

# Synthesis, X-Ray Crystallography and DFT Studies of Ni(II) Complex with Tetradentate

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**Abstract** The paper presents a combined experimental and computational study of new compound {Bis(2R)-2-hydroxy-3-(iminomethyl)cyclohexanol}benzene Nickel(II) complex. The structure of consists of isolated neutral molecules in which the nickel (II) center atom is situated in a slightly distorted square-planar surrounding, the complex was found as monoclinic space group P-1 with  $a = 12.133$  (6),  $b = 15.017$  (7),  $c = 15.393$ (7)Å,  $\alpha = 74.17$ ,  $\beta = 70.92$  (5),  $\gamma = 70.08$  and  $Z = 4$ . The complex has been characterized via single-crystal X-ray diffraction and then the conformation of the molecular structure in the ground state has been calculated using the density functional theory (DFT) methods with generalised gradient approximation (Becke)(Lee–Yang–Parr) GGA BLYP level of theory often being used to obtain more exact results and TZP basis sets, frontier molecular orbitals (FMO) were investigated theoretically. By using Dewar-Chart-Duncanson model, as a basis of the molecular orbital (MO) analysis shown the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital LUMO.

**Keywords:** Nickel (II) complexes, X-ray, DFT, MO, HOMO, LUMO, FMO

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## 1. Introduction

Polydentate Schiff base ligands are important and versatile type of ligands due to the number and variety of donor atoms (like O, N, S, etc.) that they may possess. In addition to that, Schiff base ligands play a key role in the development of coordination chemistry due to their ease of synthesis and their ability to be readily modified both electronically and sterically. Moreover, they easily form stable complexes with most of the transition metal ions. For many years, Schiff base complexes have been of major interest due to their multidisciplinary functions in catalysis, analytical and industrial in addition to their important positions in organic synthesis and enzymatic reactions. [1,2] They are once again topical in connection with self-assembling cluster complexes. [3] Schiff bases are well known for their biological activities, and it has been elucidated that their biological activity is related to their ability to coordinate to metal centers in enzymes.

Even though a number of nickel compounds are considered to have environmental toxicity and carcinogenic nature, many researchers have been interested in investigating the biological, medicinal properties and the structure chemistry of nickel complexes as some of them have shown a variety of biological activities. Among them, nickel Schiff base complexes have proven antibacterial, antimalarial, antifungal and anticancer activities. Synthesis and characterization of nickel complexes with Schiff base ligands having nitrogen and oxygen donor

atoms and evaluation of their ant proliferative properties in cancer cells and normal cells have been described [4].

Although there have been several studies on the synthesis and spectroscopic characterization of diamine Schiff base complexes [5,6] relatively few crystal structures of those complexes containing nickel(II) have been reported.

Using both theoretical methods and experimental techniques has highly interest for many years to form determination of the structural and spectroscopic properties of compounds.

On the past ten years, the computational methods calculating the electronic structure of molecular systems such DFT was found the favorite one, and the information can be Obtained from this methods such molecule geometry, vibrational frequencies, atomic charges, dipole moment, and others and this is because of its great accuracy in reproducing the experimental values of in [7,8] Normally the theoretical calculations belong to gaseous phase willing that the experimentally results belong to solid phase, then the calculated optimized structures were compared with their X-ray structure In the solid state, the differences of bond parameters between the calculated and experimentally values can be considering in outcome file. [9] Recently a whole issue of chemical reviews dedicated to computational transition metal chemistry showed how the introduction of DFT has revolutionized this field.

### 1.1. Theoretical Methods and Computational Details

The Schrödinger Equation mainly detailing wave function theory as method of determining electronic structure was

published by Schrödinger and all information for a system is contained in a wave function. Also time-independent was developed by Schrödinger Equation [10,11,12,13].

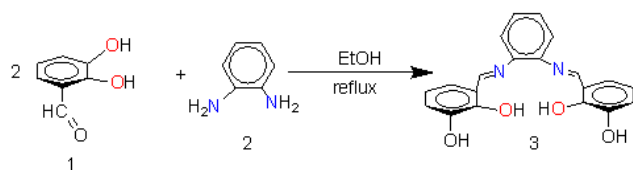
Density functional theory (DFT), discussed in detail in the following sections, is based on the use of electron density as an alternative to wave functions. There are significant advantages to a computational theory based on electron densities. The first is in relation to computational efficiency; the electron density depends on three spatial coordinates in contrast to the  $4N$  coordinates that wave function theory depends on (three spatial and one spin per electron). Therefore, large systems can theoretically be modelled. In addition, electron correlation is conceptually easier to include in DFT.

## 2. Method And Experimental

All materials were reagent grade obtained, from commercial sources and used without further purification.

### 2.1. Synthesis of the Ligand {Bis-((1R,2R)-3-(iminomethyl)cyclohexane-1,2-diol)benzene}(3)

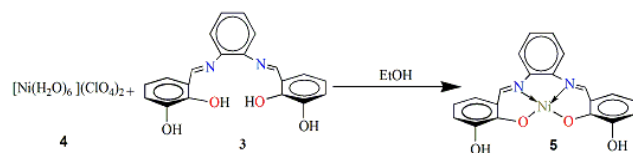
The Schiff base ligand (3) was prepared following the published procedure [14] by treatment of 2,3-dihydroxybenzaldehyde (1) with 1,2-phenylenediamine (2) in a 1:1 molar ratio, under standard reflux conditions (Scheme 1)



Scheme 1. Synthesis of the  $\{C_6H_4N_2(C_6H_3O_2H_2)_2\}$  Ligand (3)

### 2.2. Synthesis of the complex [{Bis-((1R,2R)-3-(iminomethyl)cyclohexane-1,2-diol)benzene}nickel (II)] $[Ni\{C_6H_4N_2(C_6H_3OOH)_2\}]$ (5)

The synthesis of 4 was achieved by slow addition of a solution of the  $\{C_6H_4N_2(C_6H_3O_2H_2)_2\}$  (3) in  $C_2H_5OH$  to a stoichiometric amount of  $[Ni(H_2O)_6](ClO_4)_2$  in  $C_2H_5OH$  at room temperature, which is during that time the color turned to dark red and was stirring for 3 hours under reflux. The red solid resulted in a precipitate of insoluble, was filtered and washed thoroughly with mixture of water-ethanol then with ether and dried in air and finally kept in a desiccators over silica gel. Work-up yielded  $[Ni\{C_6H_4N_2(C_6H_3OOH)_2\}]$  (5), as a red-brown material in 60% yield after slow dried in air at room temperature (Scheme 2). The resulting solid was stable at air. X-ray diffraction were obtained by recrystallization from a mixture of DMF/ethanol



Scheme 2. Synthesis of the  $[Ni\{C_6H_4N_2(C_6H_3OOH)_2\}]$  (5)

## 2.3. X-ray Crystallography

The data of the complex was collected using a Bruker SMART APEX CCD diffractometer equipped with graphite monochromated Mo K $\alpha$  radiation ( $\lambda = 0.7107 \text{ \AA}$ ) at 296 K. Absorption corrections on the data were made using SADABS. [15] The structure was solved and refined by SHELXL97 [16] and implemented in the WinGX [17] program suite. Molecular graphics were drawn by using ORTEP-3. [18] Material for publication was prepared using publCIF. [19] The structure was solved by direct-methods and refined by a full-matrix least-squares procedure on F $^2$  with anisotropic displacement parameters for non-hydrogen atoms.

## 2.4. Computational Procedures

All the calculations were performed by using Amsterdam Function 2012package (ADF2012) [20,21] package and the generalized gradient approximation (GGA) functional [22] on the personal computer with restricting a  $C(2)$  symmetry for the title complex. while nickel was modelled with a singlet- $\zeta$  basis set.

The local density approximation was employed for the optimizations, [23] along with the local exchange-correlation potential. Different electronic configurations were defined using the 'occupations' key. All structures were optimized using the gradient algorithm of Versluis and Ziegler [24]. For modeling, the initial guess of the complex was first obtained from the X-ray coordinates. The molecular structure of the title complex in the ground state (in vacuo) is optimized by GGA BLYP methods and TZP, core Large basis sets. Besides, the molecular electrostatic potential (MEP), frontier molecular orbitals (FMO) of the title complex were determined by theoretical calculation results.

## 3. Result and Discussion

### 3.1. Structural Description of the Complex $[Ni\{C_6H_4N_2(C_6H_3OOH)_2\}]$ (5)

The title complex  $[Ni\{C_6H_4N_2(C_6H_3OOH)_2\}]$  (5) was crystallizing in the monoclinic space group P-1 with three molecules in unit cell and then used ORTEP-3 [18] and finally chemcraft as shown in Figure 1.

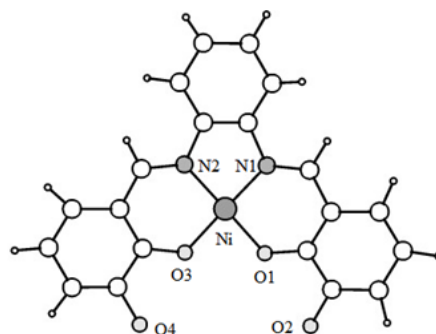


Figure 1. An Chemcraft view of the X-ray in title complex with the atomic numbering scheme. Displacement ellipsoids are shown at the 30% probability level

The asymmetric unit in the crystal structure contains the Ni(II) and four coordination {Bis-((1R,2R)-3-(iminomethyl)cyclohexane-1,2-diol)benzene} molecules.

The Ni(II) atom displays a distorted square-planar coordination geometry, with two N atoms and two O atoms from four the ligand in the equatorial plane position. Ni–N1, Ni–N2, and Ni–O1 and Ni–O3 bond lengths are 1.863Å, 1.858Å, 1.844Å and 1.868Å, respectively, and are within the average values found in a Cambridge structural database search [25,26,27] for compounds having two carbon atoms in the imines bridge. These bond lengths detailed are shown in Table 1.

**Table 1. X-ray and DFT calculated bond lengths (Å) of (5)**

Bond	Length / Å	DFT (calu.)
Ni-N(1)	1.863	1.97
Ni-N(2)	1.858	1.97
Ni-O(3)	1.868	1.98
Ni-O(1)	1.844	1.98
N(1)-C(7)	1.33	1.27
N(1)-C(8)	1.414	1.41
O(1)-C(1)	1.302	1.30

The chelate bite angle, defined by the  $\angle$  N(1)-Ni-N(2) bond angles of  $85.61^\circ$  derives from the short two-carbon phenyl bridge. The  $\angle$  O(1)-Ni-O(3),  $\angle$  O(1)-Ni-N(2) and  $\angle$  N(1)-Ni-O(3) bond angles are  $83.99^\circ$ ,  $178.91^\circ$  and  $179.41^\circ$  respectively, these bonds angles detailed are shown in Table 2. From the point of view of catalysis this is encouraging as a monomeric complex could potentially be more active than a dimer.

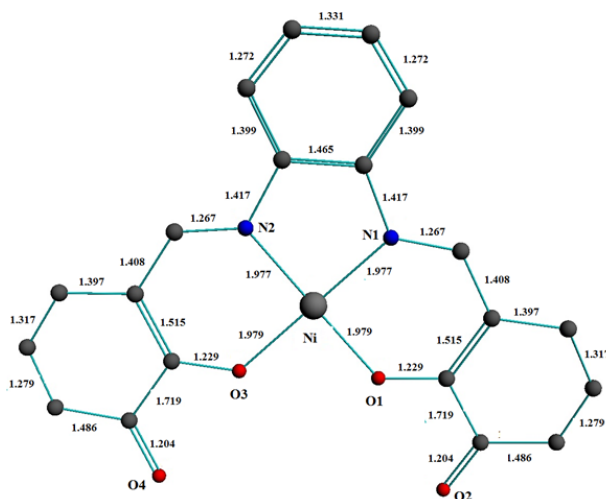
**Table 2. X-ray and DFT calculated bond angles ( $^\circ$ ) of (5)**

Fragment	Angle ( $^\circ$ )	DFT (calu.)
N(1)-Ni-N(1)	85.61	85.50
O(1)-Ni-O(3)	83.99	93.80
O(1)-Ni-N(1)	95.42	90.30
O(3)-Ni-N(2)	94.97	90.30
O(1)-Ni-N(2)	178.91	175.80
N(1)-Ni-O(3)	179.41	175.80
Ni-O(1)-C(1)	125.70	130.20

### 3.1. Structural and Electronic Properties

#### 3.1.1. Molecular Orbital (MO) Analysis

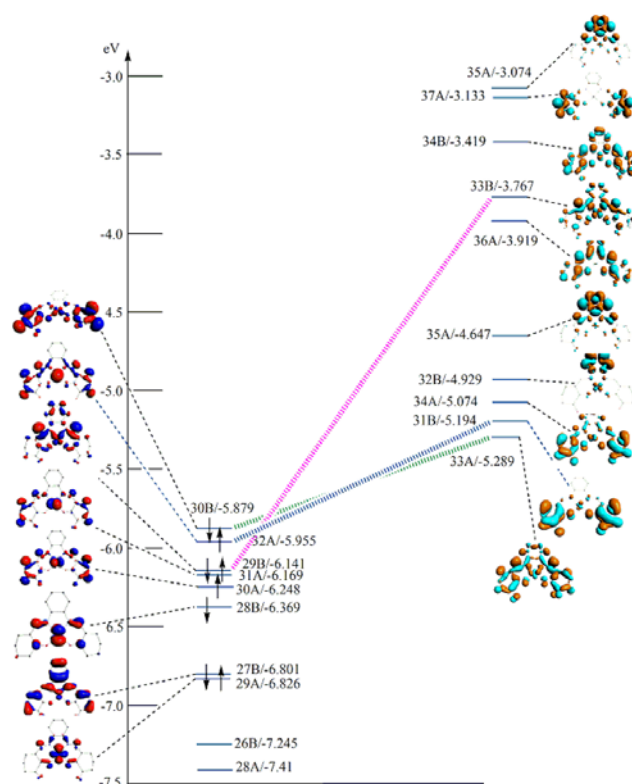
The structural view from output file from DFT showed in Figure 2. Also parameters were calculated bond lengths and bond angles of (5).



**Figure 2.** An Chemcraft view of the complex (5) with the atomic numbering shown at the 30% probability level

It is seen that there are no significant differences to the experimental values was obtained by X-ray crystal diffraction as shown in Table 1, this result serves as a validation of the computational method and it was noted here that the experimental results belong to solid phase and theoretical calculations belong to gaseous phase.

The molecular orbitals (MOs) which go to build up the total wavefunction for the system provide valuable insight into the interactions that give rise to bonding. Molecular orbitals (MOs) that for complex (5) give us more specific and detailed information about the electronic interactions occurring in a molecule. The highest occupied molecular orbital (HOMO) and the lowest lying unoccupied molecular orbital (LUMO) are named as frontier molecular orbitals (FMO) as shown in Figure 3.



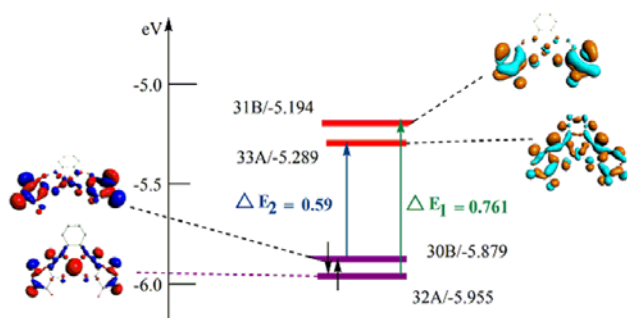
**Figure 3.** frontier molecular orbitals (FMO) of the complex (5)

The basis of the molecular orbital (MO) analysis is the Dewar-Chatt-Duncanson model, [28] which is can be used to the best describing the bonding of ligand to the metal centre.

The distributions and energy levels of the HOMO and LUMO orbitals computed for the title complex  $[\text{Ni}\{\text{C}_6\text{H}_4\text{N}_2(\text{C}_6\text{H}_3\text{OOH})_2\}]$  (5) has 30B and 32A for occupied molecular orbitals HOMO and HOMO-1 respectively and the value of energy calculated found at -5.879 eV and -5.955 eV respectively, again 33A and 31B for unoccupied molecular orbitals LUMO and LUMO+1 and the value of energy are found to be at -5.289 eV and -5.194 eV respectively, are delocalized over the metal and the ligand as indicated by the percentage % (d/Ni/ligand), the Ni/ligand orbital mixing (i.e., 6/32 and 46/20% for MO #30B and 32A, respectively).

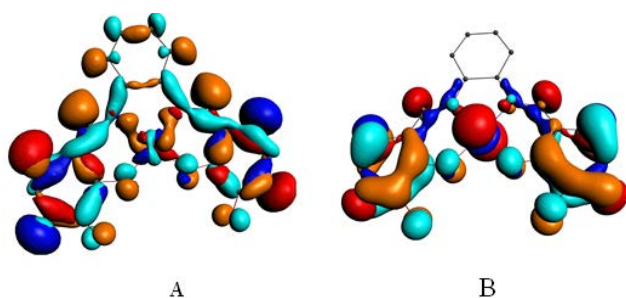
The energy separation ( $\Delta E$ ) between the HOMO & LUMO and HOMO-1 & LUMO+1 are 0.59 eV and 0.761 eV respectively Figure 4. A molecule with a large energy gap implies higher stability and lower chemical reactivity, at the meantime a small energy gap is more

polarizable and is generally associated with a high chemical reactivity and low kinetic stability and is also termed as soft molecule [29].



**Figure 4.** Energy levels of the HOMO & HOMO-1 and LUMO & LUMO+1 orbitals as they computed

In  $[\text{Ni}\{\text{C}_6\text{H}_4\text{N}_2(\text{C}_6\text{H}_3\text{OOH})_2\}]$  (5), these MOs appear to be essentially metallic, with a strong 3d orbital character and contribution from the tetradentate ligand as indicated by the percentage % (d/Ni/ligand). The 3d block is deep in energy, confirming its slight participation in the metal-ligand bonding. The MOs immediately below are slightly different in energy, and their orbital composition shows that the 3d orbital weights remain small. The clasp between HOMO with LUMO and HOMO-1 with LUMO+1 can be seen in the Figure 5, that to give more information about electronic distribution over the complex.



**Figure 5.** HOMO & LUMO (A) and HOMO-1 & LUMO+1 orbitals (B)

## 4. Conclusion

The computational chemistry presented in this paper shows that the investigation, molecular structure, molecular electrostatic, HOMO-LUMO analysis of {Bis(2R)-2-hydroxy-3-(iminomethyl)cyclohexanol}benzene Nickel(II) complex has been studied using (Becke)(Lee–Yang–Parr) GGA BLYP level and TZP basis sets calculations. They are compared with the calculated geometric parameters (bond length, bond angle) with their experimental data. It is seen that there are no significant differences, when the experimental structure is compared with theoretical structures. It was noted here that the experimental results belong to solid phase and theoretical calculations belong to gaseous phase. The predicted nonlinear optical (NLO) properties of the complex are great. Besides these sites provide information concerning the region from where the compound can undergo intermolecular interactions. At the meantime via the Dewar-Chatt-Duncanson model, as a basis of the molecular orbital (MO) analysis was showed the correlation between

the highest occupied molecular orbital (HOMO) and lowest occupied molecular orbital LUMO.

## 5. Supplementary Data

Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publications NOS. CCDC 1051307. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK, (fax: q44-1223-336033 or e-mail: deposit@ccdc.cam.ac.uk).

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