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Influence of Metal Dilution on the Light-Induced Spin Transition in Two 1D Chain Compounds: $[Fe_xZn_{1-x}(btzp)_3](BF_4)_2$ and $[Fe_xZn_{1-x}(endi)_3](BF_4)_2$ {btzp = 1,2-Bis(tetrazol-1-yl)propane and endi = 1,2-Bis(tetrazol-1-yl)ethane}

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Dedicated to Professor Jan Reedijk on the occasion of his 65th birthday

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The thermal and light-induced spin transitions in $[Fe_xZn_{1-x}(btzp)_3](BF_4)_2$ and $[Fe_xZn_{1-x}(endi)_3](BF_4)_2$ {btzp = 1,2-bis(tetrazol-1-yl)propane; endi = 1,2-bis(tetrazol-1-yl)ethane} chain compounds have been investigated by magnetic susceptibility, photomagnetism and diffuse reflectivity measurements. These compounds display a thermal spin transition and the Light-Induced Excited Spin State Trapping (LIESST) effect at low temperature. For each compound, 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. A decrease in $T_{1/2}$ induces an increase in T(LIESST). The results are discussed and compared with some other "metal-diluted" iron(II) spin crossover (SCO) complexes.

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Introduction

A challenging field of research in coordination chemistry concerns the study of bistable molecular materials. Spin crossover compounds (SCO) of 3d metal ions with d^4-d^7 electronic configurations in an octahedral environment exhibiting high-spin (HS) low-spin (LS) crossover under an external perturbation are particularly interesting. The perturbation can be either a change of temperature, application of pressure, light or a high magnetic field.[1,2] Some information can be written and erased by light irradiation, according to the so-called LIESST (Light-Induced Excited Spin State Trapping) and reverse LIESST phenomena.[3]

Since 1998, a T(LIESST) database has been maintained. T(LIESST) represents the limiting temperature above which the photoinduced information, namely the photoinduced HS fraction is erased under specific conditions.[4] Using this procedure, we have up to now compared the photomagnetic properties of more than sixty SCO compounds and reported an empirically established linear relation between the thermal spin transition ($T_{1/2}$) and the T(LIESST) temperature: $T(\text{LIESST}) = T_0 - 0.3T_{1/2}$.[5–8] This phenomenological relationship appears to reflect rearrangement processes in the coordination sphere accompanying the SCO at the metal centre. In a recent investigation, the applicability of this relationship was extended to metal-diluted SCO systems, viz. $[Fe_xZn_{1-x}(Phen)_2(NCS)_2]$[9] and $[Fe_xMn_{1-x}(bpp)_2](NCSe)_2$[10] {Phen = 1,10-phenanthroline and bpp = 2,6-bis(pyrazol-3-yl)pyridine}. It has been found in these two mixed-crystal series that the thermal spin transition $T_{1/2}$ decreases with metal dilution (decrease of x) whereas the relaxation temperature T(LIESST) remains constant. These mononuclear complexes are zero-dimensional with relatively weak cooperative interactions between the spin state changing iron(II) complex molecules transmitted through van der Waals or π stacking interactions. It has been the goal of the present study to investigate the influence of isomorphous metal dilution on T(LIESST) in SCO compounds of higher dimensionality where the iron complexes are linked together by covalent bonds. We chose the two 1D compounds $[Fe_xZn_{1-x}(btzp)_3](BF_4)_2$ and $[Fe_xZn_{1-x}(endi)_3](BF_4)_2$ {btzp = 1,2-bis(tetrazol-1-yl)propane and endi = 1,2-bis(tetrazol-1-yl)ethane} and diluted them gradually with zinc which is appropriate for the formation of isomorphous mixed-crystal series with iron(II). The two ligands endi and btzp are depicted in Scheme 1. The structures and magnetic properties of $[Fe(btzp)_3](ClO_4)_2$[11] and $[Fe(endi)_3](BF_4)_2$[12] have been previously described as well as some photomagnetic properties of $[Fe(btzp)_3](ClO_4)_2$.[11] $[Fe(btzp)_3](ClO_4)_2$ was the first reported chain compound showing the

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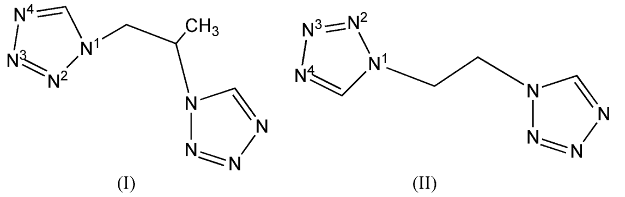
LIESST effect and both compounds crystallise in the space group $P\bar{3}c1$. The structure consists of iron atoms in an octahedral environment which alternate with three organic ligands to form cationic chains parallel to the crystallographic *c* axis. The chains in the *ab* plane are arranged in a hexagonal close-packed fashion which leaves channel-like spaces in between occupied by the anions. Single crystals of $[Fe(btzp)_3](BF_4)_2$ have not been obtained, however, it has been shown that they are isomorphous with the perchlorate analogue. The zinc(II) metal host has been selected for (i) diamagnetic response, (ii) the absence of metal-to-ligand charge transfer (MLCT) transitions in the visible range and (iii) the similar ionic radii of the iron(II) HS state and the zinc(II) ion which is expected to decrease the $T_{1/2}$ temperature with the metal dilution.



Scheme 1. Derivatives of the bis(tetrazol) ligand used in the present study. (I) 1,2-bis(tetrazol-1-yl)propane (btzp) and (II) 1,2-bis(tetrazol-1-yl)ethane (endi).

Results and Discussion

Magnetic Properties

Figure 1 and Figure 2 show the product of the molar magnetic susceptibility, χ_M, multiplied by the temperature *T* as well as the molar fraction of the high-spin state, γ_{HS}, as a function of temperature for different metal dilution factors *x* for the two mixed-crystal series $[Fe_xZn_{1-x}(btzp)_3](BF_4)_2$ and $[Fe_xZn_{1-x}(endi)_3](BF_4)_2$. The molar HS fraction was calculated from the susceptibility data taking into account that Zn^{II} is a diamagnetic ion and that the amount of iron is *x* mol for each mole of doped compound $[Fe_xZn_{1-x}(btzp)_3](BF_4)_2$ or $[Fe_xZn_{1-x}(endi)_3](BF_4)_2$. Thus the high-spin fraction is derived from the ratio $\chi_M T/[x(\chi_M T)_{HS}]$, where $(\chi_M T)_{HS}$ refers to the neat iron compound ($x = 1$) at high temperatures. This value has been taken as $3.6\,cm^3\,K\,mol^{-1}$ for $[Fe(btzp)_3](BF_4)_2$ and $3.4\,cm^3\,K\,mol^{-1}$ for $[Fe(btzp)_3](BF_4)_2$ corresponding to the values at recorded 300 K with a SQUID magnetometer. These values are in good agreement with those expected from the Curie law if a Landé factor of 2.2 is attributed to the high-spin iron(II) ion. In other words, the two pure iron compounds are completely high-spin at room temperature.

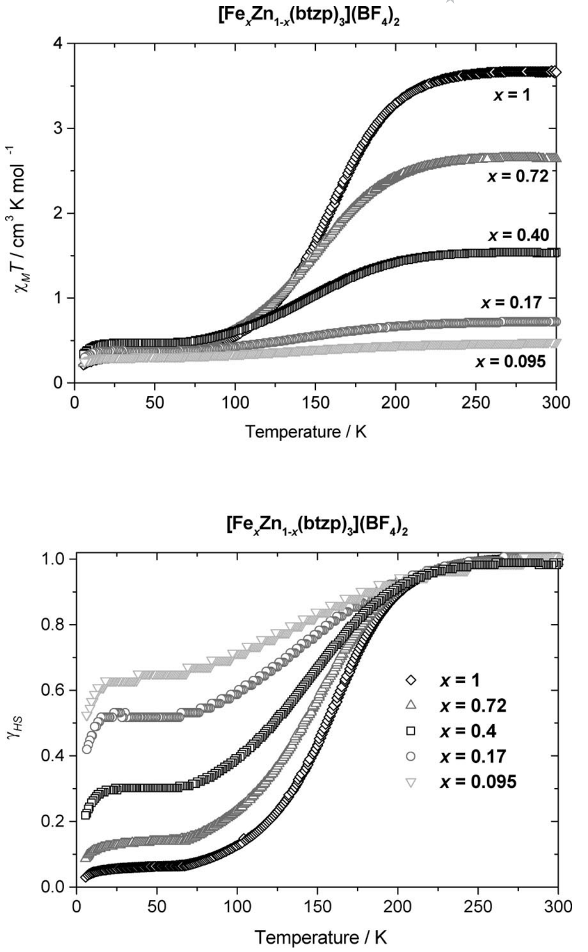


Figure 1. Evolution of the $\chi_M T$ signal as function of *x* and the HS fraction vs. *T* curves for $[Fe_xZn_{1-x}(btzp)_3](BF_4)_2$. A decrease in $T_{1/2}$ vs. *x* has already been observed in the $[Fe_xZn_{1-x}(2\text{-pic})_3]Cl_2\cdot C_2H_5OH$,[13] $[Fe_xCo_{1-x}(4,4'\text{-bis-1,2,4-triazole})_2(NCS)_2]\cdot H_2O$,[16] $[Fe_xM_{1-x}(phen)_2(NCS)_2]$ (M = Mn, Co, Ni, Zn)[14] and $[Fe_xM_{1-x}(pyrazine)_2][Pt(CN)_4]$ (M = Co, Ni) series.[17] To the best of our knowledge, the only exception is for $[Fe_xNi_{1-x}\{4,4'\text{-bis}(1,2,4\text{-triazole})\}_2(NCS)_2]\cdot H_2O$,[18] in which metal dilution leads to a decrease of the thermal spin transition hysteresis but the mean $T_{1/2}$ remains constant.

When the temperature is lowered, all samples exhibit a decrease in γ_{HS} consistent with the well documented spin transition phenomenon in which iron(II) high-spin ions ($S = 2$) at room temperature become low-spin ($S = 0$) with decreasing temperature. Both mixed-crystal series, $[Fe_xZn_{1-x}(endi)_3](BF_4)_2$ and $[Fe_xZn_{1-x}(btzp)_3](BF_4)_2$, are entirely in the HS state at room temperature ($\gamma_{HS} = 1$) for the whole dilution range under investigation ($x = 1$ to 0.093). At low temperature (10 K), the γ_{HS} value is almost 0 for $[Fe_xZn_{1-x}(endi)_3](BF_4)_2$ for values of *x* between 1.0 and 0.49. For higher dilutions, some residual HS fraction appears: $\gamma_{HS} = 0.11$ for $x = 0.29$ and $\gamma_{HS} = 0.18$ for $x = 0.093$. For the $[Fe_xZn_{1-x}(btzp)_3](BF_4)_2$ series, the residual high-spin fraction at low temperature is about 0.05 for $x = 1$. With dilution, this residual fraction increases and reaches about 0.62 for $x = 0.17$. The occurrence of a residual HS fraction at low temperature (or LS fraction at high temperature) is

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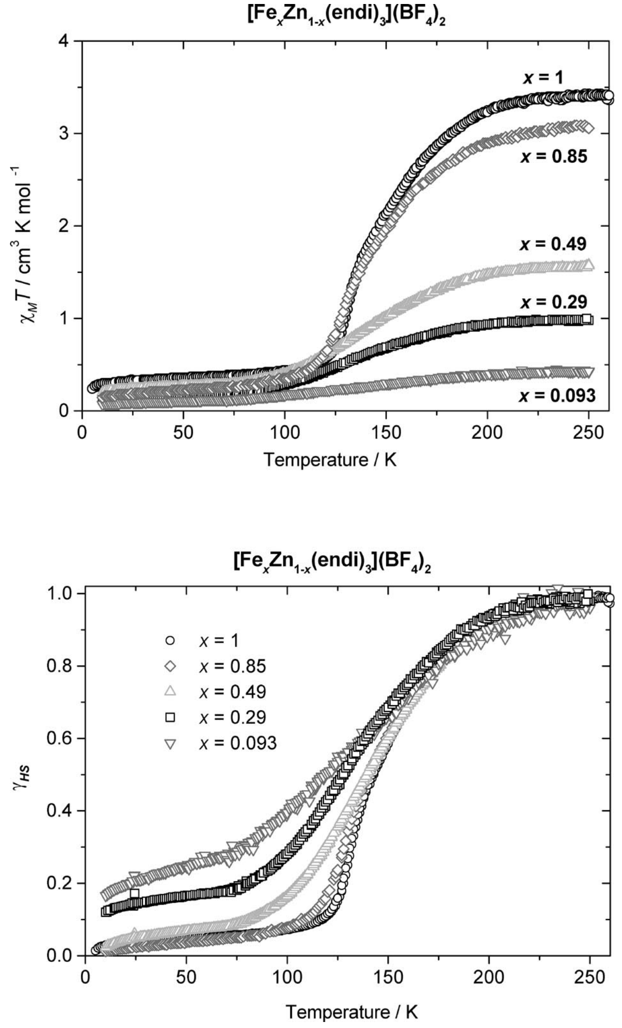


Figure 2. Evolution of the $\chi_M T$ signal as function of x and the HS fraction vs. T curves for [Fe$_x$Zn$_{1-x}$(endi)$_3$](BF$_4$)$_2$.

often discussed in terms of “positive” and “negative” lattice pressure.[13–14] Large diluting ions will exert a “negative” pressure, favouring the HS state. According to Shannon,[15] the ionic radii of divalent 3d metal ions in an octahedral environment are r(Fe^{2+} HS) = 0.78 Å, r(Fe^{2+} LS) = 0.61 Å and r(Zn^{2+}) = 0.74 Å. The radius of Zn^{2+} is thus much closer to the radius of HS Fe^{2+} than to LS Fe^{2+} and the dilution with zinc should thus favour the HS state. This can be clearly observed by the appearance of the residual HS fraction at low T. It can also be observed that with increasing dilution, the spin transition becomes more and more gradual. Similar behaviour has already been observed in earlier studies.[13,14] The abrupt character of the transition is commonly interpreted in terms of the strength of cooperativity between iron centres exhibiting the spin crossover phenomenon. Clearly, upon dilution, the distance between the iron centres becomes larger and the cooperativity decreases. One parameter which characterises the thermal spin transition is the so-called $T_{1/2}$ temperature. This temperature is defined as the temperature at which the high-spin fraction γ_{HS} is equal to the mean value of γ_{HS} at high and at low temperatures. $T_{1/2}$ as a function of dilution, x, for the two mixed-crystal series [Fe$_x$Zn$_{1-x}$(endi)$_3$](BF$_4$)$_2$ and [Fe$_x$Zn$_{1-x}$(btzp)$_3$](BF$_4$)$_2$ is reported in Figure 3 and values of $T_{1/2}$ are reported in Table 1. The $T_{1/2}$ values determined for the neat (x = 1) [Fe(btzp)$_3$](BF$_4$)$_2$ and [Fe(endi)$_3$](BF$_4$)$_2$ compounds are, respectively, 158 K and 143 K. These values are in reasonable agreement with the ones reported previously: 150 K for [Fe(btzp)$_3$](BF$_4$)$_2$[11] and 140 K for [Fe(endi)$_3$](BF$_4$)$_2$.[12] It can be observed that (i) for higher dilution (decreasing x), $T_{1/2}$ decreases, (ii) the relationship between $T_{1/2}$ and x is linear and (iii) the change in $T_{1/2}$ with varying x is more pronounced in the case of the [Fe$_x$Zn$_{1-x}$(endi)$_3$](BF$_4$)$_2$ series. A linear fit of the two graphs gives the relation between $T_{1/2}$ and x: $T_{1/2}$ = 130.0 + 28.3x for the btzp compounds and $T_{1/2}$ = 133.1 + 10.2x for the endi compounds.

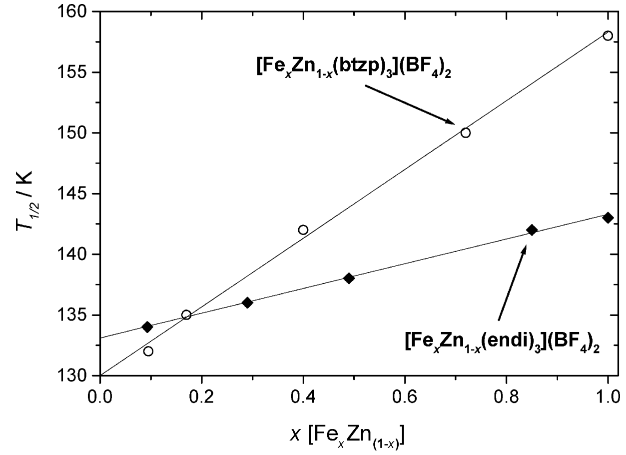


Figure 3. Concentration dependence of the transition temperature $T_{1/2}$ for (o) [Fe$_x$Zn$_{1-x}$(btzp)$_3$](BF$_4$)$_2$ and (♦) [Fe$_x$Zn$_{1-x}$(endi)$_3$](BF$_4$)$_2$. Linear fit appears as a straight line.

Table 1. Spin transition, reflectivity and LIESST parameters for the mixed-crystal series [Fe$_x$Zn$_{1-x}$(btzp)$_3$](BF$_4$)$_2$ and [Fe$_x$Zn$_{1-x}$(endi)$_3$](BF$_4$)$_2$.

	x	$T_{1/2}$ / K	T(LIESST) / K	% Photoexcitation
Btzp	1	158	46	62
	0.72	150	50	61
	0.4	142	51	79
	0.17	135	54	76
	0.095	132		
endi	1	143	61	86
	0.85	142	62	59
	0.49	138	63	63
	0.29	136	67	78
	0.093	134		

Reflectivity Properties

Diffuse reflectivity was recorded between 450 and 950 nm and at temperatures between 280 and 10 K. Typical spectra, recorded for [Fe$_{0.85}$Zn$_{0.15}$(endi)$_3$](BF$_4$)$_2$, are presented in Figure 4. The first part of the figure shows the evolution of the spectra between 280 and 90 K. It can be observed that, when decreasing the temperature, a broad band present at 850 nm tends to disappear, whereas a new and sharper band appears at 575 nm. The band at 575 nm can be attributed to a d-d transition of the LS spin complex, namely $^1A_1 \rightarrow {}^1T_1$. Indeed, it has been previously shown that the second transition for the LS state, $^1A_1 \rightarrow {}^1T_2$, was at lower wavelengths for similar tetrazole-like chains (400 nm).[19] On the other hand, the broad peak at 850 nm can be attributed to a d-d band of the HS state of the compound, namely the $^5T_2 \rightarrow {}^5E$ transition. The observed modifications between 280 and 90 K are thus related to the thermal spin transition of the compound, as confirmed by Figure 1 ($\gamma_{HS} = 1$ at 280 K and $\gamma_{HS} = 0.05$ at 90 K). At temperatures below 90 K, a decrease of the band at 575 nm can be observed, associated with a re-increase of the band at 850 nm. When the temperature is sufficiently low, relaxation of the photoinduced HS state is sufficiently slow and the light intensity at the surface of the sample is large enough to populate the photoinduced HS state. It is therefore not surprising that the band of the HS state reappears, whereas the band of the LS state disappears. It can be observed that, for all samples under study, the reflectivity at 10 K has almost the same value as at room-temperature. This means that the bleaching by irradiation of the compound, at least on the surface, is complete at low temperature. Notably, the spectra recorded at 50 K during heating and cooling are quite different, the spectra recorded in heating mode being more similar to the LS state. This phenomenon is known as the so-called LITH (Light-Induced Thermal Hysteresis) effect.[4] LITH results from the competition between LS→HS transitions induced by light and the spontaneous relaxation of the system. The width of LITH depends on the sweeping rate of the temperature. The larger the sweeping rate, the larger the hysteresis. However, even at vanishing sweeping rates, hysteresis can occur. This is linked to the cooperativity of the system. LITH can appear above a certain threshold value of cooperativity.[20]

In order to have an easy comparison between the different metal dilutions, the reflectivity as a function of the temperature was recorded at a given wavelength, namely 830 nm, for the $^5T_2 \rightarrow {}^5E$ band of the HS state (Figure 5). All the compounds exhibit the same general behaviour: starting from room temperature, the reflectivity decreases first to a temperature between 75 K and 100 K, depending on the compound. Further cooling of the compound leads to a re-increase of this reflectivity. Again this behaviour can

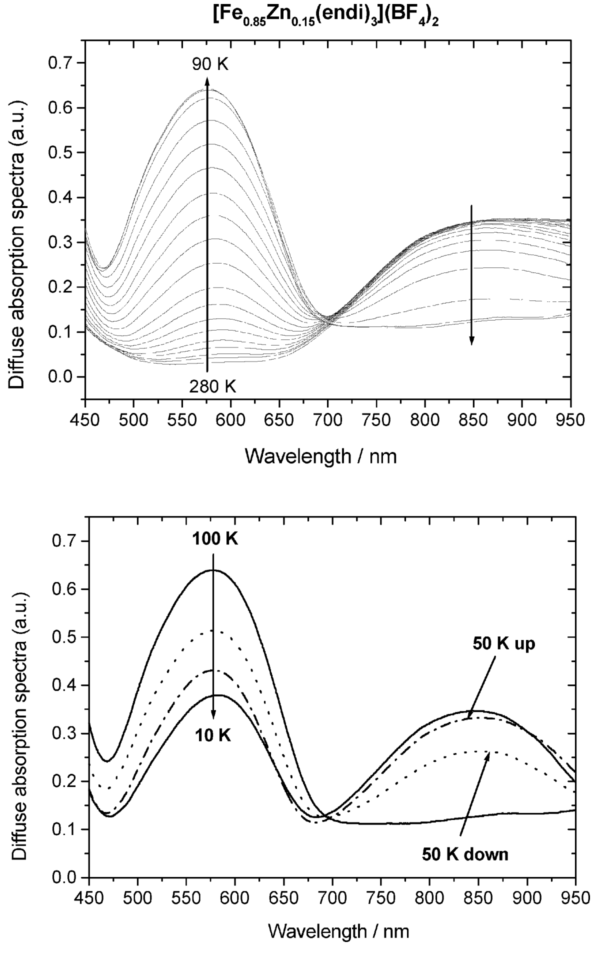


Figure 4. The changes in absorbance spectra during the cooling and heating modes for $[Fe_{0.85}Zn_{0.15}(endi)_3](BF_4)_2$.

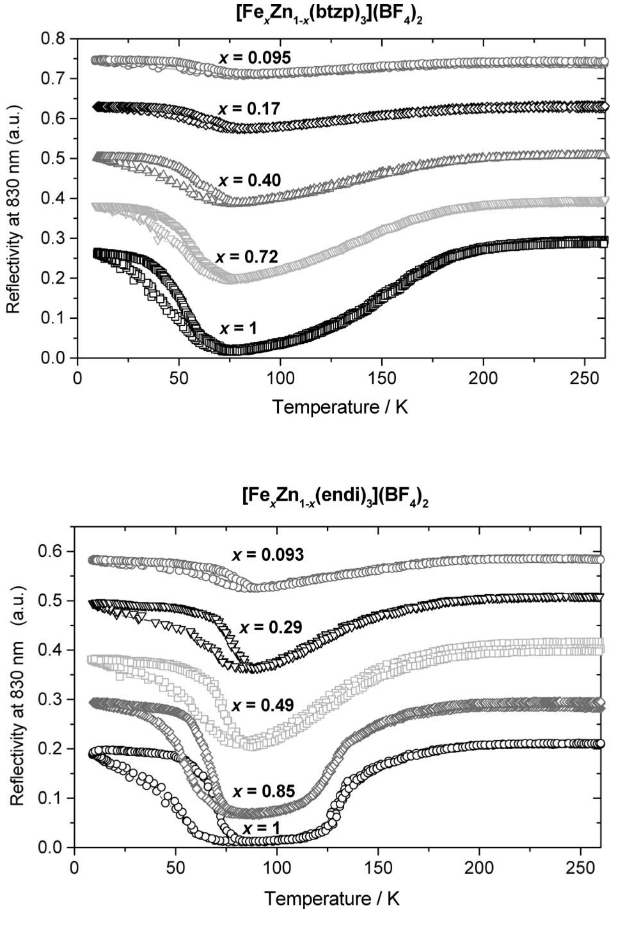


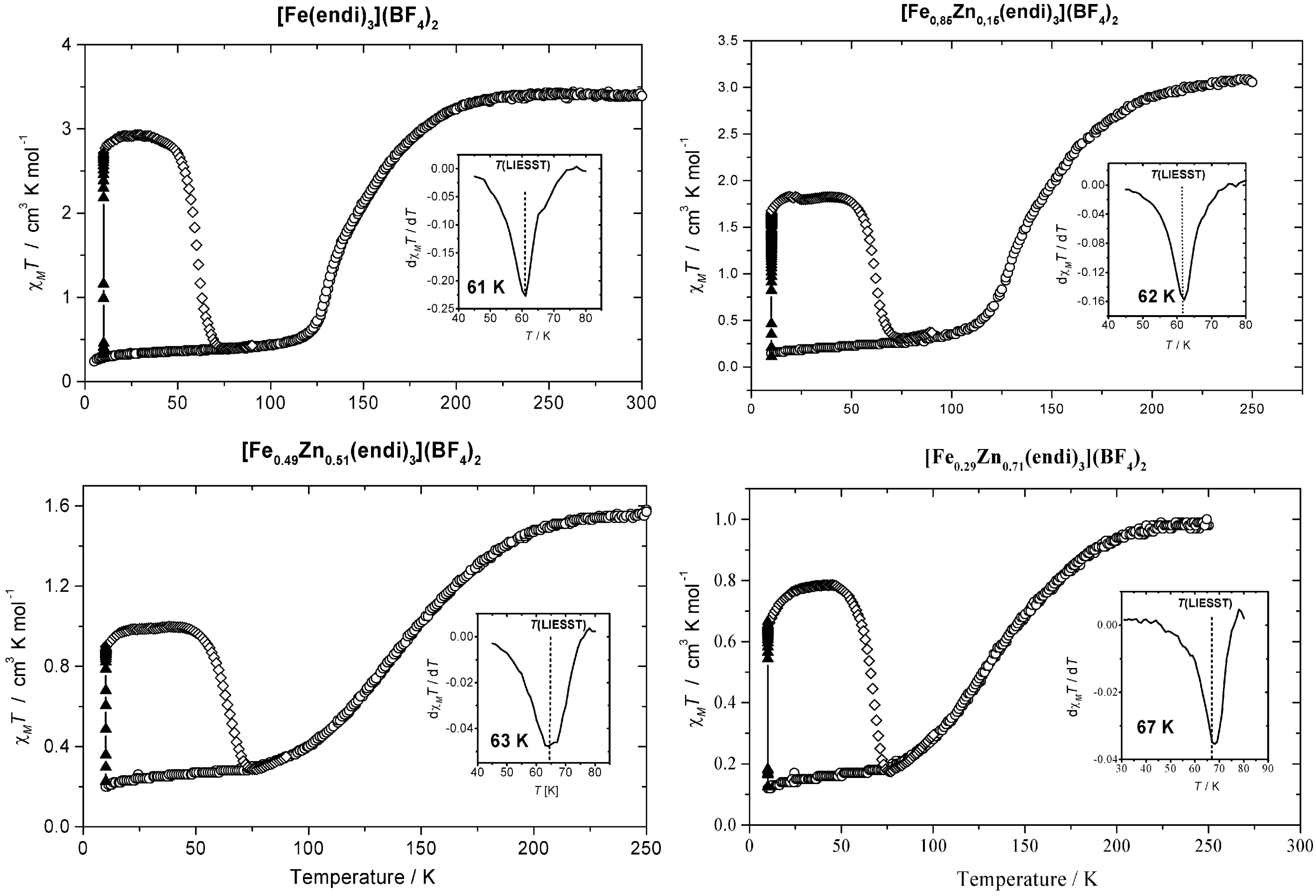
Figure 5. Thermal evolution of the reflectivity signal recorded at λ = 830 nm during the cooling and heating modes for (I) $[Fe_xZn_{1-x}(btzp)_3](BF_4)_2$ and (II) $[Fe_xZn_{1-x}(endi)_3](BF_4)_2$.

be explained: (i) at high temperature by the thermal spin transition and (ii) at low temperature by the population of a photoinduced high-spin state. When the spectra are recorded upon increasing the temperature, the signal is different, especially at low temperature and this is the LITH effect. The latter is especially large for pure iron compounds ($x = 1$). For the diluted systems the hysteresis loop of LITH becomes smaller. This is, of course, consistent with the fact that this loop is related to the cooperativity of the system. A decrease of the cooperativity of the system will lead to a decrease of the LITH loop as a mirror image of the decrease in abrupt character of the thermal spin transition.

Photomagnetism

The low spin→high spin photoconversion can also be investigated in bulk conditions using a SQUID magnetometer coupled to a CW optical source. Figure 6 and Figure 7 represent the temperature dependence of $\chi_M T$ for the different mixed-crystal systems $[\mathrm{Fe}_x\mathrm{Zn}_{1-x}(\mathrm{endi})_3](\mathrm{BF}_4)_2$ and $[\mathrm{Fe}_x\mathrm{Zn}_{1-x}(\mathrm{btzp})_3](\mathrm{BF}_4)_2$, respectively, before and after irradiation. For all complexes, a drastic increase in the magnetic signal under light irradiation was observed at 10 K. It should, however, be noticed that the amount of iron in the photoexcited high-spin state is not the same for all compounds and for none of the complexes is it quantitative. The level of percentage of photoconversion at 10 K was calculated by dividing the $\chi_M T$ value after photoirradiation by the $\chi_M T$ value at room temperature. Depending on the compound and the metal dilution, this percentage varies from 61 to 86.

After photoirradiation at 10 K, the system was heated in the dark with a temperature increase rate of 0.3 K min^{-1}. The $\chi_M T$ product first increases upon warming from 10 K due to zerofield splitting of the high-spin iron(II) ion, eventually reaching a plateau. At higher temperatures, $\chi_M T$ decreases sharply. To quantify the temperature at which the photoexcited state relaxes to the LS state, a limit temperature, T(LIESST), has been defined. T(LIESST) is defined as the minimum of the derivative $\mathrm{d}(\chi_M T)/\mathrm{d}T$ vs. T recorded during relaxation. Values of T(LIESST) are reported in Table 1. For the samples of $[\mathrm{Fe}_x\mathrm{Zn}_{1-x}(\mathrm{endi})_3](\mathrm{BF}_4)_2$, T(LIESST) has been recorded between 61 K and 63 K for x values between 1 and 0.49 and at 67 K for $x = 0.29$. Determining a T(LIESST) value for $x = 0.093$ was unsuccessful due to the weak $\chi_M T$ signal. Between $x = 1$ and $x = 0.29$, the $T_{1/2}$ values decrease from 143 K to 136 K. According to the equation, $T(\mathrm{LIESST}) = T_0 - 0.3T_{1/2}$, this should correspond to an increase of only 2 K for T(LIESST), that


$[\mathrm{Fe(endi)}_3](\mathrm{BF}_4)_2$

$[\mathrm{Fe}_{0.86}\mathrm{Zn}_{0.16}(\mathrm{endi})_3](\mathrm{BF}_4)_2$

$[\mathrm{Fe}_{0.49}\mathrm{Zn}_{0.51}(\mathrm{endi})_3](\mathrm{BF}_4)_2$

$[\mathrm{Fe}_{0.29}\mathrm{Zn}_{0.71}(\mathrm{endi})_3](\mathrm{BF}_4)_2$

Figure 6. Temperature dependence of $\chi_M T$ for $[\mathrm{Fe}_x\mathrm{Zn}_{1-x}(\mathrm{endi})_3](\mathrm{BF}_4)_2$ (○) data recorded without irradiation; (▲) data recorded with irradiation at 10 K; (✧) T(LIESST) measurement, data recorded in the warming mode with the laser turned off after one hour of irradiation.

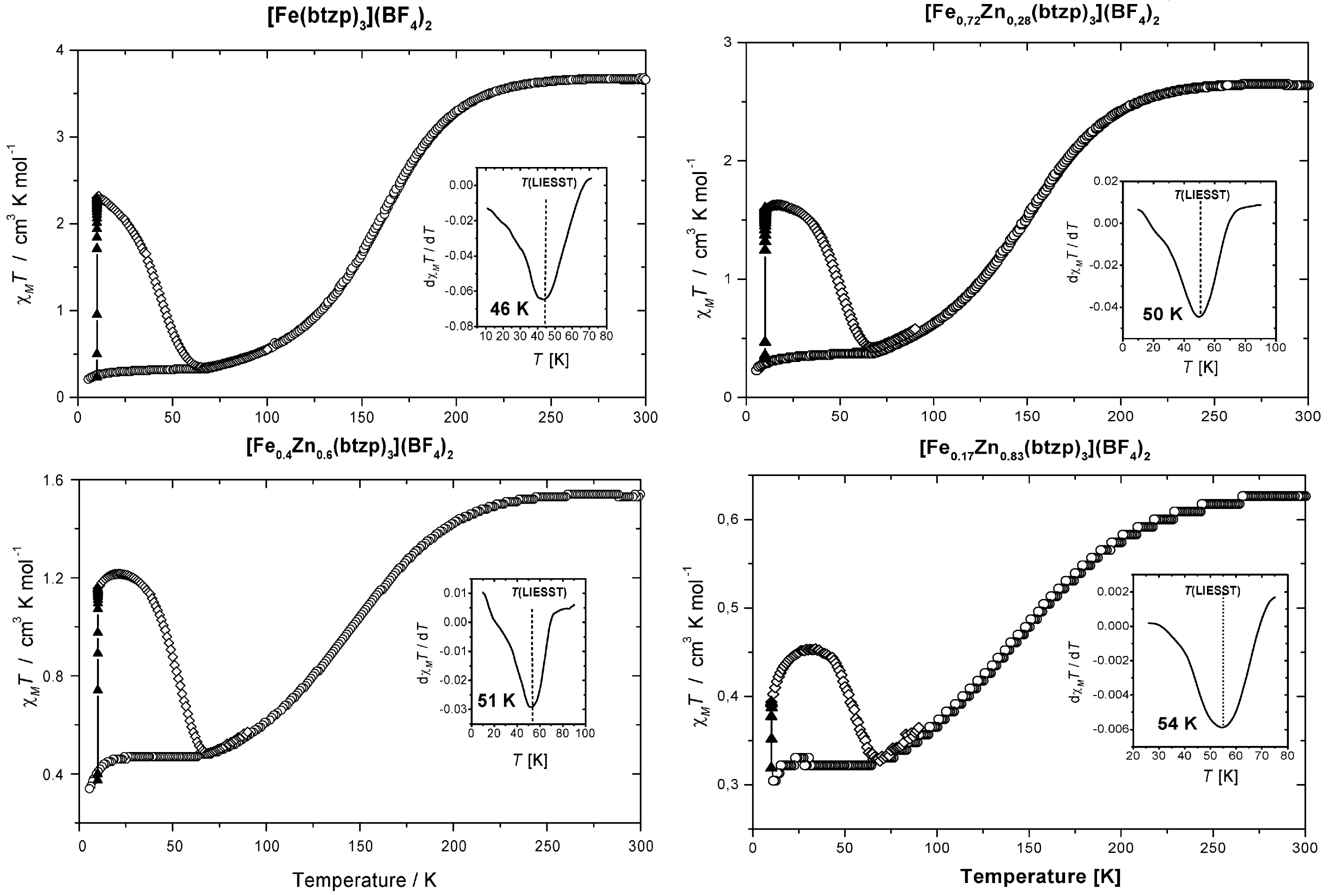


Figure 7. Temperature dependence of $\chi_M T$ for $[Fe_xZn_{1-x}(btzp)_3](BF_4)_2$ (○) data recorded without irradiation; (▲) data recorded with irradiation at 10 K; (✧) *T*(LIESST) measurement, data recorded in the warming mode with the laser turned off after one hour of irradiation.

is to say *T*(LIESST) is almost a constant value. This is indeed what is observed. For $[Fe_xZn_{1-x}(btzp)_3](BF_4)_2$ compounds, the change in *T*(LIESST) is somewhat more pronounced. It increases from 46 K ($x = 1$) to 50 K ($x = 0.72$) and 51 K ($x = 0.4$) to reach a value of 54 K ($x = 0.17$). Attempts to determine a *T*(LIESST) value for $x = 0.095$ were unsuccessful due to the weak $\chi_M T$ signal. A linear fit of these four combinations of *T*(LIESST) and $T_{1/2}$ values of the $[Fe_xZn_{1-x}(btzp)_3](BF_4)_2$ series leads to the relation $T(\text{LIESST}) = 97.7\pm7.4\text{ K} - 0.32\pm0.05\times T_{1/2}$ (*R* factor: 0.98). In other words, the $[Fe_xZn_{1-x}(btzp)_3](BF_4)_2$ samples obey the relation $T(\text{LIESST}) = T_0 - 0.3T_{1/2}$, with a T_0 factor of almost 100 K.

Concluding Remarks

In the present work, we have reported the thermal and the light-induced spin transitions of the two metal-diluted series of chain compounds $[Fe_xZn_{1-x}(btzp)_3](BF_4)_2$ and $[Fe_xZn_{1-x}(endi)_3](BF_4)_2$. These complexes display a thermal spin transition and show the Light-Induced Excited Spin State Trapping (LIESST) effect at low temperature. For each mixed-crystal sample, we have determined the thermal spin transition temperature, $T_{1/2}$, and the relaxation temperature of the photoinduced high-spin state, *T*(LIESST). Interestingly, for the $[Fe_xZn_{1-x}(btzp)_3](BF_4)_2$ series, the metal dilution seems to have a non-negligible influence on the *T*(LIESST) temperature. In the $[Fe_xZn_{1-x}(endi)_3](BF_4)_2$ compounds, the *T*(LIESST) values remain almost constant with the metal dilution. This may be interpreted in two ways: (i) the observed invariance may be due to the fact that *T*(LIESST) is not influenced by dilution or (ii) the change is too small with regards to the almost unchanged $T_{1/2}$ values. From the present study it is not possible to decide which of the two possibilities is more realistic.

Previous studies on the thermal spin crossover phenomenon have shown that any change of pressure in the lattice by chemical metal dilution or by an external stimulus affects the Gibbs free energy through a change of the molecular volume of the reaction giving rise to the additional term $p\Delta V_{HL}$.[2a] The shift of $T_{1/2}$ towards lower temperatures with increasing zinc metal dilution is a direct consequence of the negative pressure generated in the Zn host. Concerning the LIESST properties, Hauser et al.[21] have obtained evidence for an enhancement of the tunnelling rate by changing the size of the host ion (zinc, cadmium, etc) due to a vertical displacement of the HS and LS potential wells relative to each other. More precisely, in the case of zinc dilution (negative pressure effect), the HS potential is substantially shifted to lower energies relative to the LS state, both the barrier height and thickness for the tunnelling process are increased and the relaxation rate is reduced. As a consequence of this, one should expect an increase of the T(LIESST) value, in agreement with the decrease of $T_{1/2}$, according to the empirical $T(\text{LIESST}) = T_0 - 0.3T_{1/2}$ relation.[7,8] In a previous study on $[\text{Fe}_x\text{Zn}_{1-x}(\text{Phen})_2(\text{NCS})_2]$[9] and $[\text{Fe}_x\text{Mn}_{1-x}(\text{bpp})_2](\text{NCSe})_2$,[10] T(LIESST) was shown to be constant whereas $T_{1/2}$ decreases with dilution. This has been attributed to the fact that the photomagnetic properties are governed at the molecular scale while the thermal spin crossover regime is affected by both the ligand field and crystal packing effects. In the chain compounds presently studied and particularly in the $[\text{Fe}_x\text{Zn}_{1-x}(\text{btzp})_3](\text{BF}_4)_2$ series, this explanation does not seem to be pertinent. This can possibly be attributed to some interaction between the iron centres through the covalent bonds of the chain.

Contrary to the mixed-crystal series of $[\text{Fe}_x\text{Zn}_{1-x}(\text{Phen})_2(\text{NCS})_2]$[9] and $[\text{Fe}_x\text{Mn}_{1-x}(\text{bpp})_2](\text{NCSe})_2$,[10] the iron atoms in the compounds under study are not located in isolated molecules, linked only by van der Waals forces or π-π stacking but are linked by covalent bonds. This can justify the difference in behaviour between zero-dimensional mononuclear compounds and chain-like compounds. Further work is in progress to fully investigate the kinetics of these various metal dilution materials to determine the evolution of the different kinetic parameters governing the metastable HS→LS relaxation process (activation energy, frequency factor).

The determination of the kinetic parameters will also help understand the incomplete photoconversion recorded at low temperature in the present study. Incomplete photoconversion has already been observed in many SCO compounds, for instance in tetrazole derivatives such as a series of iron(II) α,ω-bis(tetrazole-1-yl)alkane complexes[19] where, depending on the carbon atom number ($n = 4$ to 9) in the bridges between the tetrazole moieties, different maximum percentages of photoexcited HS states have been reported ranging from almost complete photoirradiation ($n = 5$) to only 15% photoexcitation ($n = 8$).[19] Usually, incomplete photoirradiation can be explained by (i) a short penetration depth of the light during photoexcitation due to strong light absorption on the surface resulting in only a fraction of all the active iron(II) metal centres in the sample and/or being reached (ii) a short lifetime of the photoinduced HS state which prevents achievement of the steady state of complete LS→HS conversion. With regards to the first hypothesis, it is well known that metal dilution with zinc leads to a bleaching of the compound. Therefore, for highly metal-diluted samples, the penetration of light into the material should be facilitated and a higher degree of photoexcitation may be anticipated. The actual observation in the present study, however, is different. For instance, in the $[\text{Fe}_x\text{Zn}_{1-x}(\text{endi})_3](\text{BF}_4)_2$ family, the highest yield in photoexcitation was obtained for the neat compound so that explanation (i) does not seem to be reasonable.

It has been shown by investigating the photomagnetic properties of more than sixty iron(II) SCO compounds with nitrogen-donor ligands that a simple linear relation governs the LIESST properties of most of these compounds, $T(\text{LIESST}) = T_0 - 0.3T_{1/2}$, 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.[5–8] To date, four parallel T_0 lines have been established with values of 100, 120, 150 and 200 K.[7,8] By comparing the different $T(\text{LIESST})$-$T_{1/2}$ values and considering the chemical nature of the ligands involved, these T_0 lines have been attributed, respectively, to iron(II) complexes involving six independent monodentate ligands,[5] bidentate ligands,[5] meridional tridentate ligands[6] and 3D network solids.[22] In the present work, the $[\text{Fe}_x\text{Zn}_{1-x}(\text{btzp})_3](\text{BF}_4)_2$ derivatives appear to follow the $T(\text{LIESST}) = T_0 - 0.3T_{1/2}$ law with a T_0 factor of almost 100 K. Similar conclusions were also drawn for other spin-crossover chain complexes such as the iron(II) α,ω-bis(tetrazole-1-yl)alkane family[19] and $[\text{Fe}(\text{NCS})_2(\text{bped})_2]\cdot3(\text{ethanol})$ {bped = DL-1,2-bis(4′-pyridyl)-1,2-ethanediol}.[23] In the case of mononuclear complexes, it has been noted that materials with pronounced inherent ligand flexibility are prone to weak communication between the iron(II) SCO centres and show little tendency for photoconversion to the HS state.[7,8] Here, the inherent flexibility of the ligands linking the iron(II) SCO centres appears to have ‘no’ communicative effect on the photoexcitation properties. The T(LIESST) values on the $T_0 = 100$ K line (for monodentate discrete materials) indicate that linking SCO sites does not cause a more cooperative effect. We postulate that the coordinative bridging of iron(II) centres with flexible ligands, such as derivatives of tetrazole (present work and see ref.[19]) or bped (see ref.[22]), seems to have a negative influence on cooperativity, in contrast to the positive influence observed with short rigid ligands, each of which is linked to only one iron metal atom.

Experimental Section

General: All syntheses were carried out under nitrogen. The syntheses of the ligand btzp [1,2-bis(tetrazol-1-yl)propane] and endi [1,2-bis(tetrazol-1-yl)ethane] are described in the literature.[11,12]

Materials: The ligand [btzp] was prepared from sodium azide, triethyl orthoformate and 1,2-diaminopropane according to the general method described by Kamiya and Saito.[24] The ligand 1,2-(tetrazol-1-yl)ethane [endi] was prepared in a similar method to that used by Satoh et al.[25] The preparation of the pure compounds $[\text{Fe}(\text{btzp})_2](\text{BF}_4)_2$ and $[\text{Fe}(\text{endi})_2](\text{BF}_4)_2$ has been described earlier by Gutlich et al.[11] and Linert et al.[12] The diluted compounds $[\text{Fe}_x\text{Zn}_{1-x}]$ were synthesised according to the same procedures, replacing the iron(II) tetrafluoroborate by mixtures of iron(II) and zinc(II) in a given ratio. Iron fraction (x) values were calculated from the iron and zinc atomic percentage determined by quantitative analysis. Elemental analyses of C, H, N and F were performed and the results agreed well with the calculated data.

Physical Measurements: Photomagnetic measurements were performed using a Spectrum Physics Series 2025 Kr+ laser ($\lambda = 532$ nm) coupled by means of an optical fibre to the cavity of a MPMS-55 Quantum Design SQUID magnetometer. The optical

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power at the sample surface was adjusted to 5 mW cm^{-2} and it was verified that this resulted in no change in magnetic response due to heating of the sample. The samples consisted of a thin layer of compound the weight of which was obtained by comparison of the thermal spin crossover curve with that of a more accurately weighed sample of the same material. Our previously published standardised method for measuring LIESST data was followed.[4–8] After slowly cooling to 10 K, the sample in the low-spin state was irradiated and the change in magnetic susceptibility followed. When the saturation point had been reached the laser was switched off and the temperature increased at a rate of 0.3 K min^{-1}. The magnetisation was measured every 1 K. T(LIESST) was determined from the minimum of a d$\chi_M T$/dT vs. T plot for the relaxation process.

Reflectivity measurements were done using a custom-built reflectivity set-up equipped with a CVI spectrometer which allowed the collection of both the reflectivity spectra within the range of 450–900 nm at a given temperatures and following of the temperature dependence of the signal at a selected wavelength at 5–290 K.[26]

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[1] For general reviews on “Spin crossover in Transition Metal Compounds”, cf. P. Gütlich, H. A. Goodwin (Eds.), **2004**, *Top. Curr. Chem.* 233–235.

[2] a) P. Gütlich, A. Hauser, H. Spiering, *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 2024–2054; b) O. Kahn, C. J. Martinez, *Science* **1998**, *279*, 44; c) P. Gütlich, Y. Garcia, T. Woike, *Coord. Chem. Rev.* **2001**, *219–221*, 839–879; d) J.-F. Létard, P. Guionneau, L. Goux-Capes, *Top. Curr. Chem.* **2004**, *235*, 221–249.

[3] S. Decurtins, P. Gütlich, C. P. Köhler, H. Spiering, A. Hauser, *Chem. Phys. Lett.* **1984**, *105*, 1–4; A. Hauser, *Chem. Phys. Lett.* **1986**, *124*, 543–548.

[4] J.-F. Létard, P. Guionneau, L. Rabardel, J. A. K. Howard, A. E. Goeta, D. Chasseau, O. Kahn, *Inorg. Chem.* **1998**, *37*, 4432–4441.

[5] J.-F. Létard, L. Capes, G. Chastanet, N. Moliner, S. Létard, J. A. Réal, O. Kahn, *Chem. Phys. Lett.* **1999**, *313*, 115–120.

[6] a) S. Marcen, L. Lecren, L. Capes, H. A. Goodwin, J.-F. Létard, *Chem. Phys. Lett.* **2002**, *358*, 87–95; b) C. Carbonera, J. S. Costa, V. A. Money, J. Elhaik, J. A. K. Howard, M. A. Halcrow, J.-F. Létard, *Dalton Trans.* **2006**, 3058–3066; c) V. A. Money, J. S. Costa, S. Marcén, G. Chastanet, J. Elhaik, M. A. Halcrow, J. A. K. Howard, J.-F. Létard, *Chem. Phys. Lett.* **2004**, *391*, 273–277.

[7] J.-F. Létard, P. Gionneau, O. Nguyen, J. S. Costa, S. Marcen, G. Chastanet, M. Marchivie, L. Capes, *Chem. Eur. J.* **2005**, *11*, 4582–4589.

[8] J.-F. Létard, *J. Mater. Chem.* **2006**, *16*, 2550–2559.

[9] C. Baldé, C. Desplanches, A. Wattiaux, P. Guionneau, P. Gütlich, J.-F. Létard, *Dalton Trans.* Article in press, DOI: 10.1039/b800248g.

[10] C. Baldé, C. Desplanches, P. Gütlich, E. Freysz, J.-F. Létard, *Inorg. Chim. Acta*, article in press, DOI: 10.1016/j.ica.2008.03.124.

[11] P. J. van Koningsbruggen, Y. Garcia, O. Kahn, L. Fournès, H. Kooijman, A. L. Spek, J. G. Haasnoot, J. Moscovici, K. Provost, A. Michalowicz, F. Renz, P. Gütlich, *Inorg. Chem.* **2000**, *39*, 1891.

[12] J. Schweifer, P. Weinberger, K. Mereiter, M. Boca, C. Reichl, G. Wiesinger, G. Hilscher, P. J. van Koningsbruggen, H. Kooijman, M. Grunert, W. Linert, *Inorg. Chim. Acta* **2002**, *339*, 297.

[13] M. Sorai, J. Ensling, P. Gütlich, *Chem. Phys.* **1976**, *18*, 199–209; P. Gütlich, R. Link, H. G. Steinhäuser, *Inorg. Chem.* **1978**, *17*, 2509–2514.

[14] P. Ganguli, P. Gütlich, E. W. Müller, *Inorg. Chem.* **1982**, *21*, 3429–3433.

[15] R. D. Shannon, *Acta Crystallogr., Sect. A* **1976**, *32*, 751.

[16] J.-P. Martin, J. Zarembowitch, A. Bousseksou, A. Dworkin, J. G. Haasnoot, F. Varret, *Inorg. Chem.* **1994**, *33*, 6325–6333.

[17] T. Tayagaki, A. Galet, G. Molnar, M. Carmen Muñoz, A. Zwick, K. Tanaka, J.-A. Real, A. Bousseksou, *J. Phys. Chem. B* **2005**, *109*, 14859.

[18] J.-P. Martin, J. Zarembowitch, A. Dworkin, J. G. Haasnoot, E. Codjovi, *Inorg. Chem.* **1994**, *33*, 2617–2623.

[19] A. Absmeier, M. Bartel, C. Carbonera, G. Jameson, P. Weinberger, A. Caneschi, K. Mereiter, J.-F. Létard, W. Linert, *Chem. Eur. J.* **2006**, *12*, 2235–2243; A. Absmeier, M. Bartel, C. Carbonera, G. Jameson, F. Werner, M. Reissner, A. Caneschi, J.-F. Létard, W. Linert, *Eur. J. Inorg. Chem.* **2007**, 3047–3054.

[20] A. Desaix, O. Roubeau, J. Jeftic, J. G. Haasnoot, K. Boukheddaden, E. Codjovi, J. Linares, M. Nogues, F. Varret, *Eur. Phys. J., Part B* **1998**, *6*, 183–193.

[21] A. Hauser, *Coord. Chem. Rev.* **1991**, *111*, 275–290; J. Jeftic, A. Hauser, *J. Phys. Chem. B* **1997**, *101*, 10262–10270; H. Romstedt, A. Hauser, H. Spiering, *J. Phys. Chem. Solids* **1998**, *59*, 265–275; A. Vef, U. Manthe, P. Gütlich, A. Hauser, *J. Chem. Phys.* **1994**, *101*, 9326–9332.

[22] N. Shimamoto, S.-I. Ohkoshi, O. Sato, K. Hashimoto, *Inorg. Chem.* **2002**, *41*, 678–684.

[23] S. M. Neville, G. J. Halder, K. W. Chapman, M. B. Duriska, P. D. Southon, J. D. Cashion, J.-F. Létard, B. Moubaraki, K. S. Murray, C. J. Kepert, *J. Am. Chem. Soc.* **2008**, *130*, 2869–2876.

[24] T. Kamiya, Y. Saito, *Ger. Offen.* **1973**, 2147023.

[25] Y. Satoh, N. Marcopulos, *Tetrahedron Lett.* **1995**, *36*, 1759–1762.

[26] C. Carbonera, A. Dei, C. Sangregorio, J.-F. Létard, *Chem. Phys. Lett.* **2004**, *396*, 198–201.

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