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Synthesis, Crystal Structure and DNA-Binding of a Novel Zinc(II) Complex with 2-(2-(1*H*-Benzo[d]imidazol-2-yl)phenoxy)acetic Acid

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A novel complex of $[Zn(L)_2]$ (**1**) [HL = 2-(2-(1*H*-benzo[d]imidazol-2-yl)phenoxy)acetic acid] was synthesized and characterized by elemental analysis, IR and TG-DTG. Its crystal structure was determined by single crystal X-ray diffraction method. The complex crystallizes in orthorhombic with space group Pccn, cell parameters: a = 2.2030(2) nm, b = 0.70727(6) nm, c = 1.68856(1) nm, β = 90º, cell volume: V = 2.6310(4) nm^3, number of molecules inside the cell: Z = 4, relative molecular mass: M_r = 599.89. The crystal structure shows that the zinc(II) ion is coordination with two oxygen atoms and two nitrogen atoms from two 2-(2-(1*H*-benzo[d]imidazol-2-yl)phenoxy) acetic acids, forming a distorted capped tetrahedron coordination geometry. In addition, the interaction of complex with DNA was also studied by ethidium bromide fluorescence spectroscopy. CCDC: 901910.

Key Words: Zinc(II) complex, 2-(2-(1*H*-Benzo[d]imidazol-2-yl)phenoxy)acetic acid, Crystal structure, DNA.

INTRODUCTION

The rational design of coordination architectures based on multidentate organic ligands has attracted considerable attention, owing to the anticipations not only for novel topologies and fascinating structures, but also for new potential functional materials[1-7], *e.g.*, optical, electrical, magnetic, catalytic and microporous materials.

Transition metal coordination compounds containing benzimidazolic ligands have drawn attention from several research groups, since benzimidazoles display important properties that span from luminescence to biocidal activities[8-10]. The Zn(II) and Cd(II) complexes[11] with the ligand of pyridine-3,5-*bis*(benzimidazole-2-yl) show activity aganist bacteria (*E. coli*, *S. aureus* and *B. subtilis*) and mould (*G. cingulata*, *M. fructicola*, *A. solani*). Pd(II) and Pt(II) compouds[12] of (1*H*-benzimidazol-2-ylmethyl)-(4-methoxyl-phenyl)amine are active aganist gram-positive bacteria and gram-negative bacteria. While the Cr(III) benzimidazolic complex shows good activites in the binding and the cleavage DNA[13]. 2-(2-(1*H*-Benzo[d]imidazol-2-yl)phenoxy)acetic acid (HL) is an important benzimidazole-derivated N,O-donor ligand. In this paper, we report the synthesis, characterization, crystal structure and DNA binding property of a novel Zn(II) complex with 2-(2-(1*H*-benzo[d]imidazol-2-yl)phenoxy)acetic acid (HL).

EXPERIMENTAL

All reagents and solvents employed in the present work were of analytical grade as obtained from commercial sources without further purification. HL was prepared using similar method with slight modification based on literature[14]. Elemental analyses were carried out on Elementar Vario EL III elemental analyzer. The FTIR spectra were obtained from KBr pellets in the range 4000-400 cm^{-1} with a Nicolet NEXUS 670 FTIR spectrometer. Diffraction data were collected at 296(2) K on Bruker APEXII CCD diffractometer with graphite monochromated MoK_α radiation (λ = 0.071073 nm). A Mettler Toledo thermal analyzer TGA/SDTA 851^e was used to carry out the thermoanalytical analysis with a heating rate of 10 ºC min^{-1} from 30-800 ºC in air atomsphere. Fluorescent spectrum were recorded at room temperature on an Edinburgh FL920 phosphorimeter.

Synthesis of complex: A mixture of HL (0.0857g, 0.2 mmol), $Zn(NO_3)_2{\cdot}6H_2O$ (0.0271 g, 0.1 mmol), NaOH (0.008 g, 0.2 mmol), 5 mL of ethanol and 10 mL of water was sealed in a 25 mL Teflon-lined stainless steel vessel and heated at 140 ºC for 3 days. After the mixture was slowly cooled to room temperature, colourless crystals of the complex were obtained in 38 % yield based on $Zn(NO_3)_2{\cdot}6H_2O$. Anal. calcd. (%) for $C_{30}H_{22}N_4O_6Zn$: C, 60.01, H, 3.33, N, 9.33. Found (%): C, 59.94, H, 3.36, N, 9.31. IR (KBr, ν_{max}, cm^{-1}): 3444.4(w), 3056.6(w), 2923.4(w), 1562.3(m), 1514.4(s), 1381.7(m), 848.3(w), 726.2(m).

Crystal structure determination: A single-crystal of the title complex with dimentions of 0.051 mm × 0.047 mm × 0.032 mm was selected and mounted on a glass fiber and collected diffraction data on a Bruker Smart APEX II CCD diffractometer with graphite monochromated MoK_α radiation (λ = 0.071073 nm). Data intendity was corrected by Lorenta-polarization factors ans empirical absorption. The structure was solved with direct methods and expanded with difference Fourier techniques. Except the hydrogen atoms were generated geometrically. All calculations were performed using SHELXS-97[15] and SHELXL-97[16] program package. The crystallographic data and structural determination parameters are summarized in Table-1 and the selected bond lengths and the bond angles are listed in Table-2. CCDC No. 901910 of 1 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre.

TABLE-1
CRYSTALLOGRAPHIC DATA FOR **1**

Formula	$C_{30}H_{22}N_4O_6Zn$
Formula weight	599.89
Temperature (K)	296(2)
Wavelength (nm)	0.071073
Crystal system,	Orthorhombic
Space group	Pccn
a (nm)	2.2030(2)
b (nm)	0.70727(6)
c (nm)	1.68856(1)
β (°)	90
Volume (nm^3)	2.6310(4)
Z	4
Calculated density (g/cm^3)	1.514
Absorption coefficient (mm^{-1})	0.987
$F_{(000)}$	1232
Crystal size (mm)	0.051 × 0.047 × 0.032
$R_{(int)}$	0.0812
Completeness (%)	99.3
Goodness-of-fit on F^2	0.98
Final R indices [I>2σ(I)]	R_1 = 0.0482, wR_2 = 0.1022
R indices (all data)	R_1 = 0.1046,wR_2 = 0.1251

TABLE- 2
SELECTED BOND LENGTHS (nm) AND ANGLES (°)

Bond	Dist.	Bond	Dist.
Zn(1)-O(2)#1	0.1980(2)	Zn(1)-N(2)	0.2037(3)
Zn(1)-O(2)	0.1980(2)	Zn(1)-N(2)#1	0.2037(3)
Angle	(°)	Angle	(°)
O(2)#1-Zn(1)-O(2)	85.99(13)	O(2)#1-Zn(1)-N(2)	111.87(11)
O(2)-Zn(1)-N(2)	122.95(10)	O(2)#1-Zn(1)-N(2)#1	122.95(10)
O(2)-Zn(1)-N(2)#1	111.87(11)	N(2)-Zn(1)-N(2)#1	102.43(15)

Symmetry code: #1 -x+1/2, -y+1/2, z.

RESULTS AND DISCUSSION

Structural description: A single-crystal X-ray diffraction study reveals that the title complex crystallizes in orthorhombic system with Pccn space group. As shown in Fig. 1, the asymmetric unit of **1** composed of one Zn center and two L^- anions. The Zn center is four-coordinated to form a distorted capped tetrahedron coordination geometry by O2, O2A, N2, N2A from two distinct L^- ligands. The Zn-O bond length is

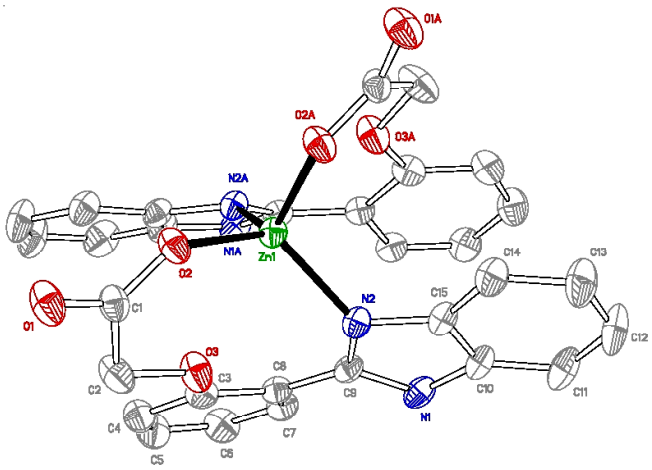

Fig. 1. View of the coordination environment of the Zn center in **1**

0.1980(2) nm and the Zn-N bond length is 0.2037(3) nm, all in the reasonable range[17,18]. The L^- ligand employs a twisted conformation and the dihedral angle between phenyl ring and the benzimidazole ring is 25.4°, the O1, O2, C1, C2, O3 atoms are in the same plane, with dihedral angle of 41.9° between the phenyl ring, respectively. The bonding carboxylate groups of the L^- ligand adopting monodentate coordination mode and one of N atoms is coordinated to the Zn center.

Interestingly, as is shown in Fig. 2, along the bc plane, the asymmetric units of the complex give rise to a 2D layered structure with the interaction of hydrogen bonds (N(1)-H(1A)···O(1)#2, 0.2762(4) nm; C(7)-H(7A)···O2, 0.3332(4) nm) (Table-3).

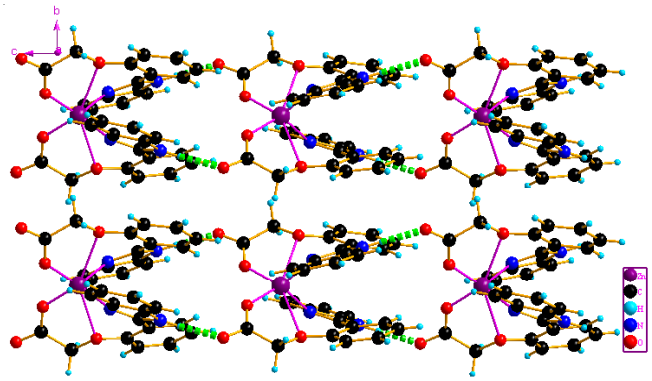

Fig. 2. 2D layered structure of **1** linked by the hydrogen bonds

TABLE-3
HYDROGEN BOND GEOMETRY FOR COMPLEX **1**

D-H···A	d(D-H) (nm)	d(H···A) (nm)	d(D···A) (nm)	∠(DHA) (°)
N(1)-H(1A)···O(1)#2	0.086	0.193	0.2762(4)	161.5
C(7)-H(7A)···O2	0.093	0.244	0.3332(4)	161.2

Symmetry code: #2 -x+1/2, y, z-1/2.

Thermogravimetric analysis: The TG-DTG curves of complex **1** is shown in Fig. 3. The first stage decomposition temperature is in the range of 120-340 °C, with a mass loss of 43.17 %, which corresponds to the elimination of one L^- ligand (calcd. 43.25 %). The second stage starts from 340-420 °C with a mass loss of 43.22 % which assigns to the removal of another L^- ligand, (calcd. 43.25 %). The final product is the

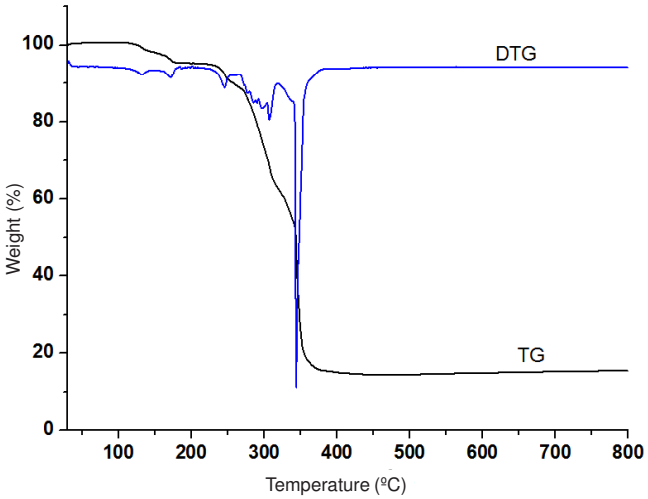

Fig. 3. TG-DTG of the complex **1**

metal oxide ZnO (13.61 %, calcd.13.50 %). The result is in good accordance with the composition of the complex.

Fluorescence quenching studies: The effects of the complex on the fluorescence spectra of ethidium bromide-DNA system are presented in Fig. 4, the fluorescence intensities of ethidium bromide bound to CT-DNA at 592 nm show remarkable decreasing trends with the increasing concentration of the complex, indicating that some ethidium bromide molecules are released into solution after the exchange with the complex which resulted in the fluorescence quenching of ethidium

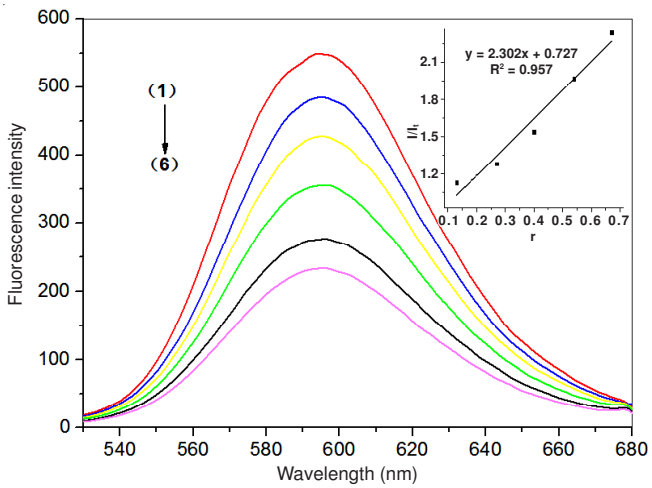

Fig. 4. Emission spectra of EB-DNA system in the absence and presence of the complex. λ_{ex} = 251 nm, $C_{EB} = 1.25 \times 10^{-7}$ mol L^{-1}, from (1-6): $r = C_{complex}/C_{DNA}$ = 0, 0.13, 0.27, 0.40, 0.54, 0.67, respectively

bromide. The quenching of ethidium bromide bound to DNA by the complex is in agreement with the linear Stern-Volmer equation: $I_0/I = 1 + K_{sq}r$[19], where I_0 and I represent the fluorescence intensities in the absence and presence of quencher, respectively. K_{sq} is a linear Stern-Volmer quenching constant, r is the ratio of the concentration of quencher and DNA. In the quenching plots (Fig. 4) of I_0/I *versus* r, K_{sq} values are given by the slopes. The K_{sq} value for the complex is 2.30. It indicating that interaction of the complex with DNA was strong and the complex may be used as a potential antitumor drug.

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