Synthesis and Structure of a Novel Two-dimensional Diphenic Acid (H₂dpa) Zinc(II) Complex

Juangang WANG, Rui SHEN, Weina WU, Jincai WU, and Ning TANG[†]

College of Chemistry and Chemical Engineering, Lanzhou University, Lanzhou 730000, P. R. China

A novel tetrahedral coordinated zinc polymer was hydrothermally prepared and characterized. It was crystallized in the monoclinic system, space group $P2_1/c$ with $a = 12.8437(1)\text{\AA}$, $b = 5.9596(1)\text{\AA}$, $c = 17.2934(2)\text{\AA}$, $\beta = 104.057(4)^\circ$, $V = 1284.06(18)\text{\AA}^3$ and $Z = 4$. The structure of the title complex consists of extended two-dimensional double helix chains.

(Received September 14, 2007; Accepted January 28, 2008; Published on web April 2, 2008)

Recently, studies of inorganic and organic hydrides have focused on the dynamic aspects of crystal engineering, porous structures, and coordination polymers.¹⁻³ Helical structures through self-organization are an essence of life and are of interest in supramolecular chemistry because helical structures are reminiscent of DNA molecules. The design and synthesis of chiral inorganic-organic materials have attracted great attention for their potential applications in enantioselective separation and catalysis. Water can play an important role in these self-assembly processes.^{4,5} Here we report on the preparation and crystal structure of a self-assembled two-dimensional supermolecular complex that is stabilized by an intricate array of coordinated water molecules.

As a typical preparation procedure, a mixture of H₂dpa (0.5 mmol), NaOH (1 mmol) and ZnCl₂·6H₂O (0.5 mmol) was suspended in 8 ml of deionized water and sealed in a 20-ml Teflon-lined autoclave. Upon heating at 180°C for three days, the autoclave was slowly cooled to room temperature. The crystals were collected, washed with deionized water and dried. The compound is stable in air and insoluble in water and common organic solvents. A white single crystal with dimensions of 0.40 × 0.09 × 0.08 mm was selected for X-ray diffraction analysis. Data collection was performed on a Bruker SMART diffractometer using Mo K_α radiation ($\lambda = 0.71073\text{\AA}$). The structure was solved by direct methods with the Shelx-97 program and expanded with a different Fourier technique. The non-hydrogen atoms were refined

anisotropically by the full-matrix least-squares method based on F^2 with all observed reflections. The hydrogen atoms were generated geometrically with isotropic thermal parameters. The experimental conditions, crystal data and structure refinement results are summarized in Table 1. The atomic coordinates and equivalent isotropic displacement parameters for the non-hydrogen atoms are listed in Table 2. The selected bond lengths and angles are listed in Tables 3 and 4. An ORTEP plot of the title complex is shown in Fig. 2.

Single-crystal X-ray diffraction study reveals that the complex is a double-helical chain structure (Fig. 3). The Zn²⁺ ion is in a tetrahedral coordination environment (Fig. 2). It is ligated to three different carboxylate oxygen atoms and one water molecule. The distance of Zn–O_{H₂O} is (1.966(3)Å) slightly

Fig. 1 Chemical structure of the title complex.

Table 1 Crystal and experimental data

Empirical formula	C ₁₄ H ₁₀ O ₅ Zn
Formula weight	323.59
Temperature	294(2)K
Wavelength	0.71073
Crystal system/Space group	monoclinic, $P2_1/c$
Unit cell dimensions	$a = 12.8437(1)\text{\AA}$ $b = 5.9596(1)\text{\AA}$, $\beta = 104.057(4)^\circ$ $c = 17.2934(2)\text{\AA}$
Volume	1284.06(18)Å ³
Z	4
Density (calculated)	1.674 Mg/m ³
Absorption coefficient	1.928 mm ⁻¹
$F(0\ 0\ 0)$	656
Crystal size	0.40 mm × 0.09 mm × 0.08 mm
range for data collection [°]	1.63 to 27.77
Index ranges	$-16 < h < 16$, $-7 < k < 6$, $-22 < l < 14$
Reflections collected/unique	7570/2944
Absorption correction	empirical
Refinement method	full-matrix least-squares on F^2
Data/restraints/parameters	2944/0/190
Goodness-of-fit on F^2	0.968
R indices	$R1 = 0.0466$, $wR2 = 0.1595$
Largest diff. peak and hole	0.804 and $-0.833\text{ e.\AA}^{-3}$

Crystallographic Data Center as supplementary publication number CCDC-660499

[†] To whom correspondence should be addressed.
E-mail: Tangn@lzu.edu.cn

Table 2 Atomic coordinates and equivalent isotropic displacement parameters for the non-hydrogen atoms. $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U_{ij} tensor

Atom	x	y	z	$U(\text{eq})$
Zn1	-0.05902	0.97444	-0.11040	0.0299
O1	0.07930	0.83499	-0.07410	0.0456
O2	-0.04335	1.13600	-0.20608	0.0398
O3	0.10541	0.77346	0.05553	0.0410
O4	0.17755	0.23490	0.13159	0.0380
O5	0.10492	0.43642	0.21295	0.0431
C1	0.17601	0.40341	0.17560	0.0303
C2	0.26444	0.57015	0.18530	0.0299
C3	0.31613	0.61184	0.12447	0.0282
C4	0.39789	0.77288	0.13765	0.0424
C5	0.42603	0.89212	0.20741	0.0502
C6	0.37275	0.85274	0.26679	0.0466
C7	0.29289	0.69540	0.25568	0.0385
C9	0.29002	0.49507	0.04506	0.0299
C10	0.20446	0.55881	-0.01769	0.0301
C11	0.18925	0.44784	-0.09049	0.0440
C12	0.25707	0.27722	-0.10064	0.0516
C13	0.34313	0.21717	-0.03884	0.0524
C14	0.35861	0.32769	0.03242	0.0445
C15	0.12494	0.73603	-0.01116	0.0303

Table 3 Selected bond lengths (Å)

Zn(1)-O(1)	1.923(3)	C(1)-O(4)	1.263(5)
Zn(1)-O(4)	1.933(3)	C(1)-O(5)	1.255(5)
Zn(1)-O(3)	1.946(3)	C(1)-C(2)	1.488(6)
Zn(1)-O(2)	1.967(3)	C(15)-C(10)	1.492(5)
C(3)-C(2)	1.396(5)	C(15)-O(3)	1.258(5)
C(3)-C(4)	1.400(5)	C15-O(1)	1.251(5)
C(3)-C(9)	1.503(5)		

Table 4 Selected bond angles (°)

O(1)-Zn(1)-O(4)	113.92(14)	O(1)-C(15)-O(3)	123.9(4)
O(1)-Zn(1)-O(3)	122.85(13)	O(1)-C(15)-C(10)	116.9(3)
O(4)-Zn(1)-O(3)	105.68(12)	O(3)-C(15)-C(10)	119.2(3)
O(1)-Zn(1)-O(2)	102.18(13)	C(2)-C(3)-C(4)	118.3(4)
O(4)-Zn(1)-O(2)	113.16(14)	C(2)-C(3)-C(9)	124.4(3)
O(3)-Zn(1)-O(2)	97.95(14)	C(4)-C(3)-C(9)	117.3(3)

longer than that of Zn-O_{COO} (1.923(3)Å, 1.933(3)Å, and 1.946(3)Å). The three carboxylate oxygen atoms of the H₂dpa ligand coordinated with Zn atoms. Each carboxylate of the H₂dpa ligands bridges three Zn²⁺ ions to form infinite right-hand or left-hand helical C-O-Zn chains. The two types of helical chains are interconnected to each other through the Zn²⁺ center to produce interesting double-helix chains.

One hydrogen atom of the coordinated water molecule links the adjacent carboxylate oxygen atom, not be coordinated with the Zn²⁺ ion in an identical chain (Fig. 4). Another hydrogen atom of the coordinated water links the adjacent carboxylate oxygen atom of neighboring chains which can not coordinated with the Zn²⁺ ion. The distance of HO-H...O_{COO} was observed to be 2.660 Å and 2.662 Å, respectively. In this way, the double-helix chains are linked through coordinated water molecules by hydrogen bonding to form an extended two-dimensional network.

Fig. 2 ORTEP plot of the title complex.

Fig. 3 Double helix chains of the title complex.

Fig. 4 Schematic diagram representing section of the coordinated water molecular linked the double helix chains by hydrogen bonds.

Acknowledgements

We are grateful for financial support of the National Science Foundation of China (20571035) and the Gansu Science Foundation of China (3ZS051-A25-003)

References

1. M. W. Hosseini and A. D. Cain, *Chem. Commun.*, **1998**, 727.
2. J. Y. Lu, *Coord. Chem. Rev.*, **2003**, 246, 327.
3. B. Moulton and M. J. Zaworotko, *Chem. Rev.*, **2004**, 101, 1629.
4. R. E. Dehl and C. A. J. Hoeve, *Chem. Phys.*, **1996**, 50, 3245.
5. C. Migchelsen, H. J. C. Berendsen, and A. J. Rupprecht, *Mol. Biol.*, **1968**, 37, 235.