



Synthesis, Crystal Structure and Luminescence Property of New Binuclear Zn²⁺ Complex

Y.Z. ZHANG¹, Z.W. YUAN^{1,*} and YU'E QIU^{2,3}

¹School of Chemistry and Pharmaceutical Engineering, Qilu University of Technology, Jinan 250353, P.R. China

²Key Laboratory of Coordination Chemistry and Functional Materials in Universities of Shandong, Dezhou University, Dezhou 253023, P.R. China

³Department of Chemistry, Dezhou University, Dezhou 253023, P.R. China

*Corresponding author: E-mail: yuanzaiwu@163.com; zhangyongzheng23@163.com

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A new zinc(II) complex, [Zn₂(L)₂·2H₂O (**1**) [L = 6-(4-pyridyl)isophthalic acid], was synthesized by hydrothermal reaction and characterized by single crystal X-ray diffraction elemental analyses and IR. The single crystal X-ray diffraction analyses reveals that the complex **1** was bridged by L ligands to form a 2-D supramolecular structures.

Keywords: Zinc(II) complex, Luminescence, 6-(4-Pyridyl)isophthalic acid, Crystal structure.

INTRODUCTION

Design and synthesis of coordination polymers constructed with transition metals and organic ligands have attracted intense attention owing to the diverse topologies and potential applications in luminescence property and magnetism¹⁻³. Recently, many metal-organic complexes with novel structures were successfully prepared by the selection of carboxylates and N-containing ligands due to their various coordination modes and structural features⁴⁻⁶. Herein, we report on the synthesis and crystal structures of one new complex, [Zn₂(L)₂·2H₂O.

EXPERIMENTAL

All the starting materials used in this work were commercially purchased and used without further purification. The elemental analyses for C, H and N were performed on an Elementar Vario Micro Cube analyzer. The IR spectra was recorded on a Thermo Nicolet IR200 FT-IR spectrometer as KBr pellets (4000-400 cm⁻¹).

Synthesis of [Zn₂(L)₂·2H₂O: A mixture of Zn(NO₃)₂·6H₂O (0.0594 g, 0.2 mmol), 6-(4-pyridyl)isophthalic acid (L) (0.0243 g, 0.1 mmol), NaOH (0.004 g, 0.1 mmol), 1,4-diazabicyclo[2.2.2]octane (DBO) (0.0112 g, 0.1 mmol) and distilled water (5 mL) was heated to 160 °C for 72 h in a 25 mL stainless steel reactor with a Teflon liner, followed by slow cooling to room temperature. The resulting reaction products were colorless block crystals that were washed with distilled water to give pure samples (Yield: 52 % based on Zn ion). Elemental anal. calcd. (%) for C₂₆H₁₈N₂O₁₀Zn₂: C, 48.06; H,

2.77; N, 4.31. Found: C, 49.62; H, 2.68; N, 4.25. Main IR frequencies (KBr, ν_{max}, cm⁻¹): 3442, 1616, 1562, 1431, 1381, 1343, 1129, 785, 768, 564, 475.

Crystal structure determination: Diffraction intensity data of the single crystals of complex **1** was collected on a Bruker SMART APEXII CCD diffractometer equipped with a graphite monochromated MoK_α radiation (λ = 0.71073 Å) by using a ω-scan mode. Empirical absorption correction was applied using the SADABS programs⁷. All the structures were solved by direct methods and refined by full-matrix least-squares methods on F² using the program SHELX 97⁸. The single suite WINGX was used as an integrated system for all the crystallographic programs⁹. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were located by geometrically calculations and their positions and thermal parameters were fixed during the structure refinement. The crystallographic data are summarized in Table-1. The data of relevant bond lengths and angles are listed in Table-2. CCDC (940144).

RESULTS AND DISCUSSION

Structure determination shows that complex crystallized in the triclinic, space group P-1. 6-(4-Pyridyl)isophthalic acid (L) is a tridentate ligand with one N-atom and two carboxyl groups. There are two independent Zn(II) ions (Zn1 and Zn2), two L ligands and two coordinated water molecules in the asymmetric unit. The selected molecular geometry parameters are listed in Table-2 and hydrogen bond geometry are listed in Table-3. The molecular structure of complex is depicted in Fig. 1.

TABLE-1
CRYSTAL DATA AND STRUCTURE
REFINEMENTS FOR COMPLEX 1

Empirical formula	C ₂₆ H ₁₈ N ₂ O ₁₀ Zn ₂
Formula weight	649.16
Crystal system	Triclinic
Space group	P -1
Unit cell dimensions (Å)	
a	10.0369(10)
b	11.3213(11)
c	11.3958(11)
α	105.6140(10)
β	95.9930(10)
γ	108.2340(10)
Volume (Å ³), Z	1159.0 (2), 2
Calcd. density (Mg m ⁻³)	1.860
Absorption coefficient (mm ⁻¹)	2.139
Crystal size (mm)	0.37 × 0.26 × 0.18
F(000)	656
θ range for data collection (°)	1.90 -27.58
Data/restraints/parameters	5142/0/363
Goodness-of-fit on F ²	0.993
Final R ² indices	R1 = 0.0338
[I > 2σ(I)]	wR2 = 0.0710
R indices (all data)	R1 = 0.0490; wR2 = 0.0771
R = Σ(F _o - F _c) / Σ F _o , wR = {Σw[(F _o ² - F _c ²) ²] / Σw[(F _o ²) ²]} ^{1/2}	

TABLE-2
SELECTED BOND LENGTHS (Å)
AND ANGLES (°) FOR COMPLEX 1

Zn(1)-O(1W)	2.091(2)	O(1W)-Zn(1)-O(5)	168.44(8)
Zn(1)-N(2)	2.107(2)	N(2)-Zn(1)-O(5)	88.04(8)
Zn(1)-N(1C)#1	2.116(2)	N(1C)#1-Zn(1)-O(5)	86.68(8)
Zn(1)-O(3D)#2	2.1237(18)	O(3D)#2-Zn(1)-O(5)	100.83(7)
Zn(1)-O(5)	2.1404(19)	O(1W)-Zn(1)-O(2W)	81.37(9)
Zn(1)-O(2W)	2.286(2)	N(2)-Zn(1)-O(2W)	85.54(9)
Zn(2)-O(7)	1.934(2)	N(1C)#1-Zn(1)-O(2W)	88.52(9)
Zn(2)-O(2A)#3	1.935(2)	O(3D)#2-Zn(1)-O(2W)	171.27(8)
Zn(2)-O(6B)#4	1.9613(19)	O(5)-Zn(1)-O(2W)	87.85(8)
Zn(2)-O(4)	2.000(2)	O(7)-Zn(2)-O(2)#3	130.04(9)
O(1W)-Zn(1)-N(2)	95.21(9)	O(7)-Zn(2)-O(6B)#4	105.46(9)
O(1W)-Zn(1)-N(1C)#1	88.89(9)	O(2)#3-Zn(2)-O(6B)#4	106.71(9)
N(2)-Zn(1)-N(1C)#1	172.19(9)	O(7)-Zn(2)-O(4)	99.95(8)
O(1W)-Zn(1)-O(3D)#2	89.91(8)	O(2)#3-Zn(2)-O(4)	104.37(9)
N(2)-Zn(1)-O(3D)#2	95.63(8)	O(6B)#4-Zn(2)-O(4)	109.02(8)
N(1)#1-Zn(1)-O(3D)#2	91.01(8)		
Symmetry transformations used to generate equivalent atoms: #1 -x,-y,-z+1 #2 -x+1,-y+1,-z+2 #3 -x+1,-y+2,-z+3 #4 -x,-y+1,-z+2			

TABLE-3
HYDROGEN BOND LENGTHS (Å) AND
BOND ANGLES (°) FOR COMPLEX 1

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O(1W)-H(1WA)...O(4)#1	0.85	2.53	2.966(3)	113.0
O(1W)-H(1WA)...O(8)#1	0.85	2.42	3.212(3)	154.8
O(1W)-H(1WB)...O(8)#2	0.85	2.18	2.739(3)	122.7
O(1W)-H(1WB)...O(1)#3	0.85	2.45	3.078(3)	131.3
O(2W)-H(2WA)...O(7)#2	0.86	2.47	3.092(3)	129.6
O(2W)-H(2WB)...O(1)#3	0.86	1.99	2.843(4)	170.3
Symmetry transformations used to generate equivalent atoms: #1 -x+1,-y+1,-z+2 #2 x,y,z-1 #3 -x+1,-y+2,-z+2				

The Zn1(II) atom is six-coordinated by two oxygen atoms (O3D and O5) of the carboxyl groups from two L ligands, two nitrogen atoms (N1C and N2) from two L ligands and two coordinated water molecules in a distorted octahedral geometry,

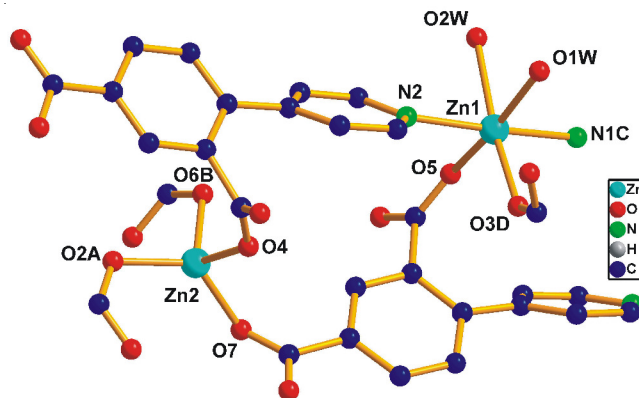


Fig. 1. Coordination environment of Zn(II) atom in complex 1. Hydrogen atoms have been omitted for clarity

while Zn2(II) ion is surrounded by four oxygen atoms (O4, O7, O2A and O6B) of four carboxyl groups from four L ligands. The Zn-M (M = O, N) distances are shown in Table-2. The Zn-O bond distances are in the range of 1.934(2) Å to 2.1404(18) Å. The Zn-N bond distances are 2.107(2) Å and 2.116(2) Å, respectively. The bond angles between the donor atoms around the Zn(II) center range from 81.37(9)° to 172.19(9)°. The carboxylic groups and N atoms of L ligand adopt monodentate bridging mode which lead to a dinuclear Zn(II) unit. The Zn(II) metal centers are connected to each other by L ligands into a 2D supramolecular structures¹⁰ (Fig. 2).

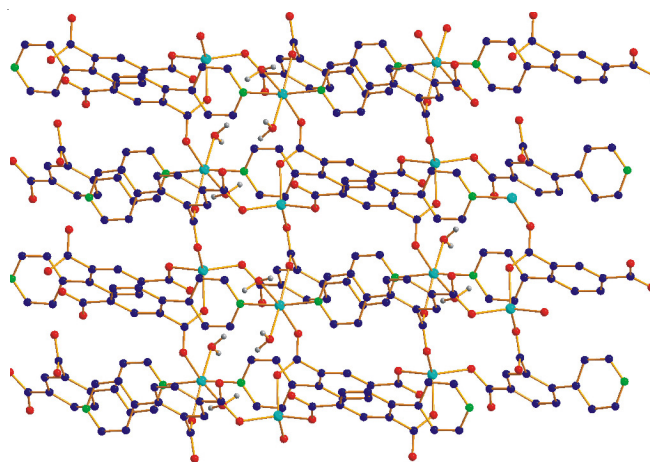


Fig. 2. Packing diagram of the complex 1 with wires or sticks. Hydrogen atoms have been omitted for clarity

Analysis of the crystal packing of complex 1 reveals the existence of multiple intermolecular O-H...O hydrogen bonds in 2D supramolecular structures between the O-H groups from coordinated water molecules and uncoordinated O-atoms from L ligands (Fig. 3), which results in the forming a latticed structure. The hydrogen bond lengths and bond angles are listed in Table-3.

Photoluminescent property: Luminescent property of complex 1 and 6-(4-pyridyl)isophthalic acid (L) were investigated in the solid state at room temperature and the emission spectra is depicted in Fig. 4. Excitation at 290 nm, the peak maxima occurs at 376 nm for complex 1. The fluorescence

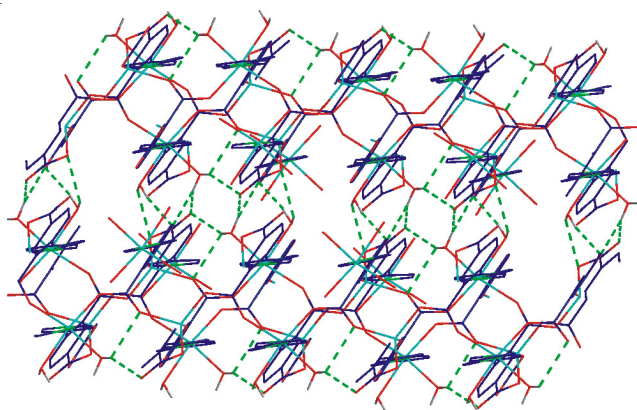


Fig. 3. 2-D supramolecular structure of complex **1** showing hydrogen bond interactions (green dashed line involving L and water molecules)

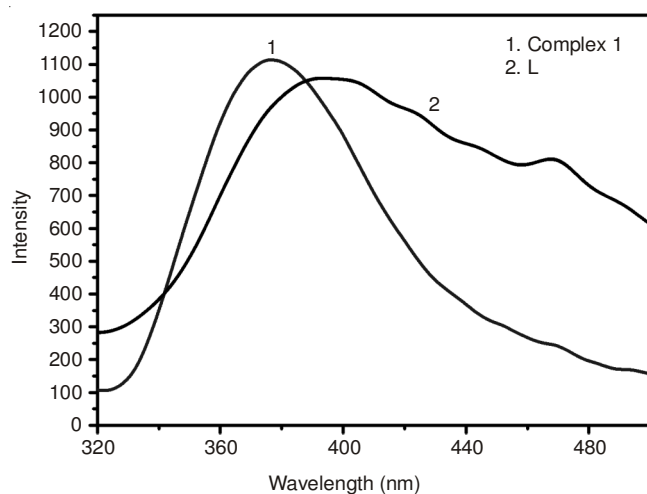


Fig. 4. Solid-state photoluminescent spectra of complex **1** and L at room temperature

spectrum of L has also been measured, showing an emission band at 392 with excitation at 270 nm. Complex **1** shows a 16 nm blue-shift compared to 6-(4-pyridyl) isophthalic acid (L).

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