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► **To cite this version:**

Rafal Kulmaczewski, Elzbieta Trzop, Laurence J Kershaw Cook, Eric Collet, Guillaume Chastanet, et al.. The role of symmetry breaking in the structural trapping of light-induced excited spin states. Chemical Communications, 2017, 53 (99), pp.13268-13271. 10.1039/c7cc07990g . hal-01662309

HAL Id: hal-01662309

<https://hal.science/hal-01662309v1>

Submitted on 9 Mar 2021

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

Received 00th January 20xx,
Accepted 00th January 20xx

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DOI: 10.1039/x0xx00000x

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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 $T_{1/2}$ 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.

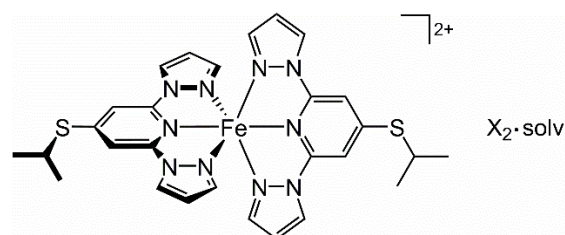
Spin-crossover (SCO) compounds^{1,2} are versatile molecular switches for use in multifunctional materials, macroscopic devices and nanoscience.^{2,3} SCO transitions can be induced by a range of stimuli including temperature, pressure and visible irradiation.^{1,4} Light induced SCO is most often measured 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 $T_{1/2}$ 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):

$$T(\text{LIESST}) = T_0 - 0.3T_{1/2} \quad (1)$$

where $T(\text{LIESST})$ 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 $T_{1/2}$ vs $T(\text{LIESST})$ plots, eq 1 is a useful predictor of $T(\text{LIESST})$ for many types of SCO materials. This includes complex salts derived from $[\text{Fe}(\text{bpp})_2]^{2+}$ (bpp = 2,6-di(pyrazolyl)pyridine), which often show good agreement to eq 1 with $T_0 = 150$ K.^{10,11}

We recently reported six compounds of general formula $[\text{FeL}_2][\text{BF}_4]_2 \cdot \text{solv}$ (**1** $[\text{BF}_4]_2 \cdot \text{solv}$, 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** $[\text{ClO}_4]_2 \cdot \text{solv}$, and report a photomagnetic and photocrystallographic study on these isostructural compounds that reveals the relationship between structure and $T(\text{LIESST})$ in unprecedented detail.



Scheme 1. Compound **1** $X_2 \cdot \text{solv}$ ($X^- = \text{BF}_4^-$ or ClO_4^- ; solv = MeNO_2 , MeCN , Me_2CO , H_2O or sf [solvent-free]).

Complexation of $\text{Fe}[\text{ClO}_4]_2 \cdot 6\text{H}_2\text{O}$ by 2 equiv L in the appropriate solvent affords **1** $[\text{ClO}_4]_2 \cdot \text{MeCN}$, **1** $[\text{ClO}_4]_2 \cdot \text{MeNO}_2$ and **1** $[\text{ClO}_4]_2 \cdot \gamma\text{Me}_2\text{CO}$ ($\gamma \approx 0.7$) after the usual work-up. **1** $[\text{ClO}_4]_2 \cdot \gamma\text{Me}_2\text{CO}$ is converted to **1** $[\text{ClO}_4]_2 \cdot \text{H}_2\text{O}$ 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** $[\text{ClO}_4]_2 \cdot \text{sf}$ was also prepared *in situ*, by annealing crystals of **1** $[\text{ClO}_4]_2 \cdot \gamma\text{Me}_2\text{CO}$ at 370 K for 1 hr on the diffractometer (ESI †). The **1** $[\text{ClO}_4]_2 \cdot \text{solv}$ and **1** $[\text{BF}_4]_2 \cdot \text{solv}$ ¹² compounds are high-spin, isostructural and phase-pure at room temperature ($P2_1/c$, $Z = 4$), while all except **1** $[\text{ClO}_4]_2 \cdot \text{MeCN}$ 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 $X = \text{ClO}_4^-$ compared to $X = \text{BF}_4^-$ 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** $[\text{ClO}_4]_2 \cdot \text{MeNO}_2$ at 102 K for 80 mins leads to a slow reduction in χ_{MT} , until the sample is fully low-spin

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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** $[\text{ClO}_4]_2 \cdot \text{solv}$ samples; and a Table of the $T(\text{LIESST})$ data plotted in Fig. 2. See DOI: 10.1039/x0xx00000x

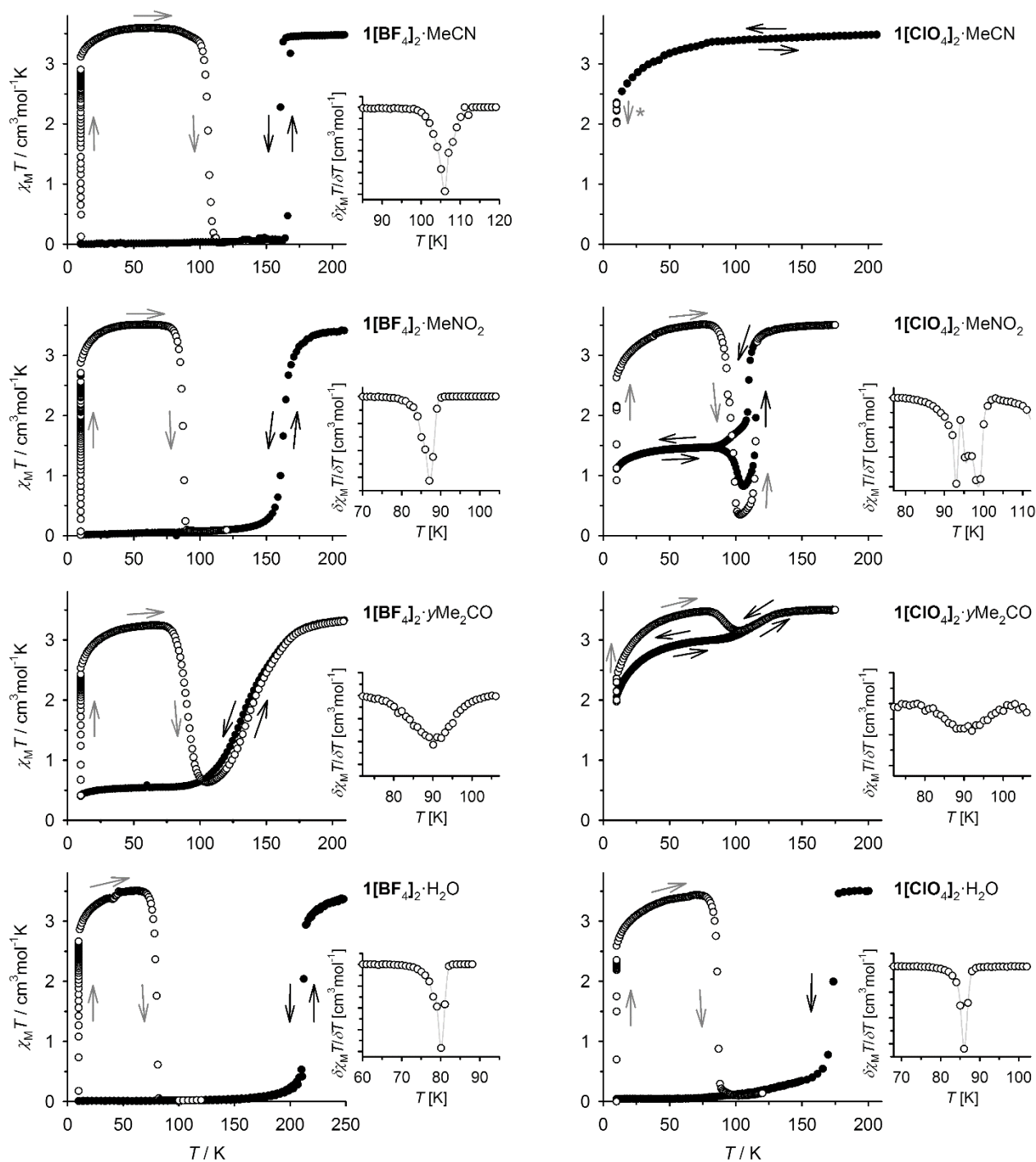


Figure 1. Temperature dependence of magnetic susceptibility data for eight $1X_2$ -solv compounds before irradiation (\bullet , black arrows), and during the T (LIESST) measurement (\circ , grey arrows). The samples were cooled to 10 K, irradiated at that temperature ($\lambda = 510$ nm), then rewarmed 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 $\lambda = 980$ nm in a reverse-LIESST experiment.¹⁷

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 $T_{1/2}$ in an SCO material.¹⁵

Seven freshly prepared $1X_2$ -solv samples showed essentially quantitative low \rightarrow 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 ($1[BF_4]_2 \cdot \gamma Me_2CO$ and $1[ClO_4]_2 \cdot \gamma Me_2CO$) showing the most gradual LIESST relaxation. An exception is $1[ClO_4]_2 \cdot MeNO_2$, whose relaxation is split into three closely spaced components. Although other explanations are possible,¹⁸ this stepped relaxation

Table 1. Thermal SCO and LIESST properties of $1[\text{BF}_4]_2\text{-solv}$ and $1[\text{ClO}_4]_2\text{-solv}$, 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 †).

	$T_{1/2}\downarrow / \text{K}$	$T_{1/2}\uparrow / \text{K}$	cooperativity	$T(\text{LIESST}) / \text{K}$
$1[\text{BF}_4]_2\text{-MeCN}$	160	167	abrupt	106
$1[\text{ClO}_4]_2\text{-MeCN}$	HS ^a	–	–	–
$1[\text{BF}_4]_2\text{-MeNO}_2$	171	–	gradual	87
$1[\text{ClO}_4]_2\text{-MeNO}_2$	102	115	gradual, incomplete	93,96,99
$1[\text{BF}_4]_2\text{-yMe}_2\text{CO}$	131	–	gradual, incomplete	91
$1[\text{ClO}_4]_2\text{-yMe}_2\text{CO}$	<100 ^b	–	gradual, incomplete	ca 90 ^c
$1[\text{BF}_4]_2\text{-H}_2\text{O}$	212	214	abrupt	81
$1[\text{ClO}_4]_2\text{-H}_2\text{O}$	173	–	abrupt	86

^aHS = high-spin between 3–300 K. ^bOnly 20 % of the SCO transition occurs before the remaining high-spin fraction is frozen in below 100 K. ^cNot included in Fig. 2.

may reflect crystallographic phase changes occurring during the LIESST relaxation process (see below).¹⁹

The $T(\text{LIESST})$ values, from the minima of the $\delta\chi_M T / \delta T$ curves, are typical for complexes of this type (Table 1 and ESI †).¹¹ However, a plot of $T_{1/2}$ vs $T(\text{LIESST})$ for these data can be interpreted in two ways (Fig. 2). At first glance, all the compounds lie on the same $T(\text{LIESST})/T_{1/2}$ line except $1[\text{BF}_4]_2\text{-MeCN}$, whose $T(\text{LIESST})$ is ca 20 K higher than for $1[\text{BF}_4]_2\text{-MeNO}_2$ despite their similar $T_{1/2}$ values (Table 1). However, comparison of these data with the literature shows an alternative picture. Only $T(\text{LIESST})$ for $1[\text{BF}_4]_2\text{-H}_2\text{O}$ and $1[\text{BF}_4]_2\text{-MeCN}$ is consistent with previous measurements. The other compounds show reduced $T(\text{LIESST})$ values, deviating increasingly from eq 1 as $T_{1/2}$ is lowered (Fig. 2).

Additional crystallographic studies on three of the materials shed light on these differences. Unexpectedly, $1[\text{BF}_4]_2\text{-MeNO}_2$ 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 isopropyl groups, anions and solvent molecules (ESI †).

In contrast, $1[\text{BF}_4]_2\text{-H}_2\text{O}$ (at 20 K) and $1[\text{BF}_4]_2\text{-MeCN}$ (at 85 K) both retain phase 1 before and after irradiation; the high-spin form of $1[\text{BF}_4]_2\text{-MeCN}$ was also characterised at 15 K, again adopting phase 1. Hence $1[\text{BF}_4]_2\text{-H}_2\text{O}$ and $1[\text{BF}_4]_2\text{-MeCN}$, which align more closely with eq 1 ($T_0 = 150\text{ K}$, 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 $1[\text{BF}_4]_2\text{-MeCN}$ at 85 K, causing an unusual 0.2 % contraction of the unit cell volume in its high-spin state. In contrast, $1[\text{BF}_4]_2\text{-H}_2\text{O}$ and $1[\text{BF}_4]_2\text{-MeNO}_2$ both undergo a more typical expansion of their normalised unit cell volume during photoexcitation experiments (ESI †).

The light-induced high-spin state of $1[\text{BF}_4]_2\text{-MeNO}_2$ (phase 3) has reduced crystallographic symmetry, and thus a lower entropy,

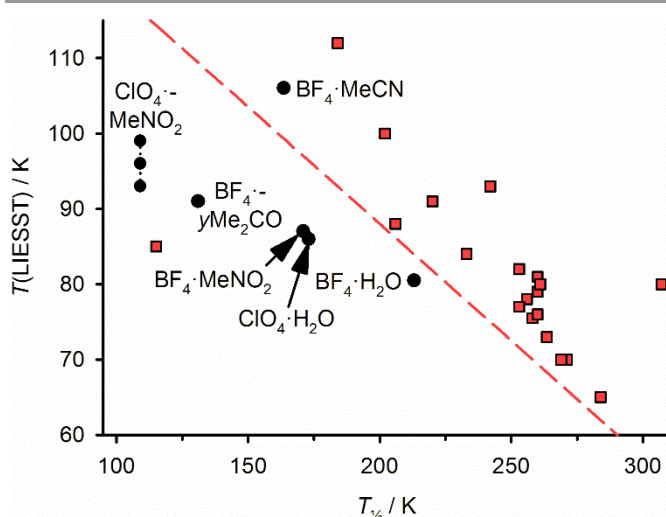


Figure 2. Plot of $T_{1/2}$ vs $T(\text{LIESST})$ for the compounds in this work (black circles; Table 1), and from previously published compounds from our laboratory (red squares; ESI †). The dashed line shows the $T_0 = 150\text{ K}$ line (eq 1) that has been proposed to apply to this family of compounds.^{10,11}

than its thermodynamic high-spin state (phase 1). That should shift the (theoretical) $T_{1/2}$ of phase 3 to a higher temperature than phase 1,²⁰ leading to a lower $T(\text{LIESST})$ 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 $1[\text{BF}_4]_2\text{-MeNO}_2$ by photoirradiation, for comparison with phase 3, have thus far been unsuccessful.

In conclusion, isostructural $1[\text{BF}_4]_2\text{-solv}$ and $1[\text{ClO}_4]_2\text{-solv}$ exhibit a complex relationship between $T_{1/2}$ and $T(\text{LIESST})$. Most of the compounds exhibit a linear $T_{1/2}$ vs $T(\text{LIESST})$ 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).

$$T(\text{LIESST}) = T_0 - aT_{1/2} \quad (2)$$

The data in Table 1 (omitting $1[\text{BF}_4]_2\text{-MeCN}$) are best fit by $T_0 = 108\text{ K}$ and $a = 0.13$ (ESI †). Moreover, $T(\text{LIESST})$ for $1[\text{BF}_4]_2\text{-MeCN}$ and $1[\text{BF}_4]_2\text{-MeNO}_2$ differ by 20 K, despite their almost identical $T_{1/2}$ values (Table 1). That can be explained by the thermodynamic consequences of an unexpected series of thermal and light-induced symmetry-breaking transitions, which are undergone by $1[\text{BF}_4]_2\text{-MeNO}_2$ but not $1[\text{BF}_4]_2\text{-MeCN}$ or $1[\text{BF}_4]_2\text{-H}_2\text{O}$. This clearly demonstrates the impact of crystallographic phase changes on $T(\text{LIESST})$,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.

This work was funded by EPSRC grants EP/K012568/1, EP/K012576/1 and EP/K00512X/1; and by the National Research Agency (ANR-13-BS04-0002), Rennes Metropole and CNRS. The Aquitaine Region is acknowledged for the development of the International Centre of Photomagnetism in Aquitaine (ICPA) platform. Support by COST network CM1305 *Explicit Control of Spin States in Technology and Biology (ECOSTBio)* is also acknowledged. Data supporting this study are available in the ESI † and at <http://doi.org/10.5518/#####>.

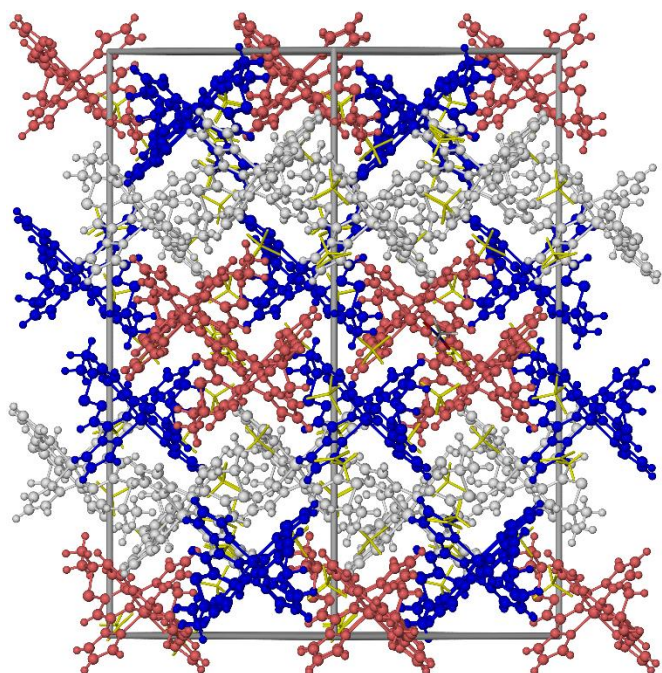


Figure 3. Packing diagram of low-spin phase 2 of $1[\text{BF}_4]_2 \cdot \text{MeNO}_2$ along the (101) crystal vector, with the b axis vertical. Cations A, B and C are coloured white, blue and red, respectively, while the anions and solvent (yellow) are de-emphasised for clarity.

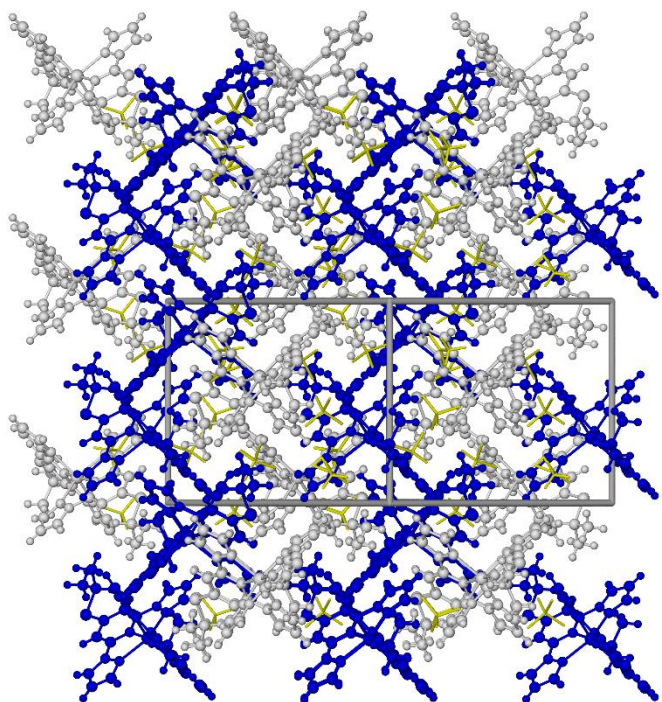


Figure 4. Packing diagram of high-spin phase 3 of $1[\text{BF}_4]_2 \cdot \text{MeNO}_2$, in the same view as Fig. 3. Cations A and B are coloured white and blue, respectively. Other details as for Fig. 3.

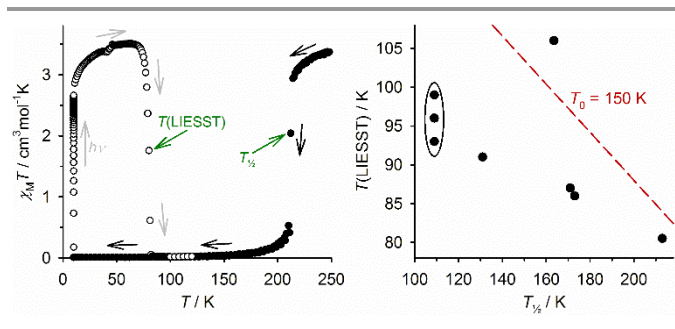
Conflicts of interest

There are no conflicts to declare.

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TOC Entry



Light-Induced Excited Spin-State Trapping (LIESST) data on six isostructural compounds show differing agreement with the well-known correlation $T(\text{LIESST}) = T_0 - 0.3T_{1/2}$ (red line). This relates to crystallographic symmetry breaking under LIESST conditions, exhibited by one member of the series but not by two others.