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Effect of the metal dilution on the thermal and light-induced spin transition in $[Fe_xMn_{1-x}(bpp)_2](NCSe)_2$: When T(LIESST) reaches $T_{1/2}$

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ABSTRACT

The thermal and light-induced spin transition in $[Fe_xMn_{1-x}(bpp)_2](NCSe)_2$ (bpp = 2,6-bis(pyrazol-3-yl)pyridine) has been investigated by magnetic susceptibility, photomagnetism and diffuse reflectivity measurements. These complexes display a thermal spin transition and exhibit the light-induced excited spin state trapping (LIESST) effect at low temperature. For each mixed-crystal system, the thermal spin transition temperature, $T_{1/2}$, and the relaxation temperature of the photo-induced high-spin state, T(LIESST), have been systematically determined. It appears that $T_{1/2}$ decreases with the metal dilution while T(LIESST) remains unchanged, suggesting that the two interconversion processes are controlled by different factors; i.e. the photomagnetic properties are governed at the molecular scale and the thermal spin crossover regime is affected by both the ligand field and crystal packing effects. For highly metal-diluted complex with $x < 0.2$, it is found that when $T_{1/2}$ reaches the T(LIESST), the complex remains HS on the whole range of temperature.

1. Introduction

In the course of the miniaturization the design of molecular materials able to store information represents a fascinating challenge for the future development of magnetic and optical data storage. In this particular context, metal ions with $3d^4$–$3d^7$ electronic configuration in an octahedral environment, exhibiting high-spin state (HS) ↔ low-spin (LS) crossover under the influence of external perturbations such as variation of temperature, application of pressure, light and high magnetic fields, are promising candidates [1–3]. The optical information can be reversibly written and/or erased by the well-known direct or reverse light-induced excited spin state trapping (LIESST) effect [4–6]. Since the discovery of this effect, many studies have been dedicated to identify the parameters allowing to influence the lifetime of the photo-induced metastable HS state.

An early attempt to correlate the spin transition temperature with the thermal relaxation temperature after LIESST was reported by Herber et al. [7,8], but it was really Hauser in 1991 who has introduced the first quantitative guideline allowing some expectation on the lifetime of the photo-induced HS state [9]. Hauser has carefully investigated the dynamics of the LIESST effect in different diluted spin crossover (SCO) materials and noticed a strong correlation between the lifetime of the LIESST state extrapolated to $T \rightarrow 0$ (i.e. in the tunnelling region [10]), expressed as $\ln k_{HL}(T \rightarrow 0)$, and the thermal spin crossover temperature, $T_{1/2}$ [11–13]. In other words, Hauser has demonstrated that the lifetime of the metastable LIESST state is inversely proportional to $T_{1/2}$ (assumed to vary with ΔE_{HL}°). This relation has become known as the inverse-energy-gap law [7]. But one of the difficulty of the inverse-energy-gap law is to properly determine the $T \rightarrow 0$ lifetime, particularly when the photo-induced HS state is very stable in the tunnelling region. For this reason, we have proposed to compare the various SCO materials by systematically measuring the T(LIESST) value [14], i.e. the limit temperature above which the light-induced magnetic HS information is erased when the temperature is increased from 10 K at a rate of 0.3 K min^{-1}. T(LIESST) represents a somewhat limiting temperature of photo-inscription: below this limit, the lifetime of the photo-induced HS state is usually of the order of days, whereas above T(LIESST), the photo-induced HS state decays in a few seconds. This method has been applied up to now to more than sixty neat SCO materials and, by comparing the various materials, a linear relation between T(LIESST) and $T_{1/2}$ temperatures has been obtained, i.e. $T(LIESST) = T_0 - 0.3\ T_{1/2}$ [15–18]. We have also proposed that factors outside the inner metal coordination sphere, such as intermolecular cooperativity, crystal packing and the identity of any anions and solvent in the material, result in only minor perturbations to T_0 for a given set of metal complexes, while the influence of the geometry and of the conformational rigidity of

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the ligand donors around the metal ion appears to be crucial [17,18]. This finding lends support to the idea that the photomagnetic properties are somehow governed at the molecular scale and then linked to the inner metal coordination sphere through intramolecular vibrations [18,19].

To pursue this study, we have recently investigated the influence of metal dilution on the T(LIESST)/$T_{1/2}$ relation [20]. Interestingly, in the metal-diluted $[Fe_xZn_{1-x}(Phen)_2(NCS)_2]$ (Phen = 1,10-phenanthroline) series, the spin transition temperature ($T_{1/2}$) has been found to decrease with the metal dilution while T(LIESST) remained unchanged. Our interpretation is that the thermal spin crossover regime is mainly governed by the thermodynamics and the cooperative interactions while the photomagnetic properties appear to be mainly controlled at the molecular scale, explaining why the use of two potential wells for interpreting the relaxation process is pertinent. In the present work, our primary objective is to investigate the effect of metal dilution in another SCO series, the $[Fe_xMn_{1-x}(bpp)_2](NCSe)_2$ (bpp = 2,6-bis(pyrazol-3-yl)pyridine). The iron(II) SCO $[Fe(bpp)_2](NCSe)_2$ complex has been selected in view of both its abrupt thermal spin transition, well defined with a small hysteresis loop of 2 K ($T_{1/2}\downarrow = 230$ K, $T_{1/2}\uparrow = 232$ K) [21], and its relatively high T(LIESST) value of about 75 K [16,22]. For each metal-diluted mixed-crystal ($0.2 \leqslant x \leqslant 1$), we have measured systematically the $T_{1/2}$ and T(LIESST) values. Two questions have been of particular interest in the present study: (i) Does the $T_{1/2}$ temperature also in this mixed-crystal series progressively approach the T(LIESST) value? (ii) What is the high temperature limit where $T_{1/2}$ becomes close to T(LIESST), i.e. when the stability of the thermally induced HS state merges with the metastability region of the photo-induced HS state? As a favourable case we have selected manganese(II) as diluting metal ion, which is characterized by a large ionic radius (r = 83 pm) with regard to the iron(II) metal radius of HS (78 pm) or the LS (61 pm) state [23], and where we can anticipate a pronounced effect on the $T_{1/2}$ temperature [24].

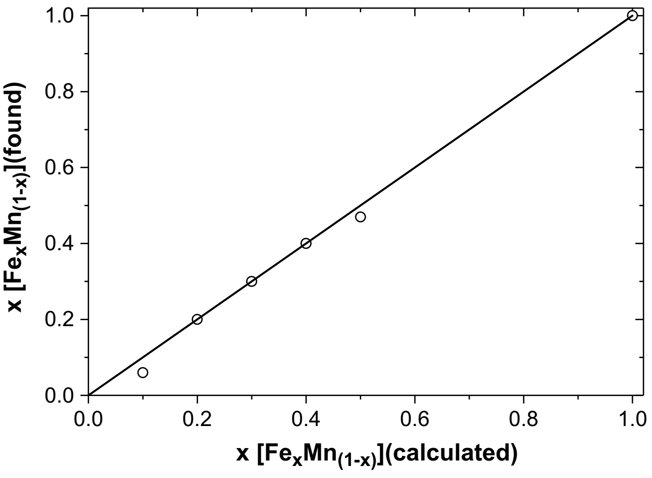

Fig. 1. Iron fraction obtained from elemental analysis vs. iron fraction calculated from the relative amounts of metallic salts used for the synthesis. The full line corresponds to the situation where x(found) = x(calculated).

Table 1
Spin transition temperature in cooling [$T_{1/2}\downarrow$] and warming [$T_{1/2}\uparrow$] modes, hysteresis width [ΔT], values at room temperature $\chi_M T$ for $[Fe_xMn_{1-x}]$, values at room temperature $\chi_{Fe}T$ for $[Fe_xMn_{1-x}]$, T(LIESST) values

x	$T_{1/2}\downarrow$ (K)	$T_{1/2}\uparrow$ (K)	ΔT (K)	$\chi_M T_{HS}$ (cm^3 mol^{-1} K)	$\chi_{Fe} T_{HS}$ (cm^3 mol^{-1} K)	T(LIESST)(K)
1	231	233	2	3.03	3.03	75
0.47	150	150	0	3.73	1.42	84
0.4	130	130	0	3.84	1.21	86
0.3	118	118	0	3.96	0.91	87
0.2	105	105	0	4.09	0.61	87
0.2	HS state			4.18	0.18	/
0	HS state			4.36	0	/

2. Experimental

2.1. Materials

The preparation of $[Fe(bpp)_2](NCSe)_2$ with bpp = 2,6-bis(pyrazol-3-yl) pyridine has been described earlier by Sugiyarto et al. [21]. The diluted compounds $[Fe_xMn_{1-x}]$ were synthesized according to the same procedure, replacing the metal salt by mixtures of iron(II) chloride and manganese(II) chloride in given ratios. The elemental analysis of C, H, N was performed, and the results agreed well with the calculated data. The values of the iron fractions (x) were calculated from the iron and manganese atomic percentages determined by quantitative analysis. The discrepancies between the found and calculated values are minor, as can be seen in Fig. 1. The X-ray powder diffraction of $[Fe(bpp)_2](NCSe)_2$, $[Mn(bpp)_2](NCSe)_2$ and diluted compounds $[Fe_xMn_{1-x}]$ have been done and all the compounds are isomorphous.

2.2. Magnetic and photomagnetic measurements

The thermal spin transition of all the investigated compounds was followed in both cooling and warming modes by measurement of magnetic susceptibility and optical reflectivity. Values are collected in Table 1.

The magnetic susceptibility measurements were obtained with a MPMS-55 Quantum Design SQUID magnetometer. Photomagnetic experiments were carried out by using the light source of a Spectra physics Series 2025 Kr$^+$ laser (λ = 647 nm, optical power adjusted to 5 mW cm^{-2}) coupled via an optical fiber to the cavity of the SQUID magnetometer. Photomagnetic samples consisted of a very thin layer of the compound. Its weight was obtained by comparing its thermal spin crossover curve with the curve recorded with a heavier and accurately weighed sample of the same compound. The procedure to measure the T(LIESST) temperature was as previously published [14,18].

The measurement of the diffuse absorption spectra and reflectivity signal were performed by using a custom-built set-up equipped with a SM240 spectrometer (Opton Laser International). This equipment allows to record 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 activated charcoal (Merck) as black standard and barium sulfate ($BaSO_4$, Din 5033, Merck) as white standard.

3. Results and discussions

3.1. Thermal spin crossover properties

Fig. 2 shows the evolution of the $\chi_M T$ product as a function of temperature (χ_M is the magnetic susceptibility for 1 mol of mononuclear entities and T is the temperature) in the dark. For the two neat $[Fe(bpp)_2](NCSe)_2$ and $[Mn(bpp)_2](NCSe)_2$ complexes, the $\chi_{Mn}T$ values at room temperature were experimentally measured as 3.03 cm^3 mol^{-1} K and 4.36 cm^3 mol^{-1} K (see Table 1). The $\chi_M T$ product of the diluted $[Fe_xMn_{1-x}]$ systems was found to increase with the metal dilution due to the paramagnetic contribution of the manganese(II) ion (d^5, $S = 5/2$), both at room temperature where