

Structural Consequences of Different Metal Compositions in the Doped Spin-Crossover Crystals $[Fe_zM_{1-z}(bpp)_2][BF_4]_2$ $(M = Ni, Zn; bpp = 2,6-Bis{Pyrazol-1-yl}Pyridine)$

Christopher M. Pask,^[a] Alexander N. Kulak,^[a] and Malcolm A. Halcrow^{*[a]}

Variable temperature crystallographic characterization of $[Fe_zZn_{1-z}(bpp)_2][BF_4]_2$ (bpp=2,6-*bis*{pyrazol-1-yl}pyridine; z = 0.88, 0.72 and 0.27) and $[Fe_zNi_{1-z}(bpp)_2][BF_4]_2$ (z = 0.83, 0.72 and 0.32) is presented. Comparison with previously published data confirms the isothermal unit cell volume change during spin-crossover (ΔV_{SCO}) behaves differently in the Zn- and Ni-doped crystals. For the FeZn crystals, the relationship between ΔV_{SCO} and z is continuous for $z \ge 0.3$ but is steeper than expected, so

Introduction

Iron(II) spin-crossover (SCO) materials^[1-6] have continued interest as switching components in nanoelectronics,^[7-9] and for micro- and macro-scale materials applications.^[10-15] They also have a fundamental role for the elucidation of dynamic processes in molecular and framework crystals.^[16-18] In the latter regard, doping spin-crossover materials with inert metal ion dopants has been an important method for probing the lattice contribution to SCO thermodynamics and kinetics.^[19,20] The temperature and form of SCO transitions in homogeneous solid solutions $[Fe_xM_{1-x}L_n]^{m+}$ (M²⁺ = Mn²⁺, Co²⁺, Ni²⁺, Zn²⁺ etc; L=a ligand; 0 < x < 1) changes systematically with dopant concentration, which is characteristic for different materials and dopants. Such measurements have led to an increasingly sophisticated understanding of lattice dynamics during SCO switching in macroscale and nanoscale materials, under thermodynamic and kinetic control.[21-24]

Dopant compounds that are isomorphous with the SCO host material generally lead to homogeneous solid solutions with a controlled metal composition. The dopant ions are distributed randomly through a solid lattice, and act as inert spacers between the SCO switching centers. This weakens the lattice cooperativity of the SCO, which becomes more gradual with temperature as the dopant concentration increases in the material.^[19,24-36] The temperature of SCO also changes with the

[a] C. M. Pask, A. N. Kulak, M. A. Halcrow School of Chemistry, University of Leeds, Woodhouse Lane, Leeds LS2 9JT, UK $\Delta V_{\text{SCO}} \approx 0$ for z = 0.27. In contrast ΔV_{SCO} in the FeNi materials shows only a small variation between $0.83 \ge z \ge 0.46$, before decreasing more strongly at higher dilution. ΔV_{SCO} in each FeZn crystal is smaller than for its FeNi analogue with a similar composition. As well as the dopant ion ionic radius, the smaller ΔV_{SCO} for the Zn-doped materials reflects their $T_{1/2}$ values, which are lower than for their FeNi counterparts. The contribution of $T_{1/2}$ to this behavior is especially evident at high metal dilution.

dopant concentration, which depends on the identity of the dopant ion. While the SCO midpoint temperature $T_{1/_2}$ is progressively lowered upon doping with large inert ions (*eg* $M^{2+} = Mn^{2+}$, Co²⁺, Zn²⁺, Cd²⁺), the smaller Ni²⁺ dopant has a much smaller influence on $T_{1/_2}$.^[25-32] These effects are usually thought to correlate with the ionic radius of the dopant ion. High \rightarrow low-spin SCO leads to a reduction of the bond lengths about the individual iron switching centers, and a contraction of the surrounding lattice. Hence, larger dopants should stabilize the high-spin state of the host material and *vice versa*.^[19] Recent work has shown more subtle structural factors also contribute to these trends, however.^[32,37]

The above phenomena are controlled by elastic interactions between the individual switching centres in a lattice, and their evolution during the SCO transition.^[23,24] Structural changes in the bulk lattice of doped iron(II) materials during SCO have been less studied, but were investigated in a crystal of [Fe_{0.46}Zn_{0.54}(ptz)₆][BF₄]₂ (ptz=1-{*n*-propyl}tetrazole).^[38] While its individual unit cell parameters showed more complicated behavior, the isothermal lattice volume change during SCO (ΔV_{SCO}) in the doped crystal was *ca* 0.5x that of the pure iron compound. Hence, ΔV_{SCO} appeared to be directly proportional to the zinc concentration in that material.

Recent work on $[Fe_zM_{1-z}(bpp)_2]X_2 (bpp = 2,6-bis{pyrazol-1-yl} pyridine; M^{2+} = Ni^{2+}, Zn^{2+} \text{ or } Ru^{2+}; X^- = BF_4^- \text{ or } ClO_4^-; Scheme 1)$ implies that relationship is more complicated, however. On one hand, ΔV_{sco} differs significantly for the three dopant ions at the composition $z \approx 0.5$.^[32] Moreover, comparison of those compounds with the isomorphous $[Fe_zNi_{1-z}(bpp)_2][ClO_4]_2$ system suggested a non-linear relationship between ΔV_{sco} and z.^[39]

To address these ambiguities, we report a wider structural characterization of $[Fe_zM_{1-z}(bpp)_2][BF_4]_2$ with different metal ratios z. This is the first crystallographic study of an isomorphous series of SCO/dopant solid solutions across a range of compositions.

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Scheme 1. The $[Fe_zM_{1-z}(bpp)_2][BF_4]_2$ materials referred to in this study $(M^{2+} = Ni^{2+}, Zn^{2+} \text{ or another divalent transition metal ion; } 0 < z < 1)$.

Results

The parent complex [Fe(bpp)₂][BF₄]₂ exhibits an abrupt spintransition at $T_{\frac{1}{2}} = 261$ K with a narrow thermal hysteresis, which does not involve a crystallographic phase change.^[40] The doped materials [Fe_zZn_{1-z}(bpp)₂][BF₄]₂ (z=0.89, 0.69, 0.51, 0.26, 0.07)^[32] and [Fe_zNi_{1-z}(bpp)₂][BF₄]₂ (z=0.95, 0.83, 0.68, 0.50, 0.30, 0.15)^[33] have been reported previously. Their SCO properties show typical trends for materials containing those dopant ions. The dependence of SCO cooperativity on z is similar in the two sets of materials, while $T_{\frac{1}{2}}$ varies between $166 \le T_{\frac{1}{2}} \le 261$ K in the zinc-doped series, and between $256 \le T_{\frac{1}{2}} \le 261$ K for the nickeldoped samples (Figure S1, Table 1).

Single crystals of three compositions from the $[Fe_zZn_{1-z}$ -(bpp)₂][BF₄]₂ and $[Fe_zNi_{1-z}(bpp)_2][BF_4]_2$ series were prepared by recrystallizing the preformed precursor compounds in the appropriate ratios. All the crystals are isomorphous with the pure iron complex (monoclinic, space group $P2_1$, Z=2),^[40] and with previously studied mixed-metal crystals with $z \approx 0.5$.^[32] Crystals of **1a** and **1b** diffracted X-rays more weakly than the other crystals, and were often twinned. Hence the full structure refinements of **1a** are less precise, while the unit cell data for **1b** show more scatter than for the other compounds. Despite those caveats, the analyses described below for these and the other compounds are all self-consistent.

Full structure refinements of each crystal were performed at 100 and 300 K, when the compounds are high-spin and lowspin respectively. The metal occupancy in 1a-1d was refined crystallographically from the 100 K datasets. However this proved to be less accurate for 2a-2d, presumably because of the proximity of Fe to Ni in the periodic table. The Fe:Ni ratio in 2a-2d was therefore estimated from their metric parameters as described below. The compositions derived for the crystals by these methods were equal to that of the starting material used, within experimental error (Table 1). EDX element maps of the samples were mostly consistent with their crystallographic stoichiometries, although a small discrepancy between the techniques for 1d may indicate local heterogeneities in that material (Figure S2).^[41]

Each full dataset was refined as a single $[Fe_zM_{1-z}(bpp)_2]^{2+}$ (M=Zn or Ni) cation site, with the partial iron and dopant metal atoms having the same atomic coordinates and displacement parameters (Figure 1). That is the usual approach adopted in studies of this type, which yields a weighted average picture of

z T _{\/>} [K] Ref. [Fe(bpp) ₂][BF ₄] ₂ 1 261 [40] M=Zn 1	Table 1. The compositions of the $[Fe_2M_{1-z}(bpp)_2][BF_4]_2$ (M=Zn or Ni) crystals in this study from their low temperature structure refinements, and their predicted SCO midpoint temperatures based on magnetic susceptibility data from samples with similar compositions (Figure S1). ^[32,33]							
[Fe(bpp)₂][BF₄]₂ 1 261 [40] M=Zn 1 1 1 1 1a 0.88(3) 251 This work 1b 0.716(15) 233 This work 1c 0.536(8) 217 [32] 1d 0.265(12) 193 This work M=Ni 2a 0.83(3) 261 This work 2b 0.72(3) 260 This work 2c 0.457(18) 260 [32] 2d 0.32(3) 259 This work		Z	<i>T</i> _{1/2} [K]	Ref.				
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2b 0.72(3) 260 This work 2c 0.457(18) 260 [32] 2d 0.32(3) 259 This work	2a	0.83(3)	261	This work				
2 c 0.457(18) 260 [32] 2 d 0.32(3) 259 This work	2b	0.72(3)	260	This work				
2d 0.32(3) 259 This work	2c	0.457(18)	260	[32]				
	2d	0.32(3)	259	This work				



Figure 1. The asymmetric unit of **1b** at 100 K, showing a partial atom numbering scheme. All the structure refinements with full atom numbering are shown in Figures S3–S8. Color code: C, white; B, pink; F, yellow; Fe/Zn, green; N, blue.

Eur. J. Inorg. Chem. 2024, 27, e202400334 (2 of 8)

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Table 2. Structural parameters which are sensitive to the metal content of the crystals, from the 100 K crystallographic refinements of **1a–1d** (M=Fe/Zn, Figure 1) and **2a–2d** (M=Fe/Ni).[a] Italicised parameters in curly brackets are weighted average values, calculated from the low-spin state of [Fe(bpp)₂][BF₄]₂ and the appropriate dopant complex. Published data for **1c** and **2c** are also included, for comparison. Full Tables of metric parameters for the new solid solutions in both spin states are in the Supporting Information.

	1 a (z=0.88)	1 b (z=0.72)	$1 c (z = 0.54)^{[b]}$	1 d (z=0.26)
M—N{pyridyl} _{average} [Å]	1.928(11) <i>{1.925(5)}</i>	1.967(6) {1.957(5)}	1.996(2) {1.993(5)}	2.048(3) {2.048(5)}
M—N{pyrazolyl} _{average} [Å]	1.985(17) {2.002(8)}	2.027(9) {2.034(8)}	2.067(4) {2.069(8)}	2.125(6) {2.124(8)}
V _{Oh} [ų]	9.79(3) {9.936(13)}	10.311(13) <i>{10.357(13)}</i>	10.799(6) {10.830(13)}	11.537(10) {11.550(13)}
γ [deg]	79.6(7) {79.4(3)}	78.2(3) {78.4(3)}	77.19(14) {77.4(3)}	75.7(2) <i>{75.9(3)}</i>
ϕ [deg]	177.1(4) {177.40(17)}	176.55(18) {176.60(17)}	175.47(8) {175.70(17)}	174.20(12) <i>{174.32(17)}</i>
Σ [deg]	90.8(13) {93.1(4)}	103.8(6) <i>{101.9(4)}</i>	113.5(2) {111.8(4)}	128.3(4) {126.9(4)}
Θ [deg]	294(3) {301}	332.6(14) {327}	362.8(6) {356}	405.9(10) {400}
	2a(z=0.83)	2 h $(z - 0.72)$	$2c(z-0.46)^{[b]}$	2d(z-0.22)
	Lu (2 – 0.05)	20(2-0.72)	2C(2=0.40)	2 u (z=0.32)
M—N{pyridyl} _{average} [Å]	1.927(5) {1.920(3)}	1.927(4) {1.933(3)}	1.959(2) {1.962(3)}	$1.979(4) \{1.977(3)\}$
M—N{pyridyl} _{average} [Å] M—N{pyrazolyl} _{average} [Å]	1.927(5) {1.920(3)} 1.995(8) {2.000(5)}	1.927(4) {1.933(3)} 2.011(6) {2.015(5)}	1.959(2) {1.962(3)} 2.041(4) {2.049(5)}	1.979(4) {1.977(3)} 2.067(8) {2.067(5)}
M—N{pyridyl} _{average} [Å] M—N{pyrazolyl} _{average} [Å] V _{Oh} [Å ³]	1.927(5) {1.920(3)} 1.995(8) {2.000(5)} 9.871(12) {9.909(7)}	1.927(4) {1.933(3)} 2.011(6) {2.015(5)} 10.011(10) {10.096(7)}	1.959(2) {1.962(3)} 2.041(4) {2.049(5)} 10.415(6) {10.538(7)}	2.067(8) {2.067(5)} 10.754(12) {10.776(7)}
M–N{pyridyl} _{average} [Å] M–N{pyrazolyl} _{average} [Å] V _{oh} [Å ³] γ [deg]	1.927(5) {1.920(3)} 1.995(8) {2.000(5)} 9.871(12) {9.909(7)} 79.5(3) {79.5(2)}	1.927(4) {1.933(3)} 2.011(6) {2.015(5)} 10.011(10) {10.096(7)} 79.1(3) {79.2(2)}	1.959(2) {1.962(3)} 2.041(4) {2.049(5)} 10.415(6) {10.538(7)} 78.38(14) {78.4(2)}	1.979(4) {1.977(3)} 2.067(8) {2.067(5)} 10.754(12) {10.776(7)} 77.8(3) {77.9(2)}
$\begin{array}{l} M {-} N \{ pyridyl \}_{average} \left[\mathring{A} \right] \\ M {-} N \{ pyrazolyl \}_{average} \left[\mathring{A} \right] \\ \mathcal{V}_{Oh} \left[\mathring{A}^3 \right] \\ \gamma \left[deg \right] \\ \phi \left[deg \right] \end{array}$	1.927(5) {1.920(3)} 1.995(8) {2.000(5)} 9.871(12) {9.909(7)} 79.5(3) {79.5(2)} 177.56(18) {177.82(11)}	1.927(4) {1.933(3)} 2.011(6) {2.015(5)} 10.011(10) {10.096(7)} 79.1(3) {79.2(2)} 177.55(14) {177.71(11)}	1.959(2) {1.962(3)} 2.041(4) {2.049(5)} 10.415(6) {10.538(7)} 78.38(14) {78.4(2)} 177.32(8) {177.43(11)}	1.979(4) {1.977(3)} 2.067(8) {2.067(5)} 10.754(12) {10.776(7)} 77.8(3) {77.9(2)} 177.25(18) {177.29(11)}
$\begin{array}{l} M = N\{pyridy \}_{average} \left[\mathring{A} \right] \\ M = N\{pyrazoly \}_{average} \left[\mathring{A} \right] \\ \mathcal{V}_{oh} \left[\mathring{A}^{3} \right] \\ \gamma \left[deg \right] \\ \phi \left[deg \right] \\ \Sigma \left[deg \right] \end{array}$	1.927(5) {1.920(3)} 1.995(8) {2.000(5)} 9.871(12) {9.909(7)} 79.5(3) {79.5(2)} 177.56(18) {177.82(11)} 91.6(5) {91.5(3)}	1.927(4) {1.933(3)} 2.011(6) {2.015(5)} 10.011(10) {10.096(7)} 79.1(3) {79.2(2)} 177.55(14) {177.71(11)} 95.0(5) {94.8(3)}	1.959(2) {1.962(3)} 2.041(4) {2.049(5)} 10.415(6) {10.538(7)} 78.38(14) {78.4(2)} 177.32(8) {177.43(11)} 102.1(3) {102.4(3)}	20 (2=0.32) 1.979(4) {1.977(3)} 2.067(8) {2.067(5)} 10.754(12) {10.776(7)} 77.8(3) {77.9(2)} 177.25(18) {177.29(11)} 108.0(5) {106.6(3)}

^[a] V_{Oh} is the volume of the octahedron defined by the FeN₆ coordination sphere.^[46] γ is the average chelate bite angle of the bpp ligands in the complex molecule, and ϕ is the trans-N{pyridyl}–M–N{pyridyl} bond angle [N(2)–M(1)–N(18) in Figure 1].^[47] Σ is a general measure of the deviation of a metal ion from an ideal octahedral geometry, while Θ more specifically indicates its distortion towards a trigonal prismatic structure.^[46] More detailed definitions and discussions of these parameters are in the cited references, and in the Supporting Information.^[b] From ref.^[32]

the randomly distributed complex molecules in the lattice.^[26,32,36,38,39,42-45] Table 2 lists structural parameters derived from the M–N distances and N–M–N angles in the 100 K structure analyses, which are sensitive to the crystal's spin state and the metal composition. These data mostly lie within experimental error of values calculated from the given ratios of the constituent compounds, confirming the metal compositions of the crystals in Table 1. Small deviations from some expected values might reflect changes to the iron or dopant complex molecular geometries when crystallized together in the doped lattices.^[32]

Thermal SCO in the crystals was monitored by variable temperature unit cell measurements, which were collected between 350–100 K in 10 K intervals. The cooling mode transition is reflected in a large decrease in the *c* dimension about $T_{1/2}$; a large increase in β ; and, much smaller increases in *a* and *b*.^[32] These combine to afford a typical contraction of ΔV_{SCO} during the high—low-spin transition, of -30.4(3) Å³ or -2.2% in the pure iron complex.^[32] All these changes reduce in magnitude as *z* decreases, and for the most dilute samples **1 d** and **2 d** the transition is only clearly delineated by *c*. Hence, the progression of SCO in these compounds was most clearly monitored through the unit cell *c* parameter.

Plots of *c vs. T* show the SCO temperature and cooperativity in the crystals mostly matches expectation, from magnetic measurements from polycrystalline samples with similar compositions (Figures 2 and 3).^[32,33] The most notable difference is that the abrupt SCO in crystals of **1b** and **2b** has a more



Figure 2. Temperature dependence of the unit cell *c* parameter in the iron/ zinc-containing crystals. Data from each compound are connected by a regression curve for clarity, and the dashed lines indicate the $T_{1/2}$ temperature expected for each crystal, based on magnetic susceptibility data.^[32] Data for 1c and the precursor complexes are reproduced from ref.^[32]

gradual low-temperature tail, which is not evident in the magnetic susceptibility data (Figure S1).

The most important result from these data is that the relationship between ΔV_{SCO} (the isothermal change in unit cell volume during the high \rightarrow low-spin transition measured at $T_{1/2}$) and z is different in **1a**-1d compared to **2a**-2d, as previously proposed (Figure 4).^[32] In zinc-doped **1a**-1d, ΔV_{SCO} decreases



Figure 3. Temperature dependence of the unit cell *c* parameter in the iron/ nickel-containing crystals. The dashed lines indicate the SCO $T_{1/2}$ expected for each sample, which are all within 2 K of each other.^[33] Other details as for Figure 2.



Figure 4. Variation of the isothermal unit cell volume change during SCO (ΔV_{SCO}) with composition for the Zn-doped (gray) and Ni-doped (blue) crystals. Data from each series are joined by a regression curve for clarity. The cyan datapoints are from a previous study of isomorphous [Fe_zNi_{1-z}- (bpp)₂][ClO₄]₂ crystals.^[39]

with z in a shallow curve, and reaches zero at $z \approx 0.3$ if that correlation is extrapolated. Consistent with that, ΔV_{SCO} for **1 d** is zero within experimental error. In contrast, in **2a–2d** the correlation between ΔV_{SCO} and z is less steep between z=0.83-0.46, and has a clear inflection point around z=0.5. The shape of that plot is confirmed by comparison of these data with two isomorphous $[Fe_zNi_{1-z}(bpp)_2][ClO_4]_2$ crystals (z=0.76 and 0.50), whose ΔV_{SCO} values closely match **2b** and **2c** (Figure 4).^[39]

 $[Fe(bpp)_2][BF_4]_2$ and the doped crystals adopt a form of the so-called "terpyridine embrace" crystal structure.^[40,48] The $[M-(bpp)_2]^{2+}$ cations associate into closely packed layers in the (001) plane *via* edge-to-face C–H··· π contacts and face-to-face π ··· π interactions between their pyrazolyl groups (Figure 5). Neighboring cation layers are stacked more loosely along the *c* axis, where they are separated by the anions in the lattice.^[49]



Figure 5. Packing diagram of **1b** at 100 K viewed perpendicular to (001), which is the plane of the terpyridine embrace layers.^[40,48] Alternate cation layers are color coded white and brown, and the BF_4^- ions are deemphasized for clarity.

The high—low-spin transition in $[Fe(bpp)_2][BF_4]_2$ results in a small expansion of the cation layers in the ab plane (Δab_{SCO} is positive in Tables 3 and 4). That reflects that the low-spin cations have a more regular D_{2d} -symmetric molecular geometry, which packs less efficiently in two dimensions.^[32] However the small expansion of the cation layers is offset by a larger contraction of the inter-layer distance along c (negative Δc_{SCO}), which leads overall to the expected contraction of the unit cell in the low-spin state (negative ΔV_{SCO}). The monoclinic unit cell angle β is also larger in the low-spin state, but this has a minor effect on the unit cell volume.

The dependence of the individual unit cell parameters on the sample composition also differs between the two series of compounds. Δc_{SCOr} which makes the largest contribution to ΔV_{SCO} , decreases upon increased doping towards zero at z=0(Figure S17). However while this occurs in a smooth curve in **1a–1d**, Δc_{SCO} for **2a–2d** shows a discontinuity near z=0.5, which resembles their $\Delta V_{\rm SCO}$ dependence in Figure 4. The expansion of the cation layers during SCO, Δab_{SCO} , behaves differently again (Figure S17). Δab_{sco} in **1a–1d** decreases nonlinearly until $z \approx 0.5$, but is equal at 0.49–0.50 Å² for 1 c and 1 d. That unexpectedly large, positive Δab_{sco} almost perfectly offsets the small negative $\Delta c_{\rm SCO}$ in 1d, leading to its observed $\Delta V_{\rm SCO}$ of effectively zero. In contrast, in 2a-2d Δab_{SCO} decreases continuously in a smooth curve with z, towards zero when z =0. The trends in $\Delta ab_{\rm SCO}$ could reflect that the size of the lowspin cation layers in 1a-1d is limited by the packing of the larger zinc dopant sites, when those are present in excess (Scheme S3).

Comparison of the unit cells of compounds from the FeZn and FeNi series with similar compositions leads to additional

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Table 3. Absolute and % isothermal changes to the unit cell parameters during high \rightarrow low-spin SCO in the [Fe_zZn_{1-z}(bpp)₂][BF₄]₂ crystals, Δx_{sco} ($x = a, b, c, \beta, V$). Data for each compound are calculated at $T_{1/2}$ (Table 1), by linear extrapolation of the low-spin and high-spin parameters to that temperature. Data for [Fe(bpp)₂][BF₄]₂ and **1c** are reproduced from ref. [32].

		∆a _{sco} [Å]	$\Delta b_{\rm sco}$ [Å]	Δc_{sco} [Å]	$\Delta\!eta_{\sf sco}$ [deg]	$\Delta ab_{\rm SCO} [{\rm \AA}^2]^{\rm [a]}$	$\Delta V_{\rm SCO}$ [Å ³]
[Fe(bpp) ₂][BF ₄] ₂	Δx _{sco}	+ 0.0231(6)	+ 0.074(2)	-0.5570(9)	+ 2.027(5)	+ 0.82(2)	-30.4(3)
	%	+ 0.27	+ 0.87	-2.93	+ 2.11	+ 1.14	-2.23
1a	$\Delta x_{\rm SCO}$ %	+ 0.034(2) + 0.40	+ 0.0655(17) + 0.78	-0.482(4) -2.60	+ 1.719(19) + 1.75	+ 0.84(7) + 1.17	-24.1(5) -1.87
1b	Δx _{sco}	+ 0.0260(11)	+ 0.0546(8)	-0.341(2)	+ 1.112(11)	+ 0.68(4)	-14.6(3)
	%	+ 0.31	+ 0.65	-1.85	+ 1.13	+ 0.95	-1.15
1c	Δx _{sco}	+ 0.0153(15)	+ 0.0428(11)	-0.222(3)	+0.666(13)	+ 0.49(6)	-8.8(4)
	%	+ 0.18	+ 0.50	-1.18	+0.69	+ 0.68	-0.65
1 d	Δx _{sco}	+0.0242(7)	+0.0352(7)	-0.1052(14)	+0.154(7)	+ 0.50(2)	+0.30(18)
	%	+0.29	+0.42	-0.57	+0.16	+ 0.70	+0.02

 $^{(a)}\Delta ab_{sco}$ denotes the change in the area of the 2D cation layers in the unit cell during SCO, where ab is the product of the *a* and *b* unit cell dimensions.

Table 4. Absolute and % isothermal changes to the unit cell parameters during high \rightarrow low-spin SCO in the $[Fe_zNi_{1-z}(bpp)_2][BF_4]_2$ crystals. Data for $[Fe(bpp)_2][BF_4]_2$ and 2c are reproduced from ref. ^[32] Other details as for Table S3.							
		∆a _{sco} [Å]	$\Delta b_{\rm sco}$ [Å]	$\Delta c_{ m sco}$ [Å]	$\Delta eta_{ m sco}$ [deg]	$\Delta ab_{ m SCO} [{ m \AA}^2]^{[a]}$	$\Delta V_{\rm SCO}$ [Å ³]
[Fe(bpp) ₂][BF ₄] ₂	$\Delta x_{\rm SCO}$	+0.0231(6)	+0.074(2)	-0.5570(9)	+ 2.027(5)	+0.82(2)	-30.4(3)
	%	+ 0.27	+0.87	-2.93	+2.11	+1.14	-2.23
2a	$\Delta x_{\rm SCO}$	+ 0.0188(10)	+0.0613(8)	-0.430(2)	+ 1.657(10)	+ 0.68(5)	-23.2(3)
	%	+0.23	+0.73	-2.34	+1.68	+0.94	-1.83
2b	$\Delta x_{\rm SCO}$	+ 0.0129(10)	+0.0472(8)	-0.373(2)	+1.379(11)	+ 0.51(5)	-21.4(3)
	%	+0.15	+0.56	-2.03	+1.39	+0.71	-1.68
2c	$\Delta x_{\rm SCO}$	-0.0041(8)	+0.021(10)	-0.264(2)	+0.800(10)	+ 0.15(4)	-18.8(3)
	%	-0.05	+0.25	-1.40	+0.83	+0.20	-1.38
2 d	$\Delta x_{\rm SCO}$	-0.0001(8)	+0.010(10)	-0.136(2)	+0.396(11)	+ 0.08(5)	-9.31(3)
	%	0.00	+0.12	-0.75	+0.40	+0.12	-0.73
^[a] Λab_{cc} denotes the	$^{[a]} \Delta a_{broc}$ denotes the change in the area of the 2D cation layers in the unit cell during SCO, where <i>ab</i> is the product of the <i>a</i> and <i>b</i> unit cell dimensions.						

insights. This is exemplified by Figure 6, which compares the temperature-dependent unit cell volumes for **1d** and **2d**. *V* is smaller for **2d** at each temperature, reflecting the smaller size of its Ni(II) complex dopant. However the slope dV/dT in each spin state is similar for both crystals, and is greater in the high temperature, high-spin state. The latter observation implies ΔV_{sco} should naturally decrease as $T_{1/2}$ shifts to lower temperatures. Figure 6 shows the main reason why $\Delta V_{\text{sco}} \approx 0$ for **1d**, but not for **2d**, is that $T_{1/2}$ for zinc-doped **1d** is *ca* 65 K lower than in nickel-doped **2d**. The interplay between dopant size and $T_{1/2}$ on the parameters in Tables 3 and 4 is evident for all compositions of these materials, with $T_{1/2}$ having the greatest influence at high dopant concentrations (Figures S15 and S16).

Linear thermal expansion coefficients (α_{V} , eq 1) and their anisotropic principle component vectors can be extracted from the variable temperature unit cell data.^[50]

$$\alpha_{\rm V} = \frac{1}{V_0} \left(\frac{\rm dV}{\rm dT} \right) \tag{1}$$

 $\alpha_{\rm V}$ correlates with the thermal compressibility of the sample, so materials with a higher $\alpha_{\rm V}$ are more susceptible to deformation, and vice versa.^[51,52] For consistency, the $\alpha_{\rm V}$ values for **1a–1d** and **2a–2d** were scaled against the reference unit cell parameters (V_0) at 100 K, the lowest temperature used in the study. Input data at 100 K for the high-spin states of the crystals were derived by linear extrapolation of the higher temperature data.

 $\alpha_{\rm V}$ and its anisotropic components $\alpha_1-\alpha_3$, in the high-spin and low-spin forms of **1a–1d** and **2a–2d**, are broadly consistent with each other and with our previous study (Tables 5, S15 and S16).^[32] The crystals are less deformable in their low-spin forms, which reflects denser crystal packing of the smaller low-spin complex molecules.^[32,38,53,54] The main contribution to that in Research Article doi.org/10.1002/ejic.202400334



Figure 6. Temperature dependence of the unit cell volumes for **1d** (white/ gray, top) and **2d** (blue, bottom), plotted on the same scale to enable comparison. The linear regression lines for the high-spin and low-spin phases used to calculate ΔV_{sco} are shown, and the magnitude of ΔV_{sco} at $T_{\frac{1}{2}}$ is indicated. Magnetic data describing SCO in both samples are also included, plotted as the high-spin fraction sample at each temperature (γ_{HS} ; Figure S1). Analogous plots for the other crystals are in Figures S15–S16.

Table 5. Linear thermal expansion parameters (α_v) and the component of the thermal expansion tensor perpendicular to the cation layers (α_3) for the nickel-doped compounds. The values are scaled against the unit cell parameters at 100 K, which were derived by linear extrapolation of the experimental data if required. Full anisotropic thermal expansion parameters for all the compounds in this work are in Tables S15 and S16.

	α _v {100 K} [1	0 ⁶ K ⁻¹]	α ₃ {100 K} [10	$lpha_{ m 3}$ {100 K} [10 ⁶ K ⁻¹]		
	High-spin	Low-spin	High-spin	Low-spin		
[Fe(bpp) ₂][BF ₄] ₂ ^[a]	209(2)	160(4)	167.0(10)	76(2)		
2a	246(6)	156(3)	177.0(14)	73(2)		
2b	227(8)	152(3)	176(2)	76(2)		
2c ^[a]	251(8)	173(6)	182(4)	81(3)		
2d	244(8)	142(3)	216(2)	71.1(16)		
$[Ni(bpp)_2][BF_4]_2^{[a]}$	168(4)		93(3)			
^[a] From ref. [32].						

this study is the component of the thermal expansion tensor perpendicular to the cation layers, α_{3} , which is 2–3x smaller in the low-spin state. The cation layers themselves are more rigid, reflecting their denser 2D molecular packing, and are less perturbed by SCO (Tables S15 and S16).^[32] While the errors are relatively large, these differences may be accentuated in the doped crystals and are not attenuated at low iron concentrations. The reason for that observation is presently unclear.

Conclusions

The behavior of the $[Fe_zM_{1-z}(bpp)_2][BF_4]_2$ lattice during SCO is unexpectedly complicated, and depends on the identity of the dopant ion 'M' as well as its concentration in the crystal. This is clear in the lattice volume change during SCO, measured as an isothermal change at $T_{1/2}$ (ΔV_{SCO} ; Figure 4). When M=Zn, ΔV_{SCO} decreases continuously with *z*, reaching zero at $z \approx 0.3$. The most dilute sample 1d (z=0.27) exhibits ΔV_{SCO} =0, within experimental error. In contrast when M=Ni, the relationship between ΔV_{SCO} and *z* has a shallow plateau around z=0.5, and tends towards zero when z=0 upon further metal dilution.

The crystal lattice in $[Fe_zM_{1-z}(bpp)_2][BF_4]_2$ has a 2D character, with closely packed layers of cations in the (001) plane which associate more loosely along *c* (Figure 5). SCO also affects their individual unit cell dimensions in different ways, particularly within the tightly packed cation layers. Since the zinc(II) dopant (ionic radius 74 pm^[55]) is much larger than the low-spin iron(II) centers (ionic radius 61 pm^[55]), high zinc concentrations in the crystal restrict structural rearrangement of the tightly packed cation layers during SCO (Figure S17). That is not observed for high concentrations of the smaller nickel(II) dopant (ionic radius 69 pm^[55]).

As well as the dopant size, the SCO transition temperature also contributes to these differences. Doping with zinc(II) progressively lowers $T_{1/2}$, whereas the effect of nickel(II) doping on $T_{1/2}$ is much smaller (Table 1; Figures 2, 3 and S1). Thus, $T_{1/2}$ for zinc-doped 1d is *ca* 65 K lower than for the corresponding nickel-doped material 2d. Moreover, the unit cell volume *V* shows a stronger positive thermal expansion (*ie dV/dT*) in the high-spin than in the low-spin form of each crystal. These observations mean that ΔV_{sco} must be smaller when $T_{1/2}$ is lower, other things being equal. That also contributes to the differences between 1a–1d and 2a–2d (Figure 4), particularly at high dopant concentrations.

Hence, contrary to a previous suggestion,^[38] ΔV_{SCO} is not directly proportional to *z* in doped SCO crystals from the $[Fe_{z}M_{1-z}(bpp)_{2}][BF_{4}]_{2}$ system. That has implications when designing SCO materials for mechanical actuation applications, for example.^[56,57] However, it is unclear if these results can be generalized to other SCO materials. The 2D character of the $[Fe_{z}M_{1-z}(bpp)_{2}][BF_{4}]_{2}$ lattice is clear in its behavior during SCO; metal doping impacts the dimensions of the strongly packed (001) plane quite differently from the loosely associated *c* axis (Figure S17). Other lattice types might behave differently under these conditions, which would be an interesting topic for future investigation.

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Experimental Section

Instrumentation

SEM images and EDX measurements were obtained using an FEI Nova NanoSEM 450 environmental microscope, operating at 3 kV.

Materials and Methods

The $[Fe_zZn_{1-z}(bpp)_2][BF_4]_2$ and $[Fe_zNi_{1-z}(bpp)_2][BF_4]_2$ compounds were prepared by the literature methods. $^{[32,33]}$ Single crystals were obtained from acetonitrile solutions of the preformed mixed-metal samples, by slow diffusion of diethyl ether antisolvent vapor.

Single Crystal Structure Analyses

Diffraction data were measured with an Agilent Supernova dual source diffractometer, fitted with an Oxford Cryostream low-temperature device. Monochromated Mo- K_{α} ($\lambda = 0.7107$ Å) radiation was used for all the measurements. Experimental details of the structure determinations are given in Table S1). All the structures were solved by direct methods (*SHELXTL*^[58]), and developed by full least-squares refinement on F^2 (*SHELXL-2018*^[59]). Crystallographic figures were produced using *XSEED*,^[60] and other publication materials were prepared using *Olex2*.^[61] Isotropic and anisotropic thermal expansion parameters were calculated with *PASCal*.^[50,62]

The fractional metal occupancies of 1a-1d in Table 1 were refined from the crystallographic data. However this was less successful for 2a-2d, whose Fe:Ni ratio was therefore estimated from the metric parameters in their low-temperature structure refinements.

Deposition numbers 2359124 (1a, T = 100 K), 2359125 (1a, T = 300 K), 2359126 (1b, T = 100 K), 2359127 (1b, T = 300 K), 2359128 (1d, T = 100 K), 2359129 (d, T = 300 K), 2359130 (2a, T = 100 K), 2359131 (2a, T = 300 K), 2359132 (2b, T = 100 K), 2359133 (2b, T = 300 K), 2359134 (2d, T = 100 K) and 23591351 (2d, T = 300 K) contain the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service.

Supporting Information Summary

The authors have cited additional references within the Supporting Information. $^{\rm [63-71]}$

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Conflict of Interests

There are no conflicts to declare.

Data Availability Statement

The data that support the findings of this study are openly available in University of Leeds library at https://doi.org/ 10.5518/1540.

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