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SOME QUANTUM CHEMICAL STUDY ON THE STRUCTURAL PROPERTIES OF THREE UNSYMMETRICAL SCHIFF BASE LIGANDS

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ABSTRACT. In this studythree Schiff base ligands derived of 2-hydroxybenzaldehyde: H_2L^1, H_2L^2 and H_2L^3 have been subjected to theoretical studies by using density functional theory (DFT) calculations. The electronic properties such as highest occupied molecular orbital (HOMO), lowest unoccupied molecular orbital (LUMO) energy, HOMO-LUMO gap energy, RHF energy, some of important bond lengths and angles, dipole moment and molecular densities have been investigated. Also the calculated IR spectra of these ligands are in good consistency with the experimental results.

KEY WORDS: Schiff base, 2-Hydroxybenzaldehydeand, 2-Aminoethanthiol, HOMO, LUMO, Band gap

INTRODUCTION

Schiff's base ligands have been in the chemistry catalogue for over 150 years [1]. The literature clearly shows that the study of this diverse ligand system is linked with many of the key advances made in inorganic chemistry. Not only have they played a seminal role in the development of modern coordination chemistry [2], but they can also be found at key points in the development of structural and theoretical chemistry [3-7], inorganic biochemistry [8], catalysis [9-11] and optical materials [12]. Also Schiff base ligands and some of their complexes have been extensively investigated for more than a century and have been employed in areas that include analytical and bioinorganic chemistry, non-linear optics, fluorescence studies, catalysis and materials chemistry [13-18].

The molybdenum Schiff base complexes have continued to play the role of one of the most important models of molybdoenzymes [19]. Complexes containing cis-dioxomolybdenum(VI) fragment dominate coordination chemistry of molybdenum(VI) [20]. Depending on the preparation method, molybdenum precursor and reaction conditions, the complexes synthesized with dibasic tridentate Schiff bases are of the type: monomeric - $Mo(O)_2(L)(S)$, which is dominant, where L = Schiff base, S = monodentate neutral ligand [21], or dimeric - $[MoO(m\text{-}O)(L)]_2$ with asymmetric double oxygen bridge [22]. On the other hand quantum chemistry calculations have been shown to be useful in the description of the relationship among the electronic structure of the molecular systems and their optical response [23].

In this paper we report some calculated structural parameters for three salen type Schiff base ligands 2-((E)-(2-mercaptoethylimino) methyl)-4-methoxyphenol (H_2L^1), 2-((E)-(2-mercaptoethylimino) methyl) phenol (H_2L^2) and 2-((E)-(2-mercaptoethylimino)methyl)-4-nitrophenol (H_2L^3) (Scheme 1). These compounds have been described by Syamal [24].

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EXPERIMENTAL

Materials and reagents

2-Hydroxy-5-methoxybenzaldehyde, 2-htydroxybenzaldehyde, 2-hydroxy-5-nitrobenzaldehyde, 2-aminoethanthiol and ethanol were used as received. Methanol was distilled from magnesium methoxide. All reactions and workups were carried out under air.

Instrumentation

The IR spectra were measured as KBr pellets on a Perkin–Elmer 780 spectrophotometer (4000–400 cm^{-1}). UV–Vis spectra were recorded as a solution (DMSO) on a 160 Shimadzu spectrophotometer. ^{1}H-NMR with using d^6-DMSO spectra were recorded on a Brucker Avance 500 MHz instrument. Micro analyses for C, H, and N were determined on a Heracuse CHN rapid analyzer.

Synthesis of Schiff base ligands

In this research, we prepared three salen-type Schiff base ligands. 2-((E)-(2-mercapto-ethylimino) methyl)-4-methoxyphenol (H_2L^1), 2-((E)-(2-mercaptoethylimino) methyl) phenol (H_2L^2) and 2-((E)-(2-mercaptoethylimino) methyl)-4-nitrophenol (H_2L^3) as literatures [24]. By condensation of 2-hydroxy-5-methoxybenzaldehyde, 2-htydroxybenzaldehyde or 2-hydroxy-5-nitrobenz- aldehyde (0.01 mol, 1.52 g, 1.22 g or 1.67 g) and 2-aminoethanthiol (0.01 mol, 0.77 g) in 40 mL methanol and the mixtures were refluxed for 4 h (Scheme 1). The three imines prepared were filtered and washed several times with cold methanol and dried in vacuum. Then the imines were readily purified by recrystallization from ethanol. ^{1}H NMR, UV–Vis spectroscopy and microanalyses were used to characterize these ligands. Some physical property of H_2L^1, H_2L^2 and H_2L^3 Schiff base compounds are given in Table 1 and the relevant results of the FT-IR measurements are given in Table 2.

Table 1. Some important properties with C, H and N analysis of H_2L^1, H_2L^2 and H_2L^3 Schiff base ligands.

Schiff base and their complexes	Formula	Formula weight (gmol^{-1})	Color	Yield (%)	C, H and N analyses Exp.(Theor.)	m.p. (^{o}C)
H_2L^1	$C_{10}H_{13}NO_2S$	211	Yellow	85	56.2(56.87), 6.0(6.16), 6.4(6.63)	118-120
H_2L^2	$C_9H_{11}NOS$	181	Yellow	91	59.5(59.66), 6.1(6.07), 7.7(7.73)	112-115
H_2L^3	$C_9H_{10}N_2O_3S$	226	Orange	56	47.6(47.78), 4.4(4.42), 12.2(12.38)	130-133

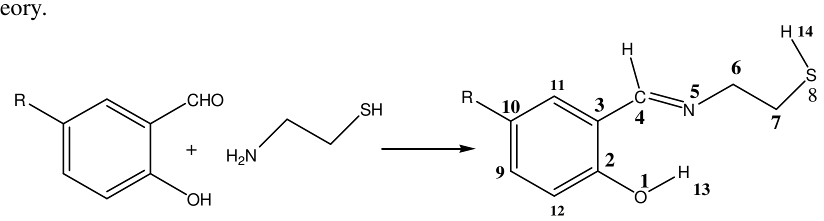
Table 2. Some important absorption bands in the FT-IR spectra (400-4000 cm^{-1}) for H_2L^1, H_2L^2 and H_2L^3Schiff base ligands.

Schiff base and their complexes	$\nu_{C=N}$ (cm^{-1})	ν_{OH} (cm^{-1})	$\nu_{C-H(imini)}$ (cm^{-1})
H_2L^1	1638	3287	2835-2995
H_2L^2	1631	3306	2905
H^2L^3	1612	3303	2976-2926

The ^{1}H NMR spectra (DMSO as an internal solvent): [H_2L^1: δ (6.8, 6.9, d, and 5.9, s, for aromatic hydrogen, 3, 3.9 aliphatic hydrogen, 3.8 methoxy protons and 8.4, s, for SH proton)], [H_2L^2: δ (7.2, 7.4, t aromatic hydrogen 5.8, s, H imine group, 3.9, t, aliphatic hydrogen, 7.0, s, SH group)], H_2L^3: δ (7, 8.1, d aromatic hydrogen, 2.8, d and 3.3, t, aliphatic hydrogen, 8.3, s,(SH group)]. The UV/Vis (DMSO), λ_{max}, nm (log ε, L mol^{-1} cm^{-1}): 2 H_2L^1: 486(4.81), H_2L^2: 449(4.72), H_2L^3: 437(4.37).

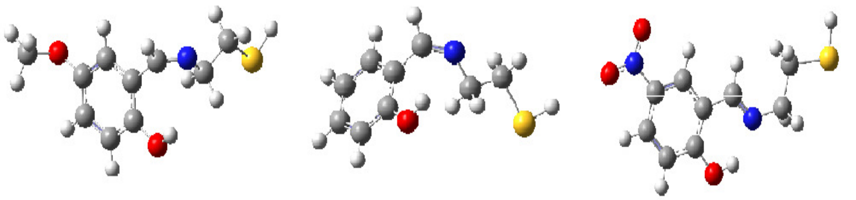
Theoretical study

Quantum chemical calculations (Density Functional Theory, B3LYP/6-31G (d)) were used to purposed the electronic parameters for H_2L^1, H_2L^2 and H_2L^3 Schiff base ligands. All density functional theory (Becke's hybrid HF-DFT procedure [25] with the Lee-Yang-Parr [26] correlation functional [B3LYP/6-31G(d)]) calculations were done by using Gaussian 03 program package [27], and all three structures of these compounds were optimized (Scheme 2). Some theoretical calculated structural properties for H_2L^1, H_2L^2 and H_2L^3 Schiff base ligands are shown in Table 3. Table 4 shows some optimized geometric parameters of H_2L^1, H_2L^2 and H_2L^3 Schiff base ligands. Some important experimentally observed picks are given in Table 5 and compared with the most intense vibrational frequencies calculated at the B3LYP/6-31G(d) level of theory.



R= OCH3 (H_2L^1), R= H (H_2L^2), R= NO_2 (H_2L^3)

Scheme 1. The preparation of H_2L^1, H_2L^2andH_2L^3Schiff base ligands.



H_2L^1 H_2L^2 H_2L^3

Scheme 2. The optimized structures of H_2L^1, H_2L^2 and H_2L^3 Schiff base ligands.

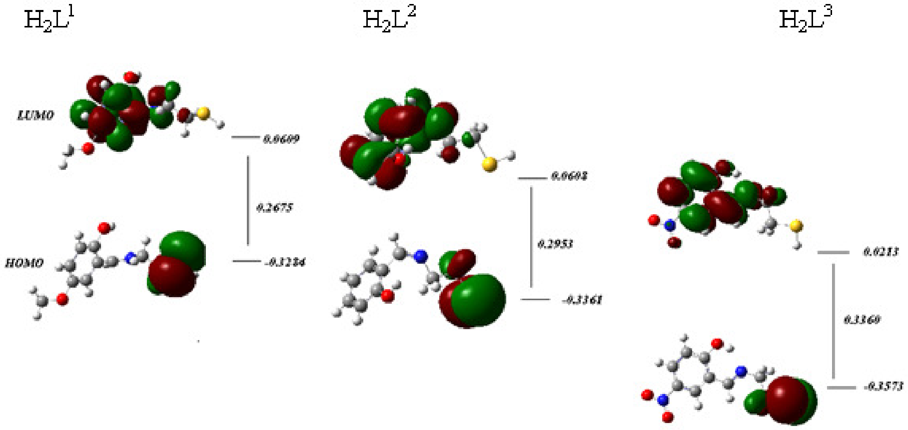
Table 3. Some calculated electronic parameters for H_2L^1, H_2L^2 and H_2L^3 Schiff base ligands.

Compound	Mulliken atomic charges			E_{HOMO} (eV)	E_{LUM} (eV)	$\mu_{(Debye)}$	E (eV)	Band gap (eV)
	O(1)	N(5)	S(8)					
H_2L^1	-0.6802	-0.1679	0.0238	-0.3284	0.0609	3.9019	-26873.7000	0.2675
H_2L^2	-0.1961	-0.1828	0.0641	-0.3361	0.0608	2.9372	-23776.5110	0.2953
H_2L^3	-0.7709	-0.4126	-0.0819	-0.3573	0.0213	4.1491	-11895.7340	0.3360

The HOMO and LUMO orbitals are very important in defining its reactivity [28]. Higher value of HOMO of a molecule has a tendency to donate electrons to appropriate acceptor molecule with low energy, empty molecular orbitals. An electronic system with a larger HOMO-LUMO gap should be less reactive than having smaller gap [29]. The larger the HOMO-LUMO orbital energy gap, the harder the molecule. The hardness has been associated with the stability of the chemical system. In the present study, the HOMO-LUMO gap the HL^3 molecule is largest than HL^2 and HL^1, respectively as shown in Table 3, which clearly indicates that HL^1 molecule is very reactive than the other. The calculated dipole moment values show that the HL^3 molecule is highly polarin nature than the other molecules.

Table 4. Some of important optimized geometries for H_2L^1, H_2L^2 and H_2L^3 Schiff base ligands.

Bond length (Å)	H_2L^1	H_2L^2	H_2L^3
C2-C12	1.388	1.388	1.394
C12-C9	1.381	1.382	1.375
C9-C10	1.389	1.393	1.392
C10-C11	1.379	1.383	1.381
C11-C3	1.397	1.397	1.388
C3-C2	1.390	1.391	1.407
C3-C4	1.491	1.491	1.467
C4-N5	1.265	1.266	1.266
N5-C6	1.463	1.463	1.461
C6-C7	1.520	1.502	1.525
C7-S8	1.888	1.888	1.885
S8-H14	1.354	1.354	1.354
C2-O1	1.379	1.377	1.344
O1-H13	0.950	0.950	0.966
H13….N5	2.718	2.706	1.861
Bond angles (°)			
H13-O1-C2	115.890	112.981	112.981
O1-C2-C3	123.120	121.986	121.986
C2-C3-C4	122.439	122.243	122.243
C3-C4-N5	128.287	122.392	122.398
C4-N5-C6	124.464	125.128	125.128
N5-C6-C7	107.309	116.457	116.457
C6-C7-S8	108.789	107.688	107.688



Scheme 3. Selected molecular orbital plots in various electronic excitations of H_2L^1, H_2L^2 and H_2L^3 Schiff base ligands.

Table 5. Some of important vibrational frequencies (cm^{-1}) of H_2L^1, H_2L^1 and H_2L^1 Schiff base ligand compared with calculated.

H_2L^1		H_2L^2		H_2L^3		Assignment
Experimental	Theoretical	Experimental	Theoretical	Experimental	Theoretical	
1180	1107	1073	1135	938	1030	$\nu_{C=C}$
1166	1140	1047	1139	1038	1033	$\nu_{C=C}$
3287	4026	3306	4025	3303	3678	ν_{O-H}
1638	1874	1631	1873	1612	1892	$\nu_{C=N}$
2995	2983	2905	2988	2926	2953	(aromatic)ν_{C-H}

RESULTS AND DISCUSSION

Three Schiff base ligands H_2L^1, H_2L^2 and H_2L^3 with NSO donor atom derived of salicylaldehyde were synthesized as literatures. A comparative study of their physico-chemical properties has been made through elemental analysis, IR, electronic spectra and ^{1}H NMR spectra. Also in the present study we have some theoretical calculations by using Gaussian 03 program to determine the best molecular configurations of the title compounds and we obtained some parameters such as the energy of the molecular orbital, E_{HOMO}, E_{LUMO}, dipole moment and Mulliken atomic charge. The results are given in Table 3. The calculated HOMO-LUMO orbital energies, dipole moments and total energy are very important physical parameters for chemical reactivity and biological activities of the studied compounds. The energy of HOMO is often associated with the electron-donating ability of a molecule; high values of E_{HOMO} are likely to indicate a tendency of the molecule to donate electrons to appropriate acceptor molecules with energy and empty molecular orbital. Therefore, the energy of LUMO indicates the ability of the molecule to accept electrons. Table 3 indicates O(1), N(5) and S(8) are the coordination sites for these ligands. Following the E_{HOMO} from Table 3 and Figure 3 looks apparently easier for the molecular to offer electrons to unoccupied d-orbital of a metal ion. The higher HOMO energy from $H_2L^1 > H_2L^2 > H_2L^3$ can be used as one of the parameters for the explanation of its good coordination performance, and R group has an important role in the complex formation by these ligands. ^{1}H NMR spectra were recorded in DMSO as an internal solvent for these ligand in our laboratory, [H_2L^1: (6.8, 6.9, d, and 5.9, s, for aromatic hydrogen, 3, 3.9 aliphatic hydrogen, 3.8 methoxy protons and 8.4, s, for SH proton)], [H_2L^2: (7.2, 7.4, t aromatic hydrogen 5.8, s, H imine group, 3.9, t, aliphatic hydrogen, 7.0, s, SH group)], H_2L^3: (7, 8.1, d aromatic hydrogen, 2.8, d and 3.3, t, aliphatic hydrogen, 8.3, s,(SH group)]. Figure 3 shows the highest molecular orbitals (HOMO) for these ligand as have major contribution from the S atomic orbital of S-H group and the lowest molecular orbital (LUMO) have major contribution from the salen rings. Table 5 shows a good agreement between the experimental with theoretical data.

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