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Synthesis, Crystal Structure and Luminescent Properties of Some Zn(II) Schiff Base Complexes: Experimental and Computational Study

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Abstract A series of Zn(II)-Schiff bases I, II and III complexes were synthesized by reaction of *o*-phenylenediamine with 3-methylsalicylaldehyde, 4-methylsalicylaldehyde and 5-methylsalicylaldehyde. These complexes were characterized using FT-IR, UV-Vis, Diffuse reflectance UV-Vis, elemental analysis and conductivity. Complex III was characterized by XRD single crystal, which crystallizes in the triclinic system, space group P-1, with lattice parameters a=9.5444(2) Å, b=11.9407(2) Å, c=21.1732(3) Å, V=2390.24(7) Å^3, D_c=1.408 Mg m^{-3}, Z=4, F(000)=1050, GOF=0.981, R1=0.0502, wR2=0.1205. Luminescence property of these complexes was investigated in DMF solution and in the solid state. Computational study of the electronic properties of complex III showed good agreement with the experimental data.

Keywords Zinc complexes · Schiff base · Luminescence

Introduction

Complexes of transition metals with Schiff bases have been investigated extensively for many years due to their relative ease of synthesis, high thermal stability and interesting properties [1–8]. These complexes have important contributions in the development of catalysis, magnetism, molecular architectures and materials chemistry [1–6]. Luminescent coordination compounds with Schiff bases have attracted much attention due to their applications as organic light emitting diodes, lasers, transistors, and fluorescent sensors for highly specific probes [9–13]. As part of our efforts in searching for new materials with high luminescence properties for organic light emitting diodes (OLED), we synthesized Zn(II) complex with a Schiff base, wherein the ligand was synthesized from the reaction of conjugated aromatic *o*-phenylenediamine with 3-methylsalicylaldehyde, 4-methylsalicylaldehyde and 5-methylsalicylaldehyde.

Experimental

Materials and Measurement

The ZnCl$_2$, *o*-phenylenediamine, 3-methylsalicylaldehyde, 4-methylsalicylaldehyde, 5-methylsalicylaldehyde and pyridine were commercially available, and were used without further purification. Infrared-spectra were recorded on a Perkin-Elmer 2000 FT-IR spectrophotometer using KBr pellets in the range 400-4000 cm^{-1}. Diffuse reflectance UV-Vis was measured using Perkin-Elmer UV/Vis Lambda 35, while the absorption spectrum in solution was measured using JASCO V-530 spectrophotometer. The fluorescence spectrum was obtained using JASCO spectrofluorometer FP-750. Quantum yields were determined for the zinc complexes using quinine sulfate in 1.0 N H$_2$SO$_4$ (Φ=0.54). Photoluminescence (PL) measurements were performed at room temperature by using Jobin Yvon HR800UV system. A He-Cd laser was used for excitation at 325 nm and the emission spectra were scanned from 330 to 1000 nm.

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Table 1 Crystal data and structure refinement for the title complex

Empirical formula	$C_{28.25} H_{24.25} N_{3.25} O_2 Zn$
Formula weight	506.63
Colour	yellow
T (K)	297(2) K
Crystal system	triclinic
Space group	P-1
a (Å)	9.5444(2)
b (Å)	11.9407(2)
c (Å)	21.1732(3)
α (°)	89.785(1)
β (°)	82.460(1)
γ (°)	87.694(1)
V (Å^3)	2390.24(7)
Z	4
D_{calc} (Mg m^{-3})	1.408
μ (mm^{-1})	1.059
$F(000)$	1050
Crystal size (mm)	0.35×0.22×0.17
θ Ranges (°)	1.71–30.00
$h/k/l$	−13/13, −16/16, −29/29
Reflections collected / unique	47405/13798 [R(int) = 0.0668]
Completeness to $\theta = 30$ (%)	99.0
T_{max} and T_{min}	0.8430 and 0.7095
Goodness-of-fit on F^2	0.981
Data / restraints / parameters	13798/0/622
Refinement method	Full-matrix least-squares on F^2
Final R indices [I>2sigma(I)]	R1=0.0502, wR2=0.1205
Largest peak and hole (e Å^{-3})	0.452 and -0.619

Fig. 1 ORTEP representation of the monomeric [Zn(pmb)(pyridine)] with the atom numbering scheme and 50% probability ellipsoids for all non-hydrogen atoms. All the hydrogen atoms and solvated pyridine have been omitted for clarity
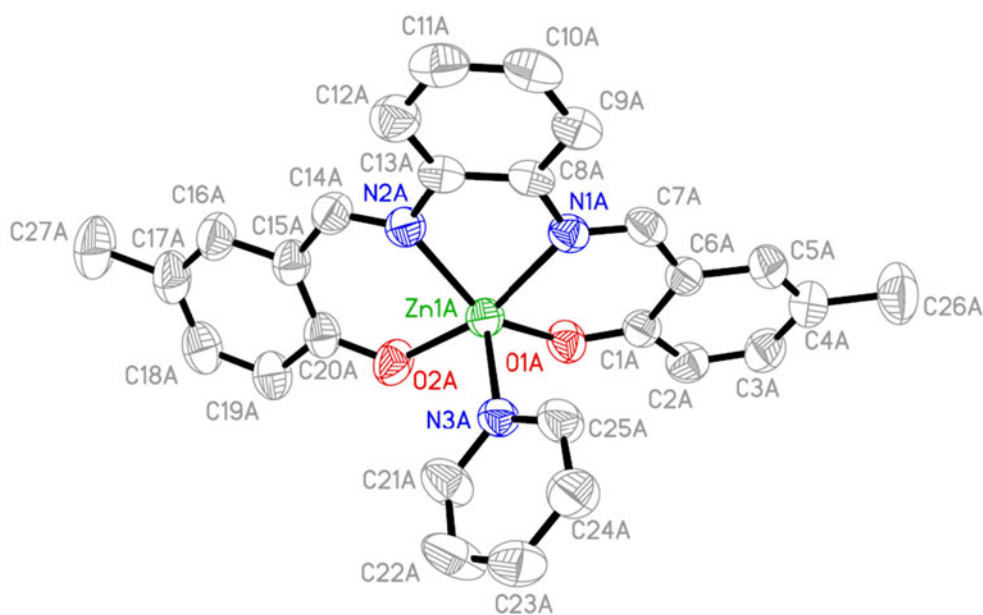
Table 2 Selected bond lengths (Angstrom) for complex III in P-1

| Bond	Bond length
Zn(1A)-O(1A)	1.968(2)
Zn(1A)-O(2A)	1.971(2)
Zn(1A)-N(2A)	2.101(3)
Zn(1A)-N(3A)	2.108(2)
Zn(1A)-N(1A)	2.125(3)
Zn(1B)-O(1B)	1.962(2)
Zn(1B)-O(2B)	1.963(2)
Zn(1B)-N(3B)	2.103(3)
Zn(1B)-N(2B)	2.110(3)
Zn(1B)-N(1B)	2.117(3)

Conductivity was measured using Cyberscan 500 conductivity meter.
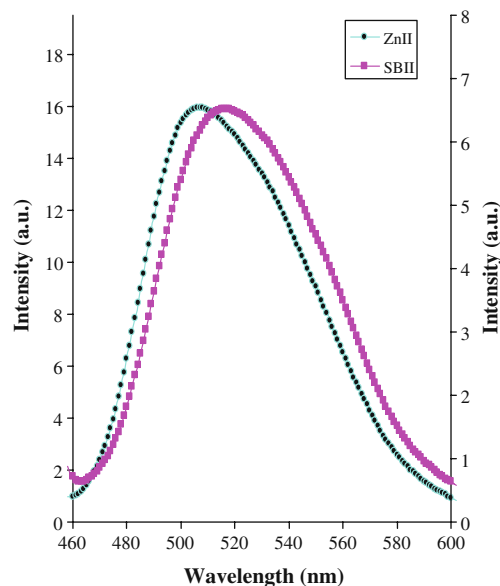
Synthesis of Complexes I, II and III

Complexes I, II and III were prepared by the same procedure using different aldehydes, for example complex III was synthesized as follows: 5-methylsalicylaldehyde (0.544 g, 4.0 mmol) was added to a solution of o-phenylenediamine (0.216 g, 2.0 mmol) in ethanol (20 ml). The mixture was refluxed under constant stirring for half an hour. Then (0.272 g, 2.0 mmol) zinc chloride in 10 ml ethanol was added, followed by (0.5 ml, 3.6 mmol)

Table 3 Selected bond angles (degrees) for complex III in P-1

O(1A)-Zn(1A)-O(2A)	98.29(9)
O(1A)-Zn(1A)-N(2A)	147.03(10)
O(2A)-Zn(1A)-N(2A)	89.09(10)
O(1A)-Zn(1A)-N(3A)	102.23(10)
O(2A)-Zn(1A)-N(3A)	96.69(10)
N(2A)-Zn(1A)-N(3A)	108.79(10)
O(1A)-Zn(1A)-N(1A)	88.73(9)
O(2A)-Zn(1A)-N(1A)	163.09(10)
N(2A)-Zn(1A)-N(1A)	76.95(10)
N(3A)-Zn(1A)-N(1A)	96.83(10)
O(1B)-Zn(1B)-O(2B)	98.27(10)
O(1B)-Zn(1B)-N(3B)	102.53(10)
O(2B)-Zn(1B)-N(3B)	100.17(11)
O(1B)-Zn(1B)-N(2B)	152.64(10)
O(2B)-Zn(1B)-N(2B)	88.33(10)
N(3B)-Zn(1B)-N(2B)	102.36(10)
O(1B)-Zn(1B)-N(1B)	88.39(10)
O(2B)-Zn(1B)-N(1B)	157.25(10)
N(3B)-Zn(1B)-N(1B)	99.55(10)
N(2B)-Zn(1B)-N(1B)	76.44(10)
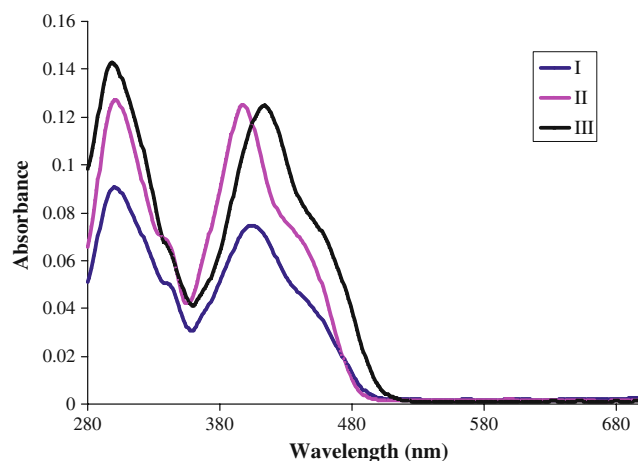
Fig. 2 UV/Vis absorption spectra of Zn(II) complexes

triethylamine. The mixture was stirred at room temperature for two hours. The yellow-orange precipitate obtained was washed with about 5 ml ethanol, dried, and then washed by copious amount of diethyl ether. The precipitate was dissolved in 20 ml of pyridine whereby yellow crystals suitable for XRD were formed after five weeks of slow evaporation of pyridine at room temperature. Orange-yellow, yield: 60.23% m.p >300 °C. IR spectrum (KBr, cm^{-1}): 3002 ν(C-H)$_{aromatic}$, 2915, 2851 ν(C-H) of CH$_3$, 1621 ν(C = N), 1583, 1525,1468 ν(C = C). UV/Vis spectroscopy (in DMF, λ_{max} nm, ε (dm^3 mol^{-1} cm^{-1})): 298 (27.03×10^3), 413 (24.07×10^3). Diffuse reflectance UV/Vis spectroscopy (solid, λ_{max} nm): 327, 379, 426 shoulder. Elemental analysis: Calculated, (found): C$_{22}$H$_{18}$N$_2$O$_2$Zn H$_2$O, C: 62.05(61.87); H: 4.73(4.28); N: 6.58(6.46). Conductivity: in DMF, 3.40 ohm^{-1} mol^{-1} L.

Fig. 3 Normalized emission spectra of Zn(II) complex II and its corresponding ligand in DMF excited at 400 nm
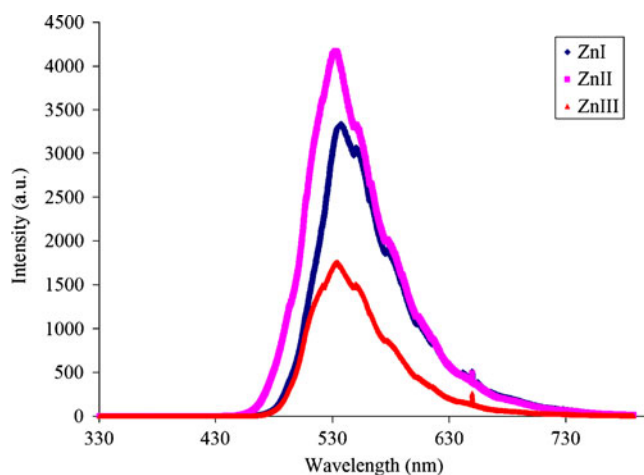
Fig. 4 Photoluminescence of Zn(II) complexes I, II and III in solid state

Synthesis and Characterization of Complex I

The synthesis and single crystal structure of this compound have been reported [14]. Yellow, yield: 75.64%, m.p>300 °C, IR spectrum (KBr, cm^{-1}): 3013 ν(C-H)$_{aromatic}$, 2927, 2901 ν(C-H) of C H$_3$, 1615 ν(C = N), 1587, 1544,1487 ν(C = C). UV/Vis spectroscopy (in DMF, λ_{max} nm, ε (dm^3 mol^{-1} cm^{-1})): 300 (26.5×10^3), 404 (22.5×10^3). Diffuse reflectance UV/Vis spectroscopy (solid, λ_{max} nm): 315, 413 and a shoulder at about 426 nm. Elemental analysis: Calculated (found): C$_{22}$H$_{18}$N$_2$O$_2$Zn H$_2$O, C: 62.05(61.83);: 4.73(4.54); N: 6.58 (6.56). Conductivity: in DMF, 7.38 ohm^{-1} mol^{-1} L.

Synthesis and Characterization of Complex II

Yellow, Yield 59.52%, m.p>300 °C, IR spectrum (KBr, cm^{-1}): 3046 ν(C-H)$_{aromatic}$, 2914, 2857 ν(C-H) of CH$_3$, 1625 ν(C = N), 1587, 1517,1470 ν(C = C). UV/Vis spectroscopy (in DMF, λ_{max} nm, ε (dm^3 mol^{-1} cm^{-1})): 297 (28.03×10^3), 397 (26.60×10^3). Diffuse reflectance UV/Vis spectroscopy (solid, λ_{max} nm): 313, 404 and a shoulder at about 426 nm. Elemental analysis: Calculated (found): C$_{22}$H$_{18}$N$_2$O$_2$Zn 1.4 H$_2$O, C: 61.31(61.39); H: 4.86(4.42); N: 6.50 (6.51). Conductivity: in DMF, 5.42 ohm^{-1} mol^{-1} L.

Computational Methods

The geometry optimization was carried out using the semi empirical PM6 level available in MOPAC 2007 [15]. Calculations of molecular orbitals were performed using Gaussian03 program [16] at the restricted Hartree-Fock (RHF) level of computation with 6-31+G(3d,3pd) basis set. Electronic absorption spectra were calculated using ZINDO/S method incorporated in Gaussian 03 [16], based on the PM6 optimized structure. The orbital diagrams were generated using the GaussView 3.09 software [16]. GaussView 3.09 was used for visualization, while AOMix [17] and Swizard [18] were used for molecular orbital analysis.

X-Ray Crystallography

The crystallographic data and structure refinement parameters for the compounds are given in Table 1. The data were collected using a Bruker SMART APEX2 CCD diffractometer [19] equipped with graphite monochromated Mo Kα (λ=0.71073 Å) radiation at 297(2)K. The structure was solved using SHELXTL [20] and refinement was carried out by full-matrix least squares on F^2. Hydrogen atoms were placed in calculated positions.

Table 4 X-ray crystallography vs. calculated selected structural parameters of complex III

Method	Atom	Connecting atom	Bond length (Å)	Connecting atom	Angle(°)	Connecting atom	Dihedral angle (°)
Experimental	Zn(1)						
	O(2)	Zn(1)	1.9619				
	O(3)	Zn(1)	1.9634	O(2)	98.2729		
	N(4)	Zn(1)	2.1171	O(2)	88.3878	O(3)	158.1522
	N(5)	Zn(1)	2.1099	O(2)	152.6487	O(3)	102.5586
	O(6)	Zn(1)	2.1033	O(2)	102.5294	O(3)	257.5670
Theoretical PM6	Zn(1)						
	O(2)	Zn(1)	2.0260				
	O(3)	Zn(1)	2.0265	O(2)	96.1167		
	N(4)	Zn(1)	2.0358	O(2)	89.2360	O(3)	167.1880
	N(5)	Zn(1)	2.0359	O(2)	165.8991	O(3)	111.6864
	O(6)	Zn(1)	2.1821	O(2)	74.9944	O(3)	-72.5169

Fig. 5 Molecular orbital surfaces of the HOMO (*left*) and LUMO (*right*) for Zn III complex
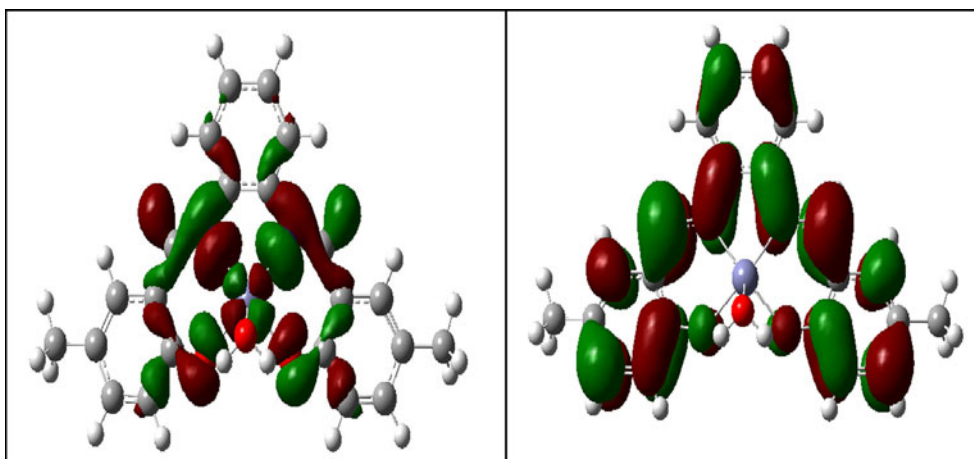
Results and Discussion

Structure Description

Complex III was crystallized from pyridine, which substitutes the coordinated water. The Zn(II) center is in a five-coordination N_2O_3 environment which is approximately square pyramidal with the N_2O_2 tetradentate Schiff-base ligand as the basal plane and the pyridine molecule in the axial position, Fig. 1.

There are two independent molecules in the asymmetric unit. The Zn atom is penta-coordinated, with the two O atoms and two N atoms forming the basal plane, and the N atom of the pyridine ring in the apical position, to give a square-pyramidal (Fig. 1 and Table 1). In molecule A, the Zn(II) ion is displaced from the basal plane (N1A/N2A/O2A/O1A) by 0.3857(4) Å, i.e Zn(II) is displaced 0.3857 (4) Å out of this mean basal plane towards the axial pyridine molecule. The pyridine ring of N3A/C21A-C25A

is attached axially to Zn1A with O1A-Zn1A-N3A-C21A torsion angle of -99.4(3).

In molecule B, the Zn(II) ion is displaced from the basal plane (N1B/N2B/O2B/O1B) by 0.3927(4)Å, i.e Zn(II) is displaced 0.3927(4) Å out of this mean basal plane towards the axial pyridine molecule. The pyridine ring of N3B/C21B-C25B is attached axially to Zn1B with O1B-Zn1B-N3B-C21B torsion angle of 96.8(3). These values are consistent with those of similar Zn(II)complex [14, 21, 22]. Selected bond distances and bond angles for the title complex were listed in Tables 2 and 3, respectively.

Electronic Spectra

Diffuse reflectance UV-Vis of all complexes: I, II and III, show two absorption bands and one shoulder. The two absorption bands at 313-327 nm and 379-413 nm correspond to the intraligand π to π* and n to π* transitions [23], respectively. The UV-Vis absorption of the Zn(II)

Fig. 6 Molecular orbital composition of complex III
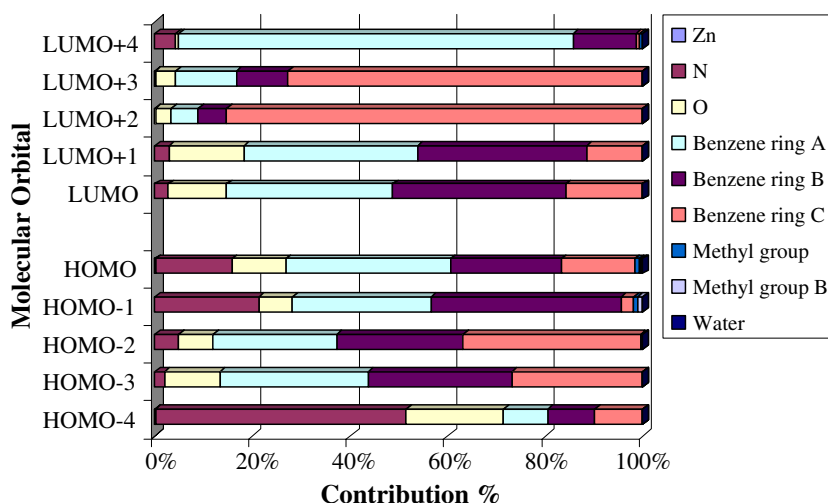
Fig. 7 Comparison of calculated and experimental absorption for complex III
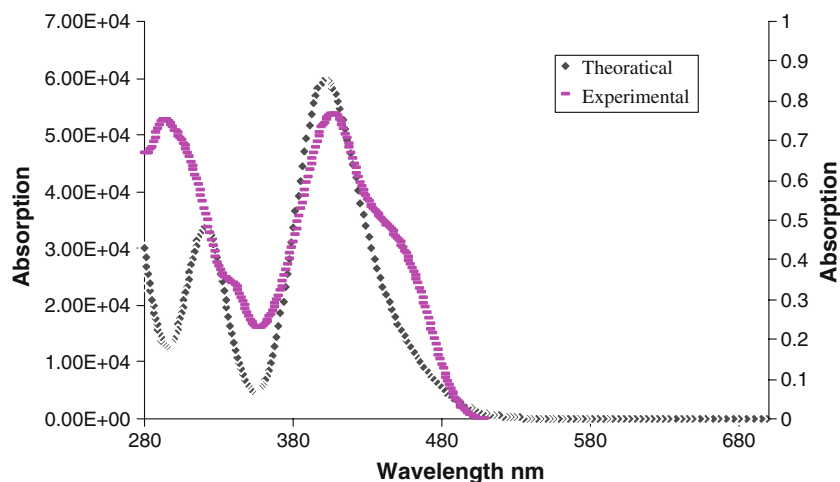
complexes in DMF, Fig. 2, shows two absorption bands at about 300 nm and 413 nm, which can be assigned to intraligand transitions. These two bands in the complexes are shifted to longer wavelengths compared to the free ligand as the effect of coordination of nitrogen and oxygen atoms to Zn(II). Comparing the bands of the complex in solid state and in DMF, the bands in DMF are shifted to lower wavelengths due to the solvent effect.

Fluorescence Spectra

The fluorescence emission spectra of complexes I, II and III show similar feature with a broad band in the region between 450 to 600 nm and a maximum at 516, 502 and 522 nm, respectively. When these complexes was excited at 400 nm, we found that, there is a red shift of about 8 nm to 26 nm in comparison with their corresponding ligands, Fig. 3, due to the coordination with zinc. Quantum yields determined using quinine sulfate as the standard were 0.2×10^{-2}, 0.19×10^{-2} and 0.36×10^{-2} for complexes I, II and III, respectively.

The solid-state photoluminescence spectra of all complexes, Fig. 4, show a broad band in the same region with a maximum at 532 nm. Two small bands at 413 nm and 686 nm were also observed. Since no d-d transition is expected in Zn(II) complexes, the bands at 413, 532 and 686 nm can be assigned to the relaxation from higher energy level to lower energy of intraligand transition. The colour of the emitted light lies in the green region. As expected for this type of complexes, the conductivity measurement shows that these complexes are non-electrolytes [24].

Computational Study

Optimized Geometry

Table 4 shows comparison between theoretical and experimental bond lengths. The optimized geometric parameters obtained from semi-empirical method PM6 in MOPAC2007 [15] represent a good agreement with those of the crystal structure, and they are the bases for calculating other

Table 5 Electronic transition data obtained by ZINDO method for complex III

State	M.O. Character	Coefficient	Character	λcal nm	λexp nm	f
$S_0 \rightarrow S_1$	HOMO-1→LUMO+1	-0.3807	ILCT	445	448 sh	0.1607
	HOMO→LUMO	0.5695	ILCT			
$S_0 \rightarrow S_2$	HOMO-1→LUMO	-0.4771	ILCT	400	405	0.7979
	HOMO→LUMO+1	0.4799	ILCT			
$S_0 \rightarrow S_3$	HOMO-3→LUMO+3	-0.1461	ILCT	324	290	0.0466
	HOMO-2→LUMO+1	0.3417	ILCT			
	HOMO-2→LUMO+2	0.1517	ILCT			
	HOMO-1→LUMO	0.3302	ILCT			
	HOMO→LUMO+1	0.3771	ILCT			
	HOMO→LUMO+2	0.2134	ILCT			

parameters, such as molecular orbitals and electronic absorption spectra, which are described below.

Molecular Orbital Analysis

The results of MO calculations, Fig. 5, shows that the electron density in the HOMO and LUMO are delocalized over the benzene rings. We found that the electron density is located near the electron-withdrawing atoms like oxygen and nitrogen. The methyl group plays a main role in the solubility of this kind of compounds in common solvents. However, their contribution to HOMO and LUMO densities is very little and almost neglectable.

In order to corroborate the delocalized nature and the relative position of the HOMO and LUMO orbitals, we have carried out molecular orbital contributions calculations on complex **III**, using AOMix [17]. For that, the structure were divided into ten molecular parts :(1) Metal center (2) Chloride (3) Oxygen atoms (4) Nitrogen atoms (5) Benzene ring A (6) Benzene ring B (7) Benzene ring C (8) Methyl group A (9) Methyl group B (10) Water. This division is schematically shown in Fig. 6.

Electronic Absorption Spectra

Figure 7 and Table 5, show the comparison between the calculated electronic absorption spectra and the experimental results. Three bands of electronic transitions have been observed in the region between 280-500 nm, at 324, 400 and 445 nm, which are in good agreement with experimental data. The results also show the adequacy of the method in reproducing experimental data.

Thermogravimetric Analysis

The thermal properties of complexes I, II and III were measured between 30-900 °C. These compounds are thermally stable until around 240 °C. Weight loss is ca. 5.20% (calc. 4.23%) for I and 5.31% (calc. 4.23%) for II and 5.3% (calc. 4.23%) for III between 100-180 °C, corresponding to loss of one coordinated water per formula unit. Compounds I, II and III are still stable until about 300 °C. Above-mentioned results indicate these compounds I,II and III have good thermal stability.

Conclusion

The synthesis, structural characterization, UV–Vis absorption, fluorescence properties and thermal stability of Schiff base-zinc complexes have been described. The results show that Zn (II) ion adopts a square-pyramidal environment and is coordinated by two nitrogen atoms, two oxygen atoms

and one coordinated water to complete the coordination number of five. The complexes showed fluorescence emission at room temperature in both solid state and in solution in addition to good thermal stability. Theoretical calculation on the geometric and electronics properties of the complexes are in good agreement with the experimental data, which suggest the calculation at this level is useful in designing similar complexes.

Supplementary Materials

Crystallographic data for the structure reported in this paper have been deposited to the Cambridge Crystallographic Data Centre as supplementary publication (No: CCDC 652743). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (Fax: (+44) 1223-336-033; E-mail: deposit@ccdc.cam.ac.uk).

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