

On the structural property of two symmetrical N₂O₂-coordination Schiff base compounds

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ABSTRACT

Disulphide derivatives of imine compounds have been the subject of intensive investigation over the past years, reflecting that they are excellent ligands for coordination to the metal ions. The disulphide group is well recognized as a potential binding site for metal ions in biological systems. In our present works we prepared two symmetrical Schiff base compounds N,N'-bis (2-hydroxy-3-methoxybenzylidene)-2,2'-(aminophenylthio) ethane [L₁] and N,N'-bis (2-hydroxybenzylidene)-2,2'-(aminophenylthio) ethane [L₂] by condensation of bis-(2-aminophenyl) disulphide with salen derivatives in absolute ethanol at room temperature. The structures of prepared compounds were checked by several spectroscopic methods. In the other part of this work the structure of these compounds have been optimized in gas phase and all quantum chemical parameters of the optimized L₁ and L₂ compounds have been discussed by some semi-empirical methods.

Keyword: Schiff base, quantum parameter, bis (2-aminophenyl) disulphide, semi-empirical method, corrosion inhibition.

INTRODUCTION

There has been considerable activity concerning the synthesis of Schiff base ligands. These compounds have significant importance in chemistry; especially in the development of Schiff base complexes, because Schiff base ligands are potentially capable of forming stable complexes with metal ions¹⁻⁶. Some imines or Schiff base compounds and their metal complexes are also noted for their significant antimicrobial activities^{7, 8} and corrosion inhibition⁹. Some organic compounds, which adsorb on the metal surface and suppress metal dissolution and reduction reaction are named inhibitors or anti corrosion materials¹⁰. In many cases, the role of inhibitors is to form a surface coating one or several molecular layers thick that serves as a barrier¹¹. Chemisorption is probably the most important type of interaction between the metal surface and an inhibitor molecule¹².

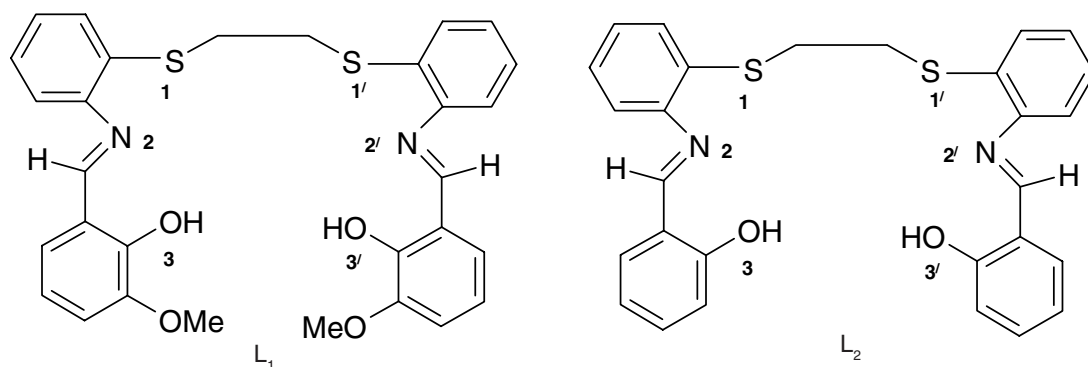
In the other hand the structure and conformations of L₁ and L₂ plays an important role in the structural properties. In the present study the correlation between the molecular structures and the coordination sites of L₁ and L₂ ligands have been investigated by using some semi-empirical quantum chemical calculations.

Recently, we have reported some new Schiff base ligands^{13,14} and in this article, we will report synthesis and the structural properties of L₁ and L₂ Schiff base compounds [Scheme 1] by the reaction of 1,2-di (ortho-aminophenylthio)ethane with 3-methoxysalicylaldehyde or salicylaldehyde.

EXPERIMENTAL

Instrumental and methods

Elemental analyses were performed on a Perkin Elmer analyzer, ¹H-NMR and ¹³C-NMR



Scheme 1: The Structure of N,N'-bis (2-hydroxy-3-methoxybenzylidene)-2,2'-(aminophenylthio) ethane [L₁] and N,N'-bis (2-hydroxybenzylidene)-2,2'-(aminophenylthio) ethane [L₂]

spectra were prepared on a Bruker AM 400 MHz, and UV-Vis spectra were reported with a Beckman DU-7000 spectrometer. FT-IR spectra were reported on a Shimadzu DR-8001. All calculation was done by a Pentium IV Personal Computer. C, H and N elemental analysis were performed on a Perkin Elmer analyzer.

MATERIAL

Salicylaldehyde, 3-methylsalicylaldehyde chloroform (reagent grade Merck) was purified and dried before use according to the standard methods.

Synthesis

L₁ and L₂ schiff base compounds [Scheme1] by the reaction of 1,2-di (ortho-aminophenylthio)ethane (0.276g, 0.001mol) with 3-methoxysalicylaldehyde (0.304 g, 0.002 mol) or salicylaldehyde (0.244g, 0.002mol) in chloroform (25mL) in the presence of one drop conc. H₂SO₄ under stirring at room temperature (6 h). The yellow solid compounds were recovered by filtration, washed with cold ethanol and dried over fused CaCl₂. The colored imines were purified by recrystallization from ethanol (yields 55-70 %). The C, H and N analytical results and some physical properties of the isolated L₁ and L₂ Schiff base ligands have been shown in Table 1.

Spectroscopic data

Spectroscopic data for L₁ Schiff base ligand

FT-IR ν_{\max} (KBr, cm⁻¹): 3500 (m, OH), 3042

(w, aromatic C-H), 1641 (s, C=N), 1184 (phenolic C-O). ¹H-NMR (Bruker AM 400 MHz, CDCl₃ solvent with TMS as an internal standard), δ 3.2 (s, 6H, CH₃), 6-8.8 (d, 14H, phenyl), 10.2 (s, 2H, OH), 7.8-8 (d, 2H, CH= N), 3.1 (4H, s, CH₂). Electronic spectra: (DMF as a solvent) λ_{\max} =286 and 353 nm.

Spectroscopic data for L₂ ligand

FT-IR ν_{\max} (KBr, cm⁻¹): 1597(m, OH), 3052 (w, aromatic C-H), 1649 (s, C=N), 1192 (phenolic C-O). ¹H-NMR (Bruker AM 400 MHz, CDCl₃ solvent with TMS as an internal standard), 6.9-8.6 (s, 16H, Phenyl), 7.25-8.32 (s, 2H, CH= N), 13.2 (s, 2H, OH), 3.3 (s, 4H, CH₂). Electronic spectra: (DMF as a solvent) λ_{\max} =278 and 349 nm.

Theoretical section

We have carried out quantum mechanical computations for L₁ and L₂ Schiff base ligands. Two structures were pre-optimized by the Molecular Mechanics method and then fully optimized at the AM1¹⁵ semi empirical-self-consistent field-molecular orbital (SCF-MO) method by using MOPACK 7.0 program package¹⁶. Also the theoretical electronic spectra were obtained for L₁ and L₂ Schiff base ligands. Theoretical calculations were performed with MOPACK 7.0 and program and geometry optimizations were used to find the coordinates of molecular structures that represent a potential energy minimum. The lowest energy, dipole moments and energy are calculated at AM1 semi-empirical method. The values of dipole moments, energies and heat of formations for L₁ and L₂

molecules are listed in Table 2. In Table 3, the atomic charges of S, N (in C=N group) and O (in OH group) atoms of the molecules are given. Some important theoretical electronic spectral data have been shown in Table 4.

RESULTS AND DISCUSSION

The reaction of 1,2-di (ortho-aminophenylthio) ethane with 3-methoxysalicylaldehyde or salicylaldehyde in chloroform in the presence of one

Table 1. Some important physical properties and analytical results for L₁ and L₂ Schiff base ligands

Compound	Formula weight g/mol	color	m.p. (°C)	yield %	Percentage of elements Calc. (Found)		
					C	H	N
L ₁ (C ₃₀ H ₂₈ N ₂ O ₄ S ₂)	544	Yellow	175	55	66.176(67.10)	5.145(5.02)	5.147(5.32)
L ₂ (C ₂₈ H ₂₄ N ₂ O ₂ S ₂)	330	Yellow	180	70	69.421(68.95)	4.958(4.35)	5.875(5.11)

Table 2: Calculated values of dipole moment (D), heat of formation (kcal/mol) and energy (kcal/mol) for L₁ and L₂ Schiff base compounds by AM1 semi-empirical method

Compound	Dipole moment (Deby)	HOMO (eV)	LOMO (eV)	Band gap (eV)	Heat of formation (Kcal./mol)	Energy (Kcal./mol)
L ₁	5.21	-7.977	-0.383	7.554	-17.11	-145463.77
L ₂	3.49	-8.075	-0.369	7.706	70.219	-123519.88

Table 3. Charges density on the S, N, O atoms of L₁ and L₂ Schiff base compounds calculated by AM1 semi-empirical method

Compound	S1	S1'	N2	N2'	O3	O3'
L ₁	0.1999	0.1882	-0.2679	-0.2735	-0.4600	-0.4829
L ₂	0.155	0.195	-0.150	-0.152	-0.244	-0.240

Table 4: Some theoretical electronic bands of L₁ and L₂ Schiff base compounds calculated by AM1 semi-empirical method

Compound	λ (nm)	
L ₁	344.38	252.74
L ₂	341.9	226.4

drop conc. H₂SO₄ under stirring at room temperature (6 h) afforded two Schiff base ligands, N,N'-bis (2-hydroxy-3-methoxybenzylidene)-2,2'-(aminophenylthio) ethane [L₁] and N,N'-bis (2-hydroxybenzylidene)-2,2'-(aminophenylthio) ethane [L₂]. Optimized molecular structure parameters of the L₁ and L₂ molecules are summarized in Table 1 and Table 2. The coordination sites (N and O) atoms exhibit a substantial negative charge, S atoms in the two structures have positive charges and they have not any role in coordination properties of these

imines. The OCH₃ group is a donor electron group and plays a major role in designing of N and O coordination sites of L₁ imine. The negative charge on the coordination sites for L₁ (N₂, N₂' and O₃ and O₃') are bigger than the negative charge on the coordination sites for L₂ (see Table 2). Table 3 is shown the theoretical electronic bands for L₁ and L₂ molecules, the lowest energy bands of the electronic spectra for these compounds (344.3 and 341.9 nm) are attributed to the HOMO→LUMO transitions (97→98 for L₁ and 85→86 for L₂) and this bands are related to π→π* transitions. The highest energy bands of the calculated electronic spectra (252.7 and 226.4 nm) are attributed to 97→99 electronic transition for L₁ and 83→87 for L₂ and related to π→π* transitions.

On the other hand, we can study the ability of quantum chemistry and select corrosion inhibitors. Because when two molecular systems

react, the energy variation along the reaction coordinate is due to the geometric distortion of the reagent molecules and to the interaction energy between them. The interaction of molecular orbitals results in a decrease of the energy of the lower orbital and an increase of the energy of the higher orbital. The extent of energy change is inversely proportional to the difference in energy of the MO prior to interaction and is directly proportional to the products of the MO coefficients at one site of interaction. According to Fukui's frontier orbital approximate, interactions between frontier MO only, highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) of both reactants are frequently considered, since the inverse dependence of stabilization energy on orbital energy difference ensures that terms involving the frontier MO will be larger than others (Table 3). So L₁ is a good corrosion inhibitor.

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