Electronic Supplementary Material (ESI) for Dalton Transactions

SUPPORTING INFORMATION

Cu(I), Co(II) and Fe(II) coordination polymers with pyrazine and benzoate as ligands. Spin crossover, spin canting and metamagnetism phenomena

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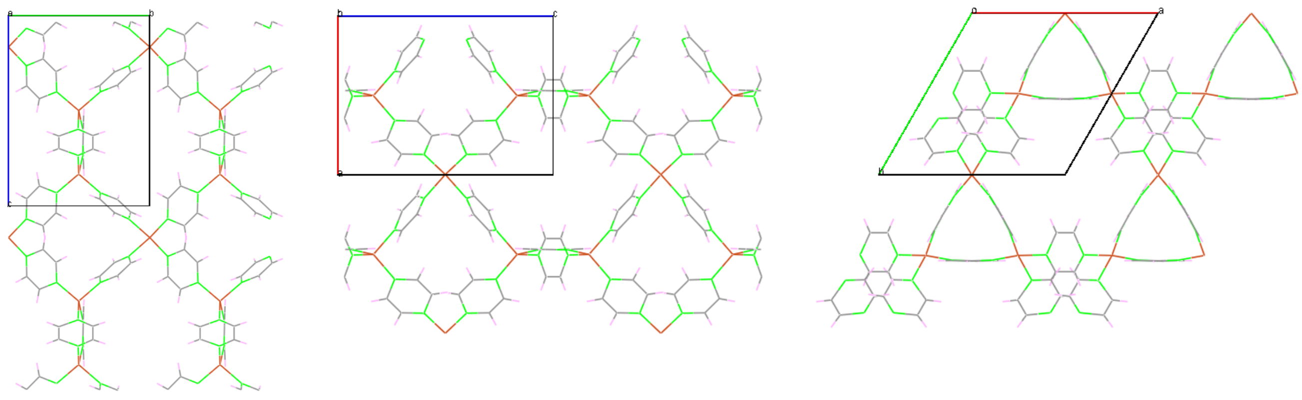
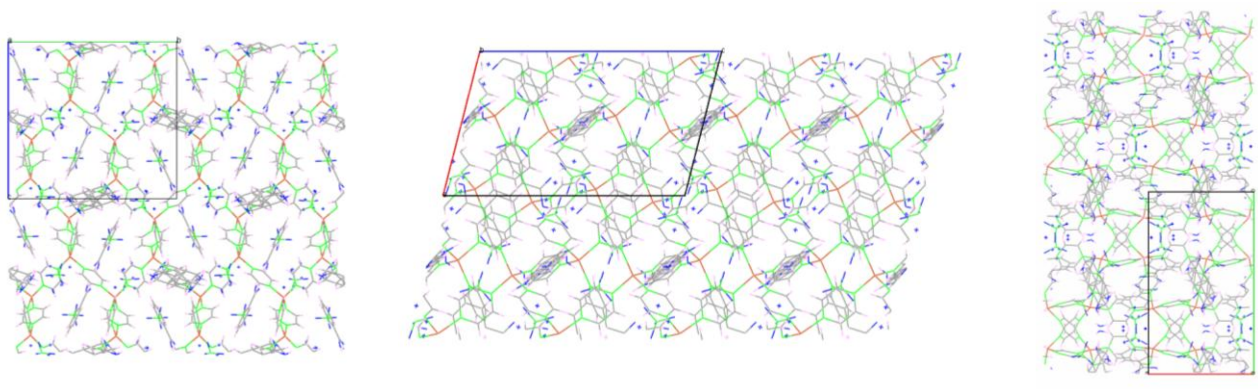


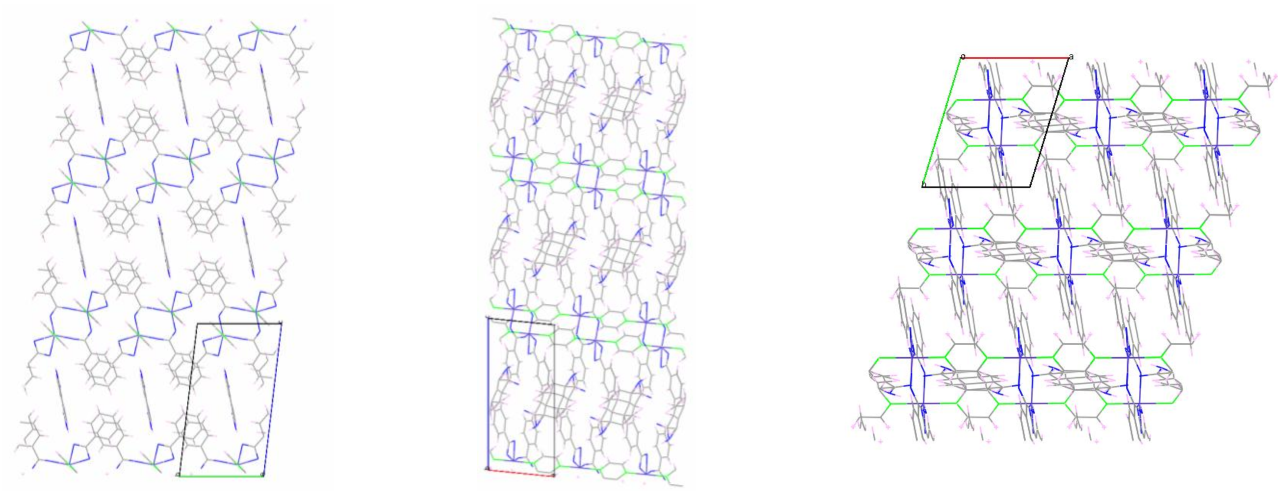
(a) **(b)** **(c)**

Figure S1. Projections of the crystal packing of compound **1** along the crystallographic (a) *a*, (b) *b* and (c) *c* axes, respectively. The counterions and solvent molecules placed in the channels are nor depicted in these pictures.



(a) **(b)** **(c)**

Figure S2. Crystal packing of compound **2** along the crystallographic (a) *a*, (b) *b* and (c) *c* axes, respectively. The solvation benzoic acid molecules are disordered over two symmetry related positions.



(a) (b) (c)

Figure S3. Crystal packing of compound **3** along the crystallographic (a) *a*, (b) *b* and (c) *c* axes, respectively. Compound **4** is isotructural to **3**. The solvation benzoic acid molecules are disordered over two symmetry related positions.

Table S1. Selected bond lengths and angles (Å,º) of compounds **1** and **2**.[a]

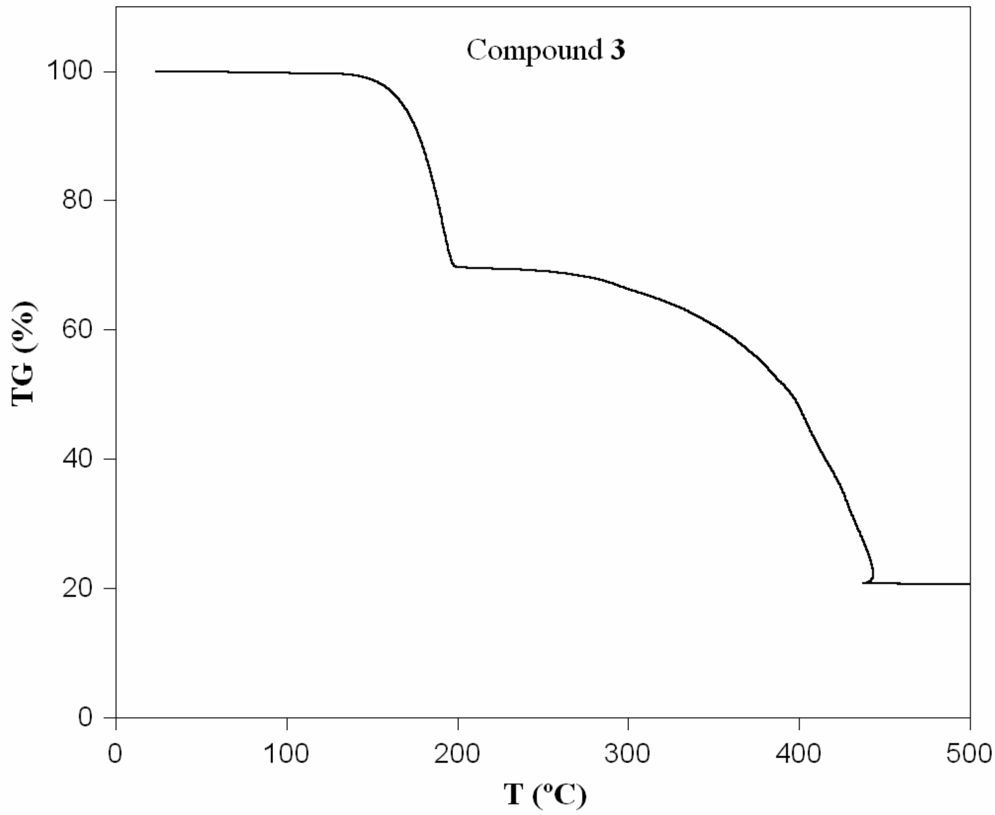
Compound **1**		Compound **2**			
Cu1–N1	2.055(8)	Cu1–N1	2.078(3)	Cu2–N2	2.036(3)
Cu1–N2	2.022(10)	Cu1–N3	2.023(3)	Cu2–N4^{i}	2.024(3))
		Cu1–N5	2.082(3)	Cu2–N7^{ii}	2.035(3)
		Cu1–N6	2.000(3)	Cu2–N8	2.068(3)
N1–Cu1–N1^{i}	100.5(5)	N1–Cu1–N3	104.05(12)	N2–Cu1–N4^{i}	108.16(12)
N1–Cu1–N2	122.8(4)	N1–Cu1–N5	114.24(12)	N2–Cu1–N7^{ii}	100.31(12)
N1–Cu1–N2^{i}	103.5(3)	N1–Cu1–N6	101.13(12)	N2–Cu1–N8	118.88(12)
N2–Cu1–N2^{i}	105.3(6)	N3–Cu1–N5	100.38(12)	N4^{i}–Cu1–N7^{ii}	127.94(12)
		N3–Cu1–N6	133.83(12)	N4^{i}–Cu1–N8	101.70(12)
		N5–Cu1–N6	103.61(12)	N7^{ii}–Cu1–N8	101.21(11)

[a]Symmetry codes: for **1** (i) x, x–y, –z; for **2** (i) –x, –y, –z + 1; (ii) x, -y+1/2, z+1/2.

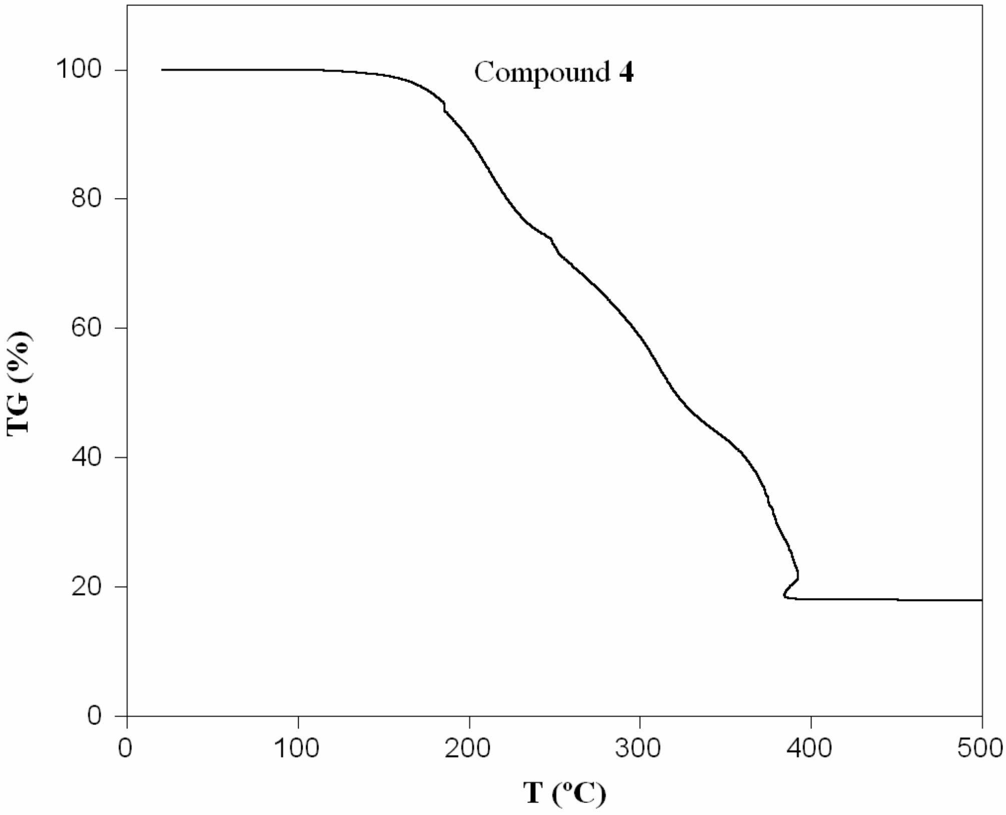
Table S2. Selected bond lengths and angles (Å,º) of compounds **3** and **4**.[a]

Compound **3**	*100 K*	*293 K*	Compound **4**	*293 K*
Co1–N1	2.172(3)	2.183(2)	Fe1–N1	2.253(5)
Co1–N2	2.160(4)	2.179(2)	Fe1–N2	2.228(5)
Co1–O1	2.160(3)	2.161(2)	Fe1–O1	2.181(5)
Co1–O2	2.168(3)	2.160(2)	Fe1–O2	2.230(5)
Co1–O3	2.000(3)	1.990(2)	Fe1–O3	2.023(5)
Co1–O4^{i}	2.008(3)	1.999(2)	Fe1–O4^{i}	2.038(4)
Co1···Co1^{i}	4.1635(13)	4.1736(8)	Fe1···Fe1^{i}	4.098(3)
Co1···Co1^{ii}	7.1207(3)	7.1488(4)	Fe1···Fe1^{ii}	7.268(7)
N1–Co1–N2	179.26(13)	178.90(8)	N1–Fe1–N2	178.0(2)
N1–Co1–O1	90.79(12)	91.28(7)	N1–Fe1–O1	89.97(18)
N1–Co1–O2	85.73(12)	86.32(8)	N1–Fe1–O2	86.61(19)
N1–Co1–O3	86.83(12)	86.95(9)	N1–Fe1–O3	89.2(2)
N1–Co1–O4^{i}	88.01(12)	88.12(8)	N1–Fe1–O4^{i}	88.27(19)
N2–Co1–O1	89.80(12)	89.71(7)	N2–Fe1–O1	91.83(18)
N2–Co1–O2	94.17(12)	93.75(9)	N2–Fe1–O2	93.56(19)
N2–Co1–O3	93.60(13)	93.50(9)	N2–Fe1–O3	91.6(2)
N2–Co1–O4^{i}	91.26(12)	90.78(8)	N2–Fe1–O4^{i}	89.76(19)
O1–Co1–O2	60.80(11)	60.33(7)	O1–Fe1–O2	59.71(18)
O1–Co1–O3	91.78(12)	91.92(8)	O1–Fe1–O3	90.6(2)
O1–Co1–O4^{i}	154.70(13)	153.86(8)	O1–Fe1–O4^{i}	149.6(2)
O2–Co1–O3	151.41(12)	151.24(9)	O2–Fe1–O3	149.96(18)
O2–Co1–O4^{i}	93.92(12)	93.56(8)	O2–Fe1–O4^{i}	89.9(2)
O3–Co1–O4^{i}	113.37(13)	114.13(9)	O3–Fe1–O4^{i}	119.7(2)

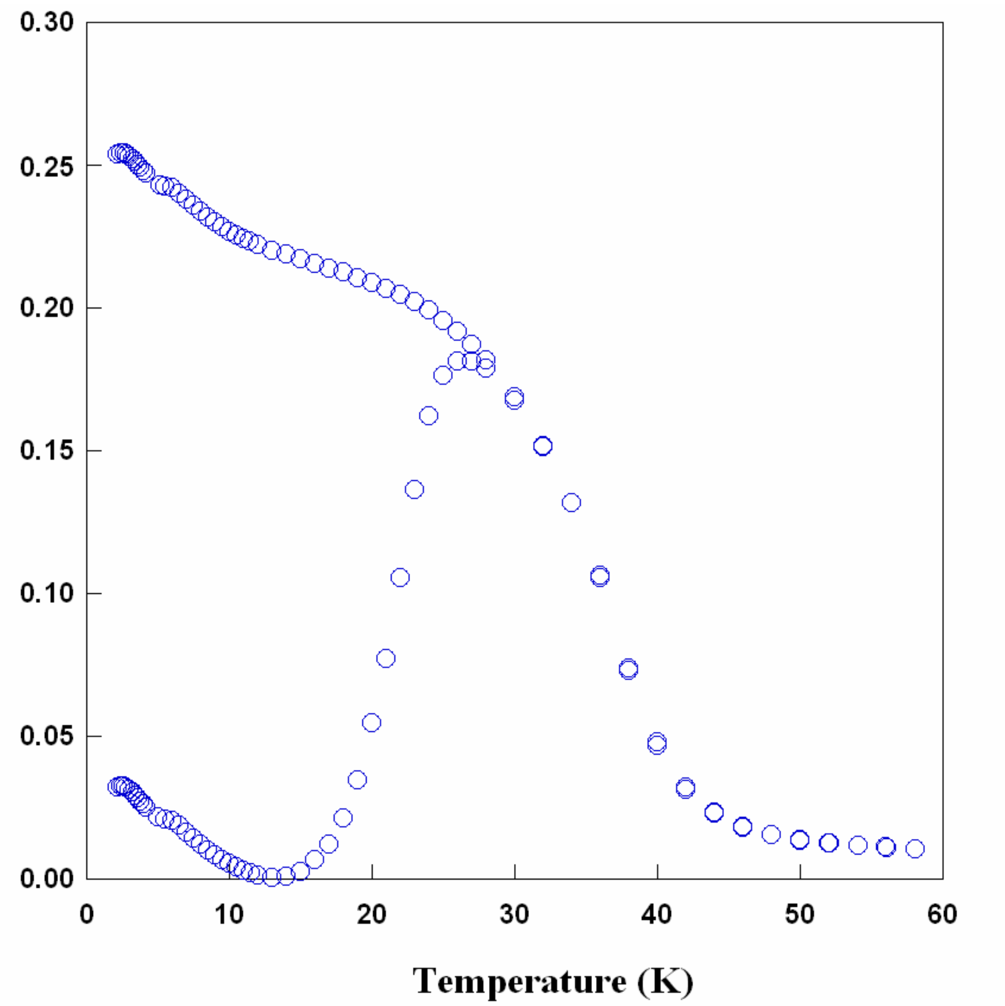
[a]Symmetry codes: (i) –x+1,–y+1,–z+2; (ii) x+1,y,z.



Figures S4. Thermogravimetric curve under synthetic air atmosphere of compound **3**.



Figures S5. Thermogravimetric curve under synthetic air atmosphere of compound **4**.



Figures S6. Field cooling (FC) and zero-field cooling (ZFC) magnetization curves for compound **3** under an applied magnetic field of 100 Oe.

Hydrothermal Synthesis of $[Cu^{II}_2(Bz)_4(pyz)]_n$

A mixture of $Cu(ClO_4)_2 \cdot 6H_2O$ (0.250 g, 0.67 mmols), pyrazine (0.053 g, 0.67 mmols) and sodium benzoate (0.097 g, 0.67 mmols) in 16 mL of water, pH 6-7, was fully stirred at 25 ºC, sealed in a 23 mL Teflon-lined autoclave and heated at 160 ºC for 24 h. Then, the autoclave was slowly cooled (2.5 ºC/h) to ambient temperature. It results in a mixture of green ($[Cu^{II}_2(Bz)_4(pyz)]_n$ (Bz= benzoate, pyz= pyrazine)) and red crystals (compound **1**). The mixture was separated by hand. Compound $[Cu^{II}_2(Bz)_4(pyz)]_n$ was washed with cold water and dried in air (0.051 g, 22.1 % yield based on Cu). Anal. Calc. for $C_{32}H_{24}N_2O_8Cu_2$: C 55.57 %, H 3.50 %, N 4.05 %, Found: C 54.47 %, H 3.27 %, N 3.78 %.