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**N,N'-DIPYRIDOXYL(ETHYLENEDIAMINE) SCHIFF-BASE LIGAND
AND ITS SQUARE-PYRAMIDAL COPPER(II) COMPLEX:
SYNTHESIS, EXPERIMENTAL AND THEORETICAL CHARACTERIZATION**

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A new tetradentate N,N'-dipyridoxyl(1,2-ethylenediamine) [=H₂ES] Schiff-base ligand and its Cu(II) salen complex [Cu(ES)(H₂O)] are synthesized and characterized by IR, UV-Vis, ¹H NMR, mass spectrometry, and elemental analysis. Their optimized geometries and theoretical vibrational frequencies are computed by using the density functional theory method where the B3LYP functional was used. Also, the ¹H NMR chemical shifts of the H₂ES ligand are calculated at the same computational level. In the optimized structure of the free ligand, two pyridine rings are not in the same plane. In the structure of the complex, the Schiff-base ligand acts as a dianionic tetradentate ligand in the N,N,O⁻,O⁻ manner, so that the coordinating atoms occupy equatorial positions. The H₂O ligand occupies the axial position of the square-pyramidal complex. The calculated results are consistent with the experimental ones, confirming the suitability of the optimized structures for the H₂ES ligand and its Cu(II) complex.

Keywords: DFT, IR assignment, NMR, Schiff base, salen, copper(II).

INTRODUCTION

Schiff bases due to structural varieties and very unique characteristics are the most versatile studied ligands in coordination chemistry [1, 2] and their metal complexes play an important role in the development of inorganic chemistry [3—6].

A variety of applications, including biological [7—10], analytical [11, 12], and industrial use as catalysts [13—20], make the Schiff-base ligands and their complexes be of great importance.

Mainly due to their variety in coordination geometry, magnetism, catalysis, spectroscopic properties and their biochemical significance, the copper complexes are very interesting and attractive. The biological activities of Cu(II) salen complexes have been widely studied, especially in the DNA-binding and cleaving properties [21—23], and catalysis of some reactions such as hydrogen peroxide decomposition [1, 20]. Also, salen complexes of copper have been widely used as catalysts for the oxidation of alcohols [13, 14, 24, 25].

Analytical [11, 12] and catalytic [13, 14] applications of the Cu(II)-Schiff base complexes with the ethylenediamine bridge have been studied. It has been shown that the catalytic activity of the Cu(II) salen complexes is influenced by the chain length of the Schiff base [26]. In the continuation of our studies [27], here we report the synthesis and experimental characterization of the N,N'-dipyridoxyl(1,2-ethylenediamine) (=H₂ES) ligand and its Cu(II) complex, which have two carbonic ethylenediamine bridge. Also, the geometry optimization of the ligand and the Cu complex and a theoretical assignment of the IR and ¹H NMR spectra have been performed using the DFT method.

EXPERIMENTAL

Material and methods. All of the used chemicals and solvents were purchased from Merck, except for pyridoxal hydrochloride that was obtained from Fluka. They were used as received. Melting points were measured by an electrothermal 9100 melting point apparatus. Elemental analysis (C, H, N) was made on a Heraeus CHN—O-Rapid elemental analyzer. The IR spectra were recorded with a Perkin Elmer 783 infrared spectrophotometer and the UV-Vis spectra were measured on a Shimadzu UV-Vis 2500 spectrophotometer. Mass spectra were recorded on a Shimadzu-GC-Mass-Qp 1100 Ex. The ^1H NMR spectrum was recorded on a Bruker Drx-500 Avance spectrometer (500.13 MHz) with $(\text{CD}_3)_2\text{CO}$ as a solvent.

Synthesis of the H_2ES ligand. Pyridoxal hydrochloride (611 mg, 3 mmol) was dissolved in 5 ml of methanol, and then was added to methanolic Et_3N (303 mg, 3 mmol in 5 ml). This mixture was stirred for a few minutes. Then, a methanolic solution of ethylenediamine (90 mg, 1.5 mmol in 5 ml) was slowly added to the mixture. The mixture was stirred for 5 hours. The yellow solid was filtered, washed with cold methanol and dried in air (Yield: 96.5 %, Decomp. P.: 208.4 °C).

The elemental analysis results for the H_2ES species confirm the proposed formula. Anal. Calc. for $\text{C}_{18}\text{H}_{22}\text{N}_4\text{O}_4$: C, 60.3; H, 6.2; N, 15.6. Found: C, 59.9; H, 6.2; N, 15.1 %. Also, the decomposition mass losses of the H_2ES ligand were found in consistent with the proposed formula weight, which may be taken as extra evidence for the correctness of this formula (MS: m/z (%) 358 (M^+)).

Synthesis of the $[\text{Cu}(\text{ES})(\text{H}_2\text{O})]$ complex. Methanolic NaOH (5 mg, 0.12 mmol) was added to the dissolved H_2ES Schiff-base ligand (22 mg, 0.06 mmol) in 15 ml of methanol. Then a solution of $\text{Cu}_2(\text{CH}_3\text{COO})_4 \cdot 2\text{H}_2\text{O}$ (12 mg, 0.06 mmol) in 5 ml of methanol was added dropwise to the ligand solution. The mixture was stirred for 1–2 hours at room temperature. After filtering, the product was washed with cold methanol and dried at 50 °C (Yield: 89.1 %).

The results of elemental analysis are good in agreement with the proposed formula for the the Cu(II) complex, $[\text{Cu}(\text{ES})(\text{H}_2\text{O})]$. In the mass spectrum, molecular ion peak, m/z (M^+) was observed at 438 and its data of elemental analysis was: Anal. Calc. for $\text{CuC}_{18}\text{H}_{22}\text{N}_4\text{O}_5$: C, 49.4; H, 5.1; N, 12.8. Found: C, 49.2; H, 5.1; N, 12.3 %.

THEORETICAL

All the present calculations have been performed using the gradient-corrected DFT method with the B3LYP functional [28]. The GAUSSIAN-98 program package [29] was used with its default procedures. Geometries of the H_2ES ligand and its Cu complex were optimized at 6-31G(*d,p*) basis sets except for the Cu atom where LANL2DZ basis sets were used.

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_2ES ligand and its Cu(II) complex and the ^1H NMR chemical shifts of the ligand at the same computational level. The ^1H NMR chemical shifts of H_2ES were predicted with respect to tetramethylsilane (TMS), where the GIAO method was used for the prediction of DFT nuclear shieldings [30].

Due to reasons such as the use of finite basis sets and incomplete treatment of electron correlation, the DFT vibrational frequencies are usually higher than the experimental ones. This can be corrected by applying the scaling of wavenumbers. The scale factor of 0.9614 was used for the calculated wavenumbers in this work [31].

RESULTS AND DISCUSSION

Geometry optimization. In this work, structural parameters of the H_2ES ligand and its Cu(II) complex have been determined, which are in agreement with the experimental structural data reported for the Schiff-base ligands [1, 2, 20, 32–40] and Cu(II) complexes [1, 5, 20, 34–46] with the ethylenediamine $-\text{N}(\text{CH}_2)_2\text{N}-$ bridge. Their optimized structures with atom labeling are shown in Figs. 1 and 2 respectively.

The optimized structure of the H_2ES molecule is V shape, so that two pyridine rings are not in the same plane, but their planes make approximately a 20° dihedral angle to each other. The calculated

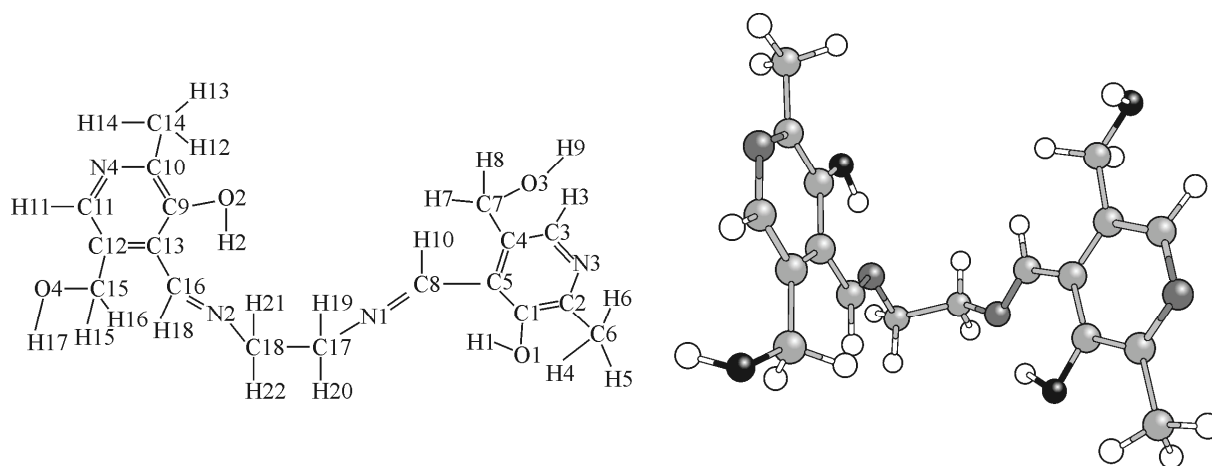


Fig. 1. Structure and B3LYP optimized geometry of N,N'-dipyridoxyl(ethylenediamine) together with its labeling

C3—C1—C9—C11 and C1—C3—C10—C12 dihedral angles are 22.9° and 15.1° respectively. The ligand molecule is twisted, so that any substituted group is in the opposite orientation relative to the corresponding group on another pyridine ring (Fig. 1).

The pyridine rings are essentially planar and the bond distances of C=C (138.8—141.9 pm) and C=N (132.8—134.8 pm) bonds in these rings are in the expected range [47]. The pyridine-carbon bond lengths for the —CH₂OH and —CH₃ substitutions are 152.2 pm and 150.4 pm respectively, which are appropriate sizes for the pyridine-carbon bond. The substituted groups are essentially in the same plane with the pyridine rings. For example, the calculated C6—C2—C1—C5, C7—C4—C5—C1, H11—C11—N4—C10, C8—C5—C1—C2, and C16—C13—C9—C10 dihedral angles are 179.7° , 179.1° , 179.2° , and 179.2° respectively.

The phenolic C—O bond lengths (134.1 pm) are shorter than the alcoholic ones (141.7 pm), but for the O—H bond lengths, the alcoholic ones (96.7 pm) are shorter than the phenolic ones (100.0 pm). The phenolic hydrogens are engaged in intramolecular-hydrogen-bond interactions with the azomethine-nitrogen atoms. This results in longer bond lengths for the phenolic O—H bonds in comparison with the alcoholic ones.

The calculated OH...N hydrogen bond lengths are about 169.0 pm, showing a strong hydrogen bond. This interaction decreases the electron density in the binding region of the phenolic O—H bonds. Hence, the phenolic O—H bonds are longer than the alcoholic ones. In addition, the electron attraction property of the aromatic rings decreases the electron density in the region of phenolic O—H bonds, too. These cases will cause the acidity of the phenolic protons to be greater than that of the alcoholic ones.

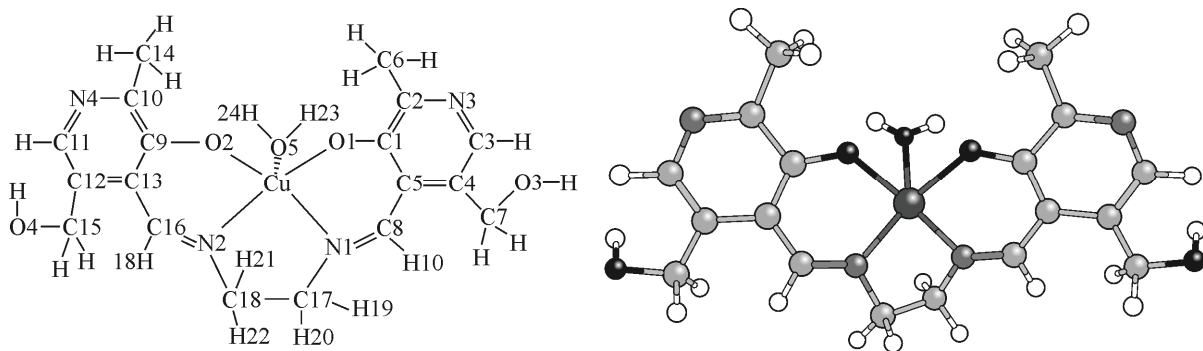


Fig. 2. Structure and B3LYP optimized geometry of the [Cu(ES)(H₂O)] complex together with its labeling

Due to the complex formation, a number of structural parameters of the ligand have changed, the most important of which have been presented below. In the ligand, the phenolic —OH groups are essentially in the same plane with the corresponding pyridine rings; the H1—O1—C1—C2 and H2—O2—C9—C13 dihedral angles are 0.5° and 0.7° respectively. However, they are in the opposite orientation to each other. During the complex formation, two substituted pyridine rings rotate around the C17—N1 and C18—N2 single bonds, which puts them roughly in the same plane. This provides structural requirements for the complex formation. The O1—O2 and N1—N2 distances decrease from 669.3 pm and 299.0 pm for the free ligand to 281.6 pm and 265.8 pm for the Cu complex respectively.

Deprotonated BS^{2-} acts as a tetradentate dianionic ligand that has an N,N,O⁻,O⁻ binding mode via the deprotonated phenolic oxygens and the azomethine nitrogens. In the square-pyramidal Cu(II) complex (Fig. 2), four coordinated atoms of BS^{2-} occupy equatorial positions, where they are roughly in the same plane. The calculated O2—O1—N1—N2, O2—O1—N1—Cu, and O1—N1—N2—Cu dihedral angles are 7.2° , 0.4° , and 6.8° respectively. The axial position of the square-pyramid complex has been occupied by the H₂O ligand.

The Cu—O1 and Cu—O2 bond lengths are 194.3 pm and 195.0 pm respectively, which are much shorter than the Cu—O5 ones (257.4 pm). This indicates that the phenolic oxygens form stronger Cu—O bonds in comparison with the O5 atom of the water ligand. The azomethine nitrogens (N1 and N2 atoms) occupy two other equatorial positions of the square-pyramidal complex, where the Cu—N1 and Cu—N2 bond lengths are 199.4 pm and 198.8 pm respectively. The O1—Cu—O2, N1—Cu—N2, O1—Cu—N2, and O2—Cu—N1 angles are 94.6° , 83.8° , 168.7° , and 174.8° respectively.

By complexation, the phenolic C—O bond length decreases from 134.1 pm for the free ligand to 129.9 pm for the complex, which demonstrated that the electron density has increased in this bond region. Deprotonation of the phenolic oxygens increases their electron density and the phenolic C—O bond regions.

Coordination of the azomethine nitrogens and their electron donation causes the electron density to decrease in the C8—N1 and C16—N2 bond regions, and hence, the lengths of these bonds increase from 128.7 pm for the ligand to 129.6 pm for the Cu complex.

In the —N(CH₂)₂N— bridge region, by complexation, the N1—C17—C18—N2 dihedral angle decreases from 68.5° to 44.1° . The C17—C18 bond length (153.9 pm) undergoes no notable change. The N—C—C angle of the ethylenediamine bridge slightly decreases from 110.8° (for the ligand) to 108.0° (for the complex).

In the complex, there is a resonance in the regions of the phenolic C—O bond, the pyridine ring, and the azomethine C=N bond. This causes the reduction of C5—C8 and C16—C13 bond lengths from 145.9 pm and 146.0 pm for the free ligand to 143.8 pm and 143.7 pm for the complex respectively.

The calculated parameters for the H₂ES and its Cu(II) complex are well in agreement with the previously reported values for the similar salen ligands and complexes, especially the compounds involving the ethylenediamine bridge [1, 2, 5, 20, 32—46].

Electronic spectra. The electronic spectra of the H₂ES and its Cu(II) complex were recorded in deuterated methanol solutions. In the UV-Vis spectrum of the H₂ES ligand, two absorption bands appeared at 207 nm and 335.5 nm, which are attributed to the π — π^* transitions of the aromatic rings and the π — π^* transitions of azomethine chromophore respectively [48—50]. By the complex formation, in the UV-Vis spectrum of the Cu complex, these absorption bands undergo a considerable red shift, which leads to the appearance of more intense bands at 238.5 nm and 378.5 nm respectively [48—50].

¹H NMR spectra. In Table 1, the experimental and theoretical ¹H NMR chemical shifts (δ) of the H₂ES Schiff-base ligand are given, where the atom positions are numbered as in Fig. 1.

The calculated chemical shifts are in good agreement with the experimental values, which confirms the suitability of the optimized geometry for H₂ES. The only exception is the chemical shift of the alcoholic protons (H9 and H17), where the calculated chemical shifts are significantly lower than

Table 1

Experimental and theoretical ^1H NMR chemical shifts of N,N' -dipyridoxyl(ethylenediamine) in the $(\text{CD}_3)_2\text{CO}$ solution, δ [ppm]

Atom position	Exp.	Theor.	Atom position	Exp.	Theor.	Atom position	Exp.	Theor.	Atom position	Exp.	Theor.
^1H NMR											
H1	14.36	13.29	H21	4.20	4.21	H8	4.81	5.08	H13	2.51	2.49
H2	14.36	13.22	H19	4.20	3.43	H15	4.81	5.02	H14	2.51	2.21
H10	9.04	8.39	H22	4.20	3.43	H16	4.81	4.91	H6	2.51	2.18
H18	9.04	8.39	H4	2.51	2.49	H7	4.81	4.83	H17	4.81	0.08
H3	7.62	8.33	H5	2.51	2.49	H20	4.20	4.21	H9	4.81	0.08
H11	7.62	8.33	H12	2.51	2.49						

the experimental ones. It is notable that the alcoholic protons can be engaged in intermolecular hydrogen bonds. On the other hand, the experimental data are obtained from $(\text{CD}_3)_2\text{CO}$ solutions, while the calculations correspond to the isolated molecule in the gas phase. Obviously, the solvent molecules interact with the alcoholic proton.

The appearance of a signal at 14.36 ppm is assigned to the phenolic protons (H1, H2), where their engagement in the intramolecular hydrogen bond interaction (O—H...N) shifts their signals upfield [27, 51].

Vibrational spectroscopy. Now, a theoretical investigation of IR and NMR spectra is accounted as an important tool for the identification of chemical species, especially analyzing the proposed geometries for compounds with an undetermined structure [27, 52].

The selected vibrational frequencies of the H_2ES ligand and its Cu(II) complex are gathered in Table 2. The vibrational modes were analyzed by comparing the previously reported data [41, 53–55] with the results of our DFT calculations.

In the $3600\text{--}2000\text{ cm}^{-1}$ spectral region of the IR spectra, an overlap of the stretching vibrations of the O—H bonds with each other and with C—H stretching modes leads to band broadening [27, 54, 55]. In Table 2, the deconvolution of this region is given. In the ligand spectrum, the most intense band is related to the stretching vibrations of the phenolic O—H bonds. These vibrations appear at lower energies than the alcoholic O—H ones, which is consistent with the weaker phenolic O—H bonds with respect to the alcoholic ones. Also, the stretching vibrations of the aromatic C—H bonds involve lower frequencies than the aliphatic ones. For the complex spectrum, the O—H stretching vibrations of the H_2O ligand involve the most intense band at 3471 cm^{-1} .

An important diagnostic for the mode of ligands coordination is the energy value of the very intense band in the $1660\text{--}1500\text{ cm}^{-1}$ region of the IR spectra of Schiff-base ligands and complexes [27, 41, 52–54]. By complexation, the symmetrical stretching modes of C8=N1 and C16=N2 bonds shifts to lower energy by 11 cm^{-1} in comparison with the free H_2ES ligand (1623 cm^{-1}), confirming the ligand coordination through the azomethine nitrogens (N1 and N2 atoms) [27, 53, 54]. Other intense bands at 1396 cm^{-1} and 1416 cm^{-1} in the spectra of the ligand and the complex respectively are attributed to the some stretching vibrations (Table 2).

The stretching vibrations of phenolic C—O bonds appear at 1248 cm^{-1} of the ligand spectrum, which are shifted by 34 cm^{-1} to higher frequencies in the spectrum of the complex, indicating that the electron density in the phenolic C—O bond region (and thereby the strength of these bonds) are increased by the deprotonation and coordination of the phenolic oxygens.

Some new bands appear in the IR spectrum of the Cu(II) complex in comparison with the ligand one. The band at 630 cm^{-1} was assigned to the wagging mode of the H_2O ligand respectively, confirming the coordination of the H_2O ligand to the Cu(II) central atom. Also, the asymmetric stretching vibration of the Cu—O bonds is exhibited at 678 cm^{-1} as a weak band.

Table 2

Selected experimental and calculated IR vibrational frequencies (cm^{-1}) of the N,N' -dipyridoxyl(ethylenediamine) ligand and its Cu(II) complex

Experimental frequencies		Calculated frequencies				Vibrational assignment
Ligand	Complex	Ligand	Intensity	Complex	Intensity	
—	—	—	—	441	38	$\nu(\text{Cu—N, Cu—O})$
—	630 (s)	—	—	579	306	$\delta_{\text{wagging}}(\text{O—H}) \text{H}_2\text{O}$
—	678 (w)	—	—	649	26	$\nu_{\text{asym}}\text{Cu—O}$
712 (w)	756 (w)	718	13	713	8	Breathing
883 (s)	—	834	107	—	—	$\delta_{\text{out-of-plane}}(\text{O—H})$ phenolic
1016 (s)	1003 (m)	1025	89	1028	43	$\delta(\text{CH}) \text{Me}^{\text{a}} + \nu(\text{ph-C})$
1075 (m)	1047 (s)	1074	49	1033	77	$\nu_{\text{asym}}(\text{ph-C—O}) \text{alc}^{\text{b}}$
1204 (m)	1221 (m)	1200	102	1185	157	$\nu(\text{ph-C}) + \nu(\text{C1—C2, N3—C3, C4—C5, C9—C10, N4—C11, C13—C12})$
1248 (s)	1282 (m)	1278	62	1280	120	$\nu(\text{C—C, C—C})$
1285 (m)	1331 (s)	1355	77	1361	207	$[\delta_{\text{twisting}}(\text{CH}_2) + \delta_{\text{in-plane}}(\text{OH})] \text{alc}^{\text{b}}$
1396 (vs)	1416 (vs)	1371	68	1348	—	$\delta_{\text{wagging}}(\text{CH}_2)$ bridge ^c
		1395	106	1403	283	$\nu(\text{C1—O1}) + \nu(\text{ring}) + \nu(\text{ph-C})$ Left ^d
1469 (w)	1468 (w)	1401	177	1413	61	$\nu(\text{C9—O2}) + \nu(\text{ring}) + \nu(\text{ph-C})$ Right ^e
		1436	47	1435	53	$\delta_{\text{scissoring}}(\text{CH}_2)$ bridge ^c
1623 (vs)	1612 (vs)	1636	177	1618	613	$\nu(\text{C8—N1})$
		—	—	1630	143	$\nu(\text{C16—N2})$
2934 (w, sh)	2906 (w)	—	—	1626	72	$\delta_{\text{scissoring}}(\text{H}_2\text{O})$
		2875	35	2859	56	$\nu_{\text{sym}}(\text{CH}) \text{alc}^{\text{b}}$
2968 (m)	2967 (w)	2886	70	2906	24	$\nu_{\text{sym}}(\text{CH})$ bridge ^c
		2891	61	2912	44	—
		2930	18	2930	18	$\nu_{\text{sym}}(\text{CH}) \text{Me}^{\text{a}}$
		—	—	—	—	—
3285 (br, s)	3471 (m, br)	2945	20	2938	23	$\nu_{\text{asym}}(\text{CH}) \text{alc}^{\text{b}}$
		2951	141	2979	30	$\nu(\text{C}_8\text{H}_{10}) + \nu(\text{C}_{16}\text{—H}_{18})$
		2956	36	2964	26	$\nu_{\text{asym}}(\text{CH})$ bridge ^c
		2981	14	2980	11	$\nu_{\text{asym}}(\text{CH}) \text{Me}^{\text{a}}$
		3038	6	3038	14	—
		2995	389	—	—	$\nu(\text{O—H})$ phenolic
		3003	351	—	—	—
		3081	9	3085	24	$\nu(\text{C—H})$ aromatic
—	—	3658	20	—	—	$\nu(\text{O—H}) \text{alc}^{\text{b}}$
		—	—	3661	23	—
		—	—	3599	31	$\nu_{\text{sym}}(\text{O—H}) \text{H}_2\text{O}$
		—	—	3673	115	$\nu_{\text{asym}}(\text{O—H}) \text{H}_2\text{O}$

^a Substituted —CH_3 groups.

^b Substituted $\text{—CH}_2\text{OH}$ groups.

^c $\text{N}(\text{CH}_2)_4\text{N}$ bridge region of molecules.

^d Left side of the molecule.

^e Right side of the molecule.

Abbreviation: w — weak; m — medium; s — strong; vs — very strong; sh — shoulder; br — broad.

CONCLUSIONS

The H₂ES Schiff-base ligand and its Cu(II) complex have been synthesized and experimentally characterized. The optimized geometries, ¹H NMR chemical shifts, and IR vibrational frequencies of these species have been calculated by the DFT method. The calculated results are in good agreement with the experimental evidence, confirming the suitability of the optimized geometries.

The free H₂ES molecule is not planar and two pyridine rings make a 20° dihedral angle to each other. By complex formation, the four N,N,O,O⁻ coordinating atoms of the dianionic tetradentate ES²⁻ ligand are put roughly in the same plane to each other. These atoms occupy the equatorial positions of the square-pyramidal Cu(II) complex, where the axial position is occupied by the H₂O ligand.

The intramolecular hydrogen bonds between the phenolic protons and the azomethine nitrogens changes the chemical shifts of the phenolic protons to 14.36 ppm in the ¹H NMR spectrum of the free ligand.

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