A Probe of the Ligand Substituent Effects on the Spin Crossover of Fe(II) Complexes

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SUPORTING INFORMATION

Description of solvathomorph 2b; Synthesis and Structure

[Fe(met1,3bpp)₂**](ClO**₄)₂·H₂O (2b). To a solution of Fe(ClO₄)₂·6H₂O (0.017 g, 0.065 mmol) and ascorbic acid (~2 mg) in dry acetone (10 mL) was added dropwise a solution of met1,3-bpp (0.027 g, 0.12 mmol) in dry acetone (10 mL). The resulting dark yellow solution was stirred for 40 minutes at room temperature. Afterwards, the solution was filtered and layered with toluene (volume 1:1). Yellow crystals of the complex [Fe(met1,3-bpp)₂](ClO₄)₂·H₂O (2b) suitable for X-ray diffraction were obtained after 4 days. Yield: 43.2%,EA, calcd (%) for C₂₄H₂₂Cl₂FeN₁₀O₈, **2b**(-H₂O), (found): C, 40.87 (41.04); H, 3.14 (3.01); N, 19.86 (19.06).



Figure S1. Molecular representation of $[Fe(met1,3bpp)_2](ClO_4)_2 \cdot H_2O$ (**2b**) at 100 K with heteroatoms labelled. Only H atoms of N–H groups shown (in yellow). Dashed lines are H-bonds.



Figure S2. Sheet organization of the cations in **2b**, emphasizing the $\pi \cdots \pi$ and C–H $\cdots \pi$ interactions formed by each complex with its four immediate neighbours within the sheet ("terpy embrace").

	2b
Formula	$C_{24}H_{24}CI_2FeN_{10}O_9$
FW (g mol⁻¹)	723.28
<i>Т</i> (К)	100(2)
Wavelength (Å)	0.7749
Crystal system	monoclinic
Space group	Сс
a (Å)	11.916(6)
b (Å)	11.884(6)
<i>c</i> (Å)	19.902(15)
β (°)	98.552(13)
V (Å ³)	2787(3)
Ζ	4
$ ho_{calcd}$ (g cm ⁻³)	1.724
µ (mm⁻¹)	1.015
Independent reflections (Rint)	6063 (0.0846)
restraints / parameters	487 / 419
Goodness-of-fit on <i>F</i> ²	1.015
Final <i>R</i> 1 / w <i>R</i> 2 [<i>I</i> >2 <i>σ</i> (<i>I</i>)]	0.1380 / 0.3254
Final R_1 / w R_2 [all data]	0.1474 / 0.3337
largest diff. peak and hole ($e \text{ Å}^3$)	1.997 / –2.752
Flack parameter	0.351(6)
Fe1–N3	1.90(2)
Fe1–N8	1.91(2)
Fe1–N5	1.955(19)
Fe1–N1	1.96(2)
Fe1–N6	1.979(19)
Fe1-N10	1.99(2)

 Table S1. Crystal data and Fe–N bond lengths for compound 2b

		2	3			
Formula	C24H22CI	2 FeN 10 O 8	$C_{26}H_{26}CI_2FeN_{10}O_8$			
FW (g mol ⁻¹)	705	5.26	733.32			
Т (К)	100(2)	300(2)	100(2)	298(2)		
Wavelength (Å)		0.71	073			
Crystal system		mono	oclinic			
Space group	C	2/c	P2	21/n		
a (Å)	41.290(9)	42.2075(12)	8.2654(3)	8.3260(5)		
b (Å)	8.0448(15)	8.1769(3)	37.8383(12)	38.4690(19)		
<i>c</i> (Å)	17.843(4)	18.2952(5)	9.5096(3)	9.6130(5)		
β (°)	108.946(14)	111.307(2)	96.203(2)	95.768(3)		
V (Å ³)	5606(2)	5882.6(3)	2956.7(2)	3063.4(3)		
Ζ	8	3	4			
$ ho_{ m calcd}$ (g cm ⁻³)	1.671	1.593	1.647	1.590		
µ (mm⁻¹)	0.798	0.760	0.760	0.733		
Independent reflections (<i>R</i> _{int})	3428 (0.1117)	4843 (0.0427)	7392 (0.0564)	3964 (0.0766)		
restraints / parameters	82 / 415	82 / 414	0 / 428	197 / 471		
Goodness-of-fit on F ²	1.059	1.051	1.031	1.019		
Final <i>R</i> ₁ / w <i>R</i> ₂ [<i>I</i> >2 <i>σ</i> (<i>I</i>)]	0.0700 /	0.0579/	0.0462 /	0.0591 /		
Final D / wD [all data]	0.1355	0.0838 /	0.0969 /	0.1483		
Final R_1 / WR_2 [all data]	0.1553	0.1806	0.1066	0.1749		
largest diff. peak and hole (<i>e</i> ų)	0.881 / -0.412	0.640 / -0.599	0.948 / -0.555	0.406 / -0.523		
<fe–n></fe–n>	1.96(4)	2.16(2)	1.95(4) 88 7	1.95(4)		
Θ	367.8	378.2	367.2	367.1		

Table S2. Crystal data, average Fe–N bond lengths and distortion parameters for compounds 2 and 3 $\,$

D–H…A	D–H (Å)	H…A (Å)	D–A (Å)	D–H…A (°)	
2 (100 K)					
N5–H5…O5	0.90(2)	1.87(3)	2.759(9)	172(8)	
N10–H10…O3	10–H10····O3 0.90(2)		2.999(10)	138(7)	
N10–H10…O4	0.90(2)	2.20(4)	3.017(10)	151(7)	
3 (100 K)					
N5–H5…O8	0.88	2.00	2.878(3)	175.0	
N10–H10…O4	0.88	1.96	2.832(3)	172.7	

Table S3. Hydrogen bonding in the structures of compounds 2 and 3 at 100 K.

Table S4. Selected $\pi \cdots \pi$ and C-H $\cdots \pi$ interactions in the structures of compounds 2 and 3 at 100 K

interaction	labels	Distance (Å) (π : centroid)	Compd.
<i>π</i> ··· <i>π</i> (1)	Cg(N1 N2 C2 C3 C4)…Cg(N4 N5 C10 C11 C12)	3.566	2
$C-H\cdots \pi$ (1)	C1-H1B…Cg(N9 N10 C22 C23 C24)	3.272	2
С−Н…π (2)	C12-H12…Cg(N6 N7 C14 C15 C16)	2.584	2
С−Н…π (2)	C24-H24…Cg(N4 N5 C10 C11 C12)	3.320	2
С−Н…π (2)	C24-H24…Cg(N6 N7 C14 C15 C16)	4.219	2
С−Н…π (2)	C15-H15…Cg(N1 N2 C2 C3 C4)	3.154	2
<i>π</i> … <i>π</i> (1)	Cg(N6 N7 C15 C16 C18)…Cg(N9 N10 C23 C24 C25)	3.635	3
$C-H\cdots \pi$ (1)	C25-H25…Cg(N1 N2 C2 C3 C5)	2.978	3
C−H…π (2)	C16-H16…Cg(N4 N5 C11 C12 C13)	3.118	3
C−H…π (3)	C3-H3…Cg(N6 N7 C15 C16 C18)	3.321	3

Table S5. Selected bond distances (Å) in the structures of compounds 2 and 3.

	2	2	3	3
	(100 K)	(300 K)	(100K)	(298K)
Fe1–N3	1.900(6)	2.121(4)	1.908(2)	1.909(5)
Fe1–N8	1.913(6)	2.117(3)	1.907(2)	1.912(5)
Fe1–N4	1.960(6)	2.175(4)	1.965(2)	1.965(5)
Fe1–N9	1.972(6)	2.184(4)	1.966(2)	1.968(5)
Fe1–N1	1.987(6)	2.191(4)	1.9682(19)	1.968(5)
Fe1–N6	2.013(6)	2.197(3)	1.975(2)	1.985(5)



Figure S3. View of the lattice of $[Fe(met1,3bpp)_2](CIO_4)_2$ (**2**), perpendicular to the *ac* crystallographic plane and thus, along the sheets of cations, emphasizing the two interlayer separations. Code: balls, Fe; red, O; green, Cl; grey, C. Hydrogen not shown.



Figure S4. View of the lattice of $[Fe(dimet1,3bpp)_2](ClO_4)_2$ (**3**), perpendicular to the *bc* crystallographic plane and thus, along the sheets of cations, emphasizing the two interlayer separations. Code: balls, Fe; red, O; green, Cl; grey, C. Hydrogen not shown.



Figure S5. Experimental powder X-ray diffraction (PXRD) diffractograms (black traces) and the corresponding diagrams simulated from the single crystal X-ray diffraction data (red traces and vertical lines) form compounds **2** and **3**.

Determination of excess heat capacity from DSC measurements and details of modelization with the domain model.

For all compounds, a lattice heat capacity was estimated from data below and above the anomaly associated with the SCO process (dashed lines in Figure S5). Excess enthalpy and entropy were derived by integration of the excess heat capacity with respect to T and $\ln T$, respectively.

The phenomenological domain model developed by Sorai¹ was applied to measure the cooperative character of the SCO, as it is widely used to analyse the SCO behaviour in cases where calorimetric data are available. It is based on hetero-phase fluctuations and gives a measure of cooperativity through the number of like-spin molecules (here the SCO centres) *n* per interacting domain, the larger the domain the more cooperative the transition. According to this model, the HS excess heat capacity can be written as:

$$\Delta C_{p} = \frac{n(\Delta H_{sco})^{2}}{RT^{2}} \frac{\exp\left[\frac{n\Delta H_{sco}}{R}\left(\frac{1}{T} - \frac{1}{T_{sco}}\right)\right]}{\left\{1 + \exp\left[\frac{n\Delta H_{sco}}{R}\left(\frac{1}{T} - \frac{1}{T_{sco}}\right)\right]\right\}^{2}}$$
Eq. S1

The experimental data were thus fitted to Eq. S1 using ΔH_{SCO} as derived from integration of ΔC_p vs. *T*. The resulting best-fit parameters are given in Table 1 (full red lines in Figure 5). For n = 1 the model is equivalent to a pure solution behaviour (van't Hoff equation) with no cooperative effects.

For compound **2**, two fits were performed. First, ΔC_p data were fit to Eq. S1 as described above, i.e. a simple Sorai's domain model (blue line in Fig. Sxxx below), giving n = 118.7 and $T_{SCO} = 182.1$ K, reproducing quite well the sharp peak, but not the broader anomaly below it. A second fit of the data to an expression with two components, i.e. two terms as in Eq. S1 with different n and T_{SCO} , was done (red line in Fig. S6 below) giving $n_1 = 128.7$ and $T_{SCO} = 182.1$ K and $n_2 = 9.9$ and $T_{SCO} = 185.6$ K, yielding a good simulation of the experimental data. Of course this does not mean there are two materials present with two behaviors. Rather, the sharper peak could correspond mainly to the structural component of the SCO, since a sharp variation of cell parameters are observed at the same temperature. The n and T_{SCO} given in Table 1 are those of the sharp component of this second fit.

¹ a) M. Sorai, S. Seki, J. Phys. Chem. Solids 1974, 35, 555-570; b) M. Sorai, Y. Nakazawa, N. Nakano, Y. Miyazaki, Chem. Rev. 2013, 113, PR41-PR122



Figure S6. Molar heat capacity of **1a/1b** (top, previously published²), **2** (middle) and **3** (bottom) at constant pressure as derived from DSC measurements. The dashed lines are the estimated lattice heat capacity used to obtain the excess heat capacity.

² C. Bartual-Murgui, C. Codina, O. Roubeau, G. Aromí, Chem. Eur. J. 2016, 22, 12767-12776



Figure S7. Excess heat capacity for compound 2. The blue and red full lines are the fits to the Sorai's domain model with respectively one and two components (see above).



Figure S8. 300 MHz ¹H NMR spectra of complexes **1** (top), **2** (middle) and **3** (bottom) in d_4 –MeOH.

Table S6. Paramagnetic shifts measured for TMS at different temperatures on a 600MHz spectrometer, by ¹H NMR in 0.005M d_4 -methanol solutions, for complexes **1**, **2** and **3**, and the corresponding *XT* values calculated with Evans method.³

	Complex 1			Complex 2			Complex 3		
T (K)	$X_{p}T$	<i>∆v</i> (Hz)	Δδ (ppm)	X_pT	<i>∆v</i> (Hz)	Δδ (ppm)	$X_{p}T$	<i>∆v</i> (Hz)	Δδ (ppm)
298	2.24	87.6	0.146	2.96	121.8	0.203	2.02	83.4	0.139
273	1.75	74.4	0.124	2.76	124.2	0.207	1.22	54	0.09
263	1.49	65.4	0.109	2.57	119.4	0.199	0.93	42	0.07
253	1.18	53.4	0.089	2.29	110.4	0.184	0.63	28.8	0.048
243	0.9	42	0.07	1.95	97.8	0.163	0.42	18.6	0.031
233	0.64	30	0.05	1.53	79.2	0.132	0.26	10.8	0.018
223	0.44	21	0.035	1.09	58.2	0.097	0.15	5.4	0.009
213	0.32	15	0.025	0.78	42.6	0.071	0.06	0.15	0.00025
203	0.2	9	0.015	0.42	22.8	0.038			
193				0.15	6.6	0.011			

The paramagnetic susceptibility of the complexes studied was calculated as follows;

$$\chi_p = \chi_{tot} + \chi_d$$

Where χ_{tot} , χ_p and χ_d are the total, the paramagnetic and the diamagnetic molar susceptibility respectively. The diamagnetic correction is determined using Pascal's constants. The formula to obtain χ_{tot} from the ¹H NMR data is;

$$\chi_{tot} = \frac{3000\Delta\nu}{4\pi\nu_o c}$$

Where Δv is the chemical shift in Hz, v_o is the spectrometer frequency in Hz and c is the concentration in mol/L.

³ S. K. Sur, *J. Magn. Reson.*, 1989, **82**, 169-173.



Figure S9. DFT optimize structures HS



Figure S10. DFT optimize structures LS