

## Hydrothermal synthesis and crystal structure of a new coordination polymer: $[Zn_1(deta)(btec)(H_2O)_2]_n$

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**Abstract:** A new metal–organic compound  $[Zn_1(deta)(btec)(H_2O)_2]_n$  where (deta= Diethylenetriamine) and (btec= benzenetetracarboxylic acid) (**I**) was hydrothermally synthesized from an aqueous solution of  $Zn(NO_3)_2 \cdot 6H_2O$ , (deta) and (btec). Compound **I** crystallize in the monoclinic system with the  $P2_1/c$  space group. The unit cell parameters are  $a= 9.6716(5) \text{ \AA}$ ,  $b= 14.3776(8) \text{ \AA}$ ,  $c= 13.5306(8) \text{ \AA}$ ,  $\beta= 105.311(3)^\circ$ ,  $Z= 4$ ,  $V= 1814.71(18) \text{ \AA}^3$  and  $D_x= 1.657 \text{ g/cm}^3$ . The refinement converged into  $R= 0.045$ ,  $R_w= 0.048$ . The structure, determined by single crystal X-ray diffraction, consists of a network of  $ZnO_4$  centers, tetrahedrally coordinated by pyromellitate anions giving rise to a two-dimensional sheet structure. The connectivity resembles a 4-connected network in which each Zn atom is connected to four btec anions and each btec anion is linked to four  $Zn^{2+}$  ions.

**Keywords:** Hydrothermal synthesis; X-ray diffraction; Crystal structure; Thermal decomposition.

### Introduction

The synthesis and structure of inorganic–organic hybrid compounds constitute one of the most flourishing areas of research in solid-state chemistry. During the 90's, multifunctional benzene carboxylic acids have been successfully employed for the preparation of a new class of metal–organic frameworks<sup>1-5</sup>.

The use of multidentate organic ligands and metal ions to construct metal-organic frameworks (MOFs) has attracted much attention<sup>6</sup> due to their fascinating molecular and/or supramolecular structural diversity<sup>7</sup> and enormous potential applications as new functional material in gas storage and separation, magnetic materials, ion-exchange<sup>8-14</sup>, catalysis<sup>15</sup>, etc. The rigid aromatic polycarboxylate ligands, such as 1,4-benzenedicarboxylate (1,4-bdc)<sup>16-17</sup>, 1,3-benzenedicarboxylate (m-bdc)<sup>18-19</sup>, 1,2-benzenedicarboxylate (1,2-bdc)<sup>20-21</sup>, 1,3,5-benzenetricarboxylate (1,3,5-btc)<sup>22-23</sup>, have been widely used as bridging ligands for the design and synthesis of porous materials with robust structures and high porosity.

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DOI: <http://dx.doi.org/10.13171/mjc.2.4.2013.03.05.10>

The high symmetry 1,2,4,5-benzenetetracarboxylic ( $H_4btec$ ) molecule is a potential diverse charge and rigid multidentate ligand, its eight oxygen atoms can possibly induce a variety of coordination modes and interesting structures through complete or partial deprotonation of its four carboxyl groups, and it can form bridges between metallic centers by two to four carboxyl groups, generating various molecular architectures. In addition,  $H_4btec$  can act not only as hydrogen bond donors but also as acceptors owing to the existence of protonated and/or deprotonated carboxyl groups with intermolecular hydrogen bonds and  $\pi$ - $\pi$  interactions<sup>24-26</sup>.

The introduction of ancillary ligands can be considered to occupy some coordination sites, inhibit the expansion of the polymeric frameworks, induce new structural evolution, and obtain the desired low dimensional coordination polymers. The chelate ligand such as *deta* is regarded as excellent N-donor candidates for maintaining the one dimensionality of the coordination polymers and constructing supramolecular structure via hydrogen bonds and  $\pi$ - $\pi$  interactions.

The variations in the possible binding modes of the four acid groups of the pyromellitic acid along with the different coordination preferences of the metal ions can give rise to a variety of interesting structures. We have been focusing our attention on the preparation of new benzene carboxylate coordination polymers, especially those involving  $H_4btec$  in the presence of organic amine molecules, by employing hydrothermal methods. During the course of these investigations, we have now isolated a new zinc pyromellitate,  $[(NH(NH_2)_2(CH_2)_4)[Zn(C_{10}H_2O_8)].2H_2O$ , compound **I**, with a layer structure. In this paper, the synthesis, structure and properties are presented.

## Experimental Section

The title compound was synthesized under hydrothermal conditions in the presence of Diethylenetriamine. In a typical synthesis, 0.1655g of pyromellitic acid (Acros Organics) was dispersed in 9 ml of  $H_2O$ . To this, 0.1975g of zinc nitrate hexahydrate (Acros Organics 98%) was added under constant stirring. Finally, we add 0.1344g of Diethylenetriamine (Acros Organics) and the mixture was homogenized for 15 min at room temperature, was sealed in a 23ml PTFE-lined stainless-steel autoclave and heated at 120°C for 60 h. The pH of the initial reaction mixture was  $\sim 5$  and did not change appreciably after the reaction. Then the product obtained is filtered and washed with a small amount of distilled water. The chemical purity of the product was tested by EDAX measurements (Fig. 1) presents the EDAX spectrum of  $[(NH(NH_2)_2(CH_2)_4)[Zn(C_{10}H_2O_8)].2H_2O$  which reveals the presence of all non-hydrogen atoms: Zn, C, O and N. Elemental analysis give these results: for observed we have C 44.16%, N 9.32%, O 18.40%, Zn 28.12%; whereas for calculated we find C 62.08%, N 11.23%, O 19.42%, Zn 7.26%.

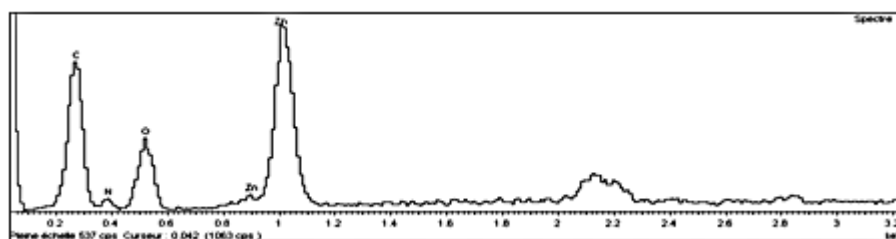


Figure 1 Typical EDAX spectrum of  $[(\text{NH}(\text{NH}_2)_2(\text{CH}_2)_4)[\text{Zn}(\text{C}_{10}\text{H}_2\text{O}_8)].2\text{H}_2\text{O}$  showing the presence of Zn, O, N and C

#### Single crystal structure determination

The unit-cell dimensions were refined using X-ray diffraction data collected with a Kappa Apex II diffractometer of Bruker AXS at  $T = 100\text{K}$ . The structure of  $[(\text{NH}(\text{NH}_2)_2(\text{CH}_2)_4)[\text{Zn}(\text{C}_{10}\text{H}_2\text{O}_8)].2\text{H}_2\text{O}$ , was analyzed with the crystallographic CRYSTALS program<sup>27</sup>. The structure was solved by conventional Patterson and difference-Fourier techniques. The chemical crystal data, the parameters used for X-ray diffraction data collection and strategy used for the crystal structure determination and their results, are listed in Table 1. Selected bond distances and angles are given in Table 4. Structural graphics were created by the DIAMOND program<sup>28</sup>. The asymmetric unit is shown in (Fig. 2).

**Table 1.** Crystallographic data for  $[(\text{NH}(\text{NH}_2)_2(\text{CH}_2)_4)[\text{Zn}_1(\text{C}_{10}\text{H}_2\text{O}_8)].2\text{H}_2\text{O}$ .

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Chemical formula	$\text{Zn}(\text{C}_{10}\text{O}_8\text{H}_2)(\text{N}_3\text{C}_4\text{H}_{13}).2\text{H}_2\text{O}$
Formula weight (g mol <sup>-1</sup> ):	472.71
Crystal system:	Monoclinic
Space group:	$P2_1/c$
$a$	$9.671(5)$ (Å)
$b$	$14.377(8)$ (Å)
$c$	$13.530(8)$ (Å)
$\beta$	$105.311(3)$ (°)
$V$	$1814.71(18)$ (Å <sup>3</sup> )
$Z$	4
$2\theta^{\circ}\text{max}$	$27.483$ with Mo $K\alpha$
$T$ (K)	100
$D_x$	$1.730$ Mg m <sup>-3</sup>
	$-12 \leq h \leq 12$
	$0 \leq k \leq 18$
	$0 \leq l \leq 17$
$\mu$	$1.42$ mm <sup>-1</sup>
Data collection instrument:	Bruker APEXII diffractometer
Radiation, monochromator	graphite $\lambda = 0.71073$ Å
Measured reflections:	29513
Unique reflections:	4134
$R$	$0.045$ and $R_w = 0.049$

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## Results and Discussion

### Crystal Structure

The structure of  $[(\text{NH}(\text{NH}_2)_2(\text{CH}_2)_4)[\text{Zn}(\text{C}_{10}\text{H}_2\text{O}_8)].2\text{H}_2\text{O}$ , Compound I, is formed of a network of tetrahedral coordinated by Zn carboxylate units btec. It also contains 28 non-hydrogen atoms. The Zn atom is tetrahedrally coordinated by four oxygen atoms from four different carboxylic groups with an average Zn–O distance of 1.968 Å. The O–Zn–O angles are in the range  $101.69(11) - 122.59(12)^\circ$  (av.  $109.48^\circ$ ). Of the eight oxygen atoms belonging to the four carboxylate units of btec, only four atoms make C–O–Zn and the remaining are terminal. This shows that the four oxygen atoms of the carboxylate group have monodentate connectivity (Fig.2). The bonded oxygen atoms of the carboxylate groups have C–O distances

in the range 1.276(5)–1.290(5)Å and the other terminal C–O distances are in the range 1.228(5)–1.260(5)Å. The O–C–O bond angles have an average value of 125.1°.

The monodendate connectivity of the btec acid has not been observed frequently. Similar monodendate connectivity of the btec acid has been observed before in the literature<sup>29-34</sup>. The present compound adds another example to this family of compounds. The various structural parameters observed in the present compound are in agreement with those observed before. A compound of the formula  $[\text{Zn}(\text{btec})^{4-}]$  would result in a net negative charge of  $-2$ . The presence of half a molecule of piperazine and one molecule of dimethylamine would account for a total of  $+2$  charge, assuming both are protonated, maintaining charge neutrality. In addition, the compound also possesses two molecule of water in the interlamellar region, of which one [O(200)] has a refined site occupancy factor (SOF) of 0.78.

The structure of  $[(\text{NH}(\text{NH}_2)_2(\text{CH}_2)_4)[\text{Zn}(\text{C}_{10}\text{H}_2\text{O}_8)].2\text{H}_2\text{O}$ , compound **I**, consists of a network of tetrahedral Zn centers coordinated by the btec carboxylate units (Fig. 2). The connectivity between these units gives rise to a two-dimensional hybrid layered structure in the *bc* plane as shown in (Fig. 3).

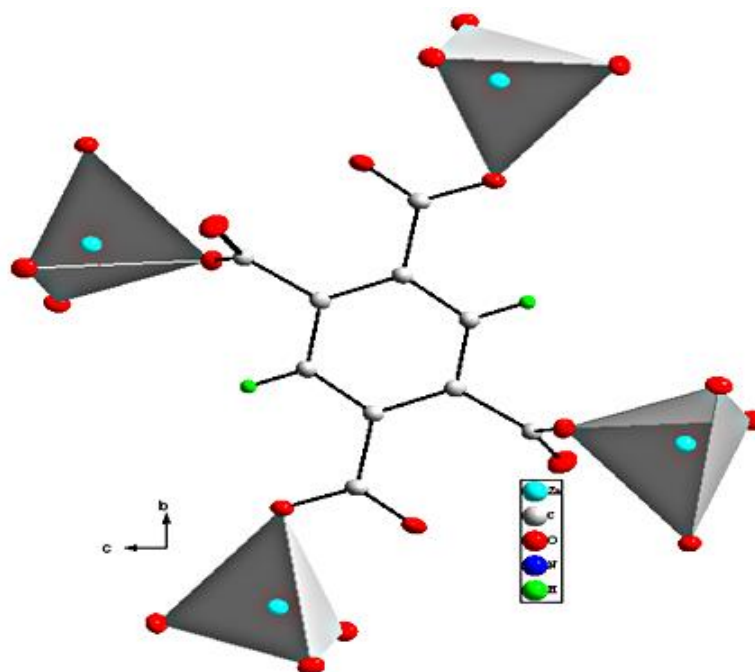


Figure 2. Connectivity between the acid and Zn of  $[(\text{NH}(\text{NH}_2)_2(\text{CH}_2)_4)[\text{Zn}_1(\text{C}_{10}\text{H}_2\text{O}_8)].2\text{H}_2\text{O}$  in the *bc* plane.

The structure resembles a 4-connected network in which each Zn atom is connected to four btec anions and each btec anion is linked to four  $\text{Zn}^{2+}$  ions. This type of connectivity observed in the compound **I** is reminiscent of the zinc coordination polymer reported previously<sup>35</sup>. The packing of the hybrid layers in the *ac* plane shows that the layers are separated by diethylenetriamine (Fig. 3). The water molecules also occupy the interlamellar region. While diethylenetriamine occupies the spaces where the two layers are closest. The structure can also be described as a hydrogen bond assembly between the hybrid layer and the diethylenetriamine molecule. This gives rise to supra-molecularly organized one dimensional channels, wherein the water molecules are located. Reactive decomposition and transformation of amines and other reactants under hydrothermal conditions have been

encountered before<sup>36</sup>. Similar behavior has also been observed in a few hydrothermal syntheses of phosphate based open-framework structures<sup>37-39</sup>. It is likely that other similar metal–organic frameworks (MOFs) can be prepared employing hydrothermal methods in the presence of other organic amine molecules.

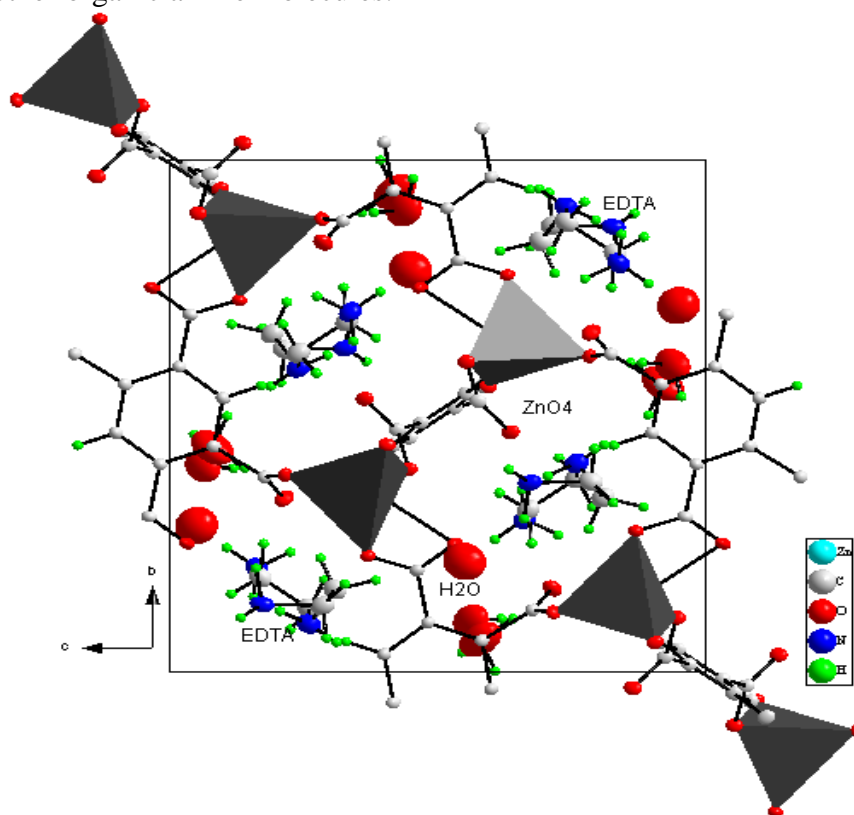


Figure 3. The projection structure of  $[\text{NH}(\text{NH}_2)_2(\text{CH}_2)_4][\text{Zn}(\text{C}_{10}\text{H}_2\text{O}_8)] \cdot 2\text{H}_2\text{O}$ , in the  $bc$  plane showing a single layer.

#### Thermal Behavior

The thermogravimetry curve and the three-dimensional representation of the powder diffraction patterns obtained during the decomposition of  $[(\text{NH}(\text{NH}_2)_2(\text{CH}_2)_4)[\text{Zn}(\text{C}_{10}\text{H}_2\text{O}_8)] \cdot 2\text{H}_2\text{O}$  in air dynamics and the temperature range of 25 to 900°C (heating rate = 5°C/h) are shown in (Figs. 4 and 5), respectively. The thermal decomposition of the title compound takes place in several steps. In the first stage, the compound loses 2 water molecules in the temperature range 50.9–177°C (observed weight loss, 11.96%; calculated weight loss, 11.39%). The second step of the decomposition (temperature range 177–378°C) corresponds to the loss of the amine molecule (observed weight loss, 72.24%; calculated weight loss, 70.01%). Thus, leading to the anhydrous phase,  $[\text{Zn}(\text{C}_{10}\text{H}_2\text{O}_8)]$ , amorphous to X-rays until 220°C (Fig. 5). At this temperature, some diffraction lines emerge from the background in the TDXD plot. While the TG curve does not weight loss. From these observations, it can be concluded that the anhydrous phase crystallizes. The last transformation corresponds to the formation of zinc oxide ZnO, which crystallise immediately after the beginning of the decomposition of  $[\text{Zn}(\text{C}_{10}\text{H}_2\text{O}_8)]$  (observed weight loss 15.8%, calculated weight loss 18.6 %).

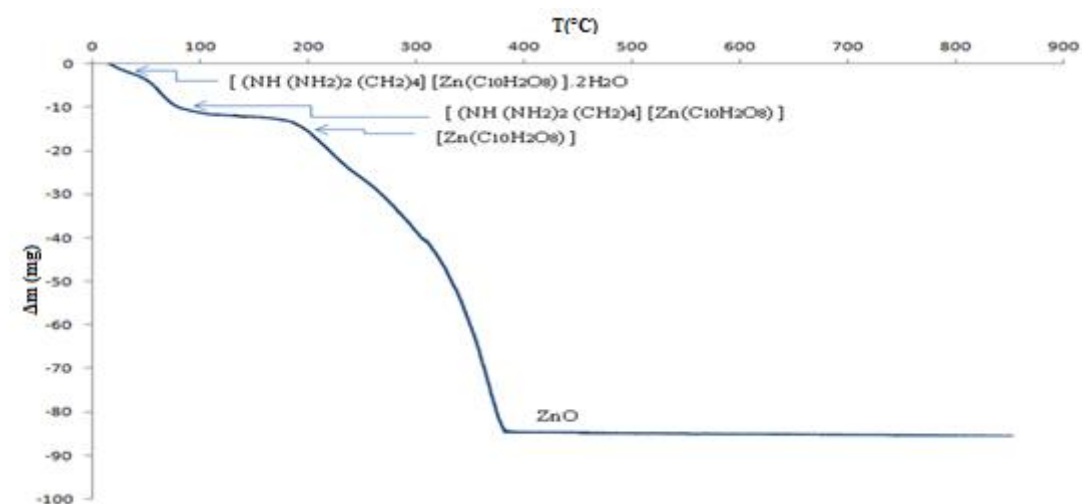


Figure 4. TG curve for the decomposition of  $[(\text{NH}(\text{NH}_2)_2(\text{CH}_2)_4) [\text{Zn}(\text{C}_{10}\text{H}_2\text{O}_8)].2\text{H}_2\text{O}$  in air ( $5^\circ\text{C h}^{-1}$ ).

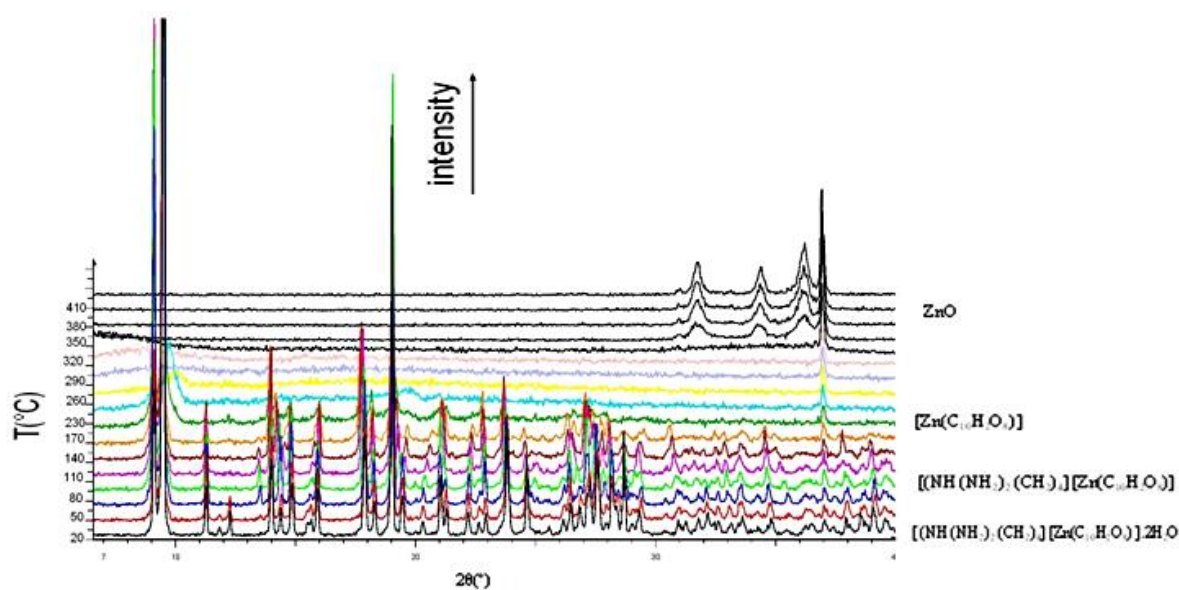


Figure 5. TDXD plot for the decomposition of  $[(\text{NH}(\text{NH}_2)_2(\text{CH}_2)_4) [\text{Zn}_1(\text{C}_{10}\text{H}_2\text{O}_8)].2\text{H}_2\text{O}$  in air, ( $30^\circ\text{C h}^{-1}$  from 20 to 450 °C).

### Infrared Spectroscopy

IR reflection spectrum of the title compound was measured with a Perkin-Elmer BX FTIR spectrometer, in the  $4000\text{--}250\text{ cm}^{-1}$  region at ambient temperature, with KBr pellets. The IR spectrum of the title compound is shown in (Fig. 6). It shows characteristic absorption bands at  $761$  and  $863\text{ cm}^{-1}$  due to the vibrations of the CH aromatic and  $1439\text{ cm}^{-1}$  due to the vibrations of aliphatic groups  $\text{CH}_2$ . The bending and stretching vibrations of water molecules appear as a band at  $1609\text{ cm}^{-1}$  and a broad band at  $3421\text{ cm}^{-1}$ , respectively. The bands situated at  $2861\text{ cm}^{-1}$  can be assigned to the bending vibrations of  $\text{CH}_2$  group. A sharp peak at  $1089\text{ cm}^{-1}$  is due to the vibrations of the CN group. A broad peak at  $3335\text{ cm}^{-1}$  is related to the vibrations of the NH group.

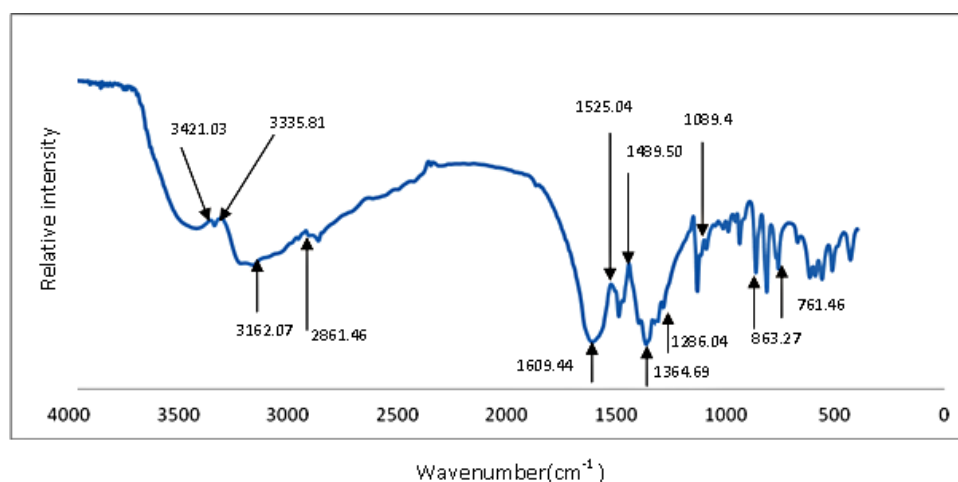


Figure 6. Infrared spectrum of  $[\text{NH}(\text{NH}_2)_2(\text{CH}_2)_4][\text{Zn}(\text{C}_{10}\text{H}_2\text{O}_8)] \cdot 2\text{H}_2\text{O}$ .

## Conclusion

In this work, we report a metal–organic complex  $[\text{Zn}_1(\text{deta})(\text{btec})(\text{H}_2\text{O})_2]_n$  (**I**), which is prepared by the hydrothermal synthesis route. It crystallizes in the monoclinic symmetry, space group  $P2_1/c$ . Compound **I** exhibits a novel three-dimensional network constructed from bridging btec and deta mixed ligand. The compound **I** obtained not only prove the strong capability of hydrothermal reactions in preparing a new organic-inorganic hybrid material with mixed organic ligands, but also confirm that coordination polymers can be designed and synthesized according to the connection between the hard-organic ligands and metal ions. But also, further proves the strong capability of hydrothermal reactions in preparing a metal–organic material with mixed organic ligands. The thermal decomposition of the precursor, studied by TG and TDXD, proceeds through several stages giving rise to zinc oxide.

## Acknowledgement

This work is supported by the minister of superior education and research.

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