



## A TWO-DIMENSIONAL SUPRAMOLECULAR Zn(II) SYSTEM ASSEMBLED VIA HYDROGEN BONDS ESTABLISHED BETWEEN THE TEREPHTHALATE DIANION AND THE TRIETHANOLAMINE LIGAND

Andrei CUCOS,<sup>a,\*</sup> Carmen PARASCHIV,<sup>a,\*</sup> Catalin MAXIM,<sup>b</sup> Gabriela SBARCEA,<sup>a</sup>  
Violeta TUDOR<sup>b</sup> and Marius ANDRUH<sup>b,\*</sup>

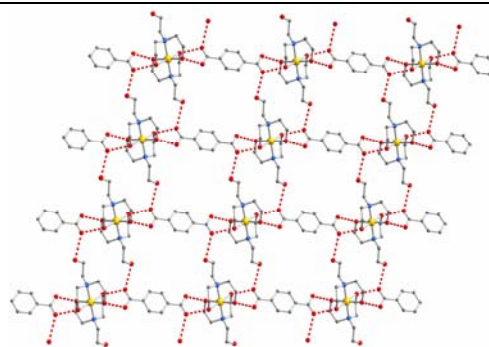
<sup>a</sup>National Institute for Research and Development in Electrical Engineering ICPE-CA, Splaiul Unirii 313, 030138-Bucharest, Roumania

<sup>b</sup>Inorganic Chemistry Laboratory, Faculty of Chemistry, University of Bucharest, Str. Dumbrava Roşie 23, 020464-Bucharest, Roumania

\* Corresponding authors: andrei.cucos@icpe-ca.ro (A.C.); carmenparaschiv@yahoo.com (C.P.); marius.andruh@dnt.ro (M.A.)

Received August 6, 2015

A new mononuclear complex,  $[Zn(H_3tea)_2] \cdot (1,4-bdc)$  **1** ( $H_3tea$  = triethanolamine,  $1,4-H_2bdc$  = 1,4-benzenedicarboxylic acid), was synthesized and characterized by single crystal and powder X-ray diffraction, IR spectroscopy, and thermal analysis under air atmosphere using the hyphenated TG-FTIR technique. Investigation of the crystal structure of **1** revealed a two-dimensional (4,4) supramolecular motif, generated from the interconnection of  $[Zn(H_3tea)_2]^{2+}$  cations and terephthalate anions through hydrogen bond interactions.



### INTRODUCTION

During the last decades, significant progress has been made in understanding the nature of intermolecular interactions and their subsequent use in the formation of solid-state structures.<sup>1-4</sup> The concept of the supramolecular synthon was assigned to intermolecular interactions by Desiraju in 1995,<sup>5</sup> describing the association of two complementary fragments to form a motif that links two molecules together. Owing to their directionality and specificity, hydrogen bonds are the most effective and widely used non-covalent tools for the self-assembly of small molecular components into ensembles with predefined

structural features and many hydrogen-bonded motifs have been described as synthons.<sup>6-9</sup> Furthermore, these supramolecular aggregates may have unique properties as a consequence of the combined features of the weakly bound entities.

Along with the coordination bond, hydrogen bonding is a key organizing force in crystal engineering due to the influence it may have on the stabilization of the lattice structure through weak interactions, e.g. between chains and layers. The chemistry of coordination polymers is among the research areas that have developed and benefitted from the synergism between coordination and hydrogen bonding, a rich variety of structures and topologies being described.<sup>10</sup> In particular,

\* Corresponding authors: carmenparaschiv@yahoo.com; marius.andruh@dnt.ro

carboxylate-based systems, especially three-dimensional porous metal organic frameworks (MOFs) have attracted considerable attention as a result of their suitability for gas storage, sorption, separation, catalysis, sensing, and recognition.<sup>11,12</sup>

The association of polyalcohol amines and carboxylates can lead to the formation of systems with different dimensionalities and topologies. Recently, several works described Zn(II) coordination polymers assembled in the presence of amino-alcohols and rigid aromatic carboxylic acids.<sup>13-15</sup> Amino-alcohols may accomplish a variety of functions to facilitate the formation of new structures: coordination to the metal ions (as chelating, bridging or terminal ligands), deprotonation of the oxygen atoms of the polycarboxylic acids, template molecules. Moreover, they may be highly efficient as structure-directing agents because of their ability to act as hydrogen bond donors. Carboxylate anions are very popular in the construction of metal coordination networks as bridging or terminal ligands, but they can also serve as hydrogen bond acceptors for the second-sphere coordination.<sup>16</sup> Herein we present a supramolecular 2-D Zn(II) system assembled via hydrogen bonds, with the dianion of terephthalic acid as a H-bond acceptor, while triethanolamine acts as a H-bond donor.

## RESULTS AND DISCUSSION

The reaction between zinc(II) nitrate, triethanolamine and 1,4-benzenedicarboxylic acid led to a mononuclear complex,  $[\text{Zn}(\text{H}_3\text{tea})_2] \cdot (1,4\text{-bdc})$  **1**. Triethanolamine was used not only as a ligand, but also to deprotonate the terephthalic acid. Compound **1** crystallizes in the *P*-1 triclinic space group, with cell parameters and structure refinement details given in Table 1. The structure consists of centrosymmetric mononuclear  $[\text{Zn}(\text{H}_3\text{tea})_2]^{2+}$  units and uncoordinated

terephthalate anions in a ratio of 1:1 so that no further anions are required. The triethanolamine molecule is not deprotonated and coordinates as a tridentate chelating ligand toward Zn1 ions through the nitrogen and two oxygen atoms, while the third OH group remains uncoordinated. The Zn(II) ion lies on an inversion center and is hexacoordinated, with a nearly perfect octahedral geometry: two nitrogen and four oxygen atoms from two  $\text{H}_3\text{tea}$  molecules [ $\text{Zn1-N1} = 2.1293(15)$ ;  $\text{Zn1-O1} = 2.1498(14)$ ;  $\text{Zn1-O2} = 2.1228(13)$  Å]. Selected bond distances and angles for compound **1** are collected in Table 2.

The mononuclear units are interconnected with the terephthalate anions through strong hydrogen bonds established between the coordinated hydroxyl groups of the  $\text{H}_3\text{tea}$  molecules and the carboxylate oxygen atoms [ $\text{O2} \cdots \text{O4} = 2.563$  Å;  $\text{O5} \cdots \text{O1}' = 2.637$  Å;  $' = -x, -y, -z$ ] to afford a supramolecular chain growing along the direction of the diagonal of the crystallographic *ac* plane (Fig. 1). The chains are further connected through weaker hydrogen bonds involving the uncoordinated OH groups of the triethanolamine and the terephthalate oxygen atoms acting as double hydrogen bond acceptors [ $\text{O5} \cdots \text{O3}'' = 2.947$  Å;  $'' = -x, -y, 1-z$ ], resulting in a two-dimensional (4,4) layered motif of rhombic meshes parallel to the crystallographic *ac* plane (Fig. 2). Details of the H-bonding scheme for **1** are given in Table 3. The meshes are characterized by angles of 72.27 and 107.73°, while the separations between the Zn(II) ions are 9.20 and 14.72 Å. The 2-D layers are aligned in a slipped parallel fashion, so that the formation of channels in the crystal lattice is prevented.

The experimental X-ray powder pattern is in perfect agreement with that calculated from single-crystal data, proving the purity of compound **1** (Fig. 3).

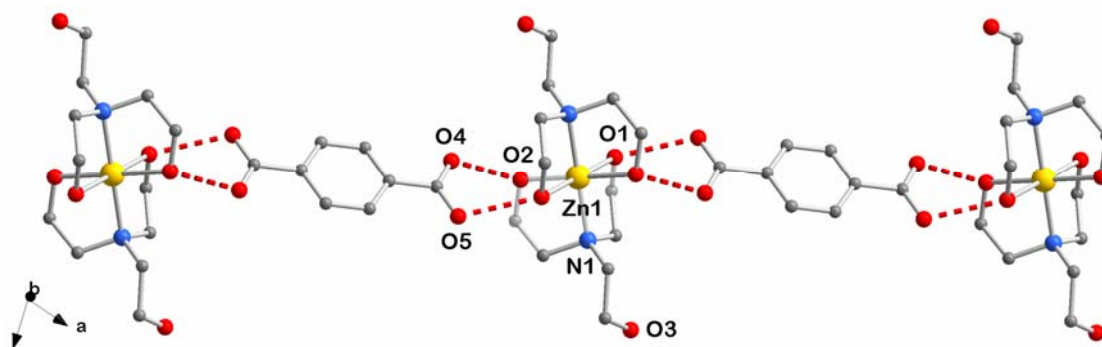


Fig. 1 – Perspective view of a fragment of the supramolecular chain in **1** growing along the direction of the diagonal of the crystallographic *ac* plane.

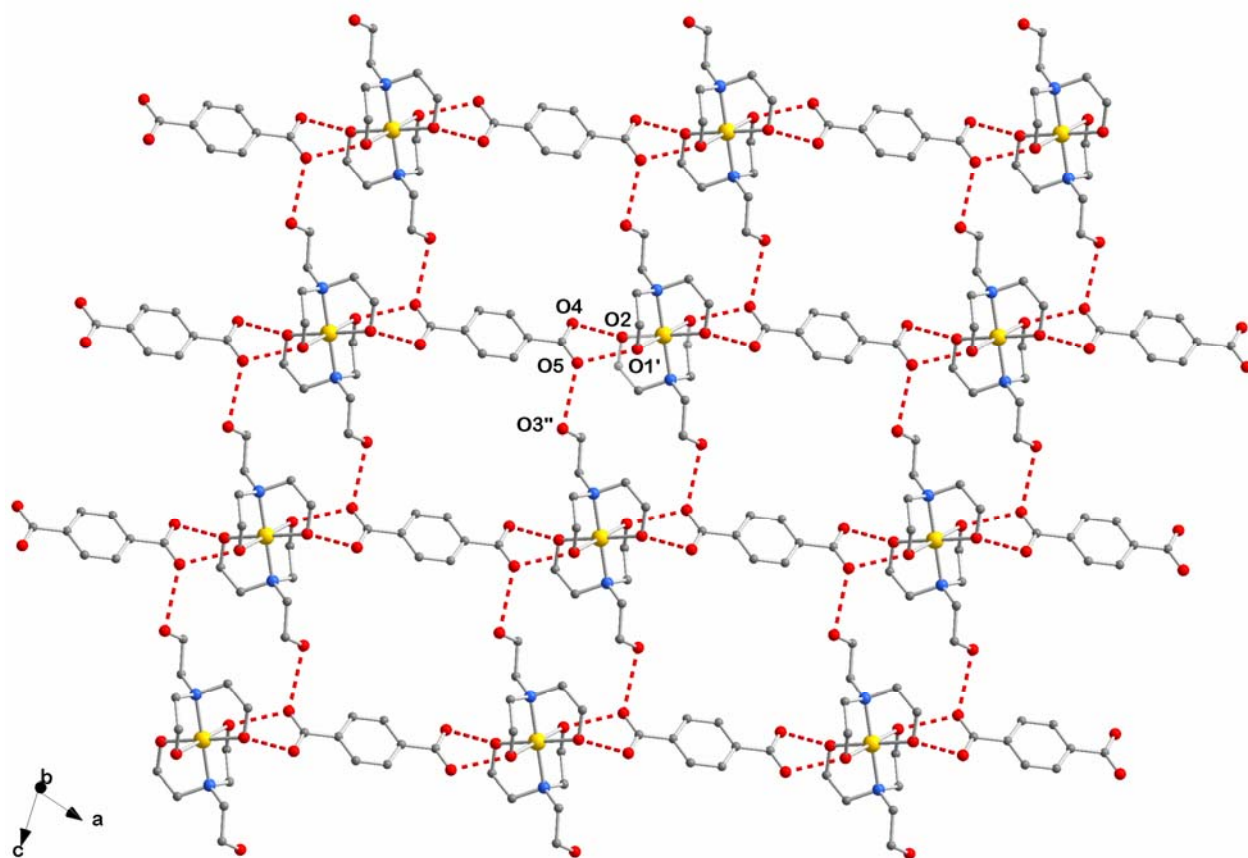


Fig. 2 – A view of the (4, 4) rectangular layer through hydrogen bonds growing parallel to the crystallographic *ac* plane (symmetry code: ' = -*x*, -*y*, -*z*; '' = -*x*, -*y*, 1-*z*).

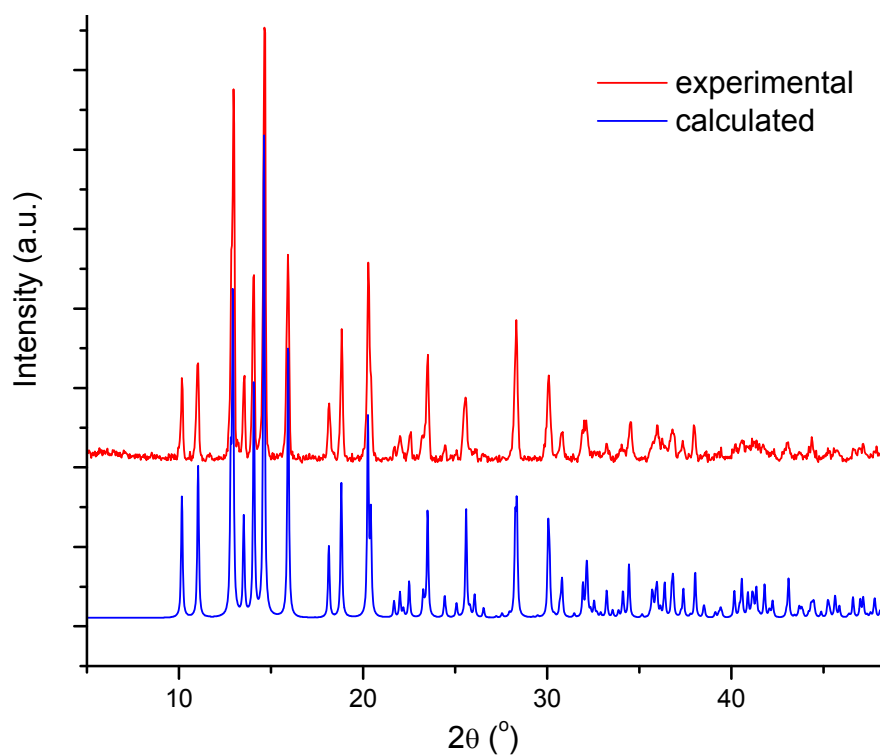


Fig. 3 – Powder X-ray diffraction patterns of **1** (above: experimental; below: calculated from single crystal X-ray diffraction data).

### Thermal stability studies

In order to investigate the thermal stability of **1**, TG-FTIR experiments were carried out in synthetic air between room temperature and 600 °C. Compound **1** is stable up to about 170 °C, as no mass loss is observed in the TG curve (Fig. 4). A sharp endotherm with a minimum at 180 °C in the DTA curve suggests a melting process, closely followed by the onset of the decomposition process. The decomposition is complex, as indicated by three main DTG peaks at 232, 396 and 490 °C, accompanied by the corresponding peaks in the Gram-Schmidt curve at 232, 408 and 497 °C. In the DTA curve, three exothermal peaks are also observed, with maxima at 371, 414 and 497 °C, the latter one being the most intense. The decomposition ends at 520 °C with the formation of the expected amount of ZnO as final residue (calculated: 15.4%, found: 15.7%).

The 2D plot of FTIR spectra (Fig. 5) shows that the decomposition starts with a slight release of methanol and a significant evolution of water vapors, indicating that triethanolamine ligands decompose first. At about 240 °C a strong release of CO<sub>2</sub> suggests the oxidation of the aliphatic side chains of H<sub>3</sub>tea ligands. At higher temperatures

CO<sub>2</sub> may also originate from the complete decarboxylation of terephthalic ligands, as confirmed by the observation of a band assigned to benzene at about 400 °C. No traces of benzoic acid, indicative of partial decarboxylation of terephthalate anions, were detected. The CO<sub>2</sub> band (around 2300 cm<sup>-1</sup>) reaches its maxima at about 410 °C and 500 °C, being the most intense of all observed FTIR bands. The bands attributed to CO and H<sub>2</sub>CO can also be seen in the FTIR spectra, together with some unidentified bands at 2800 – 3000 cm<sup>-1</sup> and 1000 – 1200 cm<sup>-1</sup> that can be assigned to C–H and C–O stretching vibrations, respectively. The methane's band is observed in the 400-520 °C temperature range, corresponding to the third mass loss.

The present paper illustrates that complementary hydrogen bond donors and acceptors can be matched in order to form high-dimensional hydrogen bonded aggregates. The non-covalent solid state assembly of the mononuclear cationic complex [Zn(H<sub>3</sub>tea)<sub>2</sub>]<sup>2+</sup> with the dianion of the terephthalic acid led to a new 2-D supramolecular system which shows a good thermal stability, comparable with the one noticed for coordination polymers.

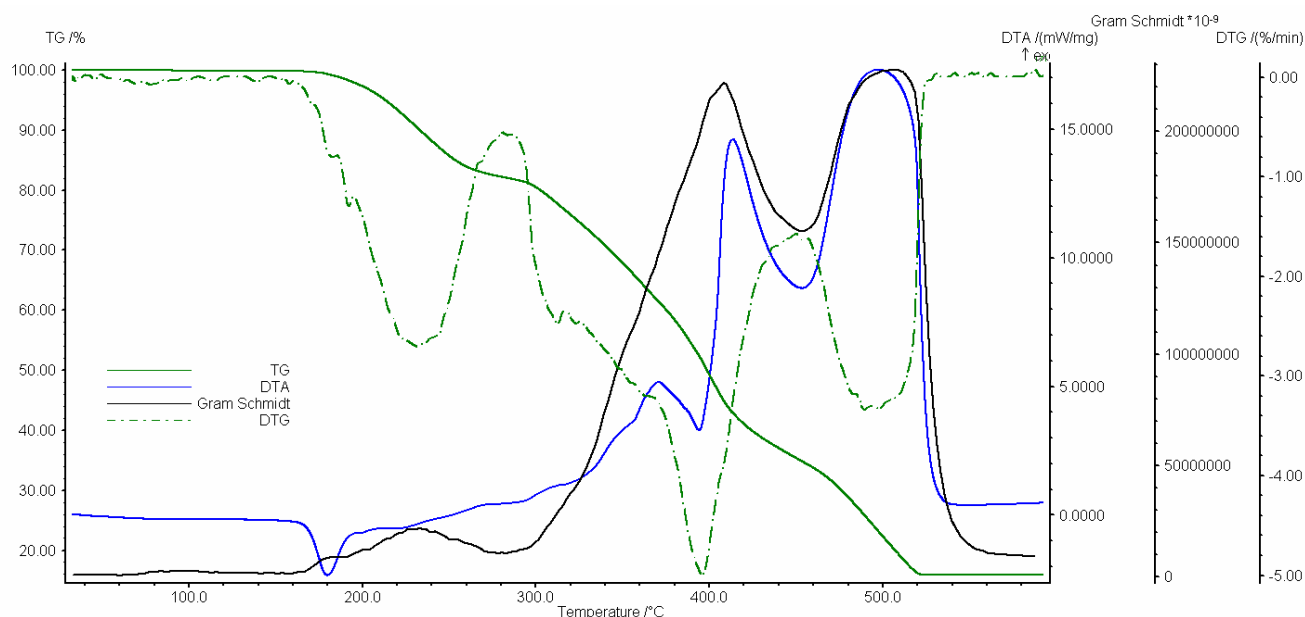


Fig. 4 – TG, DTG, DTA and Gram Schmidt curves for compound **1**.

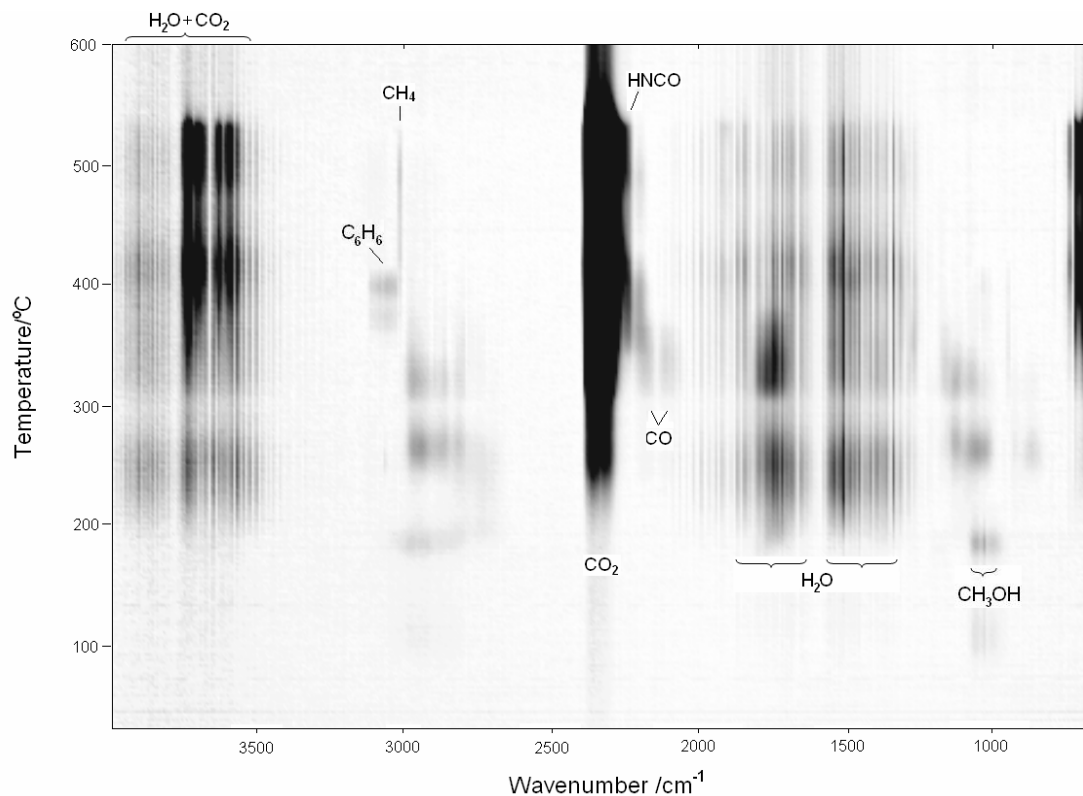
Fig. 5 – 2D plot of FTIR spectra of evolved gases from the decomposition of **1**.

Table 1

Crystallographic data, details of data collection and structure refinement parameters for **1**

Empirical formula	$C_{20}H_{34}ZnN_2O_{10}$
M (g mol <sup>-1</sup> )	527.88
Temperature (K)	293(2)
Wavelength (Å)	0.71073
Crystal system	triclinic
Space group	<i>P</i> -1
<i>a</i> [Å]	7.9877(2)
<i>b</i> [Å]	8.8265(3)
<i>c</i> [Å]	9.2016(4)
$\alpha$ [°]	89.095(2)
$\beta$ [°]	72.295(3)
$\gamma$ [°]	66.086(2)
<i>V</i> [Å <sup>3</sup> ]	560.64(4)
<i>Z</i>	1
$\rho$ (calcd) [Mgm <sup>-3</sup> ]	1.564
$\mu$ [mm <sup>-1</sup> ]	1.155
<i>F</i> (000)	278
Gof (for <i>F</i> 2)	1.107
Final <i>R</i> , <i>wR</i> [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )]	0.0306, 0.0785
$\Delta\rho_{\max}$ and $\Delta\rho_{\min}$ [e Å <sup>-3</sup> ]	0.605 and -0.358

Table 2

Selected bond distances (Å) and angles (°) for compound **1**

Zn1–N1	2.1293(15)	O1–Zn1–N1	82.81(6)
Zn1–O1	2.1498(14)	O1–Zn1–N1 <sup>i</sup>	97.19(6)
Zn1–O2	2.1228(13)	O2–Zn1–N1	82.14(6)
C1–O1	1.429(3)	O2–Zn1–N1 <sup>i</sup>	97.87(6)
C4–O2	1.427(3)	O2–Zn1–O1	90.52(5)
C6–O3	1.382(3)	O2–Zn1–O1 <sup>i</sup>	89.49(5)

<sup>i</sup> = -x, -y, -z

Table 3

Hydrogen bonding parameters in **1**<sup>a</sup>

D–H···A	D–H/Å	H···A/Å	D···A/Å	D–H···A/°
O2–H2O···O4	0.820(19)	1.745(19)	2.563(2)	175.1(19)
O1–H1O···O5 <sup>i</sup>	0.82(3)	1.82(3)	2.637(2)	172(4)
O3–H3···O5 <sup>ii</sup>	0.82	2.22	2.954(3)	149

<sup>i</sup> = -x, -y, -z; <sup>ii</sup> = -x, -y, 1-z

<sup>a</sup> D and A stand for donor and acceptor, respectively.

## EXPERIMENTAL

### Materials and methods

All starting materials were of reagent grade quality and were used as received from commercial sources without further purification.

Methanolic solutions (10 mL each) of zinc(II) nitrate hexahydrate (0.297 g, 1 mmol) and triethanolamine (0.298 g, 2 mmol) were mixed together, yielding a clear solution. Separately, 1,4-benzenedicarboxylic acid (0.166 g, 1 mmol) and triethanolamine (0.298 g, 2 mmol) were mixed with MeOH (15 mL). The resulting suspension was stirred under heating until complete dissolution of 1,4-H<sub>2</sub>bdc, then cooled to room temperature and added to the zinc-triethanolamine solution. A small quantity of unidentified white precipitate formed and it was removed by filtration. The slow evaporation of the resulted clear solution yielded compound **1** as colorless crystals. Yield: 76%. IR (KBr, cm<sup>-1</sup>): 3419w, 2986w, 2892w, 1521m, 1497m, 1453m, 1429m, 1374vs, 1352s, 1229s, 1149m, 1095m, 1056s, 1006s, 919m, 894s, 793s, 753vs, 621w.

### Physical Measurements

IR spectrum was recorded on KBr pellets in the 4000–400 cm<sup>-1</sup> range using a Bruker TENSOR 27 FTIR Spectrometer. PXRD diffractions pattern was recorded on a Bruker D8 ADVANCE diffractometer. The TG/DTG/DTA+FTIR measurement was performed on a Netzsch STA 409 PC thermal analyzer coupled to a Bruker Tensor 27 FTIR spectrometer equipped with a TG-IR gas cell. The sample was placed in a cylindrical Al<sub>2</sub>O<sub>3</sub> holder and heated in synthetic air flow (100 ml min<sup>-1</sup>, purity 99.999%), from room temperature to 600 °C, at a heating rate of 10 °C min<sup>-1</sup>. An empty Al<sub>2</sub>O<sub>3</sub> holder was used as a reference. The FTIR spectra were collected continuously during measurements in the wavenumber range 4000 – 650 cm<sup>-1</sup> at a resolution of 4 cm<sup>-1</sup>.

### Crystal structure determination

X-ray diffraction measurements were performed on STOE IPDS II diffractometer operating with a Mo-Kα (λ = 0.71073 Å) X-ray tube with a graphite monochromator. The structure was solved by direct methods and refined by full-matrix least squares techniques based on *F*<sup>2</sup>. The non-H atoms were refined with anisotropic displacement parameters. Calculations were performed using SHELX-97<sup>17</sup> crystallographic software package. A summary of the crystallographic data and the structure refinement for **1** is given in Table 1. CCDC reference number: 1419265.

*Acknowledgements:* Financial support from the Roumanian Ministry of Education CNCS-UEFISCDI (Project PN-II-RUTE-2012-3-0390) is gratefully acknowledged.

## REFERENCES

- See, for example: (a) J. J. Perry IV, J. A. Perman and M. J. Zaworotko, *Chem. Soc. Rev.*, **2009**, *38*, 1400; (b) M. J. Zaworotko, *Chem. Commun.*, **2001**, *1*; (c) S. Subramanian and M. J. Zaworotko, *Coord. Chem. Rev.*, **1994**, *137*, 357.
- (a) J.-M. Lehn, "Supramolecular Chemistry: Concepts and Perspectives"; VCH: Weinheim, Germany, 1995; (b) J.-M. Lehn, *Angew. Chem. Int. Ed.*, **1990**, *29*, 1304.
- (a) M. W. Hosseini, *Coord. Chem. Rev.*, **2003**, *240*, 157; (b) M. W. Hosseini, *Acc. Chem. Res.*, **2005**, *38*, 313.
- (a) A. E. Reed, L. A. Curtis and F. Weinhold, *Chem. Rev.*, **1988**, *88*, 899; (b) D. S. Lawrence, T. Jiang and M. Levett, *Chem. Rev.*, **1995**, *95*, 2229; (c) R. Chakrabarty, P. S. Mukherjee and P. J. Stang, *Chem. Rev.*, **2011**, *111*, 6810; (d) R. Dey, B. Bhattacharya, E. Colacio and D. Ghoshal, *Dalton Trans.*, **2013**, *42*, 2094; (e) D. Cinčić, T. Friščić and W. Jones, *Chem. Eur. J.*, **2008**, *14*, 747; (f) B. Sarma, N. K. Nath, B. R. Bhogala and A. Nangia, *Cryst. Growth Des.*, **2009**, *9*, 1546.
- G. R. Desiraju, *Angew. Chem. Int. Ed.*, **1995**, *34*, 2311.
- (a) M. C. Etter, *Acc. Chem. Res.*, **1990**, *23*, 120; (b) M. C. Etter, *J. Phys. Chem.*, **1991**, *95*, 4601.
- (a) G. R. Desiraju, *Acc. Chem. Res.*, **2002**, *35*, 565; (b) G. R. Desiraju, in: F. Vögtle, J. F. Stoddart, M. Shibasaki (Eds.), "Stimulating Concepts in Chemistry", Wiley VCH, Weinheim, 2000, p. 293.
- (a) A. M. Beatty, *Coord. Chem. Rev.*, **2003**, *246*, 131; (b) C. B. Aakeröy and K. R. Seddon, *Chem. Soc. Rev.*, **1993**, *22*, 397; (c) I. A. Baburin, V. A. Blatov, L. Carlucci, G. Ciani and D. N. Proserpio, *Cryst. Growth Des.*, **2008**, *8*, 519.
- (a) J. Bernstein, R. E. Davis, L. Shimon and N.-L. Chang, *Angew. Chem. Int. Ed.*, **1995**, *34*, 1555; (b) L. J. Prins, D. N. Reinhoudt and P. Timmerman, *Angew. Chem. Int. Ed.*, **2001**, *40*, 2382; (c) A. R. A. Palmans, J. A. J. M. Vekemans, H. Kooijman, A. L. Speck and E. W. Meijer, *Chem. Commun.*, **1997**, 2247.
- See, for example: (a) N. L. Rosi, M. Eddaoudi, D. T. Vodak, J. Eckert, M. O'Keeffe and O. M. Yaghi, *Science*, **2003**, *300*, 1127; (b) H. Furukawa and O. M. Yaghi, *J. Am. Chem. Soc.*, **2009**, *131*, 8875; (c) L. J. Murray, M. Dinca and J. R. Long, *Chem. Soc. Rev.*, **2009**, *38*, 1294; (d) P. M. Suh, H. J. Park, T. K. Prasad and D.-W. Lim, *Chem. Rev.*, **2012**, *112*, 782; (e) J.-R. Li, R. J. Kuppler and H.-C. Zhou, *Chem. Soc. Rev.*, **2009**, *38*, 1477.
- See, for example, special issues on metal organic frameworks in: (a) *Chem. Rev.* **2012**, *112*, 673-1268. (b) *Chem. Soc. Rev.* **2009**, *38*, 1201-1508.

12. (a) G. Ferey, C. Mellot-Draznieks, C. Serre, F. Millange, J. Dutour, S. Surble and I. Margiolaki, *Science*, **2005**, *309*, 2040. (b) S. S. Y. Chui, S. M. F. Lo, J. P. H. Charmant, A. G. Orpen and I. D. Williams, *Science*, **1999**, *283*, 1148. (c) H. K. Chae, D. Y. Siberio-Perez, J. Kim, Y.-B. Go, M. Eddaoudi, A. J. Matzger, M. O'Keeffe and O. M. Yaghi, *Nature*, **2004**, *427*, 523.
13. M. J. Manos, E. E. Moushi, G. S. Papaefstathiou and A. J. Tasiopoulos, *Cryst. Growth Des.*, **2012**, *12*, 5471.
14. (a) G. Xu, J. Lv, P. Guo, Z. Zhou, Z. Du and Y. Xie, *CrystEngComm*, **2013**, *15*, 4473. (b) G. Xu, M. Xie, X. Li, W. Shi, H. Yu, Y. Hu, X. Xun and Y. Xie, *CrystEngComm*, **2015**, *17*, 3677.
15. C. Paraschiv, A. Cucos, S. Shova, A. M. Madalan, C. Maxim, D. Visinescu, B. Cojocaru, V. I. Parvulescu and M. Andruh, *Crystal Growth Des.*, **2015**, *15*, 799.
16. A. Ballabh, D. R. Trivedi and P. Dastidar, *Crystal Growth Des.*, **2005**, *5*, 1545.
17. G. M. Sheldrick, *Acta Crystallogr.*, **2008**, *A64*, 112.

