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Synthesis and characterization of Schiff's base-based chemosensor and its detection potential of Fluoride ions

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Abstract. The development of selective and sensitive chemical sensors to overcome fluoride ions is needed, especially for applications in chemical and biological processes. One of the chemical compounds that can act as sensors is the Schiff base compound group. This study aims to synthesis a Schiff base based on salicylaldehyde and as a fluoride ion sensor. The one-pot synthesis approach was carried out in room terms by mixing salicylaldehyde with hydrazine hydrate or phenylenediamine with a molar ratio of 2: 1 in ethanol solvent under stirring for 24 hours. The bright yellow crystal was obtained with a yield of 80% for salicylaldazine (SB). The compounds in the dimethyl sulfoxide (DMSO) solvent tend to be colorless, but in the presence of F⁻ ions, the solution turns orange. The results indicate an interaction between SB1 with F⁻ ions in solution.

1. Introduction

Schiff bases, compounds derived from the primary amine condensation reaction with the carbonyl group, are gaining attention as "Privileged ligand " by researchers due to the stability and the attractive structural design [1,2]. Schiff Base is a compound with a typical structure $R[1]C = NR'$. They can be considered sub-classes imine, either secondary ketimine or secondary aldimine, depending on its structure. Schiff Base is widely used as an analytical reactant because they allow it and inexpensively determine some organic and inorganic substances [3]. Azine is a potential ligand because of two imine groups. Therefore, it has recently been used as ligands in coordination chemistry [4]. Previously reported that azines developed for selective ion-optical sensors. Azines mixture between opioid antagonists and ketone steroids has shown various metal complexes on their anti-microbial and anti-fungal properties [5].

Salicylaldazine is one of the ligands that belongs to the Azometine class. One of the compounds derived from the azomethine class, namely Azine. They are used in bonding formation reactions, polymerization, and in liquid crystal design. Azine exhibits a fascinating biological and conductive optical nature and is widely used as a substance [6]. Recently, due to the simplicity, a high degree of specificity and low detection limit, much effort has been devoted to developing fluorescent anion detection [7].

Anions play a significant role in a wide variety of chemical and biological processes. Fluoride is one of the most studied anions. Broad attention has been paid to the design and production of selective and



adaptive optical sensors for fluoride ion. Two salicyldazine-based compounds will be studied in this study.

2. Materials and methods

2.1. Materials

The tools used in this study are spectrophotometer FTIR Perkin Elmer Spectrum 100, Spectrophotometer UV-Vis BMG Lab-Tech Fluorostar Omega, Diffractometer Xpert MPD with $\text{CuK}\alpha(1.54\text{\AA})$, Magnetic stirrers with hot plate, A&D analytical balance HR250 AZ, Whatman No. 42 filter paper, and glass tools. The ingredients used in this study are ethanol, Salicylaldehyde Chemicraft Ltd $\geq 98\%$ BM = 122,12 g/mol, and Hydrazine hydrate Wako Pure Chemical 80%, BM = 50,06 g/mol.

2.2. Method

Salicylaldehyde (20 mmoles) was dissolved at room temperature in ethanol (50 ml), and hydrazine hydrate (10 mmoles) was added. The reaction mixture was stirred for 24 hours at room temperature. The obtained yellow precipitate was filtered after completing the reaction and washed several times with cold ethanol to produce the SB [8]. The yield is 80%. The melting point of the product was 220-222 °C. *Anal. calculated for $C_{14}H_{12}N_2O_2$: C, 69.99; H, 5.03; N, 11.66. Found: C, 70.36; H, 4.91; N, 11.78. 1H NMR (400 Hz, DMSO- d_6), δ : 11.1 (s, 2H, OH), 9.0 (s, 2H, N=CH), 7.6–7.7 (m, 2H, Ar-CH), 7.3–7.4 (m, 2H, Ar-CH), 6.9–7.0 (m, 4H, Ar-CH).*

The Fluoride ion binding properties of SB was then carried out by dissolving the SB in DMSO, then measured the UV-Vis spectra [9].

3. Results and discussion

The percentages of elemental analysis of both ligands are close to the calculated values. Both ligands have a low melting point range, suggesting that the high purity of the synthesized compound. Once the reaction is completed, light yellow deposits are formed (Figure 1). Then deposits and filtrates are separated with filter paper, and the results are done to maximize the net weight gained after the constant weight of dry deposits was obtained with a yield of 1.732 grams (80%).

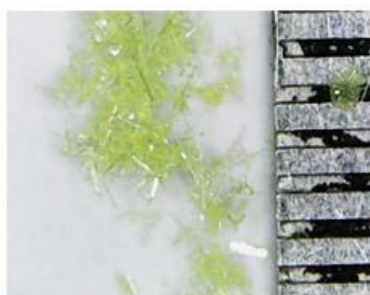


Figure 1. Salicyldazine crystal.

3.1. The UV-Vis spectra of Salicyldazine

The salicylaldehyde has two absorption bands in the UV region (Figure 2), which are at 298 and 357 nm, respectively. The aromatic ring's absorption band is located at a wavelength lower than 200 nm [10], and it did not observe. The $\pi \rightarrow \pi^*$ transition of C=O on the aldehyde group is located at 298 nm. Because of the presence of intramolecular hydrogen bond between the phenolic hydroxyl and the carbonyl of aldehyde, the molecule presents a dienylic $\pi \rightarrow \pi^*$ transition of enonyl transition of C=C-C=O around 357 nm [11,12].

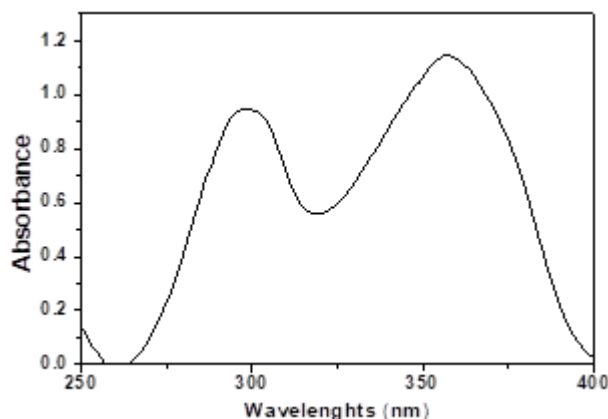


Figure 2. Spectrum Absorbance Salicylaldazine 15 mM in DMSO solvent.

3.2. The UV-Vis spectra of Salicylaldazine

The IR spectra shown in Figure 3 exhibited strong absorptions around 1621 cm^{-1} , 1566 cm^{-1} , and 1276 cm^{-1} , which are attributed to the azomethine (C=N), aromatic benzene (C=C), and phenolic oxygen (C-O) functional groups, respectively [13][14]. The weak and broad peak of hydroxyl (OH) indicated the presence of intermolecular hydrogen bond formed between phenolic hydrogen with azomethine nitrogen ($\text{OH}\cdots\text{N}=\text{C}$).

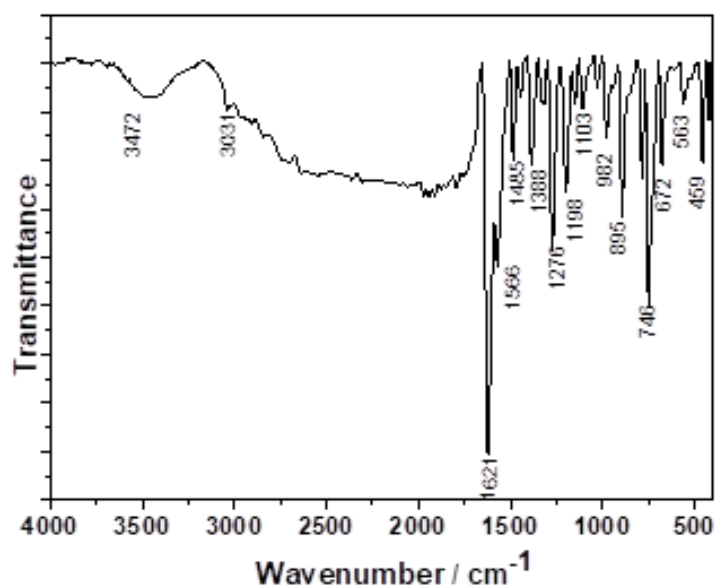


Figure 3. Spectrum FTIR Ligand Salicylaldazine.

3.3. The UV-Vis spectra of Salicylaldazine

The powder-XRD (PXRD) was used to obtain crystallographic information. The diffractogram (Figure 4) corresponds to a single phase of monoclinic system. The pattern was then refined using Le Bail method. Based on refinement result the SB include to the monoclin crystal system, space group of P 21/C, with cell parameter a, b, c and β of 8.5395 (Å), 6.3979 (Å), 12.258 (Å) and 93.945° , correspondingly. The results indicate a similar structure with the previously reported by Jain and Kumar [10], Granados et al. [15].

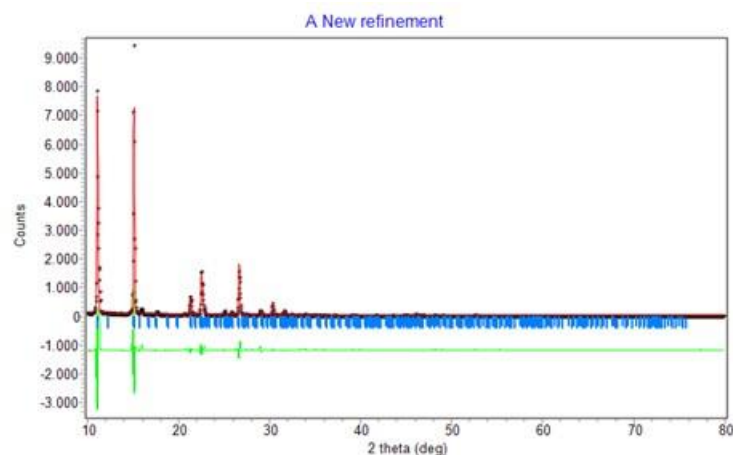


Figure 4. Diffractogram Salicylaldazinein Rietica program.

3.4. Salicylaldazine interaction with Fluoride ion

The salicylaldazine compound was screened for fluoride ion detection by measuring the UV-Vis spectra, as shown in Figure 5. In the presence of fluoride, a new peak at 455 nm was observed, possible binding models of SB was proposed, which was shown in Scheme 2. Upon binding of fluoride anions, the C=N isomerization of SB was restricted, and the intramolecular charge transfer interaction between electron-rich imine (C=N⁻) and electron-deficient fragments was enhanced, which were responsible for the spectral behaviours [16].

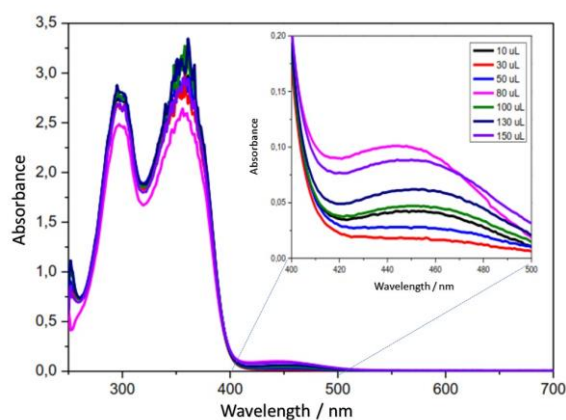


Figure 5. Fluoride ion detection with salicylaldazine in DMSO.

4. Conclusion

The salicylaldazine was synthesized successfully by refluxing salicylaldehyde with hydrazine. The yellowish crystal was obtained indicating the salicylaldazine has a high crystallinity as it also confirmed from diffractogram. The salicylaldazine shows a new peak at the visible area in the presence of fluoride ion. The peak indicating the intermolecular interaction between OH- group with fluoride ion via hydrogen bond.

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