Multi-modal sensing in spin crossover compounds

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Electronic Supplementary Information (ESI)

Structures supplementary details

Similar lattice parameters and the same symmetry can be found for **1**, **2** and **3**, in the temperature range explored (from 100K to 300K). One crystallographically independent complex molecule has been found in the asymmetric units. Crystals show channels, aligned along crystallographic axis *c*, filled with solvent molecules. In all the structures there is a solvent molecule coordinated to a ligand tetrazole ring: water for **1** (lying on a C2 axis with 0.5 occupancy), methanol for **2** and ethanol for **3**. Other disordered molecules have been modelled in remaining voids of **1** and **2**: 0.75 water in dried crystals and 0.25 methanol in the methanol exposed ones.

Crystals exposed to ethanol have slow spin transition kinetics, even slower when the crystal is cooled down. It is, in fact, possible to freeze an HS crystal and still see the yellow colour for several minutes at 100K, even collecting a full diffraction dataset in the meantime. This situation is metastable and evolve to the red LS crystal form.

Structure of "inactive" red blocks (**4**) have a different unit cell showing half iron complex molecule in the ASU and an additional ligand molecule not coordinated to any metal (Figure 1SIDN). The additional free ligand molecule forms strong stacking interactions with neighbour complex molecules. This alternative crystal form has no cavities and this result is compatible with insensitivity to alcohol exposure and better temperature resistance.

Essential crystal and refinement data are reported in Table 1SIND for crystals of **1**, **2**, **3** and **4**. Full iron coordination sphere angles and bond lengths are reported in Table 2SIND.

Figure 1SIND. ASU content for “inert” crystals **4** (50% probability ellipsoids)

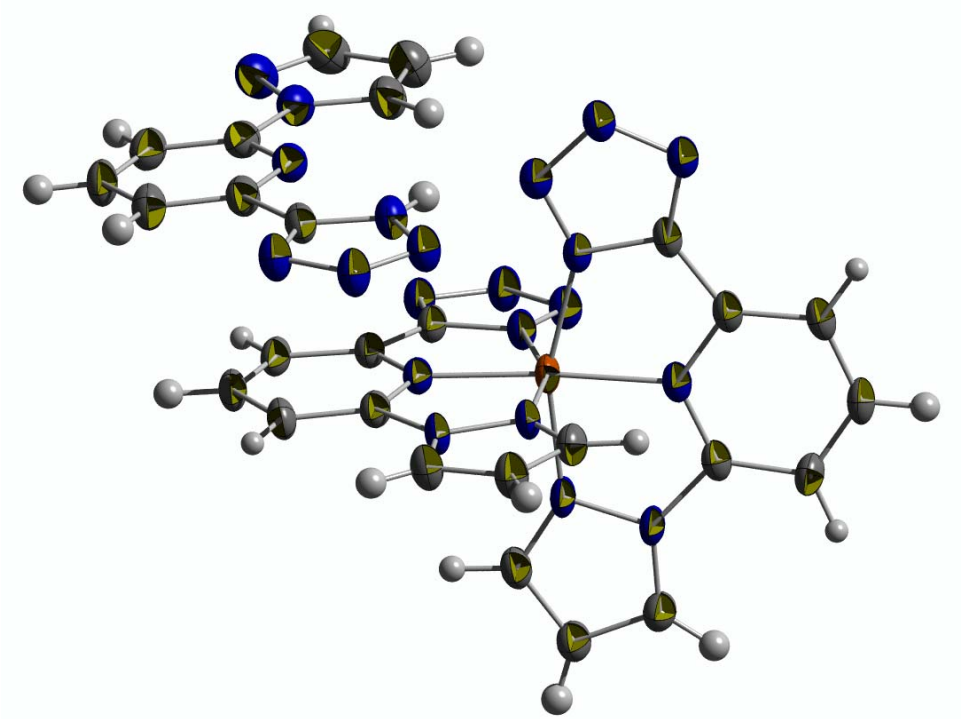

Table 1SIND. Crystal data and structure refinement for crystals **1**, **2**, **3** and **4,**

	Dried Crystals (**1**)	Dried Crystals (**1**)	Crystals with Methanol (**2**)	Crystals with Methanol (**2**)	Crystals with Ethanol (**3**)	Crystals with Ethanol (**3**)	Inactive form (**4**)
Moiety Formula	$C_{18}H_{12}FeN_{14}\cdot 1.25H_2O$	$C_{18}H_{12}FeN_{14}\cdot 1.25H_2O$	$C_{18}H_{12}FeN_{14}\cdot 1.25CH_4O$	$C_{18}H_{12}FeN_{14}\cdot 1.25CH_4O$	$C_{18}H_{12}FeN_{14}\cdot C_2H_6O$	$C_{18}H_{12}FeN_{14}\cdot C_2H_6O$	$C_{18}H_{12}FeN_{14}\cdot 2C_9H_7N_7$
Empirical Formula	$C_{18}H_{14.5}FeN_{14}O_{1.25}$	$C_{18}H_{14.5}FeN_{14}O_{1.25}$	$C_{19.25}H_{17}FeN_{14}O_{1.25}$	$C_{19.25}H_{17}FeN_{14}O_{1.25}$	$C_{20}H_{18}FeN_{14}O$	$C_{20}H_{18}FeN_{14}O$	$C_{36}H_{26}FeN_{28}$
Formula weight (Da)	502.79	502.79	520.32		526.33	526.33	906.70
Temperature (K)	300(2)	100(2)	300(2)	100(2)	300(2)	100(2)	100(2)
Wavelength (Å)	0.700	0.700	0.700	0.700	0.700	0.700	0.800
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space Group	*C 2/c*	*C 2/c*	*C 2/c*	*C 2/c*	*C 2/c*	*C 2/c*	*I 2/c*
a (Å)	23.784(7)	23.709(1)	24.495(16)	23.843(5)	24.389(49)	23.815(29)	16.407(3)
b (Å)	14.518(1)	14.472(2)	14.671(3)	14.824(3)	14.586(5)	14.299(5)	9.768(2)
c (Å)	15.534(2)	15.326(49)	16.712(9)	15.571(2)	16.985(21)	17.265(5)	23.226(5)
α (°)	90	90	90	90	90	90	90
β (°)	127.854(5)	127.617(14)	131.374(24)	129.178(9)	131.23(4)	131.676(33)	90.32(3)
γ (°)	90	90	90	90	90	90	90
V ($Å^3$)	4235.2(14)	4165(13)	4507(4)	4266.3(13)	4544(11)	4391(6)	3722.3(13)
Z	8	8	8	8	8	8	4
ρ ($g\cdot cm^{-3}$)	1.577	1.603	1.534	1.620	1.539	1.592	1.618
F(000)	2052	2052	2132	2132	2160	2160	1856
μ (mm^{-1})	0.725	0.737	0.684	0.723	0.679	0.702	0.654
θ min,max (°)	1.7, 29.1	1.7, 28.2	1.7, 28.2	1.7, 29.1	1.7, 29.0	1.8, 28.2	2.0, 28.1
Resolution (Å)	0.72	0.74	0.74	0.72	0.72	0.74	0.85
Total refl. collctd	22923	28897	47402	44022	16910	30881	10920
Independent refl.	5749	5222	5675	5846	5987	5480	3051
Obs. Refl. [Fo>4σ(Fo)]	4969	4385	5025	5409	3904	3994	2545
I/σ(I) (all data)	37.4	58.0	39.4	171.8	7.9	61.7	12.9
I/σ(I) (max resltn)	12.9	11.6	14.2	58.6	2.3	9.1	9.3
Completeness (all data)	0.98	0.98	0.99	0.98	0.95	0.99	0.95
Completeness (max resltn)	0.95	0.95	0.96	0.95	0.92	0.97	0.92
Rmerge (all data)	0.010	0.022	0.021	0.014	0.056	0.022	0.071
Rmerge (max resltn,)	0.054	0.104	0.086	0.048	0.256	0.230	0.118
Multiplicity (all data)	3.8	4.4	6.2	5.7	2.5	4.6	3.3
Multiplicity (max resltn)	3.8	4.4	6.3	6.0	2.2	4.4	3.1
Data/restraint/parameters	5749/9/328	5222/9/339	5675/26/341	5846/36/368	5987/0/330	5987/0/329	3051/0/308
Goof	1.049	1.110	1.046	1.079	1.030	1.059	1.024
R[I>2.0σ(I)], wR2 [I>2.0σ(I)]	0.0323, 0.0851	0.0756, 0.1530	0.0338, 0.1001	0.0458, 0.1231	0.0514, 0.1429	0.0596, 0.1573	0.0423, 0.1096
R (all data), wR2 (all data)	0.0383, 0.0907	0.0956, 0.1693	0.0367, 0.1030	0.0484, 0.1254	0.0767, 0.1635	0.0879, 0.1933	0.0532, 0.1175

Table 2SIND. Bond lengths (Å) and angles (°) in iron coordination sphere

	Dried Crystals published	Dried Crystals (**1**)	Dried Crystals (**1**)	Crystals with Methanol (**2**)	Crystals with Methanol (**2**)	Crystals with Ethanol (**3**)	Crystals with Ethanol (**3**)	Inactive form (**4**)
T (K)	180	300	100	300	100	300	100	100
Fe-N1	1.968(4)	1.978(1)	1.971(5)	2.198(1)	1.970(2)	2.201(2)	1.981(3)	1.969(2)
Fe-N7	1.949(4)	1.962(1)	1.968(6)	2.213(1)	1.965(2)	2.210(3)	2.039(3)	1.950(2)
Fe-N5	1.916(3)	1.912(1)	1.907(4)	2.144(2)	1.910(2)	2.146(4)	1.929(4)	1.909(2)
Fe-N12	1.918(3)	1.912(1)	1.908(4)	2.152(2)	1.912(2)	2.156(5)	1.920(4)	1.909(2)
Fe-N8	1.971(4)	1.980(1)	1.975(5)	2.162(1)	1.986(2)	2.159(3)	2.054(3)	1.969(2)
Fe-N14	1.959(4)	1.971(1)	1.958(5)	2.204(1)	1.976(2)	2.207(2)	1.991(3)	1.950(2)
N1-Fe-N7	160.04(14)	159.75(5)	160.0(2)	147.22(4)	159.91(6)	147.11(10)	159.31(13)	160.30(8)
N1-Fe-N5	80.08(15)	79.85(5)	79.8(2)	74.68(6)	79.98(6)	74.64(13)	85.30(14)	79.95(9)
N1-Fe-N12	101.77(15)	103.86(5)	104.6(2)	102.14(6)	102.02(6)	99.64(14)	96.64(14)	103.52(9)
N1-Fe-N8	92.20(17)	92.41(5)	92.7(2)	95.65(5)	92.40(6)	94.77(11)	87.40(12)	94.81(13
N1-Fe-N14	92.34(16)	92.78(5)	92.8(2)	94.17(6)	92.12(7)	94.45(10)	95.97(13)	90.23(9)
N7-Fe-N5	79.98(15)	79.92(5)	80.2(2)	72.59(5)	79.93(6)	72.59(9)	74.03(13)	80.36(9)
N7-Fe-N12	98.19(14)	96.36(5)	95.4(2)	110.09(5)	98.07(6)	112.71(9)	104.04(13)	96.10(9)
N7-Fe-N8	91.27(16)	92.30(5)	91.8(3)	98.26(6)	91.56(7)	99.11(11)	98.59(13)	90.23(9)
N7-Fe-N14	91.14(16)	89.52(5)	89.5(2)	89.98(5)	90.91(7)	90.05(11)	85.68(12)	91.39(13)
N5-Fe-N12	177.48(16)	176.22(5)	175.6(2)	165.81(4)	177.18(6)	163.83(8)	175.35(12)	174.99(13)
N5-Fe-N8	102.26(14)	101.00(5)	100.8(2)	118.90(4)	102.28(6)	120.27(9)	109.67(12)	103.52(9)
N5-Fe-N14	97.88(15)	99.07(5)	99.1(2)	93.88(6)	97.88(6)	92.96(14)	91.74(13)	96.11(9)
N12-Fe-N8	79.45(15)	79.71(5)	79.8(2)	74.96(5)	79.70(6)	74.83(8)	74.70(12)	79.94(9)
N12-Fe-N14	80.39(16)	80.15(5)	80.1(2)	72.39(5)	80.12(7)	72.17(12)	83.86(13)	80.37(9)
N8-Fe-N14	159.83(14)	159.86(5)	159.9(2)	147.20(5)	159.81(6)	146.77(10)	158.55(12)	160.30(8)
Colour	Deep Red	Deep Red	Deep Red	*Bright Yellow*	Deep Red	*Bright Yellow*	Deep Red	Bright Red
Spin Status	**LS**	**LS**	**LS**	***HS***	**LS**	***HS***	**LS**	**LS**
CCDC	956141	1055429	1055430	1055431	1055432	1055433	1055434	1055435