Supplementary Materials: Synthesis, Structures and Properties of Cobalt Thiocyanate Coordination Compounds with 4-(hydroxymethyl)pyridine as Co-ligand

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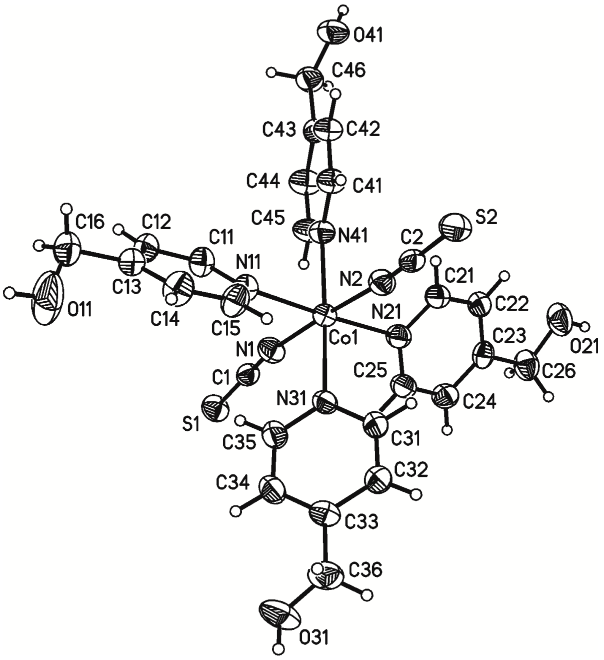

Figure S1. Crystal structure of compound **1** with labeling and displacement ellipsoids drawn at the 50 % probability level.

Table S1. Selected bond lengths (Å) and angles (°) for **1**.

Co(1)-N(1)	2.1010(19)	Co(1)-N(21)	2.1678(18)
Co(1)-N(2)	2.0989(19)	Co(1)-N(31)	2.1694(17)
Co(1)-N(11)	2.1792(17)	Co(1)-N(41)	2.1719(17)
N(1)-Co(1)-N(11)	89.22(7)	N(2)-Co(1)-N(41)	92.22(7)
N(1)-Co(1)-N(21)	90.01(8)	N(21)-Co(1)-N(11)	176.28(7)
N(1)-Co(1)-N(31)	88.18(7)	N(21)-Co(1)-N(31)	92.66(7)
N(1)-Co(1)-N(41)	90.56(7)	N(21)-Co(1)-N(41)	88.30(7)
N(2)-Co(1)-N(1)	177.21(8)	N(31)-Co(1)-N(11)	90.95(7)
N(2)-Co(1)-N(11)	91.11(7)	N(31)-Co(1)-N(41)	178.42(7)
N(2)-Co(1)-N(21)	89.84(7)	N(41)-Co(1)-N(11)	88.07(7)
N(2)-Co(1)-N(31)	89.04(7)		

Table S2. Hydrogen bonding for compound **1**. Symmetry transformations used to generate equivalent atoms: A: −x+2,y-1/2,−z+3/2, B: −x+1,y+1/2,−z+3/2, C: x+1,y,z, D: x-1,y,z.

D-H…A	d(D-H)	d(H…A)	d(D…A)	<(DHA)
O(11)-H(1O)...S(1A)	0.84	2.49	3.308(3)	164.2
O(21)-H(2O)...S(2B)	0.84	2.57	3.334(3)	152.4
O(31)-H(3O)...S(2C)	0.84	2.45	3.288(3)	173.8
O(41)-H(4O)...S(1D)	0.84	2.51	3.308(3)	158.9

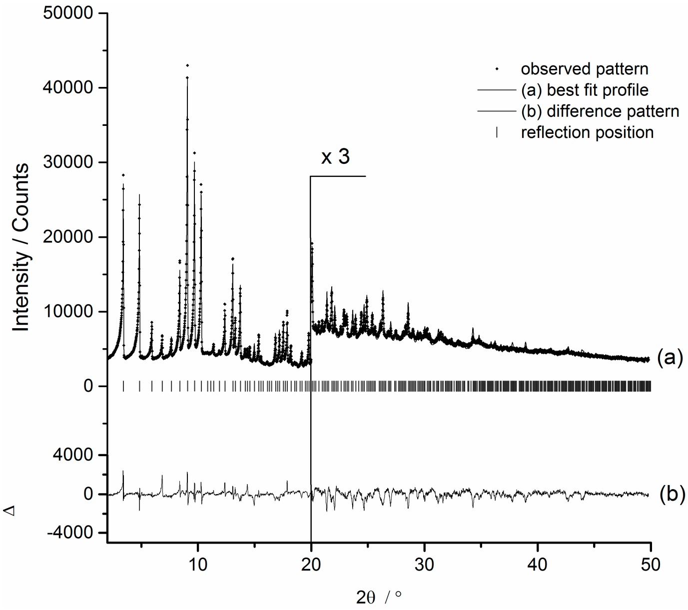

Figure S2. Scattered X-ray intensities of compound **1-H$_2$O** as a function of the diffraction angle 2θ. The observed pattern (diamonds), the best Rietveld fit profiles (line) and the difference curve between the observed and the calculated profiles (below) are shown. The high angle area (>20° 2θ) is enlarged for clarity.

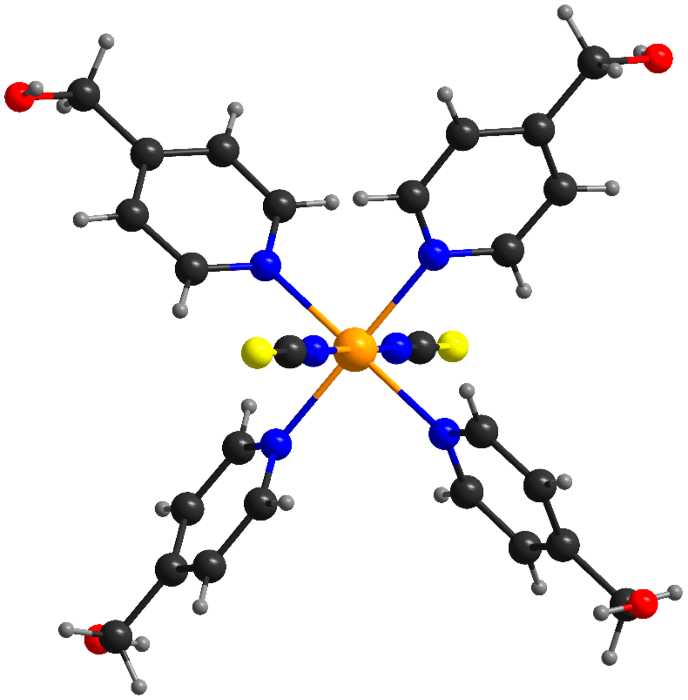

Figure S3. Crystal structure of compound **1-H$_2$O** showing the Co coordination.

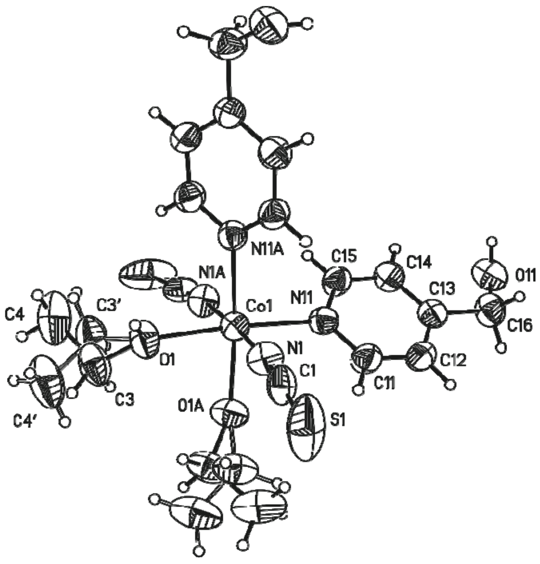

Figure S4. ORTEP plot of compound **2** with labeling and displacement ellipsoids drawn at the 50% probability level.

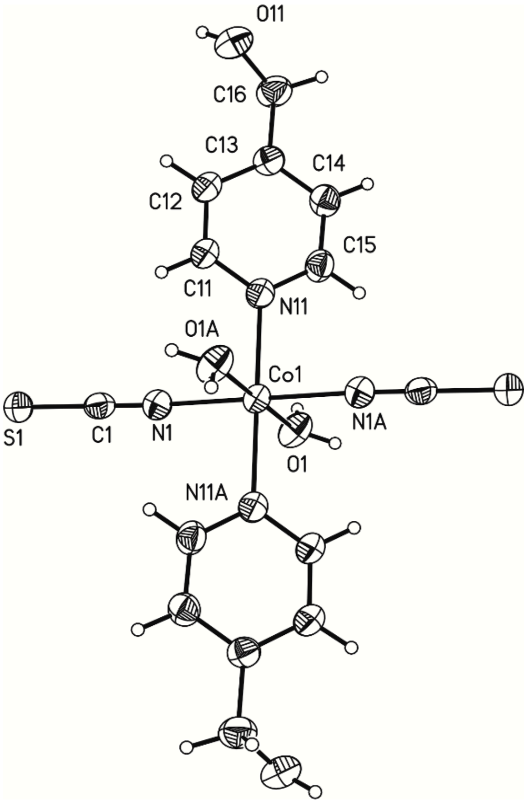

Figure S5. ORTEP plot of compound **3** with labeling and displacement ellipsoids drawn at the 50% probability level.

Table S3. Selected bond lengths (Å) and angles (°) for compound **2** and **3**.

Compound **2**			
Co(1)-N(1)	2.078(3)	Co(1)-O(1)	2.121(2)
Co(1)-N(11)	2.158(2)		
N(1A)-Co(1)-N(1)	176.82(14)	O(1A)-Co(1)-O(1)	86.26(12)
N(1A)-Co(1)-O(1A)	87.31(9)	O(1A)-Co(1)-N(11A)	175.51(9)
N(1)-Co(1)-O(1A)	90.37(9)	O(1)-Co(1)-N(11A)	89.33(8)
N(1A)-Co(1)-N(11A)	91.90(10)	N(11A)-Co(1)-N(11)	95.10(12)
N(1)-Co(1)-N(11A)	90.24(9)		

Table S3. *Cont.*

Compound **3**			
Co(1)-N(1)	2.085(3)	Co(1)-O(1)	2.101(2)
Co(1)-N(11)	2.180(3)		
N(1A)-Co(1)-N(1)	180.00(11)	O(1A)-Co(1)-O(1)	180.00(11)
N(1)-Co(1)-O(1)	90.68(11)	O(1A)-Co(1)-N(11A)	90.78(10)
N(1)-Co(1)-O(1A)	89.32(11)	O(1)-Co(1)-N(11A)	89.22(10)
N(1)-Co(1)-N(11)	88.80(10)	N(11A)-Co(1)-N(11)	180.0
N(1)-Co(1)-N(11A)	91.20(10)		

Table S4. Hydrogen bonding for compound **2** and **3**. Symmetry transformations used to generate equivalent atoms for compound **2**: A: −x + 1, y, −z + 1/2, B: x − 1/2, −y + 1/2, z + 1/2, C: −x + 3/2, y − 1/2, −z + 1/2 D: −x + 3/2, −y + 1/2, −z+1. Symmetry transformations used to generate equivalent atoms for compound **3**: A: −x + 1, −y + 1, −z + 1, B: x + 1/2, −y + 3/2, −z + 1, C: x - 1/2, −y + 3/2, −z + 1, D: −x + 3/2, y + 1/2, z.

Compound **2**				
D-H…A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
C(14)-H(14)...S(1B)	0.95	2.92	3.760(3)	148.3
C(15)-H(15)...N(1A)	0.95	2.66	3.138(4)	111.9
O(11)-H(11O)...S(1B)	0.84	2.35	3.179(2)	171.5
O(21)-H(21O)...O(11D)	0.84	1.83	2.677(3)	179.0
C(21)-H(21B)...N(1)	0.99	2.59	3.129(15)	114.3
Compound **3**				
D-H…A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O(11)-H(11)...S(1B)	0.84	2.37	3.198(3)	170.1
O(1)-H(1O1)...S(1C)	0.84	2.45	3.277(2)	167.9
O(1)-H(2O1)...O(11D)	0.84	1.93	2.749(4)	166.4

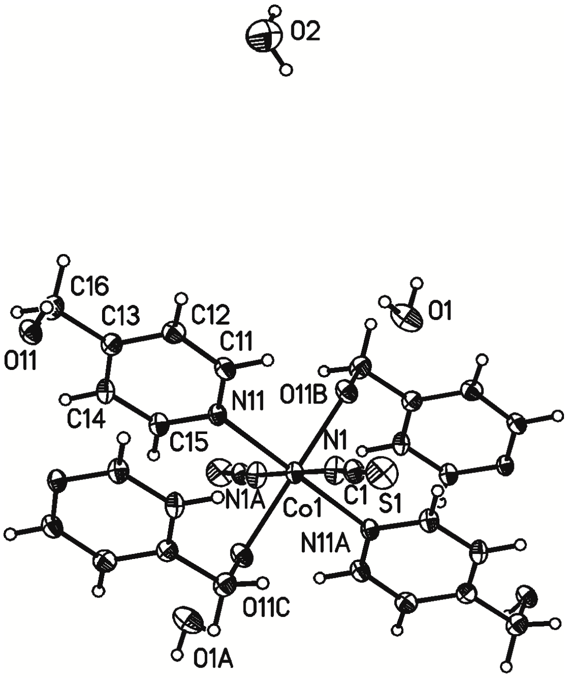

Figure S6. Crystal structure of compound **4** with labeling and displacement ellipsoids drawn at the 50% probability level.

Table S5. Selected bond lengths (Å) and angles (°) for compound **4**.

Co(1)-N(1)	2.078(2)	Co(1)-O(11B)	2.1407(15)
Co(1)-N(11)	2.1597(18)		
N(1)-Co(1)-N(1A)	180.00(11)	O(11B)-Co(1)-O(11C)	180.00(7)
N(1)-Co(1)-O(11B)	88.19(7)	O(11B)-Co(1)-N(11)	89.55(6)
N(1)-Co(1)-O(11C)	91.81(7)	O(11C)-Co(1)-N(11)	90.45(6)
N(1)-Co(1)-N(11A)	90.24(7)	N(1)-Co(1)-N(11)	89.76(7)
N(11A)-Co(1)-N(11)	180.0		

Table S6. Hydrogen bonding for compound **4**. Symmetry transformations used to generate equivalent atoms: A: − x + 2, −y, −z + 1, B: −x + 2, −y + 1, −z + 1, C: x, y−1, z, D: x, y + 1, z, E: x−1, y, z, F: −x+2, −y, −z, G: −x+1, −y + 1,−z.

D-H…A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O(1)-H(1O1)...S(1E)	0.84	2.98	3.614(2)	134.0
O(1)-H(1O1)...S(1F)	0.84	2.73	3.410(2)	139.0
O(2)-H(1O2)...S(1E)	0.84	2.54	3.324(3)	155.3
O(1)-H(2O1)...O(2G)	0.84	1.93	2.762(3)	173.4
O(11)-H(11O)...O(1D)	0.84	1.86	2.703(2)	179.8

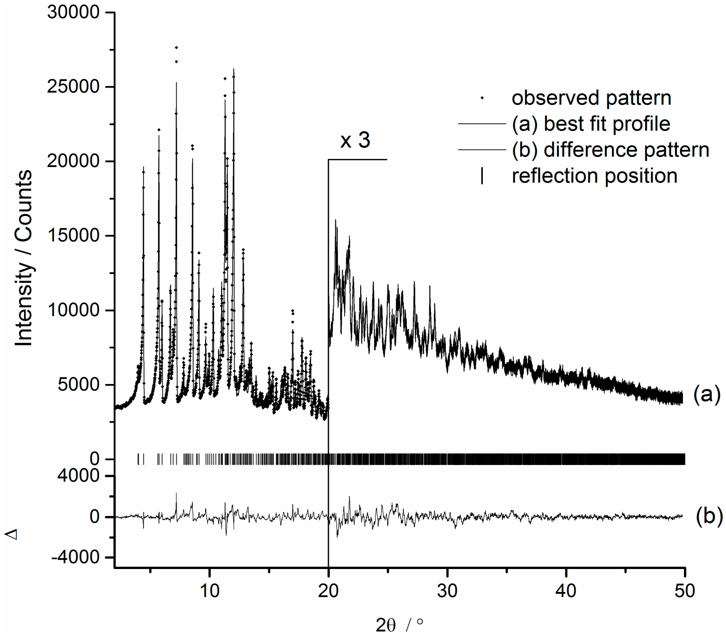

Figure S7. Scattered X-ray intensities of compound **5** as a function of the diffraction angle 2θ. The observed pattern (diamonds), the best Rietveld fit profiles (line) and the difference curve between the observed and the calculated profiles (below) are shown. The high angle area (>20° 2θ) is enlarged for clarity.

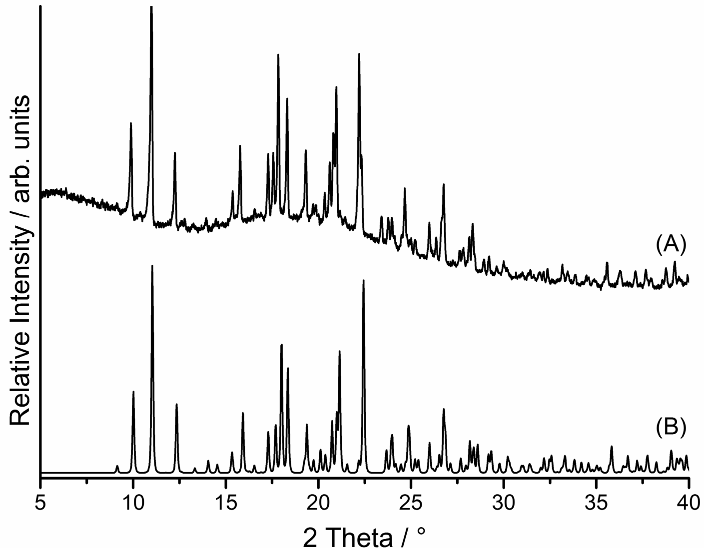

Figure S8. Experimental (**A**) and calculated (**B**) XRPD pattern (λ = 1.540596 Å) for compound **1**.

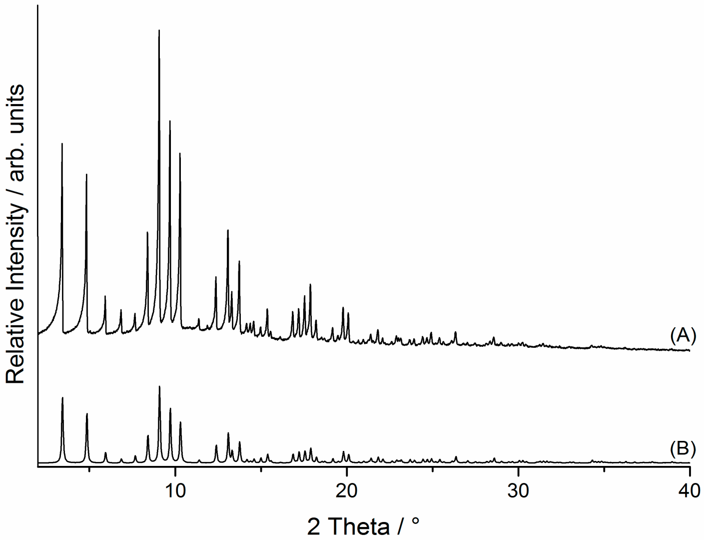

Figure S9. Experimental (**A**) and calculated (**B**) XRPD pattern (λ = 0.7093 Å) for **1-H_2O**.

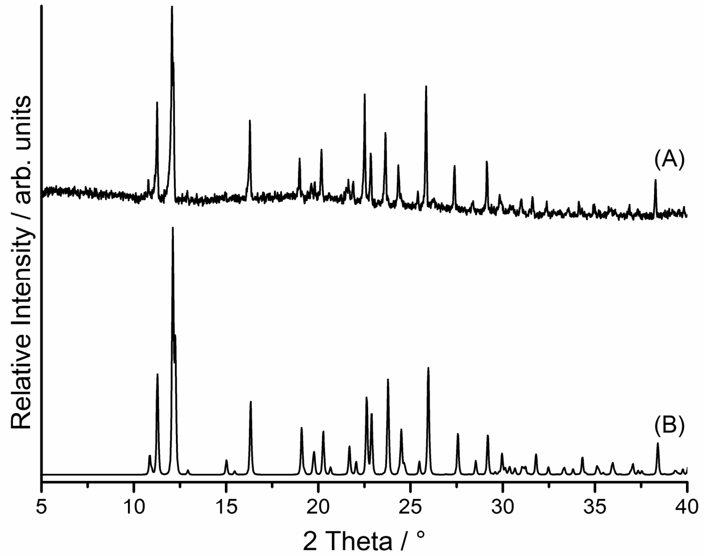

Figure S10. Experimental (**A**) and calculated (**B**) XRPD pattern (λ = 1.540596 Å) for compound **2**.

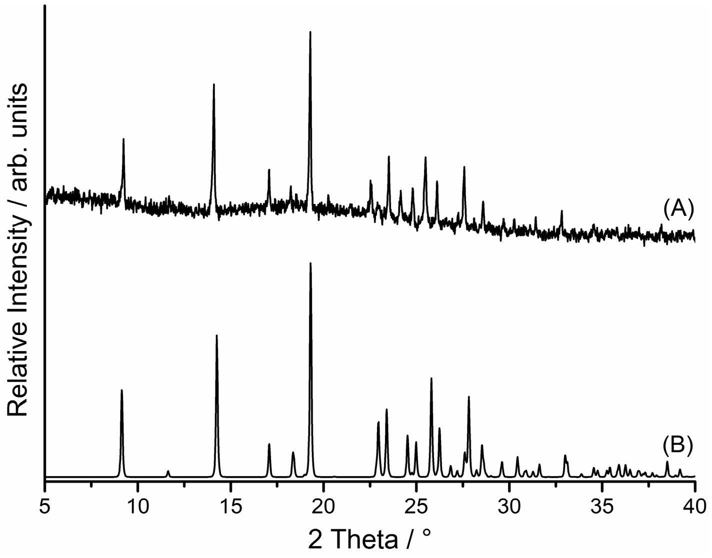

Figure S11. Experimental (**A**) and calculated (**B**) XRPD pattern (λ = 1.540596 Å) for compound **3**.

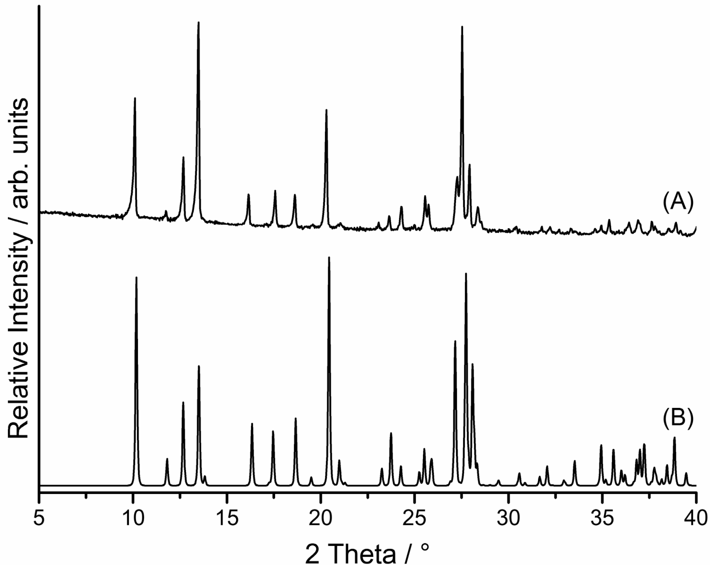

Figure S12. Experimental (**A**) and calculated (**B**) XRPD pattern (λ = 1.540596 Å) for compound **4**.

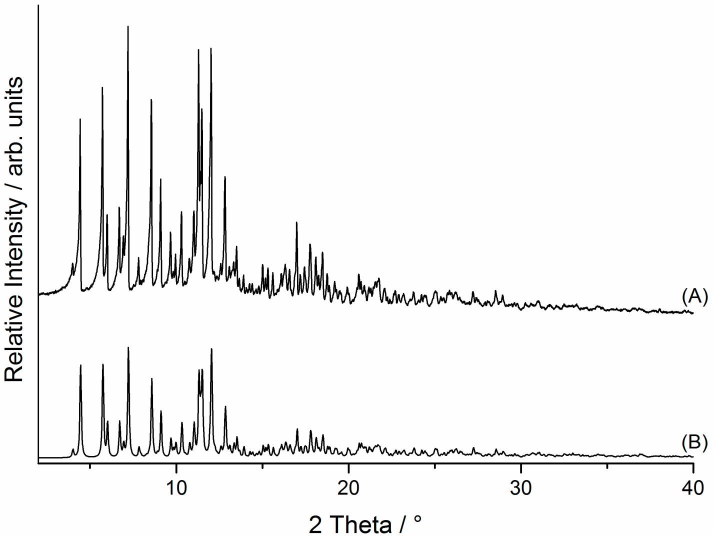

Figure S13. Experimental (**A**) and calculated (**B**) XRPD pattern (λ = 0.7093 Å) for compound **5**.

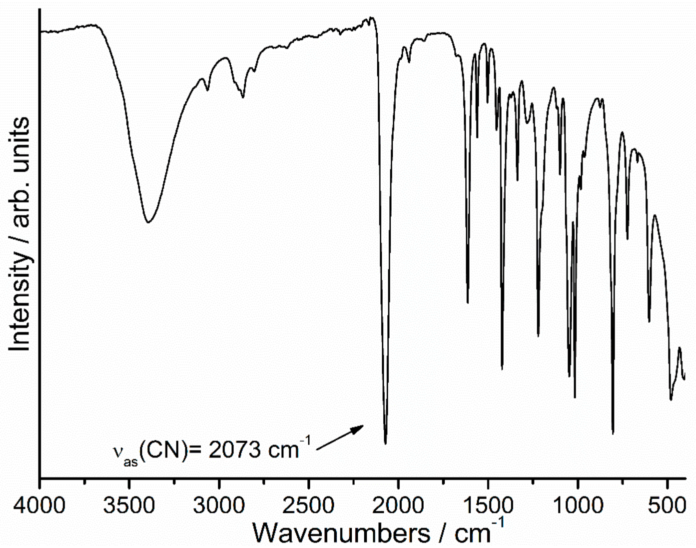

Figure S14. IR spectra of compound **1**. The value of the CN stretching vibration is given.

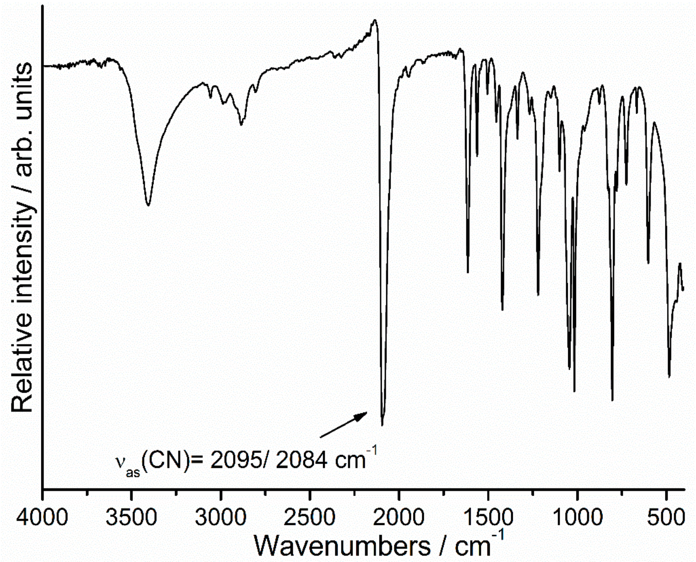

Figure S15. IR spectra of compound **1-H$_2$O**. The value of the CN stretching vibration is given.

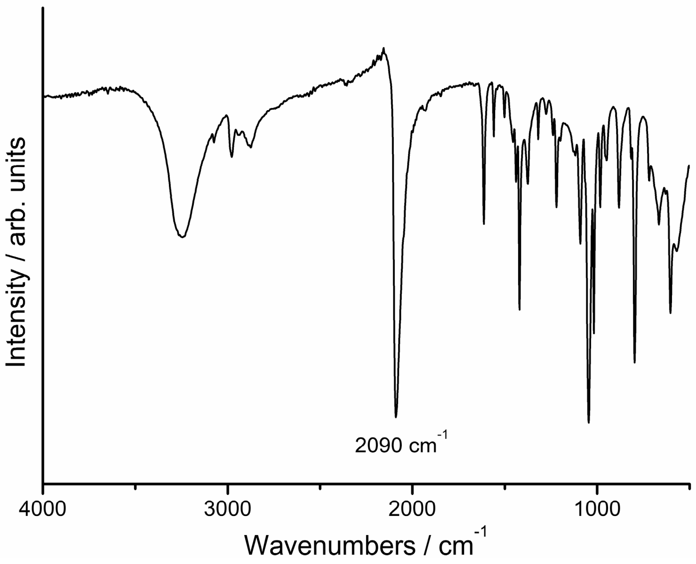

Figure S16. IR spectra of compound **2**. The value of the CN stretching vibration is given.

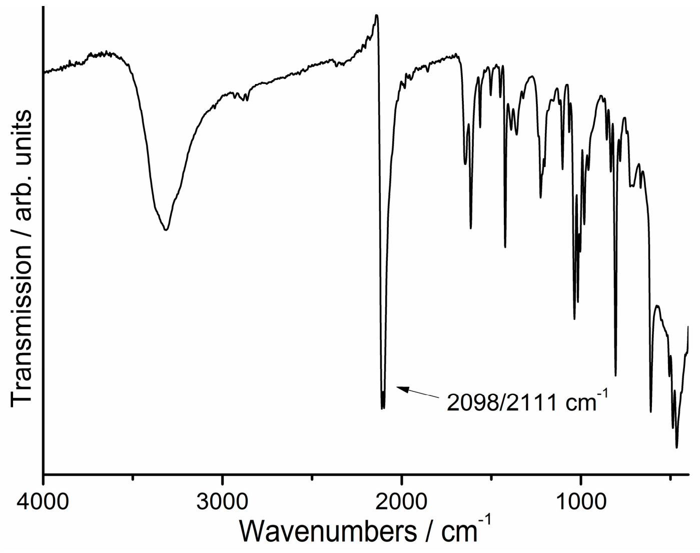

Figure S17. IR spectra of compound **3**. The CN stretching vibration is given.

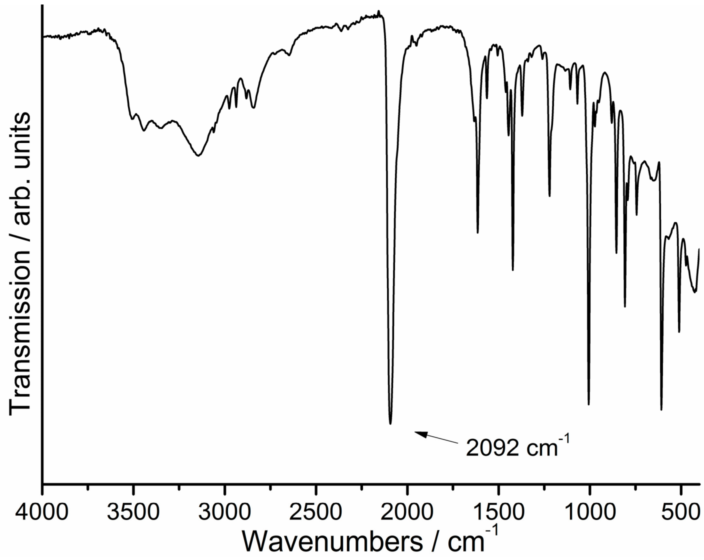

Figure S18. IR spectra of compound **4**. The value of the CN stretching vibration is given.

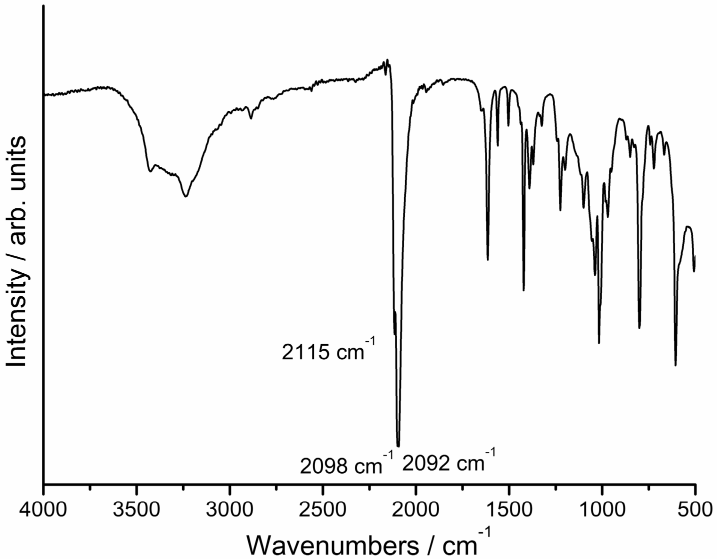

Figure S19. IR spectra of compound **5**. The value of the CN stretching vibration is given.

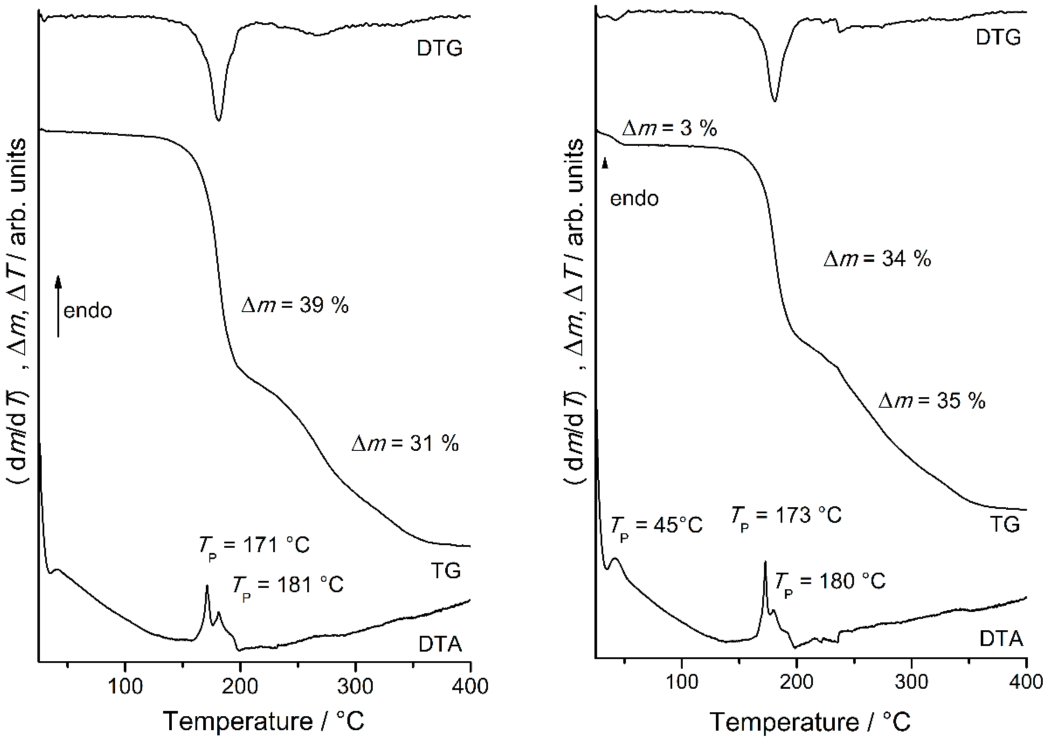

Figure S20. TG, DTA and DTG curves of compound **1** and **1-H$_2$O** at a heating rate of 1 °C/min measured in nitrogen atmosphere.

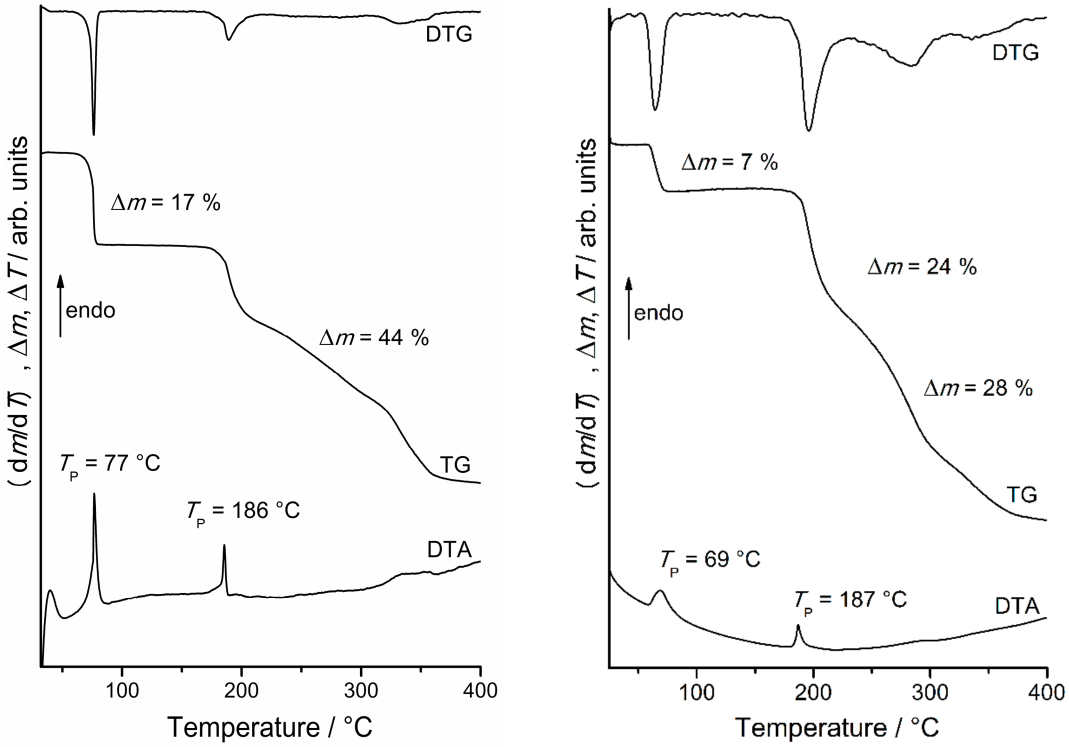

Figure S21. TG, DTA and DTG curves of compound **2** at 1 °C/min and of **3** at 4°C/min measured in nitrogen atmosphere.

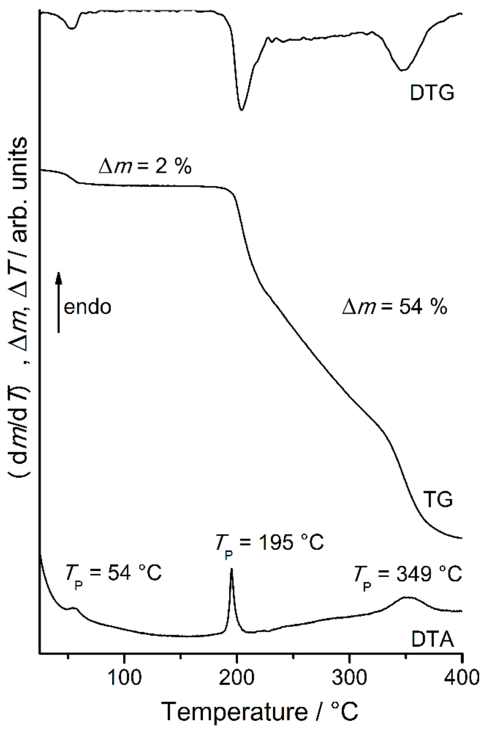

Figure S22. TG, DTA and DTG curves of compound **4** measured in nitrogen atmosphere with a heating rate of 4 °C/min.

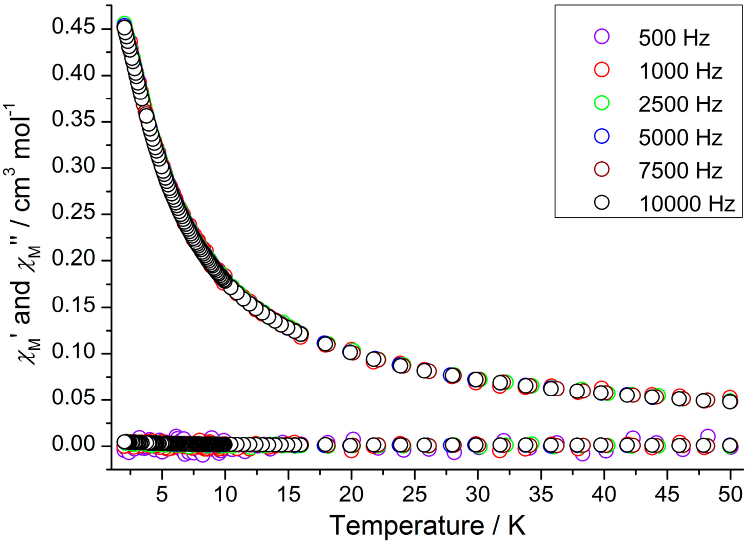

Figure S23. Temperature dependence of the AC susceptibility for compound **5** (H_{DC} = 0 Oe; H_{AC} = 3 Oe).

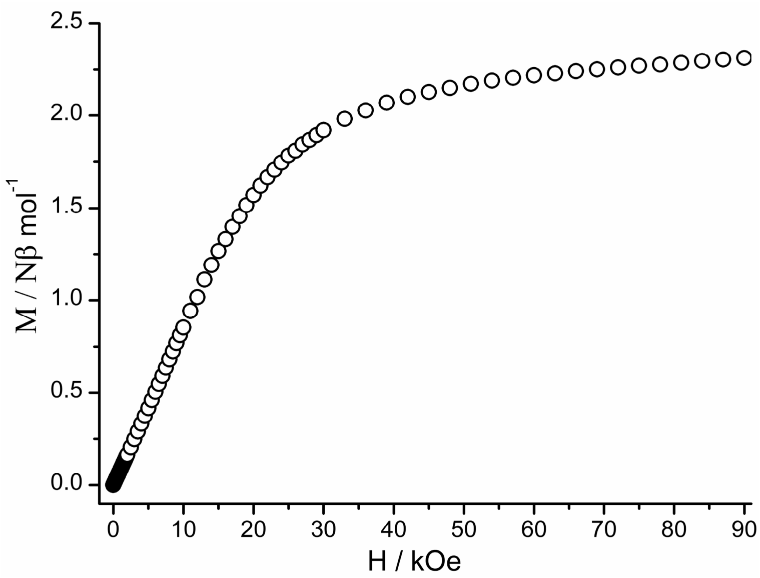

Figure S24. Field dependence of the magnetization for compound **5** measured at 2 K.