

## **Study of temperature and flexibility of ligands effects on coordination polymers formation from cyclobutanetetracarboxylic acid.**

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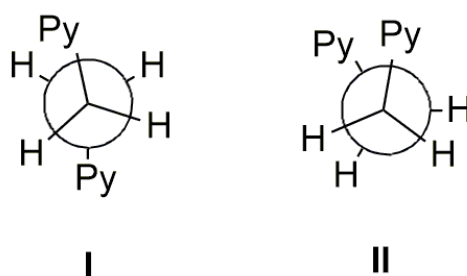
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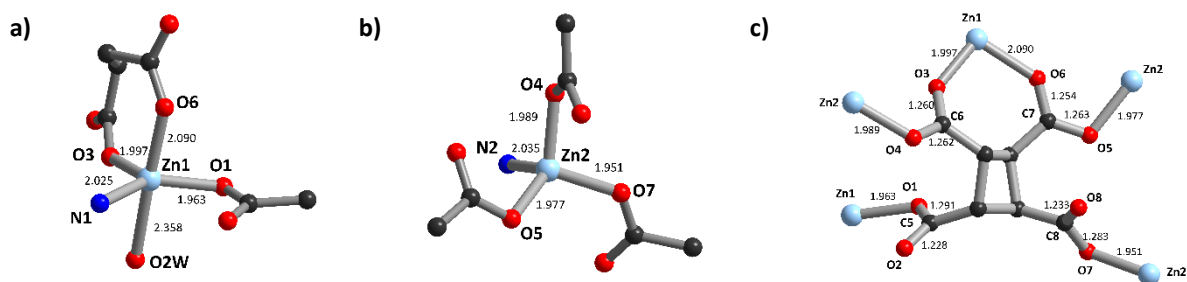
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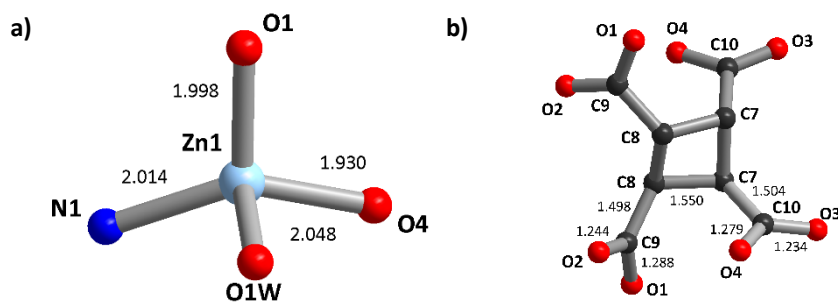
**Table S1.** X-ray diffraction experimental details.

	1	2	3
<b>Crystal data</b>			
<b>Chemical formula</b>	C <sub>20</sub> H <sub>22</sub> N <sub>2</sub> O <sub>11</sub> Zn <sub>2</sub>	C <sub>10</sub> H <sub>10</sub> NO <sub>5</sub> Zn	C <sub>16</sub> H <sub>20</sub> N <sub>2</sub> NiO <sub>7</sub> ·H <sub>2</sub> O
<b>M<sub>r</sub></b>	597.13	289.56	429.06
<b>Crystal system, space group</b>	Monoclinic, <i>P2<sub>1</sub>/c</i>	Monoclinic, <i>P2<sub>1</sub>/c</i>	Monoclinic, <i>P2<sub>1</sub>/c</i>
<b>Temperature (K)</b>	293	293	293
<b>a, b, c (Å)</b>	15.023 (2), 10.1643 (13), 18.196 (3)	5.8438 (13), 12.088 (3), 15.288 (3)	12.956 (2), 9.8991 (10), 16.960 (2)
<b>β (°)</b>	114.233 (2)	99.975 (5)	109.750 (2)
<b>V (Å<sup>3</sup>)</b>	2533.6 (6)	1063.7 (4)	2047.2 (4)
<b>Z</b>	4	4	4
<b>Radiation type</b>	Mo Kα	Mo Kα	Mo Kα
<b>μ (mm<sup>-1</sup>)</b>	1.95	2.32	0.99
<b>Crystal size (mm)</b>	0.45 × 0.15 × 0.10	0.45 × 0.40 × 0.37	0.40 × 0.35 × 0.25
<b>Data collection</b>			
<b>Diffractometer</b>	Rigaku, AFC-7 diffractometer		
<b>Absorption correction</b>	Multi-scan Jacobson, R. (1998), Private communication		
<b>T<sub>min</sub>, T<sub>max</sub></b>	0.704, 0.813	0.370, 0.434	0.700, 0.800
<b>No. of measured, independent and observed [I &gt; 2σ(I)] reflections</b>	21935, 4737, 4124	12846, 2115, 1760	23825, 3874, 3289
<b>R<sub>int</sub></b>	0.028	0.044	0.029
<b>(sin θ/λ)<sub>max</sub> (Å<sup>-1</sup>)</b>	0.655	0.664	0.653
<b>Refinement</b>			
<b>R[F<sup>2</sup> &gt; 2σ(F<sup>2</sup>)], wR(F<sup>2</sup>), S</b>	0.032, 0.079, 1.05	0.036, 0.092, 1.10	0.033, 0.088, 1.06
<b>No. of reflections</b>	4737	2115	3874
<b>No. of parameters</b>	336	160	268
<b>No. of restraints</b>	6	2	8
<b>H-atom treatment</b>	H atoms treated by a mixture of independent and constrained refinement.		
<b>Δρ<sub>max</sub>, Δρ<sub>min</sub> (eÅ<sup>-3</sup>)</b>	0.36, -0.51	0.33, -0.70	0.31, -0.37
Computer programs: <i>CrystalClear</i> , <sup>1</sup> <i>Superflip</i> , <sup>2</sup> <i>SHELXL2013</i> , <sup>3</sup> <i>SHELXLE</i> , <sup>4</sup> <i>DIAMOND 3.3k</i> , <sup>5</sup> <i>PLATON</i> , <sup>6</sup> and <i>publCIF</i> . <sup>7</sup>			

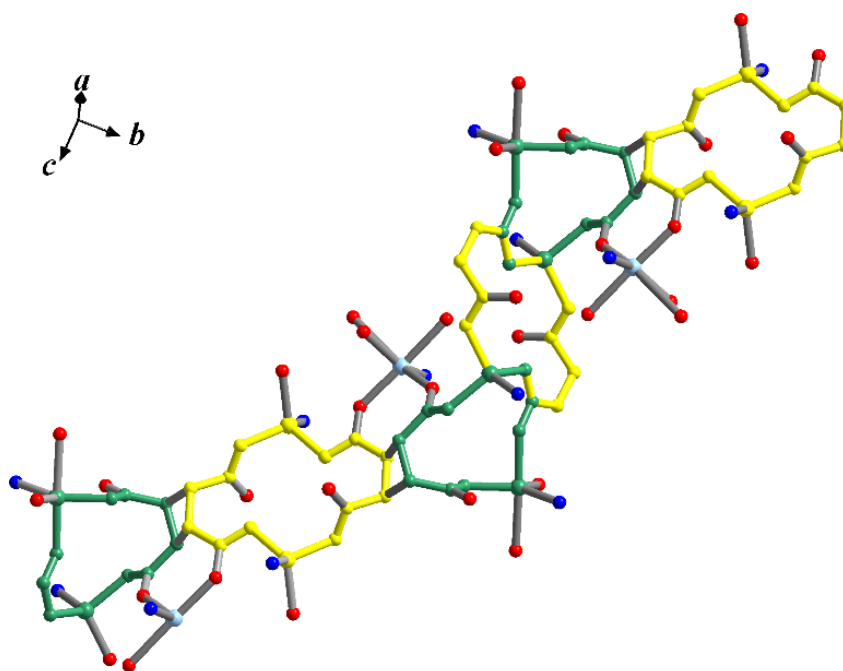
**Fig. S1** Diagram I and II represents anti and gauche conformation for 4,4'-bpe ligand, respectively.



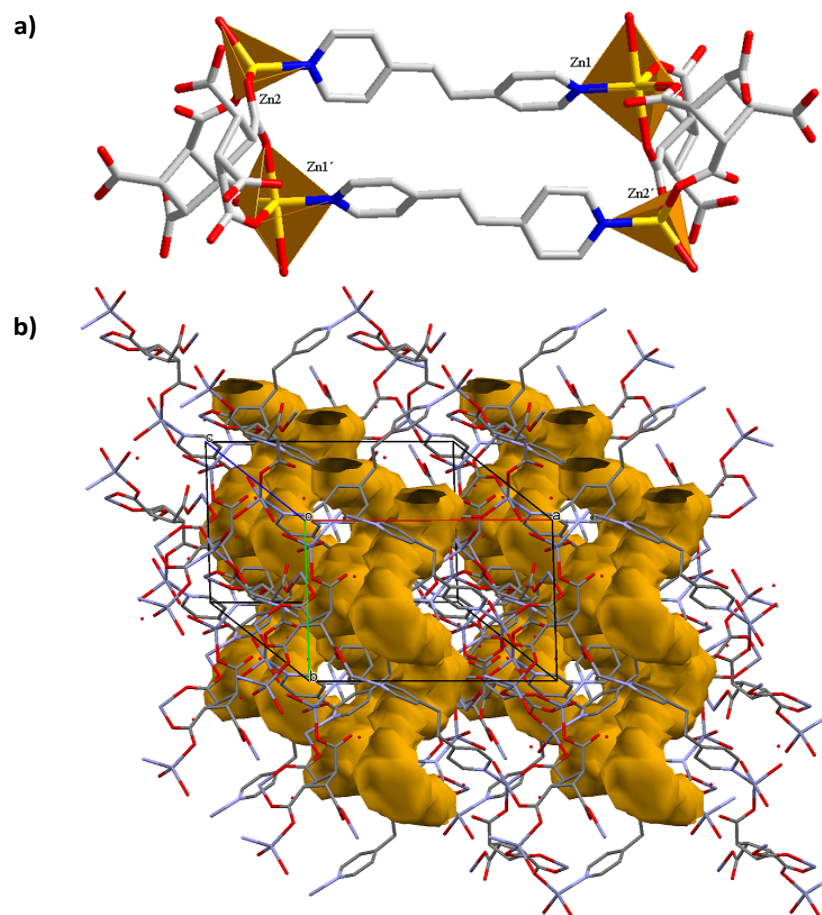
**Fig. S2** *a)* and *b)* Schematic representation of the bonds distances to bonds involved in the coordination sphere of the Zn1 and Zn2 ions. *c)* Comparatively shows the distances of links to carboxylates groups, where the O3–O4–C6 carboxylate group is that shares its negative charge between Zn1 and Zn2 ions via resonance, as discussed in the section of compound **1**.



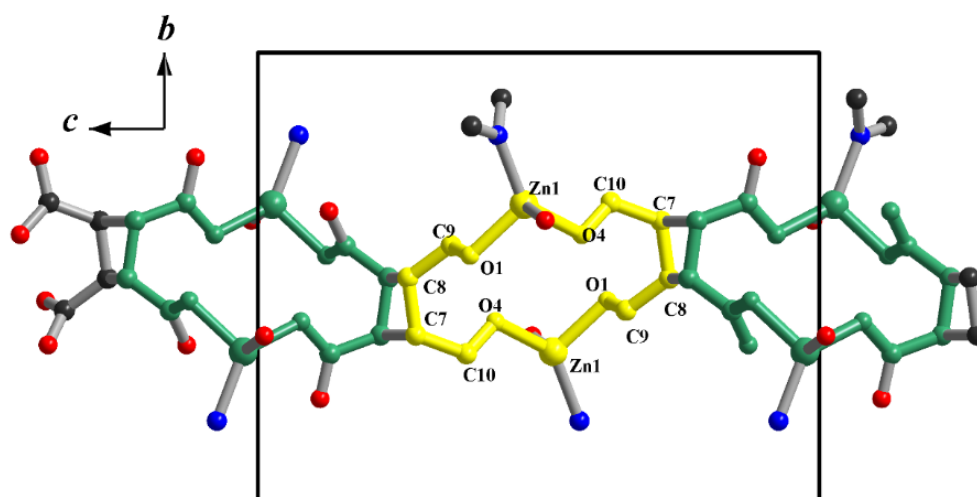
**Fig. S3** *a)* Schematic representation of the bonds distances to bonds involved in the tetrahedral coordination sphere of the Zn1 ion for compound **2**. *b)* Shows the bonds distances to carboxylates groups.



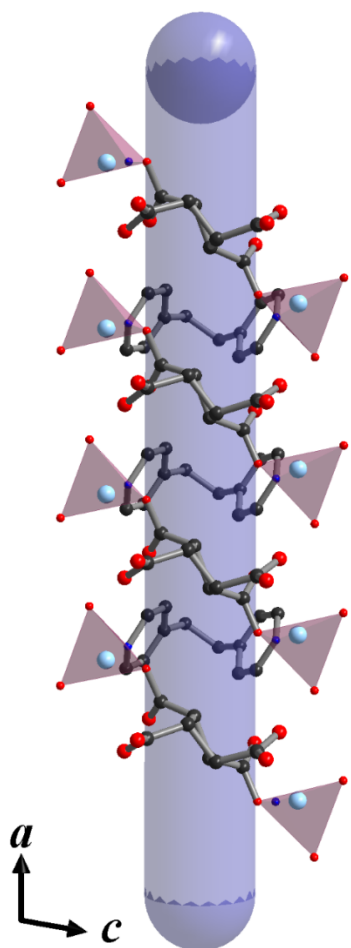
**Fig. S4** Pre-organized supramolecular structure type ring of 11 (green color) and 12 (yellow color) members.



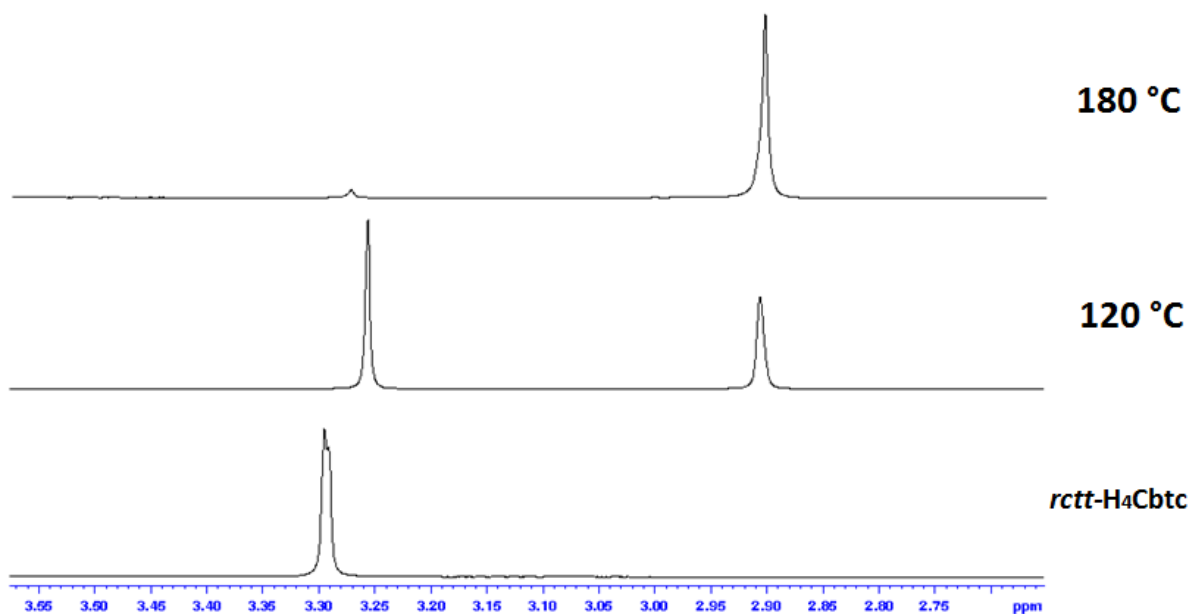
**Fig. S5.** (a) Cyclic structure generated by Zn1 and Zn2 metal centers in the **1** along the [010]-direction. (b) Supramolecular channels 1-D imaginary extended along *b*-axis. The water molecules left this channel formed by voids volume. These channels are illustrated with voids calculate in facilities Mercury program.



**Fig. S6.** Pre-organized supramolecular structure type ring of 12 (green and yellow color) members.



**Fig. S7.** Extract from the crystal packing of **2**. This shows helicoid motif connection presenting the 4,4'-**bpe** ligand between zinc ions to another at unit of translation.



**Fig. S8.**  $^1\text{H-NMR}$  spectra for the resulting solid from the reaction mixture at (a) 120 and (b) 180  $^{\circ}\text{C}$ , respectively. In both spectra the signal for the methine hydrogen in *rctt*- and *rtct-cbtc* was observed at 3.26 and 2.90 ppm, respectively. Moreover, (c)  $^1\text{H-NMR}$  spectrum for the starting ligand, *rctt-cbtc* isomer with a chemical shift for the methine hydrogen of 3.28 ppm. This shift is consistent with that reported in the ref. 16c by a deviation from  $\Delta\delta/\text{ppm} = 0.22$ .

**Table S2.** Selected Geometric parameters for the structure **1-3**.

<b>1</b>		<b>2</b>		<b>3</b>	
<b>Bond distances (Å)</b>					
Zn1—O1	1.963(2)	Zn1—O4	1.929(2)	Ni1—O1	2.066(2)
Zn1—O3 <sup>i</sup>	1.997(2)	Zn1—N1	2.011(3)	Ni1—O1W	2.074(2)
Zn1—N1	2.025(2)	Zn1—O1	1.997(2)	Ni1—O2W	2.104(2)
Zn1—O6	2.090(2)	Zn1—O1W	2.045(2)	Ni1—O3W	2.113(2)
Zn1—O2W	2.358(2)			Ni1—N1	2.073(2)
Zn2—O7	1.951(2)			Ni1—N2 <sup>i</sup>	2.082(2)
Zn2—O5	1.977(2)				
Zn2—O4	1.989(2)				
Zn2—N2 <sup>ii</sup>	2.035(2)				
C8—O7	1.283(3)				
C5—O2	1.228(3)				
C5—O1	1.291(4)				
C6—O3	1.261(3)				
C6—O4 <sup>i</sup>	1.262(3)				
C7—O6 <sup>iii</sup>	1.254(3)				
C7—O5	1.263(3)				
C8—O8	1.233(3)				
<b>Bond angles (°)</b>					
O1—Zn1—O3 <sup>i</sup>	112.14(9)	O4—Zn1—O1	105.2(1)	O1—Ni1—O1W	83.93(6)
O1—Zn1—N1	135.49(9)	O1—Zn1—N1	112.8(1)	O1—Ni1—O2W	85.48(6)
O3 <sup>i</sup> —Zn1—N1	110.47(9)	O1—Zn1—O1W	98.4(1)	O1—Ni1—O3W	92.07(6)
O1—Zn1—O6	88.79(8)	O4—Zn1—N1	137.4(1)	O1—Ni1—N1	90.19(7)
N1—Zn1—O6	95.83(9)	O4—Zn1—O1W	95.6(1)	O1—Ni1—N2 <sup>i</sup>	172.17(7)
O1—Zn1—O2W	88.84(9)	N1—Zn1—O1W	97.4(1)	O1W—Ni1—O2W	89.86(6)
O3 <sup>i</sup> —Zn1—O2W	79.43(8)			O1W—Ni1—O3W	175.93(6)
O3 <sup>i</sup> —Zn1—O6	100.32(7)			O1W—Ni1—N1	89.03(7)
N1—Zn1—O2W	86.74(9)			O1W—Ni1—N2 <sup>i</sup>	92.35(7)
O6—Zn1—O2W	177.31(9)			O2W—Ni1—O3W	90.62(6)
O7—Zn2—O5	104.48(8)			O2W—Ni1—N1	175.62(7)
O7—Zn2—O4	102.59(8)			O2W—Ni1—N2 <sup>i</sup>	87.63(7)
O5—Zn2—O4	123.50(8)			O3W—Ni1—N1	90.19(7)
O7—Zn2—N2 <sup>ii</sup>	120.1(1)			O3W—Ni1—N2 <sup>i</sup>	91.71(7)
O5—Zn2—N2 <sup>ii</sup>	109.48(9)			N1—Ni1—N2 <sup>i</sup>	96.66(8)
O4—Zn2—N2 <sup>ii</sup>	97.77(8)				
<b>Torsion angle (°)</b>					
C11—C19—C20—C16	168.3(4)	C3—C6—C6 <sup>i</sup> —C3 <sup>i</sup>	-49.9(6)	C7—C15—C16—C12	69.5(3)

Symmetry codes 1: (i)  $-x, y-1/2, -z+1/2$ ; (ii)  $x-1, -y+1/2, z-1/2$ ; (iii)  $-x, y+1/2, -z+1/2$ .Symmetry codes 2: (i)  $-x+1, y, -z+1/2$ .Symmetry codes 3: (i)  $-x+1, y, -z+3/2$ .

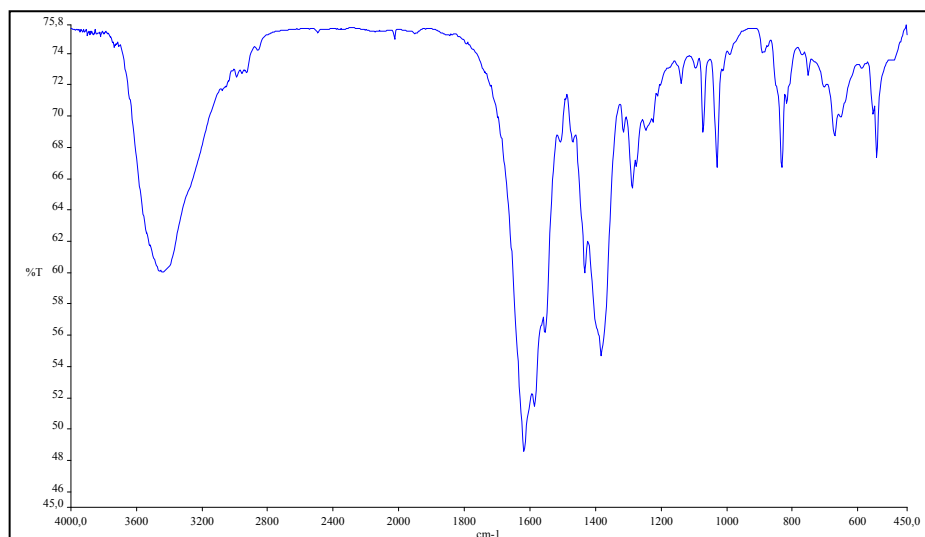
**Table S3.** Hydrogen-bond geometry for compounds **1-3**.

D—H...A	D—H (Å)	H...A (Å)	D...A (Å)	D—H...A (°)
<b>1</b>				
O1W—H1B...O2W <sup>vi</sup>	0.84(2)	2.11(3)	2.921(4)	163(7)
O2W—H2B...O8 <sup>vii</sup>	0.84(2)	2.11(2)	2.922(4)	165(6)
O3W—H3A...O7 <sup>i</sup>	0.86(2)	1.95(2)	2.792(3)	167(4)
O3W—H3B...O1 <sup>iv</sup>	0.85(2)	2.01(2)	2.848(4)	169(5)
Symmetry codes: (i) -x, y-1/2, -z+1/2; (iii) -x, y+1/2, -z+1/2; (iv) x, -y+1/2, z+1/2; (v) -x, -y+1, -z.				
<b>2</b>				
O1W—H1W...O1 <sup>ii</sup>	0.85(2)	1.93(2)	2.775(3)	170(4)
O1W—H2W...O2 <sup>iii</sup>	0.85(2)	1.99(2)	2.808(3)	162(4)
Symmetry codes: (ii) -x+1, -y+1, -z+1; (iii) x-1, y, z.				
<b>3</b>				
O1W—H1A...O3	0.85(2)	2.04(2)	2.872(2)	170(2)
O1W—H1B...O3 <sup>ii</sup>	0.85(2)	2.97(2)	3.676(2)	141(2)
O2W—H2A...O3 <sup>ii</sup>	0.86(2)	1.86(2)	2.707(2)	174(3)
O2W—H2B...O4	0.85(2)	2.01(2)	2.851(2)	172(3)
O3W—H3A...O2	0.87(2)	1.84(2)	2.676(2)	162(3)
O3W—H3B...O2 <sup>iii</sup>	0.84(2)	1.96(2)	2.791(2)	173(3)
O4W—H4A...O4	0.85(2)	1.99(2)	2.826(4)	168(6)
Symmetry codes: (ii) -x, -y+1, -z+1; (iii) -x, -y, -z+1.				

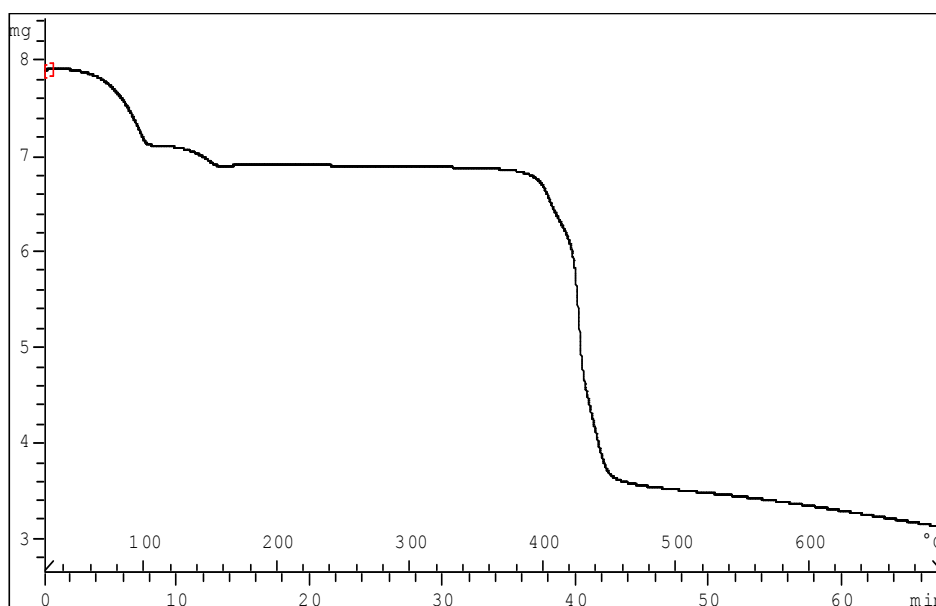
**FT-IR spectra and TG analyses for compounds 1.**

The IR spectra of compounds **1** depicted in Fig. S8. In the infrared spectrum of compound **1**, the characteristic absorption bands are observed: an intense band between 3600-3000 cm<sup>-1</sup> are attributed of O—H stretching. The absence of the band at 1718 cm<sup>-1</sup> of the starting acid ligand shows that all the carboxylic groups are involved in the coordination to the cation metal, two sharp and intense bands around 1619 and 1384 cm<sup>-1</sup> that are attributed at asymmetric and symmetric stretching of carboxylate anion, respectively. Around this same region are overlapped stretching C=N and C=C. The bands range in 1289-1030 cm<sup>-1</sup> correspond to C—H bending in the plane and between 833-672 cm<sup>-1</sup> to C—H bending out of plane.





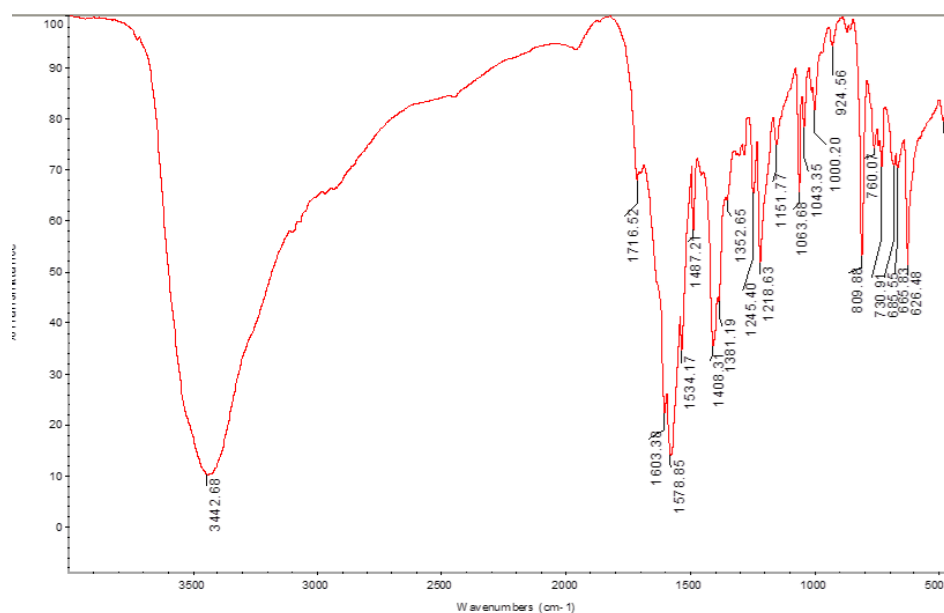
**Fig. S9.** View of infrared spectrum of compounds **1**.



**Fig. S10.** View of TGA plot for compounds **1**.

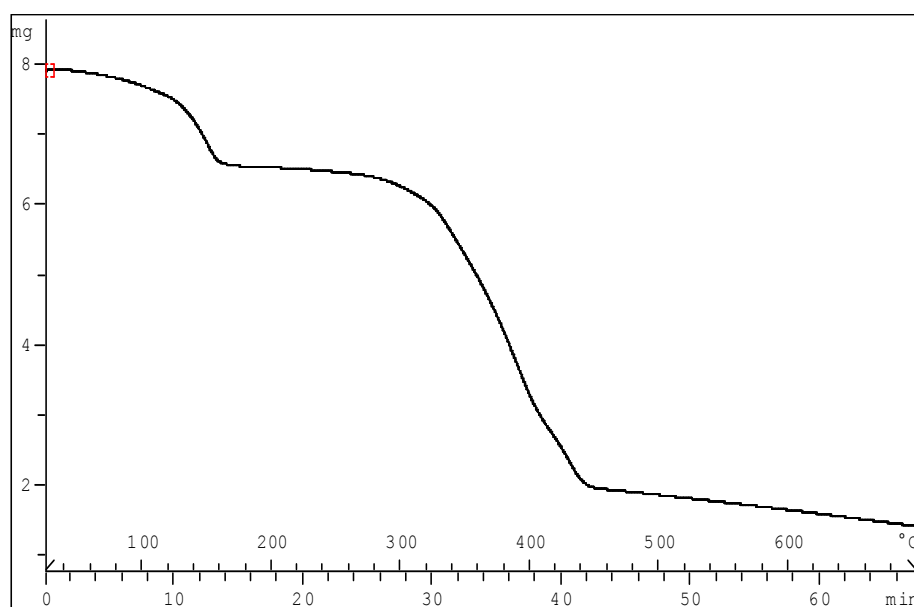
### **FT-IR spectra and TG analyses for compounds **3**.**

The IR spectra of compounds **3** depicted in Fig. S11. In the infrared spectrum, the characteristic absorption bands are observed: an intense band between 3600-3000  $\text{cm}^{-1}$  are attributed of O—H stretching. The absence of the band at 1718  $\text{cm}^{-1}$  of the starting acid ligand shows that all the carboxylic groups are involved in the coordination to the cation metal, two sharp and intense bands around 1619 and 1384  $\text{cm}^{-1}$  that are attributed at asymmetric and symmetric stretching of carboxylate anion, respectively. Around this same region are overlapped stretching C=N and C=C. The bands range in 1289-1030  $\text{cm}^{-1}$  correspond to C—H bending in the plane and between 833-672  $\text{cm}^{-1}$  to C—H bending out of plane.

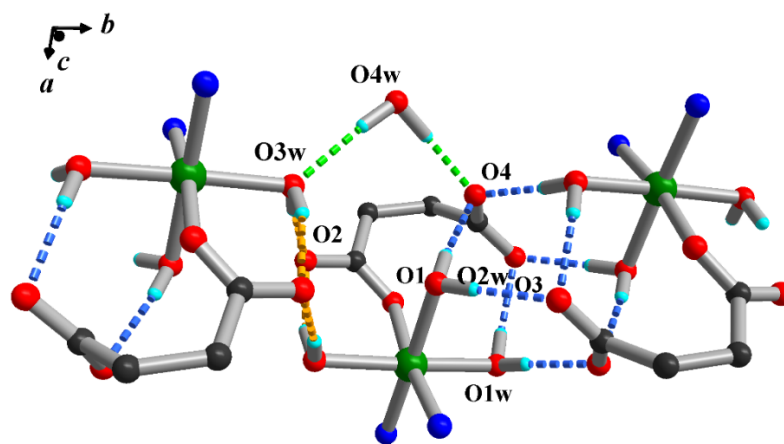


**Fig. S11.** View of infrared spectrum of compound **3**.

For **3**, the TGA curve shows that the first weight loss of 8.17%, occurring from 31.10 to 175.34 °C, corresponds to the loss of solvent molecules (calculated 23.24%). A second weight loss occurs up to 200 °C at 58.25 % (w/w), which is associated with the partial decomposition of the organic ligands (C<sub>15</sub>H<sub>3</sub>O<sub>4</sub>N<sub>2</sub> calculated value 56.14 %). The resulting residue unidentified stabilizes at around 630 °C, which could be associated with the formation of nickel oxide and carbon.



**Fig. S12.** View of TGA plot for compound **3**.



**Fig. S13.** Viewing molecule O4w acting as a bridge between the water molecule, O3w, and the coordinating oxygen atom, O4, from the carboxylate group, after performing the DFT-optimization for the bulk crystal packing compound **3**.

## References

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