Electronic Supplementary Information (ESI)

Crystal structures and solid-state CPMAS ^{13}C NMR correlations in luminescent zinc(II) and cadmium(II) mixed-ligand coordination polymers constructed from 1,2-bis(1,2,4-triazol-4-yl)ethane and benzenedicarboxylate

Hesham A. Habib, [a] Anke Hoffmann,[b] Henning A. Höppe [a] and Christoph Janiak*,[a]

[a] *Institut für Anorganische und Analytische Chemie, Universität Freiburg, Albertstr. 21, D-79104 Freiburg, Germany. E-mail: janiak@uni-freiburg.de; Fax: 49 761 2036147; Tel: 49 761 2036127*
[b] *Institut für Makromolekular Chemie, Universität Freiburg, Stefan-Meier-Sr. 31, D-79104 Freiburg, Germany.*

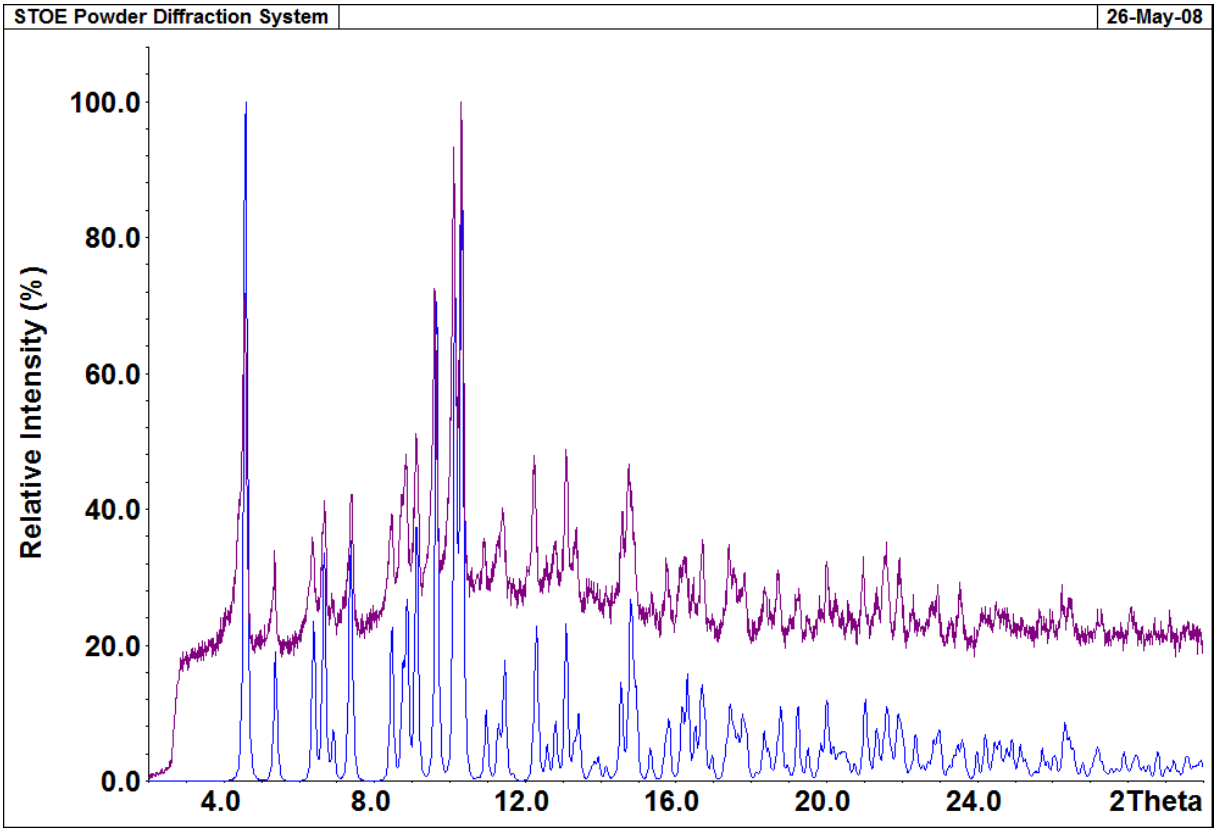

Fig. S1 X-ray powder diffractogram. Blue curve is simulated from single-crystal X-ray data of $^{3}_{\infty}${[Zn_2(μ_2-bdc)$_2$(μ_4-btre)]} (**1**). Purple curve is measured on a crystal sample of **1**.

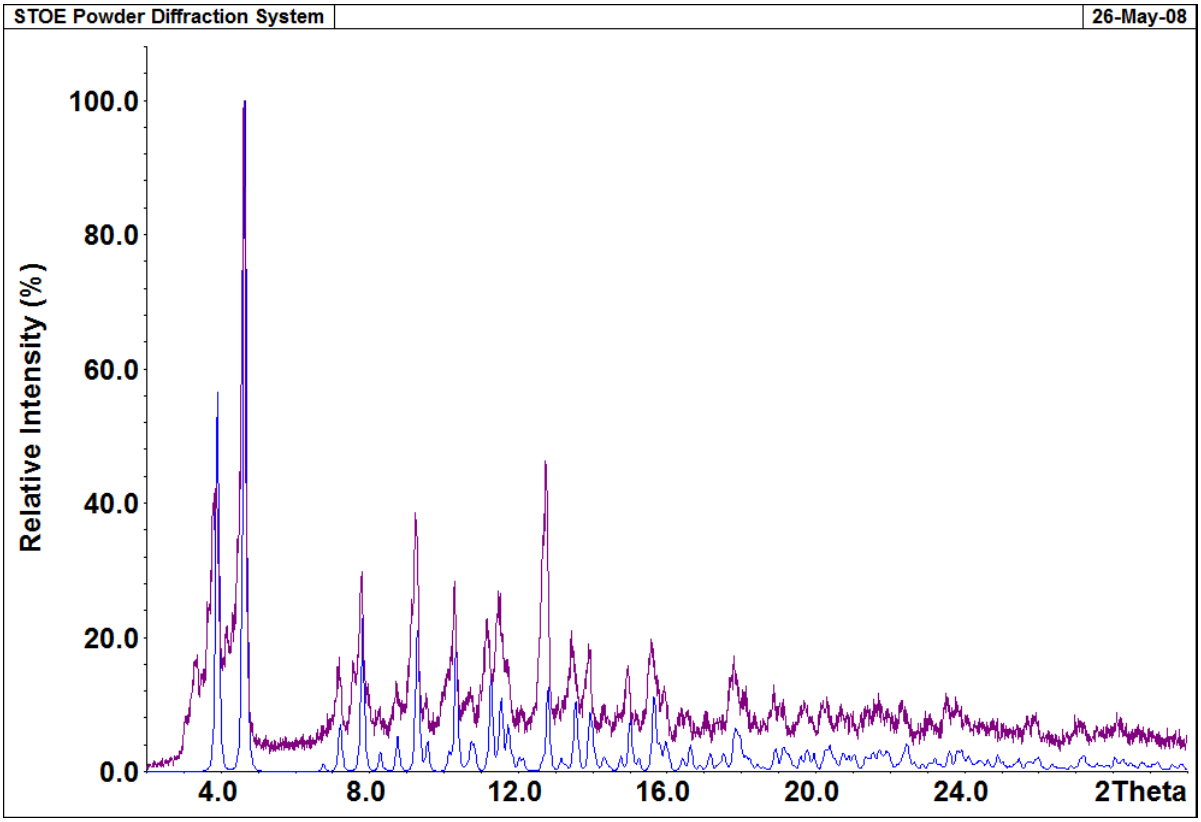

Fig. S2 X-ray powder diffractogram. Blue curve is simulated from single-crystal X-ray data of $^{3}_{\infty}\{[Cd_2(\mu_4\text{-bdc})(\mu_4\text{-btre})_2](NO_3)_2\cdot H_2O\}$ (**2**). Purple curve is measured on an air-dried crystal sample of **2**.

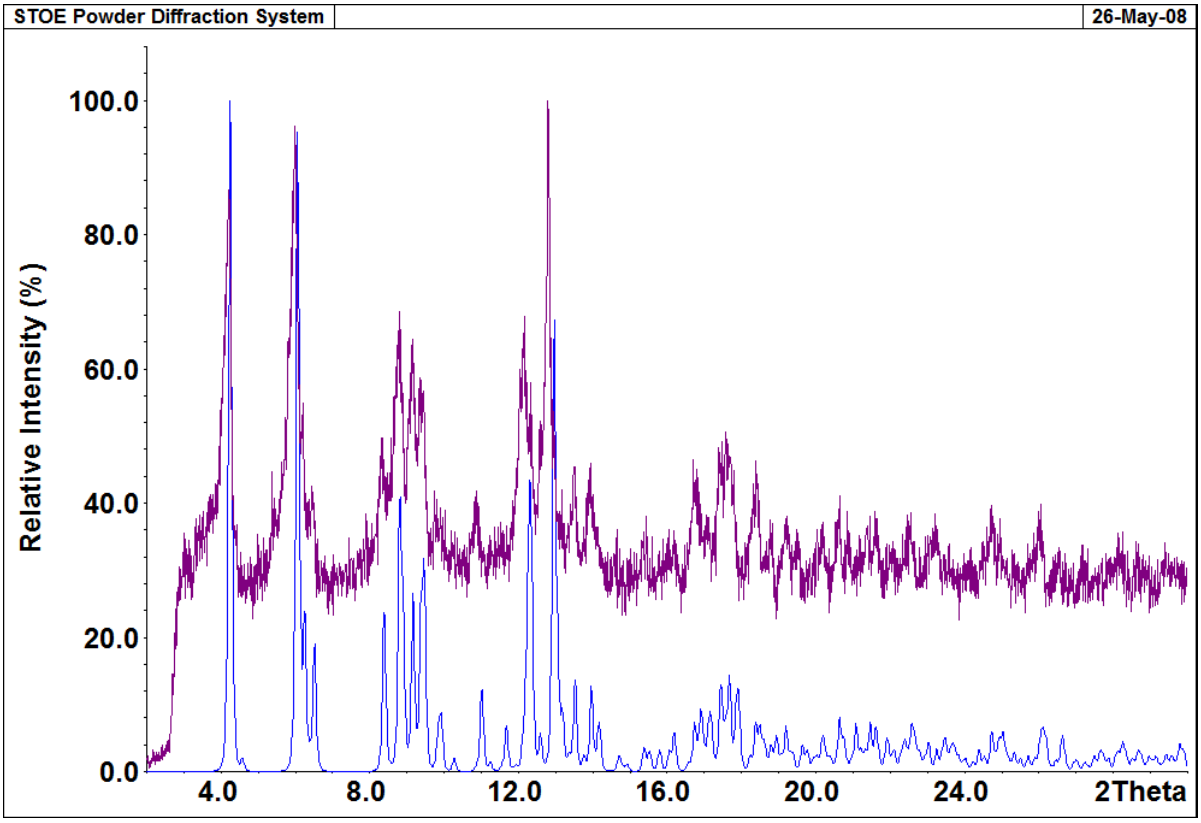

Fig. S3 X-ray powder diffractogram. Blue curve is simulated from single-crystal X-ray data of $^{2}_{\infty}\{[Zn_2(\mu_3\text{-ip})_2(\mu_2\text{-btre})(H_2O)_2]\cdot 2H_2O\}$ (**3**). Purple curve is measured on an air-dried crystal sample of **3**.

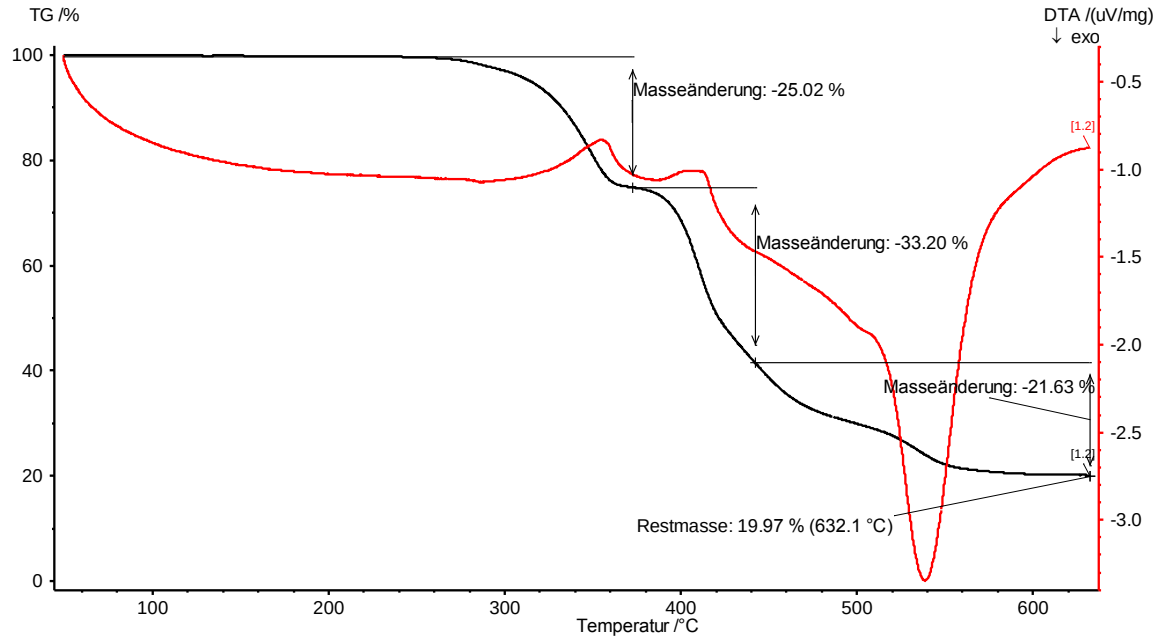

Fig. S4 Thermogravimetric analysis of $^{3}_{\infty}\{[Zn_2(\mu_2\text{-bdc})_2(\mu_4\text{-btre})]\}$ (**1**) under nitrogen after a vacuum cycle. Thermogravimetric analyses were carried out on a simultaneous thermoanalysis apparatus STA 409 from Netzsch under nitrogen (heating rate: 10 K min^{-1}, N_2 flow rate: 75 ml/min).

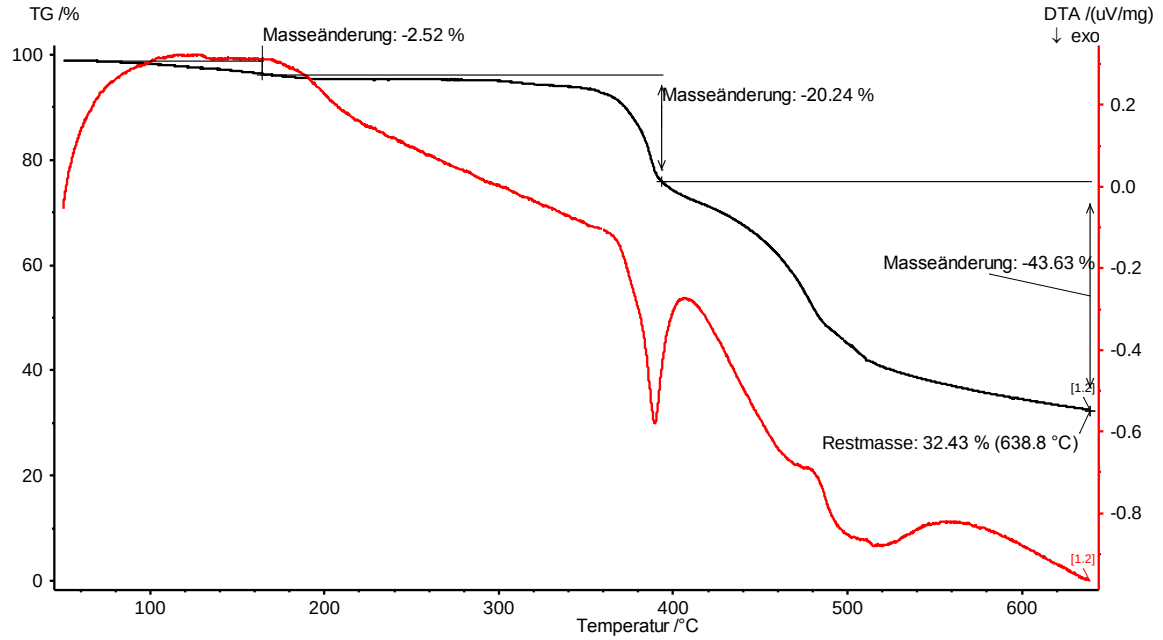

Fig. S5 Thermogravimetric analysis of $^{3}_{\infty}\{[Cd_2(\mu_4\text{-bdc})(\mu_4\text{-btre})_2](NO_3)_2\cdot H_2O\}$ (**2**) under nitrogen after a vacuum cycle. Thermogravimetric analyses were carried out on a simultaneous thermoanalysis apparatus STA 409 from Netzsch under nitrogen (heating rate: 10 K min^{-1}, N_2 flow rate: 75 ml/min).

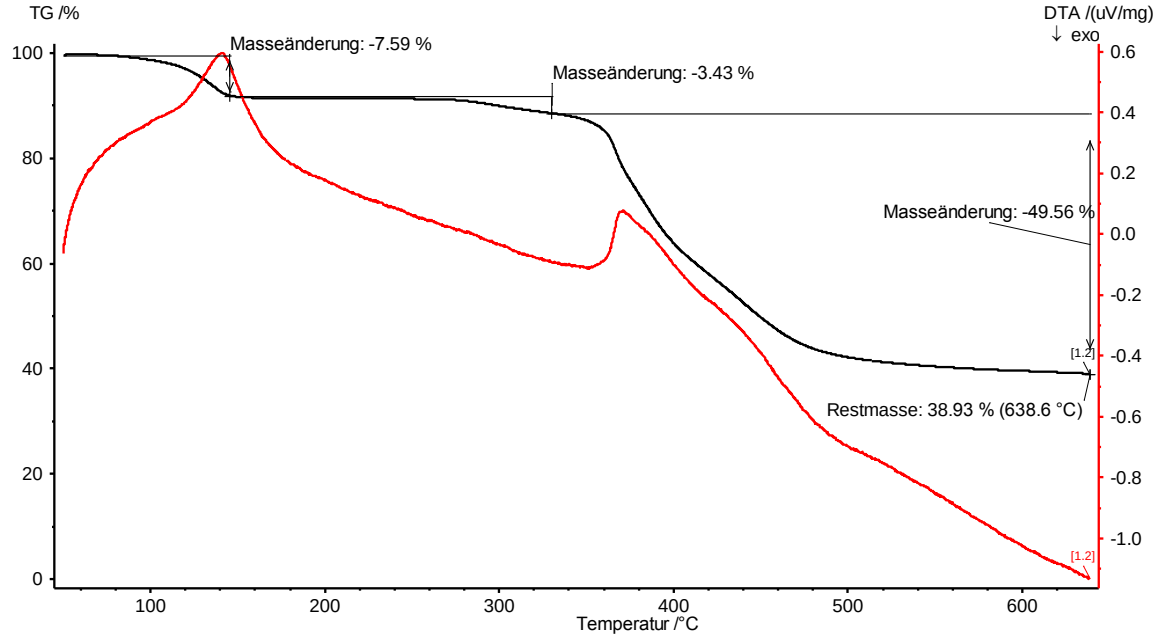

Fig. S6 TGA of $^{2}_{\infty}\{[Zn_2(\mu_3\text{-ip})_2(\mu_2\text{-btre})(H_2O)_2]\cdot 2H_2O\}$ (**3**) under nitrogen after a vacuum cycle. (Netzsch STA 409, heating rate: 10 K min^{-1}, N_2 flow rate: 75 ml/min).

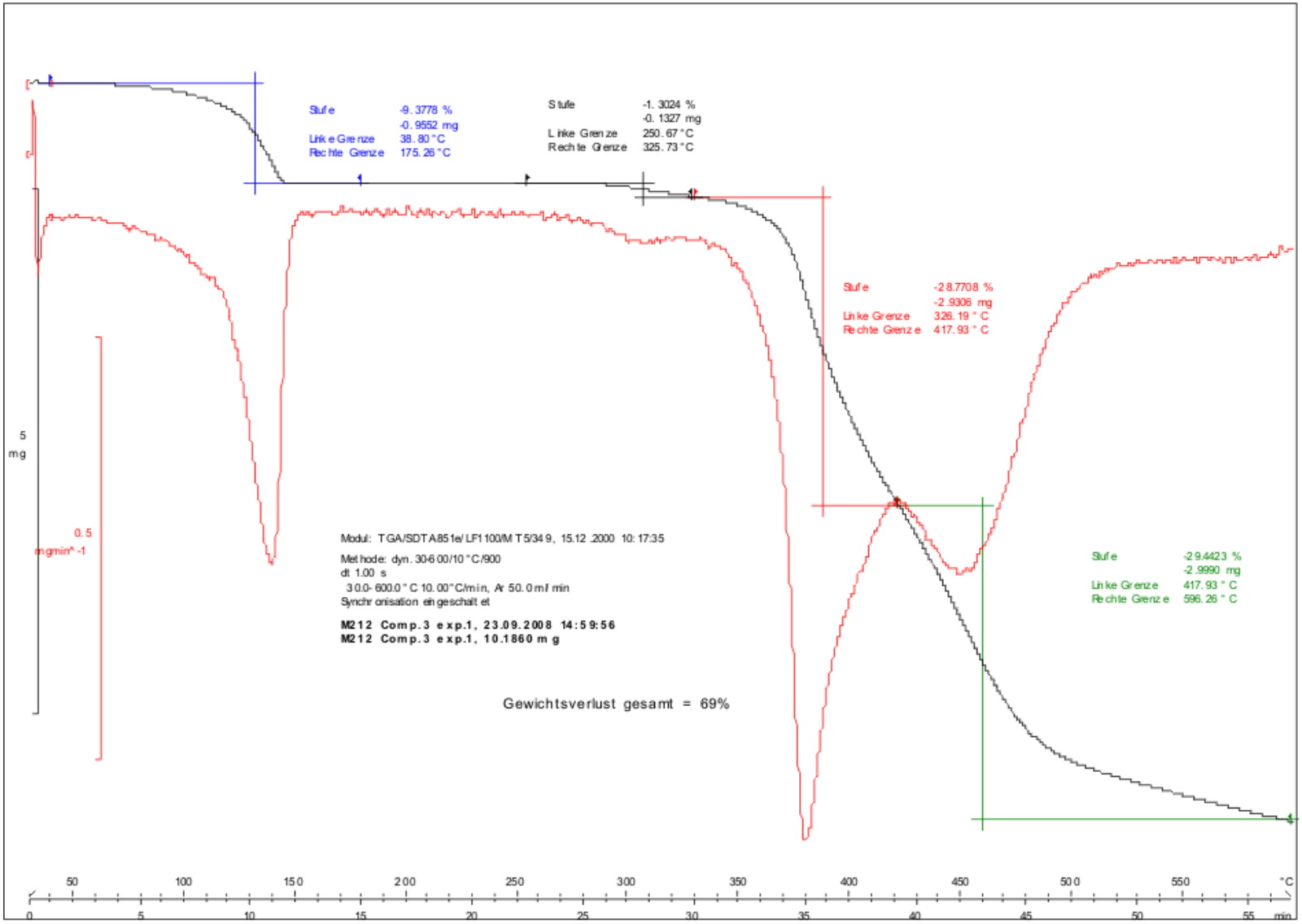

Fig. S7 TGA of $^{2}_{\infty}\{[Zn_2(\mu_3\text{-ip})_2(\mu_2\text{-btre})(H_2O)_2]\cdot 2H_2O\}$ (**3**) (Mettler TGA/SDTA 851e coupled with the Nicolet Nexus 470 gas phase FTIR and the Balzers Quadrupole MS. Experiments under Argon (60 ml/min) in 900 µl alox crucibles, with 10°C/min.)

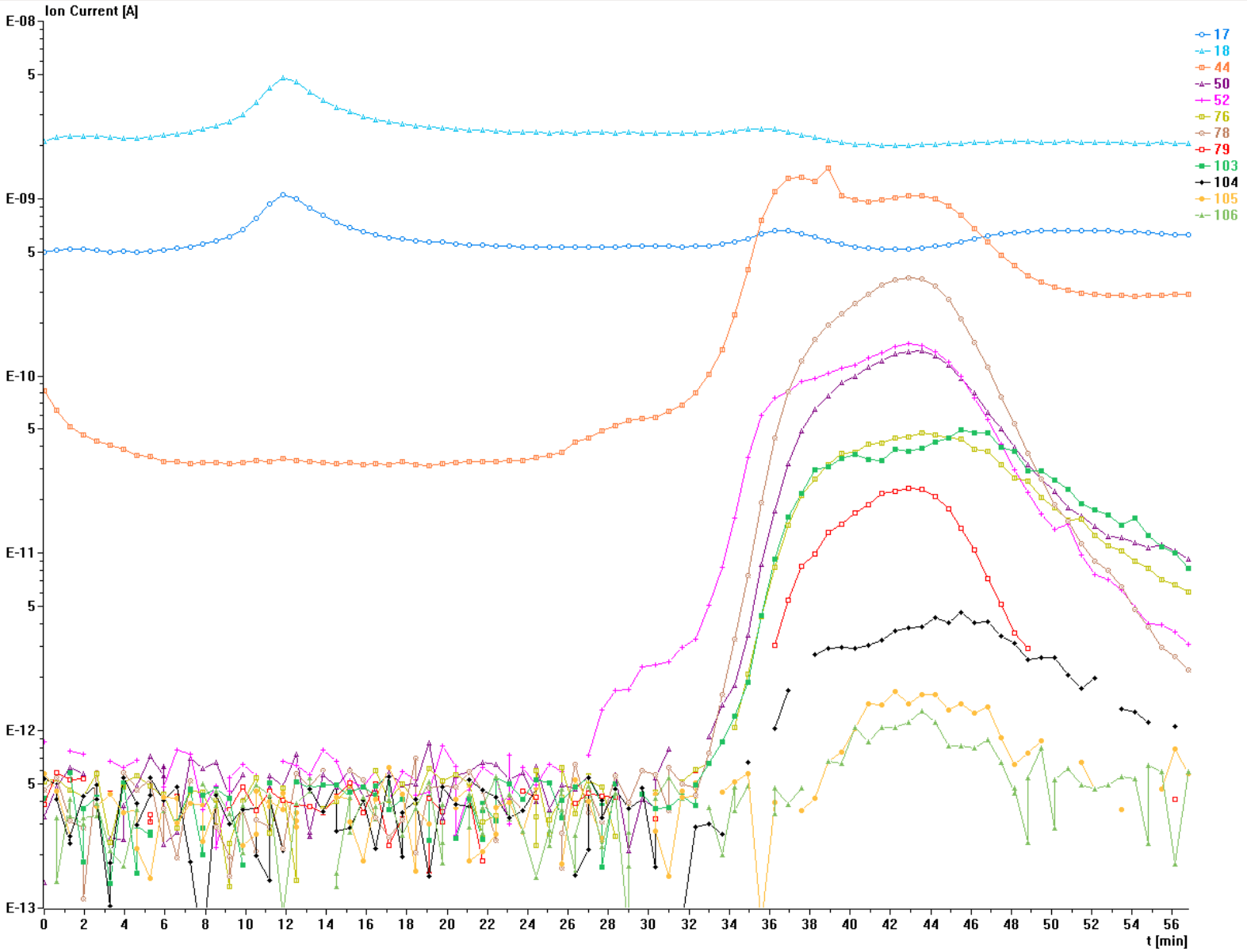

Fig. S8 TGA-MS ion current curves of $^{2}_{\infty}\{[Zn_2(\mu_3\text{-ip})_2(\mu_2\text{-btre})(H_2O)_2]\cdot 2H_2O\}$ (**3**) as a function of time (for correlation with temperature see the abscissa in Fig. S7) (Mettler TGA/SDTA 851e coupled with the Nicolet Nexus 470 gas phase FTIR and the Balzers Quadrupole MS)

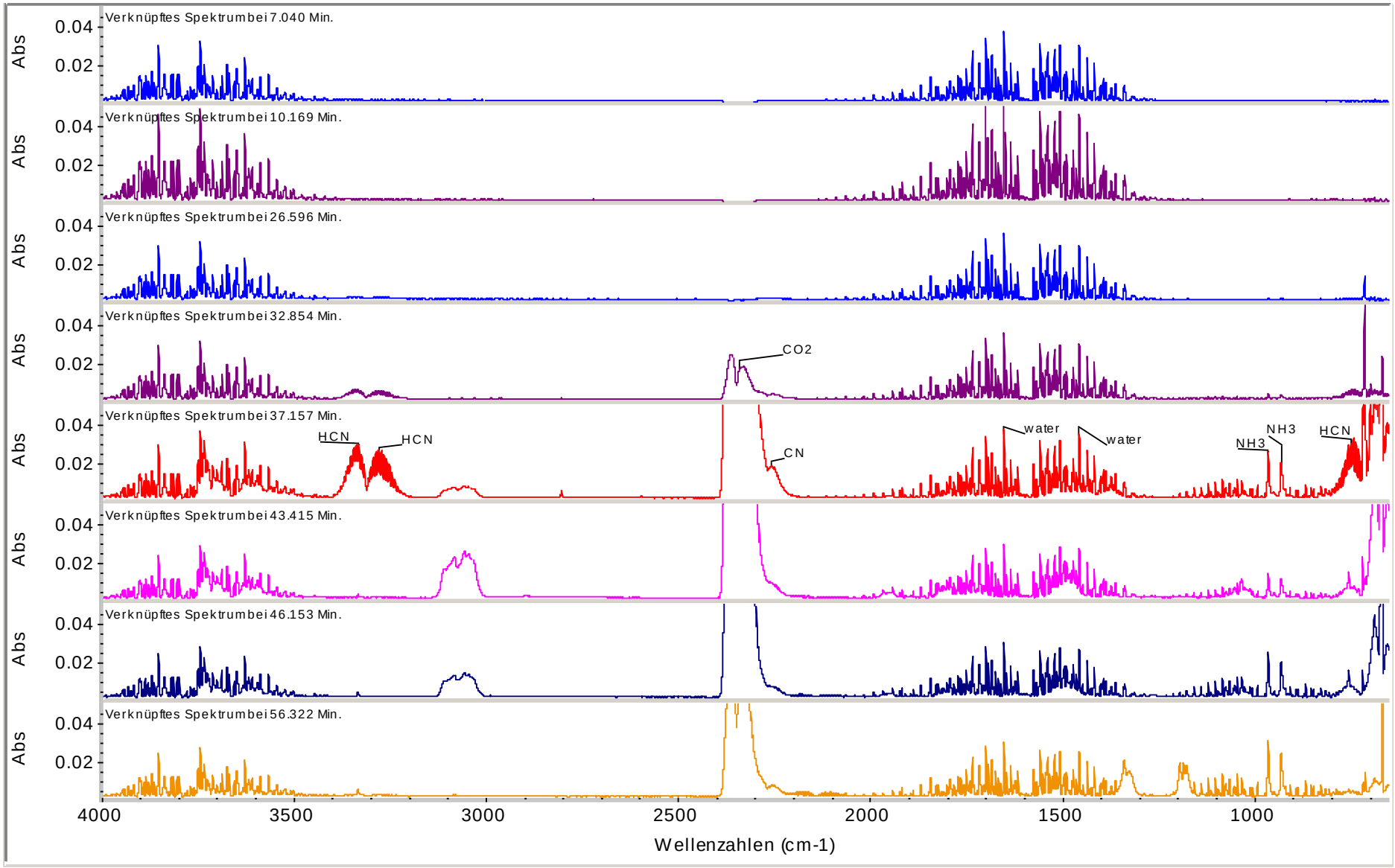

Fig. S9 TGA-IR spectra of $^{2}_{\infty}\{[Zn_2(\mu_3\text{-ip})_2(\mu_2\text{-btre})(H_2O)_2]\cdot 2H_2O\}$ (**3**) as a function of time (for correlation with temperature see the abscissa in Fig. S7) (Mettler TGA/SDTA 851e coupled with the Nicolet Nexus 470 gas phase FTIR and the Balzers Quadrupole MS).

Hydrogen bonding interactions

The structures of the metal complexes of **1**-**3** been positively evaluated with respect to C–H···O/N hydrogen bonding. Details of the C–H···O/N bonding scheme were calculated by the program PLATON.[i] Structural parameters for the C–H···O/N bonding interactions in some of the compounds of **1**-**3** (Fig. S7 to S9) below a cutoff criterion of 3.0 Å, are collected in Table S1. The structures of the of **2** and **3** often contain a considerable number of water molecules as metal-aqua ligands or/and as solvent of crystallization. In **3**, the incorporation of water of crystallization is obviously due to the presence of the additional nitrogen donor atoms and the formation of O5–H5A···N2 bonds. In view of the large number of oxygen and nitrogen atoms in these compounds, they are good candidates for the study of the possible role of C–H···O/N bonds in the crystal packing. The water and the nitrate molecules in **2** and **3** play an important role in the stabilization of the crystal phases.

Table S1. Selected geometrical parameters for C–H···O/N hydrogen bonds in compounds **1**-**3**.

Compound	C–H···O/N [Å]	C–H [Å]	H···O/N [Å]	C···O/N [Å]	D–H···A [°]
1	C1–H1···O4 ^{7}	0.94	2.46	3.02(2)	118
	C2–H2···O2 ^{8}	0.94	2.37	3.22(2)	150
	C10–H10···O1 ^{8}	0.94	2.57	3.34(2)	140
2	C1–H1···O7 ^{8}	0.94	2.55	3.28(2)	134
	C1–H1···O8 ^{8}	0.94	2.58	3.36(2)	140
	C2–H2···O6 $^{6'}$	0.94	2.58	3.50(1)	165
	C2–H2···O8 $^{8'}$	0.94	2.42	3.26(2)	148
	C3–H3B···O7 ^{8}	0.98	2.44	3.12(2)	126
	C4–H4···O5	0.94	2.46	3.32(2)	152
	C5–H5···O5 ^{1}	0.94	2.29	3.13(2)	148
	C5–H5···O3 $^{2'}$	0.94	2.38	3.22(2)	149
	C6–H6A···O7 ^{2}	0.98	2.56	3.44(2)	149
	C13–H13···N2 ^{6}	0.94	2.62	3.39(5)	139
	C13–H13···N5 ^{6}	0.94	2.62	3.36(5)	136
3	O5–H5A···N2 ^{2}	0.78(3)	2.05(3)	2.81(2)	163(3)
	O5–H5B···O3 $^{2'}$	0.82(3)	1.97(3)	2.76(2)	160(3)
	O6–H6A···O5	0.92(4)	2.08(4)	2.95(3)	158(3)
	O6–H6B···O4 ^{1}	0.95(4)	2.08(4)	2.965(3)	154(3)
	C1–H1···O2	0.94	2.33	3.040(2)	132
	C1–H1···O6 $^{2'}$	0.94	2.50	3.223(3)	134
	C3–H3A···O4 $^{1'}$	0.98	2.59	3.525(2)	161
	C3–H3B···O6 $^{2'}$	0.98	2.39	3.096(3)	129

Symmetry relations:

for **1**: 7 = –3/2–x, 1/2–y, –1–z; 8 = 1/2+x,1/2–y,1/2+z.

for **2**: 1 = x, –1+y, z; 2 = –x, y, 1/2–z; 2' = –x, –1+y, 1/2–z; 6 = 1/2–x, 1/2+y, 1/2–z; 6' = 1/2–x, –1/2+y, 1/2–z; 8 = 1/2+x,1/2–y,1/2+z; 8' = 1/2+x, –1/2–y, 1/2+z.

for **3**: 1 = x, 1+y, z; 1' = –1+x, 1+y, 1+z; 2 = –x, 2–y, 1–z; 2' = 1–x, 1–y, 1–z;

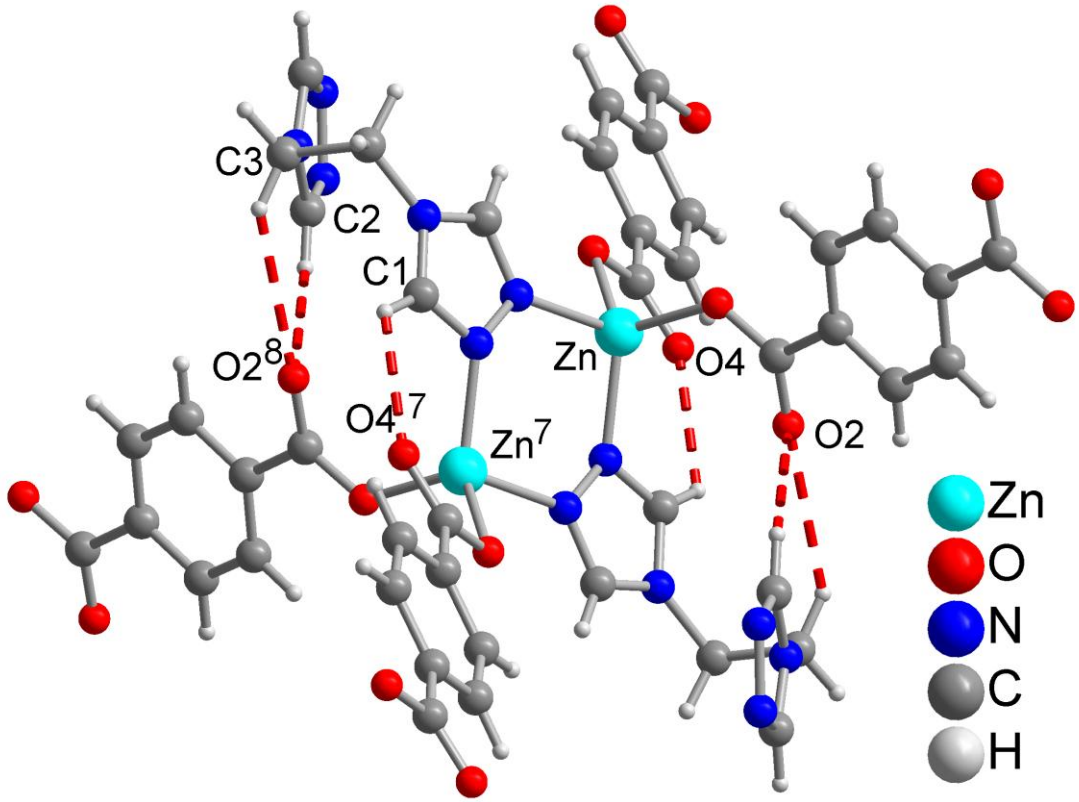

Fig. S10 Selected hydrogen bonds in compound **1**. For details see Table S1

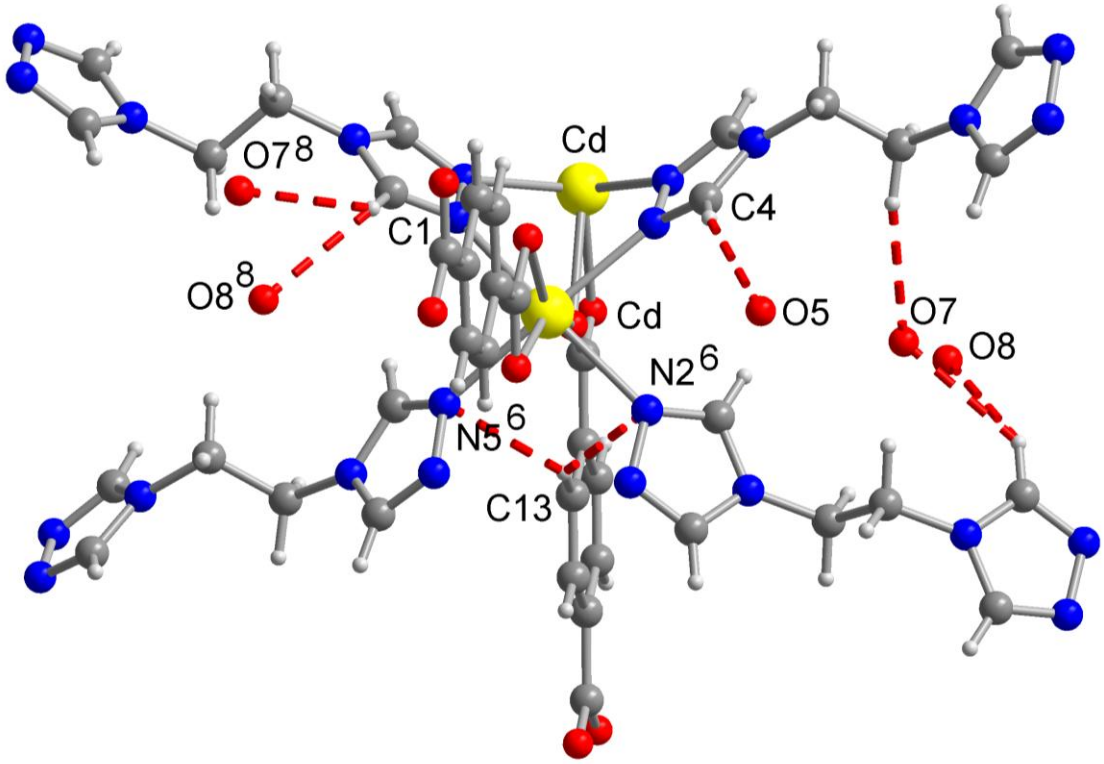

Fig. S11 Selected hydrogen bonds in compound **2**. For details see Table S1. O5, O7 and O8 belong to the disordered nitrate anions.

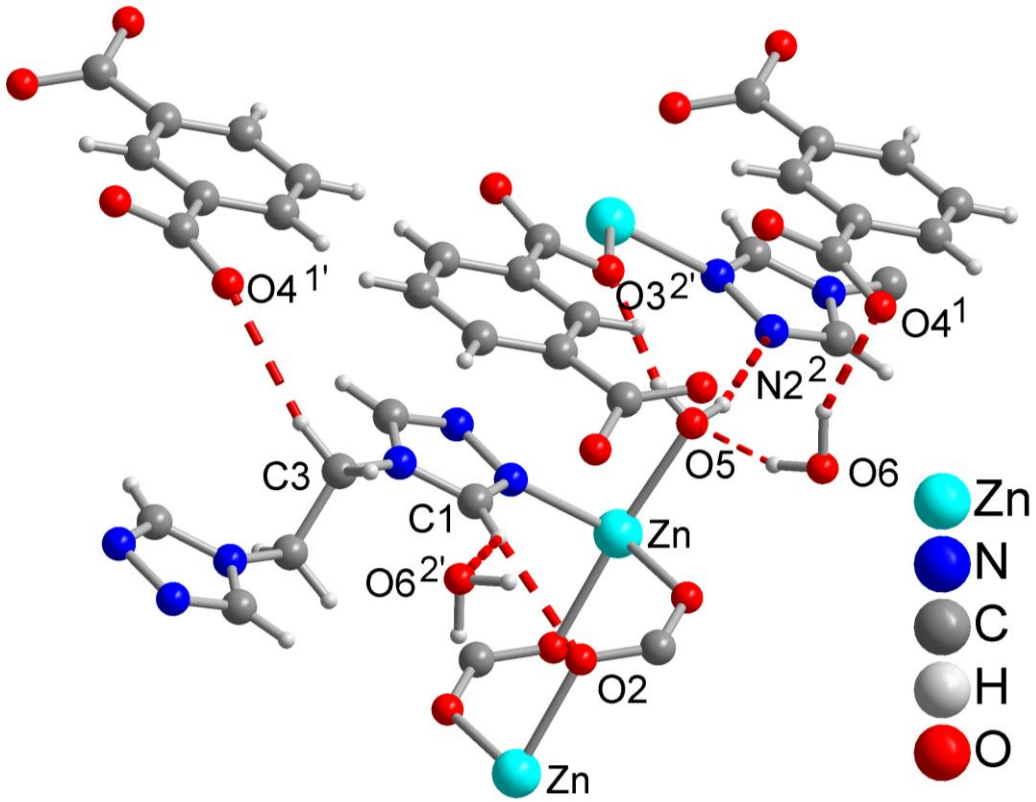

Fig. S12 Selected hydrogen bonds in compound **2**. For details see Table S1.

[i] (a) A. L. Spek, *Acta Crystallogr.*, 1990, *A46*, C34; (b) A. L. Spek, PLATON Version 29-11-98, in: L. J. Farrugia (Ed.), Windows implementation, University of Glasgow, 1998.