Supplementary material (ESI) for Dalton Trans.

Electronic Supplementary Information (ESI)/Supporting information

for

$^{2}_{\infty}[Cu_2(\mu_5\text{-btb})(\mu\text{-OH})(\mu\text{-}H_2O)]$ a two-dimensional coordination polymer built from ferromagnetically coupled Cu_2 units (btb = benzene-1,2,3-tricarboxylate)

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Thermal stability: Compound **2** shows the first weight loss in the TGA (Fig. S2) from 80-140 °C which corresponds to the removal of the two coordinated and four crystal water molecules (obs. 17.3, calcd. 16.9%). The second weight loss in the temperature range 180-240 °C is assigned to a btb-ligand decarboxylation (obs. 8.5, calcd. for CO_2 6.9%). A gradual weight loss due to ligand decomposition between 300-520 °C then leaves cadmium oxide, CdO (remaining mass obs. 21.9, calcd. 20.1%). An air-dried sample of compound **3** shows the first weight loss in the TGA (Fig. S3) in the temperature range 80-200 °C which is assigned to the removal of the six aqua ligands and the remaining crystal water (obs. 22.2, calcd. for $8H_2O$ 20.4%). This suggests that about two of the four crystal water molecules were lost upon air-drying or during the vacuum cycle in the TGA (hence calculations based on $[Zn(H_2O)_6](H_2btb)_2]\cdot 2H_2O$). A gradual weight loss due to decomposition of only *one* H_3btb molecule between 300-500 °C (obs. 34.6, calcd. 33.3%) apparently leaves a Zn-Hbtb species up to 640 °C (obs. 42.8, calcd. 43.4).

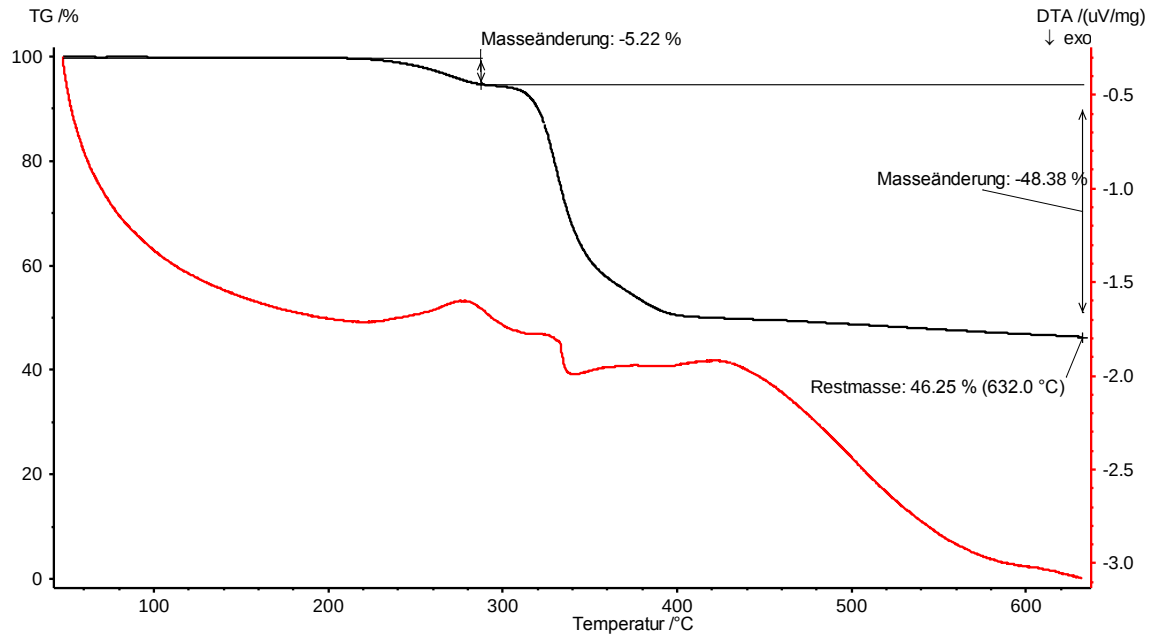

Fig. S1 Thermogravimetric analysis of $^{2}{}_{\infty}[Cu_2(\mu_5\text{-btb})(\mu\text{-OH})(H_2O)]$ (**1**) under nitrogen after a vacuum cycle. Thermogravimetric analyses were carried out on a simultaneous thermoanalysis apparatus STA 409 from Netzsch under nitrogen (heating rate: 10 K min^{-1}, N_2 flow rate: 75 ml/min).

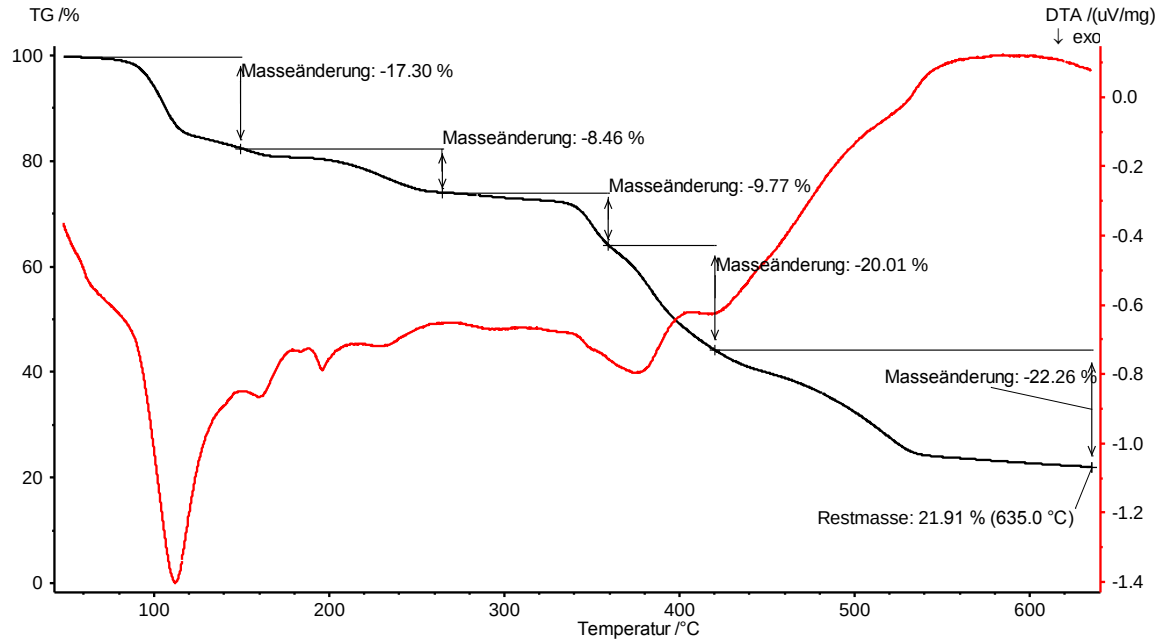

Fig. S2 Thermogravimetric analysis of $[Cd(H_2btb)_2(H_2O)_4]\cdot 2H_2O$ (**2**) under nitrogen after a vacuum cycle. Thermogravimetric analyses were carried out on a simultaneous thermoanalysis apparatus STA 409 from Netzsch under nitrogen (heating rate: 10 K min^{-1}, N_2 flow rate: 75 ml/min).

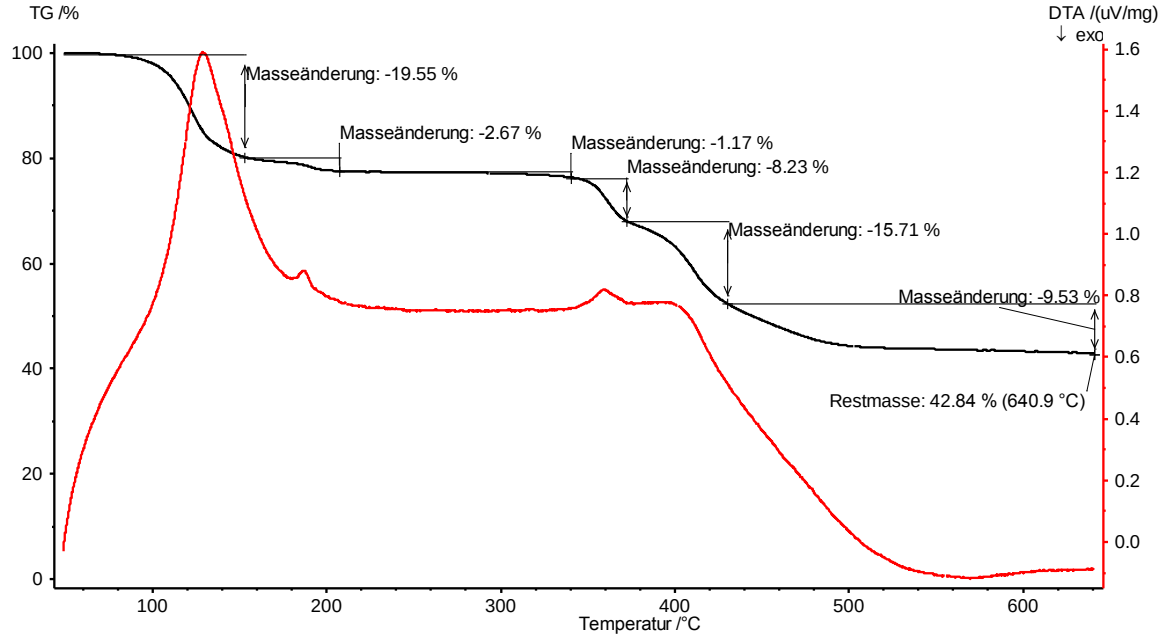

Fig. S3 Thermogravimetric analysis of $[Zn(H_2O)_6](H_2btb)_2]\cdot 4H_2O$ (**3**) under nitrogen after a vacuum cycle. Thermogravimetric analyses on a simultaneous thermoanalysis apparatus STA 409 from Netzsch under nitrogen (heating rate: 10 K min^{-1}, N_2 flow rate: 75 ml/min).

The crystal packing of 2 is dictated by hydrogen bonding without any π interactions (Fig. S4). Adjacent molecular complexes of **2** are connected through strong hydrogen bonding into strands along *c* between the aqua ligands and from the aqua to the carboxylic groups. These hydrogen-bonded strands are extended along *b* into a 2D hydrogen-bonded network through H bonds from the crystal water molecule (O3) bridging between carboxylate groups (Table S1). The non-polar aromatic regions of the btb ligands separate the 2D nets along the *a* direction (not shown).

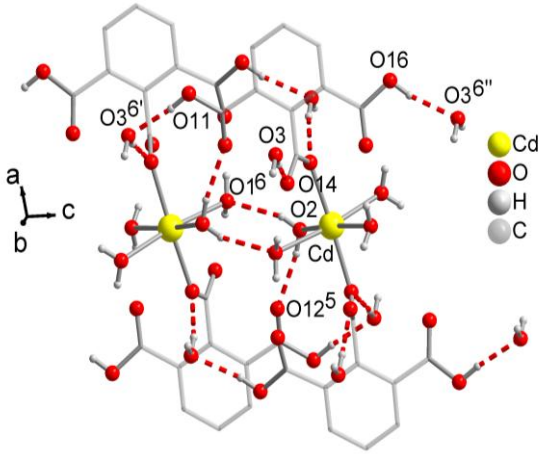

Fig. S4 Hydrogen bonding network (dashes) for the crystal packing of **2** (see Table S1 for details). Carbon atoms and C–C bonds depicted semi-transparent in stick representation with C-H bonds omitted for clarity.

Table S1 Hydrogen bonding interactions in $[Cd(H_2btb)_2(H_2O)_4]\cdot 2H_2O$ (**2**).[a]

D–H···A	D–H [Å]	H···A [Å]	D···A [Å]	D–H···A [°]
intramolecular				
O1–H1A···O14^{2}	0.74(3)	2.07(3)	2.737(2)	152(3)
O1–H1B···O15	0.82(3)	2.00(3)	2.752(2)	153(3)
intermolecular - along c				
O2–H2B···O16	0.77(2)	2.13(2)	2.845(2)	155(3)
O2–H2A···O12^{5}	0.81(3)	1.94(3)	2.737(2)	169(3)
O11–H11···O3$^{6'}$	0.84(3)	1.81(3)	2.647(2)	173(3)
O16–H16···O3$^{6''}$	0.82(3)	1.85(3)	2.662(2)	169(3)
intermolecular - along b				
O3–H5B···O13^{1}	0.75(3)	1.94(3)	2.687(2)	171(3)
O3–H5A···O14	0.79(3)	1.89(3)	2.679(2)	176(3)

[a] D = Donor, A = acceptor. For found and refined atoms the standard deviations are given. Symmetry relations: 1 = x, 1+y, z; 2 = –x, y, 0.5–z; 5 = –x, –y, –z; 6 = x, –y, –0.5+z; 6' = x, 1–y, –0.5+z; 6'' = x, 1–y, 0.5+z

X-ray powder diffractograms

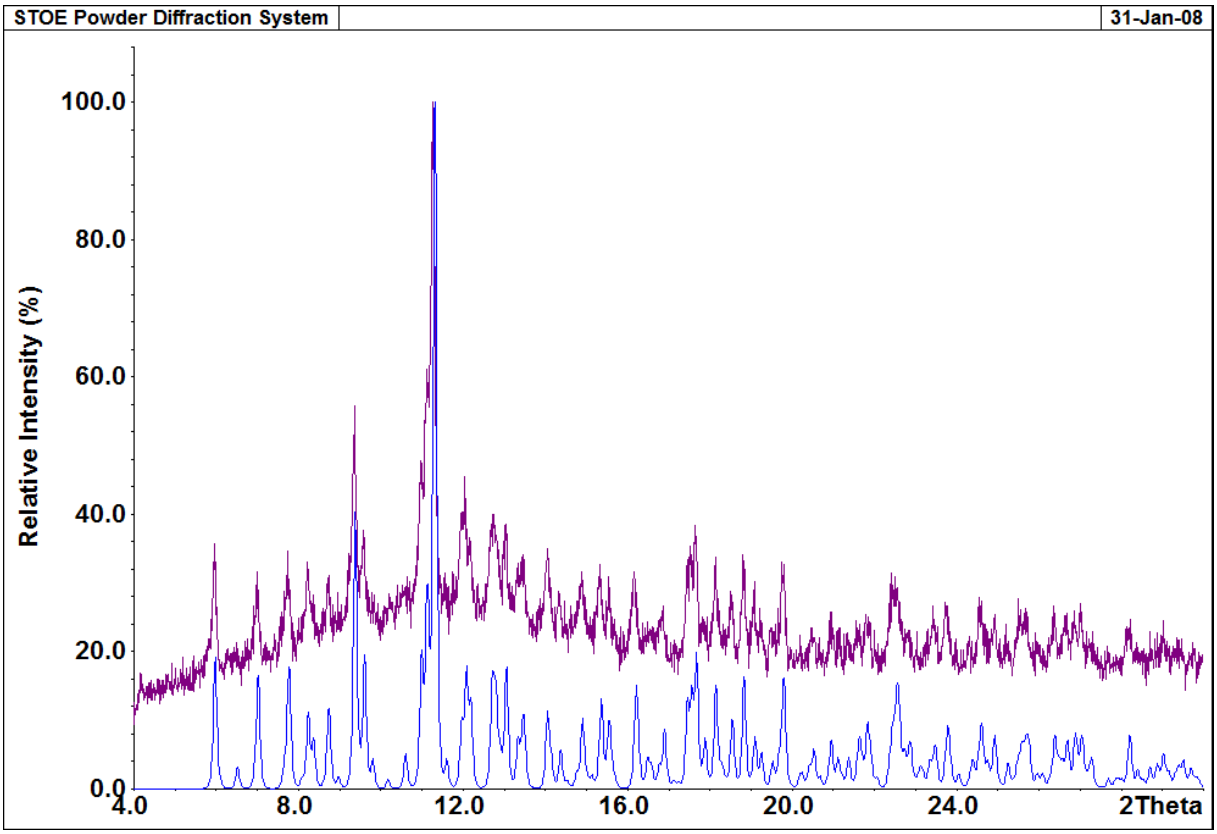

Fig. S5 X-ray powder diffractogram. Blue curve is simulated from single-crystal X-ray data of $^{2}{}_{\infty}[Cu_2(\mu_5\text{-btb})(\mu\text{-OH})(H_2O)]$ (**1**). Purple curve is measured on a microcrystalline sample of **1**.

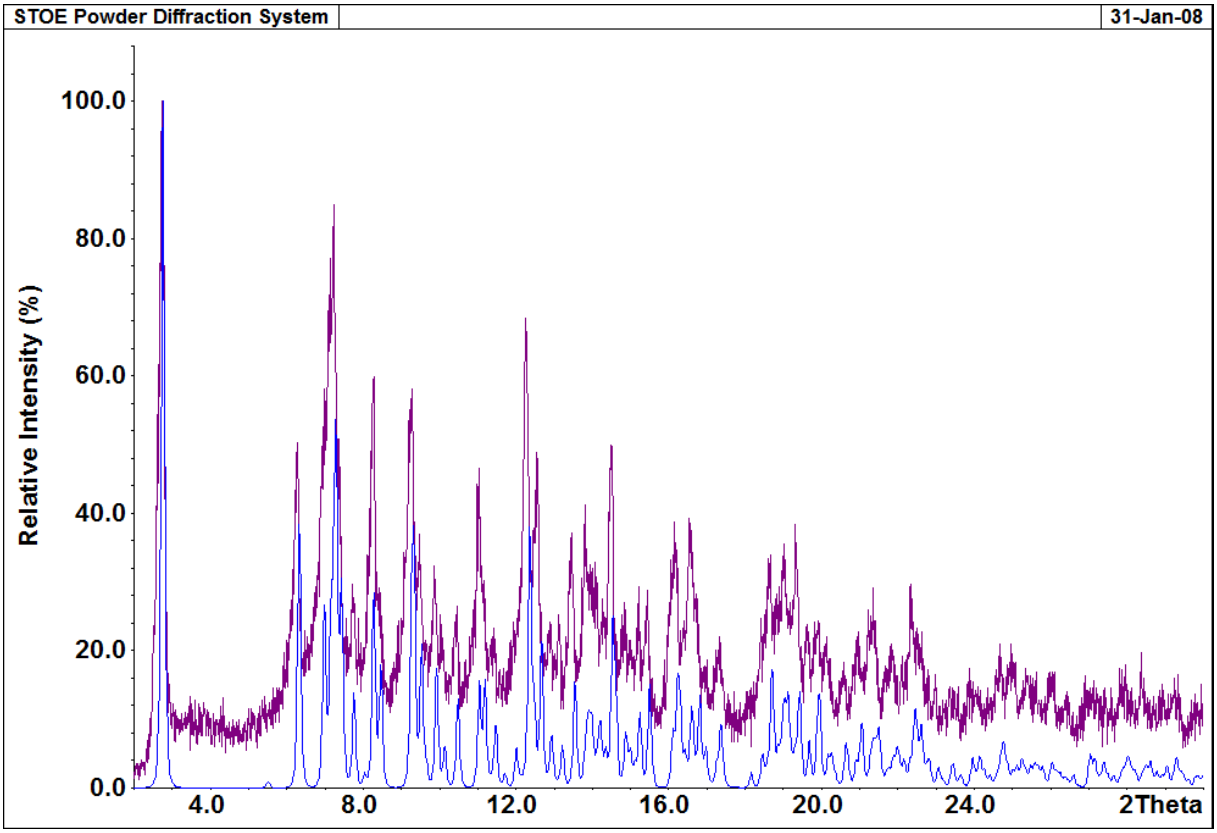

Fig. S6 X-ray powder diffractogram. Blue curve is simulated from single-crystal X-ray data of $[Cd(H_2btb)_2(H_2O)_4]\cdot 2H_2O$ (**2**). Purple curve is measured on a microcrystalline sample of **2**.