

## SPECTROSCOPIC STUDY OF SOLVENT EFFECTS ON THE PHOTOPHYSICAL PROPERTIES OF N,N'-BIS(SALICYLIDENE)-1,2-ETHYLENEDIIMINE

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## Abstract

The effects of H<sub>2</sub>O, methanol and ethanol as solvents on the spectroscopic properties of N,N'-bis(salicylidene)-1,2-ethylenediimine (Salen) Schiff base were studied. The absorption and emission of Salen were recorded in solution mixtures of; water-acetonitrile, methanol-acetonitrile and ethanol-acetonitrile. The position and intensities of the absorption bands are sensitive to the solvent ability of hydrogen bonding. The use of water-acetonitrile solvent mixture significantly enhances the intensity of the absorbance band of Salen centered at 404 nm. The enhancement occurs at the expense of the absorbance band around 317 nm as indicated by an appearance of one isosbestic point at 336 nm. This  $\pi \rightarrow \pi^*$  electron transition produces a strong emission at 505 nm that was not observed in pure acetonitrile solution. Methanol and ethanol show the same effect.

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Keywords: Salen; Schiff Base; Isosbestic Point; Tetradentate Ligand; HOMO; LUMO

Received: January 27, 2023

Accepted: February 8, 2023

Published: February 14, 2023

## Introduction

Schiff base chemistry was known for several decades. A particular class of Schiff base ligands is that of a tetra-dentate (O  $\curvearrowright$  N  $\curvearrowright$  N  $\curvearrowright$  O) Salen-type, N,N'-bis(salicylidene)-1,2-ethylenediimine. Salen ligand can be synthesized by the condensation of ethylenediamine with 2 equivalents of salicylaldehyde (Figure 1).<sup>1(a,b,c)</sup>

The tunable optical properties and the wide range of application of Salen made this ligand particularly interesting among researchers in a wide range of studies including optical materials,<sup>2</sup> fluorescent supramolecular materials<sup>3, 4</sup> and biological applications.<sup>5</sup> Electron donating and electron accepting substituents added to the bridging ethylene or even to the benzene rings, influence the  $\pi$ -conjugation of the ligand which accordingly affects its photophysical properties.<sup>6</sup>

In theory, a tetra-dentate ligand like Salen should have the ability to bind to metal ions and form thermodynamically stable coordination compounds due to its chelating effect. Xiang et.al reported on the ability of this class of ligands to coordinate to a variety of non-transition metal cations and produce fluorescent metal complexes.<sup>7</sup>

In this article, we are reporting on the optical sensitivity of Salen towards hydrogen-bonding solvents like water and alcohols (H<sub>2</sub>O, MeOH, and EtOH). The effect of these solvents on the absorbance and fluorescence of the plain Salen, without any special substituents added to the backbone of the ligand that can affect its  $\pi$ -conjugation properties, will be discussed. The UV-Vis and emission spectra of Salen were recorded using a variety of solution mixtures of; water-acetonitrile, water-methanol and water-ethanol, and the results were interpreted and compared to those recorded in pure acetonitrile solvent and those reported in the literature.

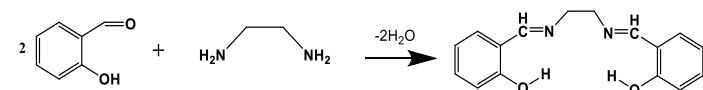


Figure 1. Synthesis of Salen.

## Experimental Methods

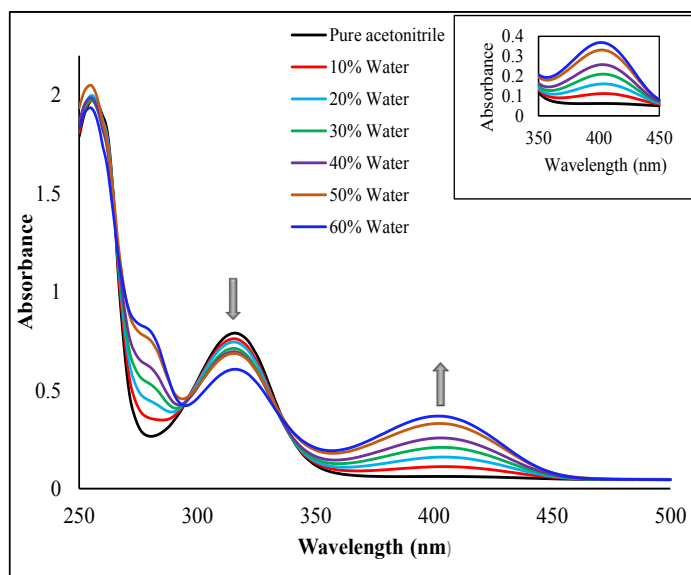
Salen was prepared in house according to Figure 1 following literature techniques.<sup>6</sup> The absorbance and fluorescence of the ligand were recorded using water-acetonitrile mixture of the ratios: 10%, 20%, 30%, 40%, 50% and 60% and compared to those measured in pure acetonitrile. UV-Vis Agilent 8453 and Photon Technology International (PTI) were used for the absorbance and fluorescence recording respectively.

## Results and Discussion

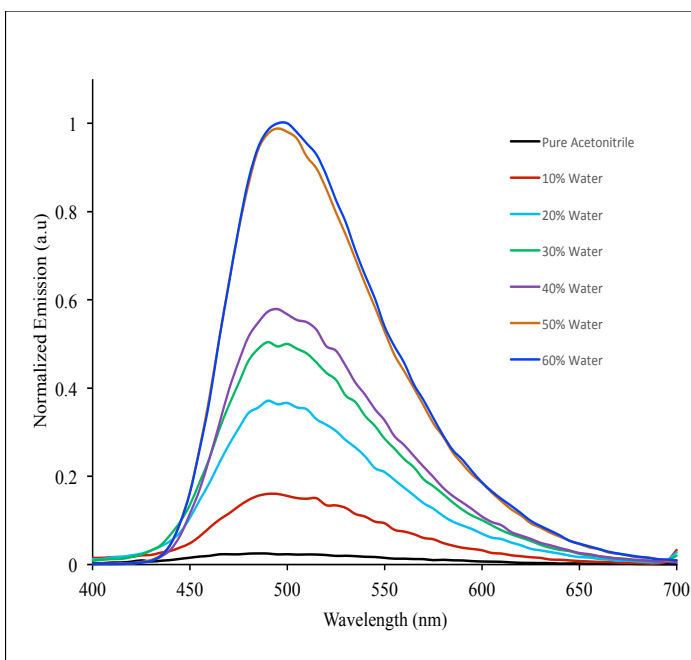
The UV-Vis absorption of Salen in acetonitrile solution shows two major absorption bands; an intense band centered around 256 nm attributed to  $\pi \rightarrow \pi^*$  transition and a broad absorption band centered around 317 nm attributed mainly to the  $\pi \rightarrow \pi^*$  transition with some  $n \rightarrow \pi^*$  transition involving molecular orbitals from C=N chromophore.<sup>8(a,b)</sup> In addition, the much lower intensity absorption band around 404 nm is attributed the  $\pi \rightarrow \pi^*$  transition involving the N=C group and the benzene ring.<sup>6</sup> The energy gap between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of the chromophore, is directly affected by the  $\pi$ -conjugated bridging between the N=C groups. For example, using 1,2-phenylendiimine bridging moiety enhances the  $\pi$ -conjugation and as a result it lowers the energy gap between the HOMO and the LUMO, resulting in a red-shift in the absorption spectra. In the case of  $\pi$ -nonconjugated bridge, polar solvents however, seem to have the same effect by stabilizing the excited state ( $\pi^*$ ) causing a significant change in the intensity and the wavelength of the  $\pi \rightarrow \pi^*$  absorption band.<sup>9, 10</sup> Using a hydrogen bonding solvent (H<sub>2</sub>O, MeOH, and EtOH) drastically weakens the contribution of nonbonding electrons (n) to the (n- $\pi$  conjugation). Thus, the electron transition responsible for the 317 nm band gains  $\pi \rightarrow \pi^*$  character with much larger probability.<sup>9</sup> This effect can be easily observed in the UV-Vis absorption of Salen in acetonitrile/H<sub>2</sub>O solvent mixtures. The increase of the percent of H<sub>2</sub>O in the acetonitrile/H<sub>2</sub>O solution mixtures drastically enhances the intensity of the absorption band centered around 404 nm and that occurs at the expense of the absorption at 317 nm, evidenced by the

appearance of an isosbestic point  $\sim 336$  nm in the spectra. **Figure 2** illustrates the effect of the percent of  $H_2O$  in the acetonitrile solution on the UV-Vis spectra of Salen.

The emission of the compound in acetonitrile solution is very weak compared to the literature.<sup>6</sup> Although the  $\pi \rightarrow \pi^*$  band at 404 nm is a strong emitter in the visible reign, no emission was detected using  $6.18 \times 10^{-3}$  M acetonitrile Salen solution. However, a significant enhancement in the emission, centered at 505 nm, is observed as the water content in the acetonitrile solution of Salen is increased while the molar concentration of Salen remains unchanged (**Figure 3**). This is due to the enhancement that occurs in the absorbance band at 404 nm. The most intense emission is obtained using 60%  $H_2O$ -acetonitrile solvent mixture when  $\lambda_{ex}$  of 375 nm is used. Attempts to prepare a stoichiometric *pure* aqueous solution of Salen have failed due to the low solubility of Salen in water.

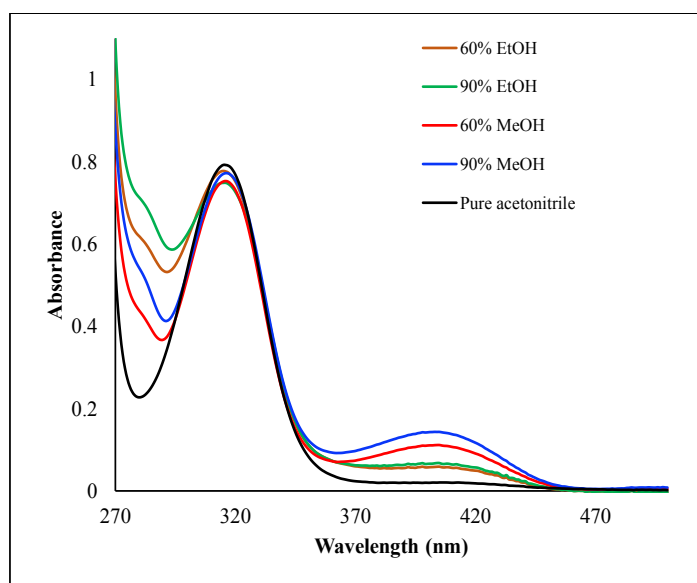


**Figure 2.** Absorbance of  $6.18 \times 10^{-3}$  M Salen in water / acetonitrile solvent mixtures.



**Figure 3.** Normalized emission spectra of  $6.18 \times 10^{-3}$  M Salen in pure acetonitrile

The effect of methanol and ethanol, as hydrogen bonding solvents, on the spectroscopic properties of Salen were also examined. The solution mixtures used in this part of the study were 60% and 90% alcohol-acetonitrile of each alcohol. The effect, as noticed from the UV-Vis measurements, resembles that of water to a large extent (**Figure 4**). Moreover, results indicate that methanol has higher effect on the conjugation structure of Salen as evidenced by the percent enhancement in the intensity of the absorbance band at 404 nm compared to ethanol. For example, the enhancement in the UV-Vis band intensity at 404 nm using the 60% methanol mixture compared to the same mixture of ethanol reaches 67%. This result is attributed to the stronger hydrogen bonding formed between methanol and Salen. In conclusion, the effect of the three solvents used in this study on the spectroscopic characters of Salen is a function of the strength of the hydrogen bonding between the solvent and Salen which comes in the order of  $H_2O > MeOH > EtOH$ .



**Figure 4.** Absorbance of  $2.08 \times 10^{-4}$  M Salen in methanol-acetonitrile and ethanol-acetonitrile solvent mixtures.

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