Supplementary Information

Hydrogen-bonded Networks of $[Fe(bpp)_2]^{2+}$ Spin Crossover Complexes and dicarboxylate anions: structural and photomagnetic properties

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Table S1 Intermolecular hydrogen bonds in the crystal structure of **1**·$4H_2O$.[a]

D···A	$d_{D\cdots A}$/Å
N(1)···O(4)#1	2.612(18)
N(5)···O(2)#2	2.768(12)
N(6)···O(3)	2.673(2)
N(10)···O(1W)	2.700(9)
O(1)···O(3W)	2.727(2)
O(2)···O(2W)	2.844(15)
O(2)···O(4W)#3	2.790(2)
O(3)···O(1W)#4	2.745(7)
O(1W)···O(4W)#5	2.717(7)
O(2W)···O(2W)#6	2.861(4)
O(2W)···O(3W)#3	2.842(19)
O(3W)···O(4W)	2.756(13)

[a] Symmetry transformations used to generate equivalent atoms:

#1 $x-1, -y+1/2, z-1/2$ #2 $-x, y-1/2, -z+3/2$
#3 $x-1, y, z$ #4 $x+1, y, z$
#5 $x-1, -y+1/2, z+1/2$ #6 $-x, -y+1, -z+2$

Table S2 Intermolecular hydrogen bonds in the crystal structure of **2**·2MeOH·H_2O.[a]

D···A	$d_{D\cdots A}$/Å
N(1)···O(3)#1	2.649(6)
N(5)···O(4)#2	2.641(6)
N(6)···O(6)	2.679(7)
N(10)···O(8)	2.592(6)
N(11)···O(1)	2.591(6)
N(15)···O(2)#3	2.704(7)
N(16)···O(3S)	2.638(6)
N(20)···O(1W)#4	2.635(6)
O(2)···O(4S)#5	2.731(9)
O(3)···O(1S)#1	2.784(8)
O(5)···O(2S)#3	2.702(6)
O(5)···O(2W)#3	2.811(8)
O(6)···O(1W)	2.793(7)
O(7)···O(3S)	2.591(7)
O(1W)···O(2W)	2.780(8)
O(2W)···O(2S)#6	2.806(8)

[a] Symmetry transformations used to generate equivalent atoms:

#1 $-x, -y+1, -z+2$ #2 $-x+1, -y+1, -z+2$
#3 $x-1, y, z$ #4 $x, y+1, z$
#5 $x+1, y, z$ #6 $-x+1, -y, -z+1$

Table S3 Intermolecular hydrogen bonds in the crystal structure of **2**·5H_2O.[a]

D···A	$d_{D\cdots A}$/Å
N(1)···O(1W)#1	2.651(9)
N(5)···O(2)#2	2.584(11)
N(6)···O(3B)#1	2.885(15)
N(6)···O(9W)#1	2.520(11)
N(10)···O(3A)#3	2.705(13)
N(10)···O(4B)#3	2.567(13)
O(1)···O(2W)	2.938(12)
O(1)···O(3W)	2.924(11)
O(2)···O(1W)#4	2.739(11)
O(3B)···O(8W)#5	2.849(15)
O(4A)···O(10W)	2.572(13)
O(4A)···O(8W)	2.883(15)
O(1W)···O(2W)	2.724(8)
O(3W)···O(3W)#6	2.811(6)
O(4W)···O(6W)	2.702(8)
O(5W)···O(6W)#7	2.960(8)
O(7W)···O(8W)#7	2.910(8)
O(7W)···O(10W)	2.499(8)
O(8W)···O(9W)#1	2.458(7)

[a] Symmetry transformations used to generate equivalent atoms:

#1 $x-1, y, z$ #2 $x, y-1, z$ #3 $x-1, y-1, z$
#4 $x, y+1, z$ #5 $x+1, y, z$ #6 $-x, -y+1, -z-1$
#7 $-x+1, -y+1, -z$

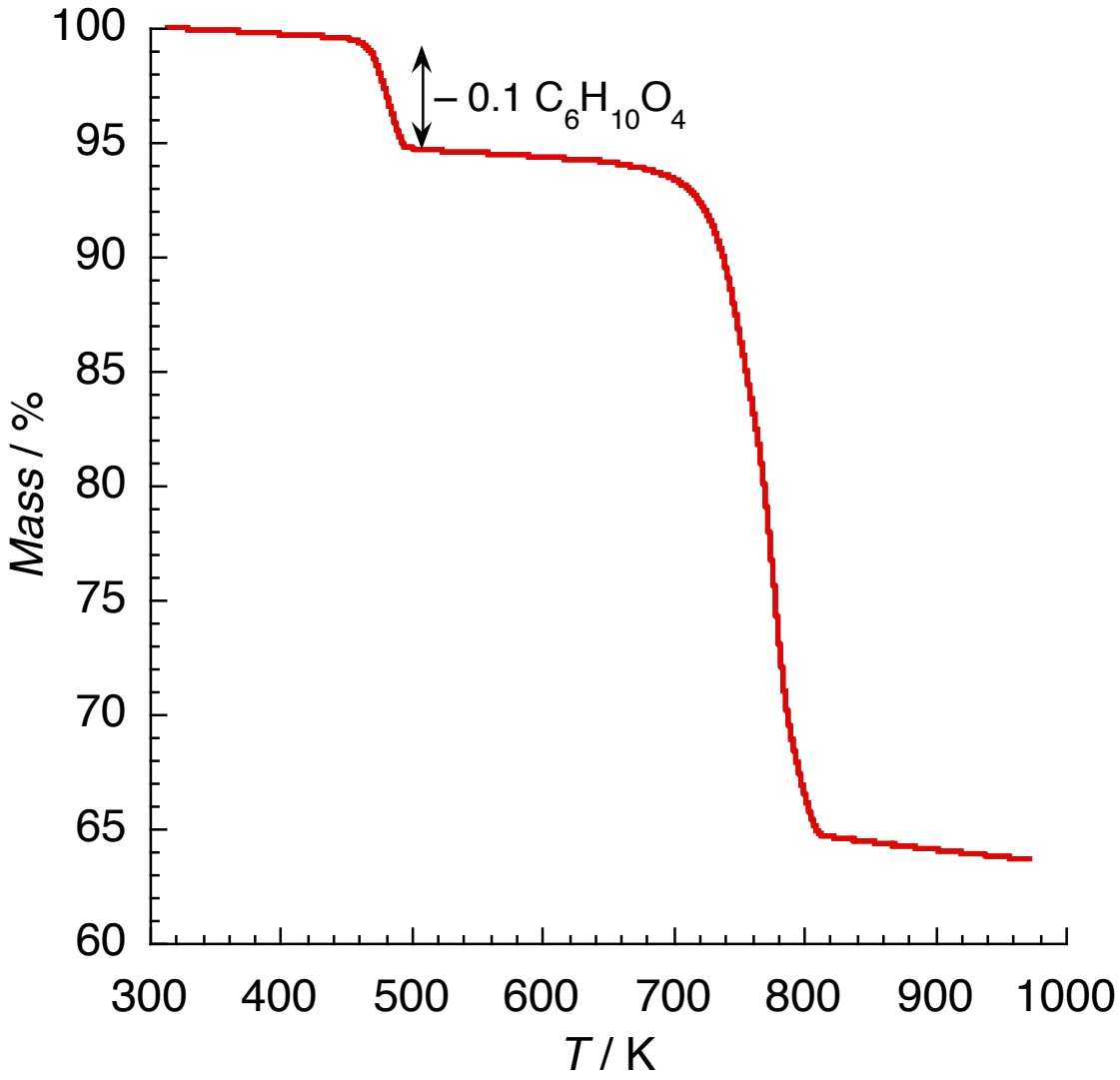

Fig. S1. Thermogravimetric analysis of $Ba(C_6H_8O_4) \cdot 0.1\ C_6H_{10}O_4$. The plot shows the loss of the adipic acid content. Water molecules of crystallization are not present in this salt.

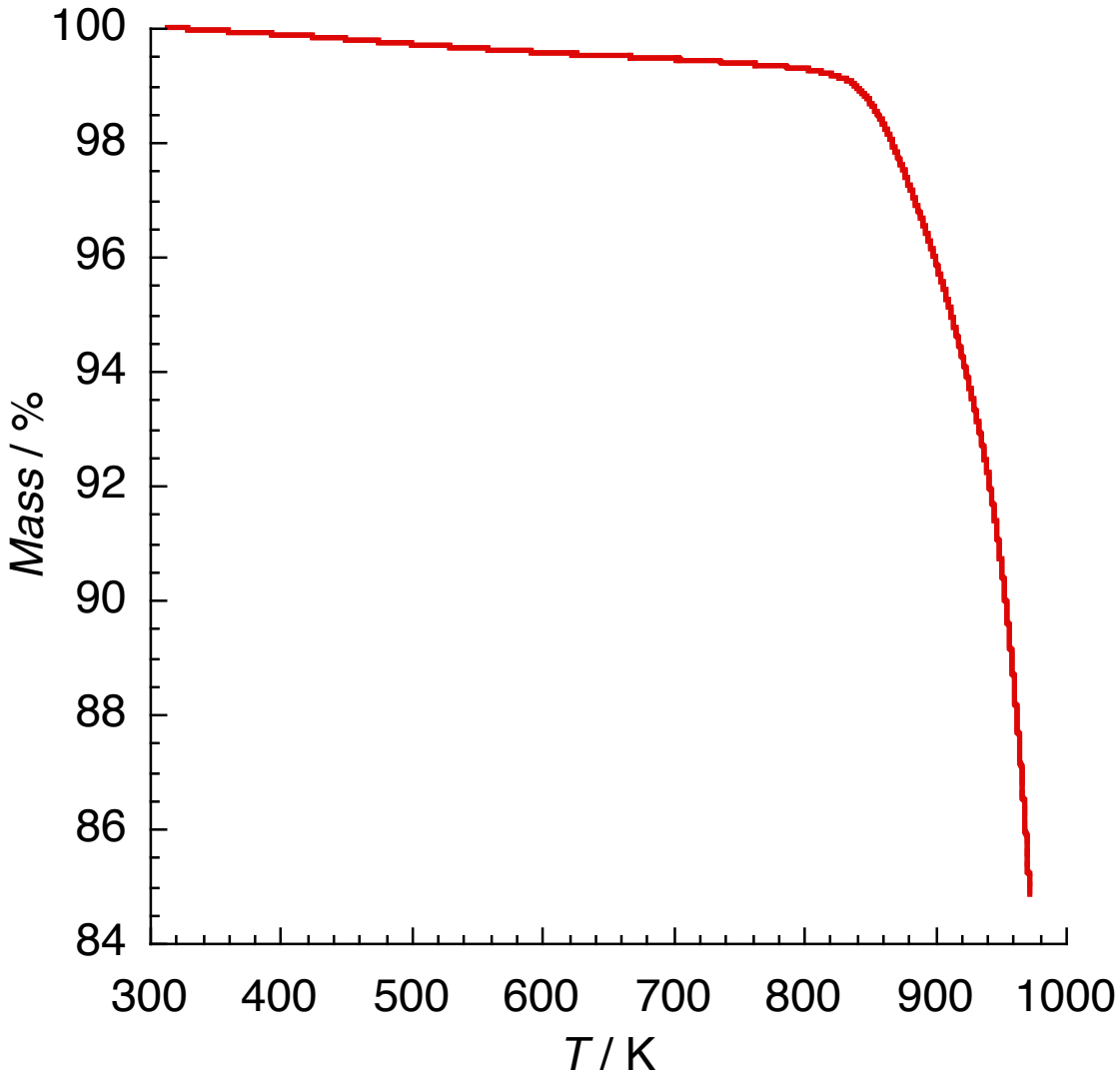

Fig. S2. Thermogravimetric analysis of $Ba(C_8H_4O_4)$. The plot confirms the anhydrous character of this salt.

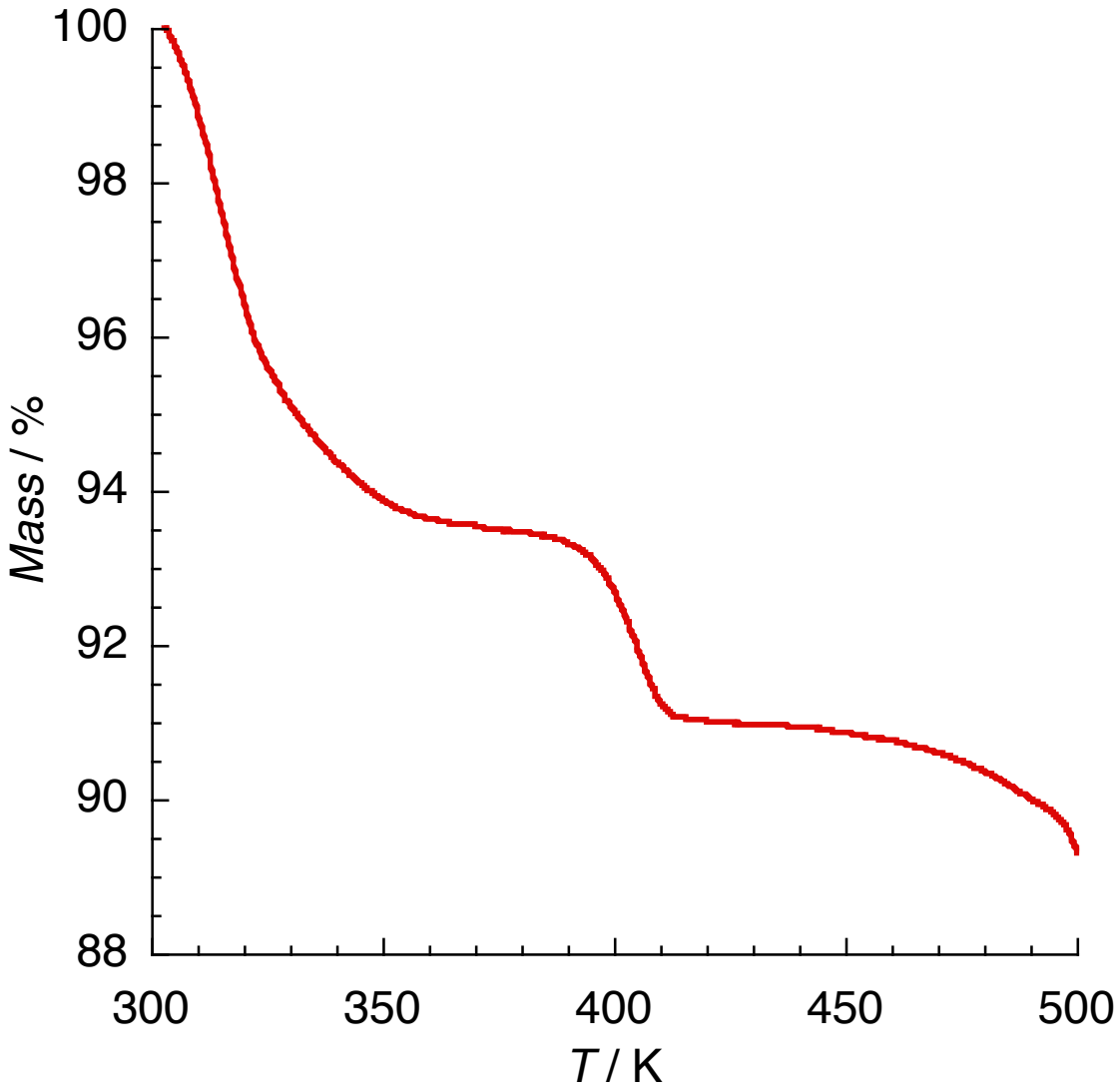

Fig. S3. Thermogravimetric analysis of **1**·4H_2O.

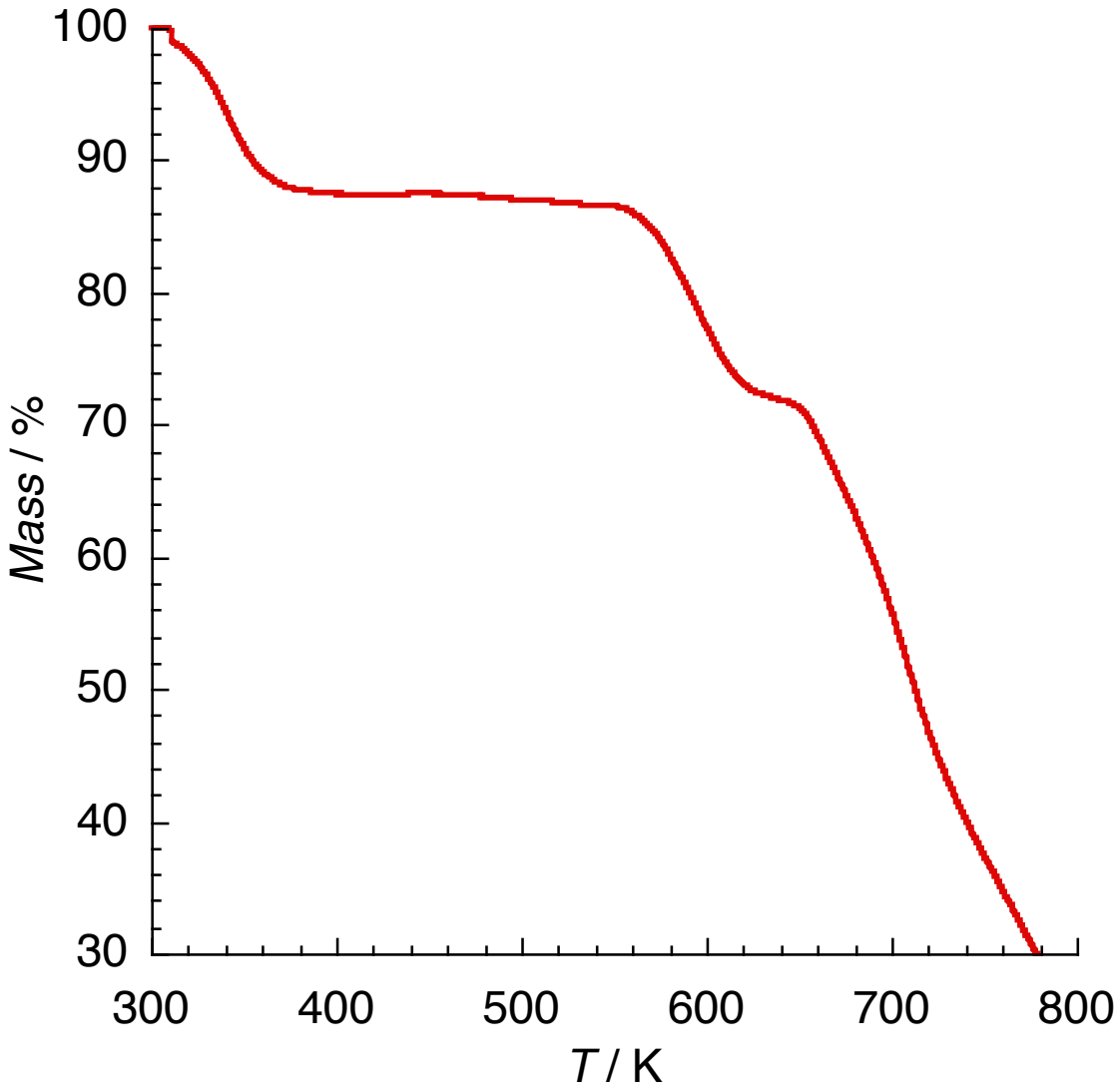

Fig. S4. Thermogravimetric analysis of **2**·5H_2O.

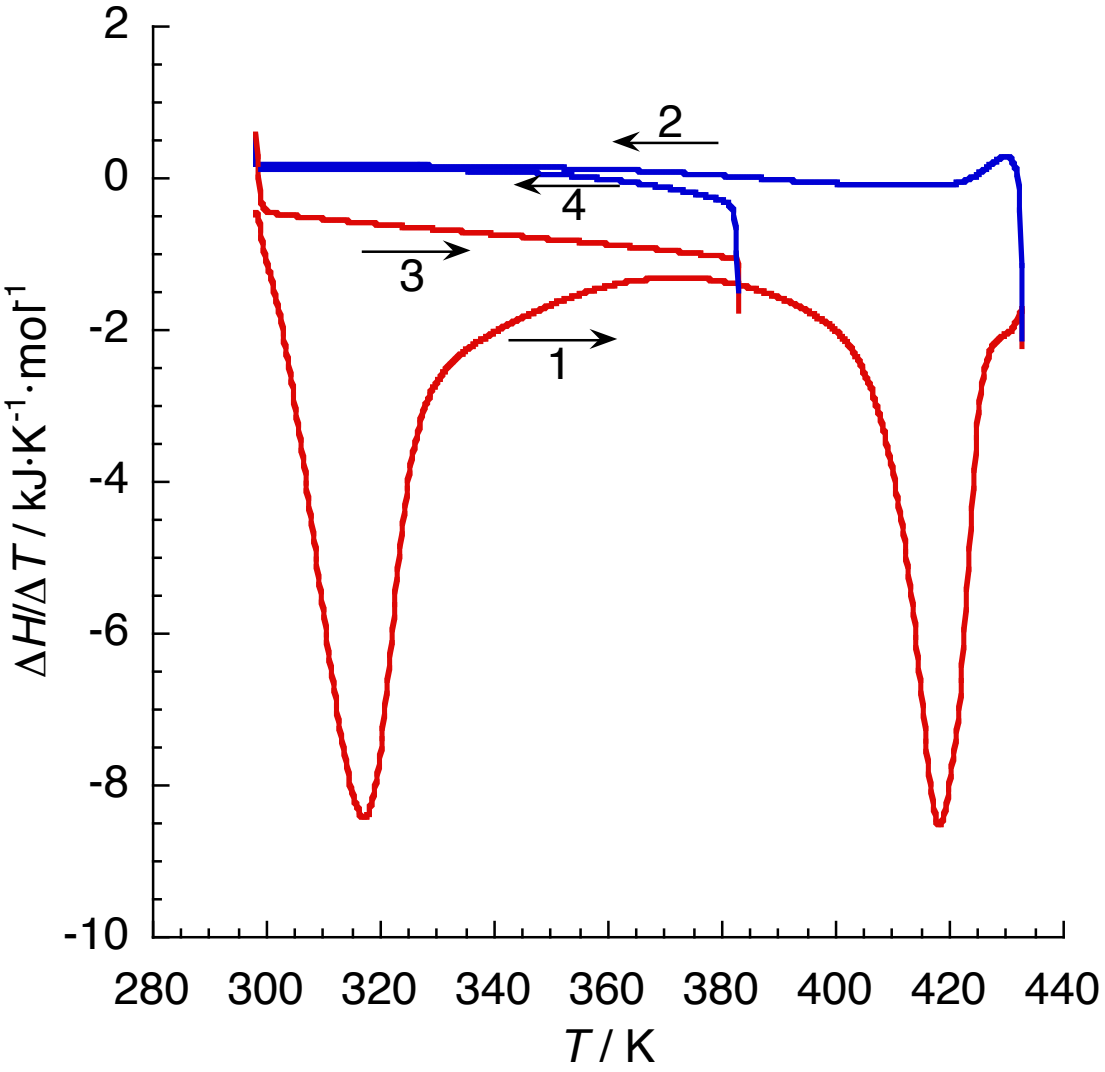

Fig. S5. Differential scanning calorimetry of **1**·4H_2O. Curve 1: first heating (dehydration process). Curve 2: first cooling. Curves 3 and 4: second temperature cycle.

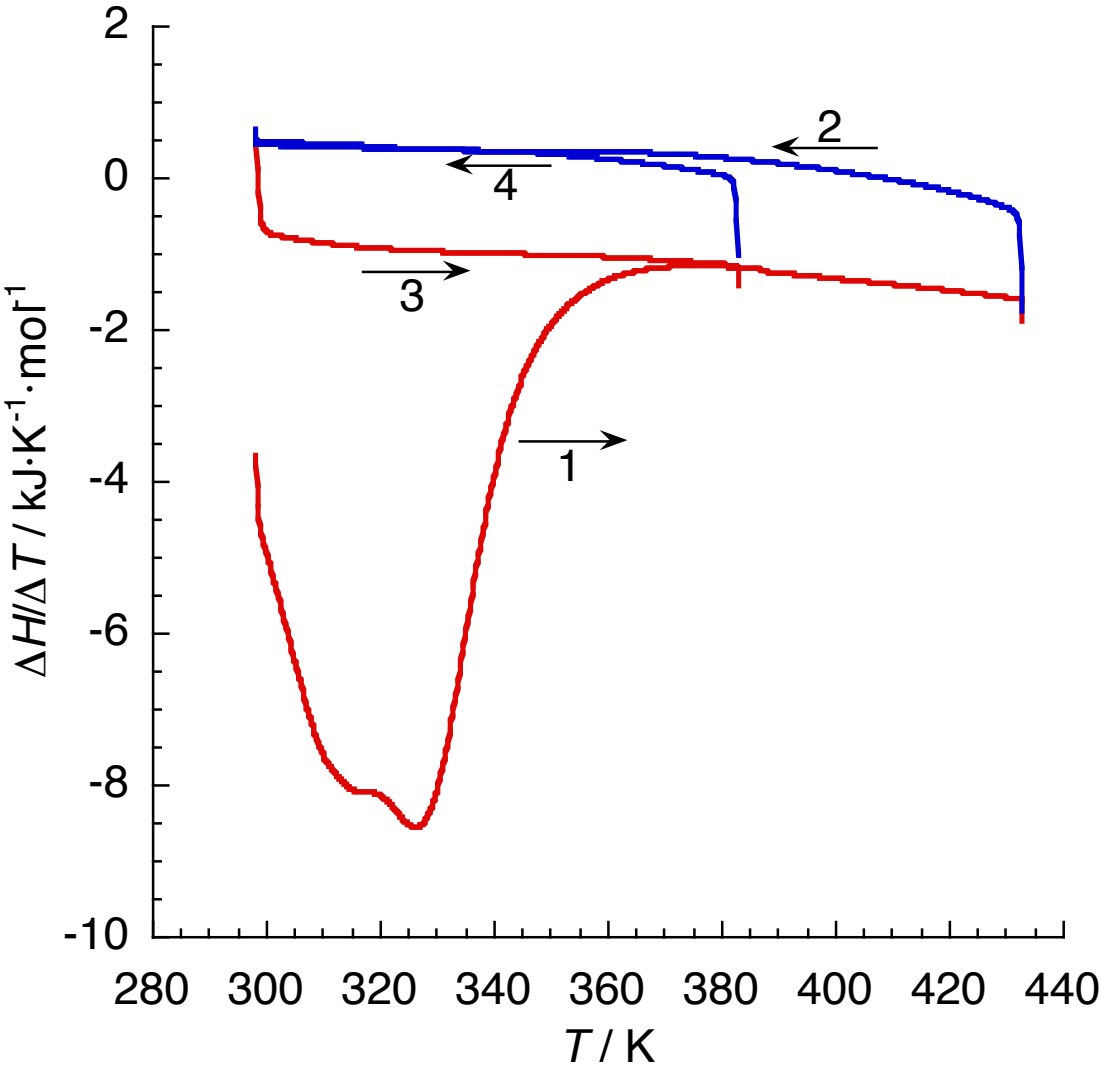

Fig. S6. Differential scanning calorimetry of **2**·5H_2O. Curve 1: first heating (dehydration process). Curve 2: first cooling. Curves 3 and 4: second temperature cycle.

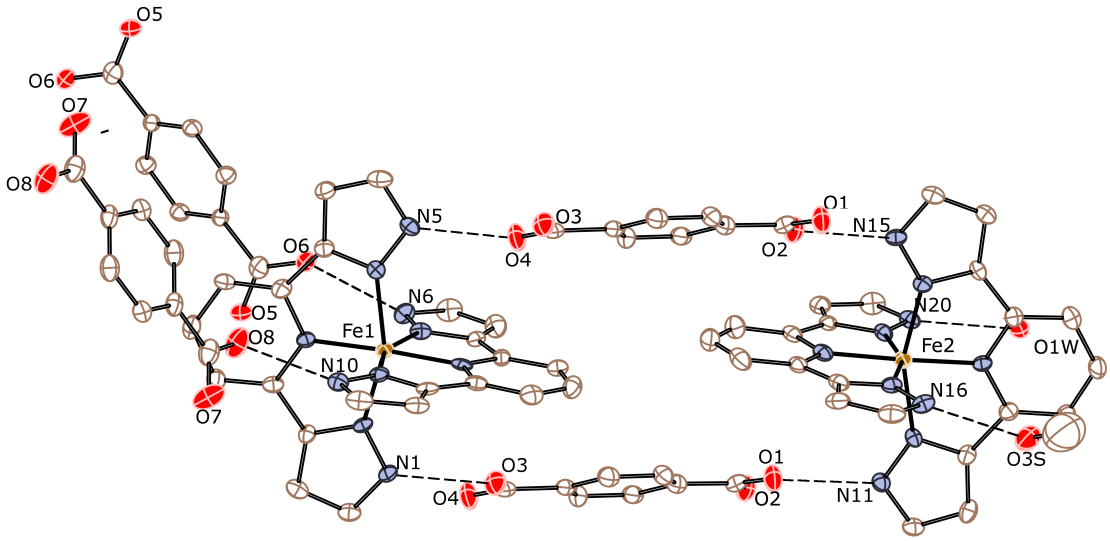

Fig. S7. Thermal ellipsoid plot of the crystal structure of **2**·2MeOH·H_2O showing the two inequivalent $[Fe(bpp)_2]^{2+}$ cations, the three crystallographically independent terephthalate anions and the two solvent molecules present in the second coordination sphere of the Fe2 site. Dashed lines refer to H bonds. Thermal ellipsoids are drawn at the 50 % probability level.

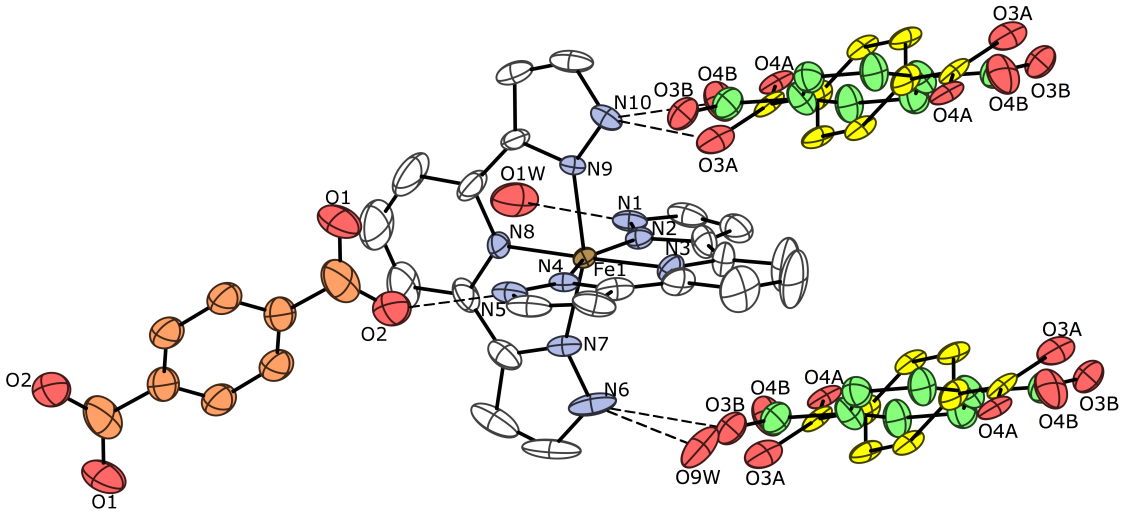

Fig. S8 Thermal ellipsoid plot of the crystal structure of **2**·5H_2O showing the second coordination sphere of the iron(II) complexes. Two terephthalate anions are disordered into two positions, A (yellow) and B (green). Thermal ellipsoids are drawn at the 50 % probability level.

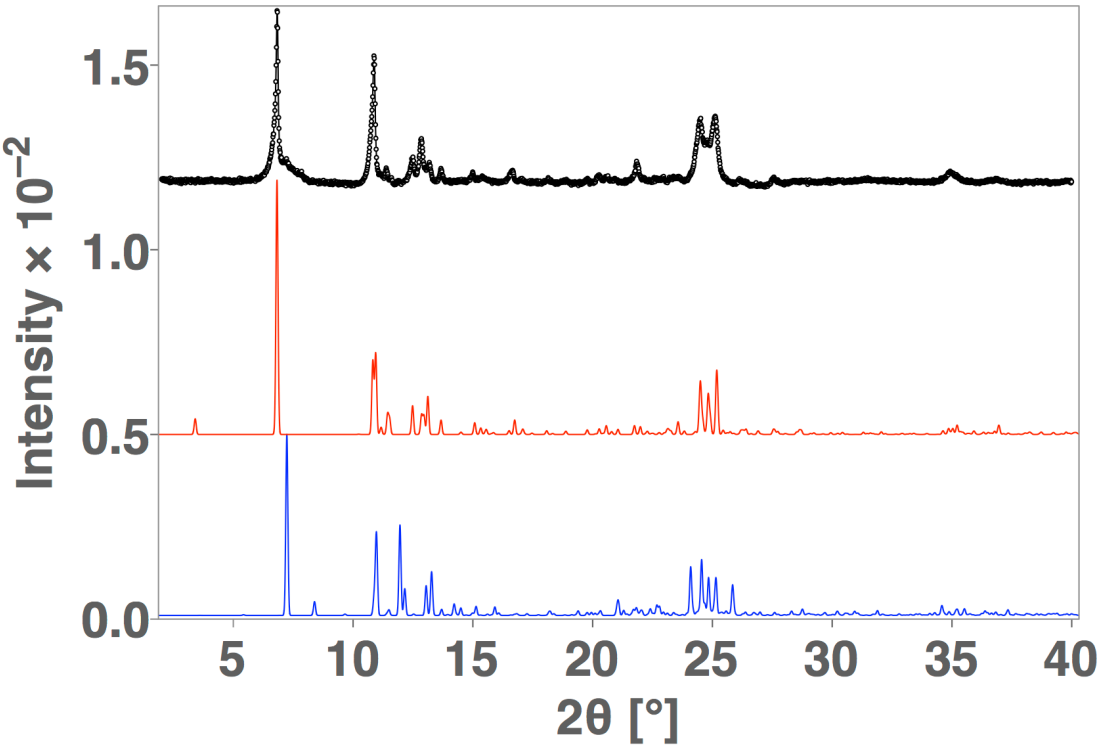

Fig. S9 Comparison of the powder diffractogram of **2**·5H_2O with simulations obtained from single crystal data of **2**·5H_2O and **2**·2MeOH·H_2O (red and blue lines, respectively).

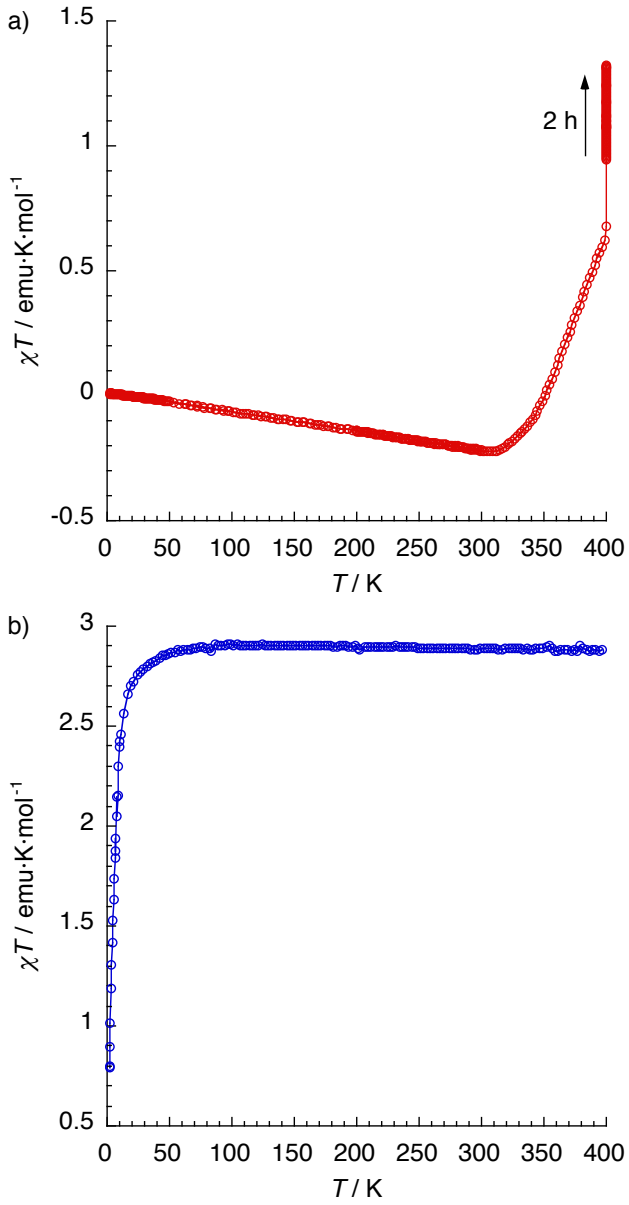

Fig. S10 Thermal variation of the χT product of a) an as synthesized sample of **1**·4H_2O; b) a dehydrated sample of **1**. No diamagnetic corrections were applied.

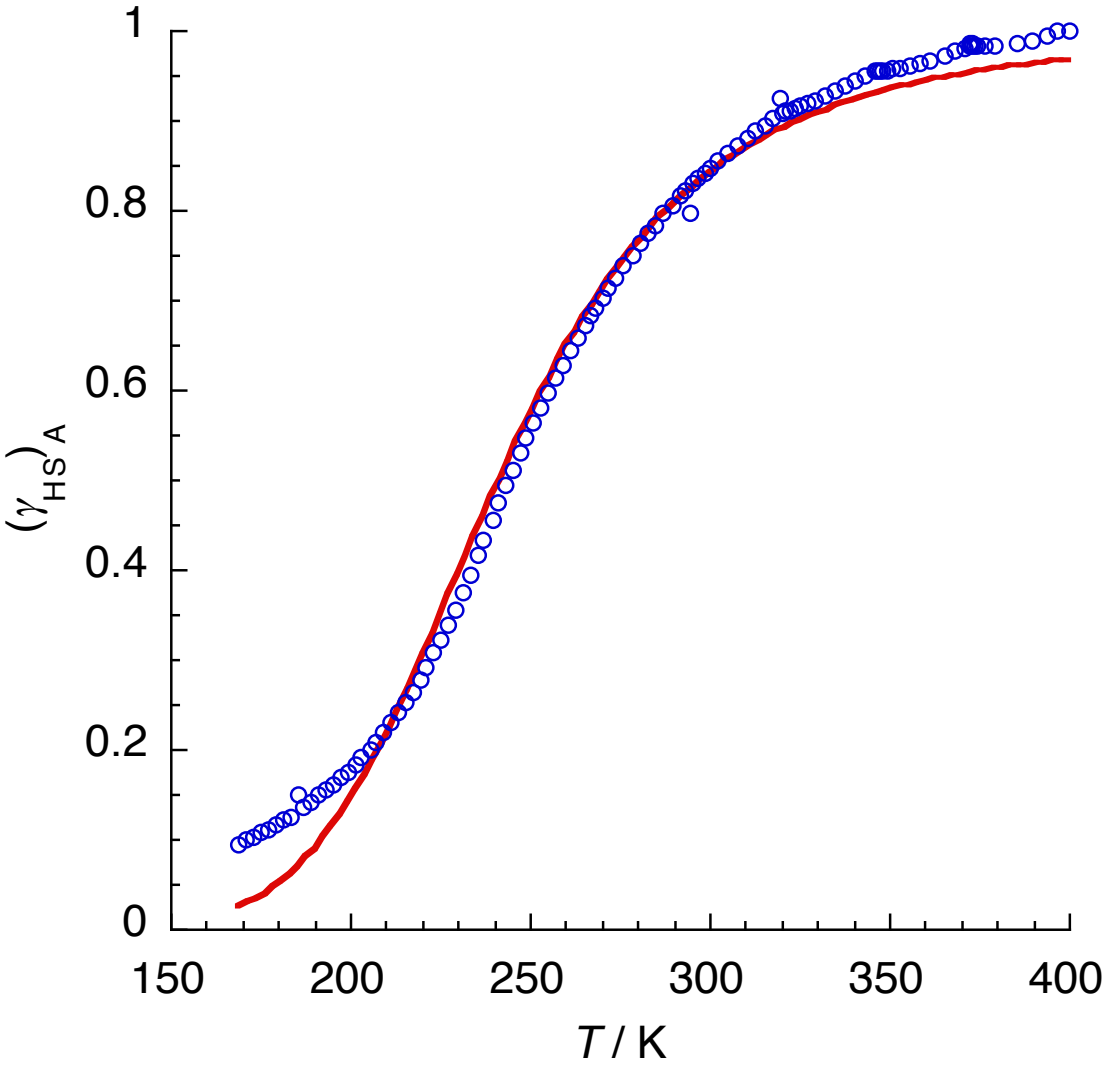

Fig. S11. Temperature dependence of the fraction of high-spin centers corresponding to iron site A , $(\gamma_{HS})_A$, of compound **2**. $(\gamma_{HS})_A$ was calculated from the overall fraction of high-spin centers γ_{HS} following the equation $(\gamma_{HS})_A = 2\gamma_{HS} - 1$. The red line corresponds to the best fit to a Boltzmann distribution with thermodynamic parameters ΔH = 17.2 ± 0.3 kJ·mol^{-1} and ΔS = 57.8 ± 1.2 J·K^{-1}·mol^{-1}