Bull. Chem. Soc. Ethiop. **2014**, 28(2), 315-319.
Printed in Ethiopia
DOI: http://dx.doi.org/10.4314/bcse.v28i2.17
ISSN 1011-3924

SHORT COMMUNICATION

SYNTHESIS AND CRYSTAL STRUCTURE OF A POLYMERIC ZINC(II) COMPLEX DERIVED FROM 4-NITROPHENYLACETIC ACID AND PROPANE-1,3-DIAMINE

Gui-Hua Sheng[1], Xiao-Shan Cheng[2], Zhong-Lu You[2,*] and Hai-Liang Zhu[1,*]

[1]School of Life Sciences, Shandong University of Technology, ZiBo 255049, P. R. China
[2]Department of Chemistry and Chemical Engineering, Liaoning Normal University, Dalian 116029, P. R. China

(Received September 10, 2013; revised May 7, 2014)

ABSTRACT. A new polymeric zinc(II) complex, $[ZnL_2(PDA)]_n$, has been prepared by the reaction of zinc sulfate, 4-nitrophenylacetic acid, and propane-1,3-diamine (PDA) in water. Structure of the complex has been characterized by single-crystal X-ray diffraction. The complex crystallizes as orthorhombic space group *Pnma*, with unit cell dimensions a = 15.732(1) Å, b = 23.912(1) Å, c = 5.5565(3) Å, V = 2090.2(2) Å^3, Z = 4, R_1 = 0.0427, wR_2 = 0.0968, S = 1.048. The Zn atom is coordinated in a tetrahedral geometry. Single crystals of the complex are stabilized by hydrogen bonds and $\pi\cdots\pi$ interactions.

KEY WORDS: 4-Nitrophenylacetic acid, Zinc complex, Crystal structure, Hydrogen bonding

INTRODUCTION

Carboxylic acids are a kind of interesting ligands for the preparation of metal-organic frameworks (MOFs) [1-4]. Zinc is a very important element in biological systems, functions as the active site of hydrolytic enzymes, such as carboxypeptidase and carbonic anhydrase [5, 6]. Zinc complexes with carboxylate ligands have been widely reported for their versatile structures and applications [7-10]. 4-Nitrophenylacetic acid is structurally similar to carboxylic acids. However, no zinc complexes derived from 4-nitrophenylacetic acid have been reported so far. In the present paper, a new polymeric zinc(II) complex, $[ZnL_2(PDA)]_n$, where L is 4-nitrophenylate, PDA is propane-1,3-diamine, is reported.

EXPERIMENTAL

Materials and measurements. Commercially available 4-nitrophenylacetic acid, and propane-1,3-diamine were purchased from Aldrich and used without further purification. Other solvents and reagents were made in China and used as obtained. C, H and N elemental analyses were performed with a Perkin-Elmer elemental analyser. Infrared spectra were recorded on a Nicolet AVATAR 360 spectrometer as KBr pellets in the 4000–400 cm^{-1} region.

Synthesis of $[ZnL_2(PDA)]_n$. An aqueous solution (10 mL) of $ZnSO_4$ (0.1 mmol, 28.8 mg) was added to an aqueous solution (10 mL) of 4-nitrophenylacetic acid (0.2 mmol, 36.2 mg) and propane-1,3-diamine (0.2 mmol, 14.8 mg) with stirring. The mixture was stirred for 1 h at ambient condition to give a clear colorless solution. The resulting solution was allowed to stand in air for several days. Colorless block-shaped crystals suitable for X-ray single crystal analysis were formed at the bottom of the vessel. The isolated product was washed three times with water, and dried in a vacuum over anhydrous $CaCl_2$. Yield, 27 mg (54% based on Zn). M.p.

*Corresponding author. E-mail: hailiang_zhu@163.com

200.0-202.0 ºC. Anal. calcd. for $C_{19}H_{22}N_4O_8Zn$ (FW 499.8): C, 45.66; H, 4.44; N, 11.21. Found: C, 45.75; H, 4.56; N, 11.08%. IR data (KBr, cm^{-1}): 3301 (m), 3262 (m), 3169 (w), 3108 (w), 3079 (w), 2945 (m), 2883 (w), 2837 (w), 1638 (s), 1601 (s), 1589 (s), 1509 (s), 1421 (m), 1372 (s), 1345 (s), 1307 (m), 1271 (s), 1200 (m), 1158 (m), 1114 (m), 1049 (w), 1033 (w), 971 (m), 939 (w), 871 (w), 858 (m), 818 (m), 719 (s), 682 (w), 640 (w), 630 (w), 581 (w), 508 (m), 476 (w).

X-Ray diffraction. Diffraction intensities for the complex were collected at 298(2) K using a Bruker D8 VENTURE PHOTON diffractometer with Mo$K\alpha$ radiation (λ = 0.71073 Å). The collected data were reduced using SAINT [11], and multi-scan absorption corrections were performed using SADABS [12]. The structure was solved by direct method and refined against F^2 by full-matrix least-squares methods using SHELXTL [13]. All the non-hydrogen atoms were refined anisotropically. H atoms were placed in idealized positions and constrained to ride on their parent atoms. The ratio of the maximum and minimum residual density was 4.6. The crystallographic data for the complex are summarized in Table 1. Selected bond lengths and angles are given in Table 2.

Table 1. Crystallographic and experimental data for the complex.

Formula	$C_{19}H_{22}N_4O_8Zn$
FW	499.8
Crystal shape/color	block/colorless
Crystal size/ mm	0.20 × 0.20 × 0.17
Crystal system	Orthorhombic
Space group	*Pnma*
a/Å	15.732(1)
b/Å	23.912(1)
c/Å	5.5565(3)
V/Å^3	2090.2(2)
Z	4
T/K	298(2)
μ/mm^{-1}(Mo-Kα)	1.231
D_c/g cm^{-3}	1.588
Reflections/parameters	1991/154
Independent reflections	1621
Restraints	0
Index ranges/ *h*, *k*, *l*	-15, 19; -28, 24; -6, 6
F(000)	1032
T_{min}	0.7909
T_{max}	0.8181
Goodness of fit on F^2	1.048
R_1, wR_2 [$I \geq 2\sigma(I)$][a]	0.0427, 0.0968
R_1, wR_2 (all data)[a]	0.0578, 0.1031
Largest diff. peak and hole/e Å^{-3}	1.112, -0.240

[a] $R_1 = \sum||F_o|-|F_c||/\sum|F_o|$, $wR_2 = [\sum w(F_o^2-F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$.

Table 2. Selected bond lengths (Å) and angles (°) for the complex.

Zn1-O4	1.977(2)	Zn1-N3A	2.026(3)
Zn1-N2	2.030(3)		
O4-Zn1-O4B	93.25(12)	O4-Zn1-N3A	108.51(10)
O4-Zn1-N2	108.02(9)	N3A-Zn1-N2	125.70(14)

Symmetry codes: A: 1/2 + *x*, *y*, 3/2 – *z*; B: *x*, 1/2 – *y*, *z*.

RESULTS AND DISCUSSION

Structure description of the complex. The molecular structure of the complex is shown in Figure 1. The complex is a propane-1,3-diamine bridged polymeric zinc(II) species. The Zn atom is coordinated by two N atoms from two bridging PDA ligands, and two carboxylate O atoms from two 4-nitrophenylate ligands, forming a tetrahedral geometry. The bond lengths related to the Zn atom are comparable to those observed in similar zinc complexes with carboxylate and amine ligands [14, 15]. The bond angles related to the Zn atom are in the range 93.2(1)–125.7(1)° indicating the tetrahedral coordination is somewhat distorted.

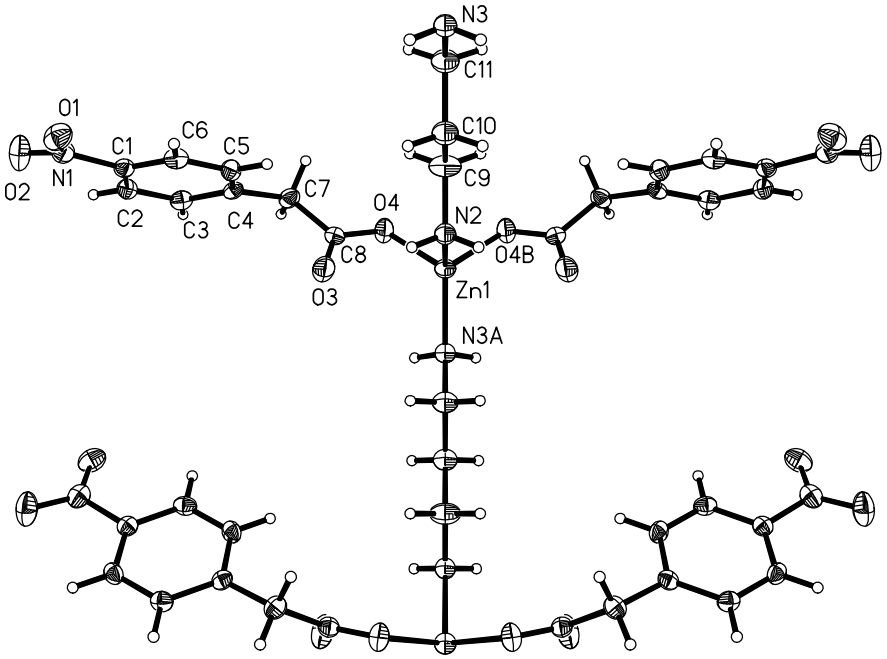

Figure 1. Molecular structure of the complex at 30% probability displacement.

In the packing diagram of the compound shown in Figure 2, the [ZnL_2] units are linked through PDA ligands, forming 1D chains along the *a* axis. The chains are further linked *via* intermolecular N–H···O hydrogen bonds (Table 3) to form 2D layers parallel to the *ab* plane. The layers are further stack along the *c* axis *via* π···π interactions (Table 4).

Table 3. Geometrical parameters for hydrogen bonds.

Hydrogen bonds	*D*–H (Å)	H···*A* (Å)	*D*···*A* (Å)	*D*–H···*A* (°)
N3–H3B···O2$^{\#1}$	0.90	2.23	3.126(3)	173(3)
N3–H3A···O2$^{\#2}$	0.90	2.23	3.126(3)	173(3)
N2–H2B···O4$^{\#3}$	0.90	2.33	3.090(4)	142(3)
N2–H2A···O4$^{\#4}$	0.90	2.33	3.090(4)	142(3)

$^{\#1}$ – *x*, – *y*, 2 – *z*; $^{\#2}$ – *x*, 1/2 + *y*, 2 – *z*; $^{\#3}$ *x*, 1/2 – *y*, 1 + *z*; $^{\#4}$ *x*, *y*, 1 + *z*.

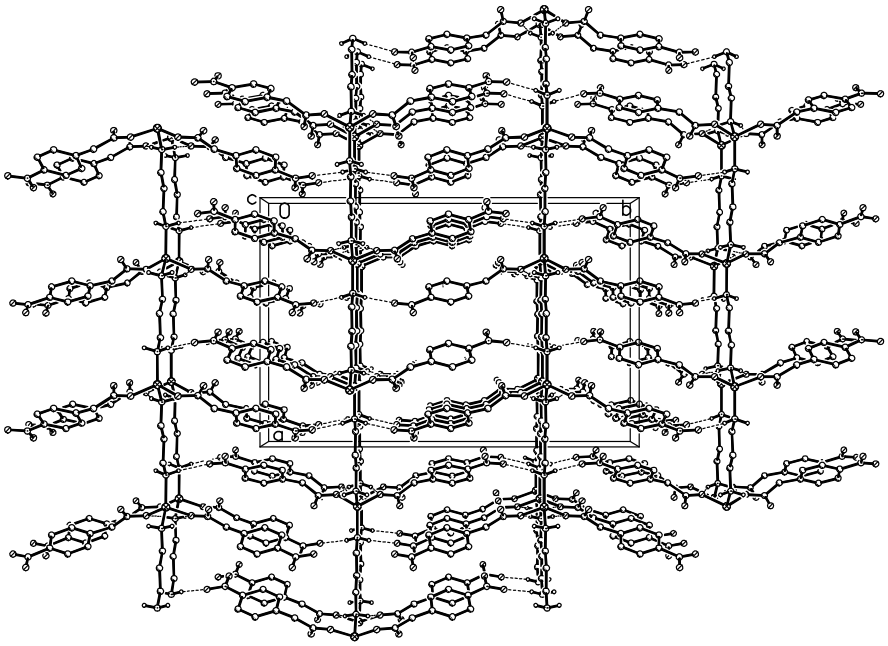

Figure 2. Molecular packing of the complex, viewed along the *c* axis. Hydrogen bonds are drawn as dashed lines. Hydrogen atoms not related to hydrogen bonds are omitted for clarity.

Table 4. Parameters between the planes for the complex.

Cg	Distance between ring centroids (Å)	Dihedral angle (º)	Perpendicular distance of *Cg*(I) on *Cg*(J) (Å)	Beta angle (º)	Gamma angle (º)	Perpendicular distance of *Cg*(J) on *Cg*(I) (Å)
*Cg*1-*Cg*1$^{\#5}$	4.842	58.99	2.083	5.55	64.52	4.819
*Cg*1-*Cg*1$^{\#6}$	3.907	0.00	3.315	31.93	31.93	3.315

Symmetry codes: #5: 1/2 – *x*, – *y*, 1/2 + *z*; #6: – *x*, – *y*, 1 – *z*. *Cg*1 is the centroid of C1-C2-C3-C4-C5-C6.

IR spectra of the complex. The infrared spectrum of the complex was consistent with the structure as determined by X-ray diffraction. Features corresponding to benzene ring puckering exist in the region between 820 and 600 cm^{-1}. Asymmetric and symmetric C–O stretching modes of the fully deprotonated, ligated carboxylate groups were substantiated by strong, broadened bands at 1601 and 1372 cm^{-1}.

Supplementary data. The crystallographic data for the structure has been deposited with the Cambridge Crystallographic Data Centre (CCDC 957482). Copies of the data can be obtained free of charge on application to the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (e-mail for deposition: deposit@ccdc.cam.ac.uk).

REFERENCES

1. Kang, Z.-X.; Ding, J.-Y.; Fan, L.-L.; Xue, M.; Zhang, D.-L.; Gao, L.-X.; Qiu, S.-L. *Inorg. Chem. Commun.* **2013**, 30, 74.
2. Wu, J.; Wang, F.-M.; Liu, J.-Q.; Li, K.-B.; Xu, D.-H. *Synth. React. Inorg. Met.-Org. Nano-Met. Chem.* **2013**, 43, 1231.
3. Li, L.-J.; Wang, L.-Z.; Yang, X.-Y.; Wang, G.-Y.; Tian, C.; Du, J.-L. *Russ. J. Coord. Chem.* **2013**, 39, 239.
4. Pintado-Sierra, M.; Rasero-Almansa, A.M.; Corma, A.; Iglesias, M.; Sanchez, F. *J. Catal.* **2013**, 299, 137.
5. Wang, S.-F.; Tian, G.-R.; Zhang, W.-Z.; Jin, J.-Y. *Bioorg. Med. Chem. Lett.* **2009**, 19, 5009.
6. Koziol, L.; Valdez, C.A.; Baker, S.E.; Lau, E.Y.; Floyd, W.C.; Wong, S.E.; Satcher, J.H.; Lightstone, F.C.; Aines, R.D. *Inorg. Chem.* **2012**, 51, 6803.
7. Liu, Y.-L.; Yue, K.-F.; Shan, B.-H.; Xu, L.-L.; Wang, C.-J.; Wang, Y.-Y. *Inorg. Chem. Commun.* **2012**, 17, 30.
8. Crees, R.S.; Cole, M.L.; Hanton, L.R.; Sumby, C.J. *Inorg. Chem.* **2010**, 49, 1712.
9. Kumar, U.; Singh, M.; Thirupathi, N. *Polyhedron* **2013**, 55, 233.
10. Katsoulakou, E.; Dermitzaki, D.; Konidaris, K.F.; Moushi, E.E.; Raptopoulou, C.P.; Psycharis, V.; Tasiopoulos, A.J.; Bekiari, V.; Manessi-Zoupa, E.; Perlepes, S.P.; Stamatatos, T.C. *Polyhedron* **2013**, 52, 467.
11. Bruker, SMART and SAINT. Bruker AXS Inc., Madison, Wisconsin, USA. **2002**.
12. Sheldrick, G.M.: SADABS. *Program for Empirical Absorption Correction of Area Detector*, University of Göttingen, Germany. **1996**.
13. Sheldrick, G.M.: SHELXTL V5.1 *Software Reference Manual*, Bruker AXS, Inc., Madison, Wisconsin, USA.
14. Guilera, G.; Steed, J.W. *Chem. Commun.* **1999**, 16, 1563.
15. Friese, S.J.; Kucera, B.E.; Junior, L.Q.; Tolman, W.B. *Inorg. Chem.* **2006**, 45, 8003.