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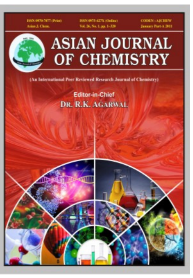

Synthesis, Crystal Structure and Fluorescent Properties of Dinuclear Zinc Complex

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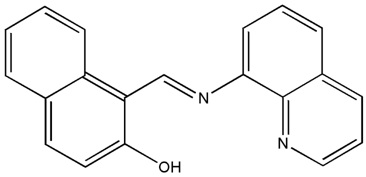
A dinuclear zinc complex $[Zn_2(qnal)_2(CH_3COO)_2]$ (Hqnal: N-(8'-quinolyl)-2-hydroxy-1-naphthaldimine) was synthesized and characterized by X-ray crystallography. The complex crystallizes in monoclinic system, space group C2/c with a = 40.00(3), b = 7.690(5), c = 27.492(16) Å, β = 120.446(11)°, V = 17290(8) Å^3, Z = 8. D_c = 1.537 g/cm^3, M_r = 843.48, F(000) = 3456, $\mu(MoK_\alpha)$ = 1.374 mm^{-1}, S = 1.033, R = 0.0403 and wR = 0.1049 for 4454 observed reflections ($I > 2\sigma(I)$). It exhibits a 3D supramolecular architecture constructing by π-π stacking interactions between quinolyl and naphthyl rings and shows luminescent property in the yellow region.

Keywords: Zinc complex, Crystal structure, Dinuclear, Fluorescence.

INTRODUCTION

The rational design and construction of coordination complexes have attracted considerable attention in recent decades, due to their intriguing structural diversities and potential applications as functional materials[1,2]. As we known, Schiff base ligands are favorite candidates for building coordination complexes because of their simple synthesis and versatility[3]. Also, Schiff base complexes have remained an important and popular area of research owing to their diverse range of applications in catalysis, magnetic properties and optical properties[4]. Derivatives of 8-aminoquinoline been extensively studied in great detail as a result of their interesting photophysical properties[5, 6]. An aromatic Schiff base, N-(8'-quinolyl)-2-hydroxy-1-naphthaldimine (Hqnal) (**Scheme- I**), has been known for many decades to be a photochromic compound. Hence, Hqnal is widely used as a fluorescent chemosensor[7,8] for Al^{3+} and Cu^{2+}. Taking its photophysical properties into account, we reported a new dinuclear zinc complex with N-(8'-quinolyl)-2-hydroxy-1-naphthaldimine ligand, $[Zn_2(qnal)_2(CH_3COO)_2]$ (**1**). Herein, we reported the synthesis, crystal structure and fluorescent property of the Zn(II) complex.



Scheme-I: Chemical structure of Hqnal

EXPERIMENTAL

The ligand N-(8'-quinolyl)-2-hydroxy-1-naphthaldimine was synthesized by coupling of 2-hydroxyl-1-naphthyl aldehyde and 8-aminoquinoline in methanol, according to a previously reported method[9]. Other materials used in syntheses were of reagent grade and obtained commercially without further purification. Elemental analyses for carbon, hydrogen and nitrogen were recorded on a Vario EL III elemental analyzer. Infrared spectra were performed on a Nicolet A370 FT-IR spectrometer using KBr pellets in the range of 4000-400 cm^{-1}. The luminescence spectra were carried out with a Shimadzu RF-5301 spectrophotometer.

Synthesis of $[Zn_2(qnal)_2(CH_3COO)_2]$: A solution of $Zn(CH_3COO)_2 \cdot 2H_2O$ (43.9 mg, 0.2 mmol) in 15 mL of methanol was added to a solution of N-(8'-quinolyl)-2-hydroxy-1-naphthaldimine (59.46 mg, 0.2 mmol) in 15 mL of methanol, resulting in a brown-yellow solution mixture. Reddish brown crystals suitable for X-ray diffraction were obtained after two weeks, in 49 % yield based on Zn. Anal. calcd (%) for $C_{44}H_{32}N_4O_6Zn_2$: C, 62.67; H, 3.82; N, 6.64. Found: C, 62.71; H, 3.85; N, 6.62. Selected IR (KBr pellet, cm^{-1}): 3440(s), 3035(w), 1649(m), 1615 (s), 1571(s), 1535(s), 1504(m), 1459(s), 1387(s), 1366(s), 1317(m), 1300(m), 1256(w), 1196(m), 827(m), 751(m).

Structure determination: A colorless crystal with sizes of 0.35 mm × 0.19 mm × 0.13 mm was selected for measurement. Diffraction data were collected using a Bruker Smart Apex II CCD diffractometer operating at 296(2) K. Intensities were collected with graphite monochromatized MoK_α radiation ($\lambda = 0.71073$ Å), using the *phi* and omega scan technique ($1.18 < \theta < 25.50°$). Data reduction was made with the Bruker SAINT package. Absorption correction was performed using the SADABS program. A total of 22667 reflections were collected, of which 6750 were unique with $R_{int} = 0.0449$ and 4590 were observed with $I > 2\sigma(I)$. The structure was solved by direct methods and refined on F^2 by full-matrix least-squares using SHELXL-2000 with anisotropic displacement parameters for all non-hydrogen atoms. H atoms were introduced in calculations using the riding model on their parent atoms with $U_{iso}(H) = 1.2\ U_{eq}(C, O)$. All computations were carried out using the SHELXTL-2000 program package[10]. A summary of crystallographic data and refinement parameters is given in Table-1.

TABLE-1
CRYSTALLOGRAPHIC DATA AND DETAILS OF THE EXPERIMENT AND REFINEMENT FOR (**1**)

Complex	**1**
m.f.	$C_{44}H_{32}N_4O_6Zn_2$
m.w.	843.48
Crystal system	Monoclinic
Space group	C2/c
a (Å)	40.00(3)
b (Å)	7.690(5)
c (Å)	27.492(16)
β (deg)	120.446(11)
V (Å^3)	7290(8)
Z	8
ρ_{calcd} (g/cm^3)	1.537
μ (mm^{-1})	1.374
F(000)	3456
Limiting indices h, k, l	$-45 \le h \le 48$, $-8 \le k \le 9$, $-32 \le l \le 33$
θ Range for data collection, deg	1.18 - 25.50
Reflections collected/	22667
Unique reflections (R_{int})	6750 (0.0449)
Goodness-of-fit on F^2	1.033
Final R indices ($I>2\sigma(I)$)	$R_1 = 0.0403$, $wR_2 = 0.1049$
R indices (all data)	$R_1 = 0.0713$, $wR_2 = 0.1280$
$\Delta\rho_{min}$/ $\Delta\rho_{min}$, e Å^{-3}	-0.365 and 0.373

RESULTS AND DISCUSSION

Structure description: The molecular structure of the complex is presented in Fig. 1 and the major bond lengths and bond angles are summarized in Table-2. In the molecular structure, two zinc ions are connected through the coordination of two acetates to form a dinuclear structure. The distance between Zn(1) and Zn(2) is 3.559 Å. In complex (**1**), both of the zinc atoms are five-coordinated with severely distorted trigonal-bipyramidal geometries which were observed in other Zn compounds[11]. In the coordination geometry, the apical positions are occupied by one oxygen atom and one nitrogen atom of one qnal$^-$. The equatorial plane is completed by one nitrogen atom and two oxygen atoms from two acetates. The Zn-O bond distances are from 1.993(3) to 2.090(3) Å and Zn-N distances are in the range of 2.097(3) and 2.156(3) Å, which are comparable to those reported in other zinc complexes[12]. There are two types of acetate coordination modes, namely, monodentate and bidentate bridges in the title complex which are recorded in documents[13]. The dihedral angles (5.23 and 8.94°) between the quinolyl and naphthyl rings on each ligand are found to be different, which are similar in $[Fe(qnal)_2][Pd(dmit)_2]_5$·acetone (dmit = 4,5-dithiolato-1,3-dithiole-2-thione)[14] and $[Fe(qnal)_2]·CH_2Cl_2$[15].

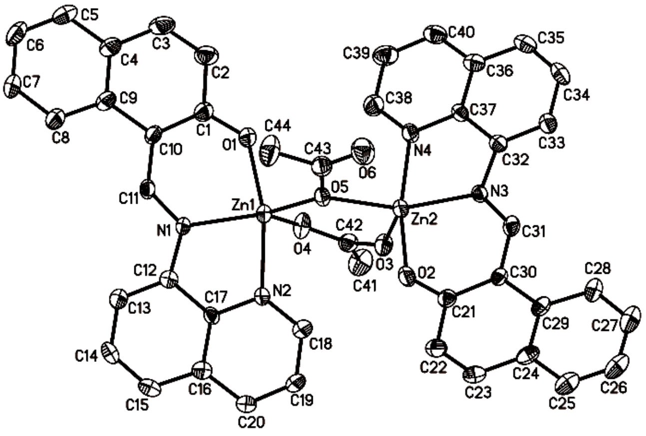


Fig. 1. Molecular structure of complex (**1**)

In the crystal lattice, there are some weak intermolecular interactions of extensive π-π stacking interactions between quinolyl and naphthyl rings, which from neighboring entities form a three-dimensional framework and stabilize the crystal structure as Fig. 2 depicted.

Fluorescent properties: The fluorescent properties of ligand Hqnal and the present Zn(II) complex have been measured in the solid state at room temperature upon 382 nm excitation.

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

Bond	Distance	Bond	Distance	Bond	Distance
Zn(1)-N(1)	2.097(3)	Zn(1)-N(2)	2.156(3)	Zn(1)-O(1)	2.016(3)
Zn(1)-O(4)	2.014(3)	Zn(1)-O(5)	2.031(3)	Zn(2)-N(3)	2.100(3)
Zn(2)-N(4)	2.119(3)	Zn(2)-O(2)	1.993(3)	Zn(2)-O(3)	2.090(3)
Zn(2)-O(5)	2.090(2)				
Angle	(°)	Angle	(°)	Angle	(°)
O(4)-Zn(1)-O(1)	95.87(13)	O(1)-Zn(1)-N(2)	166.31(11)	O(5)-Zn(1)-N(1)	131.14(12)
O(4)-Zn(1)-O(5)	104.05(11)	O(1)-Zn(1)-O(5)	92.96(12)	N(1)-Zn(1)-N(2)	78.59(12)
O(4)-Zn(1)-N(1)	124.48(12)	O(1)-Zn(1)-N(1)	87.86(11)	O(4)-Zn(1)-N(2)	93.43(13)
O(5)-Zn(1)-N(2)	94.50(12)	O(2)-Zn(2)-O(3)	93.98(12)	O(2)-Zn(2)-O(5)	93.95(11)
N(3)-Zn(2)-N(4)	79.50(12)	O(2)-Zn(2)-N(3)	88.04(11)	O(5)-Zn(2)-O(3)	95.75(11)
O(3)-Zn(2)-N(4)	93.86(12)	O(3)-Zn(2)-N(3)	118.54(11)	O(5)-Zn(2)-N(3)	145.45(10)
O(2)-Zn(2)-N(4)	167.36(11)	O(5)-Zn(2)-N(4)	95.12(12)		

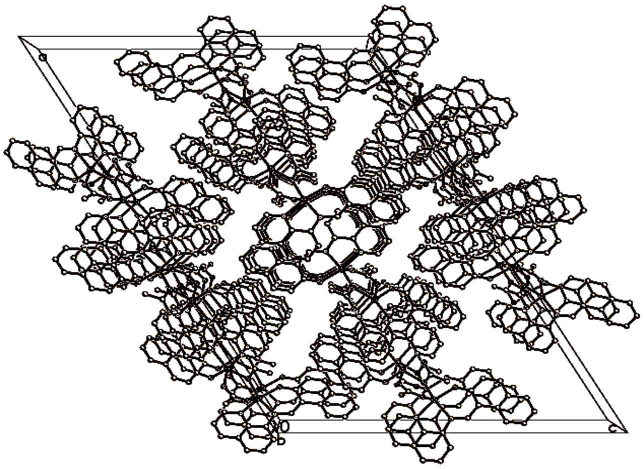


Fig. 2. 3D supramolecular architecture of the title compound along the a-axis

According to the Fig. 3, the free Hqnal molecule exhibits intense peak at 557 nm and weak board emission at 630 nm. While, complex (**1**) displays a strong peak at 579 nm and a shoudler emission 630 nm in the yellow region. Therefore, the fluorescent peaks of (**1**) are probably contributed to the ligand-centered transitions (π-π^*) of Hqnal[16].

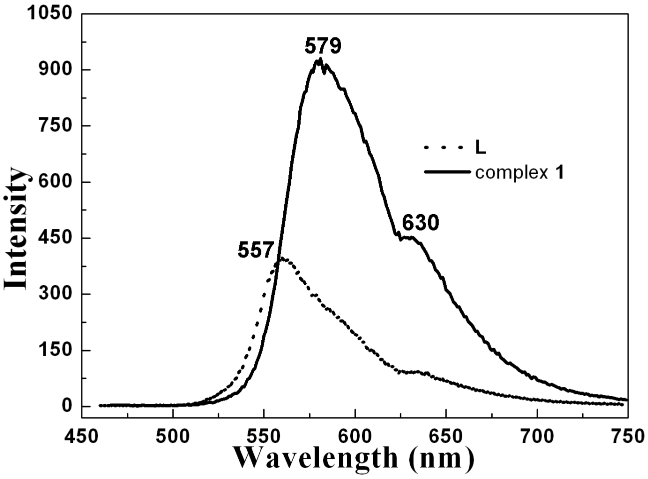


Fig. 3. Solid-state emission spectra of Hqnal and Zn(II) complex at room temperature

Conclusion

In summary, a new 3D suparmolecular architecture zinc(II) complex has been synthesized and characterized. The stability of the structure in the solid was strengthened by the extensive π-π stacking interactions of ligands. Fluorescent properties reveal that there are ligand-centered transitions (π-π^*) of Hqnal in the solid compound.

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