Crystal Structure of $\text{Zn}(\text{phth})_2(\text{H}_2\text{O})_2$ [phth = *o*-phthalate]

Wu WEN,^{*,**} Xie JIMIN,^{*†} Yawen XUAN,^{**} and Naixiang YUAN^{**}

^{*}Department of Chemistry, Jiangsu University, Zhen Jiang, 212003, P. R. China

^{**}Department of Chemistry, Zhou Kou Normal University, He Nan, 466001, P. R. China

The coordination polymer $\text{Zn}(\text{phth})_2(\text{H}_2\text{O})_2$ (phth = phthalate) (**1**), with the formula $\text{C}_{16}\text{H}_{14}\text{ZnO}_{10}$ was synthesized and the crystal structure was determined by single-crystal X-ray diffraction. The complex belongs to a monoclinic system, space group $P2_1/c$ with $a = 8.2995(17)\text{\AA}$, $b = 14.341(3)\text{\AA}$, $c = 7.1992(14)\text{\AA}$, $\beta = 102.14(3)^\circ$. The Zn complex forms one-dimensional zigzag chains *via* a π - π stacking interaction of phthalate. The adjacent zigzag chains may also be paired under the direction of supramolecular recognition and attraction through both π - π stacking and hydrogen-bonding interactions into molecular zippers, which are further interlinked into a three-dimensional supramolecular network by these non-covalent interactions.

(Received August 24, 2007; Accepted October 11, 2007; Published on web December 18, 2007)

A metal-organic coordination polymer has particular and special structure characteristics with some caves, holes and channels,¹ which can be used in selected catalysis, molecular recognition, reversible exchange of host-guest molecules (ions) and super-purity separation.² In the past ten years, polymers with bridging ligands have been widely investigated.³ Many metal compound containing phthalate ligands have been studied concerning their magnetic and spectroscopic properties.⁴ Here, we report on the synthesis and crystal structure of the title compound.

Potassium hydrogenphthalate (1 mmol) and KOH (1 mmol) were dissolved in 50 mL of an EtOH/H₂O (V:V = 1:1) solution, and then the resultant solution was added into 10 mL double-distilled water containing $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ (1 mmol). A single crystal suitable for X-ray structural analysis was obtained by slowly evaporating from ethanol at room temperature. Colorless crystals were obtained in a yield of up to 65.42%. A crystal having dimensions of $0.20 \times 0.18 \times 0.16$ mm was chosen for X-ray diffraction studies. Measurements were made on a Rigaku-RAXIS-IV diffractometer with graphite-monochromatized Mo K_α radiation ($\lambda = 0.71073 \text{\AA}$) at 291 K. The structure was solved by direct methods using SHELXS-97, and refined by full-matrix least-squares techniques anisotropically for all non-H atoms. All H atoms were added according to theoretical calculations; H5F and H5E were refined using a riding model. The crystal data and the experimental parameters are listed in Table 1. A chemical diagram of the title compound is shown in Fig. 1. The final positional parameters

for all non-hydrogen atoms are given in Table 2. Selected bond lengths and bond angles are summarized in Table 3. The hydrogen-bonding distances and angles are presented in Table 4. The molecular structure of the title complex is illustrated in Fig. 2. The complex asymmetry unit consists of one Zn(II) ion, two phthalate anions, and two H₂O molecules. The Zn(II) ion is four-coordinated to form a distorted square by O(1) (bond length $1.982(2)\text{\AA}$) of a phthalate anion as well as two O atoms from two water molecules, bond length, $2.055(3)\text{\AA}$. The Zn(II) is located at the distorted square center ($\text{O}(1)^{\#1}\text{-Zn}(1)\text{-O}(1)$ 180° , $\text{O}(1)\text{-Zn}(1)\text{-O}(5)^{\#1}$ $81.1(1)^\circ$, $\text{O}(1)^{\#1}\text{-Zn}(1)\text{-O}(5)^{\#1}$ $98.9(1)^\circ$, and

Table 1 Crystal and experimental data

Formula: $\text{C}_{16}\text{H}_{14}\text{O}_{10}\text{Zn}$
Formula weight 431.64
Crystal size (mm): $0.20 \times 0.18 \times 0.16$
Crystal system: monoclinic
Space group: $P2_1/c$ $Z = 2$
$a = 8.2995(17)\text{\AA}$
$b = 14.341(3)\text{\AA}$ $\beta = 102.14(3)^\circ$
$c = 7.1992(14)\text{\AA}$
$V = 837.7(3)\text{\AA}^3$
$D_x = 1.711 \text{ g/cm}^3$
$\theta_{\text{max}} = 25.49^\circ$ with Mo K_α
No. of reflections measured = 2717
No. of reflections used = 1467
No. of parameters = 137
$R = 0.0415$
$(\Delta/\sigma)_{\text{max}} = 0.000$
$(\Delta\rho)_{\text{max}} = 0.362 \text{ e \AA}^{-3}$
$(\Delta\rho)_{\text{min}} = -0.464 \text{ e \AA}^{-3}$
Measurement: Rigaku-R-AXIS-IV
Program system: Sheldrick SHELXS-97
Structure determination: direct methods
The final positional Refinement: full matrix

CCDC 660810 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

Fig. 1 Structural chemical diagram.

[†] To whom correspondence should be addressed.
E-mail: xiejm391@sohu.com or chinawuwen@126.com

Table 2 Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$)

	x	y	z	U(eq)
Zn(1)	0	0	0	31(1)
O(1)	2296(3)	473(1)	576(4)	34(1)
O(2)	1035(3)	1715(2)	1111(4)	37(1)
O(3)	1405(3)	3369(2)	1203(4)	37(1)
O(4)	3145(3)	4338(2)	568(4)	41(1)
O(5)	-590(3)	300(2)	-2853(4)	45(1)
C(1)	3998(3)	1833(2)	1371(4)	23(1)
C(2)	5427(4)	1264(2)	1690(5)	28(1)
C(3)	7043(4)	1627(2)	2062(5)	35(1)
C(4)	7252(4)	2576(2)	2073(5)	35(1)
C(5)	5855(4)	3154(2)	1723(5)	32(1)
C(6)	4213(3)	2809(2)	1376(4)	23(1)
C(7)	2352(4)	1321(2)	993(4)	26(1)
C(8)	2855(4)	3555(2)	1006(4)	28(1)

Table 3 Selected bond lengths ($\text{\AA}$) and angles ($^\circ$)

Zn(1)-O(1)	1.915(2)
Zn(1)-O(5)	1.971(3)
O(1)-C(7)	1.250(4)
O(2)-C(7)	1.261(4)
O(3)-C(8)	1.292(4)
C(2)-C(3)	1.368(4)
C(4)-C(5)	1.370(5)
O(1)#1-Zn(1)-O(1)	180.00
O(1)-Zn(1)-O(5)	89.12(10)
C(7)-O(1)-Zn(1)	111.6(2) ^a
C(2)-C(1)-C(6)	119.0(2)
C(2)-C(3)-C(4)	119.4(3)
C(1)-C(6)-C(8)	128.4(3)
O(4)-C(8)-O(3)	120.2(3)
O(4)-C(8)-C(6)	119.8(3)

Symmetry transformations used to generate equivalent atoms: #1 $-x$, $-y$, $-z$.

Table 4 Hydrogen bonds [$\text{\AA}$ and $^\circ$]

D-H...A	d(D-H)	d(H...A)	d(D...A)	$\angle(\text{DHA})$
D-H...A	d(D-H)	d(H...A)	d(D...A)	$\angle(\text{DHA})$
O(5)-H(5F)...O(4)#2	0.86(2)	1.82(2)	2.667(3)	166(5)
O(5)-H(5E)...O(3)#3	0.871(19)	1.94(2)	2.794(3)	166(4)
O(3)-H(3E)...O(2)	0.84(5)	1.57(5)	2.404(3)	172(5)

Symmetry transformations used to generate equivalent atoms: #1 $-x+2$, $-y$, $-z+2$ #2 $-x+2$, $y-1/2$, $-z+3/2$ #3 x , $-y+1/2$, $z-1/2$.

C(7)-O(1)-Zn(1) 111.6(2) $^\circ$. #1 $-x$, $-y$, $-z$.

As shown in Fig. 3, the zinc complex forms one-dimensional zigzag chains via a π - π stacking interaction of phthalate, which belongs to a face-to-face form with a distance of about 3.694 $\text{\AA}$. A 3D network structure is formed by a π - π stacking interaction of phthalate and hydrogen bonds of two phthalates coordinated to zinc atoms, obviously observed in Fig. 4. Another O-H...O hydrogen bond is between the water molecule coordinated to zinc atoms and phthalate, involving the H(5E) atom with O(3)^{#3} (O(5)-H(5E) = 0.871(19) $\text{\AA}$, H(5E)...O(3)^{#3} = 1.94(2) $\text{\AA}$, H(5E)...O(3)^{#3} = 2.794(3) $\text{\AA}$, $\angle$ O(5)-H(5A)...O(4A) = 166(4) $^\circ$)

Fig. 2 Molecular structure along with atom labeling.

Fig. 3 One-dimensional zigzag chains.

Fig. 4 Hydrogen-bonding and π - π stacking interactions of the title compound.

and the H(5F) atom bound to O(5) (O(5)-H(5F) = 0.86(2) $\text{\AA}$, H(5F)...O(4)^{#2} = 1.82(2) $\text{\AA}$, O(5)...O(4)^{#2} = 2.667(3) $\text{\AA}$, $\angle$ O(5)-H(5F)...O(4)^{#2} = 166(5) $^\circ$). #1 $-x+2$, $-y$, $-z+2$, #2 $-x+2$, $y-1/2$, $-z+3/2$, #3 x , $-y+1/2$, $z-1/2$ (Table 4).

References

1. C. S. Gu, S. Gao, L. H. Huo, Z. B. Zhu, H. Zhao, and J. G. Zhao, *Chinese J. Struct. Chem.*, **2004**, 9, 1073.
2. C. Lirage, C. Egger, M. Npgues, and G. J. Ferey, *Mater. Chem.*, **1998**, 8, 743.
3. X. M. Chen, and J. W. Cai, "Analysis of Single Crystal Structure", Science Press, Beijing **2003**, 9, 118.
4. G. Adiwidjaja, E. Rossmanith, and H. Küppers, *Acta Cryst.*, **1978**, B34, 3079.