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Research Article

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Some Theoretical Study on the Interaction Between of a Salen Schiff-base Ligand with Zn (II), Cd (II) and Hg (II) Ions

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ABSTRACT

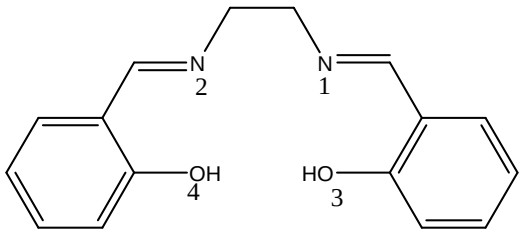
A theoretical study based on the optimum angle and distance between salen Schiff base and Zn (II), Cd (II) and Hg (II) ions was conducted. These investigations were carried out based on ab-initio calculations, to estimate the pair wise interaction energy between the two molecules. In this study the geometries of metal complexes of Zn (II), Cd (II) and Hg (II) ions with salen Schiff base were studied.

Key words: Schiff base, Theoretical study, Schiff base, Interaction, Salen, DFT.

INTRODUCTION

The Schiff bases derived from salicylaldehyde (salen) as polydentate ligands are known to form very stable complexes with transition metal ions [1]. The resulting salen complexes have attracted increasing attention, mainly due to their peculiar properties [2-6] and their reactivity mainly in the area of binding small molecules. Schiff bases reagents are becoming increasingly important in the pharmaceutical, dye, and plastic industries as well as for liquid-crystal technology and mechanistic investigations of the drugs used in pharmacology, biochemistry, and physiology [7]. However, despite extensive scientific reports on the synthesis, characterization, and crystalline structure of the transition metal–salen complexes, there have been only limited reports on the use of salen molecules as ionophores in ion-selective studies [8-14].

Quantum chemical calculations have been shown to be useful in the description of the relationship among the electronic structures of the molecular systems. Salen Schiff base has four coordination sites, two nitrogen atoms from the imino groups and two oxygen atoms in hydroxyl groups [Scheme 1].



Scheme 1. The structure of Salen Schiff base compound (H^2L)

Computational method

In this paper first the ab initio calculations at Austin model 1 (AM1) [15] level were used for the calculation of salen molecule. AM1 is a popular method for calculation of the electronic molecular properties. The geometrical optimization calculations were performed using Gaussian 03 program [16] on a Pentium IV computer. The optimized geometry with negative charge density on coordination sites are shown in Fig.1. In the other of this study we have some theoretical investigation on the electronic property of salen complex of these ions, the interaction between salen and three bivalence metal cations Zn (II), Cd (II) and Hg (II), were investigated by theoretical method and the optimum distance, angle, heat of formation and density charges on all atoms were obtained (Fig. 2). There have been several theoretical studies investigating the interaction of above metal cations with salen Schiff base ligand, in this study we will write about the structural property of salen and its complexes.

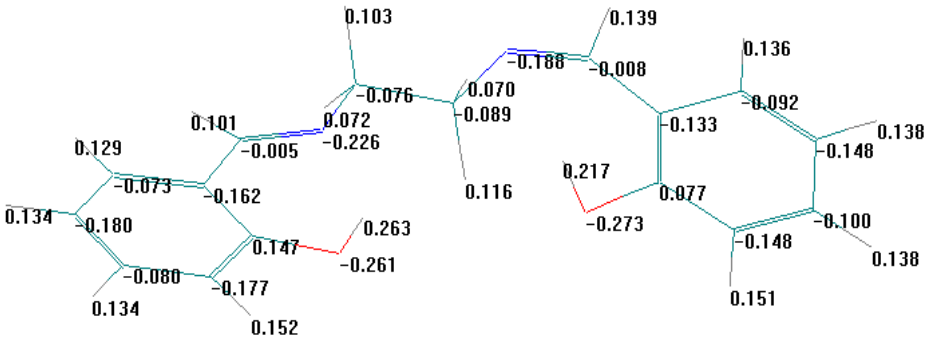


Fig. 2. Optimized geometry for H^2L Schiff base ligand

Fig. 2 shows **H^2L** Schiff base ligand has four atoms as its coordination sites for to binding to the metal ions in the complex formation (two N atoms in the imin groups and two O atoms from the hydroxyl groups).

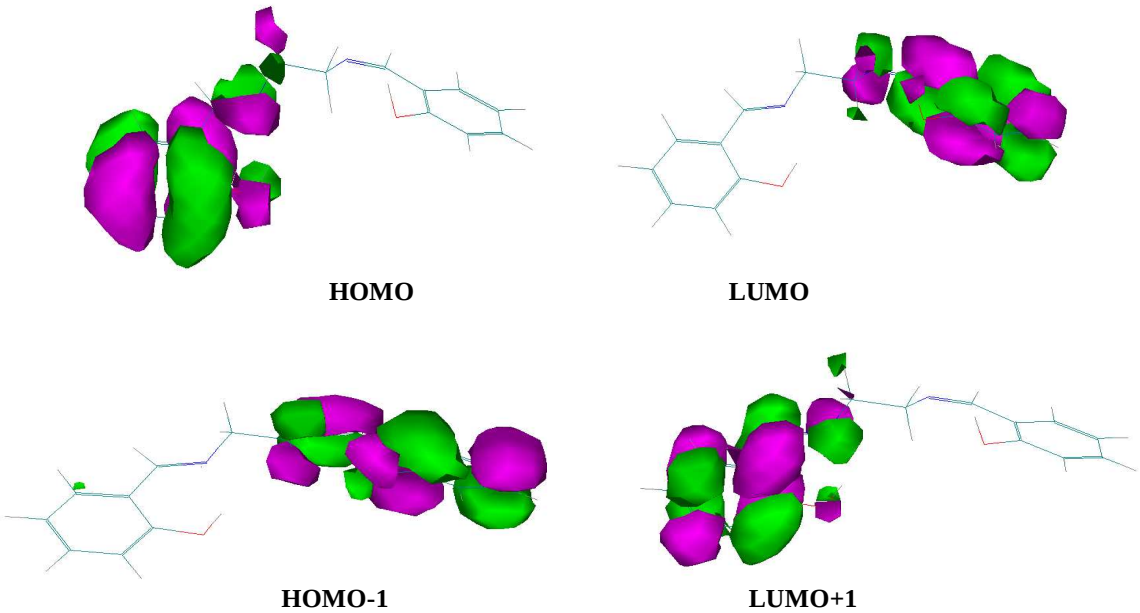


Fig. 3. Plot of HOMO, LUMO, HOMO-1 and LUMO+1 calculated molecular orbital levels for H^2L Schiff base ligand

The effect of the molecular structure on the chemical reactivity has been object of great interest in several disciplines of chemistry. The quantum chemical calculations have been widely used to study the reaction mechanisms and to interpret the experimental results as well as to solve chemical ambiguities. This is a useful approach to investigate the mechanisms of reaction in the molecule and its electronic structure level and electronic parameters can be obtained by means of theoretical calculations using the computational methodologies of quantum chemistry [17]. The advancement in methodology and implementations has reached a point where predicted properties of reasonable accuracy can be obtained from density functional theory (DFT) calculations [18] see Table 1. Fig.3 shows the plot of highest occupied molecular orbital (HOMO), lowest unoccupied molecular orbital (LUMO), HOMO-1 and LUMO+1 molecular orbital level for **H^2L** Schiff base ligand, these molecular orbitals are located on the salicylidene group.

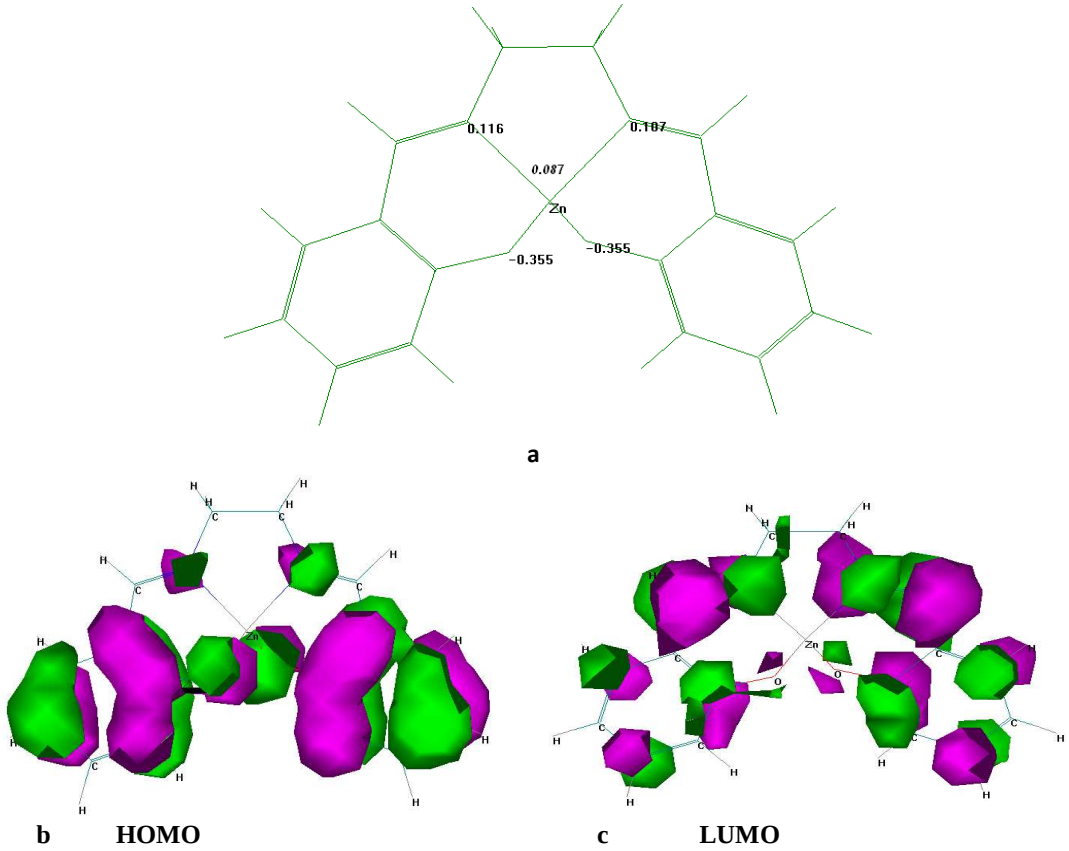
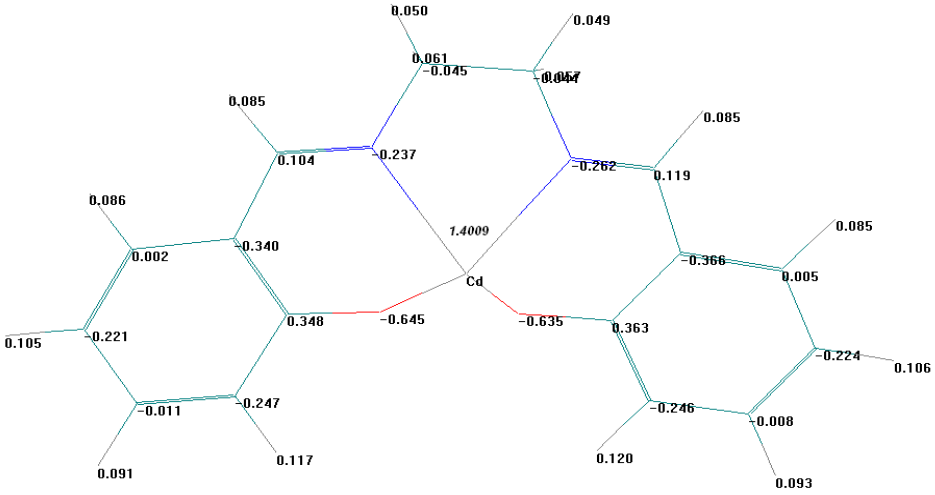


Fig. 4. (a) The optimized geometry of ZnL complex, calculated net charges are shown for all atom in the structure, (b) HOMO level, (c) LUMO level for Zn L complex



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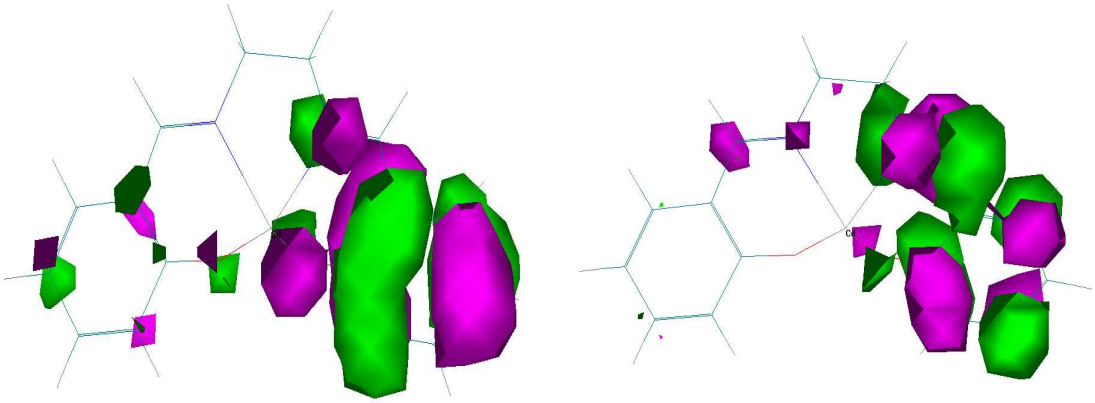
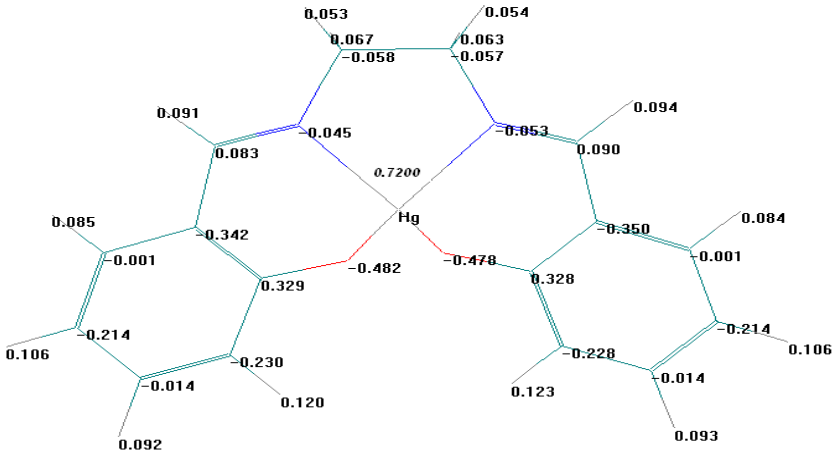


b HOMO c LUMO

Fig. 5. (a) The optimized geometry of CdL complex, calculated net charges are shown for all atom in the structure, (b) HOMO level, (c) LUMO level for Cd L complex



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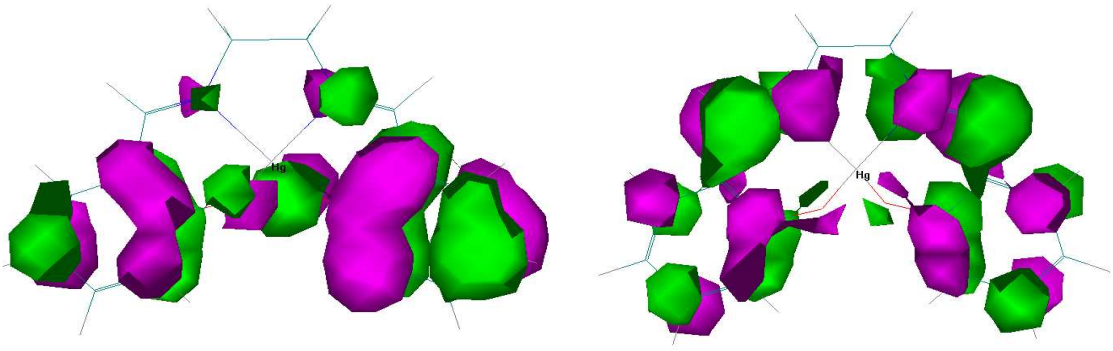

b HOMO c LUMO

Fig. 5. (a) The optimized geometry of HgL complex, calculated net charges are shown for all atom in the structure, (b) HOMO level, (c) LUMO level for Hg L complex
Fig. 6 shows the optimized hexahydrated metal cations.

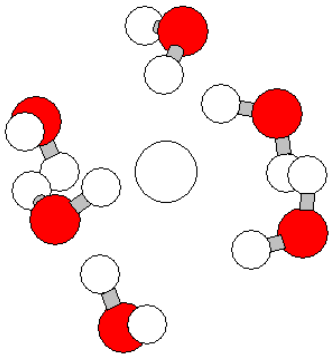

Fig. 6. Optimized hexaaquated metal cations, [M $(OH_2)_6$], M=Zn (II), Cd (II) or Hg (II)

Table 1. Some calculated data for ligand (H^2L) and their complexes with Zn (II), Cd (II) and Hg (II)

Compound	MW g/cm^3	HOMO eV	LUMO eV	Δ (Band gap) eV	ΔH_f Kcal/mol	E_{total}	$E_{interaction}$ Kcal/mol (ΔE)
H^2L	268.32	-8.835	-0.3523	8.483	9.39874	-122.0699	-
ZnL	331.67	-7.9973	-0.5228	7.4745	57/1057	-3782.8502	-2381.2413
CdL	378.70	-7.8535	-0.1946	7.6589	78.0780	-3757/4279	-2332.2881
HgL	466.89	-7.8514	-0.3249	7.5265	6.6237	-3816.8522	-2396.7392
$Zn(OH_2)_6$	173.46	-8.5652	1.8146	6.7506	-265.7910	-1279.5390	-
$Cd(OH_2)_6$	220.49	-6.7207	3.9806	2.7401	-293.7679	-1303.0659	-
$Hg(OH_2)_6$	308.68	-7.2646	2.9287	4.3359	-300.7751	-1298.0431	-

$$E_{interaction}=E_{system}-(E_{cation}+E_{ligand})$$

H^2L Schiff base was investigated in the present work which have four anchoring sites (two imines, CH=N and two OH groups) az coordination sits, and forming metal complexes, see Figs. 4, 5 and 6.

Figs. 2 has a clear picture of the ligand selectivity for various metal ions, their binding to the metal ions was investigated by Gaussian 03 software calculation and the binding energy (intraction energy, $_{\Delta E}$) was calculated using Eq. (1) [19].

$$\Delta E= \Delta E_{complex} -(\Delta E_{ligand}-\Delta E_{cation}) \qquad \text{Eq. 1}$$

Where; $\Delta E_{complex,}$ $\Delta_{Eligand}$ and ΔE_{cation} are the total energies of the complex, un-complexd ligand and metal ion, respectively.

CONCLUSION

H^2L and their metal complexes with Zn (II), Cd (II) and Hg (II) were optimized and then the optimized structures were again optimized with density functional theory (DFT). Full geometry optimizations were performed and each species was found to be at minimum energy. The optimized structures of H^2L and their metal complexes with Zn (II), Cd (II) and Hg (II) are visualized in Figs. 2, 4 and 5, respectively. Many of the important atomic charges are presented in these figures (2, 4 and 5). From Figs. 2, 4 and 5, it becomes obvious that the charge differences on the atoms that interact with Zn (II), Cd (II) and Hg (II) ions are greater. These changes indicate that these ions receive a part of their charge from the same atoms in H^2L ligand molecule. Therefore, a weak bonding was formed between coordination sits of ligand and metal ions. Hence, N atom in imine group and O atom in hydroxyl groups in H^2L are coordinated to metal ions and those that have the most interaction with this molecule. The binding energy (ΔE) was calculated using Eq. (1). Table 1 show that H^2L Shiff base ligand could possibly be used as a selective and suitable ligand to interact with these metal ions.

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