



Synthesis and Crystal Structure of 3D-Supramolecular Zinc Complex Derived from Pyridine-2,5-dicarboxylate and Oxalate

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A novel complex, $Zn_2(Hpdc)_2(Ox)(H_2O)_4$ (H_2pdc = pyridine-2,5-dicarboxylic acid, Ox = oxalate), has been hydrothermally synthesized and characterized by the elemental analyses, IR spectrum and single crystal X-ray diffraction. Crystal structure analysis reveals that the compound crystallizes in monoclinic space group $P2(1)/n$, features an interesting 3D-supramolecular network *via* hydrogen bonding and π - π stacking interactions. Cell unit parameter for the compound: $a = 10.2152(3) \text{ \AA}$, $b = 9.6535(3) \text{ \AA}$, $c = 10.3594(2) \text{ \AA}$, $\beta = 105.664^\circ$, $V = 983.63(5) \text{ \AA}^3$, $Z = 2$, $M_r = 623.05$, $D_c = 2.104 \text{ g/cm}^3$, $\mu = 2.536 \text{ mm}^{-1}$, $F_{(000)} = 628$, $T = 150(2) \text{ K}$, $R = 0.0356$, $wR = 0.0612$ for 2510 reflections with $I > 2\sigma(I)$.

Key Words: Crystal structure, Zinc, Pyridine-2,5-dicarboxylic acid, Hydrogen bond.

INTRODUCTION

Crystal engineering of supramolecular architectures based on metal and organic building blocks has received increasing attention owing to their potential applications in exchange and sorption, catalysis, electrical conductivity and magnetism *etc*¹. Pyridine dicarboxylic acids have been widely used as organic building block for the construction of organic-inorganic hybrid materials, which are of great interest in recent years. This kind of ligand combines the advantages of both organic multicarboxylic acid and hetero aromatic compound. Pyridine-2,5-dicarboxylic acid (pdc) is one of such typical examples due to the chelating ability of carboxylic acid and heterocyclic nitrogen group in the chelating mode to catch various metal ions to be amenable to the formation of extended coordination complex structures²⁻¹¹. However, few examples of metal-pyridine-2,5-dicarboxylate compounds containing oxalate ligand have been reported so far^{12,13}. In this work, we reported a novel Zn(II) complex $[Zn_2(Hpdc)_2(Ox)(H_2O)_4]$ with 3D-supramolecular structure based on hydrogen bonding and π - π stacking interactions.

EXPERIMENTAL

All the reagents and solvent employed were commercially available and used as received without further purification.

Pyridine-2,5-dicarboxylic acid (H_2pdc , $C_7H_5NO_4$, $\geq 98.0\%$, Alfa Aesar), zinc nitrate hexahydrate $[Zn(NO_3)_2 \cdot 6H_2O, \geq 98\%$, Riedel-de Haën], Guanine ($C_5H_5N_5O$, $\geq 99.0\%$, Fluka). The C, H and N microanalyses were carried out with Perkin-Elmer 240 elemental analyzer in the Microanalysis Laboratory of the University of Aveiro. The FT-IR spectra were recorded from KBr pellets in the range of $4000-400 \text{ cm}^{-1}$ on a Mattson 7000 spectrometer.

Synthesis: The compound was synthesized by mixing 0.167 g (1 mmol) of pyridine-2,5-dicarboxylic acid (H_2pdc), 0.3 g (1 mmol) of $Zn(NO_3)_2 \cdot 6H_2O$, 0.080 g (0.5 mmol) of guanine with 15 g of distilled water in a Teflon lined autoclave. The mixture was stirred for 0.5 h and then heated at 120°C for 3 days. Small amount of white powder was removed from the colourless mother liquor by filtration. The filtrate was evaporated for 1 week and block crystals were collected (Yield: 0.105 g, 31.8 %). Anal. (%) found (calcd.) for $C_{16}H_{16}N_2O_{16}Zn_2$: C, 30.92 (30.84); H, 2.51 (2.59); N, 4.39 (4.50). IR (KBr, ν_{max} , cm^{-1}): 3468(br), 3407(br), 2654(m), 2519(m), 2362(m), 1936(w), 1700(s), 1643(s), 1606(s), 1576(s), 1486(w), 1434(m), 1398(s), 1364(s), 1282(s), 1253(s), 1172(m), 1132(m), 1043(s), 896(m), 868(m), 802(s), 756(s), 688(m), 660(m), 567(w), 536(m), 502(w), 413(w), 358(w).

Crystal structure determination: A single crystal of compound with dimensions of $0.08 \text{ mm} \times 0.06 \text{ mm} \times 0.02$

mm was selected for crystallographic data collection at 150(2) K and structure determination on a Bruker SMART APEX CCD diffractometer with graphite-monochromatic MoK α radiation ($\lambda = 0.71073 \text{ \AA}$). A total of 11683 reflections were collected in the range of $2.94^\circ \leq \theta \leq 28.69^\circ$, of which 2510 reflections were unique with $R_{\text{int}} = 0.0550$. The data were integrated using the Siemens SAINT program¹⁴. With the intensities corrected for Lorentz factor, polarization, air absorption and absorption due to variation in the path length through the detector faceplate. Empirical absorption and extinction corrections were applied. The structure was solved by direct methods and expanded using Fourier techniques and SHELXTL program¹⁵ system was used in the solution and refinement of the structure. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were added according to theoretical model. The final full-matrix least-squares refinement including 183 variable parameters for 2510 reflections with $I > 2\sigma(I)$ and converged with unweighted and weighted agreement factors of

$$R_1 = \frac{\sum(|F_o| - |F_c|)}{\sum|F_o|} = 0.0356 \quad (1)$$

$$\text{and } wR_2 = \left\{ \frac{\sum[w(F_o^2 - F_c^2)^2]}{\sum w(F_o^2)^2} \right\}^{1/2} = 0.0612 \quad (2)$$

where $w = 1/[\sigma^2(F_o^2) + (0.0734P)^2 + 4.665P]$ and $P = (F_o^2 + 2F_c^2)/3$. The maximum and minimum peaks on the final difference Fourier map are corresponding to 0.569 and -0.429 e/Å³, respectively.

RESULTS AND DISCUSSION

The selected bond lengths and bond angles are given in Table-1. Fig. 1 shows the building unit of the present Zn(II) compound. The compound crystallizes in the monoclinic lattice with P2(1)/n space group. The asymmetric unit of this structure consists of one Zn atom, one Hpzdc⁻ ligand, half of oxalate anion and two coordinate water molecules. The Zn atom has a distorted octahedral coordination environment, where six positions are occupied one pyridyl nitrogen N(1), one carboxyl oxygen atom O(3), two oxalate oxygen atoms [O(1A), O(2)] and two coordinate water molecules [O(7), O(8)]. The Zn-O bond lengths are in the range of 2.0763(17)-2.149917(3) Å with slightly longer Zn-O(1A) bond [2.149917(3) Å]. The Zn-O bond lengths are in agreement with those Zn-pdc compounds¹⁶⁻¹⁸.

TABLE-1
SELECTED BOND LENGTHS [Å] AND ANGLES [°]

Zn(1)-O(2)	2.0764(17)	Zn(1)-N(1)	2.0992(18)
Zn(1)-O(8)	2.080(2)	Zn(1)-O(3)	2.1485(18)
Zn(1)-O(7)	2.091(2)	Zn(1)-O(1A)	2.1499(17)
C(1)-O(1)	1.254(3)	C(1)-O(2)	1.259(3)
C(2)-O(4)	1.240(3)	C(8)-O(6)	1.305(3)
C(2)-O(3)	1.273(3)	C(8)-O(5)	2.239(2)
O(2)-Zn(1)-O(8)	96.50(8)	O(2)-Zn(1)-O(7)	89.23(8)
O(8)-Zn(1)-O(7)	87.92(10)	O(2)-Zn(1)-O(3)	95.95(7)
O(8)-Zn(1)-N(1)	91.24(9)	O(7)-Zn(1)-N(1)	100.77(8)
O(8)-Zn(1)-O(1A)	97.13(9)	O(7)-Zn(1)-O(3)	87.43(9)
N(1)-Zn(1)-O(1A)	90.52(7)	N(1)-Zn(1)-O(3)	77.35(8)
O(2)-Zn(1)-O(1A)	78.93(7)	O(3)-Zn(1)-O(1A)	89.98(7)
O(4)-C(2)-O(3)	125.6(2)	O(6)-C(8)-O(5)	124.8(3)

Symmetry codes: A: $-x + 1, -y, -z + 2$.

The Hpzdc⁻ ligand behaves as bidentate ligand chelating a Zn atom through oxygen O(3) and pyridyl nitrogen N(1) atoms,

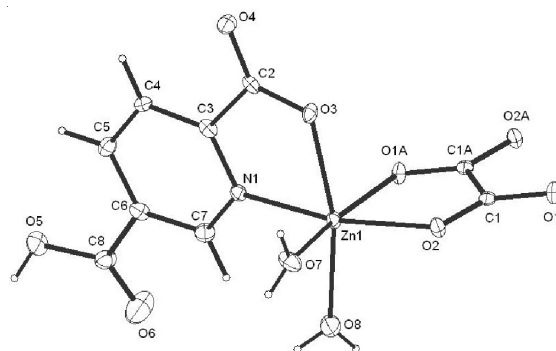


Fig. 1. Building unit of zinc(II) complex with the labeling scheme (50% probability)

while the carboxyl oxygen atom O(5) is protonated. Each oxalate anion serves as a tetradentate ligand, chelating and bridging two Zn atoms into dimer with the Zn...Zn distance of 5.4997(4) Å (Fig. 2). Strong hydrogen-bonding interactions are observed between the dinuclear unit through carboxyl oxygen, oxalate oxygen and the coordinate water molecules (Table-2). As a consequence, the equivalent dinuclear units are connected into a three dimensional supramolecular network through comprehensive hydrogen bonding and π - π stacking interactions (Fig. 3).

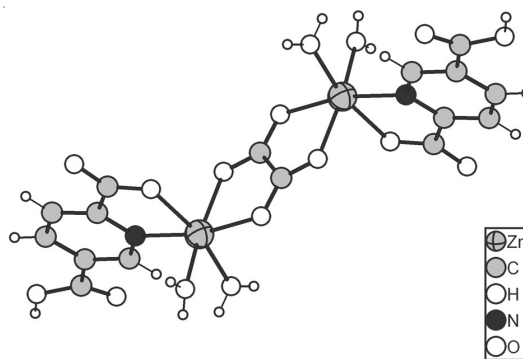


Fig. 2. Dimer unit structure of zinc(II) complex

TABLE-2
HYDROGEN BOND DISTANCES AND [Å] AND ANGLES [°]

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O(5)-H(5A)...O(3B)	0.98(4)	1.63(4)	2.604(3)	174(3)
O(5)-H(5A)...O(4B)	0.98(4)	2.63(4)	3.202(3)	118(3)
O(7)-H(7A)...O(1C)	0.72(4)	2.19(4)	2.901(3)	169(4)
O(7)-H(7B)...O(4D)	0.74(4)	2.13(4)	2.820(3)	157(4)
O(8)-H(8A)...O(2C)	0.79(4)	2.08(4)	2.856(3)	166(4)
O(8)-H(8B)...O(4E)	0.79(4)	2.06(4)	2.808(3)	158(4)

Symmetry codes: B $x, y+1, z$ C $-x+1/2, y+1/2, -z+3/2$ D $-x, -y, -z+2$ E $x+1/2, -y+1/2, z-1/2$.

Conclusion

A novel zinc(II) complex with 3D-supramolecular structure has been synthesized and characterized by IR, elemental analysis and X-ray diffraction analysis.

Supplementary material

Crystallographic data for the structure reported in this communication have been deposited with the Cambridge Crystallographic Data Center as supplementary publication No. CCDC 862056.

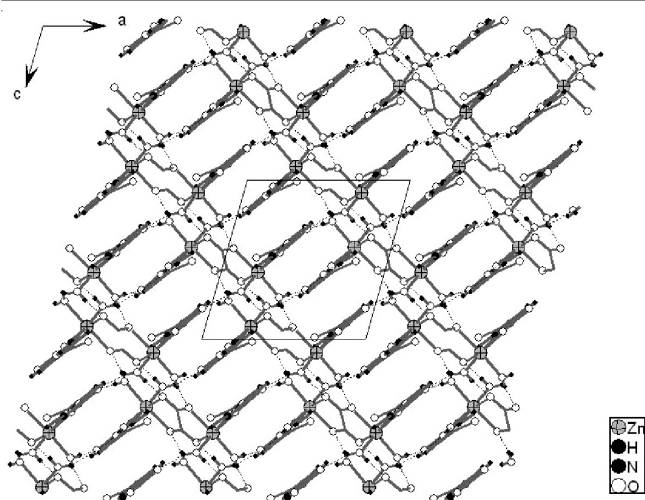


Fig. 3. Packing diagram of zinc(II) complex along the b-axis

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