



Hydrothermal Synthesis, Crystal Structure of Zinc(II) Complex of *bis*(2-Benzimidazole) and Aromatic Carboxylate Ligands

GUO-DONG FENG* and LUAN JIANG

Key Laboratory of Functional Coordination Compounds, Department of Chemistry and Chemical Engineering, Baoji University of Arts and Science, No. 1 Hi-Tech Avenue, Baoji 721013, Shaanxi, P.R. China

*Corresponding author: Tel: +86 917 3566589; E-mail: fengguodong00805@163.com

(Received: 26 April 2011;

Accepted: 12 November 2011)

AJC-10657

A novel one-dimensional zinc(II) complex: $[\text{Zn}_2\text{L}_2(\text{H}_2\text{C}_3\text{PIm})_2]_n$ (**1**) with 2-carboxymethylbenzoic acid (H_2L) and 2,2'-(1,3-propanediyl)*bis*(1*H*-benzimidazole) ($\text{H}_2\text{C}_3\text{PIm}$) has been synthesized by means of hydrothermal method and characterized by X-ray single-crystal diffraction. The crystal is of triclinic, space group P-1 with $a = 1.3354(5)$ nm, $b = 1.3991(5)$ nm, $c = 1.4245(5)$ nm, $\alpha = 83.617(5)^\circ$, $\beta = 70.742(5)^\circ$, $\gamma = 70.913(5)^\circ$, $V = 2.3744(15)$ nm³, $D_c = 1.451$ g cm⁻³, $Z = 2$, $F(000) = 1068$, $\text{Goof} = 1.073$, $R_1 = 0.1067$, $wR_2 = 0.3379$. The complex **1** shows a novel one-dimensional (1D) zigzag chain structure along the a axis and further extended into a 2D supramolecular structure through N-H...O hydrogen bonding interactions. The π - π packing interactions contribute to the formation of the three-dimensional supramolecular architecture and stabilize the crystal structure.

Key Words: Zn(II) complex, Crystal structure, 2-Carboxymethylbenzoic acid, *Bis*(1*H*-benzimidazole).

INTRODUCTION

Recently, owing to their variety of intriguing architectures and topologies and their potential applications in microelectronics, nonlinear optics and catalysis¹⁻⁴, the formation of metal-organic framework (MOF) structures has been aroused more and more interests. However, the rational design and synthesis of MOFs with unique structure and function is still hard work. Many of MOFs are constructed by assembly of metal ions with an appropriate organic ligand, especially a bridging ligand containing nitrogen, oxygen or sulfur atoms⁵. The *bis*(2-benzimidazoles) and some substituted *bis*(2-benzimidazolyl)-alkanes containing N-donors are also particularly attractive as excellent building blocks with charge, which can lead to a variety of connection modes with metal centers and provides abundant structural motifs^{6,7}. In this area, mononuclear⁸, dinuclear⁹ and a 1D chain structure¹⁰ have been reported. Comparatively, The 2-carboxymethylbenzoic acid (H_2L), as a family rigid organic O-donors are especially interesting because of their various coordination modes to metal ions¹¹ and their abilities to act as H-bond acceptors and donors to assemble various supramolecular structures¹². On the basis of above results, we report the syntheses and crystal structure of a new coordination polymer $[\text{Zn}_2\text{L}_2(\text{H}_2\text{C}_3\text{PIm})_2]_n$ based on the mixed ligands of aromatic carboxylates, 2-carboxymethylbenzoic acid (H_2L) and N-donor ligands, 2,2'-(1,3-propanediyl)-*bis*(1*H*-benzimidazole) ($\text{H}_2\text{C}_3\text{PIm}$).

EXPERIMENTAL

All chemical reagents were of analytical grade and used without further purification. The $\text{H}_2\text{C}_3\text{PIm}$ ligand was prepared according to the reported method¹³. The emission/excitation spectra were recorded on a Varian Cary Eclipse spectrometer. The single-crystal structure of the compound **1** was determined on a Bruker APXII CCD diffractometer.

The compound **1** was prepared by the mixture of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (0.148 g, 0.5 mmol), $\text{H}_2\text{C}_3\text{PIm}$ (0.182 g, 1 mmol), H_2L (0.0498 g, 0.3 mmol) and H_2O (16 mL) was heated at 165 °C for 3 days in a 25 mL Teflon-lined stainless steel vessel under autogenous pressure. After the reaction mixture was slowly cooled down to room temperature, colourless block crystals were obtained. Yield: 70 %.

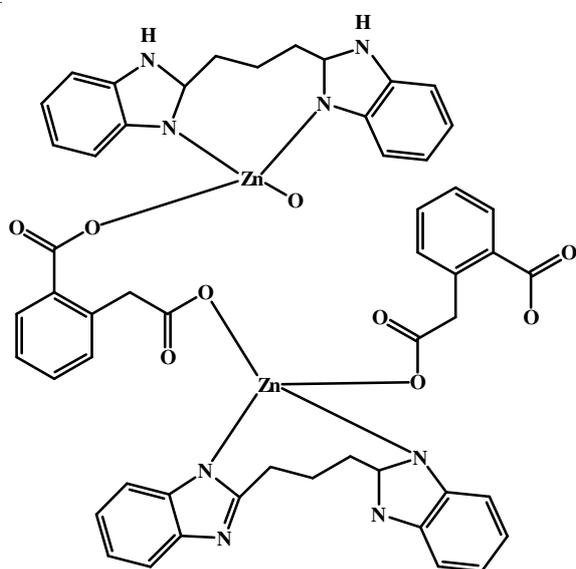
Structure determination: A colourless block single crystal of compound **1** with 0.12 mm × 0.14 mm × 0.16 mm was carefully selected under a polarizing microscope and were mounted on a glass fiber and used for X-ray diffraction analyses. Single crystal structure determination by X-ray diffraction measurements were performed using a Bruker APXII CCD diffractometer with graphite monochromated MoK_α ($k = 0.71069$ Å) radiation in the range of $2.97 \leq \theta \leq 25.50^\circ$ ($-14 \leq h \leq 16$, $-16 \leq k \leq 16$, $-14 \leq l \leq 17$) at 293 K. Absorption corrections were applied using the multi-scan technique¹⁴. A total of 15126 reflections including 8802 unique ones were collected, of which 8802 with $I > 2\sigma(I)$ were considered as

observed and used in the succeeding refinements. The structure was solved by the direct method and refined by full-matrix least-square techniques on F² using SHELXL-97¹⁵. All of the non-hydrogen atoms were refined anisotropically¹⁶. The H atoms attached to C atoms were positioned geometrically, with U_{iso} values derived from U_{eq} values of the corresponding C atom. The final R = 0.1067 and wR = 0.3379, S = 1.073, ($\Delta\rho$)_{max} = 2.965 and ($\Delta\rho$)_{min} = -0.777 e/Å³.

Crystallographic data for the structural analysis(es) have been deposited with the Cambridge Crystallographic Data Centre, CCDC No.: 822133 for the compound **1**.

RESULTS AND DISCUSSION

Crystal structure: The molecular structure, ORTEP drawing, 1D zigzag chain structure and 2D waveliness structure of the compound **1** are illustrated in **Scheme-I** and Figs. 1-3, respectively. Selected bond distances and angles for the complex are shown in Table-1. The single crystal X-ray analysis shows that the asymmetrical unit of the compound **1** contains two Zn(II) ions, two H₂C₃PIm ligands, two H₂L molecules. As shown in Fig. 1, the two Zn sites show a distorted tetrahedral geometry, being connected by two O atoms from two H₂L ligands. The remaining two coordination sites are occupied by two N atoms from one H₂C₃PIm ligand. The Zn-O bond lengths are in the range 1.947(3)-1.965(3) Å and the Zn-N bond lengths are in the range 2.012-2.021(4) Å. The Zn(II) atoms are bridged by H₂L ligand with an intramolecular Zn-Zn distance of 8.709 Å.



Scheme-I: Molecular structure of the compound **1**

It is noticeable that H₂L anion in compound **1** shows two types of coordination modes with Zn ions through the carboxylate groups: (i) The monodentate H₂L ligand links Zn1 atom with the carboxylate groups of the formylate (**Scheme-IIa**). (ii) The monodentate H₂L ligand coordinates Zn2 atom with the carboxylate groups of the acetate (**Scheme-IIb**). Through the special coordination modes, each H₂L anion acts as a μ_2 -bridge linking two Zn atoms into one-dimensional (1D) zigzag chain structure along the a axis. Owing to the multiple

TABLE-1
SELECTED BOND LENGTHS (nm) AND ANGLES (°)

Bond length	nm	Angles	(°)
Zn(1)-O(8)	0.1947(7)	O(8)-Zn(1)-O(4) ⁱ	104.5(3)
Zn(1)-O(4) ⁱ	0.1949(7)	O(8)-Zn(1)-N(5)	119.7(3)
Zn(1)-N(5)	0.2015(9)	O(4) ⁱ -Zn(1)-N(5)	102.8(4)
Zn(1)-N(7)	0.2021(8)	O(8)-Zn(1)-N(7)	104.3(3)
Zn(2)-O(5)	0.1959(7)	O(4) ⁱ -Zn(1)-N(7)	118.2(3)
Zn(2)-O(2)	0.1965(8)	N(5)-Zn(1)-N(7)	108.2(3)
Zn(2)-N(2)	0.2012(9)	O(5)-Zn(2)-O(2)	102.0(3)
Zn(2)-N(4)	0.2018(10)	O(5)-Zn(2)-N(2)	105.1(4)
O(4)-Zn(1) ⁱⁱ	0.1949(7)	O(2)-Zn(2)-N(2)	115.8(4)
O(4)-C(25)	0.1286(13)	O(5)-Zn(2)-N(4)	110.5(4)
O(3)-C(25)	0.1209(13)	O(2)-Zn(2)-N(4)	111.2(4)
O(1)-C(26)	0.1198(13)	N(2)-Zn(2)-N(4)	111.5(4)

Symmetry code: ⁱx - 1, y, z; ⁱⁱx + 1, y, z.

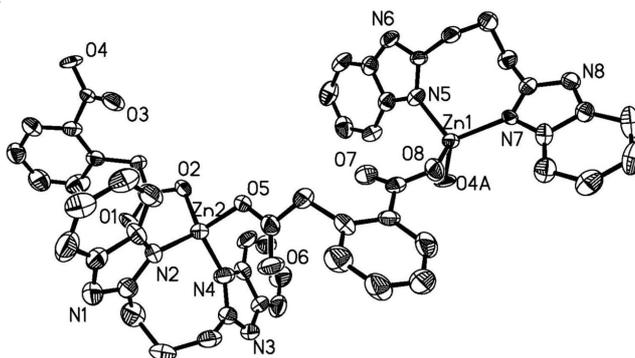
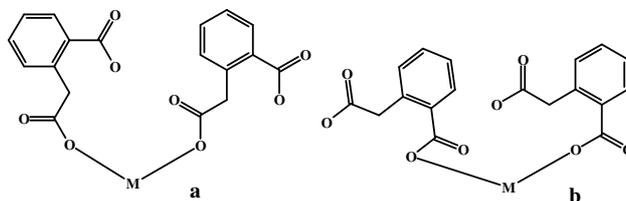


Fig. 1. Coordination environment of Zn(II) atom in compound (**50 %** thermal ellipsoids). Symmetry code: A: -1+x,y,z



Scheme-II: Coordination modes of the H₂L with metals

nitrogen atoms in the H₂C₃PIm ligand, hydrogen-bonding interactions are formed. As a result, the 1D zigzag chain structure is further linked to form a two-dimensional network with the features a waveliness structure by the intermolecular hydrogen bonds (N(8)-H(111)-O(3)ⁱ = 2.727(14), N(6)-H(222)-O(7)ⁱⁱ = 2.767(14), i = 1-x, 1-y, 1-z, 1/2-z, ii = -x, 1-y, 1-z) (Fig. 3). Moreover, the π - π stacking interactions ($d_{\text{face to face}} = 3.325$) among H₂C₃PIm ligands play important roles in the formation of 3D supramolecular structure. Hydrogen-bonding details for complex **1** are given in Table-2.

TABLE-2
DISTANCE (nm) AND ANGLES OF HYDROGEN-BONDING FOR COMPOUND

D-H	d(D-H)	d(H...A)	<DHA	d(D...A)
N(8)-H(111)-O(3) ⁱ	0.86(12)	1.87(11)	174(15)	2.727(14)
N(6)-H(222)-O(7) ⁱⁱ	0.78(12)	2.03(13)	159(13)	2.767(14)

Symmetry code: ⁱ1-x, 1-y, 1-z, 1/2-z; ⁱⁱ-x, 1-y, 1-z.

Conclusion

In summary, a novel one-dimensional (1D) zinc(II) coordination polymer with the ligand (H₂C₃PIm) and aromatic ligand

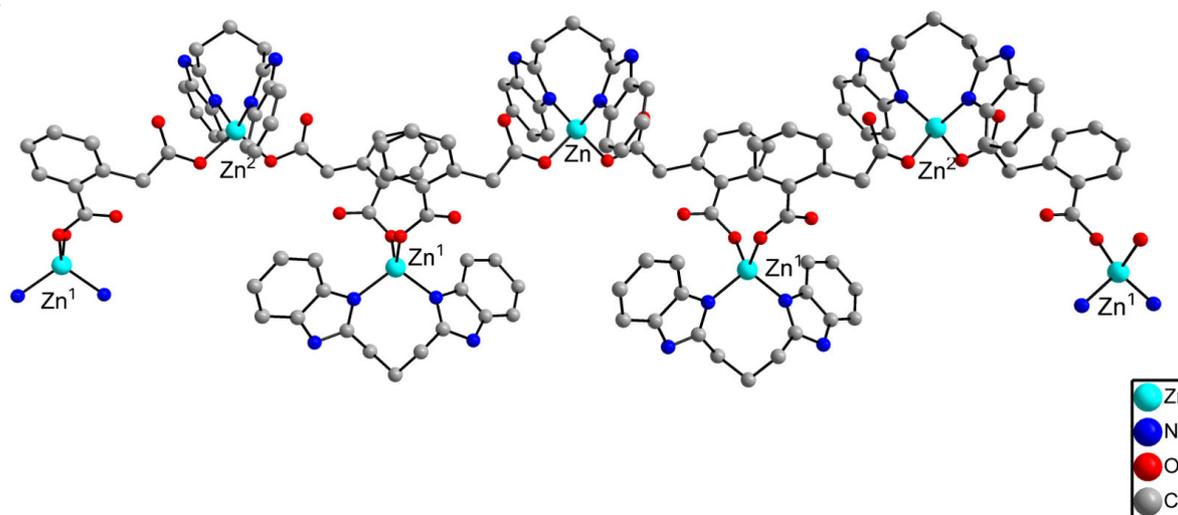


Fig. 2. Views of the 1D zigzag chain structure of compound **1** viewed down along the *a*-axis. Colour code: Zn, teal; C, gray; N, blue; O, red

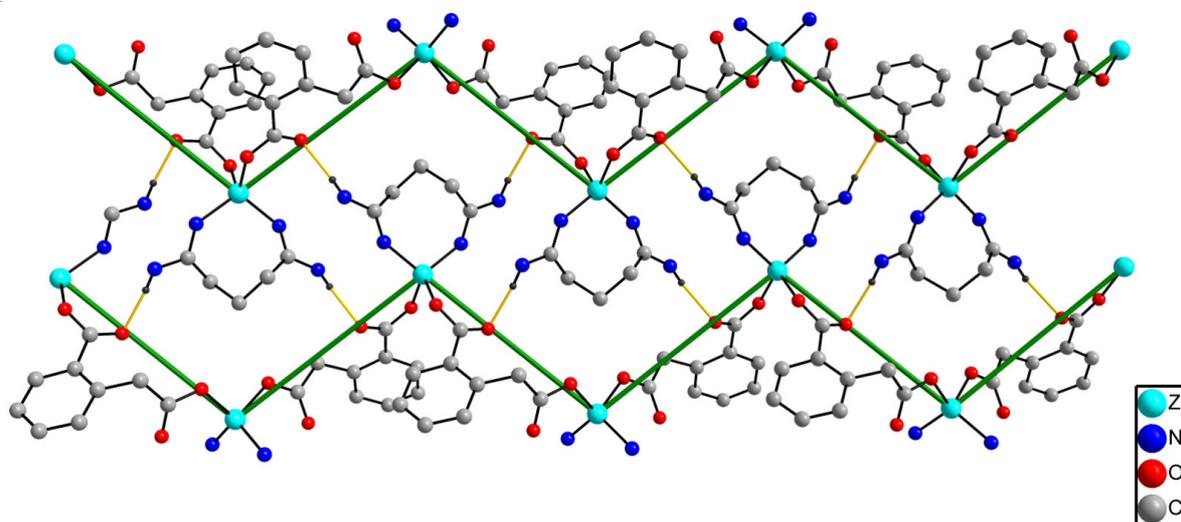


Fig. 3. View of the 2D waveliness structure in compound **1**. Colour code: Zn, teal; C, gray; N, blue; O, red. (benzimidazole cycles in ligands are omitted for clarity, the hydrogen-bonds are shown as the thick yellow stick)

(H₂L) has been synthesized in hydrothermal reaction condition. Single crystal X-ray diffraction analyses revealed that two distorted tetrahedral Zn (II) centers are bridged by H₂L ligand through the different coordination mode. It is found that the special coordination mode the plays a very important role in building the 1D zigzag chain structure along the *a* axis. The weak π - π packing interactions existing in the complex stabilize the crystal structure. Consequently, the successful syntheses of the compounds indicate that it is promising to build up unusual architectures *via* transition metals and imidazole-carboxylate ligands.

ACKNOWLEDGEMENTS

This work was financially supported by the Foundation for Young Teachers of Baoji University of Arts and Science (No. ZK1020).

REFERENCES

- O.M. Yaghi, M. O'Keeffe, N.W. Ockwig, H.K. Chae, M. Eddaoudi and J. Kim, *Nature*, **423**, 705 (2003).
- A.J. Blake, N.R. Champness, P. Hubberstey, W.S. Li, M.A. Withersby and M. Schröder, *Coord. Chem. Rev.*, **183**, 117 (1999).
- S. Kitagawa, R. Kitaura and S. Noro, *Angew. Chem. Int. Ed.*, **43**, 2334 (2004).
- N.W. Ockwig, O. Delgado-Friedrichs, M. O'Keeffe and O.M. Yaghi, *Acc. Chem. Res.*, **38**, 176 (2005).
- R. Wang, L. Han, F. Jiang, Y. Zhou, D. Yuan and M. Hong, *Cryst. Growth Des.*, **5**, 129 (2005).
- J.Y. Lu and V. Schauss, *Inorg. Chem. Commun.*, **6**, 1332 (2003).
- Y.-B. Wang, X.-J. Zheng, W.-J. Zhuang and L. Jin, *Eur. J. Inorg. Chem.*, 1355 (2003).
- V. Arora, M. Gupta and P. Mathur, *Indian J. Chem.*, **38**, 1219 (1999).
- G.A. Van Albada, M.T. Lakin, N. Veldman, A.L. Spek and J. Reedijk, *Inorg. Chem.*, **34**, 4910 (1995).
- G.A. Van Albada, N. Veldman, A.L. Spek and J. Reedijk, *J. Chem. Crystallogr.*, **30**, 69 (2000).
- V.A. Blatov, L. Carlucci, G. Ciani and D. M. Proserpio, *Cryst. Eng. Commun.*, **6**, 378 (2004).
- M. Du, X.J. Jiang and X.J. Zhao, *Inorg. Chem.*, **45**, 3998 (2006).
- L.Y.W. Lilian and M.J. Madeleine, *J. Am. Chem. Soc.*, **79**, 5706 (1957).
- T. Higashi, Program for Absorption Correction, Rigaku Corporation, Tokyo, Japan (1995).
- SHELXTL, Version 5.1, Siemens Industrial Automation, Inc. (1997).
- G.M. Sheldrick, SHELXTL-97, Program for the Refinement of Crystal Structure, University of Göttingen, Germany (1997).