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EXPERIMENTAL AND THEORETICAL CHARACTERIZATION OF N,N′-BIS(2,4-DIHYDROXYBENZYLIDENE)-1,2-DIAMINOBENZENE SCHIFF BASE AND ITS Cu(II) COMPLEX

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A new Schiff base ligand N,N′-bis(2,4-dihydroxybenzylidene)-1,2-diaminobenzene $[=H_2L]$ and its Cu(II) complex $[Cu(L)]$ are synthesized and characterized by IR, UV-Vis, NMR, mass spectrometry and elemental analysis. Also, the computational prediction of optimized geometries, IR spectra and NMR chemical shifts is performed using the density functional theory (DFT) method. The DFT optimized geometry of the ligand is not planar, so the three benzene rings are located in separate planes. The phenolic protons are engaged in the intramolecular hydrogen-bonding interactions. In the optimized geometry of the square comlex, dianionic L^{2-} acts as a tetradentate ligand, which occupies four coordination positions in the N, N, O$^-$, O$^-$ manner. The consistency between the calculated and experimental results confirms the validity of the optimized structures for the H_2L ligand and its Cu complex.

K e y w o r d s: Schiff base, copper, IR assignment, NMR, DFT, resorcinol.

INTRODUCTION

Schiff bases are of great importance, especially due to their biological [1, 2] and catalytic [3, 4] activities. The coordination of Schiff base ligands to metal ions improves their biological activities [5, 6]. Copper Schiff base complexes have been used as catalysts for the oxidation of alcohols [7, 8]. Also, biological activities of these complexes have been widely studied, especially the DNA-binding and DNA-cleaving properties [9, 10] and mimic of galactose oxidase [11].

On the other hand, resorcinol derivatives are widely used in the synthesis of a number of products [e.g., 12, 13], well-known chelating reagents in spectrophotometric determination of metal ions [13, 14], separation of trace metal ions [15], and acid-base titrations as an indicator [16].

In continuation of our studies [17—20] and hopping to biological and catalytic applications, herein we report the synthesis and characterization of a new Schiff base ligand ($=H_2L$) and its Cu(II) complex. The spectroscopic approaches and elemental analysis have been used. In addition, optimized geometries of the ligand and the Cu complex have been calculated using DFT method and a theoretical assignment of the IR and NMR spectra was made. The validity of the optimized structures has been evaluated by comparing the theoretical and experimental results.

EXPERIMENTAL

Materials and methods. All of the used chemicals and solvents were obtained from Merck. They were used without further purification. Melting points were measured by an electrothermal 9100 mel-

ting point apparatus. Elemental analysis (C, H, N) was performed using a Heraeus elemental analyzer CHN-O-Rapid. The percentage of Cu in the complex was also measured using a Shimadzu AA-670 GV/7 atomic absorption spectrometer. IR spectra of a KBr disc were recorded on a Buck 500 infrared spectrophotometer and electronic spectra were recorded on a Shimadzu UV-Vis 2550 spectrometer. Mass spectra of the H_2L ligand and the Cu complex were recorded on Shimadzu-GC-Mass-Qp 1100 Ex and Varian mat CH-7 mass spectrometers respectively. ^1H and ^{13}C NMR spectra were obtained on a Bruker Drx-500 Avance spectrometer (500.13 MHz) with $(CD_3)_2CO$ as a solvent.

Synthesis of the H_2L ligand. A solution of 1.88 g (13.61 mmol) of dihydroxybenzaldehyde and 0.72 g (6.66 mmol) of benzene-1,2-diamine in toluene (150 ml) was refluxed under vigorous stirring with a Dean-Stark for 3 h. The resulting suspension was kept at room temperature prior to being filtered, washed with ethanol (2×10 ml), and dried with diethyl ether (2×10 mL) to afford a deep red solid. The solid was recrystallized for further purification. (Yield: 73 %, m.p.: 225 °C).

Synthesis of the Cu complex. A solution of $Cu_2(CH_3COO)_4 \cdot 2H_2O$ (10 mg, 0.05 mmol) in 5 ml of methanol was dropwise added to the methanolic solution of the H_2L Schiff base ligand (17.4 mg, 0.05 mmol) in 45 minutes. The solution was stirred for 2 h at 50—60 °C. After 2 days, the precipitate was filtered and recrystalized in acetonitrile for further purification (Yield: 75 %).

Computational details. All calculations have been performed using gradient-corrected density functional theory with the Beck—Lee—Young—Parr exchange correlation functional (B3LYP) [21], as implemented in the Gaussian-98 program package [22]. The 6-311+G(d,p) basis set was employed, except for Cu atom in which the LANL2DZ basis set [23] was used with including effective core potential functions.

Geometries of the H_2L ligand and its Cu complex were fully optimized in vaccum. The optimized geometries were confirmed to have no imaginary frequency of the Hessian. Then, the gas-phase optimized geometries were used to compute theoretical vibrational frequencies of the H_2L ligand and its Cu(II) complex. Also, the ^1H and ^{13}C NMR chemical shifts of H_2L were predicted at the same computational level with respect to tetramethylsilane (TMS). The GIAO method was used for the prediction of DFT nuclear shieldings [24].

The DFT vibrational frequencies are usually higher than the experimental ones, which can be corrected by applying the procedure of scaling the wavenumbers. Here, the scale factor of 0.9614 was used for the calculated wavenumbers [25].

RESULTS AND DISCUSSION

Geometry optimization. Since no single crystals have been prepared for the investigated ligand, theoretical calculations could be considered as complementary to or replacement for experimental methods in the determination of its structural parameters. Here, the structural parameters of the H_2L ligand and its Cu(II) complex have been theoretically calculated, which are in agreement with the structural data reported for the Schiff base ligands [26—28] and complexes [29—36] with the 1,2-diaminobenzene —$N(C_6H_4)N$— bridge. Optimized geometries of the H_2L ligand and the Cu complex with their atom labeling are shown in Figs. 1 and 2 respectively.

In the optimized geometry of H_2L species, three benzene rings are essentially planar; however, each of the benzene rings is in the separate plane. The C=C bond distances (138.9—141.7 pm) in these rings are in the expected range [36, 37].

The resorcinol OH groups are in the same plane with the benzene ring. For example, the C3—C2—C1—O1 and C2—C1—O1—H1 dihedral angles are 179.9° and 178.7° respectively. Also, the C1—C2—C3—O3 and C2—C3—O3—H4 dihedral angles are 180.0° and 179.6° respectively, which are –179.9° and 179.5° respectively in the Cu complex.

The two side benzene rings make a dihedral angle of approximately 50.0° to each other, while each of them has a dihedral angle of about 40.0° with the middle benzene ring (Fig. 1). The calculated C2—C6—C13—C9, C3—C5—C12—C10, and C4—C1—C16—C19 dihedral angles are 50.1°, 51.4°, and 142.5° respectively.
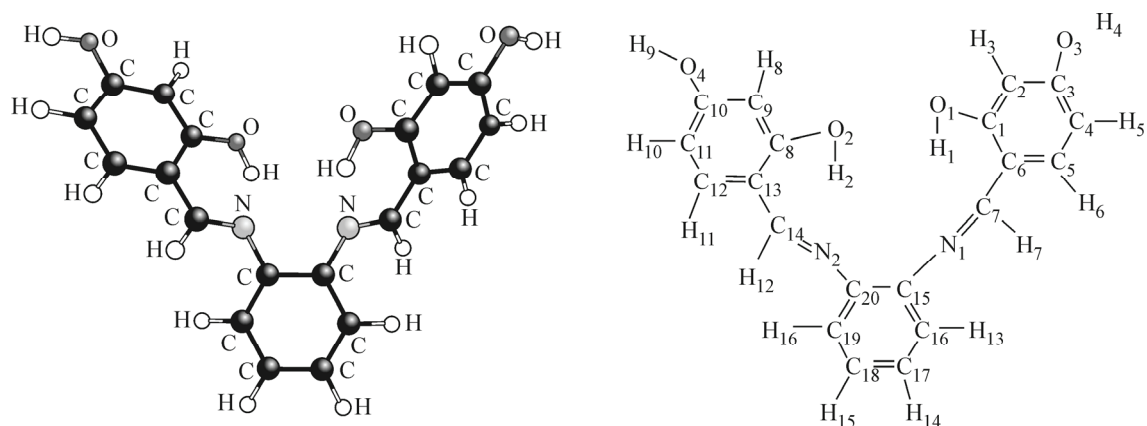
Fig. 1. Structure and B3LYP optimized geometry of the N,N′-bis(2,4-dihydroxybenzylidene)-1,2-diaminobenzene together with its labeling
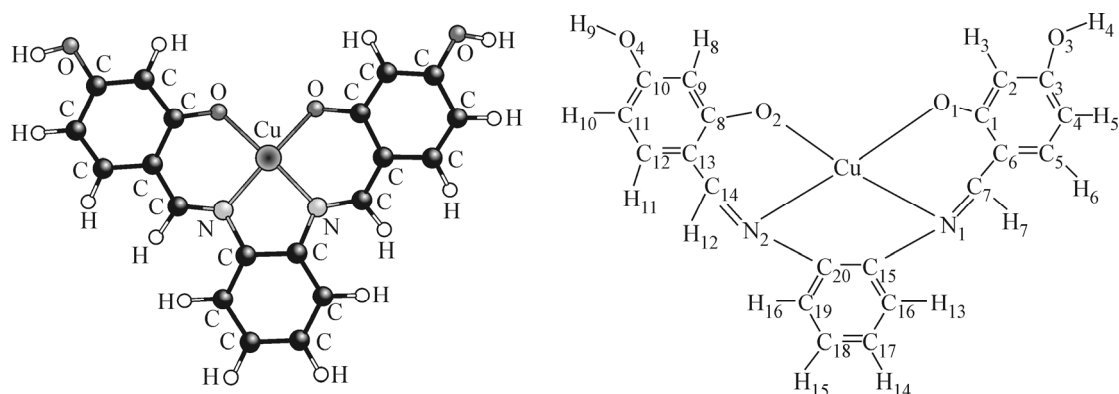

Fig. 2. Structure and B3LYP optimized geometry of the [Cu(L)] complex together with its labeling

Previously, the crystal structure of the Cu complex has been reported by Niu *et al*. In this work, its geometry has been optimized using DFT methods. For comparison, some of the experimental and theoretical structural parameters are given in Table 1. As seen, the calculated data are in good agreement with the experimental ones, confirming the suitability of our calculation for the investigated compounds.

In the complex structure, the ligand is more planar than the free form. Going from the free ligand to the Cu complex, the N1—C15—C20—N2, O1—N1—N2—O2 and C1—C7—C14—C8 dihedral

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Some experimental and calculated structural parameters of the Cu *complex*

Bond length (pm)	Exp	Cal	Angle (deg.)	Exp	Cal	Dihedral angle (deg.)	Exp	Cal
Cu—O1	190.3	193.6	O1—Cu—O2	86.5	90.8	N1—N2—O2—O1	−0.3	0.1
Cu—N1	194.1	198.6	N1—Cu—N2	84.0	83.3	O2—O1—N1—Cu	−0.4	−0.4
C1—O1	130.8	128.6	Cu—O1—C1	127.1	128.5	O1—C1—C2—C3	179.2	179.4
C1—C2	140.8	141.9	N1—Cu—O1	94.8	93.0	O1—C1—C6—C7	6.1	−1.2
C1—C6	142.7	145.0	C6—C7—N1	126.1	126.9	C1—C6—C7—N1	−0.5	−0.1
C7—N1	130.4	131.0	C7—N1—C15	122.5	123.2	C5—C2—C9—C12	0.1	−0.2
N1—C15	142.0	140.9	N1—C15—C20	114.3	115.7	N1—C15—C16—C17	178.0	179.9
C15—C20	140.4	141.8	N1—C15—C16	126.3	125.1	C6—C1—C8—C13	0.5	−0.2

angles vary from 6.0°, 48.7°, and 50° respectively to 0.0°, –0.1°, and –0.1° respectively. Also, both of the C2—C6—C13—C9 and C3—C5—C12—C10 dihedral angles of the Cu complex are –0.1°. The C2—C6—C15—C17 and C10—C12—C20—C18 dihedral angles decrease from –143.0° and –142.5° for the ligand to 173.4° and –174.6° respectively. Therefore, the three benzene rings are roughly in the same plane in the structure of the complex.

Both of the C15—N1 and C20—N2 bond lengths are 140.4 pm, which is an appropriate size for the single C—N bond, while both C7—N1 and C14—N2 are 129.0 pm, corresponding to the double C=N bond. The C7=N1 and C14=N2 bonds are in the same plane with the corresponding benzene rings. For example, the C7—C6—C5—C4 dihedral angle is 179.2° and 179.1° in the free and coordinated ligand respectively.

In free H_2L, the H1 and H2 atoms are engaged in intramolecular hydrogen bonds with the N1 and N2 atoms respectively, forming two six-membered rings. The calculated N…H hydrogen bond length and the N—O distance are 173.6 pm and 262.9 pm respectively. The N…H hydrogen bonding decreases the electron density in the binding region of the O1—H1 and O2—H2 bonds. Hence, the O1—H1 and O2—H2 bonds (99.4 pm) are longer than the O3—H4 and O4—H9 bonds (96.3 pm) by 3.1 pm.

Deprotonated L^{2-} acts as a dianionic tetradentate ligand that has an N, N, O$^-$, O$^-$ binding mode via the deprotonated phenolic oxygen and azomethine nitrogen atoms. In the structure of the Cu(II) complex (Fig. 2), four coordinated atoms are roughly in the same plane with the Cu^{2+} ion. The calculated O2—N2—N1—O1 and O1—O2—N2—Cu dihedral angles are –0.1° and –0.4° respectively. Rotation around the C15—N1 and C20—N2 single bonds put roughly the two side-benzene rings in the same plane. This provides structural requirements for the complex formation.

By complexation, the deprotonation of phenolic oxygen atoms results in a decrease in the C1—O1 and C8—O2 bond lengths, in comparison with the free H_2L ligand, from 133.7 pm to 128.6 pm. However, the C3—O3 and C10—O4 bond lengths are about 136 pm in both free and coordinated ligand.

The calculated Cu—O1 and Cu—O2 bond lengths are 193.6 pm, which are 5 pm shorter than the Cu—N1 and Cu—N2 ones. The coordination of azomethine nitrogen atoms to Cu results in the elongation of the C—N bonds of L^{2-}. The C7—N1 and N2—C14 bond lengths increase from 129.0 pm for the H_2L to 131.0 pm for the Cu(II) complex. Also, the C15—N1 and C20—N2 bond lengths are elongated by 1.0 pm to 140.9 pm in the complex.

In comparison with free H_2L, the complexation results in a considerable decrease in the O1—O2 and N1—N2 distances, from 418.3 pm and 276.5 pm for H_2L to 275.8 pm and 263.9 pm for the Cu complex. The DFT calculated parameters for the H_2L ligand and its Cu(II) complex are consistent with the previously reported data for the similar salen ligands and complexes [26—36].

Chemistry. In this work, the H_2L Schiff base and the $[Cu^{II}(L)]$ complex were newly synthesized and characterized by the elemental and spectroscopic (IR, UV-Vis, ^1H NMR and Mass) analysis.

Elemental analysis and mass spectroscopy. The elemental analysis results for the H_2L ligand (Anal. Calc. for $C_{20}H_{26}N_4O_4$: C, 68.96; H, 4.63; N, 8.04. Found: C, 67.69; H, 4.90; N, 8.29 %) and the Cu complex (Anal. Calc. for $CuC_{21}H_{30}N_4O_6$: C, 54.84; H, 4.38; N, 6.09; Cu, 13.82. Found: C, 54.83; H, 4.21; N, 6.26; Cu, 13.93 %.) confirm the proposed formulas. In addition, the molecular ion peaks m/z (M^+) observed in the mass spectra of the ligand and the complex (348 and 459 respectively) were found to be consistent with the proposed formula weight, which may be taken as extra evidence for the correctness of the proposed formulas for the studied species. Therefore, the elemental analysis as well as the mass spectra data proposed that one H_2O molecule and one CH_3OH molecule were present in the precipitated complex.

Electronic spectra. The electronic spectra of the H_2L ligand and its Cu complex were recorded in a deuterated methanol solution. The absorption bands at 241 nm and 293 nm of the ligand spectrum are assigned to the π—π* transitions of benzene rings. The maximum absorption bands at 327 nm and 420 nm are attributed to the π—π* and n—π* transitions of the azomethine group respectively [38, 39].

Experimental and theoretical ^{1}H *and* ^{13}C NMR *chemical shifts of*
N,N′-*bis*(2,4-*dihydroxybenzylidene*)-1,2-*diaminobenzene ligand in the* $(CD_3)_2CO$ *solution*, δ, ppm

Atom position	Exp.	Theo.	Atom position	Exp.	Theo.	Atom position	Exp.	Theo.	Atom position	Exp.	Theo.
^{1}H NMR						^{13}C NMR					
H1	13.40	13.23	H13	6.40	7.11	C1	163.9	172.07	C17	127.4	130.99
H2	13.40	13.23	H16	6.40	7.11	C8	163.9	172.07	C18	127.4	130.99
H7	8.75	8.65	H3	6.34	6.76	C3	163.3	167.83	C16	119.8	123.00
H12	8.75	8.65	H8	6.34	6.76	C10	163.3	167.83	C19	119.8	123.00
H6	7.35	7.30	H5	6.30	6.11	C7	162.9	165.17	C6	112.6	119.46
H11	7.35	7.30	H10	6.30	6.11	C14	162.9	165.17	C13	112.6	119.46
H14	7.35	7.30	H4	10.27	3.99	C15	142.4	151.95	C4	108.2	108.75
H15	7.35	7.30	H9	10.27	3.99	C20	142.4	151.95	C11	108.2	108.75
						C5	134.8	138.54	C2	102.8	107.16
						C12	134.8	138.54	C9	102.8	107.16

In the complex spectrum, the red shift of the π—π* transitions of benzene rings to 230 nm and 260 nm confirms the ligand coordination to the Cu^{2+} ion. An observed absorption band at 357 nm is attributed to the *d*—π* transition band of the complex, as a MLCT transition to the π* orbital of azomethine C=N [29]. The absorption band at 410 nm is assigned to the *d*—*d* transition of the complex.

NMR spectra of the H₂L. The theoretical and experimental ^{1}H NMR and ^{13}C NMR chemical shifts (δ) of the H₂L ligand are listed in Table 2, where the atom positions are numbered as in Fig. 1. As seen, the DFT chemical shifts are consistent with the experimental values, confirming the suitability of the optimized geometry for H₂L. The only exception is the H4 and H9 hydrogen atoms, where the calculated chemical shifts are significantly lower than the experimental ones. It is notable that the experimental data are from $(CD_3)_2CO$ solutions, while the calculations correspond to the isolated molecule. Obviously, the solvent molecules interact with the —OH protons. Also, H4 and H9 can be engaged in intermolecular hydrogen bonds.

The appearance of a signal at 13.40 ppm is attributed to the H1 and H2 phenolic protons (H1, H2), where their engagement in the intramolecular hydrogen bond interaction (O—H…N) shifts their signals upfield [17, 18, 40].

Vibrational spectroscopy. A theoretical analysis of the spectra is used as an important tool for the identification of chemical compounds [17—20, 41]. In this work, the vibrational modes were analyzed by comparing the DFT and experimental IR spectra. The assignment of the selected vibrational frequencies of the H₂L ligand and its Cu(II) complex are gathered in Table 3.

In the 3600—2000 cm^{-1} spectral region of the IR spectra, the overlapping of stretching vibrations of the O—H bonds with each other and with the C—H stretching modes leads to band broading [17—20, 42, 43]. In Table 2, the deconvolution of this region is given. In the ligand spectrum, the most intense band is attributed to the stretching vibrations of the O1—H1 and O2—H2 bonds. These vibrations appeared at lower energies than the corresponding vibrations for the O3—H4 and O4—H9 bonds, which can be attributed to the engagement of H1 and H2 in the intramolecular hydrogen bond interaction. For the spectrum of the complex, the most intense band is predicted to be related to the O—H stretching vibrations of the water and methanol molecules.

The energy value of the very intense band in the 1660—1500 cm^{-1} region of the IR spectra is an important diagnostic for the coordination mode of Schiff bases [17—20, 42, 44, 45]. By complexation, the symmetrical stretching modes of C7=N1 and C14=N2 bonds shift to lower energy by 9 cm^{-1} in comparison with the free H₂L ligand (1615 cm^{-1}), confirming the H₂L coordination through the azomethine nitrogen atoms (N1 and N2) [17, 42, 45].

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Selected experimental and calculated IR vibrational frequencies (cm^{-1}) *of the*
N,N′-*bis*(2,4-*dihydroxybenzylidene*)-1,2-*diaminobenzene ligand and its* Cu *complex*

Experimental frequencies		Calculated frequencies		Vibrational assignment
Ligand	Cu Complex	Ligand	Cu Complex	
—		—	482	υ(Cu—N, Cu—O)
745 (w)	756 (w)	757	776	Breathing of benzene rings
1159 (m)	1112 (w)	1174	1153	υ(C15—N1, C20—N2)
1280	1276	1223	1223	υ(C3—O3, C10—O4, C6—C7, C13—C14)
1361 (m)	1353 (w)	1342	1347	δ_{ip}(C7—H7, C14—H12)
1427 (m,sh)	1441 (m)	1405	1423	υ(C1—O1, C8—O2)
1496 (s)	1521 (s)	1485	1496	υ(C=C) benzene rings
1615 (vs)	1606 (vs)	1594	1576	υ(C7—N1)+υ(C14—N2)
			1578	υ(C7=N1, C14=N2)+υ(C=C) benzene bridge [1]
		1608	1597	υ(C=C) benzene ring of resorcinol moieties
2927 (w,br)	2938 (w)	2913	2976	υ(C7—H7, C14—H12)
		3035, 3051, 3070	3154, 3172, 3185, 3196, 3201, 3209	υ(C—H) aromatic
		3054	—	υ_{sym}(O1—H1, O2—H2)
		3064	—	υ_{asym}(O1—H1, O2—H2)
	3478 (m,br)	3085	3085	υ(C2—H3, C9—H8)
		3684	3684	υ(O3—H4, O4—H9)
—	3733 (m)	—		υ(O—H) methanol, υsym(O—H) H$_2$O, υasym(O—H) H$_2$O [a]

[1] Bridge = N(C$_6$H$_4$)$_4$N bridging region of molecules; sci, scissoring; wag, wagging; op, out-of-plane; ip, in-plane; w, weak; m, medium; s, strong; vs, very strong; br, broad; sh, shoulder.
[a] Refs: 17—19, 45.

The stretching vibrations of the C1—O1 and C8—O2 bonds appeared at 1427 cm^{-1} of the ligand spectrum. Upon complexation, this band shifts to higher frequencies by 14 cm^{-1}, indicating an increase in the electron density in the bonding region of C1—O1 and C8—O2 by the deprotonation and coordination of O1 and O2 phenolic oxygens (Table 3).

The calculated structural parameters of the studied ligand and the complex and the assignment results of their vibrational frequencies and NMR chemical shifts could be useful in the identification of similar compounds.

CONCLUSIONS

In this work, the H$_2$L ligand and its [Cu(L)] complex have been synthesized and characterized by the elemental analysis, UV-Vis, NMR and IR spectroscopies.

The proposed formulas for both ligand and complex are in agreement with the experimental results. In continuation, their geometries were optimized using the DFT methods. The optimized geometries show that the H$_2$L species is not planar, with a 50° dihedral angle between the two side benzene rings.

In the free ligand, the H1 and H2 phenolic protons are engaged in the intramolecular hydrogen bond (—O—H…N), which affects considerably their NMR chemical shifts and the strength of their O—H bonds, too.

The dianionic L^{2-} ligand is coordinated to the Cu^{2+} ion in a tetradentate manner with N, N, O^-, O^- donor sites of resorcinol OH and azomethine N. The four coordinating atoms of L^{2-} are in the same plane with each other and the Cu atom.

The calculated structural parameters are in good agreement with the reported results for the similar compounds. In addition, the DFT calculated IR frequencies and NMR chemical shifts are well in agreement with the experimental results, confirming the validity of the optimized geometries for the ligand and its Cu complex.

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