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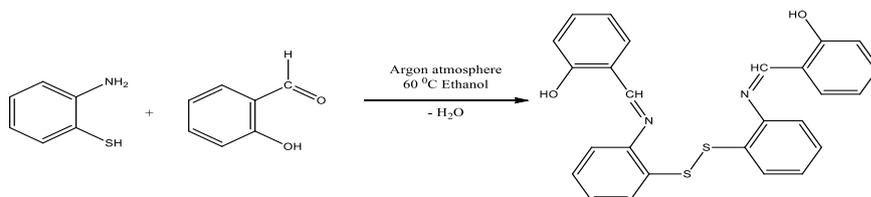
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Synthesis and Structural Characterization of $N_2S_2O_2$ Type Dimeric Schiff Base

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Abstract – A interesting hexadentate $N_2S_2O_2$ donor dimeric Schiff base ligand, $L_2HA(2-(2-(2-(2-(2-(2-hydroxybenzylideneamino)phenyl)disulfanyl)phenylimino) methyl)phenol)$, was synthesized by the condensation of 2 - aminothiophenol and salicylaldehyde under the argon atmosphere. Structural investigations on the ligand have been made based on spectral data. The ligand was characterized by FT-IR, UV-vis, 1H and ^{13}C NMR spectroscopy. L_2HA was isolated and their structures were determined by X - ray crystal structure analysis.



Keywords –
Dimeric Schiff base,
2 - aminothiophenol,
 $N_2S_2O_2$ donor set,
Disulphides.

1. Introduction

Schiff bases have remained an important and popular area of research due to their simple synthesis, versatility, and diverse range of applications and Schiff bases have played an important role in the development of coordination chemistry as they readily form stable complexes with the transition metals [1-4].

Multidentate Schiff bases have been widely used as ligands, because they can easily attached to metal ions due to the formation of high stability of coordination compounds. Metal

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complexes of S-, N-, and O-chelating ligands have attracted the considerable attention because of their biological [5-6], electrochemical [7], physicochemical [8] and analytical [9,10] properties. The interest in sulfur donor chelating agents has grown very rapidly. Coordination chemistry is focused on potential applications of macrocyclic thio Schiff bases and their metal complexes.

Compounds containing disulfide moiety play a vital role in chemistry and biochemistry. The dimeric form of thio Schiff bases are interesting class of compounds with a wide range of pharmacological applications. Molecules which contained disulfide bonds, appeared in a variety of biologically active target molecules with properties such as anti-bacterial [5-6], anti-microbial [11], anti-fungal [12], anti-tumor and anti-cancer activity.

In addition interesting electrochemical properties of some Schiff bases containing disulfide bonds have been tested in several applications. Dimeric Schiff bases showed anti-corrosive effects on mild steel [13-14], colorimetric sensor [9], polymeric materials, and bioactive compounds.

In this study hexadentate $N_2S_2O_2$ donor sets has been prepared from the condensation of 2-aminothiophenol and salicylaldehyde under the argon atmosphere. The ligand was determined by X-ray diffraction method and spectroscopic analyze method.

2. Experimental

2.1. Analytical Methods and Physical Measurements

The reagents 2-aminothiophenol (Merck), salicylaldehyde (Merck) were commercial products and were used as received. All the reagents used were of AR grade and the solvents were distilled and purified by the standart methods. IR spectras were acquired using a Shimadzu FT-IR Spectrophotometer by ATR apparatus. NMR studies were carried out with 400 MHz Bruker NMR Spectrometer. UV-vis spectras were acquired using PG Instruments T80 dual-beam Spectrophotometer.

2.2. Synthesis

The ligand was synthesized by the condensation reaction under the argon atmosphere. A quantity 2-aminothiophenol 0,050 mol (6,25 g) was dissolved in 10 ml of hot ethanol. 0,050 mol (6,10 g) of salicylaldehyde was added to this solution and the mixture was stirred at 60 °C. The precipitated compound was removed by filtration, washed with methanol and dried in vacuum. The crude product was recrystallized in CH_2Cl_2 / CH_3OH (1/2). Color: yellow. Yield % 78. m.p. : 163–165 °C [14]. (FT-IR ATR cm^{-1}): 1610 $\nu(C=N)$, 1563 $\nu(Ar - C=C)$, 1278 $\nu(Ar - C-O)$, 747 $\nu(C - S)$. 1H NMR ($CDCl_3$; 400 MHz) δ =12.93 (s, 2H); δ =8.64 (s, 2H); δ =7.69 (dd, j =7.6Hz, 1.2Hz; 2H); δ =7.46-7.42 (m, 4H); δ =7.29-7.17 (m, 6H); δ =7.09 (d; j =7.2Hz, 2H); δ =6.99 (t; j =7.2 Hz, 2H). ^{13}C - NMR ($CDCl_3$; 100 MHz) δ =162.81 (2C); 161.18 (2C); δ =146.29 (2C); δ =133.72 (2C); δ =132.66 (2C); δ =131.63 (2C); δ =127.78 (2C); δ =127.68 (2C); δ =127.18 (2C); δ =119.27 (2C); δ =119.19 (2C); δ =117.67 (2C); δ =117.48 (2C). UV-vis (λ_{max} nm): λ_1 =220, λ_2 =260, λ_3 =400 (CH_2Cl_2).

3. Result and Discussion

3.1. Spectroscopic Analysis of the Ligand

The IR spectra of the ligand showed a strong band in the region 1610 cm^{-1} which is the characteristic frequency of the azomethine $\nu(\text{C}=\text{N})$ group and also a band that appeared at 1278 cm^{-1} due to phenolic C–O stretching and aromatic C=C stretching appeared at 1563 cm^{-1} . Moreover, a band assigned to $\nu(\text{C}-\text{S})$ at 747 cm^{-1} is found, in agreement with the disulfide bond described in the crystal structure.

Schiff base ligand (H_2LA) was characterized by ^1H NMR and ^{13}C NMR spectroscopies. According to the ^1H NMR spectra, the Ar–OH proton of the ligand appeared as a singlet at 12.93 ppm due to effect of phenolic OH and hydrogen bonding. The Ar–SH proton was not appeared in the spectra for ligand. The azomethine proton of H_2LA appeared as a singlet at 8.64 ppm. The aromatic region was a set of doublets, triplets and multiplets in the range 7.69–6.69 ppm for ligand. In addition ^{13}C -NMR showed, the number of carbon atoms in the compound was observed to are in conformity with structure. The electronic spectrum of the ligand in dichloromethane shows absorption bands at 220 nm, 260 nm and 400 nm which can be assigned to the transition of $\pi\rightarrow\pi^*$ aromatic ring, azomethine group and the transition of $n\rightarrow\pi^*$ respectively.

3.2. Description of the Molecular Structure of L_2HA

The ligand [L_2HA] was characterized by X-ray diffraction, and the ORTEP representation is shown in Fig. 1. The structure was solved with direct methods using the program SHELX97 and structure refinement on F^2 was carried out with the program SHELX97. Relevant X-ray diffraction data and selected bond lengths and angles are listed in Tables 1 and 2, respectively. This ligand crystallizes in the space group P_{bca} . The crystal structure of [L_2HA] shows in figure 1.

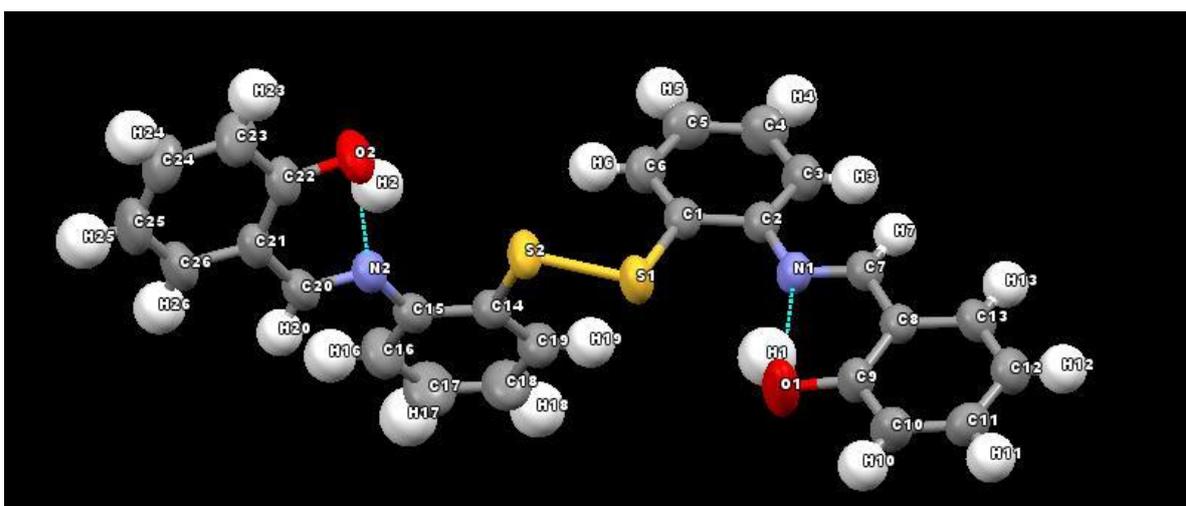


Figure 1. The ORTEP representation crystal structure of [L_2HA] ligand.

Table 1. Crystal data and structure refinement parameters for ligand [L₂HA].

Empirical formula	C ₂₆ H ₂₀ N ₂ O ₂ S ₂	Z	2
Formula weight	456.56	Density (calc.)/g cm ⁻³	1.334
Temperature/K	296(2)	F(0 0 0)	952
Wavelength (Å)	1.54184	h, k, l range	-15<h<15
Space group	P _{bca}		-15<k<15
			-21<l<21
Unit cell dimensions			
a (Å)	12.2810(5)	Θ _{range} (°)	3.83-76.26
b (Å)	12.3794(5)	Number parameters	581
c (Å)	17.1535(5)	R _{int}	0.0495
α (°)	70.404(3)	R	0.0427
β (°)	69.028(3)	R _w	0.1234
γ (°)	89.990(3)	Radiation type	CuKα
Volume/Å ³	2272.68(15)	Goodness-of-fit (GOF) on indicator	1.013

Table 2. Selected bond distances (Å) and bond angles (°) for ligand[L₂HA].

Bond distances(Å)		Bond angles(°)	
S1 - C1	1.7835(18)	C1 - S1 - S2	105.76(6)
S1 - S2	2.0245(6)	C14 - S2 - S1	105.10(6)
S2 - C14	1.7873(18)	C20 - N2 - C15	121.61(16)
N2 - C20	1.279(2)	C7 - N1 - C2	122.07(15)
N2 - C15	1.413(2)	C22 - O2 - H2	109.5
N1 - C7	1.279(2)	N2 - C20 - C21	122.03(17)
N1 - C2	1.408(2)	N2 - C20 - H20	119.0
O2 - C22	1.353(2)	C21 - C20 - H20	119.0

3.2. Conclusion

In this study we synthesized thio Schiff base ligand by the condensation of 2-aminothiophenol and salicylaldehyde under the argon atmosphere. When the reaction was performed under normal conditions, it can be observed benzothiazole derivatives [15] or monomeric thio-Schiff bases [2,4]. Then they have been characterized by the spectroscopic techniques such as UV-vis spectroscopy, FT-IR, ¹H NMR and ¹³C - NMR. In this work, we have reported only N₂S₂O₂ type dimeric Schiff base. The crystal structure of ligand was characterized by using X-ray crystallography. Hence It can be used to study biological activities and as a corrosive inhibitor due to the effects of disulphide bonds in this structure.

Acknowledgements

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