

Synthesis and characterization of a new Schiff base derived from pyridoxal and 2,3-diaminopyridine and its Cu(II) and Ni(II) complexes

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Original Research

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Schiff bases are multi-purpose ligands that are synthesized by condensing primary amines with carbonyl groups in aldehydes or ketones. In this work, my ligand, [2-methyl-4-((E)-((2-(((Z)-(3-hydroxy-5-(hydroxymethyl)-2-methylpyridine-4-yl)methylene)amino)pyridine-3-yl)imino)methyl)-5-(hydroxymethyl)pyridine-3-ol] (H_2L), was prepared from the reaction of 2,3-diaminopyridine and pyridoxal. Ni and Cu Complexes based on this ligand were also synthesized and the construction of the ligand and the complexes have been proved by experimental ways.

The construction parameters and spectral properties of ligands and their complexes were studied using density functional theory (DFT). In the tetrahedral geometry of the two complexes, the dianionic form of the Schiff base acts as a tetradentate ligand and is coordinated with Cu^{2+} and Ni^{2+} ions by two azomethine nitrogens and two phenolate oxygens. The good agreement between the experimental values the IR wave numbers and the NMR chemical shift with the values predicted by DFT shows the validity of the optimized geometries for the studied species.

Keywords: 2, 3-Diaminopyridine; Pyridoxal; Schiff base; Cu and Ni complex; DFT

1. Introduction

Schiff bases offer various advantages as ligands in coordination chemistry. This molecule is synthesized through a condensation reaction in which a $C=O$ group acts as an electrophile and an NH_2 group acts as a nucleophile. Schiff bases have attracted considerable attention in the field of coordination chemistry owing to their unique properties and structural diversity. These substances are significant organic ligands due to their bioactive properties, which include diverse capabilities such as antibacterial, antifungal, anticancer, and antiviral activities [1–4]. Recently, Schiff base compounds have been used in corrosion inhibition and surface. For instance, Furan-2-aldehyde-derived semi-carbazones that oxygen, nitrogen, and sulphur-containing heterocyclic compounds with multiple bonds tend to resist corrosion [5]. Also, Nicotinamide derivatives such as PMN, MMN, NBT, MBN [6], 4-amino-5-(substituted-phenyl)-4H-triazole-3-thiols (ATT1, ATT2, ATT4, ...) [7] and investi-

gated Schiff bases (PSCs) were prepared from amine with salicylaldehyde or benzyl aldehyde are used for corrosion inhibitions [8].

The pyridoxal Schiff bases comprising a variety of amines exhibit an extensive spectrum of hard/soft properties. This characteristic gives rise to diverse coordination modes about various metal ions. The Schiff bases that are derived from pyridoxal, and the corresponding complexes, have found extensive utilization in both industrial and biological arenas [5–15].

The insulin-enhancing properties of pyridoxal Schiff base $Vo(IV)$ complexes are exemplary, as reported in reference [15]. The complexes of dioxidovanadium(V) and pyridoxal Schiff bases exhibit properties of phosphatase inhibitors, as stated in reference [6]. In their study, researchers [9] documented the notable amoebic activities of oxovanadium(V) complexes of pyridoxal Schiff bases. The pyridoxal Schiff bases, specifically the $Cu(II)$ [10, 11, 16] complexes, exhibited remarkable anticancer activity against breast cancer.

Table 1. CHN-elemental analysis and percentage of the M^{2+} metal in structure of the studied species.

species	calculated			experimental		
	C	H	N	C	H	N
$H_2L=C_{21}H_{21}N_5O_4$	61.91	5.20	17.19	58.86	5.09	16.21
$[CuL]=C_{21}H_{19}N_5O_5Cu$	53.79	4.08	14.93	52.13	3.81	14.01
$[NiL]=C_{21}H_{19}N_5O_5Ni$	54.35	4.13	15.09	52.98	3.89	13.86

Nickel has been documented to exist in biological systems in minute quantities [17]. Additionally, it is present in several enzymatic [18]. Therefore, the Nickel complexes have garnered considerable attention due to their significant biological properties, including their efficacy as antiepileptic and anticonvulsant agents [19], as well as their ability to act as antibacterial [20], antifungal [21], antimicrobial [22], anti-proliferative [23], and anticancer agents [24, 25]. The present investigation entails a detailed account of the properties of a Schiff base denoted as H_2L , resulting from conjunction with the Ni(II) and Cu(II) cations. In addition to employing experimental methodologies, the identification of the synthesized compounds was facilitated through the use of DFT techniques.

2. General

All chemicals were Aldrich analytical grade. 1H NMR and ^{13}C NMR spectra were recorded on a Bruker DPX300 spectrometer. FT-IR spectra were recorded on 8400 Model Bruker FT-IR spectrometer $400 - 4000\text{ cm}^{-1}$. Melting points were determined in open capillaries with a "Cintex" melting point apparatus. An Elemental make Vario EL III-CHN analyzer was used for elemental analysis of CHN.

3. Experimental

3.1 Synthesis of the Schiff base (H_2L)

2 mmol (0.407 g) of pyridoxal hydrochloride, 1 mmol (0.109 g) of 2, 3-diaminopyridine and 10 mL of methanol were added to a flask and then the mixture was refluxed for 6 hours. After the end of reaction (monitored with TLC), Solvent eliminated and production, a shiny brown precipitate, was recrystallized in methanol and dried in air (Yield: %68, Dec: 170°C).

3.2 Synthesis of the Cu and Ni complexes based on pyridoxal derived schiff base

(I) Synthesis of the Cu complex

A solution of 1 mmol $CuCl_2 \cdot 5H_2O$ (0.17 g) in 10 mL 1,

4-Dioxan was added slowly to a solution of 1 mmol of Schiff base (0.409 g) in 10 mL methanol. The mixture was stirred at room temperature for 5 hours. The brown precipitate of the production was filtered, washed with cold methanol, and dried in vacuum oven. (Yield: %72, Dec: 258°C).

(II) *Synthesis of the Ni complex* A solution of 1 mmol $NiCl_2 \cdot 5H_2O$ (0.238 g) in 10 mL 1, 4-Dioxan was added slowly to a solution of 1 mmol of Schiff base (0.409 g) in 10 mL methanol, in the same condition above. The mixture was stirred at room temperature for 6 hours. (Yield= %68, Dec: 286°C , Color: dark crimson).

4. Results and discussion

This study describes the synthesis of the H_2L pyridoxal Schiff base and its Ni(II) and Cu(II) complexes. The quantitative determination of the CHN composition and the M^{2+} metal ion concentration within the complex structures have been compiled and collated in Table 1.

The computed values align satisfactorily with the empirical outcomes and confirm the authenticity of the $C_{21}H_{21}N_5O_4$ formula for the Schiff base and the $[M(C_{21}H_{19}N_5O_4)]$ formula for the produced complexes. The present study identifies the complexes as $[NiL]$ and $[CuL]$. The molecular ion peaks at m/z 407, 464, and 469 in the mass spectra of the H_2L , Ni, and Cu complexes respectively. This study shows that the M^{2+} is coordinated by the L^{2-} di anionic ligand in the investigated complexes.

4.1 Tautomerization of the H_2L Schiff base

A preceding study explored the formation of Schiff base originating from PLP (pyridoxal 5-phosphate) and PMP (pyridoxamine-5-phosphate) [26]. The empirical findings suggest that the creation of a Schiff base linking the PLP (pyridoxal-5'-phosphate) and amines is facilitated by a molecule of water. The formation of the Schiff base between PMP (pyridoxal-5'-phosphate) and ketoacids does not require the presence of a water molecule, as the proton transfer mechanism is intramolecular. In the present study,

Table 2. Relative electronic energies (E+ZPE) and 1G values for the studied species in 1, 4-Dioxan H_2L (kJ/mol) solution.

species	E+ZPE	1G
OHOH	0.00	0.00
OHNH	37.11	35.39
NHOH	34.71	31.72
NHNH	44.19	42.54

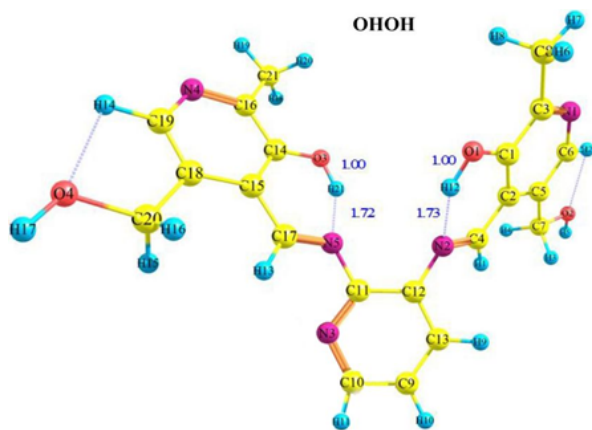


Figure 1. Optimized geometry for the most stable H₂L Schiff base tautomer.

we examine the intramolecular proton transfers involving the H₂L Schiff base.

The structure of the H₂L Schiff base comprises two phenolic –OH protons, namely the H12 and H21 atoms, which interact via intramolecular hydrogen bonds with the corresponding azomethine nitrogens. The H₂L Schiff base under investigation could potentially exist in four distinct tautomeric forms due to the potential occurrence of intramolecular-proton transfers between the azomethine nitrogens (N2 and N5) and the phenolic oxygens (O1 and O3). They are classified as OHNH, OHOH, NHHN and NHOH species in scientific literature. The optimized geometry for the most stable tautomer is shown in Figure 1.

The total of electronic and zero-point energies (E+ZPE) for all species have been determined by performing frequency calculations in the Polarizable Continuum Model (PCM). The collected result is recorded in Table 2.

The present study demonstrates that in methanolic environment of H₂L Schiff base, the OHOH tautomer is the most thermodynamically established form, as corroborated by the computed Gibbs free energy (G) values. The computed values for 1G indicate a significant magnitude that favors the OHOH tautomer. This observation confirms insignificance of tautomers in the H₂L Schiff base. Also, the high barrier energies confirm that the OHOH molecule kinetically prevents tautomerization to other tautomers.

Table 3 presents a set of structural parameters related to the OHOH species. In the non-planar configuration, the two pyridine rings of the pyridoxal moieties form a dihedral angle of approximately 30° to each other. The presence of short N2...H12 and N5...H21 indicates the formation of strong hydrogen bonds between the phenolic protons and azomethine nitrogens.

4.2 Optimized geometries of the complexes

The examination and mass spectra data show the [ML] equation for the Cu(II) and Ni(II) complexes. Since, H₂L loses the H12 and H21 phenolic protons in the presence of triethylamine, the Fukui capacities are utilized broadly to anticipate the dynamic destinations of the chemical com-

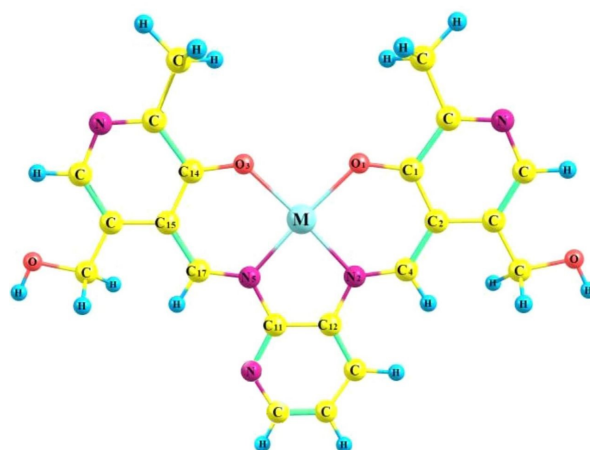


Figure 2. Optimized geometric structure for the synthesized [ML] complexes.

pounds [27]. Optimized geometry and isosurface f^- Fukui outline of L^{2-} ligand is appeared in Fig 2. The f^- Fukui outline is basically localized on the phenolate oxygens as well as the azomethine nitrogens. Since, dianionic L^{2-} forms achieve as a tetradentate ligand, arranges to the metal particles by means of two phenolate oxygens (O1 and O3) as well as two azomethine nitrogens (N2 and N5).

Geometries of the [NiL] and [CuL] complexes have been completely optimized, which are generally comparative. Optimized geometry of the explored complexes is appeared in Fig. 2. Chosen basic parameters of the complexes are recorded in Table 3. The calculated dihedral points such as the C17-N5-C11-C12, C17-N5-N2-C4 and N4-C16-C3-N1 ones illustrate that optimized geometries of the both complexes are more planar than the optimized geometry for the H₂L Schiff base. Moreover, the [NiL] complex is more planar than the [CuL] one. Within the square planar geometry of both the complexes (Fig. 2), the four coordinating atoms are generally within the same plane with the M^{2+} metal particle. By turn around the C11-N5 and C12-N2 bonds, two sides of the L^{2-} ligand lie within the same plane, roughly.

Within the optimized geometries of the H₂L Schiff base as well as the [NiL] and [CuL] complexes, the –CH₃ and –CH₂OH substitutions of the pyridoxal moieties are within the same plane with their comparing pyridine rings. The calculated basic parameters are well in steady with the comparing values detailed for comparative compounds [28–36].

4.3 NMR spectra

This research reports the experimental and DFT-predicted NMR, chemical shifts (δ) of the H₂L Schiff base and its Ni complex. These data are compiled in Table 4 and were obtained using DMSO as the employed solvent. The NMR calculations were executed on the optimized geometries pertaining to the OHOH tautomer of both H₂L and [NiL] entities. The positions of atoms are assigned numerical identification, as illustrated in Fig. 1.

According to the reported data presented in Table 4, the experimental chemical shifts are in concurrence with the DFT-

Table 3. Important structural parameters of Schiff base H₂L (OHOH tautomer) and its [CuL] and [NiL] complexes.

Bond length (pm)	H ₂ L	[CuL]	[NiL]	Angle (°)	H ₂ L	[CuL]	[NiL]	Dihedral angle (°)	H ₂ L	[CuL]	[NiL]
O3-H21	99.8	–	–	O1-H21-N5	146.5	–	–	H21-O3-C14-C15	-1.0	–	–
N5-H21	171.9	–	–	H21-O1-C14	107.7	–	–	O3-C14-C15-C17	-0.4	1.2	-1.8
C14-O3	133.9	129.1	128.8	O1-C14-C15	122.5	125.6	125.0	C14-C15-C17-N5	1	0.2	-2.1
C14-C15	141.4	143.1	143.3	C14-C15-C17	120.3	121.9	122.9	C15-C17-N5-C11	-175.5	178.9	-176.4
C15-C17	145.1	141.9	142.1	C15-C17-N5	122.1	126.9	126.9	C17-N5-C11-C12	141.5	176.0	-163.1
C17-N5	129.8	130.8	130.9	C17-N5-C11	120.5	123.1	121.9	N5-C11-C12-N2	6.0	0.5	-0.8
N5-C11	139.9	140.6	140.4	N5-C11-C12	120.0	116.0	117.1	C17-N5-C11-C10	43.4	-4.7	20.8
C11-C10	140.5	140.3	140.2	N5-C11-C10	122.4	126.0	125.0	N5-C11-C10-N3	180.1	180.1	-179.2
C10-N3	133.4	132.8	133.0	C11-C10-N3	124.4	124.2	124.4	C11-C10-N3-C9	-0.7	0.4	-1.7
N3-C9	134.0	134.0	134.0	C11-C12-N2	119.3	116.0	116.5	C15-C14-C16-C21	-179.8	180.0	180.0
C14-C16	142.0	144.9	144.4	C14-C16-N4	121.1	122.1	122.3	C15-C14-C16-N4	0.1	-0.5	0.8
C16-C21	150.2	150.1	150.2	C14-C16-C21	120.2	118.5	118.6	C15-C18-C20-O4	-179.3	-179.1	179.9
C16-N4	133.1	131.2	130.9	C15-C18-C20	121.3	121.2	121.4	C15-C18-C20-O4	-170.0	-5.5	-11.20
C18-C20	151.4	151.4	151.3	C18-C20-O4	109.5	109.9	109.9	C17-N5-N2-C4	-152.1	7.9	-5.5
C20-O4	142.3	142.3	142.1	O1-M-O3	–	92.1	105.8	C18-C15-C2-C5	-143.5	1.5	-2.3
M-O1	–	193.5	196.5	N2-M-N5	–	84.1	78.4	N4-C16-C3-N1	-160.2	-7.5	-5.5
M-O3	–	198.2	195.9	O1-M-N2	–	91.7	87.4	M-O1-C1-C2	–	-1.0	-6.3
M-N2	–	198.0	213.0	O3-M-N5	–	92.0	88.0	O3-O1-N2-M	–	0.3	2.9
M-N5	–	198.0	212.1	O1-M-N5	–	176.1	165.7	O1-N2-N5-O3	–	-0.06	-2.6
O1 ... O3	430.0	277.7	312.9					C1-O1-N5-C17	–	-173.3	147.9

calculated values, providing support for the appropriateness of the optimized geometries for both the H₂L Schiff base and the [NiL] complex. The computed ¹H NMR chemical shifts of the H12 and H21 protons of the N–H groups in the H₂L Schiff base's OHNH, NHOH, and NHNH tautomers exhibit high values of approximately 15 ppm, which conflict with the experimental chemical shifts. This finding supports the hypothesis that the H₂L Schiff base in methanol solution exists predominantly in the OHOH tautomeric form. The phenomenon whereby a peak situated at 9.31 ppm vanishes in the ¹H nuclear magnetic resonance (NMR) spectrum of

the [NiL] coordination compound serves to corroborate the deprotonation of the phenolic-OH groups upon the occurrence of complexation.

4.4 Vibrational spectroscopy

The present study used DFT calculations to ascertain the vibrational frequencies of the examined compounds. In order to perform a comparative analysis, the experimental and calculated IR spectra of all three compounds were investigated. Table 5 shows experimental and calculate vibrational wave numbers based on DFT. The synthesis of certain species

Table 4. Experimental and calculated DFT chemical shifts of the H₂L Schiff base and [NiL] complex, δ (ppm).

Atom position	¹ H NMR				¹³ C NMR			
	H ₂ L		[NiL]		H ₂ L		[NiL]	
	Exp.	Theo.	Exp.	Theo.	Exp.	Theo.	Exp.	Theo.
H13	8.02	8.81			C14		142.01	
H1	8.12	8.12	7.92	9.13	C12	135.70	135.83	
H2	6.71	7.43	7.32	8.31	C3		135.93	
H12	9.31	11.54	–		C11	127.30	128.73	
H10	6.46	7.22	6.96	8.21	C5		122.11	
H21	9.31	11.61	–		C18		122.38	
H14	7.18	7.15		7.91	C10		126.87	
H16	6.46	6.23		5.27	C16		135.71	
H4	5.12	5.13		5.12	C1	145.32	143.12	
H5	4.94	2.65	4.30		C4	146.39	147.27	
H6	2.43	2.93	3.18	3.10	C9	136.70	138.98	
H20		2.01		3.01	C17		145.11	
H7		2.91	2.34	2.21	C6	120.38	121.81	
H19		2.58		2.21	C21	11.15	11.83	
H18		2.11	2.52	2.69	C7	69.32	60.35	
H8		2.21	2.43	2.51	C2		103.81	
H15	5.16	5.81	5.95	5.21	C19		120.71	
H3	4.94	5.97	4.52	5.97	C15	114.70	102.80	
H9		6.81		8.01	C13		105.11	
H11	7.29	7.14		8.19	C20		52.52	
H17	1.24	1.36			C9	19.05	15.19	

Table 5. Experimental and DFT calculated IR vibrational wavenumbers (1/cm) of H₂L, [CuL] and [NiL] species were selected.

Experimental freq.				Calculated freq.				Vibrational assignment	
HL	[CuL]	[NiL]	HL Freq.	Intensity (km/mol)	[CuL] Freq.	Intensity (km/mol)	[NiL] Freq.		Intensity (km/mol)
2936 (vs, br)	3392 (vs, br)	3381 (vs, br)	2860 3045–3105	43 18	2840 3095–3038	50 12	2842 3093–3035	50 11	–CH ₂ groups (ν _{sym} (C–H)) aromatic hydrogens (ν _{sym} (C–H))
1080 (s)	1011 (m)	1018 (m)	1577 1067	55 155	1559 1065	21 140	1558 1060	18 145	ν(C4–N2) and ν(C=N,C=C) of the pyridine rings ν(C20–O4)+ν(C7–O2)
1387 (vs)	1313 (s)	1379 (s)	1380 687	162 8	1424 731	224 24	1425 722	280 30	ν(C14–O3) + ν(C1–O1) Breathing of the pyridine rings
660 (w)	645 (w)	550 (w)	–	–	520	95	520	84	ν _{asym} (Ni–N,Ni–O)
1194 (m)	1185 (m)	1187 (m)	1192	125	1172	255	1170	250	ν(C12–N2) + ν(C11–N5)
3328 (s)	–	–	2964 2925	37 17	3002 2915	13 17	2992 2914	18 19	ν(C4–H1) + ν(C17–H13) methyl groups (ν _{sym} (C–H))
1587 (s)	1600 (vs)	1600 (vs)	3705 3081	54 432	3705	96	3707	63	ν(O2–H5) ν(O3–H21) + ν(O1–H12)
2743 (vs, br)	–	–	1662	230	1633	432	1635	563	ν(C17=N5) + ν(C4=N2)
1458 (s)	1415 (s)	1489 (s)	2885 3095 3030	30 64 12	2863 – 3016	34 – 16	2865 – 3016	35 – 13	–CH ₂ groups (ν _{asym} (C–H)) ν(O4–H17) methyl groups (ν _{asym} (C–H))
1302 (s)	–	–	1395	27	1406	115	1400	125	ν(C18–C20) + ν(C5–C7)
881 (m)	843 (w)	764 (w)	835 –	28 –	–	–	–	–	δ _{op} (H12, H21) ν _{sym} (Ni–N,Zn–O)
1501 (vs)	1494 (vs)	1540	1269 811	63 38	1278 800	135 32	1286 802	112 28	ν(py–C) δ _{op} (aromatic hydrogens)
–	–	–	1540	130	1539	320	1541	366	pyridine rings (ν(C=N, C=C))

leads to the emergence of a broad band in the region spanning from 2000 – 3600 cm^{-1} in the IR spectra owing to the overlapping of stretching vibrations associated with O–H, N–H, and C–H bonds [37, 38]. Table 5 contains the deconvolution results obtained for the designated region of the IR spectra.

The IR spectra of Schiff base and their complexes exhibit a characteristic fingerprint region within the wavelength range of 1500 – 1660 cm^{-1} . The IR spectrum of the H₂L Schiff base exhibits a highly pronounced band at 1662 cm^{-1} , which is attributed to the stretching vibration of the imine bonds at C4=N2 and C17=N5.

The aforementioned vibration exhibits a blue shift in the infrared spectra of the [CuL] and [NiL] complexes, owing to the coordinated N2 and N4 azomethine nitrogens towards the respective metal ions of Ni²⁺ and Cu²⁺. The aforementioned blue shift represents an increase in frequency of 29 cm^{-1} and 27 cm^{-1} for the [CuL] and [NiL] complexes, respectively.

The band observed at 1380 cm^{-1} in the H₂L spectrum is attributed to the intense $\nu(\text{C1-O1})$ and $\nu(\text{C14-O3})$ stretching vibrations, which exhibit a shift towards higher frequencies in the IR spectra of the synthesized complexes. The observed phenomenon can be attributed to the deprotonation of the phenolic hydroxyl (–OH) moieties, resulting in an elevation in electron density within the bonding regions of C1-O1 and C14-O3 within the complexes. The emergence of novel bands in the infrared spectra of the analyzed complexes is attributable to the coordinative bonds between the metal and oxygen as well as metal and nitrogen, as noted by various earlier studies [37, 38]. Based on the observed data, it can be inferred that the $\nu(\text{O1-H12})$ and $\nu(\text{O3-H21})$ vibrations of the phenolic O-H bonds exhibit lower wavenumbers in comparison to the corresponding vibrations of the alcoholic O2-H5 and O4-H17 bonds.

5. Conclusion

This study involves the synthesis and investigation of a pyridoxal Schiff base H₂L and its Cu and Ni complexes characteristics. Various experimental and theoretical methods were employed for this purpose. Theoretical investigation has been conducted on the tautomerism exhibited by the Schiff base H₂L. According to the DFT computations, the H₂L Schiff base in methanol only contains the OHOH tautomer, which are the tautomer exhibiting the highest stability. The findings demonstrate a satisfactory around concurrence between the computed and the experimental data.

In the complexation process, H₂L is converted into L²⁻ species by losing two phenolic protons and performs as a tetradentate ligand, binding to the Cu²⁺ and Ni²⁺ cations using two deprotonated-phenolic oxygen atoms and two azomethine nitrogen atoms. The donated atoms occupy four coordination positions within the optimized square planar geometries in the investigated complexes.

The structures of the three compounds under investigation exhibit weak and non-covalent hydrogen bonds, specifically in the O2 ... H2 and O4 ... H14 bonds. The optimized geometries of the Cu and Ni complexes reveal the presence

of all four coordinative bonds. The M-N bonds demonstrate greater strength and covalency compared to the M-O bonds.

Ethical Approval

This manuscript does not report on or involve the use of any animal or human data or tissue. So the ethical approval is not applicable.

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Authors Contributions

All authors have contributed equally to prepare the paper.

Availability of Data and Materials

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Conflict of Interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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