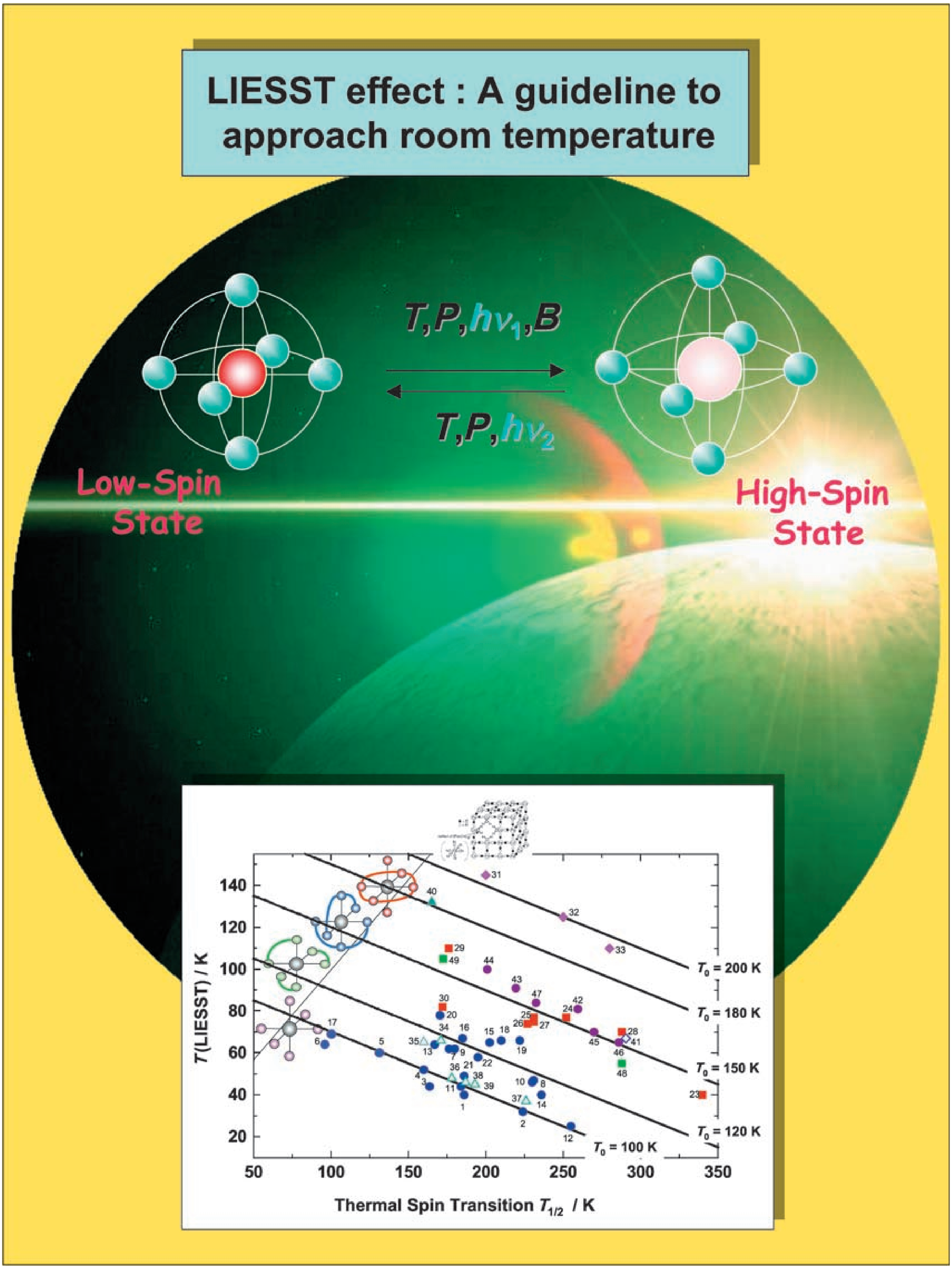
LIESST effect : A guideline to approach room temperature



DOI: 10.1002/chem.200500112

A Guideline to the Design of Molecular-Based Materials with Long-Lived Photomagnetic Lifetimes**

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Dedicated to the memory of Olivier Kahn on the occasion of the 5th anniversary of his death

Abstract: Materials presenting a stable and reversible switch of physical properties in the solid state are of major interest either for fundamental interests or potential industrial applications. In this context, the design of metal complexes showing a light-induced crossover from one spin state to another, leading to a major change of magnetic and optical properties, is probably one of the most appealing challenges. The so-denoted spin-crossover materials undergo, in some cases, a reversible photoswitch between two magnetic states, but, unfortunately, lifetimes of the photomagnetic states for compounds known so far are long enough only at low temperatures; this prohibits any applications. We have measured and collected the temperatures above which the photomagnetic effect disappears for more than sixty spin-crossover compounds. On the basis of this large data base, a correlation between the nature of the coordination sphere of the metal and the photomagnetic lifetime can be drawn. Such correlation allows us to propose here a general guideline for the rational design of materials with long-lived photomagnetic lifetimes. This result clearly opens the way towards room-temperature photonic materials, based on the spin-crossover phenomenon, which will be of great interest for future communication devices.

Keywords: coordination modes • photochromism • photomagnetism • photophysics • spin crossover

Introduction

In the last thirty years, the interest in "molecular materials" possessing a property or a set of properties relevant for industrial applications has considerably increased. This growth mainly comes from the imperative necessity of the component-size reduction for the development of future communication devices. The challenge is now to reproduce at a molecular scale the traditional electronic functions, like memories, modulators, rectifiers, transistors, switches, and wires.[1] To this aim, the spin-crossover (SCO) phenomenon, encountered in some coordination complexes possessing a 3d^n (n = 4–7) electronic configuration, is certainly one of the most promising properties offered by molecular-based materials. For instance, octahedral iron(II) (d^6) compounds exhibit a change of spin states from a paramagnetic high-spin (HS, $S=2$) state to a diamagnetic low-spin (LS, $S=0$) state, or vice versa, by tuning the temperature, by pressure effects, or through light irradiation or by applying a high magnetic

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[**] Abbreviations used in this paper: bpp = 2,6-bis(pyrazol-3-yl)pyridine, dppen = *cis*-1,2-bis(diphenylphosphino)ethylene, PM-AzA = (N-2′-pyridylmethylene)-4-(2-phenylazo)aniline, PM-BiA = (N-2′-pyridylmethylene)-4-aminobiphenyl, ptz = 1-propyltetrazole, papth = 2-(2-pyridylamino)-4-(2-pyridyl)thiazole, Hpap = 2-hydroxylphenyl-(N-2′-pyridylmethylene), tpy = 2,2′:6′,2″-terpyridine.

DOI: 10.1002/chem.200500112

pulsed field.[2] The SCO features are well-known to strongly depend on the cooperativity, that is, on the propagation of the spin-state change from one complex to the other through the material. For instance, when cooperative interactions of elastic origin are strong enough, a thermal spin transition is accompanied by a hysteresis regime that confers to these materials a memory effect.

In the view of photonic molecular device, the first evidence of the light-induced excited spin-state trapping (abbreviated as LIESST) in an iron(II) SCO material was reported by McGarvey et al.[3] in solution and then by Decurtins et al.[4] in the solid state. This phenomenon is particularly promising as it combines 1) a low addressing power (about 5 $mW\,cm^{-2}$); 2) a short addressing time (nanosecond scale), the spin transition being purely electronic in nature; 3) a perfect reproducibility over successive cycles even in a solid matrix; and 4) an optical reversibility, as the low-spin (LS, $^1A_1$)→high-spin (HS, $^5T_2$) transition can be induced with a green light and the back LS state conversion with a red light. Nevertheless, a major drawback comes from the temperature dependence. Indeed, the lifetime of the photoinduced HS state is usually long at very low temperature, for example, weeks at 20 K for $[Fe(ptz)_6](BF_4)_2$,[5] but above 50 K the relaxation process becomes thermally activated and in few seconds the stored light-induced information vanishes. In some rare cases, however, long-lived lifetimes can be observed up to 100 K,[6–10] providing that some factors are able to stabilize the photoinduced HS state. Unfortunately, to date nobody has developed a rational molecular engineering for designing an SCO complex with long-lived lifetimes. In this respect, for the past several years we have attempted to identify the key factors that account for stabilizing the light-induced metastable state.[11–15] In the present article, on the basis of the comparison of the properties of more than sixty SCO compounds, we propose a general guideline for the design of long-lived photomagnetic materials.

Photoinduced HS State

The *T*(LIESST) approach: The first attempt for a rational view of the stability of the photoinduced HS state was reported by Herber et al.[16,17] Thanks to infrared spectroscopy, the authors were able to follow the temperature dependency of the C≡N stretching mode of six different SCO materials and determined a limiting temperature above which the light-induced phenomenon is no more observable. Later on Hauser reported in 1991 the first guideline giving some expectation of the lifetime of the photoinduced HS state.[18] Hauser compared the lifetime of the photoinduced HS state in different diluted SCO materials and observed that the logarithm of the lifetime at $T\rightarrow 0$ (i.e., in the tunneling region) is inversely proportional to the thermal spin-crossover temperature, $T_{1/2}$, at which half of the molecules are found in the HS state and half in the LS state. This finding, known today as the "inverse energy-gap law", is now perfectly understood on the basis of a non-adiabatic multiphonon process in a strong vibronic coupling limit of a single configurational coordinate (SCC) model.[19] The $T\rightarrow 0$ lifetime is discussed in terms of horizontal and/or vertical displacements of the potential wells of the HS and LS states.[18,20] The difficulty of this approach is to properly determine the $T\rightarrow 0$ lifetime, in particular when the stabilization of the photoinduced HS state in the tunneling region is very effective. On the basis of this result, we decided with the late Olivier Kahn to compare the various SCO materials by a systematic measure of the *T*(LIESST) value, that is, the limiting temperature above which the light-induced magnetic HS information is erased in a SQUID cavity.[11]

Originally this approach started in partnership with the industrial Motorola Research Center;[21] the idea was to define a procedure that allowed a rapid comparison of the photomagnetic properties of a given material.[11–13] To this end, the first set of experiments concerned the study of the thermal spin-crossover properties of the material complex. A typical magnetic curve, for which the magnetic signal is expressed as the $\chi_M T$ product (χ_M stands for the molecular magnetic susceptibility and T the temperature), is shown in Figure 1. The presence of a thermal SCO behavior is reflected by a drastic change of the magnetic signal; for example, in an octahedral environment the HS iron(II) metal ion is paramagnetic ($S=2$, $(t_{2g})^6(e_g)^0$), whereas the LS iron(II) metal ion is diamagnetic ($S=2$, $(t_{2g})^4(e_g)^2$). For each SCO complex, the thermal spin transition temperature $T_{1/2}$ was measured. The second set of experiments concerns the measure of the photomagnetic properties following a well-defined protocol. The light irradiation on the material was applied at 10 K. At this temperature, the system usually behaves in a LS form and the population of the paramagnetic HS state through the LIESST phenomenon results in a drastic increase of the magnetic signal. The light irradiation is only stopped when the saturation of the signal is reached, that is, when for a given laser power (≈5 $mW\,cm^2$) the equilibrium between the population and the relaxation is reached. The temperature was then slowly increased at a rate of 0.3 $K\,min^{-1}$, while the magnetic behavior was recorded. A typical example is shown in Figure 1. Below 50 K the magnetic response of the light-induced HS state remains almost constant. The relaxation process is, in fact, governed by the non-adiabatic tunneling regime through the barrier, and the experimental timescale is negligible with respect to the lifetime of the photoinduced HS state. This behavior contrasts with the region above 50 K, at which the system reaches the thermally activated regime; this can be regarded as a tunneling from thermally populated vibrational levels of the HS state.[20] In this temperature range, the $\chi_M T$ product drastically decreases and rapidly recovers its initial value. The minimum of the $d\chi_M T/dT$ versus T curve determines the *T*(LIESST) temperature.[11]

When measured by strictly following the above protocol, that is, irradiation at 10 K and warming mode at 0.3 $K\,min^{-1}$, *T*(LIESST) value is a relevant parameter for the comparison of the photomagnetic properties of the different SCO

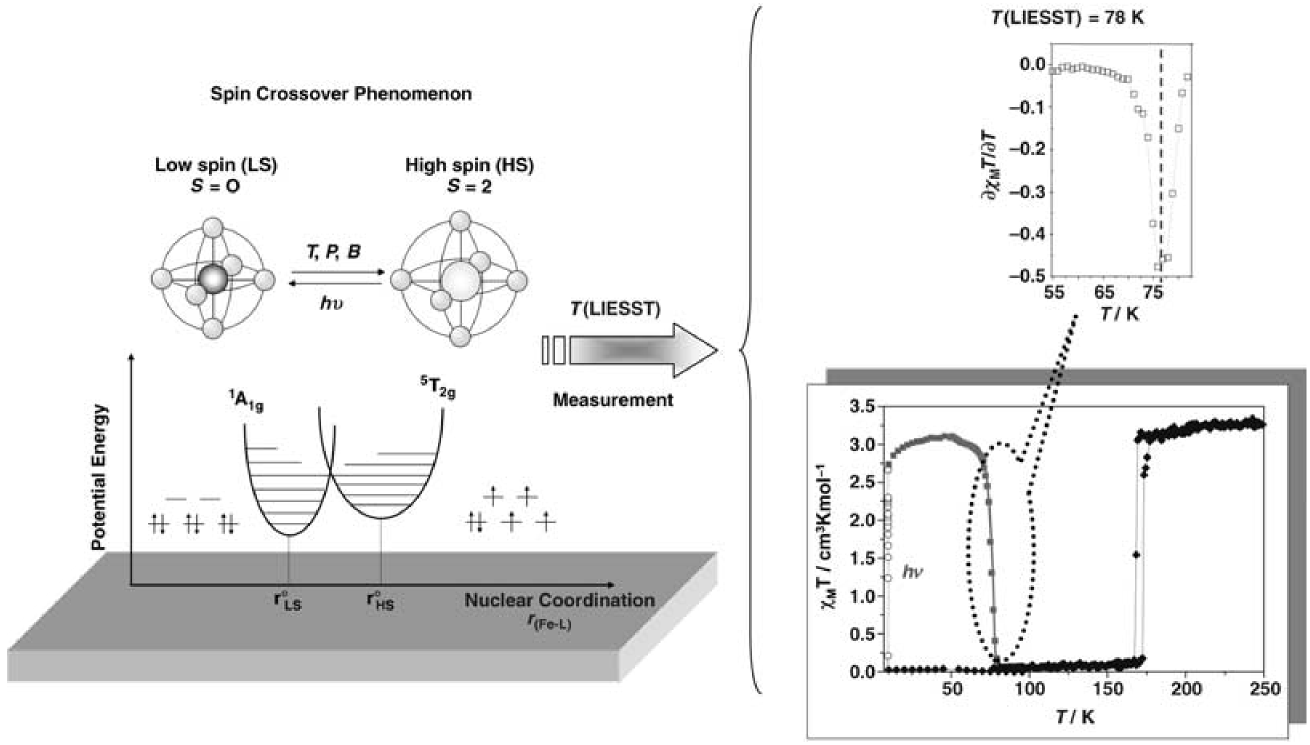

Figure 1. Schematic view of the spin-crossover phenomenon and T(LIESST) experiment recorded for the $[Fe(PM\text{-}BiA)_2(NCS)_2]$ complex. In an octahedral environment, the HS iron(II) metal ion is paramagnetic ($S=2$, $(t_{2g})^6(e_g)^0$) and the LS iron(II) metal ion diamagnetic ($S=2$, $(t_{2g})^4(e_g)^2$). Change between HS and LS states can be induced by tuning the temperature (T), the pressure (P), by applying a light irradiation ($h\nu$) or an intense magnetic field (B). Concerning the properties of the $[Fe(PM\text{-}BiA)_2(NCS)_2]$ complex, the magnetic changes recorded in the vicinity of the 170 K region correspond to the thermal spin-crossover phenomenon and those in the 10–80 K region to the LIESST effect. More precisely, the temperature dependence of $\chi_M T$ recorded in the cooling mode without irradiation is symbolized by the ◆ data points, the change recorded during 1 h of irradiation at 10 K corresponds to the ○ data points, and the behavior recorded during the warming mode (0.3 K min^{-1}) when the light irradiation was switched off corresponds to the ■ data points. The insert graph shows the derivative $d(\chi_M T)/dT$ plot as function of the temperature.

materials. A great advantage of such an approach is that in a few hours the potentiality of a material to retain the optical information is evaluated. Furthermore, the T(LIESST) temperature is a macroscopic value that intrinsically combines both the temperature-independent region and the thermally activated region. In other words, an analysis of the T(LIESST) temperatures integrates all the factors that affect the lifetime of the photoinduced HS state.

The *T*(LIESST) database: The first work based on a comparison of T(LIESST) temperatures was made in 1999.[12] In this study, the magnetic and the photomagnetic properties of twenty two SCO compounds were determined (Figure 2, samples **1**–**22**); that is, the thermal spin transition $T_{1/2}$ as well as the T(LIESST) temperatures. When all these data were plotted in a graph defined by T(LIESST) temperature versus $T_{1/2}$, we realized that by considering the chemical formula of the different complexes, the physical properties of the complexes followed some general tendencies. Most of the investigated SCO complexes in these cases are members of the $[FeL_2(NCX)_2]$ family, in which L is an aromatic unit ligand and X is a thiocyanato (=S) or selenocyanato (=Se) unit. The originality of our idea was to define a couple in which two complexes possessed the same aromatic L unit ligand but involved either a S or a Se unit. By doing this, several couples (S and Se) were found to follow the same tendency (samples **1/2**, **7/8**, **9/10**, **11/12**, **13/14**) and two virtual lines were proposed with a general equation, T(LIESST) $= T_0 - 0.3\,T_{1/2}$. The extrapolated T_0 values, at $T \rightarrow 0$, were 100 and 120 K, respectively.[12]

Three years later, this analysis was confirmed by an additional work in which the magnetic and the photomagnetic studies of eight new SCO materials were investigated (Figure 2, samples **23**–**30**).[13] The idea was to compare a series of iron(II) metal complexes possessing various $T_{1/2}$ and T(LIESST) values without changing the FeN_6 coordination sphere. The selected family was the $[Fe(bpp)_2]X_2 \cdot n\,H_2O$ series (bpp = 2,6-bis(pyrazol-3-yl)pyridine), well-known for exhibiting various thermal spin-crossover behavior depending on the nature of the anion and the degree of hydration; the iron(II) metal center is surrounded by six donor nitrogen atoms from the two ligand molecules coordinated in an octahedral meridional plane.[22–25] Moreover, in some cases unusual long-lived lifetimes have been found for the metastable HS state generated both by thermal trapping and by the LIESST effect.[6,7,26] Consequently, we systematically determined the thermal spin transition and the limit temperature of the LIESST phenomenon of all the series of hydrated

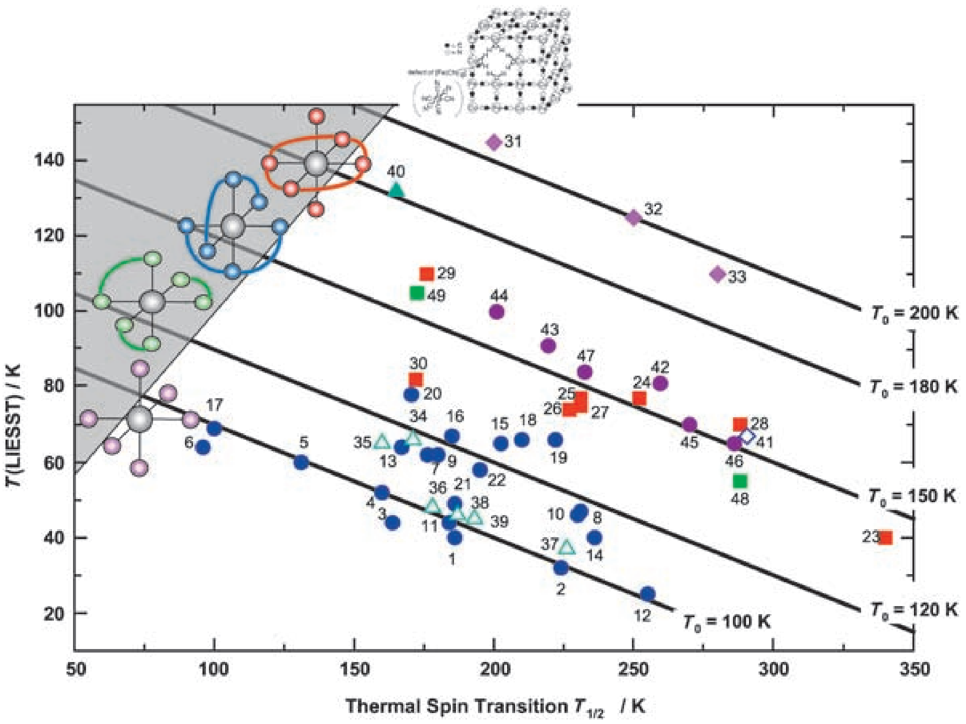

Figure 2. Variation of T(LIESST) versus $T_{1/2}$ for spin-crossover compounds. Data for the 120 and 100 K T_0 lines are reported in reference [12]. The 150 K T_0 line is the result of the linear regression obtained with the [Fe(bpp)$_2$]X$_2$·nH$_2$O family[13] and the 200 K T_0 line is based on the work of Hashimoto.[28] The region in gray is meaningless as the T(LIESST) temperature has to be inferior or at least equal to $T_{1/2}$ temperature.

and dehydrated [Fe(bpp)$_2$]X$_2$·nH$_2$O complexes, with X = PF$_6$, NCS, NCSe, BF$_4$, Br, and I.[13] Interestingly, the [Fe(bpp)$_2$]X$_2$·nH$_2$O data on the plot T(LIESST) versus $T_{1/2}$ were distributed in a such way that the T_0–0.3$T_{1/2}$ relation established earlier remained valid and a third line with a T_0 value of 150 K was proposed (samples **23–30**). What is remarkable is that for the first time the T_0 = 150 line defines some SCO complexes with a $T_{1/2}$ value around room temperature and a measurable T(LIESST) value (sample **28**). Such a result is very exciting, as it represents the first step towards the design of switchable SCO materials useable in a genuine device.[27]

In parallel, Hashimoto et al.[28] provided a new evidence for the validly of the T(LIESST) = T_0–0.3 $T_{1/2}$ relation. The selected family was the Co–Fe Prussian Blue analogues, [Na$_x$Co$_y$Fe(CN)$_6$]·zH$_2$O with atomic Co/Fe composition ratios of 1.37, 1.32, and 1.26. In such complexes, a change of electronic and spin states may be induced 1) by a gradient of temperature, that is, from room temperature Fe^{III}((t$_{2g}$)^5(e$_g$)^0, LS, S = 1/2)-CN-Co^{II}((t$_{2g}$)^5(e$_g$)^2, HS, S = 3/2) to low temperature Fe^{II}((t$_{2g}$)^6(e$_g$)^0, LS, S = 0)-CN-Co^{III}-((t$_{2g}$)^6(e$_g$)^0, LS, S = 0); and 2) by a light irradiation at 5 K with the population of the metastable Fe^{III}((t$_{2g}$)^5(e$_g$)^0, LS, S = 1/2)-CN-Co^{II} ((t$_{2g}$)^5(e$_g$)^2, HS, S = 3/2) state.[29] The authors consequently determined for each Co/Fe composition the $T_{1/2}$ and T(LIESST) temperatures and observed the presence of a new T_0 line (Figure 2, samples **31–33**) parallel to the three previous ones.[28] The T_0 value was estimated at 200 K. Of course, on one hand it is clear that the physical process involved in these Prussian Blue is not strictly speaking a pure spin-crossover phenomenon, but rather a charge-transfer-induced spin transition,[29] and any overall comparison has to be cautiously taken. On the other hand, this indicates that the T(LIESST) relation (T_0–0.3 $T_{1/2}$) is probably more general.

Photomagnetic Properties

Towards the identification of the keys parameters: Today, our database contains the T(LIESST) and $T_{1/2}$ properties of more than sixty SCO materials. A first general tendency, noticeable for all the T_0 lines (Figure 2), is a decrease of T(LIESST) with the increase of $T_{1/2}$. In others words, the higher the temperature at which the thermal spin transition occurs, the less photomagnetic information remains. Such behavior is, in fact, not so surprising. This perfectly follows the original conclusion of Hauser with the inverse energy-gap law;[18,20] The HS→LS relaxation is directly dependent on the ΔE^0_{HL} energy gap (i.e., the enthalpy factor, ΔH, at $T \rightarrow 0$), which is typically smaller than ΔH at $T_{1/2}$. Consequently, if we assume in a first approach that the entropy factor, ΔS, is almost constant for all SCO compounds, the dynamics of the relaxation and thus the T(LIESST) value become a direct function of $T_{1/2}$.

But what is more interesting is the nature of the parameters affecting the T_0 value. In a few years, the T_0 lines have been progressively shifted from 100 K to 200 K.[27] Consequently, tuning a spin state by light irradiation at room temperature (with a long-lived lifetime) appears now a plainly accessible objective. In this regard, it is has been proposed that the cooperativity factor may stabilize the photoinduced HS state.[30,31] In this context, we noticed for the [Fe(PM-L)$_2$(NCX)$_2$] family that for an almost constant $T_{1/2}$ temperature of about 170 K, the T(LIESST) value increased from 31 K, for the gradual SCO [Fe(PM-AzA)$_2$(NCS)$_2$] compound (**11**), to 78 K for the abrupt SCO [Fe(PM-BiA)$_2$-(NCS)$_2$] compound (**20**), and we proposed a general relation between the T(LIESST) temperature and the cooperativity factor (C).[30] However, it should be admitted that it is not so easy to properly disconnect the cooperativity factor from the effects of both local deformation (such as a twist of the

FeN_6 core or an elongation of the Fe−N bond length) and change of the electronic distribution (modification of the aromatic unit).[32] The X-ray structures of thermodynamic stable states (LS and HS) and metastable state (photoinduced HS) have really yet to be systematically solved. Unfortunately, to date only few articles report a careful comparison of all these structures and it is not yet possible to obtain an overall view of the effect of the cooperativity. If we consider the influence of the cooperativity on the HS→LS relaxations, it is known from the work of Hauser et al.[33] that the activation energy barrier is a function of the HS (or LS) fraction by reason of an internal pressure created by the large modification of the metal–ligand bond lengths occurring between the HS and the LS states. As a consequence, the activation energy barrier for a given HS fraction is reduced when the cooperativity is increased, and thus, as recently demonstrated by doing some theoretical simulations, the T(LIESST) temperature is slightly reduced.[34] In fact, the influence of the cooperativity on the T(LIESST) temperature appears to be very weak. This conclusion is also supported by the experimental work performed on the $[Fe(bpp)_2]X_2 \cdot n H_2O$ family (Figure 2, samples **23**–**30**).[13] The photomagnetic properties of these series was found to follow the same $T_0 = 150$ K line whatever the cooperativity; that is, from an incomplete spin conversion to a gradual or an abrupt spin transition with or without thermal hysteresis.

An additional information that we can collect from the investigation of the $[Fe(bpp)_2]X_2 \cdot n H_2O$ family (**23**–**30**) is that whatever the nature of the anion, that is, X = PF_6, NCS, NCSe, BF_4, Br, or I, the T(LIESST)/$T_{1/2}$ properties follow the same T_0 line.[13] In other words, any change outside the inner coordination sphere appears to have no effect on the final T_0 value. The role of the inner coordination sphere seems to be, consequently, particularly preponderant.

Chemical Nature of the Ligand

Role of the inner coordination sphere: The first important factor which has to be taking into account is the electronic contribution of the ligand. In this particular context, the work performed on the $[Fe(bpp)_2]X_2 \cdot n H_2O$ family (**23**–**30**) gives some interesting information. Goodwin et al.[22–25] show that the thermal SCO properties of the $[Fe(bpp)_2]X_2 \cdot n H_2O$ series are strongly affected by the degree of hydration, because the hydrated salts participated in an extended hydrogen-bonded network involving the uncoordinated NH groups of the pyrazole moieties, the anion, and the water molecules. Consequently, any change of the degree of hydration affects the electronic contribution of the ligand and modifies the thermal spin-crossover behavior. Interestingly, the photomagnetic properties of the hydrate and of the dehydrated compounds follow the same T_0 line, suggesting that the influence of the electronic factor on the T_0 factor is negligible. This idea is also supported by the results found on the $[Fe(PM\text{-}L)_2(NCX)_2]$ family (Figure 2, samples **1**–**22**), in which for a given aromatic ligand (L) the T(LIESST)-$T_{1/2}$ values of thiocyanato (X = S) and selenocyanato (Se) compounds have been found to follow the same T_0 line, independently of the electronic modification accompanying the S/Se substitution.[12]

In parallel to this electronic contribution of the ligand, which appears to be negligible, it may be anticipated if we consider the single configurational coordinate (SCC) model[19] that a horizontal displacement of the potential wells between the LS and HS state is able to affect the final T_0 value. For this, the X-ray structures of both LS and HS state have to be known. Unfortunately, as already previously mentioned,[32] to date the number of X-ray structures known in both spin states and displaying LIESST effect is small and any conclusion is hazardous. The only indirect information that we have collected has been obtained by investigating some iron(II) spin-crossover compounds with phosphorus atoms in the coordination sphere. In the particular case of the $[Fe(dppen)_2Cl_2] \cdot 2(CH_3)_2CO$, the single-crystal structures determined both in HS and LS states showed a large Δr_{HL}(Fe−P) variation (0.3 Å),[35] and the relaxation kinetics of the HS→LS conversion occurring after the LIESST effect were found to be slower than for classical FeN_6 complexes.[8] However, by looking at other iron(II)–phosphorus complexes, we realized that the T(LIESST)/$T_{1/2}$ data (Figure 2, samples **34**–**39**) remained close to the $T_0 = 100$ K and 120 K lines and that the tendency to further increase the T_0 value by tuning the iron(II) bong length is not so large.[36,37] We then focussed our attention on the distortion of the FeN_6 octahedron. Here also the determination of the structure is essential. However, by using the few X-ray data available on the mononuclear iron(II) complexes of general formula $[FeL_2(NCS)_2]$, we have obtained an exciting result; that is, the T(LIESST) value shows a linear correlation with the distortion of the metal environment sphere.[15] The stronger the distortion of the FeN_6 octahedron the higher the T(LIESST) value. Such a result confirms the assumption that the T(LIESST) value is mainly dependent from the coordination sphere, not the cooperativity. This finding has now to be extended to SCO complexes with different coordination spheres in order to propose a correlation with the magnitude of the T_0.

With regard to all these remarks, we decide to compare the different T(LIESST) versus $T_{1/2}$ values by regarding the chemical nature of the ligand involved in the inner coordination sphere. For this we arbitrarily separated the iron(II) complexes involving six independent monodentate ligands (FeL_6 coordination sphere), from those possessing three bidentate ligands (FeL_3), and those involving only two tridentate ligands (FeL_2). Interestingly, in each of these three cases (FeL_6, FeL_3, and FeL_2) the highest T(LIESST) values are found on different T_0 lines. More precisely, the highest T(LIESST) temperature of an FeL_6 complex corresponds the well-known $[Fe(ptz)_6](BF_4)_2$ complex, situated close to the $T_0 = 100$ K line (sample **5**), while for the FeL_3 systems it is the $[Fe(PM\text{-}BiA)_2(NCS)_2]$ complex (78 K, sample **20**), situated on the $T_0 = 120$ K line and for the FeL_2 compounds, it is the $[Fe(bpp)_2](BF_4)_2$ complex ON the $T_0 = 150$ K line (sample **29**). Such a finding really supports the idea that the influence of the inner coordination sphere on the T_0 value is significant.

Re-examination of the Long-Lived Lifetimes

As a continuation to this approach, it is interesting to note that the Prussian Blue complexes (**31**–**33**), which are situated on the $T_0 = 200$ K line, can be also regarded as a model of a FeL system. Similarly, Sato et al.[10] have recently reported atypical long-lived lifetimes for an iron(II) macrocyclic spin-crossover species, $[FeL(CN)_2]\cdot H_2O$ (in which L is a Schiff-base macrocyclic ligand derived from the condensation of 2,6-diacetylpyridine with 3,6-dioxaoctane-1,8-diamine), and gave a T(LIESST) temperature of 130 K. Interestingly, the position of the T(LIESST) versus $T_{1/2}$ point is in the vicinity of a virtual $T_0 = 180$ K line (Figure 2, sample **40**), which is in perfect agreement with the proposed evolution of the nature of the coordination sphere. The same analysis can be done on the exceptionally long-lived lifetime already reported for the $[Fe(papth)_2]X_2\cdot n H_2O$ system[38] (Figure 2, sample **41**)[37] or recently on some analogous of the $[Fe(bpp)_2]X_2$ complex (Figure 2, samples **42**–**47**),[39] which all contain tridentate ligands in the inner coordination sphere. Such a remark is also valid for understanding the long-lived lifetimes reported in the literature for the diluted $[Fe_{0.02}Mn_{0.98}(tpy)_2](ClO_4)_2$ complex.[9] More interestingly, some long-lived lifetimes were recently reported for some iron(III) complexes, $[Fe(pap)_2]PF_6\cdot MeOH$ and $[Fe(pap)_2]ClO_4\cdot H_2O$.[31,40] The authors attribute this unexpected result to the cooperativity. However, from our interpretation, the T(LIESST) versus $T_{1/2}$ properties of these two complexes are simply situated on $T_{0=}150$ K (Figure 2, samples **48** and **49**), in perfect agreement with the nature of the tridentate ligand involved into the coordination sphere.

Conclusion

All these findings open up exciting prospects and extensive research efforts are still required to identify the key factors involved in the stabilization of the metastable HS state. Currently, we have investigated the T(LIESST) versus $T_{1/2}$ values of more than sixty spin-crossover materials and we evidenced that a general relation appears to govern the photomagnetic properties, that is, $T(\mathrm{LIESST}) = T_0 - 0.3\,T_{1/2}$. To date, four parallel T_0 lines have been obtained with values of 100, 120, 150 and 200 K, respectively. The open challenge is now to further increase the T_0 value. From our database, it seems that changes outside the sphere (cooperativity factor, nature of the salt, degree of hydration) are relatively negligible for tuning the T_0 factor. In contrast, the influence of the coordination degree of the ligand involved into the inner coordination sphere appears to be preponderant. Based on this idea, almost all the unexplained long-lived lifetime already reported in the literature can be interpreted. Of course, this assumption has to by validated by the accumulation of further data in addition to that currently in the T(LIESST) data base, but it already constitutes an exciting guideline for elaborating new photomagnetic materials with predicted long-lived lifetimes and thus potentially relevant for industrial applications.

Acknowledgements

The authors would like to thanks all the chemists who contributed to enrich the database and also to acknowledge the Aquitaine Region of Bordeaux for supporting the technical development of the photomagnetic platform.

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