Supporting Information for the manuscript

A spin crossover ferrous complex with ordered magnetic ferric anions

Olivier Roubeau,*[a] Marco Evangelisti,[a] Eva Natividad[b]

[a] *Instituto de Ciencia de Materiales de Aragón (ICMA), CSIC - Universidad de Zaragoza, Departamento de Física de la Materia Condensada, Pl. San Francisco s/n, 50009 Zaragoza, Spain; Fax: 34 976 76123; Tel: 34 976 762461; E-mail: roubeau@unizar.es*

[b] *Instituto de Ciencia de Materiales de Aragón (ICMA), CSIC - Universidad de Zaragoza, Sede Campus Río Ebro, María de Luna, 3, 50018 Zaragoza, Spain.*

Physical Measurements.

Magnetic measurements were performed using a Quantum Design MPMS-XL SQUID magnetometer. The applied field for temperature-dependent *dc* measurements was 0.1 T, in the range of linear dependence of M vs. H. The measured values were corrected for the experimentally measured contribution of the sample holder, while the derived susceptibilities were corrected for the diamagnetism of the samples, estimated from Pascal's tables. Warming and cooling rates were of the order of 0.3 $\mathrm{Kmin^{-1}}$.

Heat capacities in the range 120-330 K were obtained by use of a differential scanning calorimeter Q1000 with the LNCS accessory from TA Instruments. The temperature and enthalpy scales were calibrated with a standard sample of indium, using its melting transition (156.6 ºC, 3296 $\mathrm{Jmol^{-1}}$). The zero-heat flow procedure described by TA Instruments was followed, using synthetic sapphire as reference compound.

Heat capacities in the range 0.35-130 K were obtained using the relaxation method and the heat capacity option of a Quantum Design PPMS set-up.

Infrared spectra of neat samples were taken on a Perkin-Elmer Spectrum 100 apparatus equipped with an ATR device.

Scanning Electron Microscopy images were taken with a JEOL JSM 6400 equipped with an Oxford Instruments INCA 300 EDS set-up for elemental analysis. For the observation of crystallites, the sample bulk was deposited onto carbon tape. EDS was performed on thick pellet to ensure a correct analysis.

Synthetic details.

1-methyltetrazole (Metz) was prepared as described in the literature (see P. L. Franke, J. G. Haasnoot, A. P. Zuur, *Inorg. Chim. Acta* **1982**, *59*, 5).

Synthesis of compound **1** $[Fe(Metz)_6](FeBr_4)_2$:

Metz (115 mg, 1.37 mmol) is added to a 10 mL ethanolic solution containing a mixture of $FeBr_2$ (26 mg, 0.12 mmol) and $FeBr_3$ (71 mg, 0.24 mmol). The deep red solution is stirred at 50 ºC for 15 min, filtrated hot over a paper filter and the filtrate is left standing at room temperature, partially covered to allow slow evaporation. Red crystalline **1** deposits within 12 hours, and is recovered by filtration after a total of 24 hours. After washing with a small amount of ethanol and diethylether, and drying in air a total of 55 mg (yield = 35 % based on Fe^{2+}) of red shiny crystalline **1** is obtained (see Fig S1), including crystals suitable for single-crystal X-ray diffraction. Similar crystalline material and yield are obtained when quantities are increased by a factor 3 and 6. Note that **1** can be obtained down to a Metz:$FeBr_2$ 6:1 molar ratio, albeit in lower yields.

Main IR bands (neat): 3136 (s), 1758 (m), 1518 (s), 1422 (m), 1298 (m), 1240 (w), 1182 (s), 1107 (vs), 1064 (w), 1020 (w), 992 (s), 880 (s), 720 (m), 682 (vs), 653 (vs) cm^{-1}. Elemental analysis: calculated (found) for $C_{12}H_{24}Fe_3N_{24}Br_8$ (**1**): C, 10.99 (11.1); H, 1.84 (1.9); N, 25.64 (25.6) %. The Fe/Br content is confirmed by SEM/EDX analysis. Relative at. % calculated (found) for $C_{12}H_{24}Fe_3N_{24}Br_8$: Fe/Br, 0.375 (0.41); Fe/N, 0.125 (0.12); Br/N, 0.333(0.29).

Synthesis of compound **2** $[Zn(Metz)_6](FeBr_4)_2$:

The exact same conditions as for **1** are used, albeit replacing $FeBr_2$ by $ZnBr_2$. The orange-red crystals of **2** are obtained in a ca. 30 % yield based on Zn(II).

Main IR bands (neat): 3135 (s), 1756 (m), 1518 (s), 1421 (m), 1299 (m), 1238 (w), 1182 (s), 1107 (vs), 1060 (w), 1029 (w), 993 (s), 881 (s), 722 (m), 682 (vs), 653 (vs) cm^{-1}. Elemental analysis: calculated (found) for $C_{12}H_{24}Fe_2ZnN_{24}Br_8$ (**2**): C, 10.91 (11.1); H, 1.83 (1.9); N, 25.45 (25.5) %.

Details of modelization of ΔC_p data with the so-called domain model.

The phenomenological domain model developed by Sorai[1] was applied here, as it is widely used to analyze the SCO behaviour in cases where calorimetric data are available. It is based on heterophase fluctuations and gives a measure of cooperativity through the number of like-spin molecules (or here the SCO centres) *n* per interacting domain, the larger the domain the more cooperative the transition. According to this model, the HS fractions can be written as:

$$\Delta C_p = \frac{n\left(\Delta_{SCO}H\right)^2}{RT^2}\,\frac{\exp\left[\dfrac{n\Delta_{SCO}H}{R}\left(\dfrac{1}{T}-\dfrac{1}{T_{SCO}}\right)\right]}{\left\{1+\exp\left[\dfrac{n\Delta_{SCO}H}{R}\left(\dfrac{1}{T}-\dfrac{1}{T_{SCO}}\right)\right]\right\}^2} \qquad \text{Eq. S1}$$

The experimental data were thus fit to Eq. S1 using $\Delta_{\mathrm{SCO}}H$ as derived from integration of ΔC_{p} vs. T, giving $n = 1.47$ and $T_{\mathrm{SCO}} = 169.2$ K (full line in inset of Figure 3). For $n = 1$ the model is equivalent to a pure solution behaviour (van't Hoff equation) with no cooperative effects.

Reference:

1) a) M. Sorai, S. Seki, *J. Phys. Chem. Solids*, 1974, **35**, 555-570; b) M. Sorai, *Top. Curr. Chem.*, 2004, **235**, 153-170.

Table S1 Relevant bond distances (Å) and angles (°) as well as short contacts (Å) in the structure of compound **1** at 296 and 104 K and **2** at 296 K.

	$[Fe(Metz)_6](FeBr_4)_2$ (**1**)		$[Zn(Metz)_6](FeBr_4)_2$ (**2**)
	296 K	104 K	296 K
M1–N1	**2.187(2)**	**2.003(2)**	2.181(4)
N1–M1–N1#1	88.89(9) 91.11(9)	88.97(9) 91.03(9)	88.69(16) 91.31(16)
Fe2–Br1	2.324(2)	2.3244(10)	2.323(2)
Fe2–Br2	2.3438(5)	2.3452(5)	2.3439(8)
Br1–Fe2–Br2	109.71(2)	109.88(2)	109.67(4)
Br2–Fe2–Br2#2	109.23(2)	109.06(2)	109.27(4)
M1···M1#3	12.9487(1)	12.683(2)	12.9404(4)
M1···Fe2	7.478(1)	7.325(1)	7.473(1)
Fe2···Fe2#4	7.489(1)	7.337(1)	7.484(1)
Fe2···Fe2#5	6.9577(1)	6.7980(14)	6.9522(3)
Br1···Fe2#5	4.634(2)	4.474(2)	4.629(2)
Br1···Br2#5	4.432(1)	4.287(1)	4.430(1)
Br2···Br2#4	4.472(1)	4.303(1)	4.469(1)
Br2···H1A	3.81	3.71	3.80

Symmetry operations: #1: x–y, x, 1–z and –x+y, –x, z; #2: –x+y, 1–x, z or 1–x, x–y, z; #3:1+x, y, z; #4:1–x, 1–y, 1–z; #5: x, y, 1+z.

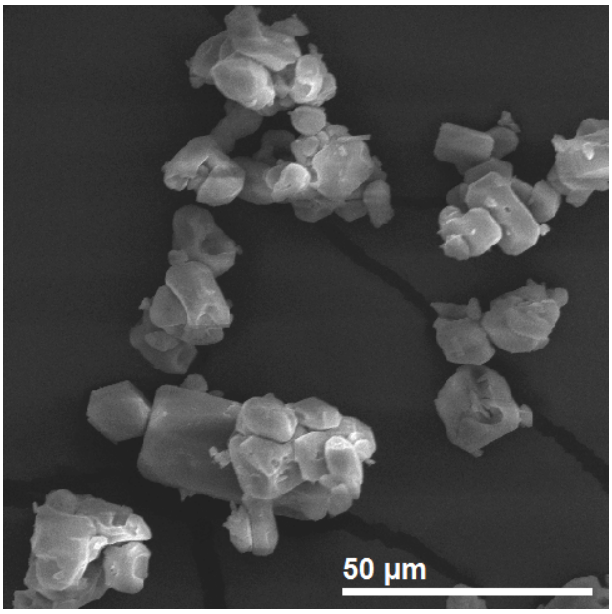

Fig. S1 Scanning Electron Microscopy image of a polycrystalline sample of **1**.

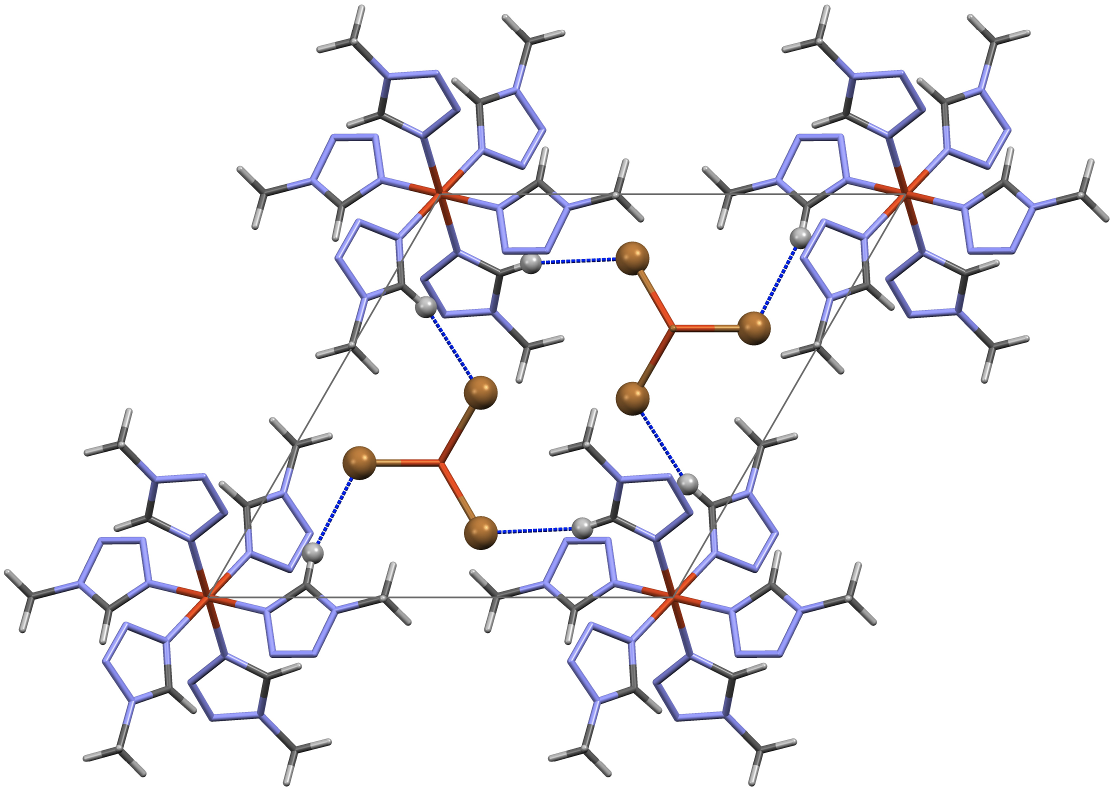

Fig. S2 Projection of the structure of **1** at 104 K in the *ab* plane showing the hydrogen bonds (light blue lines) formed by each $FeBr_4^-$ anions with three tetrazole ligand from three neighbouring $[Fe(Metz)_6]^{2+}$ complexes. Br and H atoms participating in these hydrogen bonds are represented as brown and light grey balls respectively.

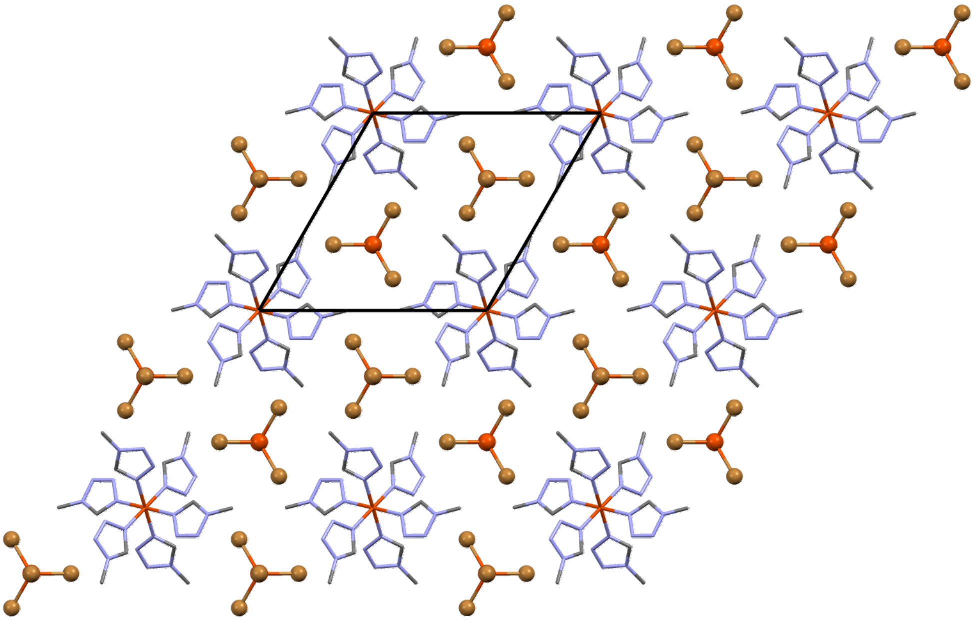

Fig. S3 Projection of the structure of **1** at 104 K in the *ab* plane highlighting the network of $FeBr_4^-$ anions represented as ball and sticks. Colour code: Fe, orange; Br, brown; N, blue, C, grey.

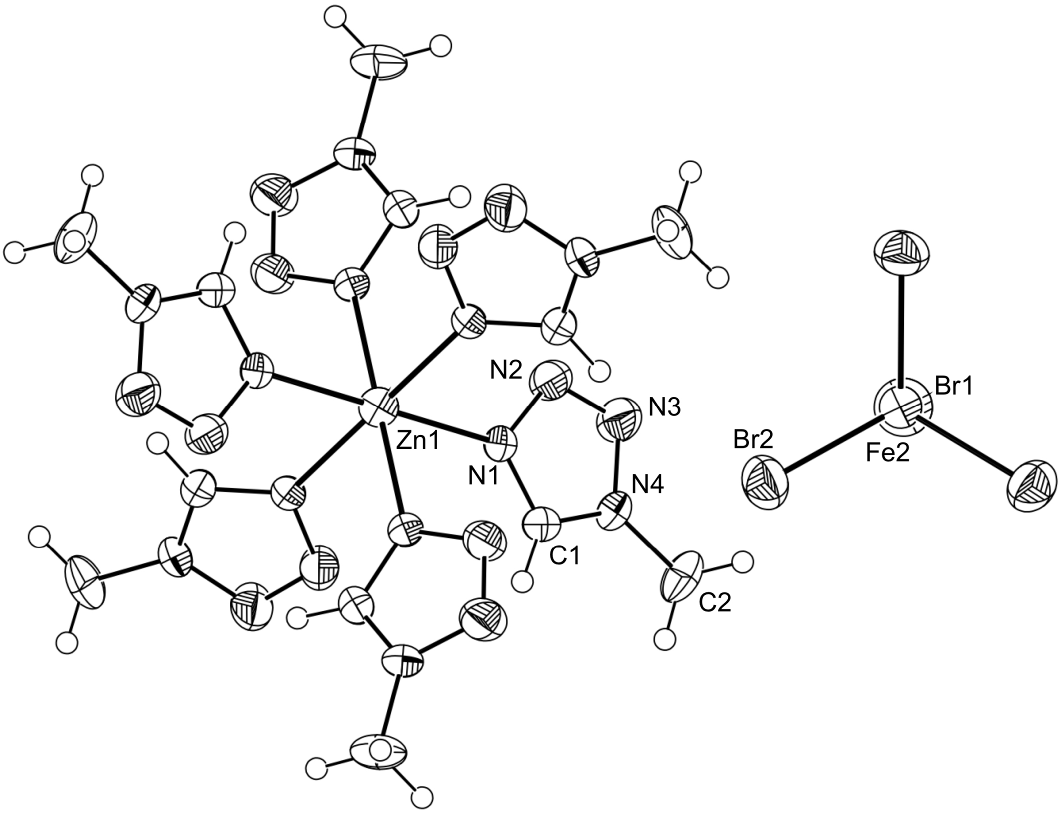

Fig. S4 ORTEP view at 50 % probability of the structure of **2** at 296 K along the *c* axis. Only non-hydrogen atoms of the asymmetric unit are labelled.