Photomagnetic properties of the \([\text{Fe}(\text{L}_{222}(\text{N}_3\text{O}_2))(\text{CN})_2]\)•\(\text{H}_2\text{O}\) complex : a fascinating example of multi-metastability

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Abstract. Today, it is known that the \([\text{Fe}(\text{L}_{222}(\text{N}_3\text{O}_2))(\text{CN})_2]\)•\(\text{H}_2\text{O}\) complex exhibits an atypical thermal spin-crossover behaviour probably connected to an unusual change of the iron(II) environment from a six to a seven coordination sphere. Here, we show that the photomagnetic properties of this derivative are also atypical. When the sample is initially prepared in the LS form, by a cooling process of 3 K/min, the light irradiation gives access to a long-lived metastable HS state with a \(T(\text{LIESST})\) value of 132 K. This photoinduced HS state is moreover characterised by a strong cooperative lattice, as reflected by the kinetic relaxations which follow a sigmoidal model and the existence of a Light-Induced Thermal Hysteresis (LITH) loop. At the opposite, when the sample is carefully placed into the LS/HS mixture state, by using a slow cooling process of less than 1 K/min, the light irradiation generates a metastable state with a \(T(\text{LIESST})\) value of only 73 K and the influence of the cooperativity is weak. The relaxation curves are indeed satisfactory fitted by using a stretched exponential model and the LITH phenomenon is not present. All these data will be discussed in term of multi-metastability.

1. Introduction

In the promising context of the development of information technology, the ability of a molecular system to exist in different electronic states is of particularly importance since logic operations can be executed. A fascinating example is given by the molecular bistability using the spin crossover (SCO) phenomenon, which is encountered in metal complexes having a 3d\(^4\)-3d\(^7\) electronic configuration. Materials of this sort have the possibility to switch from a high spin (HS) to a low spin (LS) state, and vice versa, in response to an external perturbation such as a change in temperature or pressure or on irradiation or exposure to a magnetic field [1].

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A fascinating challenge in such a context would be the design of a SCO material exhibiting not only a bistability process, but a multistability tuneable by various external perturbations. To this respect, we recently demonstrated in some iron(II) binuclear SCO complexes, the existence of both magnetic interaction and photoinduced spin conversion [2,3]. As a consequence, the photomagnetic behavior of such binuclear systems cannot be any more described in terms of two potential wells (i.e. a stable and a metastable states) but the LS/HS spin states of each metal center as well as the five HS-HS states linked to the intramolecular antiferromagnetic interaction (J) must be considered. As a continuation of this investigation of multi-metastable SCO complexes, we would like to report here the atypical behavior encountered with the [Fe(L_{222}(N_3O_2))(CN)_2]·H_2O complex, dicyano[2,13-dimethyl-6,9-dioxa-3,12,18-triazabicyclo [12.3.1]-octa-deca-1(18),2,12,14,16-pentaene]iron(II) monohydrate (Scheme 1).

Scheme 1. Ball and stick view of the molecular structure of the title iron(II) complex determined in the high spin state by X-ray diffraction.

Nelson et al. [4,5] were the first to evidence the atypical magnetic properties on the [Fe(L_{222}(N_3O_2))(CN)_2]·H_2O complex. They noticed that depending on the temperature range, the thermodynamically stable form is the HS state (at ambient temperature), the LS state (below 150 K) or the LS/HS mixture state (between 150 K and 200 K). Later on, Sato et al. [6] observed that the lifetime of the photoinduced HS state, generated through the Light-Induced Excited Spin-State Trapping (= LIESST) effect [7], was extremely long in regard to the other SCO compounds known within the literature [8], and mentioned an atypical bidirectional LIESST processes depending on the illumination history [9].

In the present work, we report the photomagnetic properties of this complex depending on the thermal history; i.e. when at low temperature the thermodynamic stable form is carefully controlled by an adequate experimental protocol. We will see that the effect is not negligible on the lifetimes of the photoinduced HS state.

### 2. Experimental Section

The thermal spin transition was followed in both cooling and warming modes by measuring the magnetic susceptibility with a MPMS-55 Quantum Design SQUID magnetometer operating at ca. 2 Tesla in the 2-340 K. These data are represented in the form of $\chi$ vs T plots, $\chi$ being the molar magnetic susceptibility corrected of the diamagnetism of the closed-shell core, and T the temperature. The $T_{1/2}^{\downarrow}$ and $T_{1/2}^{\uparrow}$ define the temperatures for which there are 50% of converted LS and of HS molecules in the cooling and warming modes, respectively.

Photomagnetic experiments were carried out by using a Kr⁺ laser coupled through an optical fiber to the cavity of the SQUID magnetometer. The sample is deposited on a very thin layer to avoid any problem of light penetration. The weight was estimated from the thermal spin crossover curve recorded with a heavier and accurately weighed sample. The laser irradiation was performed at 530.9 nm and power was fixed at 5 mW/cm² to avoid any heating problems. The T(LIESST) value defines the temperature for which the light-induced HS information was erased into the SQUID cavity [10-13]. In such a procedure, the sample was always irradiated at 10 K until photo-saturation, then in the dark the temperature was increased at the rate of 0.3 K min⁻¹. The T(LIESST) temperature was estimated from the minimum of the derivate. The Light-Induced Thermal Hysteresis (LITH) curve was investigated by maintaining the light irradiation during the cooling and the warming modes at the rate of 0.3 K min⁻¹ [10,14].
3. Results and Discussion

3.1 Synthesis and X-ray diffraction. The synthesis of the iron(II) [Fe(L_{22}(N3O2))(CN)_2]•H_2O complex was performed by using the procedure of Nelson et al. [4]; i.e. by mixing in first the 2,6-diacetylpyridine, the 3,6-dioxaoctane-1,8-diamine and the FeCl_2.4H_2O in deoxygenated methanol/aqueous solution containing Na_2S_2O_4. Then, the solution was partially concentrated, filtered into an aqueous solution of NaCN containing Na_2S_2O_4 and washed. The powder of [Fe(L_{22}(N3O2))(CN)_2]•H_2O was finally obtained by drying in vacuum the solution. Elemental analysis was in line with the expected formula: calculated for C_{17}H_{23}N_{5}O_{3}Fe C 50.89, H 5.74, N 17.46, Fe 13.93; found C 50.89, H 5.78, N 17.45, Fe 13.92.

By slow diffusion single crystals can also be obtained. In this context, we have recently reported a reinvestigation of the X-ray structure of the [Fe(L_{22}(N3O2))(CN)_2]•H_2O complex at room temperature [15]. The crystal structure of the high spin form was first reported by Sato et al. [6]. However, in the latter, the level of symmetry of the crystal packing and the iron atom site was underestimated. We reinvestigated the HS crystal structure showing that the iron ion lays on a twofold axis [15]. One consequence of importance of such feature is that, in the case of a change of the iron environment from a seven to a six coordination sphere, there must necessarily be a change in the crystal symmetry. Furthermore, a large structural change can also be predicted at low temperature by considerations of the volume of the iron coordination sphere. Indeed, the expected transition from a seven-coordinate HS iron ion to a six-coordinate iron ion would correspond to a decrease of the iron polyhedron volume from almost 60%, i.e. from 17 Å^3 to 10 Å^3 respectively. This large modification is consistent with the observation made by Sato et al [6], Collet et al. [16] and ourselves [17] of the damaging of the single crystal at low temperature. A variable temperature powder X-Ray diffraction analysis is currently underway to elucidate the low spin crystal structures of the title complex.

3.2 Magnetic properties along the thermal spin transition. The Figure 1 reports the magnetic properties obtained during the first cooling and warming mode and those found for the subsequent thermal cycles. On one hand, these data perfectly agree with those previously reported by Nelson et al. [4,5] and latter on by Sato et al. [6], but on the other hand, these data bring a new light on the experimental conditions that lead to the formation of the low temperature forms.

Firstly, we noticed that when the sample was cooled at a constant rate of 3 K/min the magnetic behaviour of the first thermal cycle was the one reported in Figure 1a. For the subsequent thermal cycles (recorded at the same cooling rate) its corresponds to the Figure 1b. More precisely, on the primary cooling mode (Figure 1a) the $\chi_{MT}$T product slightly decreases from room temperature to 164 K, then suddenly drops at around 156 K, to reach a value close to 0.5 cm^3 M mol^{-1} below 130 K. On the warming mode, the magnetic signal increases at around 165 K, then decreases in the vicinity of 170-200 K and finally increases at around 220 K. For the second (and subsequent) thermal cycle(s), only a partial spin transition takes place at $T_{1/2}^{\downarrow} = 180$ K and $T_{1/2}^{\uparrow} = 220$ K, which corresponds to a thermal hysteresis loop of 40 K. The $\chi_{MT}$T product recorded below 160 K (1.5 cm^3 M mol^{-1}) was, in this case, consistent with the equal proportion of LS/HS states found by Mössbauer measurements [5].

Secondly, by repeating several times the thermal SCO properties, we realized that if the delay between two subsequent thermal cycles exceeded 8 hours at room temperature, the system is able to recover its original properties, displayed in Figure 1a. Along this line, for intermediate delay times of 1-6 hours between two subsequent thermal cycles, we were able to record at low temperature some intermediate magnetic responses between the values found for the LS and the HS/LS forms. This part is, in fact, not the one that we would like to describe in this paper. Let us just briefly indicate that by investigating both the powder X-ray diffraction and the photomagnetic properties we were able to prove that such intermediate forms were in reality not some new phases, but just a combination of LS and LS/HS forms [17].

Thirdly, by changing the cooling rate we found that even if the sample is initially prepared into the condition where the LS form can be expected at low temperature, the HS/LS can be formed.
fact, when the cooling rate was 3 K/min the LS form was effectively measured at low temperature while with a rate of 1 K/min only the LS/HS mixture state was found.

3.3 Photomagnetism. As a continuation of this investigation, we have studied the photomagnetic properties recorded in the case where the sample at low temperature is prepared into the situation of the LS state and of the LS/HS state. As expected from the work of Sato et al. [6], we were able to observe in both cases a drastic increase of the magnetic signal when the light irradiation (\(\lambda = 530.9\) nm) was applied at 10 K.

Figure 1. Temperature dependence of \(\chi_{MT}\) for [Fe(L_222(N_3O_2))(CN)_2]*H_2O a) in a first thermal cycle and b) in a second and/or a subsequent thermal cycles. ▲ = data recorded in the cooling and warming mode without irradiation; ○ = data recorded with irradiation at 10 K; Δ = T(LIESST) measurement, data recorded in the warming mode after an optical irradiation of 24 hours. The Inset graph reports the derivate of the magnetic product as function of the temperature. The minimum of the curve gave the T(LIESST) temperature.

Concerning now the T(LIESST) curve recorded in the condition where the thermodynamic stable form is the LS/HS state (Figure 1b), we also found as previously an influence of the zero-field splitting in the 10-20 K temperature range with a slight increase of the \(\chi_{MT}\) product, and of the tunnelling regime between 20 and 60 K with an almost constant \(\chi_{MT}\) product. But in this case, the thermally activated regime which control the T(LIESST) temperature appears to be predominant above 60 K. More precisely, the T(LIESST) temperature was found at 73 K.

An elegant way to collect some information on the photo-induced HS state is to record the magnetic response under light irradiation along the cooling and warming modes. When a Light-
Induced Thermal Hysteresis (LITH) is observed it is an indication that a competition occurs between the constant photo-excitation and the self-accelerated thermal relaxation process [14]. Figures 2a and 2b present the two experiments performed, respectively, for an initial sample in the LS form and the LS/HS form. Only the former exhibits a width LITH loop with transition temperatures at 73 K for the cooling branch and 132 K for the warming branch. The photomagnetic responses of the latter during the cooling and the warming modes are identical. The cooperativity of the two photoinduced metastable states seems to be consequently strongly different.

Figure 2. LITH experiments for a sample initially prepared a) in the first thermal cycle and b) subsequent thermal cycles.

This conclusion is also supported by the kinetics study performed in the vicinity of the T(LIESST) region. Figure 3 presents a typical example of relaxation curves recorded after irradiation in the case of a thermodynamic stable LS and LS/HS forms. Both kinetic curves strongly deviate from a single exponential law; the relaxation curves deduced from an original LS state show a marked sigmoidal type behaviour with the presence of a self-acceleration factor, as predicted for high cooperative spin-crossover materials, while those with an original LS/HS form can be satisfactorily analysed with a stretched exponential mode, behaviour typical of a weak cooperative system. Such a result evidenced that this [Fe(L222(N3O2))(CN)2]•H2O complex can not be properly described by taking into account a two potential levels, constituted by a stable LS state and a metastable photo-induced HS state.

Figure 3. Time dependence of the high spin molar fraction generated by light irradiation a) at 115 K for a compound initially into the LS state and b) at 65 K for a sample initially into the LS/HS mixture state.

4. Conclusion

Nelson et al. [4,5] in the original paper proposed that between the room temperature and the low temperature region a reorganisation of the local sphere occurred from a seven- to a six-coordination. But nothing was mentioned for the photo-induced metastable HS state. In the work of Sato et al. [6], it was not clear if the thermodynamic phase before irradiation was properly the LS form or the LS/HS form (See the Insert graph of the Figure 2 in Ref. [6]). Moreover, these authors also mentioned an atypical photoinduced magnetic memory effect by a sequential irradiation with a 520 nm, 980 nm, and 1340 nm, and reported a T(LIESST) temperature of 77 K [9].

In the present work, we demonstrate that the photomagnetic properties originate within the thermal spin crossover history. Depending on the thermal pre-treatment of the complex, two different thermodynamic stable forms can be reached at low temperature, respectively the LS state and the
LS/HS state, and each of them is sensible to the light irradiation. The optical irradiation of the LS state
gives access to a metastable state with an exceptionally long-lived lifetime, $T_{(LISSST)} = 132$ K, while
LS/HS state is photo-converted into a metastable state with a $T_{(LISSST)}$ temperature of only 73 K.
The different nature of the two photoinduced HS states is also illustrated by the measurements of the
LITH loop and of the kinetic studies. The scheme 2 summarises this approach without discussing the
exact nature of the various states involved, in terms of seven- or six-coordination.

Further works are currently in progress by syntheising some analogous complexes, by
changing the multidentate $\text{N}_3\text{O}_2$ macrocyclic
Schiff-base ligand, by diluting the iron(II)
metal centers into ‘host’ matrice of zinc, cobalt
or manganese and by deuterating the water
molecule.

**Scheme 2.** Thermodynamic routes to the
different states involved along the thermal spin
crossover and the photo-induced processes

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