^{-1}. The Mössbauer spectrum measured at room temperature consists of a quadrupole doublet with a quadrupole splitting of 0.323(1) mm s^{-1} and an isomer shift of 0.121(1) mm s^{-1}, relative to α-iron. These data are typical of iron(II) in the low-spin state and are in accordance with the conclusions of Nelson et al.,[18] who reported a diamagnetic $S = 0$ low-spin iron(II)−metal center at room temperature and proposed a six-coordinate structure, where the macrocycle $L_{222}N_5$ acted as a quadridentate ligand with one

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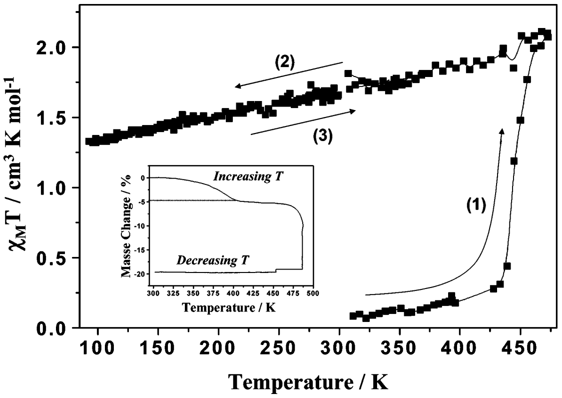

Figure 2. Temperature dependence of $\chi_M T$ scanned at 1 K min^{-1} through the ranges 290 K → 475 K → 90 K → 475 K. The inset graph shows the thermogravimetry analysis performed by using a Setaram setup operating in the temperature range 300−500 K under nitrogen atmosphere at a heating rate of 1 K min^{-1}.

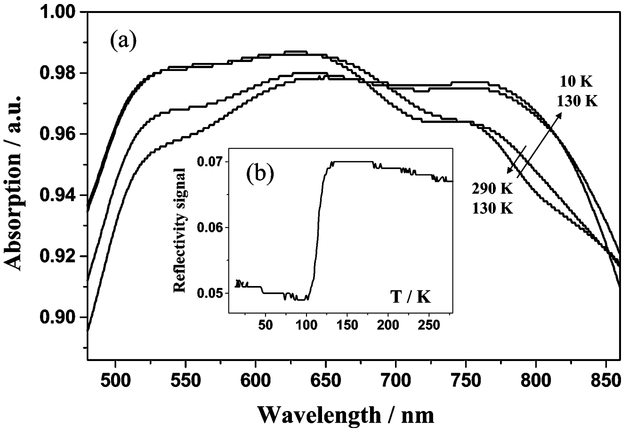

Figure 3. Diffuse absorption spectra recorded as a function of the temperature. The inset graph shows the temperature dependence of the reflectivity signal recorded at 830 nm.

secondary amine group uncoordinated. The observation of a $S = 0$ ground state excludes, in fact, the seven-coordinate pentagonal bipyramidal structure found for other Fe(II) complexes with macrocycle ligands,[19−21] as a singlet ground state is not possible for d^6 metal ions in D_{5h} symmetry.

Nelson et al.[18] also mentioned that a hemihydrate [Fe($L_{222}N_5$)$(CN)_2$]•0.5H_2O complex could be obtained by recrystallization in O_2-free ethanol.[18] In addition to that we have observed that a full dehydration phenomenon occurs if the temperature is increased up to 420 K. The thermogravimetric experiment (see insert of Figure 2) shows an intermediate plateau at around 420 K which corresponds to a weight loss of ca. 4.8% corresponding to one molecule of water before the beginning of the degradation process occurring around 480 K. This dehydration process is not without influence on the magnetic properties (Figure 2). The HS state appears to be stabilized by the loss of water, as described, e.g., by Goodwin et al.[22] for some members of the [Fe(bpp)$_2$]X_2•$n$$H_2O$ (bpp = 2,6-bis(pyrazol-3-yl) pyridine) series. This stabilization of the HS state is illustrated by the drastic increase of the magnetic signal at around 420 K and by the fact that any subsequent cooling and warming cycles do not change significantly the $\chi_M T$ product, which decreases only slightly from 2.0 at 420 K to 1.3 at 100 K.

Figure 3 reports the temperature-dependent diffuse absorption spectra of the hydrated [Fe($L_{222}N_5$)$(CN)_2$]•H_2O complex recorded in the visible range. At room temperature, the black-purple [Fe($L_{222}N_5$)$(CN)_2$]•H_2O complex displays a broad absorption band at around 650 nm, which can be assigned to the MLCT (Metal-to-Ligand Charge Transfer) transition of the LS state. The intensity of this MLCT band remains insensitive to temperature down to ca. 120 K, below which a new phenomenon occurs: the signal of the MLCT band starts to decrease. Moreover, the intensity of the absorption band between 750 and 800 nm, which is characteristic of d−d transition of the HS state, starts to reversibly increase. This behavior is illustrated by the reflectivity signal recorded at 830 nm as a function of temperature (Figure 3b), where a drastic change occurs at ca. 110 K. The reflected 830 nm signal is significantly lower in the temperature region up to ca. 110 K because of the relatively strong absorption by the photoinduced HS state. Around 110 K thermal relaxation of the metastable HS state to the LS state sets in, and the reflected 830 nm signal sharply increases due to the now less efficient absorption. These observations can be understood in regard to the extensive work of Varret et al.[23] using the reflectivity technique for studying molecular spin crossover materials. Apparently, at sufficiently low temperature the light intensity used for recording the reflectivity is able to convert, at the surface of the material, the LS state of [Fe($L_{222}N_5$)$(CN)_2$]•H_2O to the metastable HS state, according to the well-known LIESST phenomenon. This of course would imply that at low temperature the relaxation process of the photoinduced metastable state is extremely slow, which contradicts the tendency expected from the inverse energy gap law proposed by Hauser et al.[3,24] on the grounds of a nonadiabatic multiphonon relaxation model used as a guideline to estimate the lifetime of the photoinduced HS state. Hauser has carefully investigated the relaxation dynamics of the metastable HS state after LIESST in different (diluted) SCO materials and observed a correlation between the lifetime of the LIESST state extrapolated to $T \to 0$ (i.e., in the tunneling region), expressed as $\ln k_{HL}(T \to 0)$, and the thermal spin crossover temperature, $T_{1/2}$ (the temperature of 50% spin state conversion), which serves as a crude measure of the ligand field strength and thus for the energy gap ΔE^0_{HL} between the lowest vibronic levels of the HS and LS states. This relaxation model predicts that the low-temperature tunneling rates $\ln k_{HL}(T \to 0)$ increase dramatically with increasing $T_{1/2}$. In other words, if we consider the low-spin

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iron(II) $[Fe(L_{222}N_5)(CN)_2]{\bullet}H_2O$ complex possessing a $T_{1/2}$ above 400 K, we should never anticipate a photoexcitation of the LS to HS state under continuous irradiation with an appreciable lifetime of the metastable HS state. The LIESST effect should not be observable in the present case.

In order to prove that the LIESST effect does in fact occur in the present "strong-field" complex, we have performed some photomagnetic experiments using a Krypton Laser coupled through an optical fiber to the cavity of a SQUID magnetometer, where the bulk material of the compound was placed. The magnetic susceptibility data recorded of the bulk sample are shown in Figure 1 as the $\chi_M T$ vs T plot. At 10 K, before irradiation, the sample is diamagnetic in its LS electronic configuration. When the light source ($\lambda = 530.9$ nm, 5 mW cm^{-2}) is applied, the magnetic signal is found to drastically increase, and after 1 h a photostationary level is reached with a $\chi_M T$ product close to 2.4 cm^3 K mol^{-1}. The light is then switched off, and the T(LIESST) curve is measured. This type of experiment clearly confirms that a paramagnetic state is populated under light irradiation at low temperature, and we can reasonably state that the metastable HS state was populated through the LIESST phenomenon. This is further supported by the increase of the magnetic signal in the 10−20 K range, where the pronounced increase of $\chi_M T$ with increasing temperature is the well-known effect of zero-field splitting (and thermal population of the higher levels) of a HS iron(II)−metal center in pseudo-octahedral surroundings.[25]

The maximum of the T(LIESST) curve (2.86 cm^3 K mol^{-1}) reached at around 40 K indicates that the level of photoconversion is almost quantitative. Moreover, the existence of a plateau on the T(LIESST) curve is an additional proof that below 60 K the relaxation process is very slow and certainly governed by the nonadiabatic tunneling regime through the energy barrier.[24] In other words, below 60 K the time required to build up the T(LIESST) curve is negligible in regard to the lifetime of the photoinduced HS state. This behavior contrasts with the region above 80 K where the $\chi_M T$ product drastically decreases and rapidly recovers its initial value. The relaxation constant $\ln k_{HL}$ is strongly temperature dependent in this thermally activated regime, but the relaxation is still governed by a tunneling process from thermally populated vibronic levels of the HS state.[24] The minimum of the $d\chi_M T/dT$ versus T curve gives a T(LIESST) temperature of 105 K, a value which is incredibly high for a LS iron(II) compound with LS behavior up to 400 K.[16,17]

Figure 4 displays the decay kinetics for the metastable LIESST state recorded in the 10−102 K temperature range, i.e., up to the highest temperature where the decay of the metastable state can be satisfactorily monitored with a SQUID setup. As expected, the relaxation rates increase with temperature. Below 85 K, the decay is extremely slow. For instance, at 55 K and after 15 h, less than 1% of molecules have relaxed to the LS state. It is therefore almost impossible to measure completely the HS → LS relaxation and, therefore, to properly determine the decay rate $k_{HL}(T)$ at such low temperatures. The HL → LS relaxation kinetics becomes measurable in the time window of our SQUID setup only in the 90−102 K. The most striking feature of these relaxation curves is the strong deviation from single exponential with a marked stretched exponential behavior with a fast component at earlier times and a long decay process at infinite times. Such stretched exponential behaviors have already been mentioned in disordered systems, like an iron(II) spin crossover complex dispersed into a polymer matrix[26] or organized on a surface by the Langmuir−Blodgett technique.[26] For reproducing this type of curves, Hauser et al.[27] used a distribution of relaxation rates at a given temperature with a Gaussian distribution of the activation energy. Following this procedure, the relaxation curves of the $[Fe(L_{222}N_5)(CN)_2]{\bullet}H_2O$ complex can be satisfactorily fitted as illustrated by the solid lines in Figure 4. The apparent activation energy, E_a (=1600 cm^{-1}), and the apparent pre-exponential factor, k_∞ (=5 × 10^6 s^{-1}), of the activated region are calculated from the straight line of the $\ln k_{HL}(T)$ vs $1/T$ plot (Figure 5). The distribution width of the activation energy in a Gaussian approach is 130 ± 30 cm^{-1}.

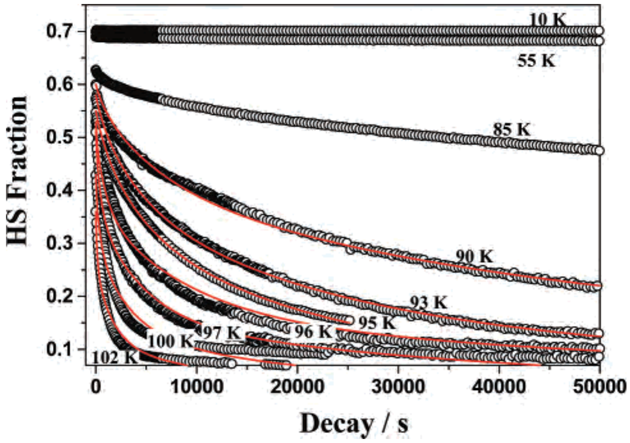

Figure 4. Relaxation curves after illumination at 10 K with the best fits obtained with a stretched exponential decay.

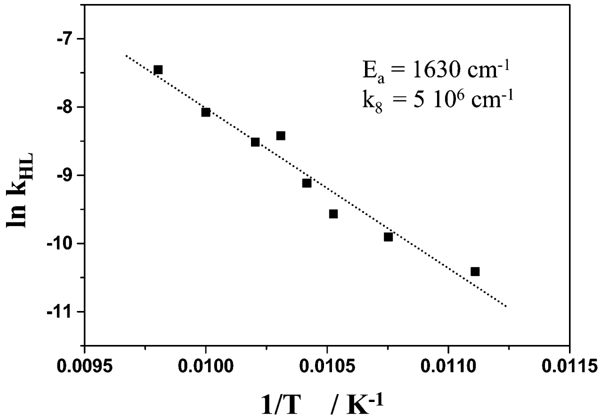

Figure 5. Pseudo-Arrhenius plot $\ln k_{HL}$ versus $1/T$.

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Table 1. Kinetic Parameters of the Photoinduced HS → LS Relaxation Process with k_{HL} the Rate Constant at a Given Temperature (T) and σ the Standard Deviation in Activation Energy According to a Gaussian Distribution

T/K	k_{HL}/s^{-1}	σ/cm^{-1}
90	3×10^{-5}	114
93	5×10^{-5}	99
95	7×10^{-5}	92
96	1.1×10^{-4}	144
97	2.2×10^{-4}	148
98	2×10^{-4}	157
100	3.1×10^{-4}	141
102	5.8×10^{-4}	157

An elegant way to account for the kinetic parameters is to use them for reproducing the experimental T(LIESST) curve. Briefly, it is now well-established that the T(LIESST) curve combines the relaxation of both the tunneling and the thermally activated regions, and we have demonstrated that for a noncooperative spin crossover the time dependence of the HS fraction at temperature T_i can be obtained by following the eq 1.[17,28]

$$\left(\frac{\partial \gamma_{HS}}{\partial t}\right)_{T_i} = -\gamma_{HS}\{k_{HL}(T \rightarrow 0) + k_{\infty} \exp(-E_a/k_B T_i)\} \quad (1)$$

The rate constant k_0 (i.e., $k_{HL}(T \rightarrow 0)$], which characterizes the relaxation in the quantum mechanical tunneling region, is estimated as an upper limit from the last complete kinetic measurement recorded at low temperature, i.e., for the [Fe($L_{222}N_5$)$(CN)_2$]•H_2O complex at 90 K (Table 1). Another difficulty arises from the fact that the relaxation process of the [Fe($L_{222}N_5$)$(CN)_2$]•H_2O complex does not follow a purely exponential behavior, as expressed by eq 1, but a marked stretched exponential behavior with a Gaussian distribution of the activation energy. We have then decided to simulate the T(LIESST) curve as a Gaussian distribution of individual T(LIESST) curves with different activation energies. Based on this, and by using the deduced parameters of k_{∞} ($=5 \times 10^6$ s^{-1}) and E_a ($=1600$ cm^{-1}) with a Gaussian distribution width of activation energy of 130 ± 30 cm^{-1}, we have calculated the T(LIESST) curve (solid line) in Figure 1. The agreement between the calculated and the experimental T(LIESST) curves are very good, which confirms that both the experimental kinetics parameters used in this simulation as well as the fitting procedure are adequate.

Discussions and Conclusion

We have shown that the iron(II)−metal center of the [Fe($L_{222}N_5$)$(CN)_2$]•H_2O complex which is low-spin up to ca. 400 K can be almost quantitatively photoconverted by light irradiation at 10 K. The study of the kinetics and the measurement of the T(LIESST) temperature (105 K) have both evidenced the atypical stability of the photoinduced metastable state. Such a situation contrasts with the tendency expected from the inverse energy gap law proposed by Hauser et al.[3,24,29] This is the second example exhibiting such an unusual behavior. Renz et al.[30] have reported on the existence of the photoinduced HS state with a long-lived lifetime for the purely low-spin complex ions $[Fe(terpy)_2]^{2+}$ (terpy = 2,2′:6′,2′′-terpyridine) doped into a corresponding inert manganese host. This phenomenon was termed strong-field LIESST effect (SF-LIESST).[30] The main difference between the present study of [Fe($L_{222}N_5$)$(CN)_2$]•H_2O and the work of Renz et al. on the $[Fe(terpy)_2]^{2+}$ complex is that in the present low-spin system, LIESST is observed in the neat compound, whereas in the terpy system the complex had to be doped into an appropriate inert matrix, otherwise it showed the expected fast relaxation even at low temperatures.[29]

From a comparison of the photomagnetic properties of all the iron(II) complexes investigated and collected in the T(LIESST)/$T_{1/2}$ database defined by Létard,[16,17] it is clear that factors like the cooperativity, the nature of the salt, or the degree of hydration, i.e., influences coming from outside the coordination sphere, do not seem to be responsible for the existence of such an unusual photophysical behavior like SF-LIESST. The main factor appears to be the inner coordination sphere, predominantly the coordination degree of the ligand.[16,17] It has been evidenced by investigating the photomagnetic properties of more than 60 iron(II) SCO compounds with nitrogen-donor ligands that a simple linear relation governs the LIESST properties of most of these compounds, $T(\mathrm{LIESST}) = T_0 - 0.3T_{1/2}$, where $T_{1/2}$ is the thermal spin transition temperature and T_0 is an empirical parameter corresponding to the y-intercept of the line defined by the data.[14,15] To date four parallel T_0 lines have been established with values of 100, 120, 150, and 200 K.[16,17] By comparing the different T(LIESST)-$T_{1/2}$ values and regarding the chemical nature of the ligands involved, these T_0 lines have been attributed, respectively, to iron(II) complexes involving six independent monodentate ligands,[14] bidentate ligands,[14] meridional tridentate ligands,[15,31] and three-dimensional network solids.[32] The [Fe($L_{222}N_5$)$(CN)_2$]•H_2O system under study involves a macrocyclic Schiff-base L_{222}-N5 ligand, which coordinates in a tetradentate manner, and interestingly the T(LIESST) value (of 105 K) is astonishingly high for a pure iron(II) low-spin complex. In other words, modifying the inner coordination sphere appears to be a promising strategy to stabilize the metastable HS state. Such an alteration around the iron(II)−metal center seems to affect the kinetics of the structural rearrangement accompanying

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the photoinduced HS → LS relaxation by acting on the vibrational properties of the inner core.[29,33]

In this context it is worth noting the work of Schenker et al.,[34] which clearly demonstrates the importance of secondary processes for the lifetime of the photoinduced HS state, such as intraligand-ligand exchange. It seems to bear some relevance to the $[Fe(L_{222}N_5)(CN)_2]\bullet H_2O$ complex of the present study, which also has a noncoordinating nitrogen atom. Of course in the absence of structural data there is no proof, but there is some likelihood that a seven-coordinate HS species is formed[18] which strongly decelerates the HS → LS relaxation to its six-coordinate LS ground state. Along that Hayami et al.[35] have recently reported a high *T*(LIESST) temperature of 130 K for an iron(II) macrocyclic spin crossover compound, the $[FeL(CN)_2]\bullet H_2O$ (L = 2,13-dimethyl-6,9-dioxa-3,12,18-triazabicyclo[12.3.1]octadeca-1(18),2,12,14,16-pentaene), in which the macrocyclic Schiff-base L acts as a pentadentate ligand.[21] It is conceivable that such a structural rearrangement as described above following the light-induced LS → HS conversion leads to a significant quasi permanent weakening of the ligand field strength, which stabilizes the LIESST state with a long lifetime even in the high-temperature region.

Such secondary processes accompanying the "pure" LIESST effect and leading to considerably longer lifetimes of the photogenerated HS state in comparison to the molecular LIESST effect alone, preferably up to room temperature, may play an important role in the context of practical applications. The challenging question is, therefore, how to further increase the *T*(LIESST) value toward the working room temperature by inducing such secondary photochemical processes accompanying the light-induced conversion to the HS state. We believe that the earlier of work of Renz et al.[30] and the present study have opened a new pathway in the area of light-induced spin crossover in transition-metal compounds, probably in particular toward practical applications.

Acknowledgment. The authors thank the DFG/CNRS bilateral program (DFG-Project Gu 95/59), the network of excellence MAGMANet (FP6-515767-2), and the Aquitaine Region for supporting the photomagnetic platform at the ICMCB institute.

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