ELECTRONIC SUPPLEMENTARY INFORMATION

Guest Induced Hysteretic Tristability in 3D Pillared Hofmann-type Microporous Metal-Organic Framework†

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Supplementary material

1. **Experimental and synthesis**
2. **Crystallographic description**
3. **Physical methods (IR/TGA)**
4. **Magnetic Data**

1. Experimental and synthesis
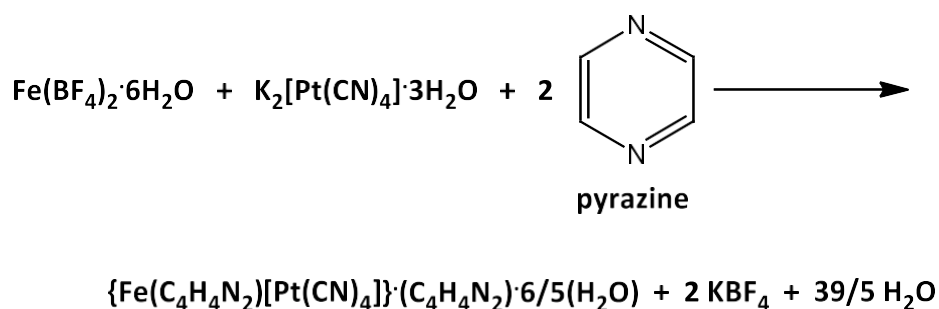
EXPERIMENTAL

All manipulations were carried out under aerobic conditions. $K_2[Pt(CN)_4] \cdot 3H_2O$ was purchased from Aldrich, $Fe(BF_4)_2 \cdot 6H_2O$ from Fluka and $C_4H_4N_2$ (pyrazine) from Merck. Nano-pure quality water was used for all reactions run.

Infrared (IR) spectra (400–4000 cm^{-1}) were recorded on a Nicolet FT-IR 6700 spectrometer with samples prepared as KBr pellets. C, H and N elemental analyses were performed on a Perkin Elmer 240B elemental analyzer. The TGA curves were obtained on a SETARAM thermal analyzer, model SETSYS-1200. The sample of approximately 8 mg was heated in platinum crucibles, in nitrogen atmosphere at a flow rate of 80 ml min^{-1}, within the temperature range 30–500 ^0C.

Magnetic susceptibility data were collected on powdered samples of **1** and **2** with a Quantum Design SQUID susceptometer in the 3-290 K temperature range, under various applied magnetic fields.

SYNTHESIS

The interaction of $Fe(BF_4)_2 \cdot 6H_2O$ with $K_2[Pt(CN)_4] \cdot 3H_2O$ and pyrazine in aqueous media-only and at room temperature, led to the isolation of compound $\{Fe(pyz)[Pt(CN)_4]\} \cdot (pyz) \cdot 1.2\ H_2O$ with a 1:1:2 molar ratio. Elemental analysis on the isolated product suggested the formulation $\{Fe(pyz)[Pt(CN)_4]\} \cdot (pyz) \cdot 1.2\ H_2O$ (**1**). The stoichiometric reaction (Reaction 1) leading to the isolation of the aforementioned compound is the following:

$$Fe(BF_4)_2 \cdot 6H_2O\ +\ K_2[Pt(CN)_4] \cdot 3H_2O\ +\ 2\quad \text{pyrazine}$$

$$\{Fe(C_4H_4N_2)[Pt(CN)_4]\} \cdot (C_4H_4N_2) \cdot 6/5(H_2O)\ +\ 2\ KBF_4\ +\ 39/5\ H_2O$$

Reaction 1

The new hydrated Fe(II)/Pt(II) species was isolated using an excess of pyrazine molecules in aqueous solution. For the synthesis of {Fe(pyz)[Pt(CN)$_4$]}·(pyz)·1.2H$_2$O (1) pyrazine (0.30 g, 3.75 mmol) was dissolved in 20 mL of nanopure water while Fe(BF$_4$)$_2$·6H$_2$O (0.08 g, 0.25 mmol) and K$_2$[Pt(CN)$_4$]·3H$_2$O (0.09 g, 0.25 mmol) were dissolved in 1 mL of nanopure water, respectively. All reagents were dissolved only at room temperature. The aqueous solution of pyrazine was placed in a 50 mL jar with stopper. Following that, a 10 mL vial was placed inside the jar and the aqueous solution of Fe(BF$_4$)$_2$·6H$_2$O was injected at the bottom of the vial. Finally, the aqueous solution of K$_2$[Pt(CN)$_4$]·3H$_2$O was injected at the bottom of the jar and the jar was closed. The resulted reaction mixture was left undisturbed at room temperature and after several hours a mixture of yellow crystalline powder and needle like crystals were formed. Single crystals were isolated by filtration and dried *in vacuo*. Yield 0.4 g (30 %). Anal. Calcd. for **1**, (C$_{12}$H$_{10.4}$FeN$_8$O$_{1.2}$Pt, M.W.: 536.84 g/mol): C, 26.84; H, 1.94; N, 20.86. Found: C, 26.99; H, 2.08; N, 20.91 %.

For the synthesis of {Fe(pyz)[Pd(CN)$_4$]}·(pyz)·1.2H$_2$O (**2**) pyrazine (0.80 g, 10.0 mmol) was dissolved in 65 mL of nanopure water while Fe(BF$_4$)$_2$·6H$_2$O (0.23 g, 0.68 mmol) and K$_2$[Pt(CN)$_4$]·3H$_2$O (0.20 g, 0.69 mmol) were dissolved in 2.5 mL of nanopure water, respectively. The aqueous solution of pyrazine was placed in an H-tube while in the two sides of the tube were injected the Fe and Pd solutions, respectively. The resulted reaction mixture was left undisturbed at room temperature and after several hours a mixture of yellow crystalline powder and needle like crystals was formed. Single crystals were isolated by filtration and dried *in vacuo*. Yield 0.4 g (30 %). Anal. Calcd. for **2**, (C$_{12}$H$_{10.4}$FeN$_8$O$_{1.2}$Pd, M.W.: 448.13 g/mol): C, 32.16; H, 2.34; N, 25.03. Found: C, 32.32; H, 2.41; N, 24.90 %.

2. Crystallographic description

Single crystals of compounds **1** and **2** were obtained from aqueous solutions according to the described synthetic procedure. Single crystals with approximate dimensions, 0.03 x 0.06 x 0.160 mm for **1** and 0.02, 0.04, 0.120 mm for **2** were taken from the mother liquor, mounted on a glass fiber using grease and immediately cooled at -113 °C. Diffraction measurements for both crystals were made on a Rigaku R-AXIS SPIDER Image Plate diffractometer using graphite monochromated Cu K$_\alpha$ radiation and using the Rigaku Nitrogen gas cryostream system, X-STREAM 2000 for cooling. Data collection (ω-scans) and processing (cell refinement, data reduction and Empirical absorption correction) were performed using the CrystalClear program package.[1] Important crystallographic

data for compounds **1** and **2** are listed in Table S1. The structures of **1** and **2** were solved by direct methods using SHELXS-97[2] and refined by full-matrix least-squares techniques on F^2 with SHELXL2014/6.[3] All non-H atoms were refined anisotropically and all Hydrogen atoms were introduced at calculated positions and refined as riding on bonded carbon atoms with $U_{iso}(H) = 1.2U_{eq}(C)$.

[1] Rigaku/MSC *CrystalClear*. Rigaku/MSC Inc., The Woodlands, Texas, USA, 2005
[2] G. M. Sheldrick, *Acta Cryst.*, **2008**, A64, 112-122
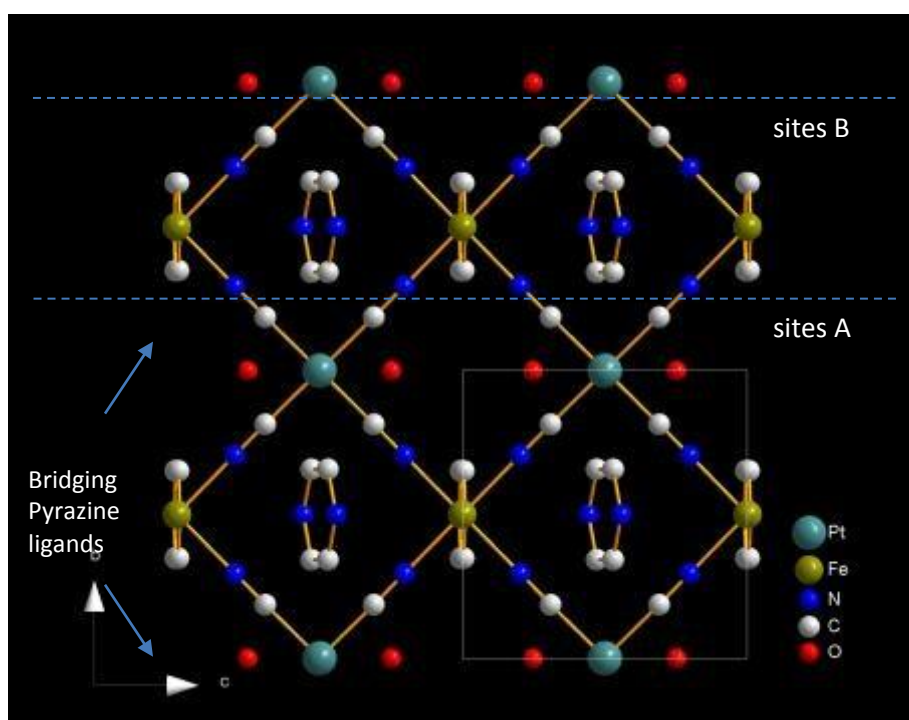[3] G. M. Sheldrick, *Acta Cryst.*, **2015**, C71, 3-8

Fig. S1 View of the structure of **1** or **2** along the a-axis. Orientation of bridging pyrazine ligands and arrangement of sites -A and -B.
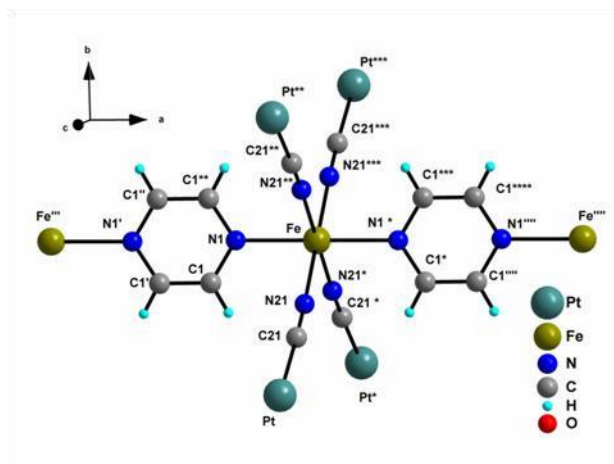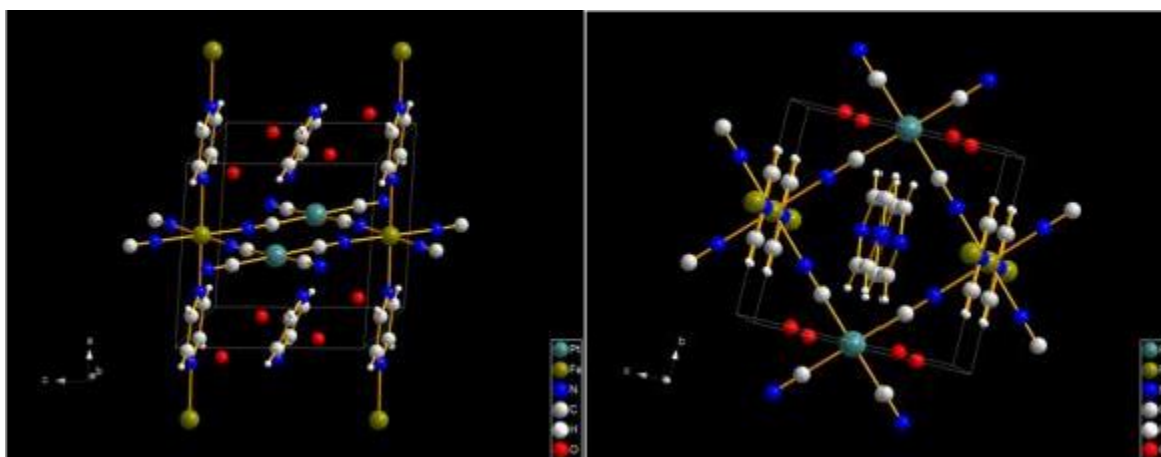
Fig. S2 A part of the structure of **1** (or **2**). Symmetry operations used to generate equivalent atoms: ('): -x,y,-z ; (''): -x,1-y,-z ; (''') : -1+x,y,z;(''''):1+x,y,z;(*):1-x,y,-z;(**):x,1-y,z; (***):1-x,1-y,-z; (****): 1+x, 1-y,z.

Figs. S3 The arrangement of pyrazine guest molecules (A-sites) and oxygen atoms (B-sites) in the lattice of **1** (or **2**). View in a direction almost parallel to -a crystallographic axis (left) and almost parallel to -b (right).

Crystallographic Tables

Table S1 Crystallographic parameters and data collection details

Identification code	**1 [CCDC: 1472612]**	**2 [CCDC: 1472613]**
Empirical formula	$C_{12}H_{10.40}FeN_8O_{1.20}Pt$	$C_{12}H_{10.40}FeN_8O_{1.20}Pd$
Formula weight	536.82	448.13
Temperature	160(2) K	160(2) K
Wavelength	1.54178 Å (Cu Kα)	1.54178 A
Crystal system	Monoclinic	Monoclinic
Space Group	P2/m	P2/m
Unit cell dimensions	a = 7.2727 (2) Å, α=90°	a = 7.2800 (1) Å, α=90°
	b = 7.4681 (1) Å, β= 95.939 (1)°	b = 7.4700 (1) Å, β= 95.880(1) °
	c = 7.4416 (2) Å, γ=90 °	c = 7.4387(1) Å, γ=90 °
Volume	402.01(2) Å ^{3}	402.40(1)
Z	1	1
Calculated density (Mg/m^3)	2.217	1.849
Absorption coefficient (mm^{-1})	23.44 mm^{-1}	16.410
F(000)	252	220
Crystal size (mm)	0.16 x 0.05 x 0.03	0.12 x 0.04 x 0.02
Theta range for data collection	8.11 to 64.99 °	8.11 to 64.98 °
Limiting indices	-8<=h<=8, -8<=k<=8, -8<=l<=8	-8<=h<=8, -8<=k<=8, -8<=l<=8
Reflections collected / unique	4331 / 742 [R(int)= 0.084]	4498 / 747 [R(int) = 0.0625]
Completeness to theta 64.98	99.0 %	99.1 %
Absorption correction	Empirical	Empirical
Max. and min. transmission	1.0 and 0.550	1.0 and 0.700
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	742/ 0 / 63	747 / 0 / 63
Goodness-of-fit on F^2	1.04	1.10
Final R indices [I>2sigma(I)]	R1 = 0.044, wR2 = 0.093 [a]	R1 = 0.0433, wR2 = 0.1055[a]
R indices (all data)	R1 = 0.046, wR2 = 0.094 [a]	R1 = 0.0446, wR2 = 0.1065[a]
Largest diff. peak and hole	2.59 and -2.5 e Å $^{-3}$	1.081 and -1.258

[a] $R_1 = \Sigma(|F_o|-|F_c|)/\Sigma(|F_o|)$ and $wR_2 = \{\Sigma[w(Fo^2-Fc^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$,
$w=1/[\sigma^2(F_o^2)+(\alpha P)^2+bP]$ and $P = ((\max F_o^2,0)+2F_c^2)/3$; a=0.0453, b=1.1717 for **1** and a=0.0442, b=1.6923 for **2**

Table S2 Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2) for **1.** U(eq) is defined as one third of the trace of the orthogonalized Uij tensor

	x	y	z	$U_{iso}{}^1/U_{eq}$
Pt	0.5000	0.0000	0.5000	0.0128 (3)
Fe	0.5000	0.5000	0.0000	0.0092 (6)
N1	0.1903 (11)	0.5000	-0.0110 (12)	0.012 (2)
C1	0.0947 (10)	0.3480 (11)	-0.0053 (10)	0.0160 (18)
H1	0.1579	0.2369	-0.0086	0.022^1
N11	0.1680 (17)	0.5000	0.4417 (17)	0.050 (4)
C11	0.0811 (10)	0.3422 (11)	0.4708 (12)	0.024 (2)
H11	0.1396	0.2319	0.4483	0.033^1
N21	0.5098 (8)	0.2944 (10)	0.2029 (9)	0.0157 (15)
C21	0.5094 (10)	0.1864 (11)	0.3101 (11)	0.0122 (18)
OW^2	0.050 (2)	1.0000	0.247 (2)	0.056 (5)

[1] isotropic displacement parameters (Å^2)

[2] the occupation factor was kept constant to the value of 0.3 during the refinement

Table S3 Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2) for **2.**
U(eq) is defined as one third of the trace of the orthogonalized Uij tensor

	x	y	z	U_{iso}[1]/U_{eq}
Pd	0.5000	0.0000	0.5000	0.0128 (3)
Fe	0.5000	0.5000	0.0000	0.0091 (4)
N1	0.1905 (7)	0.5000	-0.0112 (7)	0.0122 (12)
C1	0.0946 (6)	0.3470 (6)	-0.0060 (7)	0.0176 (11)
H1	0.1575	0.2360	-0.0107	0.025[1]
N11	0.1683 (11)	0.5000	0.4454 (11)	0.047 (2)
C11	0.0819 (6)	0.3429 (7)	0.4701 (8)	0.0236 (13)
H11	0.1395	0.2330	0.4443	0.033[1]
N21	0.5104 (5)	0.2957 (6)	0.2006 (6)	0.0160 (10)
C21	0.5072 (6)	0.1858 (7)	0.3112 (7)	0.0129 (10)
OW[2]	0.0508 (16)	1.0000	0.2493 (16)	0.054 (3)

[1] isotropic displacement parameters (Å^2)

[2] the occupation factor was kept constant to the value of 0.3 during the refinement

Table S4 Bond lengths [Å] and angles [°] for **1** and **2**

Pt-C(21)	1.990 (8)	1.979(5)
Fe-N(21)	2.149 (7)	2.130(5)
Fe-N(1)	2.245 (8)	2.246(5)
N(1)-C(1)	1.334 (9)	2.246(5)
C(1)-C(1)'	1.388 (14)	1.389(9)
N(11)-C(11)	1.365 (10)	1.353(6)
C(11)-C(11)#3	1.299 (15)	1.315(9)
N(21)-C(21)	1.135 (11)	1.164(7)
C(21)-Pt-C(21) #1	88.8 (5)	89.1(3)
C(21)-Pt-C(21)#2	180.0	180.0(1)
C(21)-Pt-C(21) #4	91.2 (5)	90.9(3)
N(21)-Fe-N(21)**	91.2 (4)	91.5(2)
N(21)-Fe-N(21)*	88.8 (4)	88.5(2)
N(21)-Fe-N(1)	89.2(2)	89.40(14)
N(21)*-Fe-N(1)	90.8(2)	90.60(14)
C(1)-N(1)-C(1)**	116.6 (9)	116.7(5)
C(1)-N(1)-Fe	121.5 (4)	121.5(3)
N(1)-C(1)-C(1)'	121.7 (4)	121.6(3)
C(11)**-N(11)-C(11)	119.4 (12)	120.4(7)
C(11)#3-C(11)-N(11)	120.3 (6)	119.7(3)
C(21)-N(21)-Fe	177.9 (7)	176.7(4)
N(21)-C(21)-Pt	178.0 (8)	179.6(5)

(#1): x,-y,z; (#2): 1-x,-y,1-z; (#3): -x,y,1-z; (#4):1-x,y,1-z

(*): 1-x,y,-z ; (**): x,1-y,z; ('): -x,y,-z

3. Physical Methods

Infrared (IR) Spectra

The IR data for **1-2** (Fig. S4) show the occurrence of three main groups of bands. These bands can be assigned to the water molecules (OH stretching; 3400-3000 cm^{-1}), the CN^{-} group (CN stretching; 2170 cm^{-1}) and the characteristic bands belonging to the pyrazine molecule (CN stretching, ring deformation and CH out of plane deformation; 1603-600 cm^{-1}.
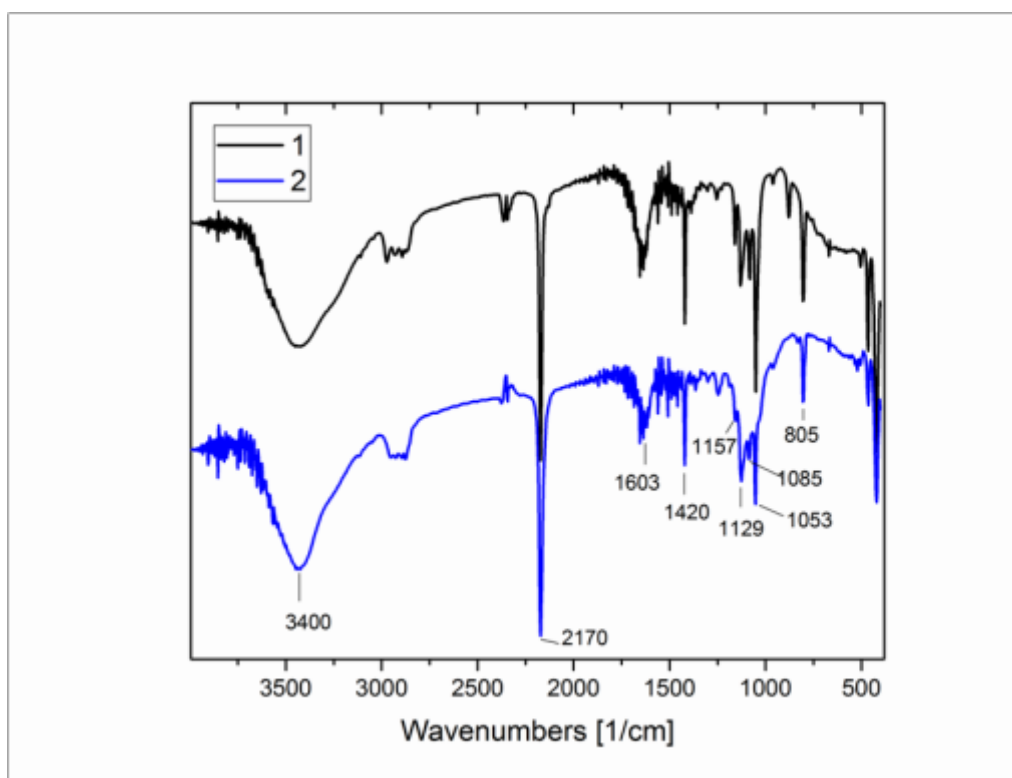

Fig. S4 Comparison of Infrared spectra for **1** and **2**.

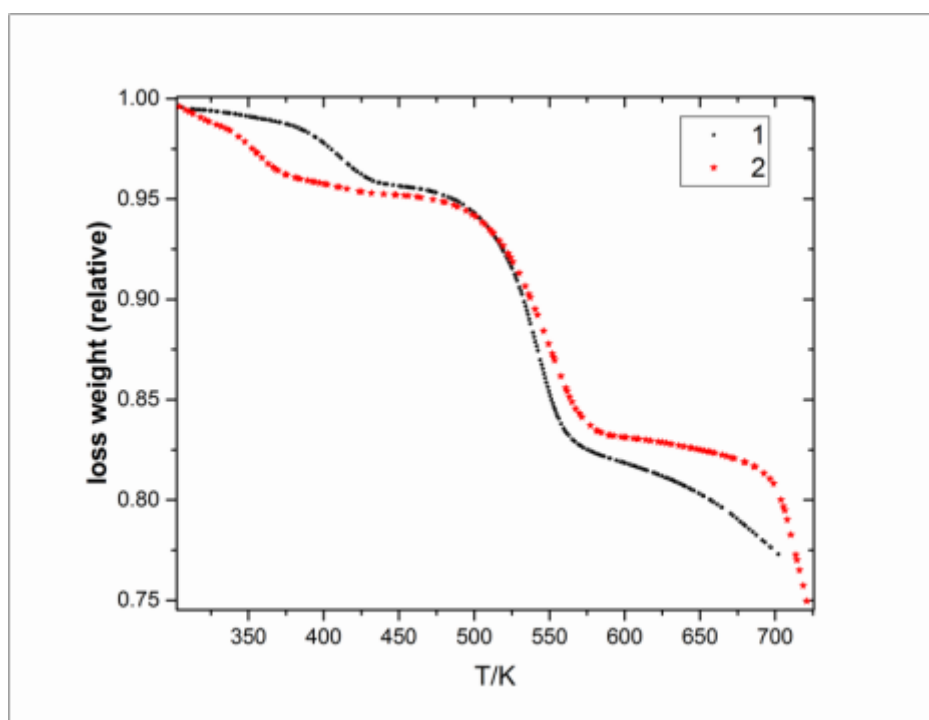**Thermogravimetric Analysis (TGA)**

Fig. S5 Water loss occurs in the temperature range of 320-430 K for samples **1**, **2**. Decomposition of these samples occurs at approximately 500 K.
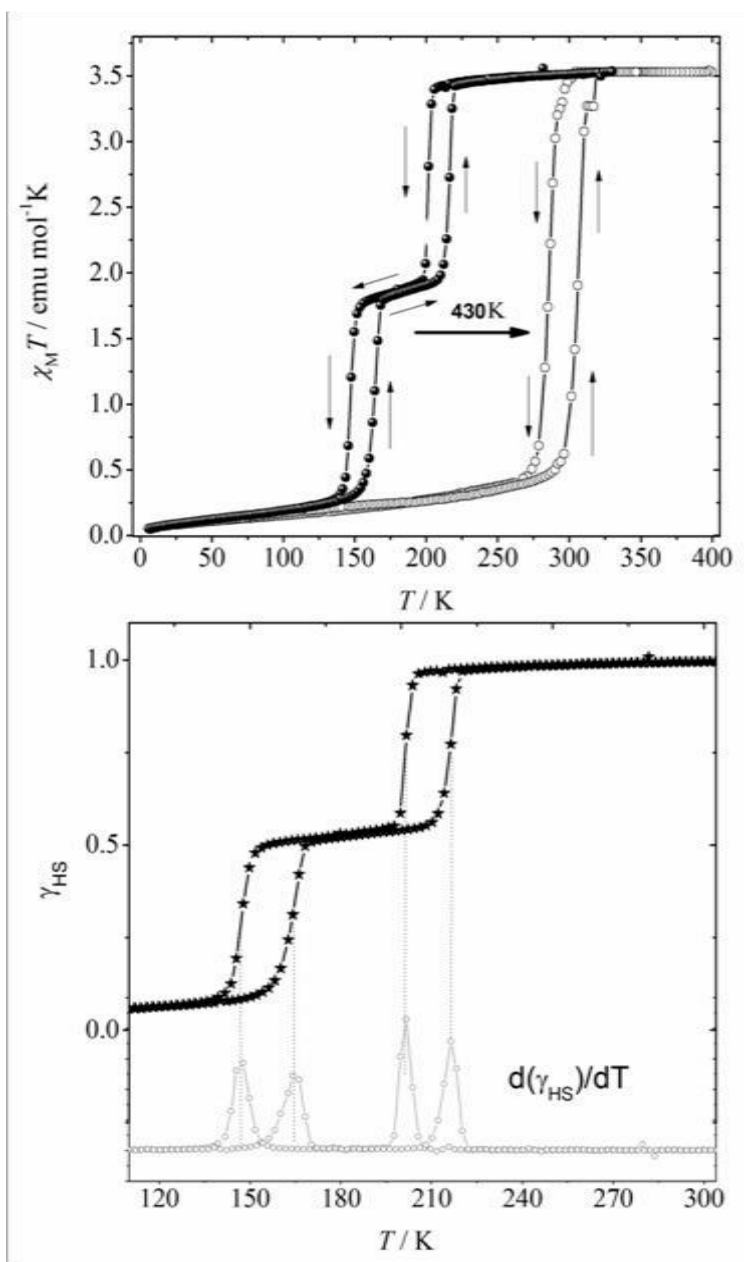
4. Magnetic Data

Fig. S6 Thermal dependence of the $\chi_M T$ product of compound **2** before and after heating to 430 K using a cooling/heating rate of 2 K/min. In the same Figure (lower) is shown the curves of $\gamma_{HS}(T)$, the molar fraction of high-spin (HS) molecules, as a function of temperature along with the derivative of $\gamma_{HS}(T)$.