Comparative Analysis of the Ni (II) Complex of the N, N'-Bis-(4-Hydroxysalicylidene)-1, 2-Diaminoethane: Combined Experimental and Theoretical Study (DFT/PW91)

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Abstract This study deals with the identification of the title compound, Ni (II) complex, by means of quantum chemical calculations. The optimized molecular structure, vibrational frequencies and corresponding vibrational assignments, ultraviolet-visible (UV-vis) spectrum of the title molecule in the ground state were evaluated using density functional theory (DFT) with the standard PW91 method using the ADF package. The results show that the obtained optimized geometric parameters (bond lengths, bond angles and dihedral angles) and vibrational frequencies were observed to be in good agreement with the available experimental results. Moreover, the calculation of the electronic spectrum was compared with the experimental ones.

Keywords DFT calculations, PW91, Vibrational frequencies, Electronic spectra, ADF

(Sunil et al, 2010). In the past decade, by increasing development of computational chemistry, electronic structure calculations using Density Functional Theory (DFT) have been used extensively to calculate a wide variety of molecular properties such as equilibrium structure, charge distribution, UV-visible, FTIR and NMR spectra, and provided reliable results which are in accordance with experimental data. Quantum chemical calculations and comparing the result with X-ray crystallographic studies of cis dioxomolybdenum(VI) Schiff base complex (Sheikhshoaie et al, 2010) a platinum dimer complex (Akbari et al, 2011) and a dioxidomolybdenum (VI) complex (Sheikhshoaie et al, 2012) have been reported recently.

1. Introduction

Metal complexes of Schiff bases derived from substituted salicylaldehydes and various aromatic amines have been widely investigated, and these compounds represent an important class of coordination chemistry (Maurya et al, 2011; Biswas et al, 2012). Transition metal complexes of tetradentate Schiff base ligands find applications as model analogues of certain metal enzymes (Tang, 2002). Furthermore, the macrocyclic derivatives of these Schiff bases was found to have many fundamental biological functions such as photosynthesis (Singh et al, 2010; Hotchandani et al, 1998) and transport of oxygen in mammalian (Anthonysamy and Balasubramanian, 2005) and other respiratory systems (Alco et al, 2010). The Schiff base complexes of transition metal ions can be applied, particularly in the development of pharmaceutical industries

2. Experimental & Discussion

2.1. Synthesis of the H₂L ligand

The Schiff base ligand, H₂L, was prepared according to the procedure described in the literature (Deligonul and Tumer, 2006). A solution of dihydroxy benzaldehyde (2 mmol in 20 mL ethanol) and the related diamine (1 mmol in 20 mL ethanol) were refluxed for 3 h. The resulting suspension was kept at room temperature prior to being filtered, washed with ethanol and dried with diethyl ether to afford the wanted Schiff base. The product was recrystallized from a suitable solvent for further purification. Orange solid, yield 92 %; m.p. > 250 °C dec.; IR (KBr, cm⁻¹), 3478, 2932, 2893, 2837, 2454, 1635, 1280. UV-Vis (DMSO) λ_{max} (nm): 280, 308, 376. Conductivity (DMSO): 2.38 Ω⁻¹ cm² mol⁻¹.

2.2. Synthesis of NiL Complex

Synthesis of Ni (II) complex of the N, N'-bis (4-hydroxy salicylidene) - 1, 2 diaminoethane, H₂L, was described

earlier (Deligonu and Tumer, 2006). A solution of the metal acetate salt (1 mmol) in absolute MeOH (10 mL) was added dropwise to the H₂L ligand (1 mmol) in absolute MeOH (10 mL) and the mixture was boiled under reflux for 2 h. The obtained NiL. 2 H₂O was filtered off and washed with Methanol, and diethyl ether. Yield 72 %; m.p. : 260 °C dec.; IR (KBr, cm⁻¹), 3471, 2923, 2896, 1612, 1287, 493, 430. UV-Vis (DMSO) λ_{max} (nm): 308, 390, 424, 522. Elemental Anal. Calc. for C₁₆H₁₄N₂O₄Ni . 2 H₂O: (393.02): C, 48.90; H, 4.62; N, 7.13. Found: C, 50.52, H, 4.86, N, 7.84%. Yield Conductivity (DMSO): 2.08 Ω^{-1} cm² mol⁻¹.

2.3. Physical Methods

The infrared spectra of the ligand and complex were recorded on a Shimadzu Prestige 8400 FT-IR spectrometer as KBr disks. Elemental CHN analyses were performed using a Heraeus CHN-O-FLASH EA 1112 elemental analyzer. The conductivity measurements were carried out in DMSO at room temperature using a Metrohm 712 conductivity meter. The electronic spectra of the compounds were recorded in DMSO on a Shimadzu 2550 (UV-Vis) spectrophotometer. Thermogravimetric analysis Ni (II) complex (TGA) was carried out using a TGA-50 SHIMADZU under air atmosphere over the temperature range of 20–1000 °C at a heating rate of 10 °C/min.

2.4. Computational Methods

All the calculations were carried out with the density

functional theory (DFT) (Schäffer et al, 2009) method and the calculations have been performed using the PW91 exchange correlation functional (Perdew et al, 1992), as implemented in the Amsterdam density functional (ADF) 2009.01 package (Velde et al, 2001). The geometry of the complex and H₂L ligand were fully optimized in gas phase using DZ, DZP and TZP basis sets (Van Lenthe and Baerends, 2003). Calculations of harmonic frequencies and electronic spectra at the fully optimized geometries of the ligand and its Ni (II) complex were performed at the PW91 level, for which the used basis set was DZP. Two scale factors, 0.9602 and 0.72, were used for correction of the calculated harmonic vibrational frequencies and singlet-singlet calculated excitations respectively (Merrick et al, 2007; Lahiri et al, 2004).

3. Results & Discussion

3.1. Molecular Geometry

The first task for the computational work is to determine the optimized geometries of the studied molecules. The gas phase optimized structures of the ligand and Ni (II) complex with labeling of the atoms are shown in figures 1 and 2, respectively. The optimized geometrical parameters (bond length, bond angles and bond dihedrals) calculated by DFT/PW91 method with the DZ, DZP and TZP basis sets are listed in Table 1 in comparison to the experimental values.

Table 1. Selected bond parameters of NiL and ligand

	H2L (calculated)			Ni L (calculated)			
	DZ	DZP	TZP	DZ	DZP	TZP	X-ray
Bond length (Å)							
C5-N4	1.339	1.320	1.324	1.321	1.304	1.308	1.295
N4-C1	1.463	1.443	1.446	1.489	1.463	1.467	1.481
C1-C2	1.542	1.530	1.536	1.522	1.514	1.518	1.516
C2-N3	1.472	1.446	1.448	1.488	1.462	1.465	1.475
N3-C6	1.311	1.292	1.295	1.320	1.303	1.300	1.297
C6-C19	1.439	1.435	1.439	1.422	1.413	1.416	1.428
C19-C20	1.434	1.424	1.429	1.441	1.439	1.443	1.417
C20-C21	1.400	1.394	1.398	1.417	1.412	1.417	1.409
C21-C22	1.390	1.387	1.391	1.382	1.377	1.382	1.385
C22-C23	1.412	1.404	1.408	1.417	1.411	1.416	1.396
C23-C24	1.390	1.381	1.383	1.384	1.373	1.376	1.369
C20-O25	1.367	1.360	1.341	1.336	1.299	1.304	1.318
C22-O27	1.406	1.365	1.372	1.409	1.367	1.374	1.363
C5-C9	1.404	1.397	1.401	1.421	1.412	1.415	1.422
C9-C10	1.430	1.416	1.42	1.429	1.415	1.418	1.422
C10-C11	1.374	1.367	1.371	1.379	1.370	1.376	1.362
C11-C12	1.426	1.419	1.422	1.416	1.410	1.414	1.402
C12-C13	1.377	1.374	1.38	1.383	1.379	1.384	1.392
C13-C14	1.432	1.425	1.428	1.421	1.415	1.418	1.398
C14-C9	1.467	1.463	1.467	1.435	1.437	1.440	1.419
C14-O8	1.308	1.277	1.282	1.335	1.298	1.303	1.305
C12-O17	1.407	1.367	1.373	1.408	1.366	1.373	1.375
N3-H29	1.541	1.639	1.677	-	-	-	-
N4-H30	1.069	1.086	1.083	-	-	-	-
O8-H30	1.642	1.546	1.551	-	-	-	-
O25-H29	1.080	1.030	1.019	-	-	-	-
O17-H31	0.998	0.981	0.974	0.997	0.981	0.981	1.088
O27-H32	0.997	0.98	0.973	0.997	0.979	0.979	0.941
C24-C19	1.413	1.402	1.407	1.422	1.413	1.417	1.418
Ni-O8	-	-	-	1.895	1.891	1.889	1.849
Ni-O25	-	-	-	1.920	1.889	1.890	1.853
Ni-N4	-	-	-	1.876	1.873	1.874	1.844
Ni-N3	-	-	-	1.874	1.871	1.871	1.824
Bond angle (°)							
O8 – Ni – N3	-	-	-	177.2	177.6	177.6	176.2
N4– Ni – O25	-	-	-	176.4	176.9	176.4	177.3
N4 – Ni – N3	-	-	-	86.6	85.9	85.8	86.4
N3 - Ni – O25	-	-	-	93.8	94.3	94.3	94.7
O25 – Ni – O8	-	-	-	85.8	85.5	85.6	84.4
O 8- Ni - N4	-	-	-	94.1	94.5	94.5	94.7
Dihedral angles(°)							
N3-Ni-N4-C5	-	-	-	186.8	186.4	186.2	174.4
Ni-O25-C20-C21	-	-	-	187.5	188.0	188.5	176.2
N4-Ni-N3-C6	-	-	-	189.9	190.0	191.1	170.6

The H₂L molecule deprotonates and then acts as a tetradentate dianionic Schiff-base ligand framework, which has a N, N, O⁻, O⁻ binding mode. The calculated C₅-N₄ (1.324 Å) and C₆-N₃ (1.295 Å) bond lengths are of the approximate value for a C=N double bond length, whereas the N₄-C₁ (1.446 Å) and C₂-N₃ (1.448 Å) bond lengths are a bit shorter than a C-N single bond. The calculated C₁₄-O₈ and C₂₀-O₂₅ bond distances are 1.282 and 1.341 Å, respectively, which are somewhat between the length of a C-O single bond (1.43 Å) and that of a C=O double bond (1.20 Å). These values suggest that electron density may be delocalized throughout the N₃-C₆-C₁₉ fragment, the aromatic ring and the C₂₀-O₂₅ bond in the right side of the ligand molecule, i.e. the

appearance of the π -electron resonance in this region. Also, in the left side of this molecule π -electrons are delocalized throughout the N₄-C₅-C₉ fragment, the aromatic ring and the C₁₄-O₈ bond. An intermolecular hydrogen bond, O₈-H₃₀...N₄ is observed in the molecule [Eshtiagh-Hosseini, 2011]. The O₈-H₃₀ bond length is 1.551 Å. This value is larger than O₂₅-H₂₉, O₁₇-H₃₁ and O₂₇-H₃₂ bond lengths, which are 1.019, 0.974 and 0.973 Å, respectively. The calculated N₄...H₃₀ distance is 1.083 Å, which demonstrates that there is a hydrogen bond between these atoms. The inter-nuclear distance determined between O₂₅ and H₂₉, N₃ and H₂₉ in the optimized geometries are 1.019 and 1.677 Å, respectively.

This longer distance is not in favor of the formation of an

intermolecular hydrogen bond of the type $O_{25}-H_{29}...N_3$. The engagement in intermolecular hydrogen bond interactions causes the longer O_8-H_{30} bond than $O_{25}-H_{29}$, $O_{17}-H_{31}$ and $O_{27}-H_{32}$. On the other hand the $C_{14}-O_8$ ($1.282 \text{ \AA}$) bond distance is shorter than $C_{20}-O_{25}$ ($1.341 \text{ \AA}$), $C_{22}-O_{27}$ ($1.372 \text{ \AA}$) and $C_{12}-O_{17}$ ($1.373 \text{ \AA}$). These values indicate that the electron density in the carbon-oxygen bond for $C_{14}-O_8$ is higher than for $C_{20}-O_{25}$, $C_{22}-O_{27}$ and $C_{12}-O_{17}$ bonds. Inversely, the electron density in the O_8-H_{30} bond is lower than in $O_{25}-H_{29}$, $O_{17}-H_{31}$ and $O_{27}-H_{32}$ bonds. Therefore, the acidic nature of the H_{30} proton of the O_8-H_{30} bond is higher than for $O_{25}-H_{29}$, $O_{17}-H_{31}$ and $O_{27}-H_{32}$. Hence, the O_8 atom has a higher ability for coordination to the metal ion than O_{25} , O_{17} and O_{27} atoms. In the complexation region, deprotonating of the phenolic OH group causes a decrease in the $C_{20}-O_{25}$ bond length, while coordination of the N_3 atom to the Ni (II) ion, leads to the elongation of the C_6-N_3 bond. Due to the existing $O_8-H_{30}...N_4$ hydrogen bond, the C_5-N_4 bond length decreases after complex-formation while the $C_{14}-O_8$ bond length increases.

From theoretical values we can find that most of the optimized bond lengths and bond angles are slightly longer and shorter than experimental values. Comparing bond angles and bond lengths of Ni (II) complex at pw91/ DZP and TZP method leads to geometrical parameters which are much closer to experimental values. The small difference between the computed values is due to the reason that calculation belongs to gaseous phase and experimental result belongs to solid phase.

Figure 3. Graphic correlation between the experimental and calculated bond lengths obtained by PW91/DZP of NiL

The correlation graphics between the experimental and calculated bond lengths Ni (II) complex that are obtained by PW91/DZP method is shown in Fig. 3 and the other graphics are similar to that. As a result, the performances of the PW91 method with the DZP and TZP basis setes with respect to the prediction of the bond lengths within the molecule were quite close. The relations between the calculated and experimental wavelength Ni (II) complex are usually linear and described by the following:

$$\begin{aligned} \text{DZ} \quad & \text{bond length exp (Å)} = 0.932 \text{ bond length calc (Å)} \\ & + 0.08, R^2 = 0.985 \\ \text{DZP} \quad & \text{bond length exp (Å)} = 0.923 \text{ bond length Calc (Å)} \\ & + 0.107, R^2 = 0.987 \end{aligned}$$

$$\text{TZP} \quad \text{bond length exp (Å)} = 0.925 \text{ bond length calc (Å)} + 0.101, R^2 = 0.987$$

The O_8-Ni-N_3 , N_4-Ni-O_{25} , N_4-Ni-N_3 , N_3-Ni-O_{25} , $O_{25}-Ni-O_8$ and O_8-Ni-N_4 bond angles are observed 176.2° , 177.3° , 86.4° , 94.7° , 84.4° and 94.7° , which calculated 177.6° , 176.9° , 85.9° , 94.3° , 85.5° and 94.5° , respectively.

Theoretical angle values for the Ni (II) complex show some deviation from the square-planer geometry. For example, the calculated angles obtained for N_4-Ni-O_{25} and O_8-Ni-N_3 are 177.26° and 176.19° respectively, instead of 180° .

3.2. HOMO–LUMO Analysis

The highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) are the main orbital take part in chemical stability. The HOMO represents the ability to donate an electron and LUMO as an electron acceptor. The HOMO and LUMO energy calculated by PW91/ DZP method. The electronic transition absorption corresponds to the transition from the ground to the first excited state and is mainly described by an electron excitation from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO). The atomic compositions of the frontier molecular orbital are shown in Fig. 4.

Figure 4. The atomic orbital compositions of the frontier molecular orbitals for NiL

In the case of our Ni complex, the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) is delocalized on the Ni center. The percentage composition of the lowest unoccupied and highest occupied molecular orbital levels for this compound are: for the HOMO level, $\%Ni = 3.66d_{x^2-y^2} + 34.08d_{xz} + 5.97d_z^2 + 2.00d_{xy}$, $\%O = 1.05p_x + 15.34p_z$, $\%N = 4.86p_z$ and $\%C = 20.54p_z$. For the LUMO level, $\%Ni = 1.28d_{yz} + 2.82d_{xz} + 50.24d_{xy}$, $\%O = 13.48p_y$, $\%N = 3.95p_x + 7.35p_y + 4.58s$ and $\%C = 0$. The detailed contributions from different fragments to the frontier orbital for the complex are given in Table 2.

Table 2. Energies (eV) and composition (%) of frontier molecular orbital's of the complex

Orbital	Energy (eV)	Ni	C	N	O
HOMO - 6	-6.245	$17.46 d_{xz} + 14.64 d_{x^2-y^2}$	$2.41 p_x + 31.58 p_z$	$5.47 p_z$	$4.26 p_y + 9.3 p_z$
HOMO - 5	-6.098	$27.20 d_{x^2-y^2} + 2.82 d_{yz} + 1.25 d_z^2$	$28.24 p_z$	$2.57 p_z$	$11.27 p_y + 10.39 p_z$
HOMO - 4	-6.043	$10.06 d_{x^2-y^2} + 4.62 d_{yz} + 5.29 d_z^2 + 18.34 d_{xz} + 1.08 d_{xy}$	$2.53 p_x + 1.05 p_y + 26.09 p_z$	-	$6.47 p_y + 10.03 p_z$
HOMO - 3	-5.825	$1.26 p_z + 7.34 d_{yz} + 1.43 d_z^2$	$2.37 p_x + 46.19 p_z$	$8.87 p_z$	$13.2 p_z$
HOMO - 2	-5.473	$2.72 d_{x^2-y^2} + 36.68 d_{yz} + 8.27 d_z^2 + 1.93 d_{xy}$	$26.6 p_z$	-	$11.45 p_z$
HOMO - 1	-5.243	$1.96 d_{x^2-y^2} + 10.01 d_{yz} + 59.35 d_z^2 + 12.76 d_{xz} + 9.82 s$	-	-	$3.71 p_y$
HOMO	-4.824	$3.66 d_{x^2-y^2} + 34.08 d_{xz} + 5.97 d_z^2 + 2.00 d_{xy}$	$20.54 p_z$	$4.86 p_z$	$1.05 p_x + 15.34 p_z$
LUMO	-3.348	$1.28 d_{yz} + 2.82 d_{xz} + 50.24 d_{xy}$	-	$3.95 p_x + 7.35 p_y + 4.58 s$	$13.48 p_y$
LUMO + 1	-2.763	$4.58 d_{yz} + 1.10 d_z^2$	$2.84 p_x + 50.25 p_z$	$1.43 p_x + 3.81 p_y + 11.16 p_z$	$6.35 p_z$
LUMO + 2	-2.693	-	$1.19 p_x + 2.02 p_y + 52.77 p_z$	$19.76 p_z$	$4.57 p_z$

3.3. UV-Vis Spectroscopy/Electronic Spectra

The UV-vis spectrum of the free ligand H₂L (recorded in DMSO) exhibits three absorption bands at 280, 308 and 376 nm. The former absorption at 280 nm can be assigned to the $\pi-\pi^*$ transition of the benzene rings. A low-intensity band in the lower energy region at 308 nm is attributable to a $\pi-\pi^*$ transition of the azomethine chromophore. The band around 376 nm is due to the $n-\pi^*$ transition of the non-bonding electrons present on the nitrogen of the azomethine group in the Schiff base (Aranha, et al, 2007; Kianfar et al, 2011)

The electronic spectrum of the complex recorded in DMSO displayed maxima in the 308, 394, 424 and 522 nm. The strongest band in the absorption spectrum appears in the 308 and 394 nm, which is predominantly due to an intra ligand charge transfer ($\pi \rightarrow \pi^*$) (Aranha, et al, 2007), and 424 nm, which is due to a Metal to ligand charge transfer (MLCT). In addition to these bands, a weak and much broader band in the 522 nm has been observed. This very weak band, which arises due to a d-d transition. In order to get a deeper understanding of the transitions occurring in NiL complex, DFT calculations have been performed. The computed excitation energies and oscillator strengths at the PW91/DZP level represent four strong absorptions at 303, 396, 412 and 507 nm. A comparison of the calculated and experimental spectrum for the Ni (II) complex are shown in figures 5 and 6, respectively.

Figure 5. UV spectrum of the Ni (II) complex, (a) experimental, (b) calculated (PW91/TZP) Main calculated transitions from table 3: (1) Excitation 10, (2) Excitation 3, (3) Excitation 2, (4) Excitation 1

Figure 6. UV spectrum of the H₂L ligand, (a) experimental, (b) calculated (PW91/DZP)

Some selected calculated absorptions associated with the excitation energies and oscillator strengths as well as the

assignments of the transitions of Ni (II) complex is given in Table 3.

The assignment of the calculated electronic transitions to the experimental absorption bands was based on an overview of the contour plots and relative energy of the highest occupied (HOMO) and lowest unoccupied (LUMO) molecular orbitals involved in the electronic transitions. The lowest energy absorptions of Ni (II) complex is in HOMO → LUMO transition at 507 nm, where HOMO corresponds to the d_{xz} orbital of Ni (II) and the LUMO is made of mainly the d_{xy} orbital of Ni (II). Therefore, the lowest energy absorption is assigned as the MMCT charge transfer. As given in Table 3, the absorptions of Ni (II) complex at 412, 396, and 303 nm attribute to the MLCT, LLCT/MLCT and LLCT/MLCT transitions, respectively. All assignments agree well with experimental values. We have drawn correlation graphics between the experimental and calculated wavelength that are obtained by PW91 method (Fig. 7). The relations between the calculated and experimental wavelength are usually linear and described by the following:

$$\lambda_{\text{Calc}}(\text{nm}) = 0.944 \lambda_{\text{exp}}(\text{nm}) + 15.58, \quad R^2 = 0.995$$

Figure 7. Graphic correlation between the experimental and calculated wavelength obtained by PW91/DZP of NiL complex

Table 3. Some selected singlet-singlet calculated excitations Ni (II) complex using PW91/DZP method

Excitation	Composition	E(eV)	Oscillator Strength(f)	λ_{theo} (Unscaled(nm))	λ_{theo} ^a (scaled(nm))	λ_{exp} (nm)	Assignment
1	H → L (96%)	1.75985	0.1100E-03	705	507	522	MMCT
2	H → L ₊₁ (85%) H ₋₁ → L (13%)	2.16675	0.1963E-01	572	412	436	MLCT(majour)
3	H → L ₊₂ (95%)	2.25157	0.6983E-02	551	396	394	MLCT+LLCT
10	H ₋₂ → L ₊₂ (76%)	2.94349	0.7667E-01	421	303	308	MLCT+LLCT

^a Scaling factor: 0.72

Table 4. Selected experimental and calculated IR vibrational frequencies (cm^{-1}) of the H_2L Salen ligand and Ni L complex

Experimental frequencies		Calculated frequencies				Vibrational assignment
Ligand	Ni(II) Complex	Ligand (Unscaled (cm^{-1}))	Ligand (scaled (cm^{-1})) ^a	Ni(II) Complex (Unscaled(cm^{-1}))	Ni(II) Complex (scaled (cm^{-1})) ^a	
3478	3471	3635	3490	3649	3503	ν (O-H)
3033	3031	3109	2985	3112	2988	ν (C-H) _{ring}
2932	2923	2955	2837	3036	2915	ν (C-H) _{imini}
2893	2896	3025	2904	3027	2906	ν_{as} (C-H) _{bridge}
2837	2823	2965	2846	2958	2840	ν_{s} (C-H) _{bridge}
2454	-	2510	2410	-	-	ν (N ₄ -H)
1635	1612	1648	1582	1616	1551	$\nu(\text{C}=\text{N})_{\text{imini}}$
1580	1556	1634	1568	1630	1565	$\nu(\text{C}=\text{C})_{\text{ring}}$
1473	1458	1540	1478	1529	1468	$\nu(\text{C}=\text{C})_{\text{ring}}$
1280	1287	1316	1263	1338	1284	ν (C-O) _{phenolic}
-	493	-	-	593	569	ν (Ni - O)
-	430	-	-	471	452	ν (Ni - N _{imini})

Abbreviations: ν , stretching; δ , bending; op, out-of-plane; ip, in-plane; s, symmetric; as, anti-symmetric; ^a Scaling factor: 0.9602

3.4. Vibrational Spectroscopy

The Selected experimental and calculated IR vibrational frequencies (cm^{-1}) of the H_2L ligand and its Ni (II) complex are listed in Table 4.

The discrepancies between the results may come from the application of the harmonic approximation for calculations performed in the vacuum. Nevertheless, all frequencies were corrected by a scaling factor, 0.9602.

Upon comparison it was found that the azomethine $\nu(\text{C}=\text{N})$ stretching vibration is found in the free ligand at 1635 cm^{-1} . This band is shifted to lower wavenumbers (1612 cm^{-1}) in the complex indicating the participation of the azomethine nitrogen in coordination (Singh et al, 2011; Durmus et al, 2011). The coordination of the azomethine nitrogen atom was further supported by the appearance of a new non-ligand absorption band at 430 cm^{-1} which may be assigned to $\nu(\text{Ni}-\text{N})$ vibration (Deligonu and Tumer, 2006). The band observed in the free ligand H_2L at 1280 cm^{-1} due to the phenol hydroxyl substituent $\nu(\text{Ar}-\text{O})$ is shifted to higher frequency value at 1287 cm^{-1} upon complexation, suggesting the coordination via hydroxyl oxygen atom ($\text{O} \rightarrow \text{Ni}$) (Shebl, 2008). This was further confirmed by the appearance of a new non-ligand absorption band at 493 cm^{-1} assignable to $\nu(\text{O} \rightarrow \text{Ni})$ vibration (Deligonu and Tumer, 2006). The free Schiff base exhibits a broad band at 2454 cm^{-1} , attributed to hydrogen bonding between the phenol hydrogen and azomethine nitrogen. The absence of this band in the spectrum of the covalently anchored complex indicates the loss of the hydrogen bond, as expected for the coordination of the deprotonated phenolic oxygen (Kianfar et al, 2010; Kianfar et al, 2011).

3.5. Thermal Analysis

Thermogravimetric analysis (TGA) has been performed to investigate the physical behavior of the complex. The TGA data are listed in Table 5 and the representative TG curve is given in Fig. 8. The TG curve show mainly three stages in the decomposition process. The first stage decomposition temperature is in the range of $26\text{--}260^\circ\text{C}$, with a mass loss of 9.00 %, which corresponds to the loss of 2 mole of water calculated (9.15 %). In the second to third stage of decomposition in the $260\text{--}600^\circ\text{C}$ temperature range, the remaining organic ligand molecule is lost, with a mass loss of 73.66 % (calcd. 71.82 %). The final decomposition product is the NiO in good agreement with the calculated weight 18.3% (19%).

Figure 8. TG curve of NiL complex

Table 5. Thermal data of NiL

Complex	Temp. Range (°C)	n#	Mass loss%		Assignment	Metallic residue
			Found	Calcd.		
Ni L. H ₂ O	26-260 260-600	1	9.00	9.15	-2H ₂ O -L	NiO
		2	73.66	71.82		

4. Conclusion

From the spectroscopic, elemental and thermal analyses data, it can be concluded that Ni (II) complex exists in an square-planar environment with the H₂L ligand coordinated as a tetradentate with a facial (O⁻, O⁻, N, N) donor. A square-planar Ni (II) complex with H₂L has been described and its geometric structure, electronic structure and spectroscopic properties thoroughly investigated by spectroscopic investigation, DFT theoretical level calculations. This has allowed us to look into the correlated relationship of geometric and electronic structure with spectroscopic properties

The electronic properties were also calculated and experimental electronic spectrum was recorded (200–800 nm) with help of UV–Vis spectrometer. The calculate geometric parameters and vibrational frequencies obtained with DFT method are in well agreement with the experimental values obtained for the investigated molecule. In summary, a very complete characterization of studied compound was given in this paper.

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