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DFT AND EXPERIMENTAL STUDY OF SYNTHESIS A NEW LIGAND AND HER COMPLEX OF METAL NI(II).

Annotation: *A novel Schiff base ligand PMBHBH [1□4-phenylene bis (methanylylidene) bis (4-Hydroxybenzohydrazide)] which has not been described in the literature Previously was synthesized by the condensation reaction of 1,4-Benzenedialdehyde (BA) with 4-hydroxybenzohydrazide (HBH). Then the reaction of this ligand with nickel (II) ion were carried out using metal chloride salt by the (1:2) molar ration respectively conduced [Ni_2(PMBHBH)Cl_4]. The ligand and it metal complex have been investigated using the density functional theory ((DFT)B3LYP/6-311++g (2d, p)) by finding the optimal structures for reacting and resulting compounds and also the calculation of cohesion and reaction energies, and finding FT-IR, UV-Vis spectra. And the comparison of theoretical and experimental results, where great agreement appeared between them.*

Key words: *Schiff base, hydrazide, Density Functional theory (DFT), structure, synthesis, IR spectroscopy, UV-Visible Spectroscopy.*

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DFT И ЭКСПЕРИМЕНТАЛЬНОЕ ИССЛЕДОВАНИЕ СИНТЕЗА НОВОГО ЛИГАНДА И ЕЕ КОМПЛЕКСА МЕТАЛЛА NI (II).

Аннотация: *Новый лиганд основания Шиффа PMBHBH [1,4-фенилен-бис (метанилилиден) бис (4-гидроксибензогидразид)], который ранее не описывался в литературе, был синтезирован реакцией конденсации 1,4-бензолдиальдегида (BA) с 4-гидроксибензогидразид (HBH). Затем проводили реакцию этого лиганда с ионом никеля (II) с использованием хлоридной соли металла в молярном соотношении (1: 2) соответственно проводимому [Ni_2 (PMBHBH) Cl_4]. Лиганд и его металлический комплекс были исследованы с использованием теории функционала плотности ((DFT) B3LYP / 6-311 ++ g (2d, p)) путем нахождения оптимальных структур для реакции и получаемых соединений, а также расчета когезии и реакции энергии, и нахождение спектров FT-IR, UV-Vis. И сравнение теоретических и экспериментальных результатов, где между ними обнаружилось большое согласие.*

Ключевые слова: *основание Шиффа, гидразид, теория функций плотности (DFT), структура, синтез, ИК-спектроскопия, УФ-видимая спектроскопия.*

1. INTRODUCTION

A Schiff base is a functional group or chemical compound containing a carbon-nitrogen double bond.it is a result of the reaction between aldehydes or ketones with amines. The electrophilic carbon atoms of aldehydes and ketones can be targets of nucleophilic attack by amines then C=O double bond is replaced by a C=N double bond. hydrazides are a special group of the Schiff base family. they are an important organic compound in the preparation of many organic derivatives such as triazole, hydrazone and others. hydrazides have a variety of various biological effects: anticonvulsant, antidepressant, analgesic, antimicrobial, antitumor, anti-platelet , vasodilator, antiviral , these compounds and their metal complexes have been reported to exhibit a wide spectrum of biological properties[1], Nowadays DFT is being applied as a computational method for calculating the structural properties of molecular systems; it provides greater accuracy in reproducing the experimental values of molecular geometry, vibrational frequencies, atomic charges, dipole moment, etc[2-3].

2 QUANTUM-CHEMICAL STUDY:

Using a Gaussian 09 package [4] have been carry out the DFT/B3LYP [6-311++G (2d, p)] [5-6] calculations for the reacting and possible resulting compounds in the reactions of synthesis of a new ligand and nickel (II) complex.

2.1 Optimized structures:

The optimized structure parameters [bond lengths (A^o) and bond angles(o)] of reactants and resultants were obtained using quantum chemical method DFT/B3LYP [6-311++G (2d, p)], GaussView5 and Gaussian09 programs, the optimized structures of reactants and resultants are shown in figure 1.

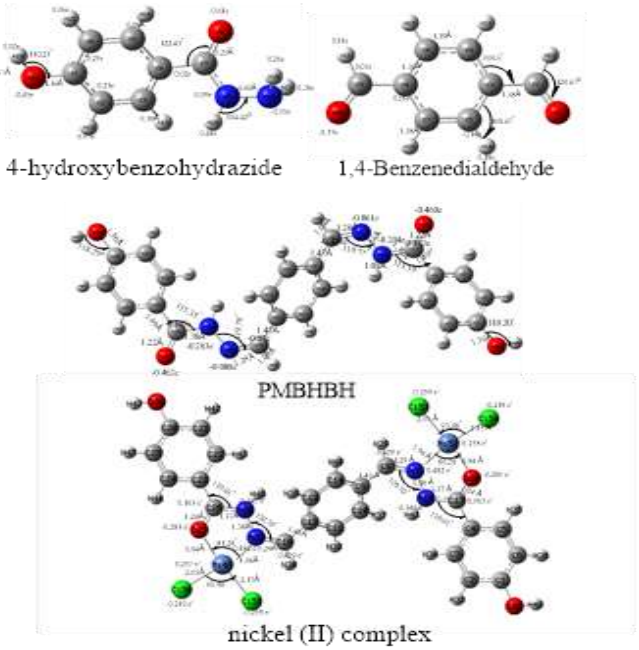


Figure 1: The optimized structures of reactants and resultant.

Table 1: Dipole moment, total electronic energy (Ei), energy of highest occupied molecule orbital (HOMO)energy of lowest unoccupied molecule orbital (LUMO) and energy gap (gap).

Compound		**Dipole moment (Debye)**	**Energies (eV)**			
Name	**Formula**		E_i	ε_{HOMO}	ε_{LUMO}	ε_{gap}
1،4 Benzenedialdehyde	$C_8H_6O_2$	4.83	-12486.0664	-7.6706	-2.9860	4.6846
4-Hydroxybenzoic hydrazide	$C_7H_8N_2O_2$	3.15	-14461.7523	-6.6740	-1.2675	5.4065
Water	H_2O	2.08	-2079.7007	-8.7723	-0.6166	8.1557
IM	$C_{15}H_{12}N_2O_3$	7.72	-24868.1195	-6.5280	-2.7336	3.7944
PMBHBH	$C_{22}H_{18}N_4O_4$	1.06	-37249.6671	-6.5030	-2.3474	4.1556
[Ni_2(PMBHBH)Cl4]	$C_{22}H_{18}N_4O_4$ Ni_2Cl_4	0.0032	-169379.9613	-6.3123	-3.8879	2.4244

2.2. Synthesis reactions:

Table 2: Energies and enthalpies* of possible reactions

The Reaction	Reaction Energy In e. V	
BA + HBH ⟶ IM+H_2O	ΔE_{R1}	-0.0015 e. V
	ΔH_{R1}	-0.0005 e. V
IM+HBH ⟶ PMBHBH+H_2O	ΔE_{R2}	0.504 e. V
	ΔH_{R2}	-0.0020 e. V
BA +2 HBH ⟶ PMBHBH+2H_2O	ΔE_R	0.5025 e. V
	ΔH_R	0.0015e.V

The values of reaction enthalpies indicate that the reaction is endothermic ($\Delta H_R > 0$), while values of reaction energies show that the favorite reaction path is throw formation the intermediate compound (IM) (figure 2).

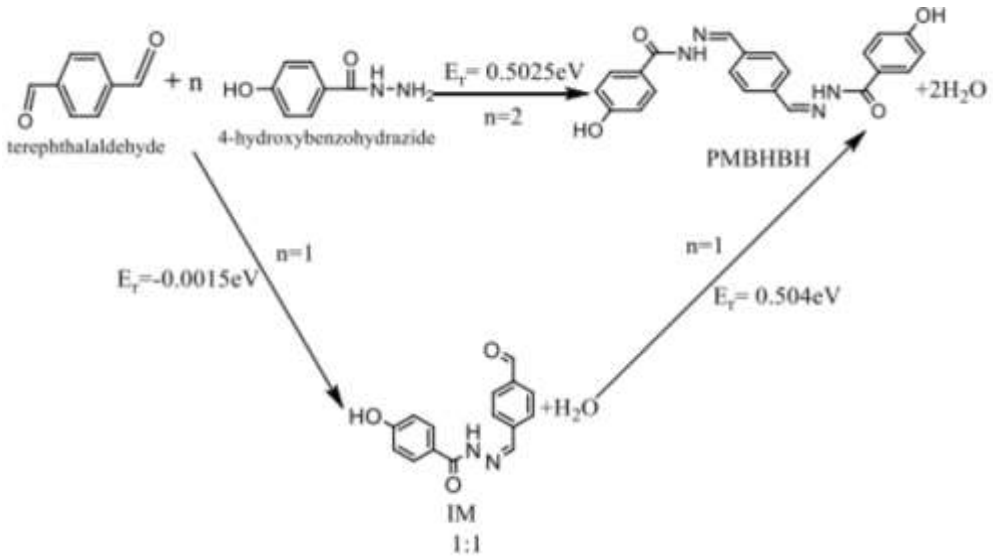


Figure 2: formation mechanism of PMBHBH

Table 3: Energies of possible reactions to complex formation

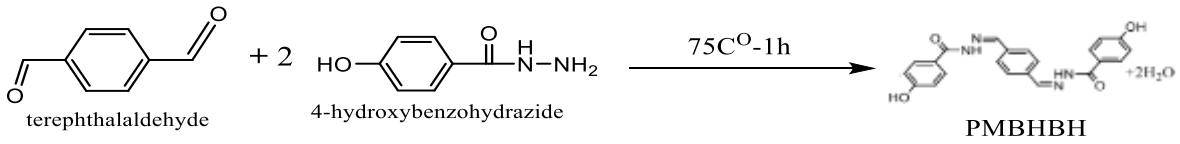
The Reaction	Reaction Energy In e.V	
PMBHBH + $NiCl_2$ ⟶ [Ni (PMBHBH) Cl_2]	E_{F1}	-1.3552 e.V
[Ni (PMBHBH) Cl_2] + $NiCl_2$ ⟶ [Ni_2 (PMBHBH) Cl_4]	E_{F2}	-2.2758 e.V
PMBHBH +2 $NiCl_2$ ⟶ [Ni_2 (PMBHBH) Cl_4]	E_F	-5.7615 e.V

The reaction energies values indicate that the preferred reaction pathway is the formation of the compound [Ni (PMBHBH) Cl_2] and then by catalysis the compound is formed [Ni_2 (PMBHBH) Cl_4]

3. EXPERIMENTAL STUDY:

3.1 Synthesis of ligand PMBHBH:

4-hydroxybenzohydrazide (2 mol, 0.30430 gr) dissolved in hot ethanol 40 ml was added to solution 1,4-Benzenedialdehyde (1 mol,0.136877 gr) respectively, with 3-5 drops of glacial acetic acid in ethanol 5 ml. The reaction mixture was stirred and gently heated under reflux on a water bath for 1h., while the mixture reaction was refluxing the precipitation was formed gradually. After cooling at room temperature the precipitated solid was filtered off by Buchner Fennel, washed with water and hot ethanol, followed by dry diethyl ether (2×5 ml), then dried in a vacuum oven, A precipitate is obtained with a white crystalline yield of (74.9%) and a melting point of (>360C^O).



terephthalaldehyde 4-hydroxybenzohydrazide PMBHBH

3.2 characterization of reactants and resultants, by comparison with quantum spectra:

• FT-IR spectrophotometer by theoretical and experimental methods: The harmonic vibrational frequencies for reactants and resultants were calculated by using (DFT/B3LYP(6-311++ G(2d,p)) method and measured by experimentally . (tables 4) explain vibration values for the basic functional groups for reactants calculated by theoretical and experimental methods.

Table 4: Vibrations of 4-hydroxybenzohydrazide and 1,4-Benzenedialdehyde calculated by theoretical and experimental method.

Compound	**Vibration mod**	**Quantum Value cm^{-1}**	**Experimental value cm^{-1}**
$C_8H_6O_2$	C-H $_{str}$	2892.83	2865.70
	C=O $_{str}$	1765.37	1693.19
	C-H $_{bend}$	1181.81	1198.54
	C-C_{str}	1212.76	1301.72
$C_7H_8N_2O_2$	C- C_{str}	1460.74	1466.60
	C=O $_{str}$	1664.13	1618.95

Vibrations of PMBHBH were calculated by theoretical method and measured by experimental method. (Figures 3), (table 5) explain vibration values for the basic functional groups for reactants calculated by theoretical and experimental methods.

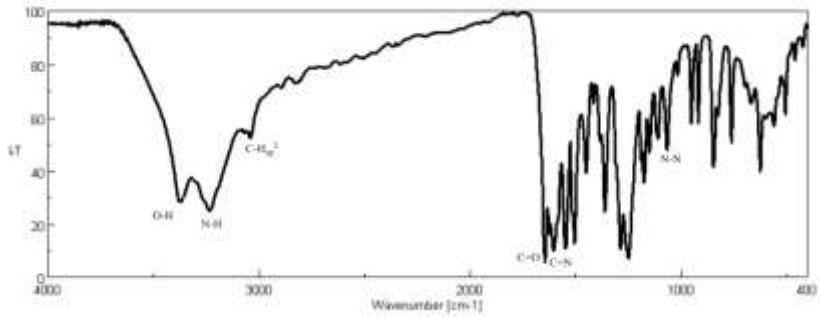


Figure 3: IR spectrum for PMBHBH by experimental method.

Table 5: Vibrations of PMBHBH calculated by theoretical and experimental method.

PMBHBH	Quantum Value cm^{-1}	Experimental value cm^{-1}
$C=N_{st.}$	1647.45	1604.48
$C-N_{st.}$	1268.05	1248.68
C=O	1697.65	1644.98
$C=C_{st}$	1525.78	1547.59
N-N	1050	1066

From (table 5) we notice converge between theoretical and experimental values for an imine ligand PMBHBH. It can be seen that the experiment has a better correlation with the calculations.

- Electronic Absorption Spectra by theoretical and experimental methods: UV-Visible spectra were calculated by theoretical method and measured by experimental method

(figure 4) for an imine ligand PMBHBH.

The spectra of PMBHBH shows peak at (343 nm) which is assigned to a (n→π*) transition and peak (302 nm) which is assigned to a$(\pi \rightarrow \pi^*)$ transition.

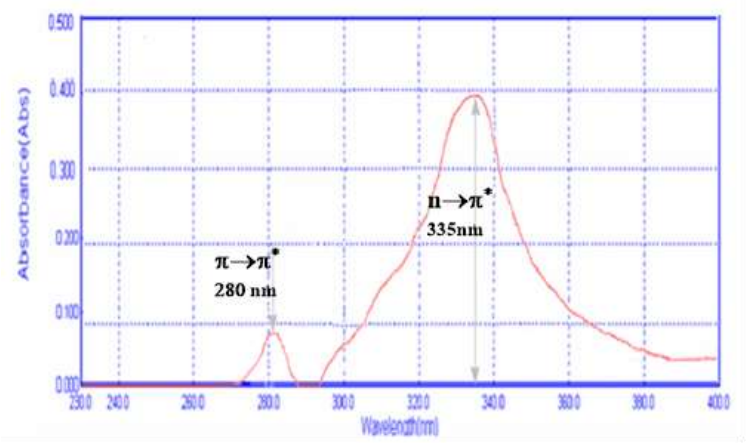
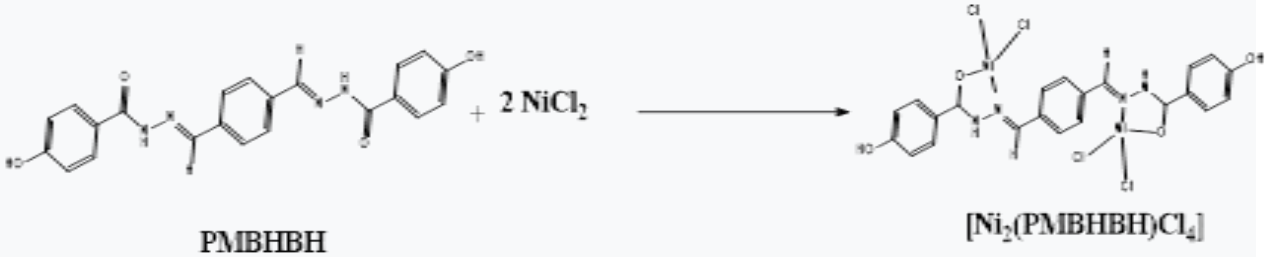


Figure 4: UV spectrum for PMBHBH by experimental method.

Within the UV spectrum of the ligand PMBHBH in DMF peak at (335nm) which is assigned to a (n→π*) transition and peak (280 nm) which is assigned to a $(\pi \rightarrow \pi^*)$ transition due to nitrogen atom and oxygen in the compound.

3.3 Synthesis of complex [Ni_2 (PMBHBH) Cl_4]:

A hot solution of potassium hydroxide KOH (20 mmol, 1.12 g) in ethanol 15 ml was added to a suspension of the ligands (10 mmol) in ethanol 50 ml respectively. To the resulting yellow solution, a hot solution of metal Nickel (II) chloride anhydrous (20 mmol) in ethanol 25 ml was added. The mixture was then refluxed, with constant stirring, for 4 hours to complete the precipitation. The resultant cooling at room temperature, then the precipitated complex compounds were filtered by Buchner Fennel, washed with hot water and ethanol, followed by dry diethyl ether (2×3 ml), then dried in a vacuum oven. A precipitate is obtained with a Dark brown crystalline yield of (86%).



3.4 characterization of resultant, by comparison with quantum spectra:

Vibrations of [Ni_2 (PMBHBH) Cl_4] were calculated by theoretical method and measured by experimental method. (Figures 5), (table 6) explain vibration values for

the basic functional groups for reactants calculated by theoretical and experimental methods.

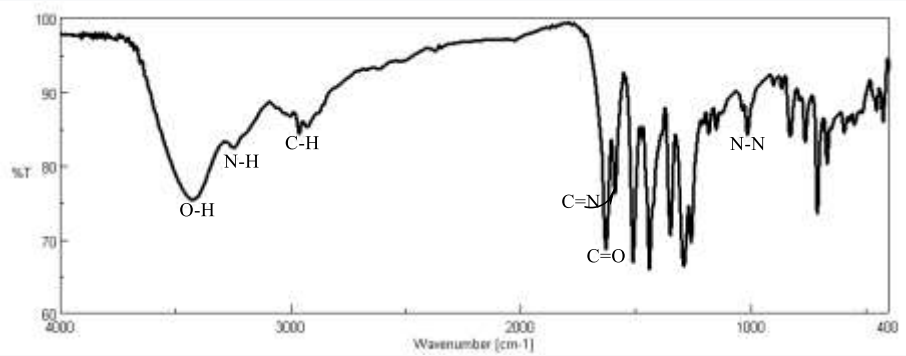


Figure5: IR spectrum for [Ni_2 (PMBHBH) Cl_4] by experimental method.

Table 6: Vibrations of [Ni_2 (PMBHBH) Cl_4] calculated by theoretical and experimental method.

[Ni_2(PMBHBH)]$^{+4}$	**Quantum Value cm^{-1}**	**Experimental value cm^{-1}**
C=$N_{st.}$	**1507**	**1590**
C=O	**1633**	**1629**
N-$N_{st.}$	**1075**	**1014**
Ni-O	**433**	**425**

- Electronic Absorption Spectra by theoretical and experimental methods: UV-Visible spectra were measured by experimental method for [Ni_2 (PMBHBH) Cl_4].Within the UV spectrum of the complex [Ni_2 (PMBHBH) Cl_4] in DMF shows the existence of 4 absorption bands assigned to the transitions, 340 nm (n→π*) ,270 nm(π →π*), and 430,835nm(d-d).

4. SUMMARY AND CONCLUSIONS:

In this work, a new imine compound, namely (PMBHBH)[1،4-phenylene bis (methanylylidene) bis (4-Hydroxybenzohydrazide)] has been synthesized and characterized by various techniques including IR, UV-Vis. The Synthesis of imine ligand PMBHBH were carried out by the condensation reaction of 1,4-Benzenedialdehyde with 4-hydroxybenzohydrazide Theoretically, two pathway

mechanisms were proposed for this process, which consists of formation of intermediate compound (IM) before the ligand (PMBHBH) is formed (I) and formation of this ligand directly (II). These two mechanisms were studied with the density functional theory (DFT/B3LYP (6-311++G (2d, p)). The theoretical calculations demonstrate that Pathway (I) is a more dominant route than Pathway II.

The DFT/B3LYP theory has been successfully employed to support the experimental findings and to evaluate some important parameters, bond length, bond angle, frequency, Mul-liken charge distribution, HOMO-LUMO energy gap (ε gap), etc. The molar ratio of reaction was (1: 2) and the reaction was endothermic and slow ,the yield was 74.9% then nickel (II) complex has been synthesized and characterized by various techniques including IR, UV-Vis the Synthesis of nickel (II) complex were carried out by the condensation reaction of PMBHBH with Nickel (II) chloride anhydrous ,the yield was 86% and were studied with the density functional theory (DFT/B3LYP(6-311++G(2d,p)). The theoretical calculations demonstrate that the reaction energies values indicate that the preferred reaction pathway is the formation of the compound [Ni (PMBHBH) Cl2] and then by catalysis the compound is formed [Ni2 (PMBHBH) Cl4] and the value of the dipole moment of the complex is very small and also the energy gap (ε gap) in the complex is smaller than that in the PMBHBH. The complex is more stable and chemically active than the PMBHBH.

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