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The Role of Symmetry Breaking in the Structural Trapping of Light-Induced Excited Spin States

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Light-Induced Excited Spin State Trapping (LIESST) data are reported for seven isostructural solvate salts from the iron(II)/2,6-di(pyrazol-1-yl)pyridine family. A complicated relationship between their spin-crossover $T_{½}$ and T(LIESST) values may reflect low-temperature thermal and light-induced symmetry breaking, which is shown by one of the compounds but not by two others.

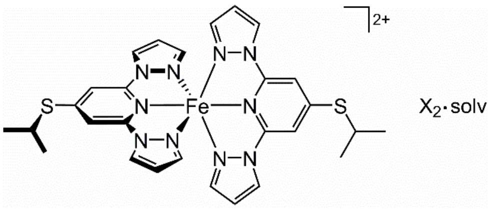
Spin-crossover (SCO) compounds[1,2] are versatile molecular switches for use in multifunctional materials, macroscopic devices and nanoscience.[2,3] SCO transitions can be induced by a range of stimuli including temperature, pressure and visible irradiation.[1,4] Light induced SCO is most often measured as a photo-conversion of a low-spin compound to a metastable high-spin state at low temperatures. This is the Light-Induced Excited Spin State Trapping (LIESST) effect.[5] The sample can only reconvert to its low-spin ground state upon heating above the activation barrier to its relaxation process, which typically lies below 150 K.

Mean-field theory of the propagation of SCO transitions through solid lattices predicts an inverse relationship between the thermodynamic SCO temperature $T_{½}$ and the lifetime of the photoinduced metastable state,[6] Some years ago an empirical relationship of this type was indeed proposed in different families of compounds (eq 1):

$$T(\text{LIESST}) = T_0 - 0.3T_{½} \qquad (1)$$

where T(LIESST) is the relaxation temperature of the kinetically trapped spin state[7,8] and T_0 reflects the rigidity of the metal ion coordination sphere.[8,9] Although there is often a degree of scatter in $T_{½}$ *vs* T(LIESST) plots, eq 1 is a useful predictor of T(LIESST) for many types of SCO materials. This includes complex salts derived from $[Fe(bpp)_2]^{2+}$ (bpp = 2,6-di{pyrazol-1-yl}pyridine), which often show good agreement to eq 1 with $T_0 \approx 150$ K.[10,11]

We recently reported six compounds of general formula $[FeL_2][BF_4]_2$·solv (**1[BF$_4$]$_2$**·solv, Scheme 1).[12] This is a rare family of isostructural SCO materials,[13] which facilitates studies of structure: function relationships underlying their SCO behaviour. We have expanded the series with the perchlorate salts **1[ClO$_4$]$_2$**·solv, and report a photomagnetic and photocrystallographic study on these isostructural compounds that reveals the relationship between structure and T(LIESST) in unprecedented detail.



Scheme 1. Compound **1X$_2$·solv** (X^- = BF_4^- or ClO_4^-; solv = $MeNO_2$, MeCN, Me_2CO, H_2O or sf [solvent-free]).

Complexation of $Fe[ClO_4]_2·6H_2O$ by 2 equiv L in the appropriate solvent affords **1[ClO$_4$]$_2$**·MeCN, **1[ClO$_4$]$_2$**·$MeNO_2$ and **1[ClO$_4$]$_2$**·*y*Me_2CO ($y \approx 0.7$) after the usual work-up. **1[ClO$_4$]$_2$**·*y*Me_2CO is converted to **1[ClO$_4$]$_2$**·H_2O in single-crystal-to-single-crystal fashion, when stored *in vacuo* at 290 K for 24 hrs and then exposed to air. Solvent-free **1[ClO$_4$]$_2$**·sf was also prepared *in situ*, by annealing crystals of **1[ClO$_4$]$_2$**·*y*Me_2CO on the diffractometer (ESI †). The **1[ClO$_4$]$_2$**·solv and **1[BF$_4$]$_2$**·solv[12] compounds are high-spin, isostructural and phase-pure at room temperature ($P2_1/c$, Z = 4), while all except **1[ClO$_4$]$_2$**·MeCN exhibit SCO upon cooling without a crystallographic phase change (Fig. 1 and ESI †). The SCO temperature and cooperativity vary between the compounds, but the high-spin state is consistently stabilised when X = ClO_4^- compared to X = BF_4^- for each solvent. That might reflect expansion of the crystal lattice by the larger ClO_4^- anion, which would favour the larger high-spin cations.[14] Any fraction of the samples that is high-spin near 100 K remains frozen in below that temperature.[15,16] Poising **1[ClO$_4$]$_2$**·$MeNO_2$ at 102 K for 80 mins leads to a slow reduction in $\chi_M T$, until the sample is fully low-spin and the warming branch of the transition proceeds monotonically (ESI †). That confirms the kinetic origin of the low-temperature spin-state trapping, and the apparent SCO hysteresis, in that material. Such kinetic effects arise when thermal trapping of the high-spin state occurs at a similar temperature to $T_{½}$ in an SCO material.[15]

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† Electronic Supplementary Information (ESI) available: experimental procedures and characterisation data; crystallographic experimental data, Figures and Tables; magnetic susceptibility data for all the compounds, measured under the same conditions as in ref. 12; kinetic studies of thermal SCO in two **1[ClO$_4$]$_2$**·solv samples; and a Table of the T(LIESST) data plotted in Fig. 2. See DOI: 10.1039/x0xx00000x

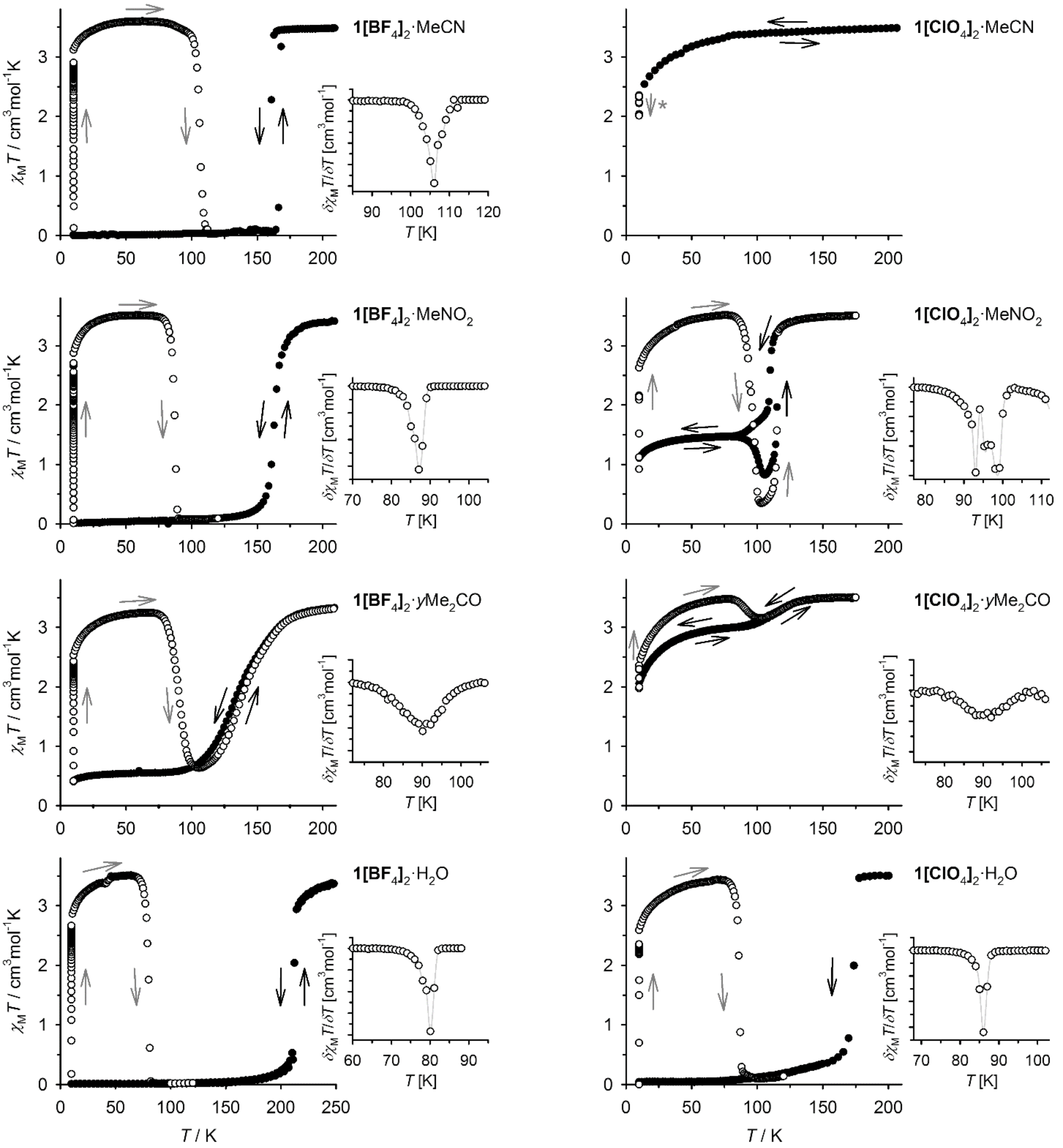

Figure 1. Temperature dependence of magnetic susceptibility data for eight $\mathbf{1X_2}$·solv compounds before irradiation (●, black arrows), and during the *T*(LIESST) measurement (○, grey arrows). The samples were cooled to 10 K, irradiated at that temperature (λ = 510 nm), then rewarmed in the dark. Scan rate 0.4 Kmin^{-1}. The insets show the first derivatives of the relaxation curves, with data points linked by spline curves for clarity. The starred compound is high-spin at 10 K, and was irradiated at λ = 980 nm in a reverse-LIESST experiment.[17]

Seven freshly prepared $\mathbf{1X_2}$·solv samples showed essentially quantitative low→high-spin photoconversion upon irradiation at 510 nm at 10 K (Fig. 1). After equilibration, warming the samples in the dark showed the high-spin forms are long-lived until *ca* 80 K, where thermal relaxation to their thermodynamic low-spin states took place.[17] The *T*(LIESST) curves are mostly monotonic but of differing abruptness, with samples exhibiting the least cooperative thermal SCO ($\mathbf{1[BF_4]_2}$·*y*Me_2CO and $\mathbf{1[ClO_4]_2}$·*y*Me_2CO) showing the most gradual LIESST relaxation. An exception is $\mathbf{1[ClO_4]_2}$·$MeNO_2$, whose relaxation is split into three closely spaced components. Although other explanations are possible,[18] this stepped relaxation may reflect crystallographic phase changes occurring during the LIESST relaxation process (see below).[19]

The *T*(LIESST) values, from the minima of the $\delta\chi_M T/\delta T$ curves, are typical for complexes of this type (Table 1).[11] However, a plot of $T_{½}$ *vs* *T*(LIESST) for these data can be interpreted in two ways (Fig. 2). At first glance, all the compounds lie on the same *T*(LIESST)/$T_{½}$ line except $\mathbf{1[BF_4]_2}$·MeCN, whose *T*(LIESST) is *ca* 20 K higher than for $\mathbf{1[BF_4]_2}$·$MeNO_2$ despite their similar $T_{½}$ values (Table 1). However, comparison of these data with the literature shows an

Table 1. Thermal SCO and LIESST properties of **1[BF$_4$]$_2$**·solv and **1[ClO$_4$]$_2$**·solv, with a temperature ramp of 0.4 Kmin^{-1}. (Figs. 1 and 2). Data for the BF$_4^-$ salts differ slightly from those in ref. 13, which were measured at a faster scan rate of 5 Kmin^{-1} (ESI †).

	$T_{½}$↓ / K	$T_{½}$↑ / K	cooperativity	T(LIESST) / K
1[BF$_4$]$_2$·MeCN	160	167	abrupt	106
1[ClO$_4$]$_2$·MeCN	HS[a]	–	–	–
1[BF$_4$]$_2$·MeNO$_2$	171	–	gradual	87
1[ClO$_4$]$_2$·MeNO$_2$	102	115	gradual, incomplete	93,96,99
1[BF$_4$]$_2$·*y*Me$_2$CO	131	–	gradual, incomplete	91
1[ClO$_4$]$_2$·*y*Me$_2$CO	<100[b]	–	gradual, incomplete	*ca* 90[c]
1[BF$_4$]$_2$·H$_2$O	212	214	abrupt	81
1[ClO$_4$]$_2$·H$_2$O	173	–	abrupt	86

[a] HS = high-spin between 3-300 K. [b] Only 20 % of the SCO transition occurs before the remaining high-spin fraction is frozen in below 100 K. [c] Not included in Fig. 2.

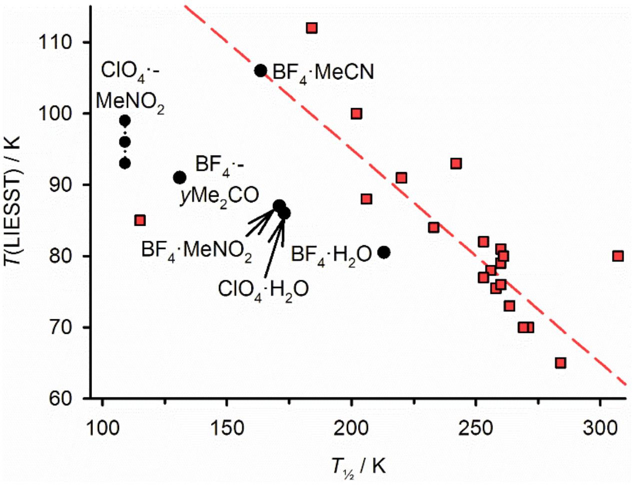

Figure 2. Plot of $T_{½}$ vs T(LIESST) for the compounds in this work (black circles; Table 1), and from previously published compounds from our laboratory (red squares; ESI†). The dashed line shows eq 1 with T_0 = 155 K, close to the T_0 = 150 K correlation that was originally proposed for this family of compounds.[10,11]

alternative picture. Only **1[BF$_4$]$_2$**·MeCN and **1[BF$_4$]$_2$**·H$_2$O lie within experimental error of the trend expected from our previous measurements. The other compounds show reduced T(LIESST) values, deviating increasingly from eq 1 as $T_{½}$ is lowered (Fig. 2). Crystallographic studies on three of the materials shed light on these differences. Unexpectedly, **1[BF$_4$]$_2$**·MeNO$_2$ undergoes a symmetry-breaking phase transition upon cooling from 100 K (phase 1; $P2_1/c$, $Z = 4$) to 15 K (phase 2; $P2_1/c$, $Z = 12$), involving a tripling of the unit cell b dimension. Three unique low-spin cations in the asymmetric unit, labelled 'A', 'B' and 'C', are grouped into layers parallel to (010). Individual layers contain either A-type molecules or alternating B and C types, with the layers arranged as A–(B/C)–(B/C)–A–(B/C)–(B/C) down the b axis (Fig. 3). Irradiation at 660 nm at 15 K transforms the crystal to a new high-spin phase (phase 3; $P2_1$, $Z = 4$), whose unit cell dimensions resemble phase 1 but which lacks the c glide plane. The 'A' and 'B' cation sites in this phase are grouped into corrugated layers along (001) (Fig. 4). The cations in phases 2 and 3 have similar metric parameters to the corresponding spin states of phase 1. The symmetry breaking is reflected in changes to the orientations of the *iso*propyl groups, anions and solvent molecules (ESI †).

In contrast, **1[BF$_4$]$_2$**·H$_2$O (at 20 K) and **1[BF$_4$]$_2$**·MeCN (at 85 K) both retain phase 1 before and after irradiation; the high-spin form

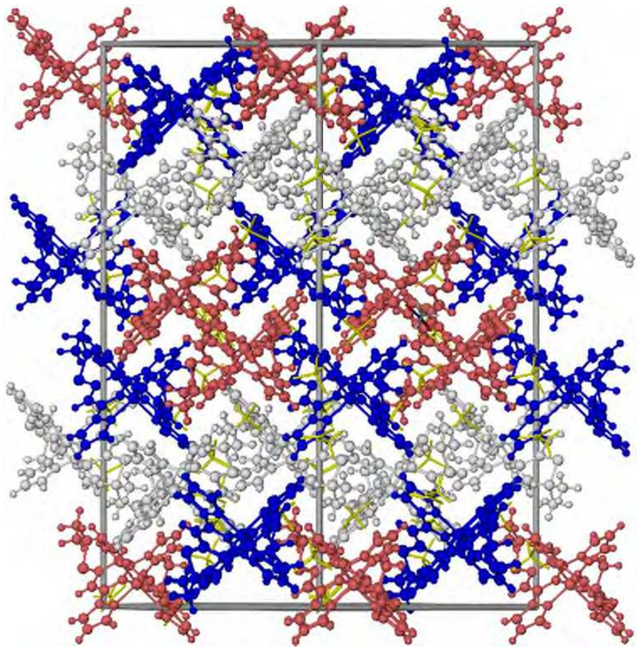

Figure 3. Packing diagram of low-spin phase 2 of **1[BF$_4$]$_2$**·MeNO$_2$ along the (101) crystal vector, with the b axis vertical. Cations A, B and C are coloured white, blue and red, respectively, while the anions and solvent (yellow) are de-emphasised for clarity.

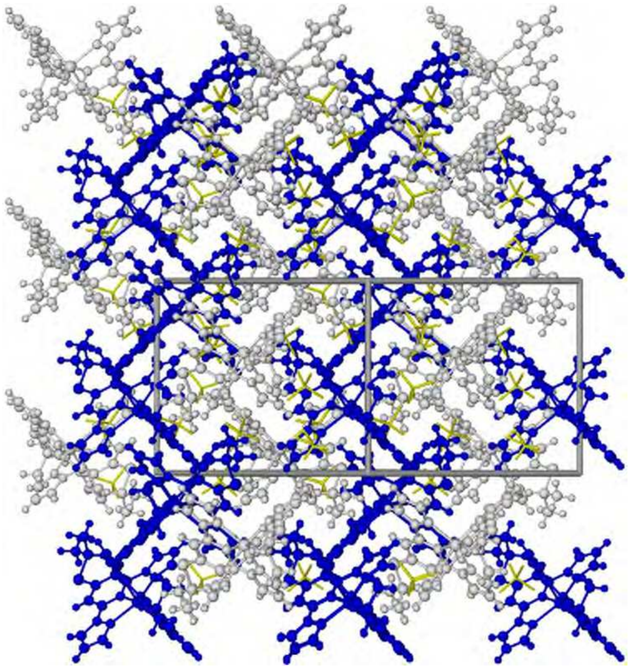

Figure 4. Packing diagram of high-spin phase 3 of **1[BF$_4$]$_2$**·MeNO$_2$, in the same view as Fig. 3. Cations A and B are coloured white and blue, respectively. Other details as for Fig. 3.

of **1[BF$_4$]$_2$**·MeCN was also characterised at 15 K, again adopting phase 1. Hence **1[BF$_4$]$_2$**·H$_2$O and **1[BF$_4$]$_2$**·MeCN, which align more closely with eq 1 (T_0 = 150 K, Fig. 2), show no evidence for symmetry breaking under these conditions. The isothermal low-spin→high-spin photoconversion of both phase 1 compounds results in an expansion of the unit cell a axis and a contraction of b and β. The reduction in β is much larger for **1[BF$_4$]$_2$**·MeCN at 85 K, causing an unusual 0.2 % contraction of the unit cell volume in its high-spin state. In contrast, **1[BF$_4$]$_2$**·H$_2$O and **1[BF$_4$]$_2$**·MeNO$_2$ both undergo a more typical expansion of their normalised unit cell volume during photoexcitation experiments (ESI †).

The light-induced high-spin state of **1[BF$_4$]$_2$**·MeNO$_2$ (phase 3) has reduced crystallographic symmetry, and thus a lower entropy, than its thermodynamic high-spin state (phase 1). That should shift the (theoretical) $T_{½}$ of phase 3 to a higher temperature than phase 1,[20] leading to a lower T(LIESST) for phase 3 as observed (eq 1).[21] This symmetry-breaking entropy change is unlikely to be electronic in origin, since the coordination geometries of the C_1-symmetric iron centers are similar in each phase. Rather, it predominantly reflects a reduction in vibrational entropy through a lifting of lattice phonon degeneracy, associated with the loss of the crystallographic glide plane and inversion center in phase 3. Attempts to access phase 1 of **1[BF$_4$]$_2$**·MeNO$_2$ by photoirradiation, for comparison with phase 3, have thus far been unsuccessful.

In conclusion, isostructural **1[BF$_4$]$_2$**·solv and **1[ClO$_4$]$_2$**·solv exhibit a complex relationship between $T_{½}$ and T(LIESST). Most of the compounds exhibit a linear $T_{½}$ *vs* T(LIESST) dependence, with a reduced slope compared to eq 1 (Fig. 2). Hence, a generalisation of eq 1 can be applied to this subset of compounds (eq 2).

$$T(\text{LIESST}) = T_0 - aT_{½} \qquad (2)$$

The data in Table 1 (omitting **1[BF$_4$]$_2$**·MeCN) are best fit by T_0 = 108 K and a = 0.13 (ESI †). Moreover, T(LIESST) for **1[BF$_4$]$_2$**·MeCN and **1[BF$_4$]$_2$**·MeNO$_2$ differ by 20 K, despite their almost identical $T_{½}$ values (Table 1). That can be explained by the thermodynamic consequences of a series of thermal and light-induced symmetry-breaking transitions, which are undergone by **1[BF$_4$]$_2$**·MeNO$_2$ but not **1[BF$_4$]$_2$**·MeCN or **1[BF$_4$]$_2$**·H$_2$O. This clearly demonstrates the impact of crystallographic phase changes on T(LIESST),[21] at least in these two compounds. Other compounds that deviate unexpectedly from eqs 1 or 2 may also exhibit unresolved structural chemistry in the LIESST experiment.

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Conflicts of interest

There are no conflicts to declare.

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