

Synthesis, Characterization and Theoretical Study of 1,2(2,2-dihydroxy benzelidenamine) Phenyl Complexes

Dina A. Najeeb¹, Ahmed Ahmed¹ and Muhammad Rahimi Yusop²

¹ Department of Chemistry, College of Science, Al-Nahrain University, Baghdad-Iraq.

² School of Chemical Sciences and Food Technology, Faculty of Science and Technology, University Kebangsaan Malaysia, 43600 UKM Bangi, Selangor, Malaysia.

Abstract

New schiff base and its metal complexes of Co(II), Ni(II), Fe(II) and Cu(II) has been synthesized from *O*-phenylenediamine and *O*-hydroxyl benzaldehyde. The ligand and its complexes were described the distinctive nature of element by elemental analysis (C,H,N), FTIR, UV-Vis, and magnetic susceptibility. Hyperchem-7 software was used in this project for a theoretical treatment of the synthesized complexes under gas phase condition. PM3 method was used to calculate: heat of formation (ΔH_f°), binding energy (ΔE_b) and total energy (ΔET) for both ligand and its complexes at 298 K. Additionally, the electrostatic potential of the free ligand (L) was calculated to see the active sites of the product complexes. According to the results of this research, the produced complexes form [ML] type composition where L ligand=1,2(2,2-dihydroxy benzeliden amine). Phenyl and M=Co, Ni, Fe and Cu. [DOI: [10.22401/JUNS.20.3.03](https://doi.org/10.22401/JUNS.20.3.03)]

Keywords: Metal complexes, Schiff base, Semiepirical PM₃, Hyperchem.7, Theoretical Study.

Introduction

The methods of the synthesis of new transition metal complexes have been extensively studied due to their probable applications in broad ranges of science. Moreover, Schiff base and its ligands have the ability to coordinate with different metals [1-4]. The necessity of Schiff base ligands and their metal complexes are due to the range of applications such as catalysts [5,6], medicine [7,8], crystal engineering [9], anti-corrosion agent [10,11]. Schiff bases are broadly explored due to the flexibility in synthesis methods, and also due to its selectivity and sensitivity for the metal ion. Furthermore, Schiff bases possesses similarities in structure with natural biological compounds in presence of azomethine group (-N=CH-) which imports in explaining the mechanism of transformation and racemization reaction in terms of biology [12, 13]. Oxygen, nitrogen etc. are the donor's centers in Schiff bases chelation for the synthesis of their metal complexes which have potential biological activities [14].

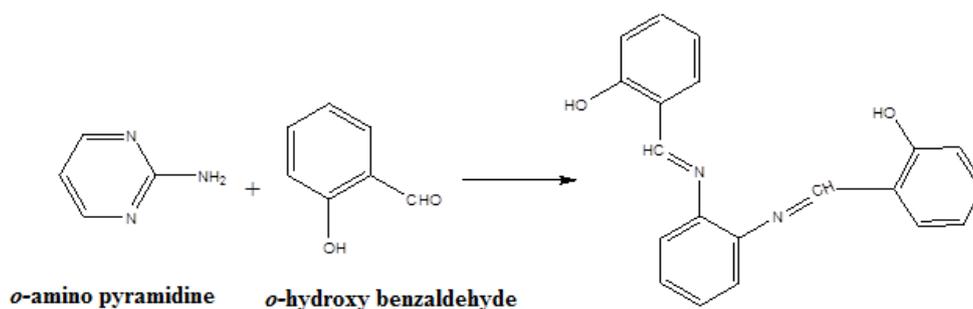
Experimental

The chemical materials that have been used in this project were analar analytical stander and purchase from Sigma-Aldrich chemical industry. The solvents used were distilled in

the purpose of high purity to be use in any test in this research under standard procedures. IR spectrometry from shimadzu (FTIR-8300) spectrophotometer were used with KBr medium disk. Ethanol was used as a reference solution in all the UV-Vis spectrometric measurements of all the complexes using Shimadzu UV-1650PC spectrophotometer with (200-1000) nm range. The magnetic susceptibility was measured for the newly prepared complexes at 25C° using (Magnetic susceptibility Balance) from Johnson Maltery.

Preparation of ligand (L)

A mixture of *o*-aminopyrimidine (0.021 mol, 2g) and *o*-hydroxyaldehyde (0.021 mol, 4.58g) dissolved in ethanol and acidified with several drops of glacial acetic acid, after that the reaction mixture was refluxed for 6-hrs by air condenser. Then the precipitated be washed, filtered and re-crystallized by ethanol, and become dry in desiccator over anhydrous (calcium chloride) vacuum. The general arrangement of ligand obtained from chemical analysis and spectral methods were shown in Scheme (1).



Scheme (1) Reaction scheme of the preparation ligand.

Metal complexes Preparation procedure

New complexes of the cationic ions of Fe(II), Co (II), Ni (II) and Cu(II) have been prepared by reacting solution of metal halides with solutions of ligands in molar ratio 1:1. The colored complexes which were separated under relatively low temperature, then the product complexes were filtered and washed with ethanol to remove unreacted chemicals, finally the precipitate were allowed to dried in oven.

Result and Discussion

Table (1) illustrates all the ligand and their complexes physical properties tested in this project. All metal complexes are colored, stable in air at room temperature. These are incapable of being dissolved in polar solvent and soluble in organic solvents and all of them are non-electrolytes in DMF [15].

Table (1)
Physical and Analytical Data measurements of the newly prepared Schiff Base and their metal Complexes.

Compound	Molecular Weight	Product color	% products	M.Pt (C°)	Found (Calc)%					(Molar) (conductance) Ohm ⁻¹ cm ² mol ⁻¹ x 10 ⁻³
					C	H	N	O	M	
Ligand(L)	316	Brown	77	235	75.00 (75.94)	5.04 (5.06)	8.83 (8.86)	10.10 (10.12)	-----	-----
[FeLCl ₂]	442.54	Brown	62	265	54.20 (54.23)	3.13 (3.16)	6.31 (6.32)	7.22 (7.23)	12.55 (12.57)	1.34
[CoLCl ₂]	445.83	Green	63	258	53.71 (53.83)	3.12 (3.14)	6.24 (6.28)	7.10 (7.17)	13.19 (13.21)	4.95
[NiLCl ₂]	445.59	Red	69	267	53.85 (53.86)	3.12 (3.14)	6.25 (6.28)	7.16 (7.18)	13.13 (13.17)	3.14
[CuLCl ₂]	450.45	Green	69	278	53.25 (53.28)	3.10 (3.10)	6.20 (6.21)	7.10 (7.10)	14.10 (14.10)	4.03

[IR spectra]

The main character of the coordination ligand and their metal ions has been determined by IR spectra as shown in Table (2). Two strong absorption bands at 1656cm⁻¹ and 3417cm⁻¹ is an indication of the azomethine (-HC=N-) and phenolic (-OH) group respectively as in Schiff base ligand. Furthermore, the hydroxyl group in ligand (I) was absorbed at (3417cm⁻¹), whereas disappeared in the IR-spectrum of the Schiff-base complexes which might be due to the

deprotonating and coordination of the main matrix to the metal ion to form (M-O).

In addition, the spectra of the prepared complexes show some new bands in between (605-642 cm⁻¹), (540-585cm⁻¹) and (388-329cm⁻¹) which might be because of the formation of (M-O), (M-N) [16] and (M-Cl) chemical bonds [17-21].

Table (2)
IR Spectral Measurements of ligand and their complexes.

Compound	ν (-OH)	ν C=N	ν M-O	ν M-N	ν M-Cl
Ligand	3417	1656	-----	-----	-----
[FeLCl ₂]		1615	605	540	388
[CoLCl ₂]		1600	624	557	368
[NiLCl ₂]		1598	637	573	346
[CuLCl ₂]		1590	642	585	329

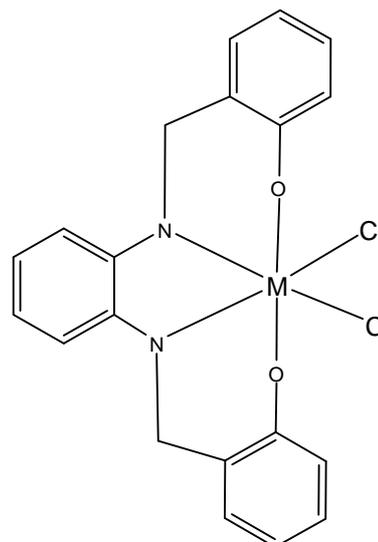
Electronic spectra and magnetic susceptibility of the complexes

The ligand (L) in ethanol was exhibited two sets of highly intense bands, the first one appeared at 36359 and 38613 cm^{-1} , and the other bands set appeared at 32998 and 31655 cm^{-1} respectively. The first bands group might be attributed to $\pi \rightarrow \pi^*$ transitions of the carbonyl group also might be due to conjugated ring system. However, the second two bands might be related to $n \rightarrow \pi^*$ transition which masked by the extension of the second band set [22]. The iron (II) complex electronic spectrum absorption at 11764 cm^{-1} band assignable to the ${}^5T_{2g} \rightarrow {}^5E_g$ transition consistent with an octahedral geometry for iron (II) complex [23-25].

The room temperature magnetic moment (5.22 μB) corresponds to an octahedral geometry of iron (II). Electronic spectra of Co(II) complex exhibit three absorbance peaks at 22779 cm^{-1} , 16339 cm^{-1} and 14925 cm^{-1} . These absorbance maxima due to ${}^4T_{1g}(\text{F}) \rightarrow {}^4T_{1g}(\text{P})$, ${}^4T_{1g}(\text{F}) \rightarrow {}^4A_{2g}(\text{F})$ and ${}^4T_{1g}(\text{F}) \rightarrow {}^4T_{2g}$, transitions correspondingly, because of the characteristics of the Co(II) metal ion octahedral geometry [26,27]. Magnetic moment is found to be 3.85 μB . A broad low intensity band noticeable at 14798 cm^{-1} which is caused by the d-d transition of the Cu(II) ion, this band is of low molar absorptivity being Laporte forbidden and could be assigned to $E_g \rightarrow {}^2T_{2g}$ transition. The band electronic absorption at 32268 cm^{-1} might be due to (LMCT) ligand - metal charge transfer which is belonging typically for copper (II) complexes with nitrogen donors.

The magnetic moment value at 1.58 μB of the complex at 25 $^\circ\text{C}$ shows similar value to the octahedral structure for the Cu (II) ion [28]. Additionally, the electronic spectrum measurement of the Ni (II) complex

might be assigned to the structure of the octahedral geometry. However, the spectrum measurements of Ni(II) complex identified two bands at 16722 and 22727 cm^{-1} , refer to the transitions ${}^3A_{2g}(\text{F}) \rightarrow {}^3T_{1g}(\text{F})$ and, ${}^3A_{2g}(\text{F}) \rightarrow {}^3T_{1g}(\text{P})$ respectively [29] provided further support by The magnetic susceptibility value in the range of 3.10 μB of the complexes. The proposed structures for the complexes that have been prepared are shown in Fig. (2).



Scheme (2): The suggest structure of the complexes where M=Fe, Co, Ni, and Cu ligand=1,2(2,2-dihydroxy benzeliden)amine). Phenyl.

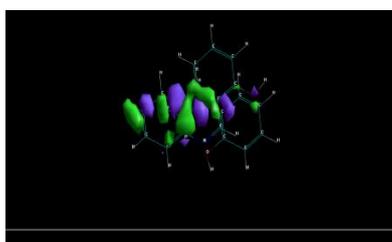
Theoretical studies of (L) ligand and their metal complexes

Hyperchem-7 software was used for semi-empirical calculation for the purpose of measuring: heat of formation ($\Delta H^{\circ}f$), binding energy (ΔEb) and total energy for ligand and its synthesized complexes, in addition to calculate the molecular orbita HOMO and LUMO for ligand and their complexes as in Table (3) [30]. The electrostatic potential (E.P) with the energy interaction of the molecular

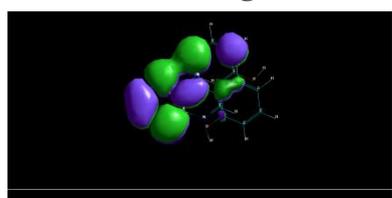
system with a positive charged center. (E.P) can be used to find reaction sites in a molecule; the positively charged molecules have a tendency to attack a molecule when its electro static potential site is powerfully negative i.e. electrophonic interaction [31]. E.P of ligand (L) and their complexes could be calculated and plotted as 2D contour to study the reactive sites of the molecules as in Fig.(4). The results of calculations show that the LUMO of transition metal ions prefer to react with the HOMO of O and N atoms of free ligands (L).

Table (3)
Total energy, Binding, Heat of formation calculations in kcal/mol and the Energy of HOMO, LUMO levels.

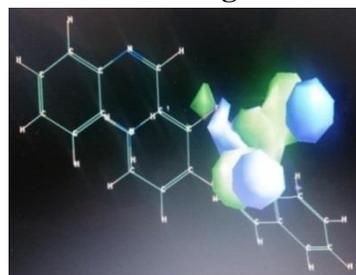
Compound	Total energy	Binding energy	Heat of formation	HOMO	LUMO
Ligand	-88362.234658	4854.897625	9968.8796934	-5.478122	-1.121363
Fe com.	-10032.733743	6123.552910	11152.476910	-7.85801	-1.334127
Co com.	-93808.158326	5674.285088	21160.821088	-8.406527	4.21399
Ni com.	-111989.7009	6252.970674	11285.394674	-7.594781	2.558232
Cu com.	-11383.5995524	8150.9244926	13213.350492	-7.503585	-4.425163



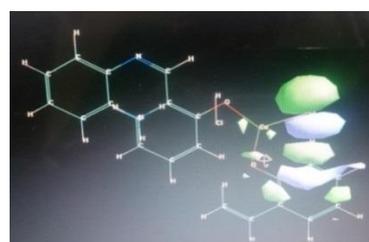
Homo of ligand



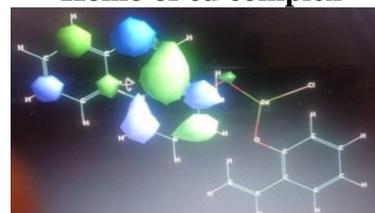
Lumo of ligand



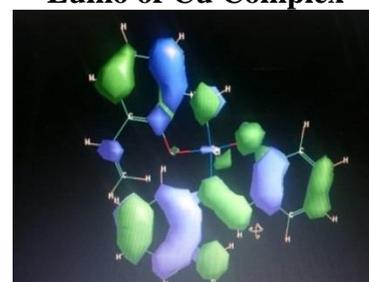
Homo of iron complex



Homo of cu complex

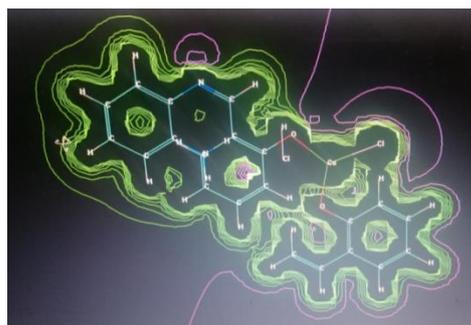


Lumo of Cu Complex

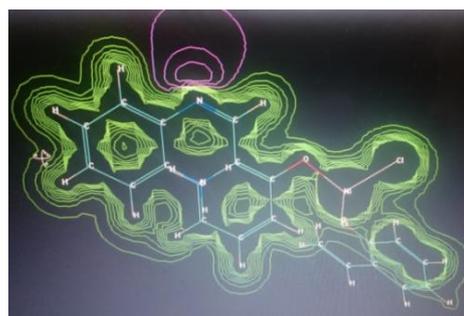


Lumo of iron complex

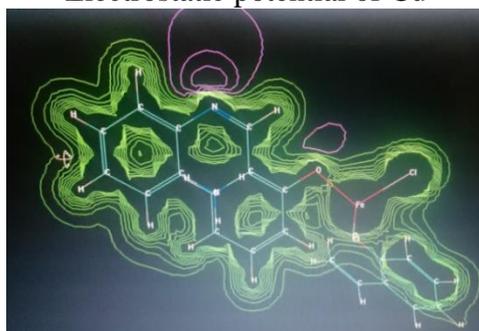
Scheme (3): HOMO and LUMO for ligand and its complexes.



Electrostatic potential of Cu



Electrostatic potential of Ni



Electrostatic potential of Fe



Electrostatic potential of Co

Scheme (4) Electrostatic Potential for prepared complexes.**Acknowledgements**

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