

SYNTHESIS, CHARACTERISATION AND FLUORESCENCE SENSING PROPERTIES OF TETRADENTATE *N,N'*-BIS(SALICYLIDENE)-1,3-PROPANEDIAMINE FOR METAL IONS DETECTION: PRELIMINARY STUDY

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Abstract: Tetradentate Schiff base ligand namely *N,N'*-bis(salicylidene)-1,3-propanediamine, containing -ONNO- donor set was successfully synthesised between salicylaldehyde and 1,3-diaminopropane using condensation reaction. The structure of the synthesised ligand was unambiguously determined by Fourier Transform Infrared (FTIR) spectroscopy, Nuclear Magnetic Resonance (NMR) spectroscopy and Thermogravimetric Analysis (TGA). The spectroscopic studies suggest that the central azomethine (C=N) group of tetradentate ligand can be assigned at vibration peak 1632 cm^{-1} and the chemical shift observed for OH proton appeared at very downfield. TGA curve shows around 80% weight loss occurred when the sample was heated at room-temperature up to $850\text{ }^{\circ}\text{C}$. Initial data show the ligand enhanced fluorescence spot upon increasing the concentration of Zn^{2+} and Pb^{2+} . The response of ligand with Zn^{2+} and Pb^{2+} also inhibits the C=N bond isomerisation and subsequently increased the intensity of fluorescence efficiency. Thus, the proposed tetradentate Schiff base ligand used as reagent sensing potentially has good capability in sensing application for metal ions detection.

Keywords: Tetradentate Schiff base, metal complexes, fluorescence sensing

Introduction

Heavy metals such as mercury (Hg), cadmium (Cd) and lead (Pb) can be described as those with definite density exceeding 5 g/cm^3 . These metals have been thoroughly studied and frequently evaluated by international organizations like WHO for their effects on human health. The toxicity of heavy metals has proven to be a major threat and the negative effects on health, environment as well as living organisms have long been recognized (Jarup, 2003). According to Kang *et al.*, (2014), in industrial and agriculture pollutants, heavy metal ions are pervasive, thus causing a major environmental issue in many places. Unlike many other pollutants, heavy metal ions are hard to degrade, yet they are easy to enrich human body through the food chain.

Zinc is the second most abundant metal ion among the varied major heavy metal ions in

the human body and thus the detection of Zn^{2+} shows considerable interest in chemistry (Hens *et al.*, 2014). The disorder of zinc ion metabolism can cause anaemia, growth retardation, skin abnormalities, and mental lethargy. In addition, deficiency of zinc can cause delayed growth, immunodeficiency, and also degeneration of the neurons. So, there is significant interest and importance for the detection of Zn^{2+} in the samples (Ackland & Michalzyk, 2006).

Lead is classified among the most harmful and cumulative pollutants of the environment that threatens all biological systems by exposure to air, water and food sources. Lead is among the most frequently found as global environmental pollutants in manufacturing areas, and animals could be exposed to lead easily. In addition, excessive consumption of lead may cause bad animal performance, poisoning and death (Assi *et al.*, 2016).

Schiff base ligand is versatile C=N (imine) compound with a wide spectrum of biological activity and complex incorporation of metals that have shown some degree of antibacterial, antifungal, antitumor and anti-inflammatory interaction. They are ketone or aldehyde condensation products with primary amines and were first reported in 1864 by Hugo Schiff (Xavier & Srividhiya, 2014). Schiff base ligands involving different donor atoms (such as N, O, S, etc.) exhibit wide biological activity and are of particular concern due to the wide variety of ways in which they have been linked to transition metal ions. Because of their coordination chemistry, Schiff bases have been considered as important ligands for decades and can be easily prepared and connected to a different type of metal ions (Joshi *et al.*, 2014). Therefore, fluorescence techniques have been commonly used in the identification of metal ions, with the benefits of sensitivity, simple operation, and real-time tracking with quick response time (Guo *et al.*, 2019). In this study, synthesis, characterisation and fluorescence sensing properties of tetradentate Schiff base ligand, *N,N'*-bis(salicylidene)-1,3-propanediamine for metal ion detection have been focused on and the preliminary studies have been carried out.

Materials and Methods

Chemicals

Pure chemicals of 1,3-diaminopropane and salicylaldehyde were purchased from Merck and Aldrich, respectively. Absolute ethanol (95%) ethanol (70%), zinc sulphate ($ZnSO_4$) and lead chloride ($PbCl_2$) were used to prepare metal ion stock solutions. The chloroform-*d* ($CDCl_3$) was available as a solvent to record 1H NMR and ^{13}C NMR spectra. All of the chemicals were used as received without further purification.

Instrumentation

Fourier-transform infrared spectroscopy (FTIR) was performed using Perkin-Elmer Spectrum 100 Spectrometer. FTIR spectrum was obtained using KBr pellet method. The absorption was recorded in the range of $4000-400\text{ cm}^{-1}$. Nuclear Magnetic Resonance (NMR) spectra of 1H

NMR and ^{13}C NMR were obtained using Bruker Avance III 400 MHz spectrometer, using $CDCl_3$ as the solvent. Thermogravimetric Analyzer (TGA) was performed using Mettler Toledo TGA/SDTA851° with a heating rate of $15\text{ }^\circ\text{C}/\text{min}$ over the temperature range between $30-850\text{ }^\circ\text{C}$. Ultraviolet-Visible (UV-Vis) spectra were recorded on a Shimadzu SPD-10A. The stock solution of ligand with the concentration of 0.01 M was diluted for several series with the new concentration of $1\times 10^{-3}\text{ M}$, $1\times 10^{-4}\text{ M}$, $1\times 10^{-5}\text{ M}$ and $1\times 10^{-6}\text{ M}$ using ethanol as solvent. The emission of data was collected using Cary Eclipse Fluorescence Spectrophotometer.

Synthesis of Ligand

Salicylaldehyde (0.4884 g, 4.00 mmol) was mixed with 10 mL of absolute ethanol in 3 neck round bottom flasks. Then, 1,3-diaminopropane (0.1482 g, 2.00 mmol) was added into that flask and the mixture was refluxed for 6 hours. The yellow precipitate was formed. The precipitate was filtered and left until totally dry. Ethanol solution was used as solvent to recrystallize the yellow precipitate.

Fluorescence Experiments

A stock solution of zinc and lead with the concentration of 0.001 M was initially prepared by dissolving metal ions in distilled water. The stock solutions were then diluted to appropriate concentrations for further experiment. All fluorescence emission spectra were recorded in the wavelength from 300 nm to 650 nm. The slit widths for excitation and emission were both 10 nm.

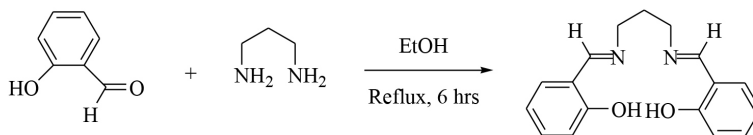
Results and Discussion

The ligand was successfully synthesized by condensation reaction between salicylaldehyde and 1,3-diaminopropane under mild conditions (Scheme 1). The reaction progress was monitored using TLC. The structure of the ligand was confirmed by FTIR and NMR spectroscopies as well as TGA. FTIR data (Table 1) show a vibration band at 1632 cm^{-1} which can be assigned to the stretch of imine ($-C=N-$) group

in the ligand molecule. The vibration band at 3457 cm⁻¹ associated with alcohol stretching group while 1582 cm⁻¹ was assigned as (-C-C

aromatic) symmetrical group in this Schiff base ligand.

Scheme 1: Synthesis route of tetradentate Schiff



base ligand

Table 1: FTIR peak assignment of tetradentate ligand

Compound	Frequency (cm ⁻¹)				
	n(O-H)	n(C=N)	n(C=C aromatic)	n(C-N)	n(C-O)
<i>N,N'</i> -bis(salicylidene)-1,3-propanediamine	3457	1632	1582	1281	1011

The ¹H NMR spectrum obtained for synthesised ligand in chloroform-*d* (CDCl₃) with their assignment is given in Figure 1. The proton of azomethine HC=N was exhibited at the downfield δ_H 8.40 ppm. The multiplet and triplet resonances were observed at shielded regions, at two different environments δ_H 2-13 – 2.16 ppm and δ_H 3.73 – 3.76 ppm accordingly which were allocated for C-CH₂-C and N-CH₂. The distinctive multiplet resonance appeared in the range of δ_H 6.89 – 7.36 ppm was attributed to the presence of aromatic protons for synthesised ligand.

Meanwhile, thermal analysis provides significant information about the structural feature and preferential ligation of the different groups directly attached to and/or associated in the compound (Soliman *et al.*, 2000). The ligand was thermally stable up to 230 °C and above this temperature it started to decompose. Figure 2 reveals a decrease in mass between the temperature regions which may be due to the dissociation of solvent and water molecules and the sample degradation (Popa *et al.*, 2006). The thermogram of tetradentate ligand shows around 90% in weight loss occurred when the sample was heated up to 850 °C

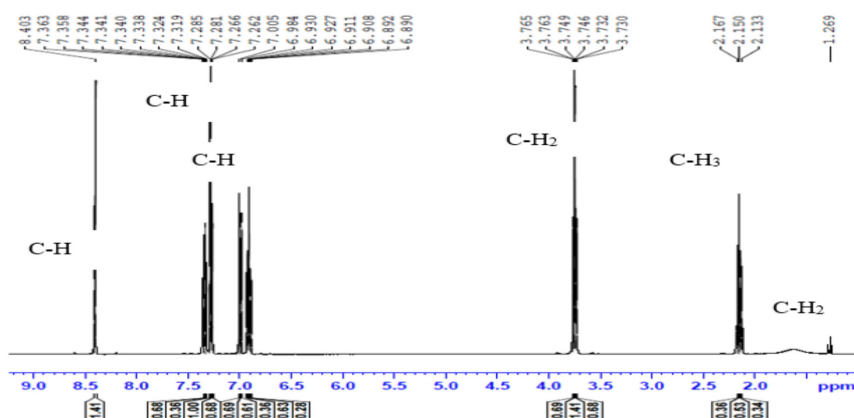


Figure 1: ¹H NMR spectrum of tetradentate Schiff base ligand

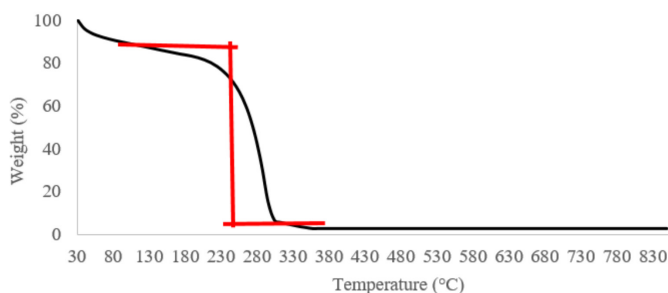


Figure 2: TGA thermogram of tetradentate Schiff base ligand

The UV-visible analysis of ligand was recorded in the 300-800 nm range in ethanol solution with the variety of concentrations between 1×10^{-2} M until 1×10^{-6} M (Figure 3). In the electronic spectra of ligand, the absorption band observed within the range of 350-450 nm was most probably due to the transition of $\pi \rightarrow \pi^*$ in the benzene ring or $n \rightarrow \pi^*$ of C=N chromophore, corresponding to the ligand (Fraser & Bosnich, 1994). It can be found that the maximum

absorption wavelength obtained at 395 nm with 1×10^{-5} M which is the most suitable for sensing reagent due to high intensity of peak (Sun *et al.*, 2014). As can be observed, the concentration of 1×10^{-5} M provides optimum shoulder in the region which involves molecular essentially localized on the C=N group and benzene ring (Asadi *et al.*, 2011). The wavelength at 395 nm was also selected as ligand excitation for fluorescence study.

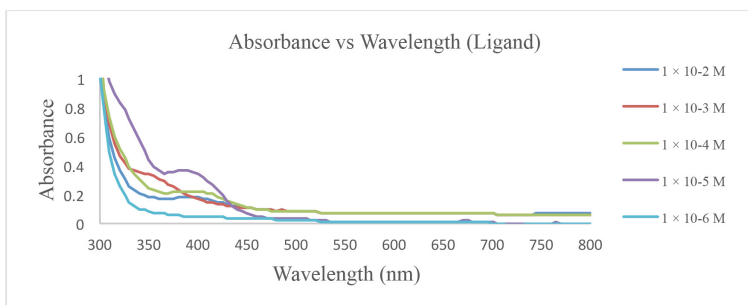


Figure 3: Progression of UV-vis spectra of ligand with different concentrations

Furthermore, the fluorescence study was investigated for 1×10^{-5} M solution using excitation wavelength at 395 nm. Two types of metal ions have been tested which are Zn^{2+} and Pb^{2+} . Excitation and emission-based response of ligand with metals ion are shown in Figure 4. The results show that the fluorescence enhancement on Pb^{2+} ion is higher compared to Zn^{2+} ion due to the excellent selectivity and sensitivity towards

Pb^{2+} with binding site of tetradentate ligand (Wan *et al.*, 2015). The fluorescence intensities were increased according to the increased concentration ion of metals and saturates after one equivalent has been achieved. Hens *et al.*, (2014) also reported that the changes of colour in solution may have occurred due to the decrease of absorption peak during the fluorescence studies.

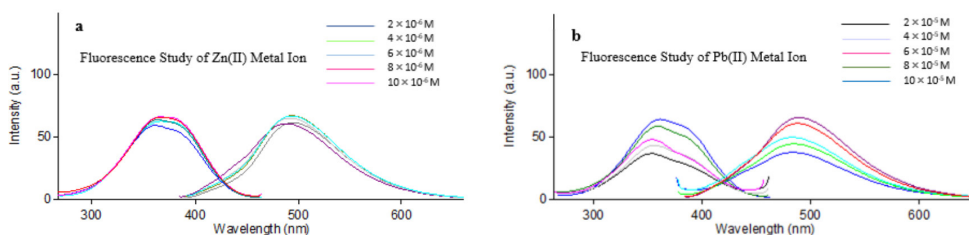


Figure 4: Fluorescence spectra of (a) Zn²⁺ and (b) Pb²⁺

Figure 5 exhibits calibration curves of metal ions for Pb²⁺ and Zn²⁺ with the ligand solution of 1 × 10⁻⁵ M. The Zn²⁺ ion that have low absorbance compared to other metal ion which leads to the formation of a stable complexes with the ligand as a sensing reagent (Andiappan *et al.*, 2018). When a higher concentration of each

metal was used, the fluorescence enhancement exhibited a linear response versus amount of the metal ion with the correlation coefficient for Zn²⁺ is 0.9895 and Pb²⁺ is 0.9876, respectively. The results indicate that the ligand can be used for metals ion detection in a wide concentration range.

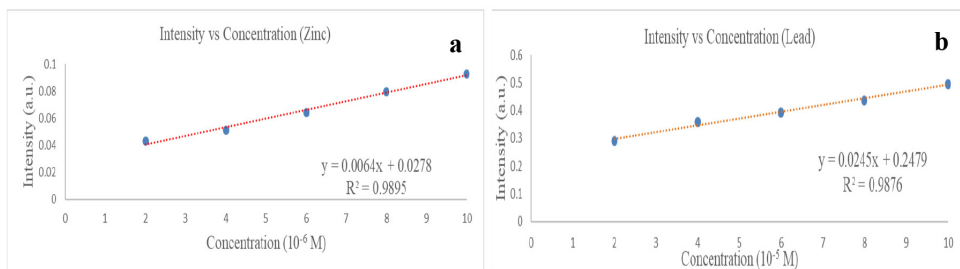


Figure 5: Fluorescence calibration curves of Zn²⁺ (a) and Pb²⁺ (b)

Conclusion

A turn-on fluorescence probe containing a Schiff base as metal binding site for zinc ion and lead ion has been synthesised through condensation reaction. The chemical structure and spectral properties were carefully characterized using FTIR spectroscopy, NMR spectroscopy and TG analysis. Selective binding with metal ions (Zn²⁺ and Pb²⁺) greatly increased the fluorescence of the probe due to the formation of a rigid structure between the imine groups. The complexation between ligand and metal produced a large chelation-enhanced fluorescence effect, leading to the fluorescence enhancement. The method allows a simple and effective way for visual Zn(II) and Pb(II) detection.

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