Above Room Temperature Spin Crossover in Thioamide-Functionalised 2,6-bis(pyrazol-1-yl)pyridine Iron(II) Complexes[†]

Max Attwood^a, Hiroki Akutsu^b, Lee Martin^c, Dyanne Cruickshank^d, Scott S. Turner^{*a}

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This work describes the synthesis of two novel functionalised 2,6-bis(pyrazol-1-yl)pyridine (bpp) ligands, namely 2,6-bis(pyrazol-1-yl)pyridine-4-carbothioamide (**bppCSNH₂**) and *N*-methyl-2,6-bis(pyrazol-1-yl)pyridine-4-carbothioamide (**bppCSNHMe**). The corresponding solvated or non-solvated Fe(II) salts, [Fe(**bppCSNH₂**)₂]₂X₂ and [Fe(**bppCSNHMe**)₂]₂X₂ (X = BF₄⁻ or ClO₄⁻) were synthesised and their properties measured by SQUID magnetometry, Evans NMR, differential scanning calorimetry and single crystal X-ray diffraction. In the solid state [Fe(**bppCSNH₂**)₂]₂²⁺ salts persist in the low spin state below 350 K. The structure of [Fe(**bppCSNH₂**)₂](BF₄)₂·2MeNO₂ shows a network of intermolecular interactions responsible for the low spin state stabilisation, relative to the prototypical [Fe(bpp)₂]²⁺ spin crossover (SCO) salts. By contrast the complexes of **bppCSNHMe** both display abrupt SCO above 300 K. [Fe(**bppCSNHMe**)₂](BF₄)₂·MeNO₂ requires solvent loss before SCO can be observed centred at 332 K. The non-solvated [Fe(**bppCSNHMe**)₂](ClO₄)₂ shows SCO centred at 325 K. Analysis of solvated and non-solvated crystal structures suggests that cooperativity is facilitated by thioamide-group interactions with neighbouring pyrazolyl and pyridyl moieties.

Introduction

Spin-crossover (SCO) materials are popular candidates for next-generation memory¹ and sensing applications. They may show exploitable switching of colour, magnetisation,^{2,3} dielectric constant,^{4,5} luminescence,⁶⁻⁸ and/or conductivity⁹ when exposed to changes in temperature, applied magnetic field, pressure or light irradiation.¹⁰ This is a result of switching between electronic low spin (LS) and high spin (HS) states in, commonly, metal complexes with d⁴-d⁷ electronic configurations. SCO may also be accompanied by exploitable distortions in complex geometry due to different occupations of the e_g antibonding d-orbitals.¹¹ An important focus is to modify metal complexes with known SCO properties in an effort to tune the transition temperature (T_{1/2}) towards room temperature (RT) and to introduce an abrupt transition with a practical hysteresis. The strategy involves working towards highly cooperative systems where the transitions are supported by intermolecular interactions such as hydrogen bonding and π-π stacking.¹²⁻¹⁶ It is often through modifying these interactions that structure-function correlations are discovered.

Fe(II) octahedral complexes have provided many examples of SCO compounds and they present a diamagnetic LS state and paramagnetic HS state.^{17,18} Switching involves the maximum change in electron multiplicity, S=0 to S=2, and the largest ΔH and ΔS for the transition. A popular series of ligands in previous work has been 2,6-bis(pyrazol-1-yl)pyridine (bpp, scheme.1) and its derivatives.

Scheme 1 The ligand 2,6-bis(pyrazol-1-yl)pyridine (bpp).

In recent years, functionalisation at the 4-pyridyl position of bpp has been used as a means of tuning SCO properties, including the T_{1/2}.¹⁹ With this in mind, we report the synthesis, structure and magnetic properties of Fe(II) salts of the thioamide derivatives **bppCSNH₂** and **bppCSNHMe** (scheme 2). We initially considered the 1D cationic chains in [Fe(II)(bppCOOH)₂](ClO₄)₂²⁰ (using ligand **2** in scheme 2), which are linked *via* a hydrogen bonding network thought responsible for the abrupt SCO at 380K. Therefore, our strategy was to aim for 1D chains but with weaker intermolecular interactions to move the SCO transition temperature towards RT. In our materials sulfur atoms have relatively low electronegativity but significant dipole and charge transfer from N to S. In addition compared to

^a Department of Chemistry, University of Surrey, Guildford, UK, GU2 7XH

^b Department of Chemistry, Graduate School of Science, Osaka University, 1-1 Machikaneyama, Toyonaka, Osaka 560-0043, Japan

^c School of Science and Technology, Nottingham Trent University, UK, NG1 4FQ

^d Rigaku Europe, Unit 44, Monument Park, Chalgrove, Oxfordshire, UK, OX44 7RW.

[†] Electronic Supplementary Information (ESI) available: Synthesis of **bppCONH₂** and **bppCONHMe**, ¹H and ¹³C-NMR spectra (Fig S1 and S2), photo of a crystal of [Fe(**bppCSNHMe**)₂](BF₄)₂·MeNO₂ at 330K and 360K showing change in colour and opacity (Fig S3), diffraction patterns complimentary to Fig S3 (Fig S4), TGA and DSC (Fig S5-S7). For ESI and crystallographic data see DOI: 10.1039/x0xx00000x

amide groups, thioamides are larger with longer bond lengths, slightly smaller bond energies and a larger rotational barrier about $S=C(NR_2)-R'$ bonds.^{21,22} The reduced electronegativity is expected to make the group a weaker hydrogen bond acceptor, although NH groups are stronger hydrogen bond donors than their corresponding amides.^{23,24}

Scheme 2 Overview of synthesis routes to **bppCSNH₂** and **bppCSNHMe** ligands

Several monomeric complexes of bpp derivatives containing S atoms are known to display SCO.^{25–30} However, the highest reported $T_{1/2}$ is 277 K for a Fe(II) complex of $bpp\equiv C_6H_4SCOMe$.²⁷ A further material using a 'back-to-back'³¹ $bpp-S-S-bpp$ ligand produced Fe(II) oligomers with a gradual SCO transition measured in solution at 245 K.³² However, it is desirable that an SCO transition occurs at, or slightly above, room temperature (*ca.* 298 K) and in that respect we have succeeded. Two complexes reported here achieve abrupt SCO above RT, significantly improving on previous S/bpp-based materials.

Experimental

Physical measurements

CHN elemental analysis was performed using an Exeter Analytical Inc. CE-440 Elemental Analyser. Differential scanning calorimetry (DSC) and thermal gravimetric analysis (TGA) were performed using TA Instruments DSC Q1000 and TGA Q500, respectively. Samples for DSC were placed inside a hermetically sealed aluminium pan and heated at a rate of 10 K/min. NMR for both ligand characterisation and Evans method measurements were performed using a Bruker AVI400NMR instrument. Magnetic properties were measured using a Quantum Design MPMS2 magnetometer on powders in aluminium foil sample holders or quartz tubes. Corrections were made for the holders and the diamagnetic contribution was estimated using Pascal's constants.³³ Single crystal X-ray diffraction were predominantly measured using a Rigaku Rapid II imaging plate system with MicroMax-007 HF/VariMax rotating-anode X-ray

generator and confocal monochromated Mo-K α radiation. The structures at 330 and 370 K were measured with a Rigaku XtalLAB Synergy-S system with a HyPix-6000HE detector and Cu-K α radiation.

Starting materials and reaction overview

All reagents, unless otherwise stated, were used as supplied without further purification. Scheme 2 shows the synthetic pathway to the ligands. 2,6-dichloropyridine-4-carboxylic acid (**1**) was synthesised according to Adamczyk *et al.*,³⁴ while 2,6-bis(pyrazol-1-yl)pyridine-4-carboxylic acid (**2**) was synthesised from **1** following Vermonden *et al.*³⁵ The amide derivatives were synthesised from the reaction of **2** with $SOCl_2$ followed by NH_4OH or NH_2Me in methanol at 75°C ($ESI^\dagger$). The thioamides can be synthesised from the amide with P_2S_5 or Lawesson's reagent.³⁶ The latter route provides higher yields, detailed below, following a modified method from Martelli *et al.*³⁷

Synthesis of **bppCSNH₂**

A solution of **bppCONH₂** (scheme 2, 0.378 g, 1.49 mmols) in THF (25 ml) was added to Lawesson's reagent (0.727 g, 1.78 mmols). The solution was stirred at RT for 2 hours. The solvent was removed at 60°C *in vacuo*, and the resultant solid was dissolved in EtOAc (100 ml). The solution was washed with 5% Na_2CO_3 soln. (100 ml), dried over $MgSO_4$, filtered, and concentrated to *ca.* 10 ml under *vacuo*. The solution was left at -20°C for two days yielding a yellow crystalline solid of **bppCSNH₂** (yield 0.255 g, 64%). 1H NMR (400 MHz, DMSO): δ 10.39 (s, 1H), 10.08 (s, 1H), 8.98 (d, $J = 2.6$ Hz, 2H), 8.13 (s, 2H), 7.91 (s, 2H), 6.68–6.65 (m, 2H). ^{13}C NMR (400 MHz, DMSO): δ 197.36, 152.96, 150.15, 143.47, 128.87, 109.2, 106.99 (Fig S1 †). Calculated for $C_{12}H_{10}N_6S$: C, 53.32; H, 3.73; N, 31.09. Found: C, 53.03; H, 3.73; N, 30.86.

Synthesis of **bppCSNHMe**

A solution of **bppCONHMe** (scheme 2, 0.457 g, 1.71 mmols) in THF (25 ml) was added to Lawesson's reagent (0.826 g, 2.14 mmols). The solution was stirred at 50°C for 3 hours. The solvent was removed at 60°C *in vacuo*, and the solid dissolved in EtOAc (100 ml), washed with 5% Na_2CO_3 soln. (100 ml), dried over $MgSO_4$, filtered and the solvent removed *in vacuo*. The crude product was purified *via* flash chromatography using 1:1 EtOAc: Petroleum Ether. The resulting solution was concentrated to *ca.* 5 ml and left at -20°C for 2 days yielding a yellow crystalline solid (yield: 0.2321 g, 48%). 1H NMR (400 MHz, DMSO): δ 10.9 (s, 1H), 8.98 (d, $J = 2.6$ Hz, 2H), 8.1 (s, 2H), 7.91 (d, $J = 1.0$ Hz, 2H), 6.70–6.64 (m, 2H), 3.21 (s, 3H). ^{13}C NMR (400 MHz, DMSO): δ 193.9, 153.48, 150.15, 143.47, 128.87, 109.21, 107.1, 34.08 (Fig S2 †). Calculated for $C_{13}H_{12}N_6S$: C, 54.91; H, 4.25; N, 29.56. Found: C, 54.64; H, 4.20; N, 31.15.

Synthesis of Fe(II) complexes

Caution! Although we have experienced no difficulties during the synthesis of metal perchlorates, in the solid state, subject to heat, these are potentially explosive. All such materials are best kept in a cool place, out of direct sunlight and used in small quantities.

Synthesis of $[\text{Fe}(\text{bppCSNH}_2)_2](\text{X})_2 \cdot \text{solvent}$ ($\text{X} = \text{ClO}_4$ or BF_4)

A solution of $\text{Fe}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ (50.3 mg, 0.139 mmols) was added to a solution of **bppCSNH₂** (75 mg, 0.278 mmols) in MeNO_2 (4 ml). The solution was heated under N_2 at reflux for 30 minutes. The solution was allowed to cool to RT giving dark red crystals (yield: 91.2 mg, 82%). Calculated for $\text{C}_{24}\text{H}_{20}\text{N}_{12}\text{S}_2\text{O}_8\text{Cl}_2\text{Fe} \cdot 0.5\text{MeNO}_2$: C, 35.63; H, 2.62; N, 21.20. Found: C, 35.86; H, 2.38; N, 21.56.

A solution of $\text{Fe}(\text{BF}_4)_2 \cdot 6\text{H}_2\text{O}$ (0.0473 g, 0.14 mmols) was added to a solution of **bppCSNH₂** (75.8 mg, 0.28 mmols) in MeNO_2 (7 ml). The solution was heated under N_2 at reflux for 20 minutes. Large dark red crystals were obtained by vapour diffusion with Et_2O (yield: 63 mg, 58%). Calculated for $\text{C}_{24}\text{H}_{20}\text{N}_{12}\text{S}_2\text{B}_2\text{F}_8\text{Fe} \cdot 2\text{MeNO}_2$: C, 35.00; H, 2.94; N, 21.98. Found: C, 35.25; H, 2.80; N, 22.51.

Synthesis of $[\text{Fe}(\text{bppCSNHMe})_2](\text{X})_2 \cdot \text{solvent}$ ($\text{X} = \text{ClO}_4$ or BF_4)

$\text{Fe}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ (36.2 mg, 0.1 mmols) was reacted with **bppCSNHMe** (56.8 mg, 0.2 mmols) in MeNO_2 (5 ml). After 30 minutes heating at reflux under N_2 , red crystals formed from the cooling reaction solution (yield: 70 mg, 86%). Calculated for $\text{C}_{26}\text{H}_{24}\text{N}_{12}\text{S}_2\text{O}_8\text{Cl}_2\text{Fe}$: C, 37.93; H, 2.94; N, 20.41. Found: C, 37.23; H, 2.63; N, 20.04.

$\text{Fe}(\text{BF}_4)_2 \cdot 6\text{H}_2\text{O}$ (41.8 mg, 0.124 mmols) was reacted with **bppCSNHMe** (70.4 mg, 0.248 mmols) in MeNO_2 (7 ml). After heating at reflux under N_2 for 30 minutes the solution was concentrated to ca. 5 ml. Vapour diffusion with Et_2O produced red crystals (yield: 49 mg, 50%). Calculated for $\text{C}_{26}\text{H}_{24}\text{N}_{12}\text{S}_2\text{B}_2\text{F}_8\text{Fe} \cdot 0.5\text{MeNO}_2$: C, 38.46; H, 2.95; N, 21.15. Found: C, 38.98; H, 2.92; N, 21.25

Results and Discussion

Crystal structures of **bppCSNH₂** and **bppCSNHMe** ligands

Table 1 contains the crystallographic parameters for all the structures obtained. The molecular structures of the ligands are shown in figure 1. There is one crystallographically independent molecule for **bppCSNH₂**, whereas there are two for **bppCSNHMe**. As with other bpp-like structures, the nitrogen donors are arranged in respective Z-conformers. The thioamide groups are not in the same plane as the rest of the ligand, due to intra-ligand steric hindrance from N-H...H-C and S...HC contacts such as N1-H...C4 and S1...H-C3 in the **bppCSNH₂** ligand. The angle between the mean planes of the bpp and CSN parts is 27° in **bppCSNH₂** and 56.6° or 59.0° in the crystallographically independent **bppCSNHMe** molecules. The larger angle in **bppCSNHMe** is due to the presence of the methyl group. The N-methylthioamide group also adopts a Z-conformation with the methyl group directed away from the pyridyl ring. ¹H-NMR of **bppCSNHMe** does not indicate E-Z isomerism. Indeed, thioamides typically present larger rotational barriers about the C-N bonds with stronger S=C-N charge transfer than the corresponding amides.^{21,22} In this case, steric interactions between the methyl and pyridyl groups prevent formation of the E-form.

Fig. 1 Molecular structures of the crystallographically independent molecules of **bppCSNH₂** (top) and **bppCSNHMe** (bottom). The atom numbering scheme and 50% thermal ellipsoids are shown. Hydrogen atoms have been omitted for clarity

Crystal structure of $[\text{Fe}(\text{bppCSNH}_2)_2](\text{BF}_4)_2 \cdot 2\text{MeNO}_2$

Unfortunately, $[\text{Fe}(\text{bppCSNH}_2)_2](\text{ClO}_4)_2 \cdot 0.5\text{MeNO}_2$ rapidly loses solvent and despite several attempts to determine the structure, no clear diffraction spots were obtained. For the BF_4 salt, the structure of $[\text{Fe}(\text{bppCSNH}_2)_2](\text{BF}_4)_2 \cdot 2\text{MeNO}_2$ is shown in figure 2. The amount of included solvent agrees with TGA data, which gives a mass loss of 10.14% between 83°C and 111°C, consistent with the loss of two MeNO_2 molecules per complex ($\text{ESI}^\dagger$).

Fig. 2 The asymmetric unit of $[\text{Fe}(\text{bppCSNH}_2)_2](\text{BF}_4)_2 \cdot 2\text{MeNO}_2$ with 50% thermal ellipsoids and atom numbering scheme. Hydrogen atoms and MeNO_2 have been omitted for clarity.

The Fe to N donor atom distances are consistent with a low spin complex at both measured temperatures, with averages of 1.944 Å (100 K) and 1.974 Å (290 K). It has been found that many complexes with R-bpp ligands display a 'terpyridine embrace' structural motif.³⁸ These structures have layers of complexes with face-to-face π - π or atom- π interactions between pyrazole rings on neighbouring molecules. By contrast $[\text{Fe}(\text{bppCSNH}_2)_2](\text{BF}_4)_2 \cdot 2\text{MeNO}_2$ forms chains

Table 1 Crystallographic data and structural refinement parameters for **bppCSNH₂** and **bppCSNHMe** ligands, and corresponding Fe(II) complexes

Compound	bppCSNH₂	bppCSNHMe	[Fe(bppCSNHMe) ₂](BF ₄) ₂ ·MeNO ₂		
Formula	C ₁₂ H ₁₀ N ₆ S	C ₁₃ H ₁₂ N ₆ S	C ₂₇ H ₂₇ FeN ₁₃ B ₂ F ₈ S ₂ O ₂	C ₂₇ H ₂₇ FeN ₁₃ B ₂ F ₈ S ₂ O ₂	C ₂₇ H ₂₇ FeN ₁₃ B ₂ F ₈ S ₂ O ₂
<i>M_r</i>	270.31	284.34	859.17	859.17	859.17
Crystal System	Orthorhombic	Orthorhombic	Monoclinic	Monoclinic	Monoclinic
Space Group	<i>Pbca</i>	<i>P2₁2₁2₁</i>	<i>P2₁/c</i>	<i>P2₁/c</i>	<i>P2₁/c</i>
<i>a</i> /Å	10.0603(4)	6.3725(2)	8.0479(3)	8.2211(3)	8.25830(10)
<i>b</i> /Å	11.0336(5)	13.6562(5)	40.9514(14)	40.8700(18)	40.8625(4)
<i>c</i> /Å	22.1907(8)	31.8638(11)	10.6303(4)	10.7721(4)	10.80570(10)
α /°	90.000	90.000	90.000	90.000	90.000
β /°	90.000	90.000	92.164(7)	94.349(7)	94.7390(10)
γ /°	90.000	90.000	90.000	90.000	90.000
<i>V</i> (Å ³)	2463.19(17)	2816.44(16)	3501.0(2)	3608.9(3)	3633.97(7)
<i>Z</i>	8	8	4	4	4
μ /cm ⁻¹	2.578	2.291	6.423	6.231	52.07
<i>T</i> /K	150	290	100	290	330
Measured Reflections	22388	27124	32972	32472	20884
Unique Reflections	2816	6444	8012	8119	6617
<i>R_i</i> , <i>I</i> > 2 σ (<i>I</i>)	0.0481	0.0325	0.0440	0.0773	0.0393
<i>R</i> , all data	0.0769	0.0384	0.0493	0.1000	0.0441
<i>wR</i> , all data	0.1032	0.0884	0.1227	0.2351	0.1111
Goodness of Fit	1.048	1.024	1.074	1.031	1.066
Spin State	N/A	N/A	LS	LS	LS

Compound	[Fe(bppCSNH₂) ₂](BF ₄) ₂ ·2MeNO ₂		[Fe(bppCSNHMe) ₂](ClO ₄) ₂		
Formula	C ₂₆ H ₂₆ B ₂ F ₈ FeN ₁₄ S ₂ O ₄	C ₂₆ H ₂₆ B ₂ F ₈ FeN ₁₄ S ₂ O ₄	C ₂₆ H ₂₄ Cl ₂ FeN ₁₂ O ₈ S ₂	C ₂₆ H ₂₄ Cl ₂ FeN ₁₂ O ₈ S ₂	C ₂₆ H ₂₄ Cl ₂ FeN ₁₂ O ₈ S ₂
<i>M_r</i>	892.16	892.16	823.41	823.41	823.41
Crystal System	Monoclinic	Monoclinic	Triclinic	Triclinic	Triclinic
Space Group	<i>C2/c</i>	<i>C2/c</i>	<i>P-1</i>	<i>P-1</i>	<i>P-1</i>
<i>a</i> /Å	51.605(2)	51.880(2)	8.2973(4)	8.2899(3)	8.2808(2)
<i>b</i> /Å	8.3203(4)	8.4111(4)	9.7480(4)	9.9601(3)	10.2621(3)
<i>c</i> /Å	16.7867(7)	17.1533(8)	20.6211(9)	20.7440(6)	20.5898(5)
α /°	90.000	90.000	81.087(7)	80.302(6)	81.158(2)
β /°	93.676(7)	94.245(7)	83.793(7)	83.941(6)	86.276(2)
γ /°	90.000	90.000	90.517(6)	89.321(6)	89.446(2)
<i>V</i> (Å ³)	7192.8(6)	7464.7(6)	1637.52(14)	1678.85(10)	1725.24(8)
<i>Z</i> value	8	8	2	2	2
μ (Mo-K α)/cm ⁻¹	6.333	6.103	8.199	7.997	6.640
<i>T</i> /K	100	290	102	290	370
Measured Reflections	32615	34048	15925	16514	18366
Unique Reflections	8201	8497	7476	7649	6085
<i>R_i</i> , <i>I</i> > 2 σ (<i>I</i>)	0.0442	0.0605	0.0564	0.0639	0.0468
<i>R</i> , all data	0.0606	0.0844	0.0791	0.0869	0.0510
<i>wR</i> , all data	0.1188	0.1827	0.1410	0.1750	0.1439
Goodness of Fit	1.045	1.014	1.038	1.052	1.088
Spin State	LS	LS	LS	LS	HS

Table 2 Selected bond lengths and bond angle parameters for low-spin (102K and 290K) and high-spin (370K) [Fe(**bppCSNHMe**)₂](ClO₄)₂.

	Bond lengths			Bond angle Parameters				
	Fe-N _{pyridyl} (Å)	Fe-N _{pyrazolyl} (Å)		α (°) ^a	Φ (°) ^b	Σ (°) ^c	Θ (°) ^d	θ (°) ^e
Low Spin at 102 K	1.898(3), 1.901(3)	1.964(3), 1.975(3), 1.979(3), 1.990(3)		80.0	175.54	91.7	288	82.7
Low Spin at 290 K	1.900(3), 1.902(3)	1.971(3), 1.974(3), 1.981(4), 1.994(3)		79.8	176.25	94.5	291	82.4
High Spin at 370K	2.104(2), 2.111(2)	2.181(3), 2.144(3), 2.155(3), 2.153(3)		73.7	171.82	155.0	463	79.8

(a) Average of four intra-ligand *cis*-N-Fe-N angles (b) *trans*-N_{pyridyl}-Fe-N_{pyridyl} angle, (c) sum of the deviations from 90° of the 12 *cis*-N-Fe-N angles: larger value indicates deviation from O_h geometry, (d) sum of the deviations from 60° of the 24 N-Fe-N angles, 6 angles per pseudo three-fold axis, measured on a projection of opposite triangular faces of the FeN₆ octahedron orientated by superimposing the face centroids: an indication of deviation from O_h geometry towards a D_{3h} triangular³⁹, (e) angle between the mean planes of the 16 C and N atoms in each bpp-like ligand moiety: together with Φ an indication of Jahn-Teller distortion in the HS state. Typical values for these parameters for a large range of bpp derivatives can be found in ref. 14

of complexes *via* intermolecular S...C close contacts: S1...C4 is 3.640 Å at 100 K and 3.668 Å at 290 K; S2...C15 is 3.658 Å at 100 K and 3.668 Å at 290 K. There is also π - π stacking between neighbouring pyrazolyl groups in each chain, where the distance between the plane C19, C20, C21 and C22, C23, C24 of a neighbouring complex is 3.432 Å. The cation chains are essentially isolated from each other, separated by anions and solvent molecules. The thioamide groups in each chain show hydrogen bonding NH...F of BF₄⁻ anions. For example at 100 K the distance between N7 and the F7 atom of one anion is 3.021 Å and the distance between the same N7 and F6 of a different anion is 2.974 Å. However, this does not connect chains together.

Crystal structures of [Fe(bppCSNHMe)₂](BF₄)₂·MeNO₂ and [Fe(bppCSNHMe)₂](ClO₄)₂

The solvated structure [Fe(bppCSNHMe)₂](BF₄)₂·MeNO₂ was determined at 100, 290 and 330 K. The structures (figure 3, top) are isostructural and all have Fe-N bond lengths and pseudo-octahedral geometry typical of low spin Fe(II).

Fig. 3 The asymmetric units of [Fe(bppCSNHMe)₂](BF₄)₂·MeNO₂ (top) and [Fe(bppCSNHMe)₂](ClO₄)₂ (bottom), at 290 K, with 50% thermal ellipsoids and atom numbering scheme. Hydrogen atoms and MeNO₂ have been omitted for clarity.

The MeNO₂ molecule sits between pyrazolyl sites on adjacent complex moieties, and its presence prevents a spin state change. Alterations including bending and twisting about the N_{pyridyl}-Fe-N_{pyridyl} bond have been considered as essential to facilitate SCO, without which a compound can become kinetically locked in a particular spin state.^{40,41} In this case, the DSC and SQUID data (*vide infra*) show that following the loss of solvent the complex becomes SCO-active. It is not unknown to observe different SCO behaviour dependant on the type or presence of solvent molecules.⁴² Unfortunately, solvent loss

from [Fe(bppCSNHMe)₂](BF₄)₂·MeNO₂ leads to the crystals becoming opaque, giving powder-like diffraction patterns (ESI[†]). Therefore, the structure of the non-solvated, SCO active, complex could not be determined.

The structure of [Fe(bppCSNHMe)₂](ClO₄)₂ (figure 3, bottom) was determined at 102, 290 K and 370 K. Within this work, this is the only compound for which we were able to obtain structures of the SCO active species. The variable temperature determination gives a rare example of obtaining both LS and HS state structures spanning room temperature. At all temperatures the compound is isostructural, crystallising in the triclinic space group P-1. At 102 K and 290 K the structure is consistent with the LS state with metal to donor N atom bond lengths averaging 1.951 Å and 1.954 Å (table 2), respectively. However, at 370 K the corresponding bond length average is 2.141 Å as expected for the HS state. Table 2 also shows various parameters calculated from bond angles as described by Hendrickson *et al.*,^{39a} and expanded upon for non-bpp SCO materials by Guionneau *et al.*^{39b} The parameters are in agreement with those typically found in a large range of complexes with bpp-based ligands.¹⁴

Fig. 4 Crystal structure of [Fe(bppCSNHMe)₂](ClO₄)₂ at 102 K, showing (top) intra-chain S...C/N van der Waals close contacts and (bottom) inter-chain hydrogen bonding. Contacts are shown with black dotted lines. In the bottom figure only one cation per chain is shown, hydrogen atoms and some anions have been omitted for further clarity.

Two types of intermolecular or interionic interactions persist across all temperatures. Firstly S...C or N close contacts result in the formation of cationic chains propagating along the crystallographic c axis (Figure 4 top). This motif is similar to that found in [Fe(bppCSNHMe)₂](BF₄)₂·MeNO₂. However, in this case the chains are connected *via* the second type of interaction: hydrogen bonding -NH₂...anion...H₂N- (Figure 4 bottom). Each complex has two distinct thioamide groups, one being more in-plane with the bpp moiety than the other. At 102 K the plane of the thioamide group is either 21.9° (containing S1) or 67.5° (S2) away from the mean plane of the bpp moiety. This structural difference persists at each measurement temperature, although the angles become successively smaller as the temperature increases. This change is most significant for the

thioamide group that is more in-plane with the bpp body. Hence, at 370 K the angles are 7.9° and 63.6°, respectively. The intra-chain intermolecular contacts depend on which thioamide groups are involved. The contact S1...C26 (3.323 Å at 102 K, 3.379 Å at 370 K) is between S atoms of the more planar **bppCSHMe** ligand and a C atom of the bpp part of the less planar ligand. At the other side of the cation the more out-of-plane thioamide group has close contacts S2 to C19, C21 and N9 of the bpp body of the neighbouring less planar ligand. In addition at 102 and 290 K there are close inter-chain contacts S1...C4 (3.430 Å at 102 K). However, at 370 K these atomic distances are no longer below the sum of the van der Waals distances. This might be a consequence of, or result in, the more planar nature of the thioamide groups as the temperature is increased. At all temperatures the cation chains are linked *via* hydrogen bonds involving the anion (figure 4 bottom) by the contacts N1...O1 (2.944 Å at 102 K, 3.070 Å at 370 K) and N1...O2 (2.883 Å at 102 K, 2.935 Å at 370 K). Overall the structural changes in the complex as a result of SCO are shown in figure 5.

Fig. 5 Overlaid capped stick representations of the 290 K LS (blue) and 370 K HS (red) molecular structures of $[\text{Fe}(\text{bppCSNHMe})_2](\text{ClO}_4)_2$. Counter ions and hydrogen atoms have been omitted for clarity.

It has been noted that bpp derived compounds that have the 'terpyridine embrace' structure tend to have similar SCO behaviour with abrupt transitions, small hysteresis widths of less than 5 K and $T_{1/2}$ between *ca.* 200 and 260 K. There are exceptions, for example when the 'terpyridine embrace' layer involves multiple π -interactions, resulting in increases in $T_{1/2}$. This is seen in a benzimidazole based compound with a transition temperature of 403 K.⁴³ Divergent behaviour also appears when the 'terpyridine embrace' is disrupted. For example $[\text{Fe}(\text{II})(\text{bppCOOH})_2](\text{ClO}_4)_2$ ²⁰ (ligand **2** in scheme 2) has cations arranged in 1D chains rather than 2D layers. In this case the structure is a result of strong $\text{bppCOOH}\cdots\text{HOOCbpp}$ hydrogen-bonding, responsible for the abrupt SCO at 380 K. As with $[\text{Fe}(\text{bppCSNHMe})_2](\text{BF}_4)_2\cdot\text{MeNO}_2$ and $[\text{Fe}(\text{II})(\text{bppCOOH})_2](\text{ClO}_4)_2$ the perchlorate salt with **bppCSNHMe** does not form a 2D layered 'terpyridine embrace' structure but forms 1D chains. These have weaker S...C/N interactions, compared to the strong hydrogen-bonding in the bppCOOH salt. However, unlike $[\text{Fe}(\text{bppCSNHMe})_2](\text{BF}_4)_2\cdot\text{MeNO}_2$ the chains are also connected *via* a hydrogen-bonding network resulting in an abrupt SCO with a small hysteresis, but with $T_{1/2}$ between the values obtained for most 'terpyridine embrace' compounds and the

hydrogen-bonded bppCOOH containing chains. This results in the observation of a $T_{1/2}$ closer to room temperature.

Magnetisation and thermal analysis

Caution! During DSC and TGA measurements of $[\text{Fe}(\text{bppCSNHMe})_2](\text{ClO}_4)_2$ the compound exploded under N_2 at 200 to 250°C. Care should be taken if using under reduced pressure or high temperatures.

Complexes containing the ligand **bppCSNHMe**

For both compounds with the **bppCSNHMe** ligand DSC measurements show changes in the thermodynamic parameters consistent with solvent loss at 110°C for the BF_4^- salt and 112°C for the ClO_4^- salt (Fig S5 and S6[†]). There is no further solid state phase transition up to 200°C or on subsequent temperature cycling after solvent loss. Solid state SQUID measurements determined that both complexes are in the diamagnetic LS state between 3 and 350 K, irrespective of any pre-heat treatment (figure 6). When considering the structure it was stated that SCO in both **bppCSNHMe** compounds is suppressed in the solid state. This is confirmed by measuring the paramagnetic susceptibility in solution using the Evans NMR method⁴⁴ Figure 7 shows the results for all compounds in nitromethane- d_3 .

Fig. 6 Molar magnetic susceptibility (χ_M) multiplied by temperature (T) vs T . Key: $\blacktriangledown$ $[\text{Fe}(\text{bppCSNHMe})_2](\text{BF}_4)_2\cdot 2\text{MeNO}_2$; $\blacklozenge$ $[\text{Fe}(\text{bppCSNHMe})_2](\text{BF}_4)_2\cdot\text{MeNO}_2$ after heating to remove solvent; $\blacksquare$ $[\text{Fe}(\text{bppCSNHMe})_2](\text{ClO}_4)_2$; $\blacksquare$ $[\text{Fe}(\text{bppCSNHMe})_2](\text{ClO}_4)_2$. Inset shows an expanded view showing thermal hysteresis for the complexes containing **bppCSNHMe**. Measurements made in the solid state by SQUID magnetometry.

Complexes containing the ligand **bppCSNHMe**

The DSC measurement of the BF_4^- salt shows behaviour consistent with irreversible solvent loss at 83.4 °C (figure 8, top). The solvent loss is confirmed by TGA which shows a mass loss of 5.4% consistent with loss of one MeNO_2 molecule per $\text{Fe}(\text{II})$ complex (Fig S7[†]). On heating after solvent loss there is no further phase transition up to 200°C. However, subsequent cycling by reducing the temperature to -100 °C and then increasing it to 200 °C shows a reversible phase change with hysteresis between 56.5 °C and 61.5 °C (figure 8, top). The calculated thermodynamic parameters are consistent with SCO

transitions in Fe(II) complexes (table 3). Since the DSC indicated that SCO required solvent loss, prior to measurement of the SQUID profile this salt was dried for 1 hour under reduced pressure at 90°C. $[\text{Fe}(\text{bppCSNHMe})_2](\text{BF}_4)_2$ then shows an SCO centred at 332 K, with a small hysteresis of 3 K. At 350 K the $\chi_{\text{M}}T$ value is still rising and so the SCO is not yet complete (figure 6).

Fig. 7 Molar magnetic susceptibility (χ_{M}) multiplied by temperature (T) vs T measured in solution by the Evans NMR method⁴⁴ in nitromethane- d_3 . Solid line is a least squares fit to SCO compounds as described in reference 45.

The DSC data for $[\text{Fe}(\text{bppCSNHMe})_2](\text{ClO}_4)_2$ shows a reversible phase transition with thermodynamic parameters typical of an SCO transition with a small hysteresis (figure 8, bottom, and Table 3). SQUID measurements were completed between 2 and 350 K, confirming that below 290 K the compound is in the LS state. Above this temperature the $\chi_{\text{M}}T$ value increases abruptly to a maximum of $3.3 \text{ cm}^3 \text{ K mol}^{-1}$, which corresponds 94% completion of the SCO (figure 6), assuming a typical value of $3.5 \text{ cm}^3 \text{ K mol}^{-1}$ for 100% HS in Fe(II) bpp complexes. Although clearly the value of $\chi_{\text{M}}T$ is still rising at 350 K. The similar temperatures at which the SCO transitions occur in the non-solvated **bppCSNHMe** complexes indicates comparable mechanisms of cooperativity and electronic environments. This also implies that the influence of the counter-anion is minimised in these structures, but that solvent inclusion in the solid state structure of the BF_4^- salt inhibits the SCO. In solution (Figure 7) both **bppCSNHMe** salts show SCO behaviour albeit with less abrupt transitions and at a lower $T_{1/2}$ when compared to the solid state measurements. This is not unusual behaviour since it is well-observed that solid state intermolecular interactions promote an abrupt transition.⁴⁴ However, this data confirms that solid state intermolecular interactions in the solvated BF_4^- salt suppresses SCO but not in the non-solvated ClO_4^- salt. It is interesting to note the order of the $T_{1/2}$ values in solution according to the fitted values. We find **bppCSNHMe**/ BF_4^- > **bppCSNHMe**/ ClO_4^- > **bppCSNH}_2/\text{ClO}_4^- > **bppCSNH}_2/\text{BF}_4^- and for the **bppCSNHMe** compounds this is the reverse in the solid state. This is further illustration of how solid state interactions can moderate the SCO parameters.⁴⁵****

Fig. 8 DSC traces for $[\text{Fe}(\text{bppCSNHMe})_2](\text{BF}_4)_2 \cdot \text{MeNO}_2$ (top) and $[\text{Fe}(\text{bppCSNHMe})_2](\text{ClO}_4)_2$ (bottom). Measurements cycled from -100 to 200 °C.

Table 3 Thermodynamic parameters calculated from DSC data for the SCO transition of **bppCSNHMe** containing Fe(II) salts.

	$T_{\uparrow}$ /K	$T_{\downarrow}$ /K	av. ΔH /kJ mol ⁻¹	av. ΔS /J K ⁻¹ mol ⁻¹
$[\text{Fe}(\text{bppCSNHMe})_2](\text{BF}_4)_2 \cdot \text{MeNO}_2$	334.7	329.7	16.4	49.4
$[\text{Fe}(\text{bppCSNHMe})_2](\text{ClO}_4)_2$	329.9	325.4	10.8	33.0

Conclusions

Our aim was to synthesise a compound with $T_{1/2}$ close to, or slightly above RT. As a starting point we considered $[\text{Fe}(\text{II})(\text{bppCOOH})_2](\text{ClO}_4)_2$, which has 1D cationic chains with strong intermolecular hydrogen bonding. This compound has SCO centred at 380 K, well above RT. On the other hand bpp complexes often have 'terpyridine embrace' structures with an SCO between 200 and 260 K, well below RT. The initial idea was to change the COOH group to

moderate (primarily weaken) the strength of hydrogen bonding in the 1D cationic chain to reduce $T_{1/2}$ from 380 K. With that in mind, we have presented a series of complexes with two thioamide functionalised bpp ligands. In the solid state two of these, the BF_4 and ClO_4 salts of Fe(II) with the ligand **bppCSNHMe**, show SCO close to the desired temperature. We were able to obtain structures of the SCO active $[\text{Fe}(\text{bppCSNHMe})_2](\text{ClO}_4)_2$ above and below the transition. The structure showed cationic chains with weaker intra-chain interactions, as was our aim. However, the interactions were van der Waals S...C/N contacts, rather weaker hydrogen-bonding as we originally desired. Hydrogen-bonding is still present but between the cations and anions.

Tuning of SCO properties is ultimately an issue of hard to control crystal engineering with typical investigations focussing on the impact of small structural alterations. However, introducing small chemical changes carries risks, such as not being able to produce a comparable isostructural series. Or, as in this work, not being able to predict the exact nature of interactions in the structure. However, there is nevertheless useful information to be gained. For the **bppCSNHMe** complexes the nature of the anion has only a small effect on the SCO $T_{1/2}$. This may imply that SCO in the solid state is mainly controlled by the nature of the intra-chain interactions and we intend to investigate this by reporting on the Fe(II) complexes of the corresponding amides. On the other hand it may imply that $T_{1/2}$ can be subtly changed by keeping the weakly linked cationic chains and moderating inter-chain interactions with different anions. We intend to investigate this by varying the anion in **bppCSNHMe** salts, away from the traditionally used ClO_4^- and BF_4^- , including anions that form more strong or weak hydrogen bonding networks.

Conflicts of interest

There are no conflicts to declare.

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References

- 1 J.E. Clements, J.R. Price, S.M. Neville and C.J. Kepert, *Angew. Chem. Int. Ed.*, 2016, **55**, 15105–15109.
- 2 S. Hayami, S. M. Holmes and M. A. Halcrow, *J. Mater. Chem. C*, 2015, **3**, 7775–7778.
- 3 P. Gütllich, A. B. Gaspar and Y. Garcia, *Beilstein J. Org. Chem.*, 2013, **9**, 342–391.
- 4 S. Bonhommeau, T. Guillon, L. M. Lawson Daku, P. Demont, J. Sanchez Costa, J.-F. Létard, G. Molnár and A. Bousseksou, *Angew. Chemie Int. Ed.*, 2006, **45**, 1625–1629.
- 5 T. Guillon, S. Bonhommeau, J. S. Costa, A. Zwick, J.-F. Létard, P. Demont, G. Molnár and A. Bousseksou, *Phys. status solidi*, 2006, **203**, 2974–2980.
- 6 B. Schäfer, T. Bauer, I. Faus, J. A. Wolny, F. Dahms, O. Fuhr, S. Lebedkin, H.-C. Wille, K. Schlage, K. Chevalier, F. Rupp, R. Diller, V. Schünemann, M. M. Kappes and M. Ruben, *Dalton Trans.*, 2017, **46**, 2289–2302.
- 7 C.-F. Wang, R.-F. Li, X.-Y. Chen, R.-J. Wei, L.-S. Zheng and J. Tao, *Angew. Chemie*, 2015, **127**, 1594–1597.
- 8 Y. Jiao, J. Zhu, Y. Guo, W. He and Z. Guo, *J. Mater. Chem. C*, 2017, **5**, 5214–5222.
- 9 M. Nihei, N. Takahashi, H. Nishikawa and H. Oshio, *Dalton Trans.*, 2011, **40**, 2154–2156.
- 10 C. Carbonera, J. Sánchez Costa, V. A. Money, J. Elhaik, J. A. K. Howard, M. A. Halcrow and J.-F. Létard, *Dalton Trans.*, 2006, 3058–3066.
- 11 M. A. Halcrow, *Chem. Soc. Rev.*, 2011, **40**, 4119.
- 12 J. A. Real, A. B. Gaspar, V. Niel and M. C. Muñoz, *Coord. Chem. Rev.*, 2003, **236**, 121–141.
- 13 R. Boča, F. Renz, M. Boča, H. Fuess, W. Haase, G. Kickelbick, W. Linert and M. Vrbová-Schikora, *Inorg. Chem. Commun.*, 2005, **8**, 227–230.
- 14 M. A. Halcrow, *Coord. Chem. Rev.*, 2009, **253**, 2493–2514.
- 15 A. Santoro, L. J. Kershaw Cook, R. Kulmaczewski, S. A. Barrett, O. Cespedes and M. A. Halcrow, *Inorg. Chem.*, 2015, **54**, 682–693.
- 16 F. Pointillart, X. Liu, M. Kepenekian, B. Le Guennic, S. Golhen, V. Dorcet, T. Roisnel, O. Cador, Z. You, J. Hauser, S. Decurtins, L. Ouahab and S.-X. Liu, *Dalton Trans.*, 2016, **45**, 11267–11271.
- 17 M.-L. Boillot and B. Weber, *Comptes Rendus Chim.*, 2018, 1–13.
- 18 K. Senthil Kumar and M. Ruben, *Coord. Chem. Rev.*, 2017, **346**, 176–205.
- 19 M. A. Halcrow, *New J. Chem.*, 2014, **38**, 1868–1882.
- 20 A. Abhervé, M. Clemente-León, E. Coronado, C. J. Gómez-García and M. López-Jordà, *Dalton Trans.*, 2014, **43**, 9406.
- 21 K. B. Wiberg and D. J. Rush, *J. Org. Chem.*, 2002, **67**, 826–830.
- 22 K. B. Wiberg and D. J. Rush, *J. Am. Chem. Soc.*, 2001, **123**, 2038–2046.
- 23 H.-J. Lee, Y.-S. Choi, K.-B. Lee, J. Park and C.-J. Yoon, *J. Phys.*

- Chem. A*, 2002, **106**, 7010–7017.
- 24 T. Mes, S. Cantekin, D. W. R. Balkenende, M. M. M. Frissen, M. A. J. Gillissen, B. F. M. De Waal, I. K. Voets, E. W. Meijer and A. R. A. Palmans, *Chem. - A Eur. J.*, 2013, **19**, 8642–8649.
- 25 L. J. Kershaw-Cook, R. Kulmaczewski, O. Cespedes and M. A. Halcrow, *Chem. Eur. J.*, 2016, **22**, 1789.
- 26 R. Kulmaczewski, E. Trzop, L. J. Kershaw-Cook, E. Collet, G. Chastanet and M. A. Halcrow, *Chem. Commun.*, 2017, **53**, 13268.
- 27 R. Chandrasekar, F. Schramm, O. Fuhr, M. Ruben, *Eur. J. Inorg. Chem.*, 2008, 2649.
- 28 M. Haryono, F. W. Heinemann, K. Petrukhov, K. Gieb, P. Miller, A. Grohmann, *Eur. J. Inorg. Chem.*, 2009, 2136
- 29 L. J. Kershaw Cook, R. Kulmaczewski, S. A. Barrett, M. A. Halcrow, *Inorg. Chem. Front.*, 2015, **2**, 662.
- 30 L. Pukenas, F. Benn, E. Lovell, A. Santoro, L. J. Kershaw Cook, M. A. Halcrow, S. D. Evans, *J. Chem. Mat. C.*, 2015, **3**, 7890.
- 31 M. Attwood, S. S. Turner, *Coord. Chem. Rev.*, 2017, **353**, 247.
- 32 (a) L. J. Kershaw Cook, H. J. Shephard, T. P. Comyn, C. Baldé, O. Cespedes, G. Chastanet, M. A. Halcrow, *Eur. Chem. J.*, 2016, **21**, 4805. (b) L. J. Kershaw Cook, J. Fisher, L. P. Harding, M. A. Halcrow, *Dalton Trans.*, 2015, **44**, 9417.
- 33 G. A. Bain and J. F. Berry, *J. Chem. Educ.*, 2008, **85**, 532–536.
- 34 M. Adamczyk, S. R. Akireddy and R. E. Reddy, *Tetrahedron*, 2002, **58**, 6951–6963.
- 35 T. Vermonden, D. Branowska, A. T. M. Marcelis and E. J. . Sudhölter, *Tetrahedron*, 2003, **59**, 5039–5045.
- 36 T. Ozturk, E. Ertas and O. Mert, *Chem. Rev.*, 2007, **107**, 5210–5278.
- 37 A. Martelli, L. Testai, V. Citi, A. Marino, I. Pugliesi, E. Barresi, G. Nesi, S. Rapposelli, S. Taliani, F. Da Settimo, M. C. Breschi and V. Calderone, *ACS Med. Chem. Lett.*, 2013, **4**, 904–908.
- 38 (a) M. L. Scudder, H. A. Goodwin, I. G. Dance, *New J. Chem.*, 1999, **23**, 685. (b) R. Pritchard, C. A. Kilner, M. A. Halcrow, *Chem. Commun.*, 2007, 577.
- 39 (a) J. K. McCuster, A. L. Rheingold, D. N. Hendrickson, *Inorg. Chem.*, 1996, **35**, 2100 (b) P. Guionneau, M. Marchivie, G. Bravic, J-F. Létard, D. Chasseau, *Top. Curr. Chem.*, 2004, **234**, 97.
- 40 J. Elhaïk, D. J. Evans, C. A. Kilner and M. A. Halcrow, *Dalton Trans.*, 2005, 1693–1700.
- 41 J. Elhaïk, C. A. Kilner and M. A. Halcrow, *Dalton Trans.*, 2006, 823–830.
- 42 (a) M.D. Gimenez-Lopez, M. Clemente-Leon, C. Gimenez-Saiz, *Dalton Trans.*, 2018, **47**, 10453 (b) S.A. Barrett, C.A. Kilner, M. Halcrow, *Dalton Trans.*, 2011, **40**, 12021.
- 43 R. Boča, M. Boča, L. Dlháň, K. Falk, H. Fuess, W. Haase, R. Jaroščiak, B. Papánková, F. Renz, M. Vrbová, R. Verner, *Inorg. Chem.*, 2001, **40**, 2035.
- 44 D.F. Evans, *J. Chem. Soc.*, 1959, 2003.
- 45 S. Rodriguez-Jimenez, S. Brooker, *Inorg. Chem.*, 2017, **56**, 13697