Supporting Information

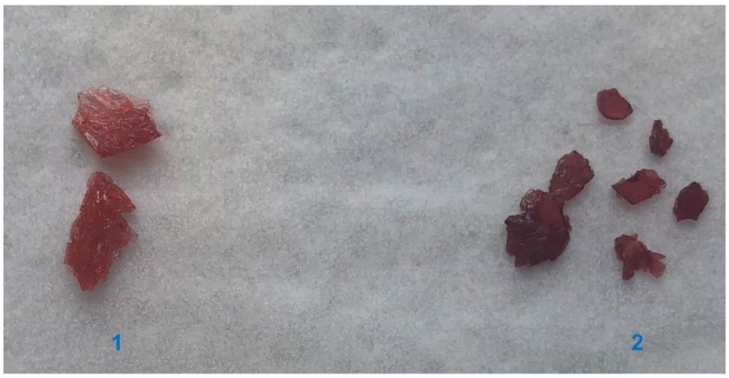

Figure S1 The bulk crystals of **1** and **2**.

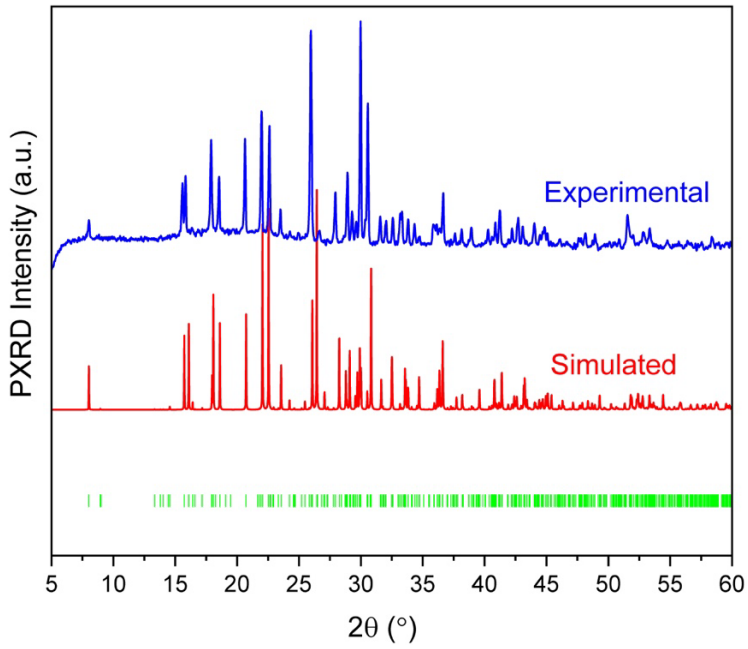

Figure S2 Experimental and simulated powder X-ray diffraction patterns for **1** with Bragg positions denoted by green vertical markers.

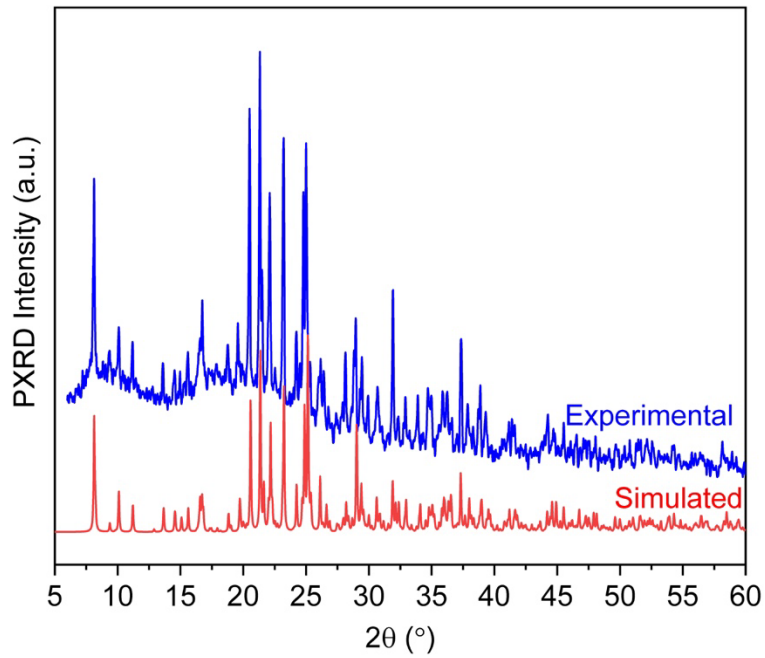

Figure S3 Same as before but for **2**.

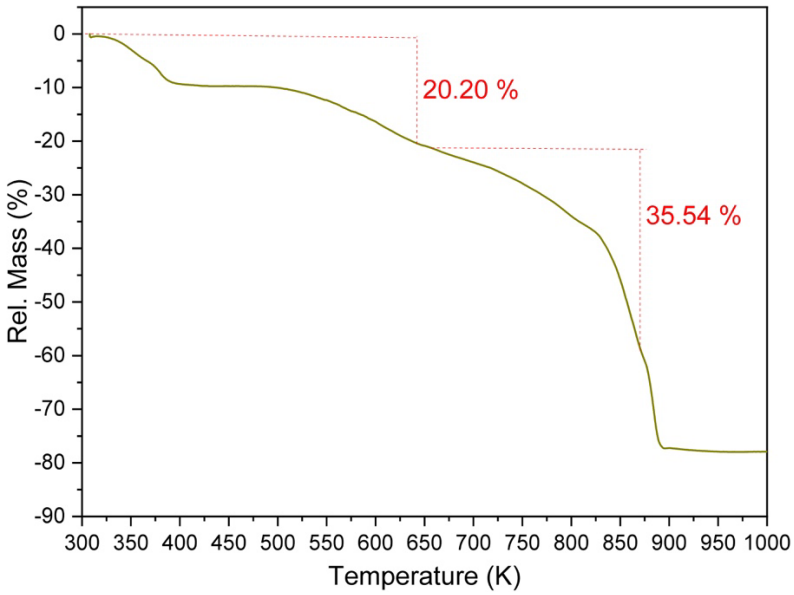

Figure S4 TGA curve for **1** with a heating rate of 5 K/min.

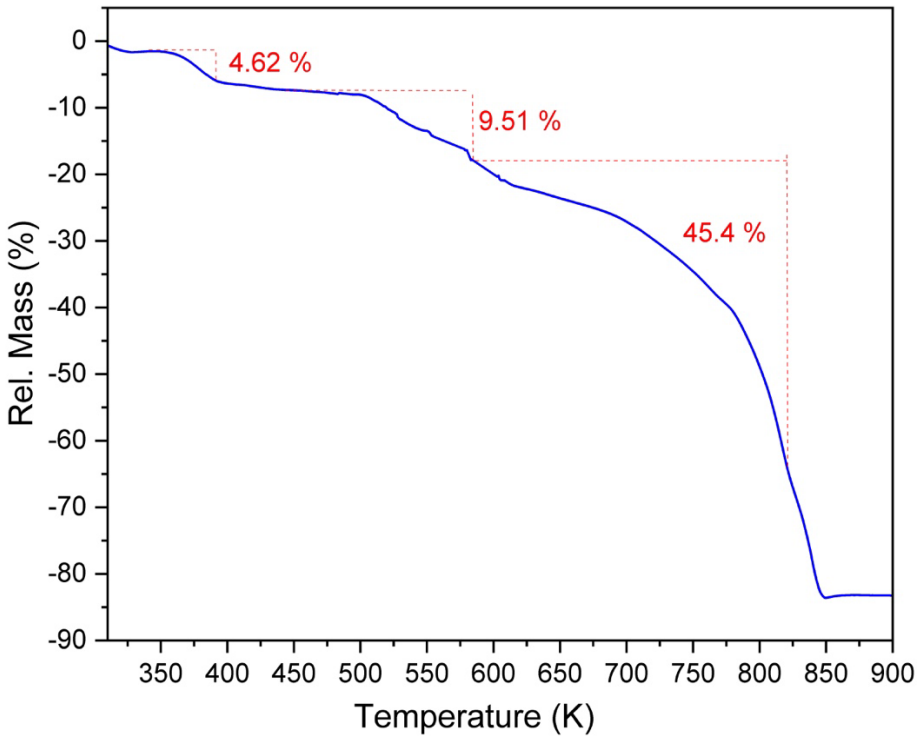

Figure S5 Same as before but for **2**.

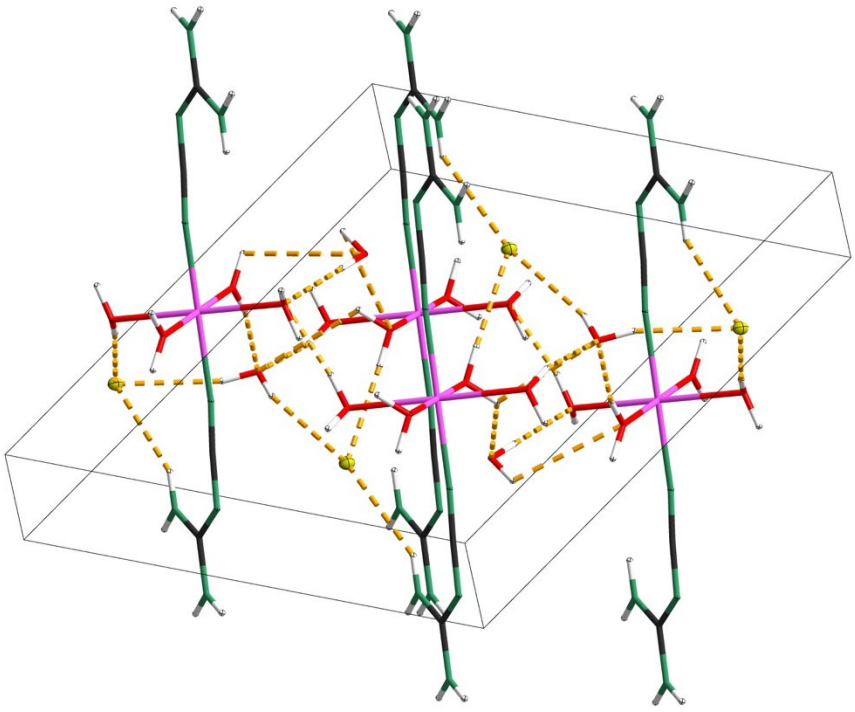

Figure S6 Hydrogen-bonding interactions between O, N and Br atoms in the crystal structure of **1**.

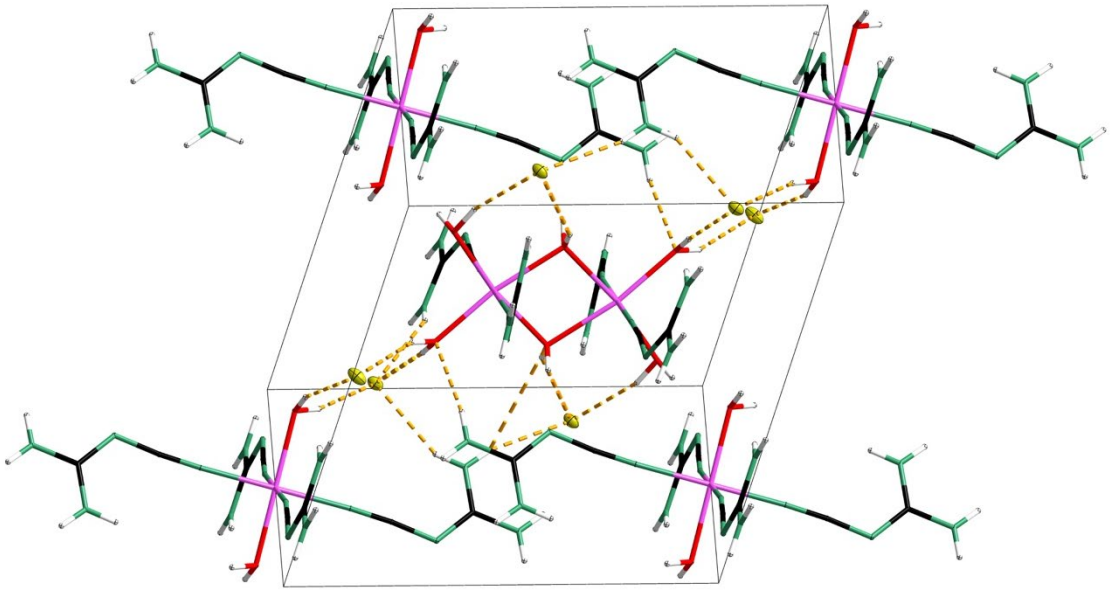

Figure S7 Same as before but for **2**.

Table S1 Assignment of Thermal Mass Loss Steps of **1**.

		1
293–600 K	calculated (crystal water and coordinated water molecules)	21.82 %
	observed	20.20 %
600–850 K	calculated (ligands)	33.94 %
	observed	35.54 %

Table S2 As before but for **2**.

		2
400–600 K	calculated (coordinated water molecules)	9.78 %
	observed	9.51 %
600–850 K	calculated (ligands)	45.62 %
	observed	45.4 %

Table S3 Crystal data and structure refinement for **1** and **2**.

	1	**2**
Empirical formula	$Co(C_2N_4H_4)_2(H_2O)_4{\cdot}2Br{\cdot}2H_2O$	$Co_3(C_2N_4H_4)_8(H_2O)_8{\cdot}6Br$
Formula weight	495.03	1473.11
Temperature / K	100	100
Crystal system	Triclinic	Triclinic
Space group	$P\overline{1}$	$P\overline{1}$
Unit cell dimensions (Å)		
	a = 6.946(2)	a = 10.731(2)
	b = 11.173(3)	b = 11.658(2)
	c = 12.485(3)	c = 12.318(2)
	α = 114.642(4)°	α = 94.173(3)°
	β = 98.284(4)°	β = 114.733(3)°
	γ = 100.028(4)°	γ = 108.593(3)°
V (Å^3)	841.5(3)	1288.0(3)
Z, ρ_{cal} (g cm^{-3})	2, 1.954	1, 1.899
Absorption coefficient, mm^{-1}	5.804	5.678
F (000)	490.0	723.0
Theta range (°)	3.7–62.052	3.75–55.132
Limiting indices		
	$-9 \le h \le 9$	$-13 \le h \le 12$
	$-14 \le k \le 15$	$-15 \le k \le 15$
	$-17 \le l \le 8$	$-15 \le l \le 16$
Reflections collected/unique	6894 / 4753 (R_{int} = 0.0165)	9103 / 5894 (R_{int} = 0.0570)
Observed [I > 2σ(I)]	3947	3753
Absorption correction	Multi-scan (SADABS)	
T_{min} / T_{max}	0.7461 / 0.6523	0.7456 / 0.5690
Completeness (%)	99.4	99.7
Data / restraints / parameters	4753 / 31 / 253	5894 / 4 / 313
Goodness	1.080	0.977
Final R indexes [$I \ge 2\sigma(I)$]	R_1 = 0.0315, wR_2 = 0.0724	R_1 = 0.0601, wR_2 = 0.1088
Final R indexes (all data)	R_1 = 0.0392, wR_2 = 0.0771	R_1 = 0.1058, wR_2 = 0.1324
Largest diff. peak and hole / e Å^{-3}	0.70 / –0.80	1.20 / –1.22

Table S4 Elemental CHN analysis for **1**.

	C (wt%)	H (wt%)	N (wt%)
Experimental	10.01	3.83	23.73
Calculated	9.71	4.07	22.64

Table S5 Bond lengths for **1**.

Atom	Atom	Length (Å)	Atom	Atom	Length (Å)
Co1	O2^1	2.180(2)	Co2	N8	2.091(2)
Co1	O2	2.180(2)	N3	C2	1.311(3)
Co1	O1^1	2.046(2)	N3	C1	1.341(3)
Co1	O1	2.046(2)	N7	C4	1.311(3)
Co1	N4	2.087(2)	N7	C3	1.341(3)

Co1	N4[1]	2.087(2)	N1	C1	1.335(3)
Co2	O3	2.142(2)	N4	C2	1.164(3)
Co2	O3[2]	2.142(2)	N2	C1	1.337(3)
Co2	O4	2.056(2)	N8	C4	1.158(3)
Co2	O4[2]	2.056(2)	N5	C3	1.333(3)
Co2	N8[2]	2.091(2)	N6	C3	1.335(3)

[1] 2–*x*, 1–*y*, 1–*z*; [2] 1–*x*, –*y*, 1–*z*

Table S6 Elemental CHN analysis for **2**.

	C (wt%)	H (wt%)	N (wt%)
Experimental	12.83	2.99	30.15
Calculated	13.04	3.08	30.43

Table S7 Bond lengths for **2**.

Atom	Atom	Length (Å)	Atom	Atom	Length (Å)
Co2	O4[1]	2.136(5)	N3	C1	1.347(9)
Co2	O4	2.136(5)	N14	C7	1.296(9)
Co2	N12	2.118(6)	N14	C8	1.353(8)
Co2	N12[1]	2.118(6)	N9	C5	1.331(10)
Co2	N13[1]	2.072(6)	N13	C7	1.165(8)
Co2	N13	2.072(6)	N15	C8	1.341(9)
Co1	O3[2]	2.218(5)	N16	C8	1.311(9)
Co1	O3	2.156(5)	N11	C6	1.303(10)
Co1	O2	2.073(4)	N11	C5	1.359(9)
Co1	O1	2.048(5)	N8	C4	1.319(9)
Co1	N5	2.062(6)	N10	C5	1.327(10)
Co1	N4	2.064(6)	N6	C3	1.303(9)
N5	C3	1.143(9)	N6	C4	1.372(9)
N4	C2	1.167(8)	N1	C1	1.327(9)
N12	C6	1.165(9)	N2	C1	1.342(9)
N3	C2	1.296(9)	N7	C4	1.326(9)

[1] 2–*x*,2–*y*,1–*z*; [2] 1–*x*,1–*y*,1–*z*

Table S8 IR bands of cyanoguanidine, **1** and **2**.

Vibration	CNGE	**1**	**2**
υ(C≡N)	2208–2163 cm^{-1}	2224–2179 cm^{-1}	2234–2189 cm^{-1}
υ(C=N)	1629 cm^{-1}	1655 cm^{-1}	1637 cm^{-1}
υ(NH)	3429 cm^{-1}	3529 cm^{-1}	3432 cm^{-1}