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Photo-induced spin-transition: the role of the iron(II) environment distortion

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The [FeL$_n$(NCS)$_2$] iron(II) spin-crossover complexes cover a wide range of magnetic behaviour. Owing to the large number of known structural and magnetic data, this series is perfectly adapted to the investigation of the structure–magnetic properties relationship. In this paper we propose a new structural parameter, denoted Θ, which is used to correlate the features of the spin-crossover phenomena with the distortion of the iron environment. In particular, this parameter has shed light on the role of such distortion on the limiting temperature of photo-inscription, known as T(LIESST). A strong dependence of T(LIESST) on Θ is clearly demonstrated. The stronger the distortion the higher the T(LIESST) value. This structure–property dependence represents, for instance, a powerful tool to estimate the highest potential T(LIESST) value for a series of complexes. This limit in the [FeL$_n$(NCS)$_2$] series is estimated to be around 120 K, which probably prevents their use in any industrial application.

1. Introduction

The ability of a transition metal ion to change its spin state is known as the spin-crossover (SCO) phenomenon. For an iron(II) ion, the change involves a diamagnetic low-spin state (LS), corresponding to a $t_{2g}^6e_g^0$ electronic configuration ($S = 0$), and a paramagnetic high-spin state (HS), corresponding to a $t_{2g}^4e_g^2$ electronic configuration ($S = 2$). Interestingly, such a magnetic state modification can be triggered by an external perturbation such as temperature, pressure, light irradiation or a pulsed magnetic field (Bousseksou *et al.*, 2000; Gütlich *et al.*, 2003). The transition from one spin state to the other is generally perfectly reversible and occurs without any fatigability even in the solid state. This is particularly interesting with regard to potential industrial applications (Jay *et al.*, 1993; Kahn & Jay Martinez, 1998). In this context one of the most promising aspects of the spin crossover is the possibility of inducing a spin-state modification by light irradiation. However, the main limitation of the light-induced spin conversion for industrial use is the temperature up to which it is possible to retain the photo-induced information. This temperature limit is denoted as T(LIESST) (Létard, Capes *et al.*, 1999), where LIESST = Light-Induced Excited Spin-State Trapping. To date, the highest T(LIESST) value in an iron(II) SCO material does not exceed 132 K (Hayami *et al.*, 2001) and the highest T(LIESST) value in all the spin-crossover materials, which is obtained for Prussian blue analogues, is 145 K (Shimamoto *et al.*, 2002). Consequently, one of the main challenges in the spin-crossover community is to find new spin-crossover compounds with higher T(LIESST) values. With this

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Table 1
Spin-crossover temperatures and values of the metal-environment distortion parameters, Θ and $\Delta\Theta$, for the [FeL$_n$(NCS)$_2$] complexes.

The labels used in the figures are defined here. Notation: ND: no low-temperature structural data available in the literature.

Compound	Label	T(LIESST) (K)	$T_{1/2}$ (K)	Θ (°) HS	Θ (°) LS	$\Delta\Theta$ (°)
[Fe(PM-TheA)$_2$(NCS)$_2$]-II^a	1	–	243	189	160	29
[Fe(btz)$_2$(NCS)$_2$]^b	2	–	215	218	156	62
[Fe(bpy)$_2$(NCS)$_2$]-II^{c,d}	3	–	213	248	143	105
[Fe(PM-TheA)$_2$(NCS)$_2$]-I^a	4	–	208	227	160	67
[Fe(PM-BiA)$_2$(NCS)$_2$]-II^a	5	34	190	207	133	74
[Fe(PM-BiA)$_2$(NCS)$_2$]-I^e	6	78	168	254	149	105
[Fe(PM-AzA)$_2$(NCS)$_2$]^f	7	46	189	214	130	84
[Fe(PM-PeA)$_2$(NCS)$_2$]^e	8	–	188	230	164	66
[Fe(abpt)$_2$(NCS)$_2$]^g	9	40	180	278	ND	ND
[Fe(phen)$_2$(NCS)$_2$]^{h,i,j,k}	10	62	176	228	128	100
[Fe(dppa)(NCS)$_2$]-*A*^{l}	11	–	176	145	ND	ND
[Fe(dppa)(NCS)$_2$]-*C*^{l}	12	–	112	152	ND	ND
[Fe(bt)$_2$(NCS)$_2$]-*A*^{m,n,o}	13	–	171	286	ND	ND
[Fe(tap)$_2$(NCS)$_2$]·CH$_3$CN^p	14	52	168	196	107	89
[Fe(dpea)(NCS)$_2$]^l	15	–	138	224	ND	ND
[Fe(PM-TeA)$_2$(NCS)$_{2.}$]·0.5CH$_3$OH^f	16	–	125	242	158	84
[Fe(dpp)$_2$(NCS)$_2$]·py^q	17	–	123	249	ND	ND
[Fe(py)$_2$bpym(NCS)$_2$]·0.25py^r	18	60	114	186	ND	ND
cis-[Fe(stpy)$_4$(NCS)$_2$]^s	19	–	110	55	ND	ND

(*a*) Marchivie *et al.* (2005); (*b*) Real *et al.* (1992); (*c*) König *et al.* (1968); (*d*) Konno & Mikami-kido (1991); (*e*) Létard, Guionneau *et al.* (1997) and Létard, Montant *et al.* (1997); (*f*) Guionneau *et al.* (1999); (*g*) Moliner *et al.* (1999); (*h*) Baker & Bobonich (1964); (*i*) König & Watson (1970); (*j*) Lee *et al.* (2000); (*k*) Müller *et al.* (1982); (*l*) Matouzenko *et al.* (1997); (*m*) Bradley *et al.* (1979); (*n*) König *et al.* (1979); (*o*) Müller *et al.* (1983); (*p*) Real *et al.* (1994); (*q*) Zhong *et al.* (1998); (*r*) Claude *et al.* (1990); (*s*) Roux *et al.* (1994).

end in sight, this paper outlines a structural parameter that accounts for the diversity of the T(LIESST) values among the iron(II) spin-crossover complexes.

2. Results and discussion

On the molecular scale, the spin transition is related to structural modifications such as metal–ligand bond length changes (König, 1987). This has been widely studied over the past 35 years (Gütlich & Hauser, 1990; Gütlich *et al.*, 1996; Kahn, 1993), but it is only recently that direct correlations have been found between the structure and magnetic properties of spin-crossover systems. For instance, in the [FeL$_n$(NCS)$_2$] series of complexes, the propagation of the spin conversion throughout the crystal, also called the cooperativity, is found to depend directly on the strength of some clearly identified hydrogen-like intermolecular interactions (Marchivie *et al.*, 2003). However, until now, no relationship between a structural feature and T(LIESST) has been shown.

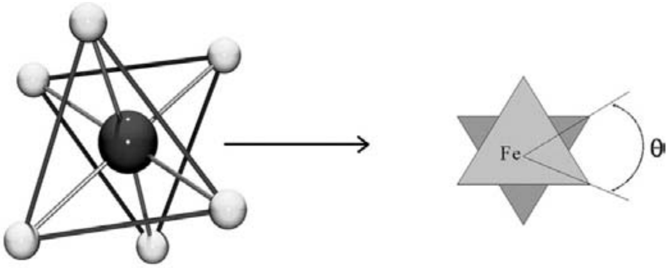

Figure 1
Metal environment in iron(II) [FeL$_n$(NCS)$_2$] complexes. Definition of the θ angle (Marchivie *et al.*, 2003).

In an earlier investigation of the [FeL$_n$(NCS)$_2$] complexes, the octahedral distortion of the metal-ion environment was estimated from the observation of the N—Fe—N angles (Guionneau *et al.*, 1999, 2001). Later, a structural parameter, denoted Σ and defined as the sum of the deviations (from 90°) of the 12 *cis* φ angles in the coordination sphere, was used to accurately evaluate the octahedral distortion. Interestingly, this parameter proved to be spin-state dependent and can thus be used to determine the spin state of the metal ion (Guionneau *et al.*, 2002). Unfortunately, Σ is not correlated to either T(LIESST) or any of the spin-crossover features (Guionneau *et al.*, 2004). However, the distortion of an octahedron can be defined in several ways. For example, the distortion parameter, denoted θ, can be introduced to account for the deviation in the Fe—N$_6$ geometry from a perfect octahedron (O_h) to a trigonal prismatic structure (D_{3h}). This parameter is derived from the trigonal twist angle (McCusker *et al.*, 1996). It is defined as the N—Fe—N angle measured on the projection of the two triangular faces of the octahedron projected along its pseudo-threefold axes on the medium plane containing the metal ion (Fig. 1).

As the value of θ depends on the orientation, we propose investigating a parameter that takes into account the 24 possible θ angles. This parameter, denoted Θ, is defined as the sum of the deviations from 60° of the 24 possible θ angles. Incidentally, this definition can be compared with the above Σ parameter definition.

$$\Theta = \sum_{i=1}^{24} \left(\left| 60 - \theta_i \right| \right).$$

Thus, Θ represents the deviation of the Fe—N$_6$ geometry from perfectly octahedral (O_h) to a trigonal prismatic structure (D_{3h}). It then becomes clear that the more distorted the octahedron the higher the Θ value. High values of Θ should therefore be found for a high-spin state, known to be strongly distorted, while lower values should be found for a low-spin state which adopts a more regular geometry (Guionneau *et al.*, 2002).

Table 1 gathers Θ parameter values which have been calculated for *ca* 20 of the complexes within the [FeL$_n$(NCS)$_2$] series. The Θ values are indeed significantly higher in the HS state than in the LS state for the same complex. These values strongly differ from one complex to another.

In an attempt to find the origin of such diversity, we decided to study the variation of Θ *versus* the cooperativity in the [Fe(PM-L)$_2$(NCS)$_2$] series (Fig. 2). For this we have used the ΔT_{80} parameter which represents the cooperativity of the system and is defined as the temperature gap needed to undergo a spin transition from 80% high spin to 80% low spin (20% high spin; Kröber *et al.*, 1994). Clearly, the more distorted the octahedron, the more abrupt the transition, *i.e.* the more ΔT_{80} decreases. However, it is particularly interesting to note that such a correlation can also be extended to additional complexes belonging to the [FeL$_n$(NCS)$_2$] family (Fig. 2). This confirms the peculiar role of the distortion of the iron environment on the cooperativity, which was previously suggested from an investigation of the twist angle (Marchivie *et al.*, 2003).

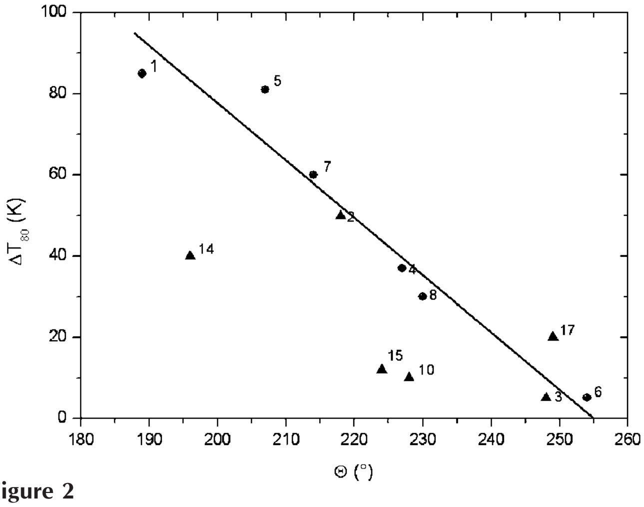

Figure 2
Plot of the trigonal distortion parameter of the metal environment in the HS state, Θ, *versus* the cooperativity ΔT_{80} parameter (see text for definition) for the [FeL$_n$(NCS)$_2$] series. Circles: [Fe(PM-L)$_2$(NCS)$_2$] complexes; triangles: other complexes of the [FeL$_n$(NCS)$_2$] complexes.

More interestingly, Θ appears to be correlated to *T*(LIESST). Indeed, the general tendency is that the higher the Θ value the higher the *T*(LIESST) value (Table 1). This correlation becomes even more obvious if ΔΘ, which is the difference between the Θ values for the HS and the LS states, is plotted as a function of *T*(LIESST) (Fig. 3). Indeed, ΔΘ increases almost linearly with *T*(LIESST). This is the first time to our knowledge that a structural parameter has been directly identified as influencing the *T*(LIESST) value. This correlation first gives crucial information to the chemists responsible for the design of new spin crossovers with high *T*(LIESST) values. Clearly, they have to design complexes with a distorted metal environment. Furthermore, beyond the simple observation and whatever fascination it creates, this correlation requires further physical investigations to be understood. In particular, it is now evident that the metal-environment distortion must be taken into account when trying to model the photomagnetic behaviour of such compounds.

Elsewhere, ΔΘ also shows a linear correlation with the thermal spin transition temperature denoted as $T_{1/2}$ (Fig. 4): the higher the ΔΘ value the lower the $T_{1/2}$ value. Consequently, $T_{1/2}$ and *T*(LIESST) are strongly linked because they depend on the same parameter. The relation between *T*(LIESST) and $T_{1/2}$ has been previously suggested, but was then only based on magnetic and photo-magnetic data without any structural considerations (Létard, Daubric *et al.*, 1999; Marcen *et al.*, 2002; Shimamoto *et al.*, 2002). Here, the dependence of *T*(LIESST) on $T_{1/2}$ is confirmed and linked with a structural feature derived from the trigonal distortion of the metal environment.

To illustrate the relationship between these two values, Fig. 5 displays the linear dependence of *T*(LIESST) and $T_{1/2}$ on ΔΘ for the [FeL$_n$(NCS)$_2$] complexes. Note that an LS to HS light-induced conversion is only possible at temperatures lower than both $T_{1/2}$ and *T*(LIESST), *i.e.* in region 3 of Fig. 5. In regions 1 and 2, the thermal HS and LS states are stable.

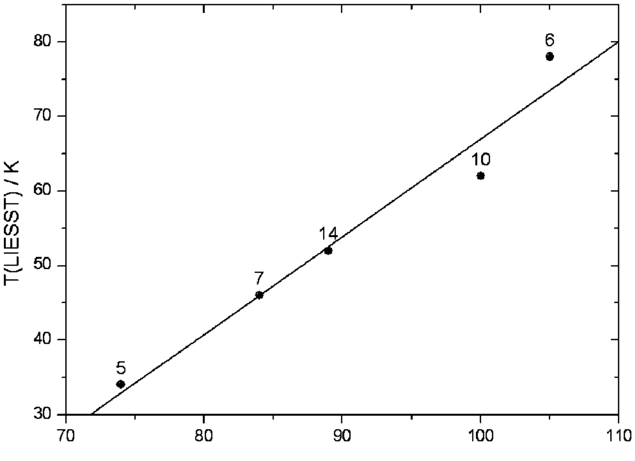

Figure 3
Plot of the variation at the spin crossover of the metal environment distortion, ΔΘ, *versus* the temperature up to which it is possible to keep the photo-induced information, *T*(LIESST), for the [FeL$_n$(NCS)$_2$] complexes.

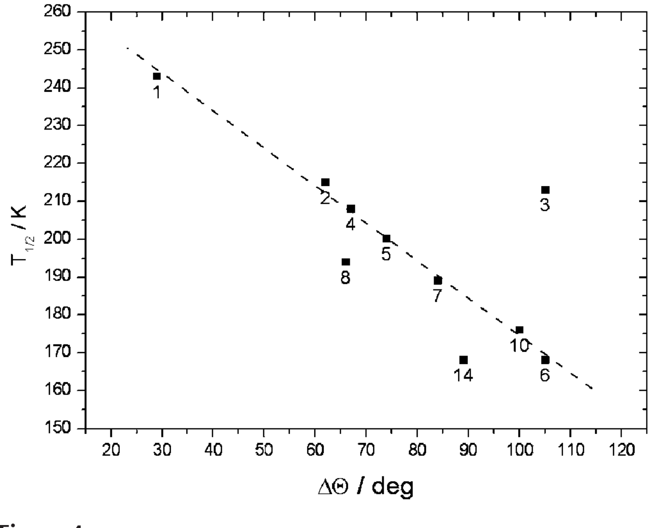

Figure 4
Plot of the variation of the distortion of the metal environment owing to the spin crossover, ΔΘ, *versus* the temperature of the thermal HS to LS conversion, $T_{1/2}$, for the [FeL$_n$(NCS)$_2$] complexes.

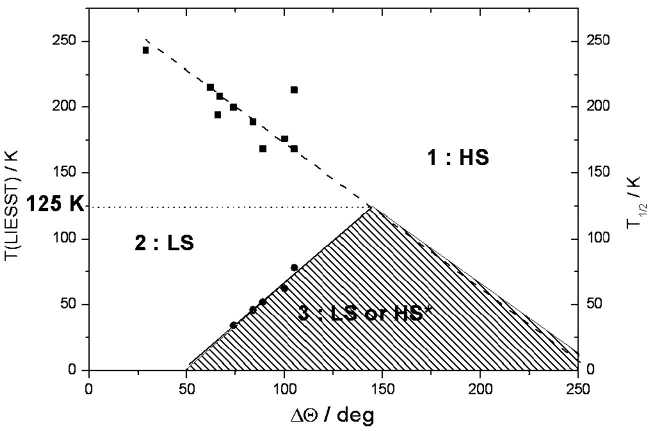

Figure 5
Variation of T(LIESST) (circle) and $T_{1/2}$ (square) as a function of the structural parameter ΔΘ (see the legends of the previous figures for the definition) for the [FeL$_n$(NCS)$_2$] complexes. Three zones are defined as a function of the possible spin state. Zone 3 corresponds to the region where a photo-induced LS to HS conversion is possible. The maximum T(LIESST) value for this series is therefore shown. HS* represents the photo-induced HS state.

The crossing point between the two lines is where T(LIESST) is equal to $T_{1/2}$. Consequently, this shows the highest T(LIESST) value obtainable for this series of complex. From our present study it appears that this temperature is around 120 K for the [FeL$_n$(NCS)$_2$] series. Incidentally, this low T(LIESST) value seems to prevent the use of these complexes in any room-temperature industrial application based on a photo-induced spin conversion. This also helps to predict that the highest T(LIESST) value for these bidentate iron(II) complexes will be obtained with a ΔΘ value of around 145°.

To summarize, photo-induced and thermal-spin transition temperatures are strongly linked to the trigonal distortion of the metal environment in [FeL$_n$(NCS)$_2$] complexes. The higher the trigonal distortion the higher the T(LIESST) value and the lower the $T_{1/2}$ value. Therefore, if such a result can be generalized, one solution to obtain high-temperature photo-induced spin-crossover systems is to design metal environment geometries such as non-octahedral high coordinated systems which are more easily deformed.

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