Electronic Supplementary Information (ESI):

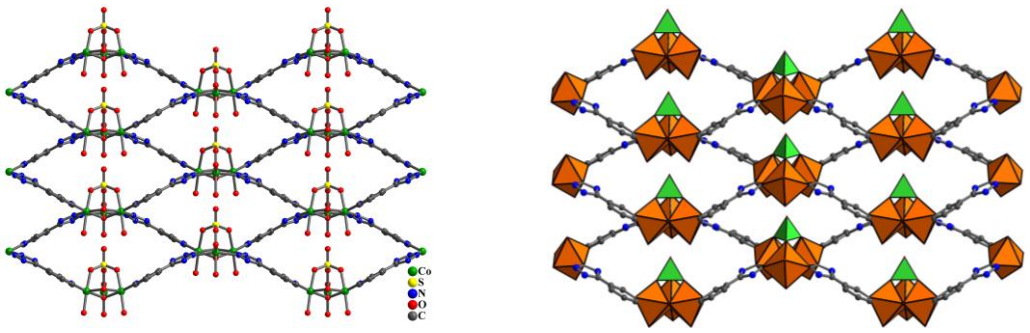
Triangle, Square and Delta-Chain Based Cobalt Tetrazolate Magnets

Ru-Xin Yao, Ying-Lian Qin，Fang Ji, Yan-Fei Zhao and Xian-Ming Zhang*[a]

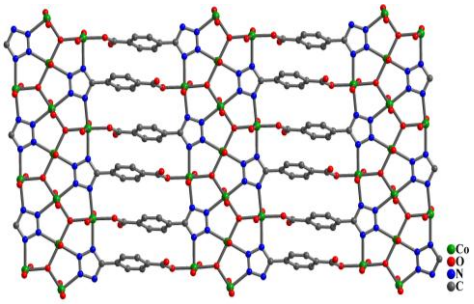
Structural Inorganic & Magnetic Material Key Laboratory of Education Ministry; School of Chemistry & Material Science, Shanxi Normal University, Linfen, Shanxi 041004, China.

Thermal properties and PXRD

Thermo gravimetric analysis (TGA) of **1-3** was performed under nitrogen atmosphere at a heating rate of 10°C min^{-1} on polycrystalline samples (Fig. S5). The TGA curves show that **3** is more stable than **1** and **2**, indicating that the 3D *bcu* framework could retain structural integrity to *ca*. 400°C, while layer frameworks of **1** and **2** to 220°C. For **1**, the initial weight loss of 11.1% (*calc.* 10.7%) in the temperature range of 220–279°C corresponds to the removal of terminal coordination water molecules. The second weight loss of 69.8% from 280 to 416°C is the decomposition of framework, and the final residue of 33.7% corresponds to CoO (*calc.* 33.5%). Similar to **1**, the first weight loss of about 19.8% (*calc.* 18.2%) in **2** corresponds to the removal of terminal coordination water molecules, which is followed by the collapse of the 2D framework. The final residue of 38.5% corresponds to the percentage of CoO (*calc.* 37.9%). For **3**, there is one-step weight loss of 48.1%, being consistent with pyrolysis of the organic ligand. The final residual weight of 51.9% is in accordance with the percentage of CoO (*calc*. 51.7%). The purity of these compounds was confirmed by comparison of experimental PXRD patterns with the simulated patterns from the X-ray single crystal data (Fig. S6).



(a) **(b)**



(c)

Fig. S1 Layer viewed along the *a*-axis of **1** (a), polyhedral diagram of 2D (4,4) layer of **1**(b), green tetrahedron represent SO_4^{2-}, orange octahedron stand for Co atom; and layer of **2** (c).

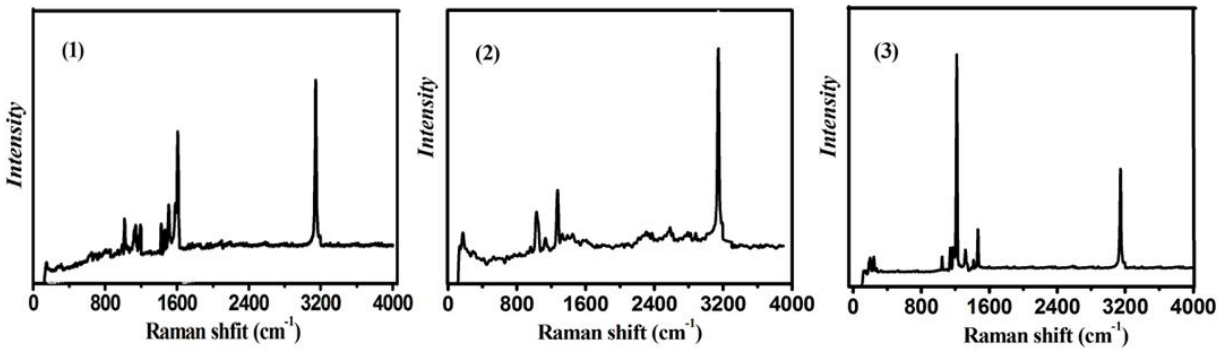


Fig. S2 Raman spectra for **1-3**.

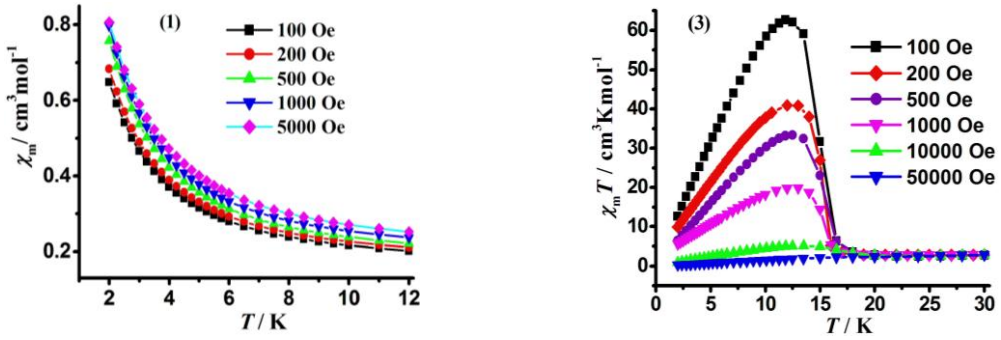


Fig. S3 Temperature dependence of the susceptibility in different applied fields of **1, 3**.

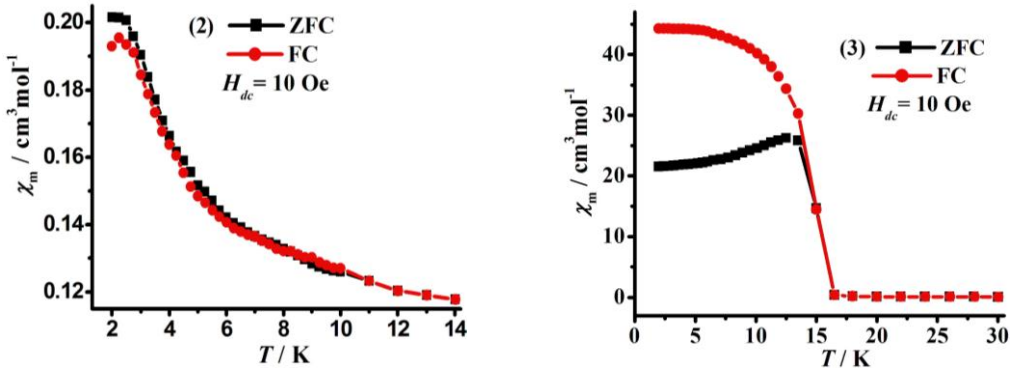


Fig. S4 FC and ZFC magnetization plots at H_{dc} = 10 Oe of **2** and **3**.

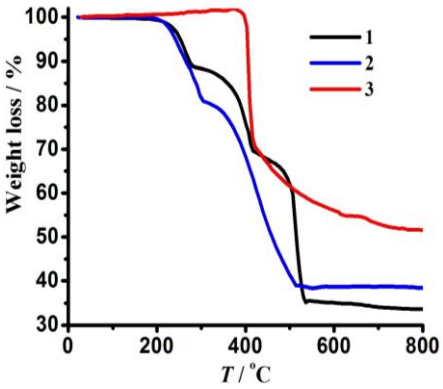


Fig. S5 TGA curves of **1-3** in nitrogen atmosphere at the heating rate of 10°C/min.

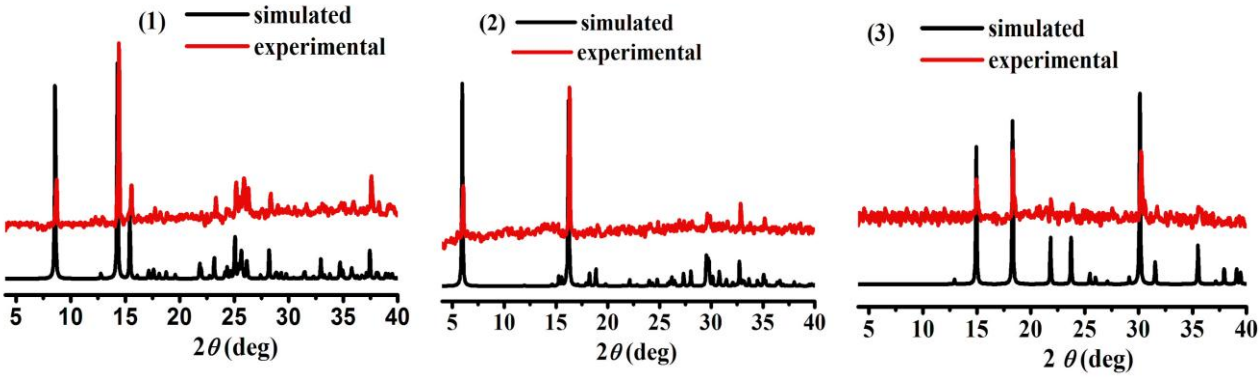


Fig. S6 The experimental and simulated PXRD patterns for **1-3**.

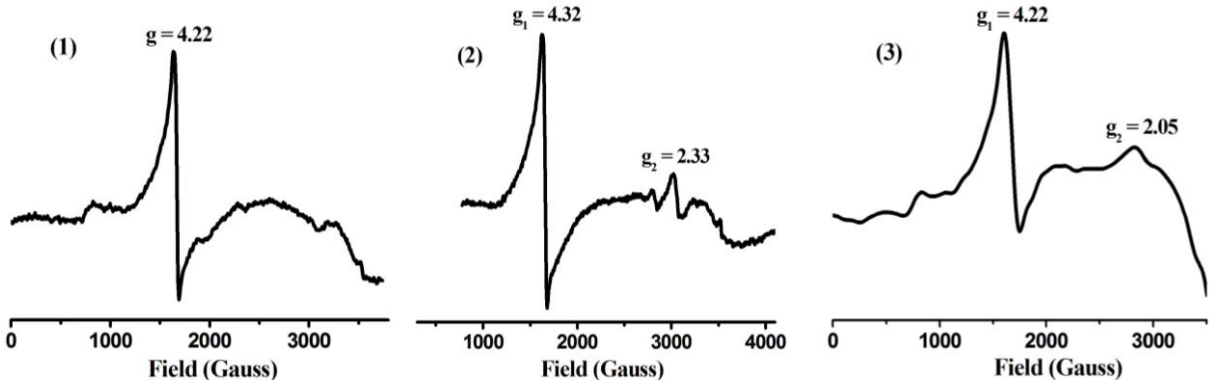


Fig. S7 ESR spectra of powdered **1-3** at room temperature.

Table S1. Bond lengths [Å] and angles [deg] for **1-3**.

Compound 1

Co(1)-O(4)	2.032(2)	Co(2)-O(4)	2.0661(13)
Co(1)-O(3W)	2.041(3)	Co(2)-O(1W)	2.075(2)
Co(1)-O(2W)	2.087(3)	Co(2)-O(2)	2.0856(19)
Co(1)-O(3)	2.104(3)	Co(2)-N(1b)	2.097(2)

Co(1)-N(3)	2.143(2)	Co(2)-O(5)	2.0981(14)
Co(1)-N(3a)	2.143(2)	Co(2)-N(4)	2.139(2)

O(4)-Co(1)-O(3W)	172.86(11)	O(4)-Co(2)-O(1W)	87.51(9)
O(4)-Co(1)-O(2W)	89.19(11)	O(4)-Co(2)-O(2)	88.79(8)
O(3W)-Co(1)-O(2W)	97.95(13)	O(1W)-Co(2)-O(2)	176.08(9)
O(4)-Co(1)-O(3)	90.77(9)	O(4)-Co(2)-N(1b)	172.15(8)
O(3W)-Co(1)-O(3)	82.10(12)	O(1W)-Co(2)-N(1b)	95.63(9)
O(2W)-Co(1)-O(3)	179.96(11)	O(2)-Co(2)-N(1b)	87.88(8)
O(4)-Co(1)-N(3)	83.84(6)	O(4)-Co(2)-O(5)	78.14(6)
O(3W)-Co(1)-N(3)	96.73(6)	O(1W)-Co(2)-O(5)	91.39(9)
O(2W)-Co(1)-N(3)	84.91(6)	O(2)-Co(2)-O(5)	86.59(8)
O(3)-Co(1)-N(3)	95.08(6)	N(1b)-Co(2)-O(5)	94.56(8)
O(4)-Co(1)-N(3a)	83.84(6)	O(4)-Co(2)-N(4)	84.06(8)
O(3W)-Co(1)-N(3a)	96.73(6)	O(1W)-Co(2)-N(4)	89.22(9)
O(2W)-Co(1)-N(3a)	84.91(6)	O(2)-Co(2)-N(4)	91.66(8)
O(3)-Co(1)-N(3a)	95.08(6)	N(1b)-Co(2)-N(4)	103.14(9)
N(3)-Co(1)-N(3a)	164.11(12)	O(5)-Co(2)-N(4)	162.14(8)
Co(1)-O(4)-Co(2)	118.31(6)	Co(2)-O(4)-Co(2a)	101.62(9)
Co(1)-O(4)-Co(2a)	118.31(6)	Co(2a)-O(5)-Co(2)	99.50(9)
Co(1)-Co(2)-Co(2)	62.93(8)	Co(2)-Co(1)-Co(2)	54.15(7)

Symmetry codes: a) x,-y+3/2,z; b) –x+3/2,-y+1,z+1/2.

Compound 2

Co(1)-O(2)	2.010(6)	Co(1)-O(1)	2.092(6)
Co(1)-O(3W)	2.070(6)	Co(1)-N(1a)	2.311(7)
Co(1)-O(2W)	2.087(6)	Co(1)-N(4b)	2.312(7)
Co(2)-O(1Wc)	2.007(5)	Co(2)-O(1)	2.064(6)
Co(2)-O(1W)	2.007(5)	Co(2)-N(2d)	2.117(7)
Co(2)-O(1c)	2.064(6)	Co(2)-N(2a)	2.117(7)

Co(3)-O(1e)	2.057(6)	Co(3)-O(4W)	2.082(6)
Co(3)-O(1)	2.057(6)	Co(3)-N(3d)	2.091(6)
Co(3)-O(4We)	2.082(6)	Co(3)-N(3b)	2.091(6)

O(2)-Co(1)-O(3W)	98.4(3)	O(1Wc)-Co(2)-O(1W)	180.0(1)
O(2)-Co(1)-O(2W)	93.0(3)	O(1Wc)-Co(2)-O(1c)	86.7(2)
O(3W)-Co(1)-O(2W)	167.9(2)	O(1W)-Co(2)-O(1c)	93.3(2)
O(2)-Co(1)-O(1)	176.1(2)	O(1Wc)-Co(2)-O(1)	93.3(2)
O(3W)-Co(1)-O(1)	84.2(2)	O(1W)-Co(2)-O(1)	86.7(2)
O(2W)-Co(1)-O(1)	84.6(2)	O(1c)-Co(2)-O(1)	180.0(2)
O(2)-Co(1)-N(1a)	94.8(3)	O(1Wc)-Co(2)-N(2d)	90.7(2)
O(3W)-Co(1)-N(1a)	88.6(3)	O(1W)-Co(2)-N(2d)	89.3(2)
O(2W)-Co(1)-N(1a)	86.4(2)	O(1c)-Co(2)-N(2d)	86.9(2)
O(1)-Co(1)-N(1a)	88.2(2)	O(1)-Co(2)-N(2d)	93.1(2)
O(2)-Co(1)-N(4b)	91.5(3)	O(1Wc)-Co(2)-N(2a)	89.3(2)
O(3W)-Co(1)-N(4b)	89.2(2)	O(1W)-Co(2)-N(2a)	90.7(2)
O(2W)-Co(1)-N(4b)	94.5(2)	O(1c)-Co(2)-N(2a)	93.1(2)
O(1)-Co(1)-N(4b)	85.6(2)	O(1)-Co(2)-N(2a)	86.9(2)
N(1a)-Co(1)-N(4b)	173.6(2)	N(2d)-Co(2)-N(2a)	180.0(2)
O(1e)-Co(3)-O(1)	180.0(3)	O(4We)-Co(3)-N(3d)	88.4(2)
O(1e)-Co(3)-O(4We)	89.5(2)	O(4W)-Co(3)-N(3d)	91.6(2)
O(1)-Co(3)-O(4We)	90.5(2)	O(1e)-Co(3)-N(3b)	94.1(2)
O(1e)-Co(3)-O(4W)	90.5(2)	O(1)-Co(3)-N(3b)	85.9(2)
O(1)-Co(3)-O(4W)	89.5(2)	O(4We)-Co(3)-N(3b)	91.6(2)
O(4We)-Co(3)-O(4W)	180.0(1)	O(4W)-Co(3)-N(3b)	88.4(2)
O(1e)-Co(3)-N(3d)	85.9(2)	N(3d)-Co(3)-N(3b)	180.0(1)
O(1)-Co(3)-N(3d)	94.1(2)	Co(3)-O(1)-Co(2)	112.1(3)
Co(2)-O(1)-Co(1)	121.2(3)	Co(3)-O(1)-Co(1)	123.4(3)
Co(1)-Co(2)-Co(3)	62.43(2)	Co(1)-Co(3)-Co(2)	61.50(2)

Co(2)-Co(1)-Co(3)	56.08(2)

Symmetry codes: a)-x+1,-y+1,-z;b)-x+1,-y+2,-z; c)-x,-y+1,-z+1; d)x-1,y,z+1; e)-x,-y+2,-z+1.

Compound 3

Co(1)-O(1a)	1.9825(14)	Co(1)-N(2)	2.156(3)
Co(1)-O(1)	1.9825(15)	Co(1)-N(1c)	2.180(3)
Co(1)-N(2b)	2.156(3)	Co(1)-N(1d)	2.180(3)

O(1a)-Co(1)-O(1)	97.73(17)	O(1)-Co(1)-N(1c)	87.05(11)
O(1a)-Co(1)-N(2b)	89.21(12)	N(2b)-Co(1)-N(1c)	91.29(11)
O(1)-Co(1)-N(2b)	172.70(11)	N(2)-Co(1)-N(1c)	97.46(11)
O(1a)-Co(1)-N(2)	172.70(11)	O(1a)-Co(1)-N(1d)	87.05(11)
O(1)-Co(1)-N(2)	89.21(12)	O(1)-Co(1)-N(1d)	85.22(10)
N(2b)-Co(1)-N(2)	83.95(16)	N(2b)-Co(1)-N(1d)	97.46(11)
O(1a)-Co(1)-N(1c)	85.22(10)	N(2)-Co(1)-N(1d)	91.29(11)
N(1c)-Co(1)-N(1d)	168.24(14)		
Co(1)-O(1)-Co(1)	125.75(16)	Co-Co-Co	90

Symmetry codes: a)-y+1,x+1/2,-z+1/2; b)-y+1,-x+1,-z+1/2; c)-x+1,-y+1,-z;d) y,x,z+1/2