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N,N′-DIPYRIDOXYL(1,2-DIAMINOCYCLOHEXANE) AND ITS Cu(II) COMPLEX: SYNTHESIS, EXPERIMENTAL AND THEORETICAL STUDIES

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In this work, the N,N′-dipyridoxyl(1,2-diaminocyclohexane) [=H_2L] Schiff-base ligand and its square complex [Cu(L)] are newly synthesized and characterized by IR, mass spectroscopy, ^{1}H NMR, and elemental analysis. The ful optimization of geometries, the ^{1}H NMR chemical shifts (for the H_2L) and their vibrational frequencies are calculated using the density functional theory (DFT) method. The optimized geometry of the ligand is not planar, but each of two pyridine rings and the cyclohexane moiety are in the separate planes. The tetradentate-dianionic L^{2-} ligand occupies the four coordination positions of the square comlex in the N, N, O⁻, O⁻ manner.

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

INTRODUCTION

Due to a variety of applications, including the analytical [1] and industrial use as catalysts [2, 3], the Schiff-base ligands and their complexes are of great importance. Also, they now attracted the attention of biochemists because of their application as models in biological, biochemical, antimicrobial, anticancer, antibacterial, and antifungal activities [4—6].

Pyridoxal is a close analogue of pyridoxine (vitamin B_6) [7], and its deficiency in a human body can lead to serious complications. Manganese dipyridoxyl diphosphate is a contrast agent for the magnetic resonance imaging of the liver [8] and a copper(II) complex of pyridoxal is used in the treatment of diabetic complications [9].

Coordination of Schiff-base ligands to metal ions improves their biological activities [10]. Copper Schiff-base complexes have been used as catalysts for oxidation of alcohols [11]. Also, the biological activities of these complexes have been widely studied, especially the DNA-binding and DNA-cleaving properties [12, 13] and mimic of galactose oxidase [14].

In continuation of our studies [15—19] and hopping to biological and catalytic applications, we report here the synthesis and spectroscopic characterization of the H_2L Schiff-base of pyridoxal and its Cu(II) complex, where H_2L is N,N′-dipyridoxyl(1,2-diaminocyclohexane). Also, the optimized geometries of the ligand and the Cu complex, the theoretical assignment of the IR and ^{1}H NMR spectra has been performed using the DFT method. By comparing the theoretical and experimental results, the validity of the proposed structures for the ligand and the complex are evaluated. The determined structural parameters of the ligand and its Cu(II) complex, and the assignment of the IR bands and ^{1}H NMR chemical shifts can be used as databases for the identification of similar compounds.

EXPERIMENTAL

Material and methods. All of the used chemicals and solvents were obtained from Merck except for pyridoxal hydrochloride which was obtained from Fluka. They were used without further purification. Melting points were measured using an electrothermal 9100 melting point apparatus. Elemental analysis (C, H, N) was carried out using a Heraeus CHN-O-Rapid elemental analyzer. IR spectra were measured on a Perkinz Elemer 783 infrared spectrophotometer. Mass spectra were recorded on a Varian mat CH-7 mass spectrometer. The ^{1}H 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. Pyridoxal hydrochloride (611 mg, 3 mmol) and NaOH (120 mg, 3 mmol) were dissolved in 15 ml of ethanol. Then, a solution of 1,2-diaminocyclohexane (171 mg, 1.5 mmol in 5 ml of ethanol) was slowly added to this mixture and refluxed for 3 h. The orange solid was filtered and washed with cold ethanol and dried in air (Yield: 61 %, m.p.: 153). Anal. Calc. for $C_{22}H_{28}N_4O_4$: C, 64.05; H, 6.86; N, 13.58. Found: C, 63.59; H, 7.95; N, 15.02 %.

Synthesis of the [Cu(L)] complex. The H_2L Schiff-base ligand (41 mg, 0.1 mmol) was dissolved in 10 ml of ethanol. Then a solution of $Cu(NO_3)_2 \cdot 3H_2O$ (24 mg, 0.1 mmol) in 5 ml of ethanol was added dropwise to the ligand solution. The mixture was refluxed for 3 h. After filtering, the filatrate was washed with cool ethanol and dried in 50 °C (Yield: 28 %). Anal. Calc. for $CuC_{22}H_{26}N_4O_4$: Cu, 13.41; C, 55.74; H, 5.97; N, 11.81. Found: Cu, 14.58; C, 55.02; H, 6.45; N, 10.93 %.

Computational details. All calculations were obtained using the gradient-corrected DFT method with the B3LYP functional [20] as implemented in the Gaussian 98 program package [21]. The 6-311+G(d,p) basis sets were used, except for the Cu atom where LANL2DZ basis sets were used.

First, the geometries of the H_2L ligand and its Cu complex were fully optimized, which were confirmed to have no imaginary frequencies 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 ^{1}H 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 [22].

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 [23].

RESULTS AND DISCUSSION

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, ^{1}H NMR and mass) analyses. The elemental analysis results for the H_2L ligand and its Cu complex confirm the proposed formulas. In addition, the molecular ion peaks (m/z (M[+])) observed in the mass spectra of the ligand and the complex (412 and 474, respectively) were found to be in agreement with the proposed formula weight, which may be taken as extra evidence for the correctness of the proposed formulas for the studied species.

Geometry optimization. Computational methods could be considered as complementary to or replacement for experimental ones in the determination of structural parameters for chemical species. Here, the structural parameters of the H_2L ligand and its Cu(II) complex have been theoretically calculated, and they are in agreement with the structural data reported for the similar compounds [15—19, 24—32]. Their selected structural parameters are listed in Table 1. Also, the optimized geometries of the H_2L ligand and the Cu complex with their atom labeling are shown in Figs. 1 and 2, respectively.

In both optimized geometries, the non-planar cyclohexane ring has a *boat* form. The pyridine rings are essentially planar, where the C=C (139.1—142.1 pm) and C=N (133.0—134.8 pm) bond distances are in the expected range [15—19, 33, 34]. The pyridine-C bond lengths for the —CH_2OH and —CH_3 substitutions are about 152 pm and 150 pm, respectively, which are the appropriate sizes for the py-C 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, and O3—C7—C4—C5 dihedral angles are 180.0°, 179.1° and −8.6°, respectively. Also, the azomethine moieties are essentially in the same plane with the pyridine rings.

Table 1

Selected structural parameters of the H_2L *ligand and the* Cu(L) *complex*

| Bond length, pm	Cu(L)	H_2L	Angle, deg.	Cu(L)	H_2L	Dihedral angle, deg.	Cu(L)	H_2L
Cu—O1	192.9	—	O1—Cu—O2	92.8	—	O2—O1—N1—Cu	−2.0	—
Cu—N1	198.6	—	N1—Cu—N2	83.9	—	O2—O1—N1—Cu	−3.7	—
O1—H1	—	99.9	Cu—O1—C1	128.4	—	H1—O1—C1—C5	—	0.7
C1—O1	128.8	134.5	C1—O1—H1	—	106.7	O1—C1—C5—C4	−179.2	179.8
C1—C2	144.9	141.8	N1—Cu—O1	92.2	—	O1—N1—N2—O2	6.1	108.0
C2—N3	131.2	133.0	O1—C1—C2	117.4	118.1	O1—C1—C2—N3	−179.4	179.7
C2—C6	151.4	150.5	C1—C2—N3	122.3	121.1	C1—C2—N3—C3	0	0.3
N1—C8	129.8	128.7	C4—C7—O3	110.0	114.2	C8—C5—C4—C7	0.3	0.7
N1—C17	147.9	146.0	C5—C8—N1	127.1	122.4	C5—C8—N1—C17	117.3	179.2
C17—C18	155.0	155.6	C8—N1—C17	120.4	119.0	C8—N1—C17—C18	39.6	126.1
N1—N2	264.4	297.1	N1—C17—C18	113.8	110.8	N1—C17—C22—N2	32.3	70.7
O1—O2	280.4	655.2	C17—C18—C19	111.9	113.8	C17—C18—C19—C20	−37.5	−63.7
O1—N1	279.6	259.9	C1—C5—C8	121.2	120.0	C8—N1—N2—C16	62.1	−86.8
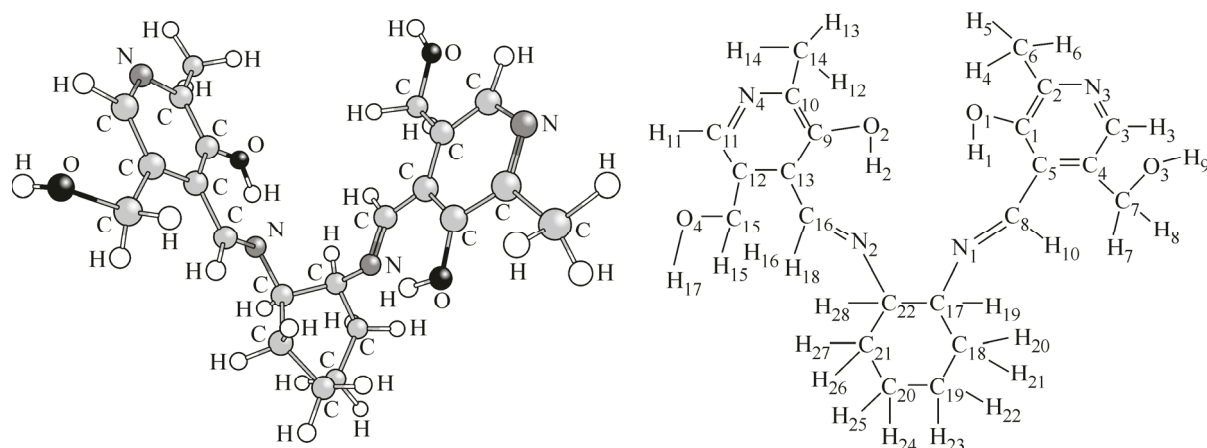
Fig. 1. Structure and B3LYP optimized geometry of N,N′-dipyridoxyl(1,2-diaminocyclohexane) together with its labeling
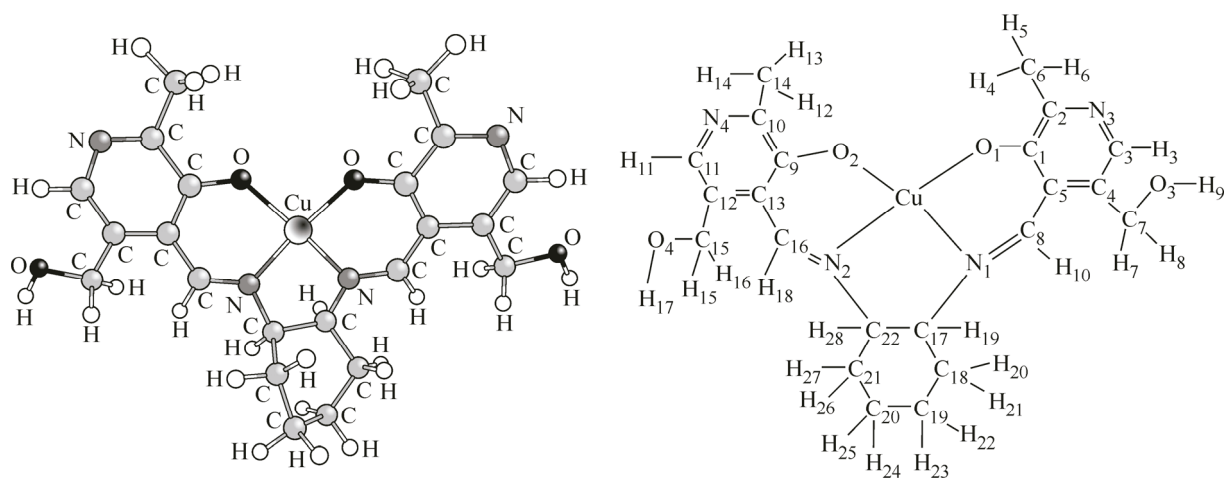

Fig. 2. Structure and B3LYP optimized geometry of the [Cu(L)] complex together with its labeling

The V shape structure of the H₂L ligand is not planar; each of the benzene rings and cyclohexane are in separate planes. The two benzene rings make a dihedral angle of approximately 50.0° to each other. For example, the calculated N3—C5—C13—N4 and C2—C1—C12—C11 dihedral angles are 51.7° and 47.9°, respectively.

The phenolic —OH groups are essentially in the same plane with the corresponding pyridine rings. Calculated H1—O1—C1—C5 and O1—C1—C5—C4 are 0.7° and 179.8°, respectively. The phenolic hydrogen atoms (H1 and H2) are engaged in the intramolecular hydrogen bond interactions with the azomethine nitrogen atoms, which elongates the phenolic O—H bonds. The calculated OH…N and N—O distances are about 169 pm and 260 pm, respectively, showing a strong hydrogen bond. Due to this interaction, the phenolic O—H bonds (100.2 pm) are longer than the alcoholic ones by 3.4 pm.

In the square complex of Cu(II) (Fig. 2), deprotonated L^{2-} acts as a dianionic tetradentate ligand, which has an N, N, O⁻, O⁻ binding mode. The deprotonated phenolic oxygen atoms and the azomethine nitrogen atoms occupy four coordination positions which 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 9.7° and –5.5°, respectively. Rotation around the C17—N1 and C22—N2 single bonds put roughly the two side-aromatic rings in the same plane, providing the structural requirements for the complex formation.

By complexation, the deprotonation of the phenolic oxygen atoms results in a decrease in the C1—O1 and C9—O2 bond lengths, in comparison with the free H₂L ligand (from 134.5 pm to 128.8 pm). However, the C7—O3 and C15—O4 bond lengths are about 142 pm in both free and coordinated ligand.

The coordination of the azomethine nitrogen atoms to Cu increases the C8—N1 and C16—N bond lengths from 128.7 pm for H₂L to 130.80 pm for the Cu(II) complex. Also, the C16—N1 and C22—N2 bond lengths are elongated by 2.4 pm to 148.6 pm in the complex.

Both C16—N1 and C22—N2 bond lengths are 146.0 pm, which is the appropriate size for the single C—N bond, while both C8—N1 and C16—N2 are 128.7 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. In the free and coordinated ligand, the N1—C8—C5—C1 dihedral angle is 0.5° and 1.3°, respectively.

In the complex structure, the ligand is more planar than in the free form. Going from the free ligand to the Cu complex, the N1—C17—C22—N2, O1—N1—N2—O2, C3—C1—C9—C11, and C4—C5—C13—C12 dihedral angles vary from 70.7°, 108.0°, –92.2°, and 45.5°, respectively, to 35.0°, 9.7°, 17.8°, and 1.9°, respectively.

In comparison with free H₂L, the complexation results in a considerable decrease in the O1—O2 and N1—N2 distances from 655.2 pm and 297.1 pm for H₂L and to 275.9 pm and 264.4 pm for the Cu complex. The calculated parameters for the H₂L ligand and its Cu(II) complex are consistent with the previously reported data for the similar Schiff-base ligands and complexes [15—19, 24—32].

NMR spectra of H₂L. In Table 2, the calculated and experimental ¹H NMR chemical shifts (δ) of the H₂L ligand are summarized, where the atom positions are numbered as in Fig. 1. The DFT chemi-

T a b l e 2

Experimental and theoretical chemical shifts of N,N′-*dipyridoxyl*(1,2-*diaminocyclohexane*) *in the* ¹H NMR *spectrum*, δ, ppm

Atom position	Exp.	Theor.	Atom position	Exp.	Theor.	Atom position	Exp.	Theor.
H1, H2	13.96	13.59	H7, H16	4.85	5.00	H4, H12	2.37	2.64
H10, H18	9.32	8.77	H28	3.67	4.45	H5, H13	2.37	2.52
H11	7.93	8.47	H19	3.67	3.93	H20—H27	1.48—1.92	2.42—1.87
H3	7.93	8.37	H6	2.37	2.77	H17	5.27	0.12
H8, H15	4.58	5.17	H14	2.37	2.71	H9	5.27	0.12

Table 3

Selected experimental and calculated IR vibrational frequencies (cm^{-1}) *of the*
N,N'-*dipyridoxyl*(1,2-*diaminocyclohexane*) *ligand and its* Cu(II) *complex*

Experimental frequencies		Calculated frequencies				Vibrational assignment
Ligand	Complex	Ligand	Intensity	Complex	Intensity	
—	—	—		546	59	υ(Cu—N, Cu—O)
723 (m)	732 (w)	713	23	721	9	Breathing of py rings
799 (w)	823 (w)	766	3	807	1.4	Breathing of cyclohexane
1043 (m)	1052 (m)	1032	65	1030	60	δ(CH)Me+υ(ph—C)
		1061	35	1079	28	υ$_{asym}$(py—C—O)$_{alc}$+ +υ$_{asym}$(C—C—C) cyclohexane
		1032	65	1057	50	C17—N1,C22—N2, (C—O)$_{alc}$
1174 (m)	1130 (m)	1197	54	1173	181	υ(ph—C)+υ(C1—C2, N3—C3, C4—C5, C9—C10, N4—C11, C13—C12)
1236 (m)	1235 (m)	1230	34	1236	55	δ$_{ip}$(C—H) aromatic
		1261	24	1281	99	υ(C—O) phenolic
1359 (m)	1357 (m)	1307	16	1306	120	δ$_{wag}$(CH$_2$) cyclohexane
		1343	50	1382	16	[δ$_{wag}$(CH$_2$)+δ$_{ip}$(OH)]alc
		1352	30	1350	70	δ(CH) Me
1395 (vs)	1401 (vs)	*28*		*1397*	281	υ(C1—O1)+υ(*ring*) *Left*
		1395	*101*	1407	89	υ(C9—O2)+υ(ring) Right
1461 (s)	1454 (s,sh)	1483	80	1482	281	υ(ph—C)
1650 (vs)	1603 (vs)	1619	162	1582	697	υ(C8—N1)
		1625	116	1592	182	υ(C16—N2)
2860 (m)	2859(m)	2884	49	2876	8	υ$_{sym}$(C17—H19, C22—H28)
		2895	28	2843	59	υ$_{sym}$(CH)$_{alc}$
2929 (s,br)	2925 (w)	2915, 2924, 2934	44, 25, 72	2916—2941	19—49	υ$_{sym}$(CH$_2$) cyclohexane
		2927	21	2914	33	υ$_{sym}$(CH) Me
		2928	20	2938	20	υ$_{sym}$(CH) Me
		2939	547	—	—	υ(O1—H1)
		2952	15	2953	26	υ$_{asym}$(CH)$_{alc}$
	2936	2953	13	2994	24	υ(C$_8$H$_{10}$)+υ(C$_{16}$—H$_{18}$)
		2977	39	2959	26	υ$_{asym}$(CH) Me
		2980, 2961, 2977	147, 43, 38	2917, 2953, 2965	60, 28, 56	υ$_{asym}$(CH$_2$) cyclohexane
		2952	13	2863	37	υ$_{asym}$(CH$_2$)$_{alc}$
		2977, 3033, 3034	14, 7, 7	3013	13	υ$_{asym}$(CH) Me
3300 (s,br)	3307 (m,br)	2993	374	—	—	υ(O2—H2)
		3084	6	3091	3	υ(C—H) aromatic
		3671	33	3717	53	υ(O—H)$_{alc}$

A b b r e v i a t i o n: sci is scissoring; wag is wagging; twi is twisting; op is out-of-plane; ip is in-plane; alc is substituted —CH$_2$OH groups; left is the left side of the molecule; right is the right side of the molecule; Me is substituted —CH$_3$ groups; w is weak; m is medium; s is strong; vs is very strong; sh is shoulder.

cal shifts are in agreement with the experimental values, confirming the suitability of optimized geometry for H_2L. The only exception is the alcoholic hydrogen atoms (H9 and H17), where the calculated chemical shifts are significantly lower than the experimental ones. It is notable that the experimental data are obtained from $(CD_3)_2CO$ solutions, while the calculations correspond to the isolated molecule. Obviously, the solvent molecules interact with the —OH protons. Also, H9 and H17 can be engaged in intermolecular hydrogen bonds.

A signal at 13.96 ppm is attributed to the H1 and H2 hydrogen atoms, where their engagement in the intramolecular hydrogen bond interaction (O—H…N) shifts their signals upfield [15—19, 35].

Vibrational spectroscopy. The theoretical analysis of the spectra is used as an important tool for the identification of chemical compounds [15—19, 31, 32]. The vibrational modes of H_2L and its Cu complex were analyzed by comparing the DFT and experimental IR spectra. Assignments of the selected vibrational frequencies are listed in Table 3.

In the 3600—2000 cm^{-1} spectral region of the IR spectra, the overlap of the stretching vibrations of O—H bonds with each other and with the C—H stretching modes leads to band broading [15—19, 36, 37]. The deconvolution of this region is given in Table 3. 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 of the O3—H4 and O4—H9 bonds, which can be attributed to the engagement of H1 and H2 in the intramolecular hydrogen bond interaction.

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 [15—19, 37—39]. In the Cu complex, the stretching vibration of C7=N1 and C14=N2 bonds is the most intense band. This band shifts to lower energy than that of the free H_2L ligand, confirming the coordination of H_2L through the azomethine nitrogen atoms (N1 and N2) [15, 16, 37, 39].

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 the 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 the O1 and O2 atoms.

CONCLUSIONS

Herein, the H_2L ligand and its [Cu(L)] complex have been synthesized and characterized experimentally. 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. Also, their ^{1}H NMR chemical shifts and IR vibrational frequencies have been calculated. The obtained results are in good agreement with the experimental evidence, confirming the validity of the optimized geometries for the ligand and the Cu complex.

The optimized geometry of the H_2L ligand is not planar. The H1 and H2 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 O1, O2 and azomethine (N1, N2). The four coordinating atoms of L^{2-} are roughly in the same plane with each other and with the Cu atom. Thus, the optimized geometry of the square complex is significantly more planar than thar of the free ligand.

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 in good agreement with the experimental results, confirming the validity of the optimized geometries for the ligand and its Cu complex.

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