Crystal Structure, Fluorescence Property and Theoretical Calculation of the Zn(II) Complex with *o*-Aminobenzoic Acid and 1,10-Phenanthroline

Zhongyu Zhang, Caifeng Bi,[*] Yuhua Fan,[*] Xia Zhang, Nan Zhang, Xingchen Yan, and Jian Zuo

Key Laboratory of Marine Chemistry Theory and Technology, Ministry of Education, College of Chemistry and Chemical Engineering, Ocean University of China, Qingdao, Shandong 266100, China
[*]E-mail: bicaifeng301@163.com (C. Bi); fanyuhua301@163.com (Y. Fan)

A novel complex [Zn(phen)(*o*-AB)$_2$] [phen: 1,10-phenanthroline *o*-AB: *o*-aminobenzoic acid] was synthesized and characterized by elemental analysis and X-ray diffraction single-crystal analysis. The crystal crystallizes in monoclinic, space group P2(1)/c with a = 7.6397(6) Å, b = 16.8761(18) Å, c = 17.7713(19) Å, α = 90°, β = 98.9570(10)°, γ = 90°, V = 2.2633(4) nm^3, Z = 4, $F(000)$ = 1064, S = 1.058, Dc = 1.520 g·cm^{-3}, R_1 = 0.0412, wR_2 = 0.0948, μ = 1.128 mm^{-1}. The Zn(II) is six coordinated by two nitrogen and four oxygen atoms from the 1,10-phenanthroline and o-aminobenzoic acid to furnish a distorted octahedron geometry. The complex exhibits intense fluorescence at room temperature. Theoretical studies of the title complex were carried out by density functional theory (DFT) B3LYP method. CCDC: 898291.

Key Words : Zn(II) complex, Crystal structure, Fluorescence, Quantum chemistry calculation

Introduction

Zinc is an essential micronutrient and plays a diverse role in many biological processes by serving as a structural component of proteins, an essential cofactor in enzymes, and a modulator of signal transductioncascades within the cell.[1,2] Zinc was successfully used in the treatment of acodermatitis enteropathica, Wilson's disease, gastrointestinal disorders, infertility and other diseases.[3] Zinc complexes with drugs have also been used for treatment of Alzheimer disease or as antibacterial, anticonvulsant, antidiabetic, antimicrobial or antiproliferative – antitumor agents.[4-7] Our study stems from the value of the Zn(II) complexes containing carboxylate ligands. By far many Zn(II) carboxylate complexes have been reported.[8-10] but rare is related about the aminobenzoic acid. In the viewpoint of constructing functional compounds, the title complex was synthesized in anhydrous solvent and its crystal structure was determined. Based on crystal data, density functional theory (DFT) studies of the title complex were performed using the Gaussian 03 program suite. The natural atomic charges distribution, molecular total energy and frontier molecular orbital energies of the complex were discussed.

Experimental

Materials and Physical Measurement. All reagents used in this work were of analytical grade. Elemental analyses were carried out with a model 2400 Perkin-Elmer analyzer. The fluorescence spectra were recorded on an F-4500 fluorimeter. The X-ray diffraction data were collected on a Bruker Smart CCD X-raysingle-crystal diffractometer. Optimizations of geometrical structures and Natural Bond Orbital (NBO) analyses of the title complexes were carried out by DFT

B3LYP method. The 6-31+G* basis set was used for C, N and O atoms, while the Effective Core Potential (ECP) and valence double-ζ LANL2DZ basis set was used for Zn atom. Atom coordinates used in the calculations were from crystallographic data, and a molecule in the unit cells was selected as the initial model. All calculations were conducted on a Pentium IV computer using Gaussian 03 program.[11-13]

Preparation of the Single Crystals of Complexes. *o*-Aminobenzoic acid (0.274 g, 2.0 mmol) was dissolved in 50 mL of anhydrous methanol. Zn(OAc)$_2$·2H$_2$O (0.219 g, 1.0 mmol) dissolved in 30 mL of anhydrous methanol was added dropwise to the above *o*-aminobenzoic acid solution and stirred for 4 h at 55 °C. Then 1,10-phenanthroline (0.198 g, 1.0 mmol) was dissolved in 10 mL of anhydrous methanol was added dropwise to the above solution and stirred for 4 h at 55 °C cooled and filtered. The filtrate was left for slow evaporation at room temperature. The wine prismatic crystals were formed 15 days later. Anal.Calcd. (%) for C$_{26}$ H$_{20}$ N$_4$ O$_4$ Zn: C, 60.30; H, 3.89; N, 10.81. Found (%): C, 60.41; H, 3.78; N, 10.89.

Crystallographic Data Collection and Structure Determination. The wine single crystal with dimensions of 0.42 × 0.40 × 0.1 mm was mounted on a Bruker Smart CCD X-raysingle-crystal diffractometer. All data were collected at 298(2) K with a graphite- monochromated MoKα radiation (λ = 0.71073 Å) by using an ω-2θ scan mode. A total of 11053 reflections were collected in the range of $2.62 \leq \theta \leq 25.02$ ($-8 \leq h \leq 9$, $-11 \leq k \leq 20$, $-20 \leq l \leq 21$), in which 3968 were independent with R_{int} = 0.0454, of which 2856 with $I > 2\sigma(I)$ were considered to be observed and used in the subsequent refinements. The structure was solved by direct methods using SHELXS-97.[14] The non-hydrogen atoms were defined with Fourier synthesis method.

Positional and thermal parameters were refined by full-

Table 1. Crystallographic data and structure refinement for complex

Empirical formula	$C_{26}H_{20}N_4O_4Zn$	Absorption coefficient (mm^{-1})	1.128
Formula weight	517.83	$F(000)$	1064
Temperature (K)	298 (2)	Crystal size (mm)	$0.42 \times 0.40 \times 0.31$
Wavelength (Å)	0.71073	θ range for data collection ($^\circ$)	2.62 to 25.02
Crystal system	Monoclinic	Limiting indices	$-8 \leq h \leq 9$
Space group	P2(1)/c		$-11 \leq k \leq 20$
a (Å)	7.6397(6)		$-20 \leq l \leq 21$
b (Å)	16.8761(18)	Reflections collected / unique	11053/ 3968 [$R_{int} = 0.0454$]
c (Å)	17.7713(19)	Completeness to $\theta = 25.01$	99.8
α ($^\circ$)	90	Max. and min. transmission	0.7213and 0.6488
β ($^\circ$)	98.9570(10)	Data / restraints / parameters	3968 / 0 / 316
γ ($^\circ$)	90	Goodness of fit on F^2	1.058
Volume, Å^3	2263.3(4)	Final R indices [$I > 2$sigma(I)]	$R_1 = 0.0412$, $wR_2 = 0.0948$
Z	4	R indices (all data)	$R_1 = 0.0670$, $wR_2 = 0.1067$
Calculated density (g/cm^3)	1.520	Largest diff. peak and hole (e. Å^3)	0.256 and -0.513

matrix least-squares method to convergence. The final cycle of refinement gave $R = 0.0412$, $wR = 0.0948$ [$I > 2(I)$] and $R_1 = 0.0670$, $wR_2 = 0.1067$ (total reflections) ($w = 1/[\sigma^2(F_o^2) + (0.0443P)^2 + 0.8358P]$, where $P = (F_o^2 + 2F_c^2)/3$). $S = 1.058$, $(\Delta\rho)_{max} = 0.256$, $(\Delta\rho)_{min} = -0.513$ e/Å^3 and $(\Delta/\sigma)_{max} = 0.000$. A summary of the key crystallographic information is given in Table 1.

Results and Discussion

Description of Crystal Structure. Non-hydrogen fractional atomic coordinates and equivalent isotropic displacement parameters, selected bond lengths and bond angles, hydrogen bond distances of the complex are listed in Tables 2, 3, and 4, respectively. Crystal structure and packing drawing of the title complex are depicted in Figures 1 and 2, respectively.

As shown in Figure 1, the complex is a neutral complex. In complex, Zn(II) is located in a very distorted octahedron coordination with six bonds to two N atoms from 1,10-phenanthroline and four carboxylate O atoms from two *o*-aminobenzoic acid molecules. There are two four-membered chelate rings (Ring 1: Zn(1)–O(1)–C(1)–O(2) Ring 2: Zn(1)–O(3)–C(8)–O(4)) and one five-membered chelate ring (Ring 3: Zn(1)–N(3)–C(19)–C(20)–N(4)). As shown in Table 1, the N(4)–Zn(1)–O(2), N(3)–Zn(1)–O(4) and O(1)–Zn(1)–O(3) bond angles deviate from 180°, indicating that Zn(II) is not coplanar with any of four coordinated atoms. Thus they can not form the plane quadrilateral in perfect octahedron.

As shown in Figure 2 and Table 4, complex forms an intermolecular hydrogen bonds N(1)–H(1A)···O(4) between the exocyclic amine group and the oxygen atom of the acetate group. The molecules are linked into extended chains parallel to the a axis and the *c* axis through the intermolecular hydrogen bond. A three-dimensional network is assembled through van der Waals' forces and intermolecular π–π interactions.[15,16]

As shown in Table 2, the cationic unit and anionic unit are

Table 2. Selected bond lengths (Å) of the complex obtained from experiment and calculations

Bond length	Exp.	Calcd.	Bond length	Exp.	Calcd.
Zn(1)–O(3)	1.981(2)	2.138	C(5)–C(6)	1.381(5)	1.403
Zn(1)–O(1)	2.051(2)	2.139	C(6)–C(7)	1.378(5)	1.389
Zn(1)–N(4)	2.107(3)	2.255	C(8)–C(9)	1.492(5)	1.485
Zn(1)–N(3)	2.112(3)	2.256	C(9)–C(14)	1.397(5)	1.407
Zn(1)–O(2)	2.277(2)	2.181	C(9)–C(10)	1.404(5)	1.424
Zn(1)–O(4)	2.560(3)	2.181	C(10)–C(11)	1.407(6)	1.414
N(1)–C(3)	1.379(4)	1.380	C(11)–C(12)	1.360(7)	1.388
N(2)–C(10)	1.357(6)	1.380	C(12)–C(13)	1.377(7)	1.403
N(3)–C(15)	1.328(4)	1.326	C(13)–C(14)	1.365(6)	1.389
N(3)–C(19)	1.362(4)	1.354	C(15)–C(16)	1.389(5)	1.410
N(4)–C(24)	1.319(4)	1.326	C(16)–C(17)	1.358(5)	1.382
N(4)–C(20)	1.360(4)	1.354	C(17)–C(18)	1.399(5)	1.414
O(1)–C(1)	1.265(4)	1.274	C(18)–C(19)	1.406(5)	1.417
O(2)–C(1)	1.253(4)	1.286	C(18)–C(25)	1.432(5)	1.437
O(3)–C(8)	1.263(4)	1.275	C(19)–C(20)	1.428(4)	1.447
O(4)–C(8)	1.260(4)	1.286	C(20)–C(21)	1.407(4)	1.417
C(1)–C(2)	1.481(4)	1.485	C(21)–C(22)	1.406(5)	1.414
C(2)–C(7)	1.401(4)	1.407	C(21)–C(26)	1.437(5)	1.437
C(2)–C(3)	1.413(4)	1.424	C(22)–C(23)	1.351(6)	1.382
C(3)–C(4)	1.400(5)	1.414	C(23)–C(24)	1.404(5)	1.410
C(4)–C(5)	1.374(5)	1.388	C(25)–C(26)	1.333(5)	1.364

linked *via* weak Zn(1)–O(4) bond, and Zn(1)–O(4) distance of 2.560 Å is longer than those of other Zn−O bonds (1.981–2.277 Å), but shorter than the sum of the van der Waals radii (2.91 Å).[17-19] The relative space positions of two *o*-aminobenzoic acid liands are different. This can be attributed to the effect of steric hindrance. And due to the steric hindrance of amino of *o*-aminobenzoic acid, the molecule of *o*-aminobenzoic acid molecule rotated to a certain angle in the molecular plane. The distances of Zn(1)–O(1) bond and Zn(1)–O(2) bond are different, and also the distances of Zn(1)–O(3) bond and Zn(1)–O(4) bond are different. Zn(1)–O(3) distance of 1.981(2) Å is shorter than Zn(1)−O(1) bonds (2.051 Å), and the distance between C(8)

Table 3. Selected bond angles (°) of the complex obtained from experiment and calculations

Bond angle	Exp.	Calcd.	Bond angle	Exp.	Calcd.
O(3)–Zn(1)–O(1)	140.61(10)	158.8	C(7)–(C6)–C(5)	118.5(3)	118.7
O(3)–Zn(1)–N(4)	110.17(10)	99.1	C(6)–C(7)–C(2)	122.4(3)	121.9
O(1)–Zn(1)–N(4)	99.82(10)	97.7	O(4)–C(8)–O(3)	120.4(3)	118.9
O(3)–Zn(1)–N(3)	103.09(10)	98.1	O(4)–C(8)–C(9)	121.7(3)	120.8
O(1)–Zn(1)–N(3)	107.36(10)	98.6	O(3)–C(8)–C(9)	118.0(3)	120.2
N(4)–Zn(1)–N(3)	78.91(11)	74.0	C(14)–C(9)–C(10)	119.7(4)	119.2
O(3)–Zn(1)–O(2)	92.28(9)	105.7	C(14)–C(9)–C(8)	117.8(3)	118.1
O(1)–Zn(1)–O(2)	59.88(9)	61.4	C(10)–C(9)–C(8)	122.5(4)	122.6
N(4)–Zn(1)–O(2)	157.54(10)	152.5	N(2)–C(10)–C(9)	122.7(4)	122.2
N(3)–Zn(1)–O(2)	97.22(10)	90.7	N(2)–C(10)–C(11)	119.4(4)	119.4
O(3)–Zn(1)–O(4)	55.90(9)	61.4	C(9)–C(10)–C(11)	117.9(5)	118.1
O(1)–Zn(1)–O(4)	99.59(10)	105.7	C(12)–C(11)–C(10)	120.4(5)	121.3
N(4)–Zn(1)–O(4)	91.59(10)	90.8	C(11)–C(12)–C(13)	122.1(5)	120.6
N(3)–Zn(1)–O(4)	152.54(10)	152.8	C(14)–C(13)–C(12)	118.6(5)	118.7
O(2)–Zn(1)–O(4)	100.82(10)	111.1	C(13)–C(14)–C(9)	121.4(4)	121.9
C(15)–N(3)–C(19)	118.0(3)	119.3	N(3)–C(15)–C(16)	122.8(4)	122.4
C(15)–N(3)–Zn(1)	129.0(2)	125.6	C(17)–C(16)–C(15)	119.7(4)	118.9
C(19)–N(3)–Zn(1)	113.1(2)	115.0	C(16)–C(17)–C(18)	119.6(4)	119.6
C(24)–N(4)–C(20)	118.1(3)	119.3	C(17)–C(18)–C(19)	117.5(3)	117.1
C(24)–N(4)–Zn(1)	128.7(3)	125.6	C(17)–C(18)–C(25)	124.5(4)	123.4
C(20)–N(4)–Zn(1)	113.2(2)	115.0	C(19)–C(18)–C(25)	118.1(3)	119.3
C(1)–O(1)–Zn(1)	95.6(2)	90.8	N(3)–C(19)–C(18)	122.4(3)	122.4
C(1)–O(2)–Zn(1)	85.6(2)	88.7	N(3)–C(19)–C(20)	117.2(3)	117.9
C(8)–O(3)–Zn(1)	105.3(2)	90.9	C(18)–C(19)–C(20)	120.4(3)	119.5
C(8)–O(4)–Zn(1)	78.4(2)	88.7	N(4)–C(20)–C(21)	122.5(3)	122.4
O(2)–C(1)–O(1)	118.9(3)	118.9	N(4)–C(20)–C(19)	117.6(3)	117.9
O(2)–C(1)–C(2)	121.2(3)	120.8	C(21)–C(20)–C(19)	119.9(3)	119.5
O(1)–C(1)–C(2)	119.8(3)	120.2	C(22)–C(21)–C(20)	117.4(3)	117.1
C(7)–C(2)–C(3)	118.1(3)	119.2	C(22)–C(21)–C(26)	124.4(3)	123.4
C(7)–C(2)–C(1)	119.2(3)	118.1	C(20)–C(21)–C(26)	118.3(3)	119.3
C(3)–C(2)–C(1)	122.7(3)	122.6	C(23)–C(22)–C(21)	119.6(4)	119.6
N(1)–C(3)–C(4)	119.2(3)	119.4	C(22)–C(23)–C(24)	119.5(4)	118.9
N(1)–C(3)–C(2)	122.0(3)	122.2	N(4)–C(24)–C(23)	122.8(4)	122.4
C(4)–C(3)–C(2)	118.8(3)	118.1	C(26)–C(25)–C(18)	121.9(4)	121.0
C(5)–C(4)–C(3)	121.0(3)	121.3	C(25)–C(26)–C(21)	121.5(4)	121.0
C(4)–C(5)–C(6)	121.1(3)	120.6			

Table 4. Hydrogen-bond geometry of complex (**1**) (Å, °)

D–H⋯A	D–H	H⋯A	D⋯A	D–H⋯A
N(2)–H(2A)⋯O(4)	0.86	2.06	2.699 (5)	130.9
N(1)–H(1A)⋯O(4)^{iv}	0.86	2.43	3.249 (4)	160.4
N(1)–H(1B)⋯O(2)	0.86	2.05	2.682 (4)	130.0
C(24)–H(24)⋯C(4)^{i}	0.93	2.66	3.544 (5)	158.1
C(6)–H(6)⋯O(2)^{i}	0.93	2.43	3.328(5)	161.2
C(7)–H(7)⋯O(3)^{i}	0.93	2.69	3.430(4)	136.7
C(11)–H(11)⋯N(1)^{ii}	0.93	2.73	3.630(5)	163.0

Symmetry codes: (*i*) *x*, −*y*+3/2, *z*−1/2; (*ii*) *x*, −*y*+3/2, *z*+1/2; (*iii*) *x*+1, *y*, *z*; (*iv*) −*x*+1, *y*+1/2, −*z*+1/2.

and Zn(1) (2.615 Å) is longer than the distance between C(1) and Zn(1) (2.513 Å). So the measured bond length of Zn(1) −O(4) (2.560 Å) is much longer than other Zn−O bonds length.

Fluorescence Properties. The fluorescence spectra of the complex in methanol solution are shown in Figure 3. The fluorescence spectra for the title complex, *o*-aminobenzoic acid and 1,10-phenanthroline were measured upon the excitation at 334 nm. The intense fluorescence peaks of complex appear at near 400 nm and may be attributed to *o*-aminobenzoic acid. The fluorescence intensity of the complex is highly increased as compared with free 1,10-phenanthroline.[20] But it is lowly decreased as compared with free *o*-aminobenzoic acid. The fluorescence change phenomenon can be attributed to the classic photoinduced electron transfer (PET) mechanism.[21] When the amine groups of the host formed a complex with the metal, the excited electron state of the *o*-aminobenzoic acid was then transferred to the LUMO of Zn(II), which induced the fluorescence quench-
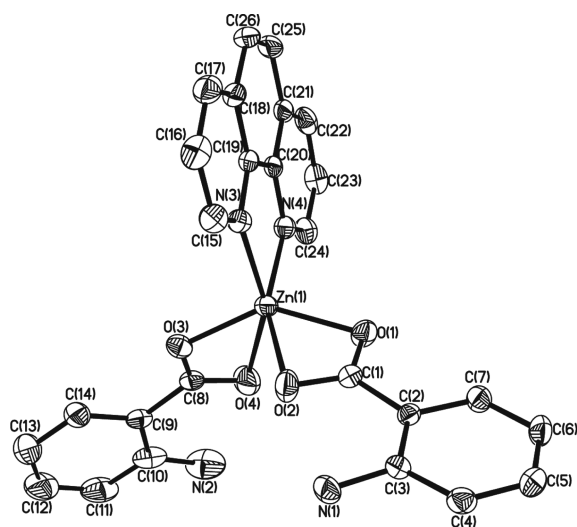
**Figure 1.** The structure of complex and the atom-numbering scheme.
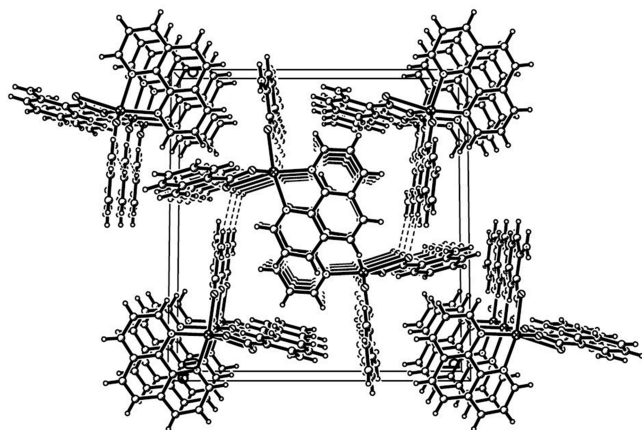
Figure 2. Packing diagram of the unit cell of complex viewed along a axis, hydrogen bonds are shown as dashed lines.

ing.

In the following functional study of the complex, however, the spectroscopic properties may be available as a suitable indicator reflecting the interaction with biological or chemical substances such as proteins, nucleic acids or other ligands in solution.

Quantum Chemistry Calculation. Comparison of important bond lengths of complex obtained from experiment and calculation is made in Table 2. Comparison of important bond angles of complex obtained from experiment and calculation is made in Table 3. The results indicate that some bond lengths and some angles data obtained from the calculations are agree with those gained from the determination. As shown in Table 2, the correspondent calculated bond lengths of the three ligands in complexes are nearly equal, although limited by the accuracy of the method, their experimental values are not equal.

The energies and components of molecular orbital are important characteristics in theoretical studies, which can predict the chemical properties. Some frontier molecular
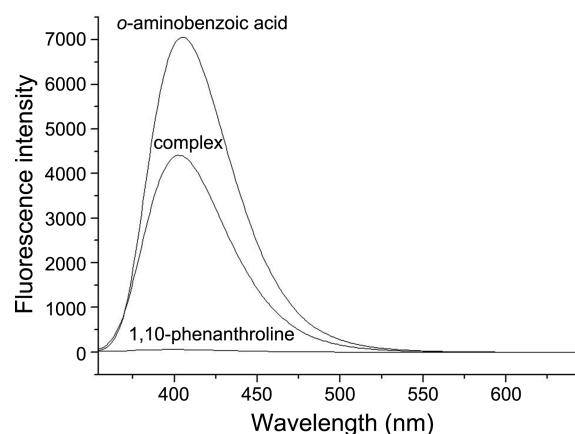
Figure 3. Fluorescence Spectra of Complexes, Free 1,10-phenanthroline and Free o-Aminobenzoic in theMethanol Solution. The concentration of each ligand andcomplex is 8.0×10^{-5} M. The excitation wavelength was 334 nm.

orbital energies and components of complexes are given in Table 5. View of the frontier molecular orbital of complex is shown in Figure 4. For the complex, the total energy is -1588.5466 a. u. The energies of HOMO, HOMO-1 and HOMO-2 orbital are -0.195, -0.196 and -0.242 a. u. respectively, the energies of LUMO, LUMO+1 and LUMO+2 orbital are -0.095, -0.092 and -0.049 a. u., respectively. The energy gap between HOMO and LUMO orbital is 0.100 a. u. The dipole moment is 7.8738 D. The energies of the molecular, HOMO, LUMO and their neighboring orbital are all negative, indicating that the complex is stable.[22-28]

The complex drug molecules or its conjugate ligands were intercalated or partially intercalated into the double helix of DNA, accompanied the π-π stacking interaction (weak interaction between the π tracks).[29,30] There are many factors which influence the interaction between complexes and DNA, including ligand planarity, plane area, the energies of LUMO and the frontier molecular orbital energy gap (ΔεL–H).[31,32] Japanese scholar Kurita used DFT method to calculate the DNA double helix model (CG/CG). Some frontier molecular orbital energy and track stereo image of the model are obtained. The energy of LUMO is 0.041 a. u., and the energies of HOMO and the occupied orbital are in the range of $-0.076 \sim -0.046$ a. u.. In this paper, the LUMO energy of the complex is -0.095 a. u.. The LUMO energy of complexes are much lower than the HOMO energy. This indicates that the complexes can accept electronics easily which are from DNA base pairs.

Geometrical structure of the complex is related to the distribution of natural atomic charge. Table 6 indicates part natural atomic charges of the complex. Natural atomic charge data show that all O and N atoms carry negative charges, the C atoms linking with O and N atoms carry positive charges, and the C atoms linking with H atoms carry negative charges. These negative charged O and N atoms are easy to coordinate with the positive charged metal ion. The charge of Zn(II) decreases from +2 to +1.693, which indicates that part of the electrons have transferred from N and O atoms to Zn

Crystal Structure of the Zn(II) Complex

Bull. Korean Chem. Soc. **2014**, Vol. 35, No. 6   1701

Table 5. Some frontier molecular orbital energies (a. u.) and components (%) of complexes

| Atom	HOMO-1	HOMO	LUMO	LUMO+1
Energy	−0.196	−0.195	−0.095	0.092
Zn1	0.20	0.17	11.61	0.34
N1	3.19	2.11	0.00	0.04
N2	3.04	2.21	0.00	0.04
N3	0.02	0.01	0.80	1.54
N4	0.02	0.01	0.79	1.55
O1	0.15	0.10	0.05	0.01
O2	0.06	0.06	0.14	0.02
O3	0.14	0.10	0.06	0.01
O4	0.06	0.06	0.14	0.02
C1	5.50	8.69	6.13	1.78
C2	13.16	5.92	5.75	3.25
C3	20.43	11.43	0.84	12.05
C4	2.94	1.85	0.36	4.17
C5	1.76	0.61	0.24	0.46
C6	1.76	1.33	3.17	1.58
C7	0.59	0.40	2.56	1.60
C8	5.00	9.15	6.27	1.75
C9	12.80	6.25	5.94	3.34
C10	19.73	12.15	0.83	11.94
C11	2.79	1.92	0.32	3.87
C12	1.69	0.65	0.23	0.47
C13	1.67	1.39	3.06	1.64
C14	0.56	0.42	2.46	1.66
C15	0.37	0.96	0.45	5.30
C16	0.64	2.32	3.48	0.41
C17	0.33	2.80	5.94	5.26
C18	0.01	1.16	1.50	3.16
C19	0.07	2.27	3.83	4.11
C20	0.05	2.38	4.12	4.11
C21	0.01	1.08	1.18	3.16
C22	0.29	2.75	5.47	5.22
C23	0.58	2.34	3.60	0.47
C24	0.31	0.95	0.49	5.34
C25	0.01	6.97	9.57	5.14
C26	0.00	6.95	8.61	5.19

(II) ion and the stable Zn(II)complex was formed.

Conclusion

The results presented here indicate a novel complex [Zn(phen)(*o*-AB)2] [phen: 1,10-phenanthroline *o*-AB: *o*-aminobenzoic acid] was synthesized and characterized by X-ray diffraction single-crystal analysis.

The Zn(II) is six coordinated by two nitrogen and four oxygen atoms from the 1,10-phenanthroline and *o*-amino-benzoic acid to furnish a distorted octahedron geometry.

The intense fluorescence peaks of complex appear at near 400 nm. But it is decreased as compared with free *o*-amino-benzoic acid. The fluorescence change phenomenon can be attributed to the classic photoinduced electron transfer (PET) mechanism.
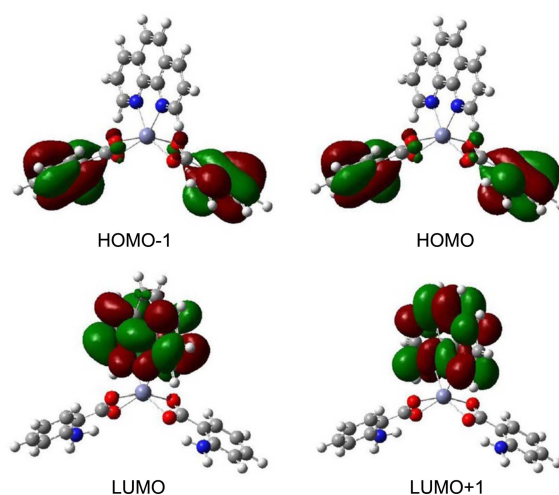
Figure 4. View of the frontier molecular orbital of complex.

Table 6. Part natural atomic charges and Mulliken Charges of the complex

Atom	Mulliken Charge	Nature Charge	Atom	Mulliken Charge	Nature Charge
Zn1	0.487	1.693	C10	−1.106	0.208
N1	−0.815	−0.850	C11	−0.172	−0.294
N2	−0.815	−0.850	C12	−0.558	−0.206
N3	−0.551	−0.551	C13	−0.105	−0.296
N4	−0.551	−0.551	C14	−0.432	−0.172
O1	−0.256	−0.817	C15	0.082	0.071
O2	−0.387	−0.840	C16	−0.530	−0.267
O3	−0.255	−0.817	C17	−0.218	−0.166
O4	−0.387	−0.840	C18	0.482	−0.100
C1	0.494	0.787	C19	−0.212	0.201
C2	1.290	−0.223	C20	−0.225	0.216
C3	−1.113	0.208	C21	0.473	−0.100
C4	−0.174	−0.294	C22	−0.214	−0.160
C5	−0.557	−0.206	C23	−0.526	−0.267
C6	−0.105	−0.296	C24	0.078	0.071
C7	−0.428	−0.172	C25	−0.419	−0.201
C8	0.512	0.781	C26	−0.426	−0.201
C9	1.181	−0.223			

1702   *Bull. Korean Chem. Soc.* **2014**, Vol. 35, No. 6

Zhongyu Zhang et al.

References

1. Murakami, M.; Hirano, T. *Cancer Sci.* **2008**, *99*, 1515-1522.
2. Erickson, J. C.; Hollopeter, G.; Thomas, S. A.; Froelick, G. J.; Palmite, R. D. *J. Neurosci.* **1997**, *17*, 1271-1281.
3. Cunnane S. C. CRC Press, Boc Raton, Florida. 1988.
4. Li, Z. Q.; Wu, F. J.; Gong, Y.; Hu, H. W.; Zhang, Y. H.; Gan, M. Y. *Chin. J. Chem.* **2007**, *25*, 1809-1814.
5. Zhou, Q. D.; Hambley, T. W.; Kennedy, B. J.; Lay, P. A.; Turner, P.; Warwick, B.; Biffin, J. R. *Inorg. Chem.* **2000**, *39*, 3742-3748.
6. Varia, M. D.; Bazzicalupi, C.; Orioli, P.; Messori, L.; Bruni, B.; Zatta, P. *Inorg. Chem.* **2004**, *43*, 3795-3797.
7. Chang, M. C. Y.; Pralle, A.; Isacoff, E. Y.; Chang, C. J. *J. Am. Chem. Soc.* **2004**, *126*, 15392-15393.
8. Zeleňák, V.; Sabo, M.; Massa, W.; Llewellyn, P. *Inorg. Chim. Acta.* **2004**, *357*, 2049-2059.
9. Baca, S. G.; Filippovab, I. G.; Gerbeleua, N. V.; Simonovb, Y. A; Gdaniecc, M; Timcoa, G. A.; Ghercob, O. A.; Malaesteana, Y. L. *Inorg. Chim. Acta* **2003**, *344*, 109-116.
10. Xu, B.; Ji, X. X.; Cai, Y.; Li, L.; Liu, G. N.; Li, C. H. *J. Mol. Struct.* **2014**, *1056-1057*, 52-55.
11. Frisch, K. D.; Trucks, G. W.; Schlegel, H. B.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A. *Gaussian03*, Revision A. 6, Gaussian, Inc., Pittsburgh PA, 2003.
12. Nagapandiselvi, P.; Baby, C.; Gopalakrishnan, R. *J. Mol. Struct.* **2014**, *1056-1057*, 110-120.
13. Alkorta, I.; Elguero, J. *J. Mol. Struct.* **2014**, *1056-1057*, 209-215.
14. Sheldrick, G. M. *SHELXTL-97*, Program for Crystal Structure Refinement, University of Göttingen, Germany, 1997.
15. Pschirer, N. G.; Ciurtin, D. M.; Smith, M. D.; Bunz, U. H. F.; Loye, H.-C. *Angew. Chem.* **2002**, *114*, 603-605.
16. Hoog, P. de.; Gamez, P.; Mutikainen, I.; Turpeinen, U.; Reedijk, J. *Angew. Chem.* **2004**, *116*, 5939-5941.
17. Bera, M.; Ribas, J.; Aromi, G.; Ray, D. *Inorg. Chem.* **2004**, *43*, 4787-4789.
18. Liu, Q. X.; Yu, J.; Zhao, X. J.; Liu, S. W.; Yang, X. Q.; Li, K. Y.; Wang, X. G. *CrystEngComm.* **2011**, *13*, 4086-4096.
19. Kim, J. C.; Cho, J.; Lough, A. *J. Inorg. Chim. Acta* **2001**, *317*, 252-258.
20. Wang, Y.; Okabe, N. *Chem. Pharm. Bull.* **2005**, *53*, 645-652.
21. Chen, Z. H.; He, Y. B.; Hu, C. G.; Huang, X. H. *Tetrahedron: Asymmetry* **2008**, *19*, 2051-2057.
22. Xia, S. W.; Xu, X.; Sun, Y. L.; Fan, Y. H.; Bi, C. F.; Zhang, D. M.; Yang, L. R. *Chinese. J. Struct. Chem.* **2006**, *25*, 197-203.
23. Xing, Y. H.; Zhang, Y. H.; Sun, Z.; Ge, M. F.; Yuan, H. Q.; Zhang, B. L. *Synth. React. Inorg., Met.-Org., Nano-Met. Chem.* **2005**, *35*, 747-753.
24. Wang, A. D.; Bi, C. F.; Fan, Y. H.; Zou, Y. N.; Xu, J. K.; Kan, Y. H. *Russ. J. Coord. Chem.***2008**, *34*, 475-479.
25. Chen, A. H.; Meng, S. C.; Zhang, J. F.; Zhang, C. *J. Mol. Struct.* **2013**, *1050*, 15-20.
26. Anbazhagan, R.; Sankaran, K. R. *J. Mol. Struct.* **2013**, *1050*, 73-80.
27. Guo, F.; Bi, C. F.; Fan, Y. H.; Wang, A. D.; Xu, J. K.; Zhang, X. *J. Ocean. Univ. Chin.* **2008**, *7*, 168.
28. Ji, N. N.; Shi, Z. Q.; Zhao, R. G.; Zheng, Z. B.; Li, Z. F. *Bull. Korean Chem. Soc.* **2010**, *31*, 881-886.
29. Clarke, M. J.; Zhu, F.; Frasca, D. R. *Chem. Rev.* **1999**, *99*, 2511-2534.
30. Clarke, M. J. *Cood. Chem. Rev.* **2002**, *232*, 69-93.
31. Kurita, N.; Kobayashi, K. *Comput. Chem.* **2000**, *24*, 351-357.
32. Rÿeha, D.; Kabeláč, M.; Ryjácek, F.; Sÿponer, F.; Sÿponer, J. E.; Elstner, M.; Suhai, S.; Hobza, P. *J. Am. Chem. Soc.* **2002**, *124*, 3366-3376.