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Study of A Tridentate Schiff-Base as A Highly Selective Fluorescent Sensor for Detection of Copper and Chromium Ions

Zeyad G. Yasseen

Chemistry – Science – IUG – Gaza

Corresponding Author: zyasseen@iugaza.edu.ps

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Abstract:

A simple and easily synthesized fluorescent sensor, Schiff base sensor (SBS), produced by condensation reaction of equal amounts of anthranilic acid and salicyladehyde. It was synthesized and characterized systemically. Both UV-vis and fluorescence spectroscopic studies indicated that the SBS sensor showed good selectivity toward the studied ions: Na^{+}, K^{+}, Cu^{2+}, Co^{2+}, Fe^{3+} , Al^{3+} and Cr^{3+}. Whereas, chromium (III) and copper (II) exhibited the largest fluorescence enhancement over the other investigated ions.

Chelation-enhanced fluorescence were shown upon the interaction of SBS sensor with some metal ions studied forming inclusion complexes. The fluorescent sensor in aqueous ethanolic solution exhibited high selectivity towards Cu^{2+} and Cr^{3+} ions, forming 2 : 1 (L : M) complex as determined by Job's plot.

The formation constants of the inclusion complexes (M^{n+}/SBS) were measured via spectrofluorometric method applying Benesi-Hildebrand equation.

Keywords:

tridentate Schiff base; fluorescence sensor; fluorescence enhancement; formation constant

Introduction:

Much attention was paid to the design and synthesis of fluorescent sensors, based on Schiff bases which display intriguing features such as high sensitivity, selectivity, rapidity and easy operational procedures through their use as sensors to identify metal ions in biological, environmental testing and sewage treatment [1-7].

Schiff bases which contain azomethine groups are the compounds synthesized by condensation of carbonyl compounds with primary amines. Schiff bases were of profound importance in experimental and theoretical studies of coordination compounds.

Several metal chelates of the ON donor moiety of Schiff bases were studied and were found to be useful models for bioinorganic processes [8-13]. They form complexes with distinct stability and provide several bonding sites with notable flexibility around metal ions involved in various functions in biological molecules and many other chemical species. Moreover, they are also widely used in electrochemical and optical sensors [14-17].

Schiff bases have received considerable attention because of their potential use as fluorescent sensors [18-20]. The design of fluorescent sensors for the detection of some metal cations is a hot research subject that is under investigation these days.

As several transition metals including iron and chromium in various oxidation states are essential to all organisms, fabrication of fluorescent sensors of these metal ions is useful for determination of these ions and assessing their roles in biological and environmental processes.

Schiff base compounds have received considerable attention because of their potential use as antibacterial, antifungal, antitumor and herbicidal active substances and as catalysts. [21-28]

Some fluorescent chemosensors have received considerable attention for the detection of metal ions such as Cu^{2+} [29, 30], Cr^{3+} [31], and Fe^{3+} [32], because their special structural properties provide an ideal mode to construct off-on fluorescent switch chemosensors.

Development of fluorescence sensors for various valent metal ions, is still a need because they play very important roles in a wide range of environmental and biological processes.

This study aimed to synthesize a tridentate Schiff base ligand and its complexation with some essential transition metal ions.

In addition, estimation of the formation constants, (K_f) for the inclusion complexes formed with the tridentate sensor used (SBS).

Experimental Section

Material

Metal salts used in this study, typically chlorides, were of analytical reagent grade quality and were supplied from Merck.

The SBS sensor was dissolved in a mixed aqueous/ethanol media (H_2O : ethanol (v/v, 1:1) forming 1.0 mM stock solution.

Equipments and procedures

Fluorescence

Spectrofluorimetric metal ion/sensor complexation studies were performed using a Perkin Elmer luminescence (series no. 70412) spectrofluorometer with both excitation and emission slits set at 10 nm. The instrument was interfaced to a computer for data collection. All titrations were performed using a 1 cm quartz cell by addition of small aliquots of metal ion work solutions of appropriate concentration to a 3 mL solution of 10 μM of initial concentration of SBS sensor in aqueous ethanolic phosphate buffer solution pH7 (1:1, v/v). During the complexation studies, the excitation wavelength was set at 325 nm, and fluorescence emission (which correspond to sensor with its inclusion complex) was monitored at 345 nm. The collected fluorescence readings were treated to eliminate dilutions effects as well as inner filter effects.

After thorough mixing, the solutions were allowed to stand at ambient temperature for 5 min. The fluorescence spectrum of SBS sensor was taken in the range of 250-500 nm. The equations and data analysis corresponding to the complexation of the studied metal ion to sensor SBS was performed using Benesi-Hildebrand equation [34].

Synthesis of the Schiff base sensor

The tridentate Schiff base (SBS), shown in Scheme 1, was synthesized by following the literature procedure [26].

An ethanolic solution containing 2 mmol of salicylaldehyde was condensed with 2 mmol of anthranilic acid and were refluxed for 2 h. Upon completion of the reaction, a light yellow product was formed. The final product was collected, washed and dried, M.P 205 ºC, [35], scheme (1).

Measuring the complexation constant

The association constants of the (SBS-metal ion) inclusion complexes were determined employing the Benesi-Hildebrand method (equation 1) [25,33]. A plot of the ratio $(F_{max} - F_0)/(F - F_0)$ *versus* 1/ [metal ion]^2 allows to obtain the association constant from the slope.

Where, F_0 is the fluorescence intensity of free sensor SBS; F is the observed fluorescence intensity at any given concentration of metal ion $[M^{n+}]$; F_{max} is the intensity at saturation point (large excess) with the metal ion; and K_a is the association constant. A plot of $(F_{max} - F_0) / (F - F_0)$ *against* $1 / [M^{n+}]^2$ produced a straight line. The value of Ka was calculated from the slope of the line obtained as described above.

Results and Discussion

The fluorescence properties of SBS sensor were evaluated with distinguished metal ions in ethanol/H_2O system (v/v, 1:1, 0.02 M Phosphate buffer, pH 7.0) at 25 °C. The sensor, SBS (10 µM) exhibited a weak fluorescence emission in the studied range (250-500 nm) upon excitation at wavelength 325 nm.

The weak fluorescence intensity is most likely associated with internal charge transfer which results in quenching of the sensor fluorescence emission.

Figure 1, depicted the fluorescence emission spectra upon addition of successive 20 µl aliquots of various studied metal ions.

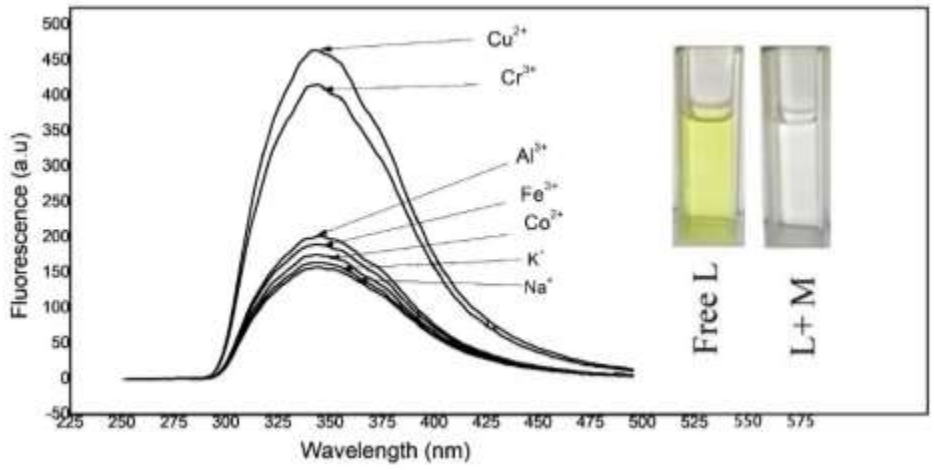


Figure (1): Emission fluorescence spectra of SBS sensor in ethanolic-water, phosphate buffered solution pH 7.0 at 25 °C). λ_{ex} = 325 nm, λ_{em} = 345 nm) titrated with different aliquots of metal ion samples.

The SBS sensor exhibited a remarkably enhanced intensity in its fluorescence emission in presence of the divalent ion (Cu^{2+}), and to a lesser extent with the trivalent ion (Cr^{3+}), both over all other examined mono/di or trivalent metal ions. The results suggested that SBS sensor is entertained by good selectivity towards both Cu^{2+} and Cr^{3+} ions over all other competitive metal ions, studied.

The emission spectra of inclusion complexes (sensor/M^{n+}) were enhanced around the emission wavelength 345 nm, while it exhibited a remarkably enhanced fluorescence emission intensity over all other metal ions examined in case of (Cu^{2+} and Cr^{3+}). The results demonstrating that SBS sensor behaves as an efficient and selective sensor abilities for these two ions; Cu^{2+} and Cr^{3+}

The calculated values of complex formation constants related to the studied metal ions with the SBS follows the order:

$Cu^{2+} > Cr^{3+} >> Al^{3+} > Fe^{3+} > Co^{2+} > K^{+} > Na^{+}$ (Table 1)

Selectivity of SBS sensor towards metal ions

To understand the selectivity of SBS sensor at 25 °C towards metal ions studied, the emission spectra of SBS sensor (10 μM) were studied upon addition of different metal ions (Na^{+}, K^{+}, Co^{2+}, Fe^{3+}, Al^{3+}, Cr^{3+}, and Cu^{2+}ions) of various concentrations in the range 1.30 to 15.0 μM. It is shown in Fig. 2 that the SBS sensor exhibited fluorescence emission band maxima at 345 nm and was drastically enhanced in presence of the studied metal ions. The fluorescence intensity of SBS was highly enhanced in presence of $Cu^{2+}$and Cr^{3+} ions at 345 nm.

On examination of the results, it can be inferred that gradual addition of metal ions to the test solution to make its concentration in the range 1.30 to 15.0 μM caused a dramatic increase in fluorescence intensity, suggesting that metallic ions enter the less polar cavity of the sensor.

Binding Stoichiometry and complex formation constants (K_f)

The binding stoichiometry SBS: metal ion was determined by Job's plot (continuous variation method) [33], applying the fluorometric titration method,

The method of continuous variations (Job's method) was performed to determine the binding stoichiometry of combination between the ligand SBS and the metal ion. The fluorescent intensity of the reaction mixture was measured upon addition of metal ion increments. Then the fluorescence intensity of the sensor alone was plot at the *y*-axis versus the percent of desired metal ion concentration to total concentration in order to determine the exact binding stoichiometry between the SBS sensor and metal ion.

Figure 2 shows the Job's plot in which maximum emission that achieved at 0.33 mol fraction of Cu^{2+}, indicating 2:1 binding stoichiometry of the complex formed between the sensor and Cu^{2+} ions.

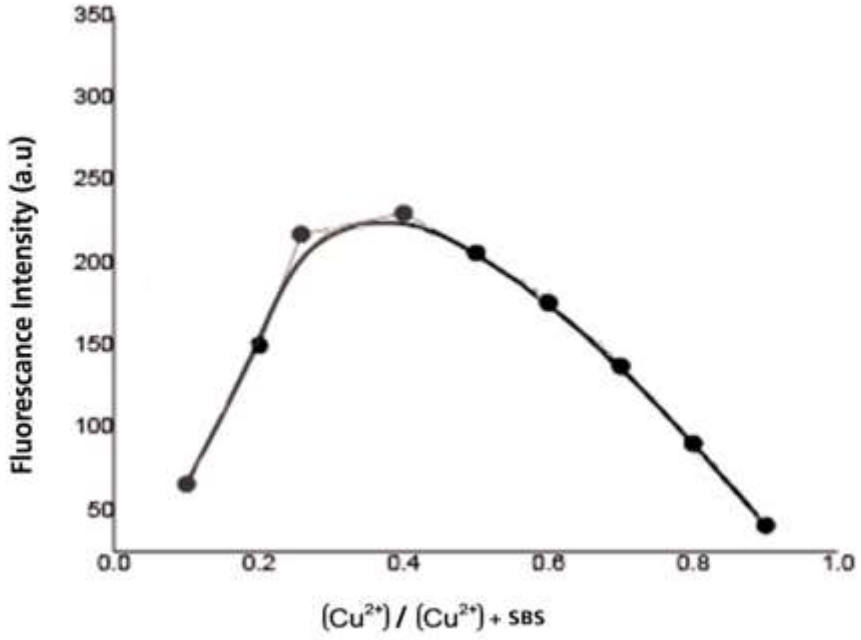
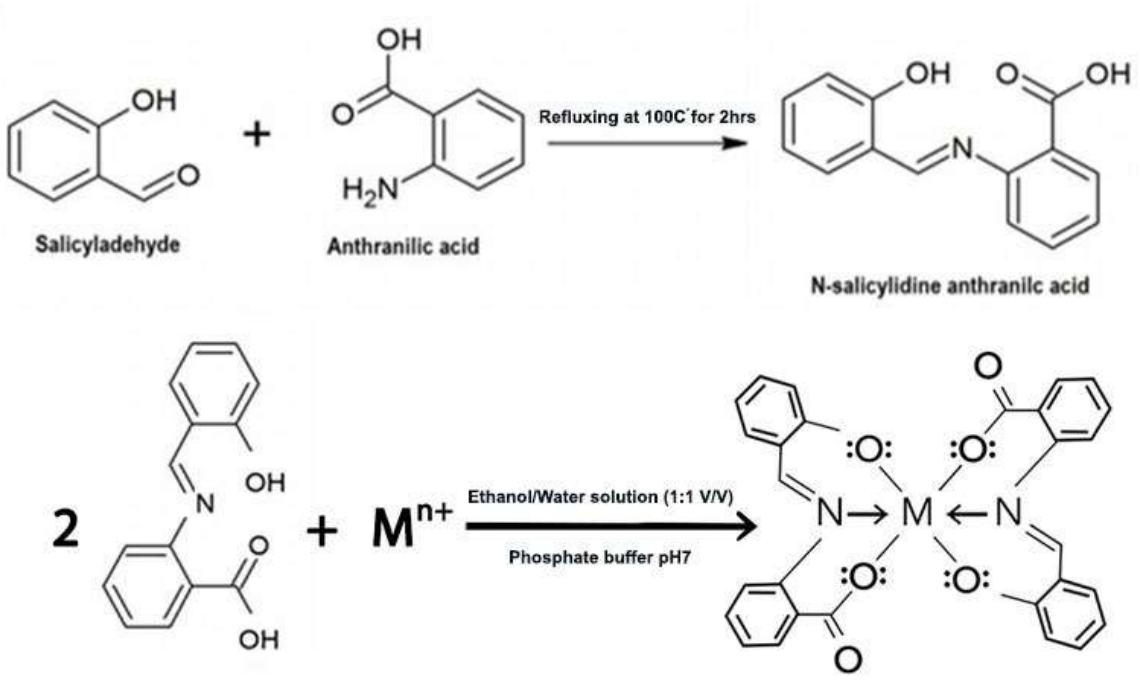


Figure (2): *Job's plot according to the method for continuous variations, indication the 2:1 stoichiometry between* ***SBS sensor*** *and* Cu^{2+} *metal ion. (λex=325 nm)*



Scheme 1: Synthesis of the tridentate sensor (SBS), and the proposed structure of the M^{n+}/SBS inclusion complex formed from connection of twofold molar amount of sensor under the given conditions.

The formation constants (K_f)

The complex formation constants were determined by monitoring fluorescence emission spectra at *λem=345 nm* and applying modified Benesi-Hildebrand equation.

The SBS metal ion inclusion complexes were obtained from the interaction of the metal ion with the tridentate Schiff base donors (NOO) in each side according to scheme 1. The formation constants were determined by monitoring fluorescence emission spectra through titration of the sensor (SBS) with the metal ions of various concentrations ranged from 1.30 μM up to 15.0 μM, at 25 °C.

The formation constants (K_f) were determined by using modified Benesi-Hildebrand equation Eq (1) [34-40].

$$\frac{(F_{max} - F_0)}{(F - F_0)} = \frac{1}{K_f [M^{n+}]^2} \quad \text{.....(1)}$$

Where, F_0 is the fluorescence intensity of free SBS sensor, F is the observed fluorescence intensity at any given concentration of metal ion in micromolar; F_{max} is the intensity at saturation

point (large excess) with the metal ion; and K_f is the formation constant of sensor-metal ion complex in (M^{-2}).

Values of the fraction $(F_{max} - F_0) / (F - F_0)$ at all points through the titration process were calculated then plot against the corresponding values of $1 / [M^{n+}]^2$.

and produced practically a straight line. The results exhibited a good linear relationship with linear fitting with slope = $(1/K_f)$ for each of the specified metal ions studied as shown in Figure 3.

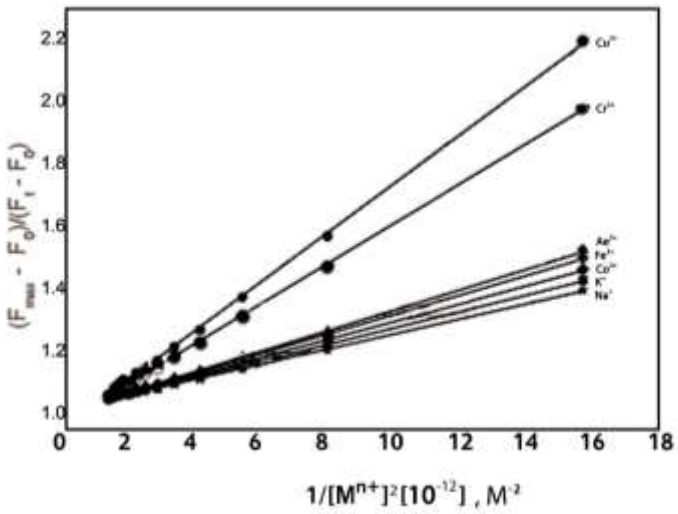


Figure (3): Typical Benesi-Hildebrand plots of 1:2 M^{n+}/SBS complexes. Where M^{n+} is the metal ion studied; Na^+, K^+, Co^{2+}, Fe^{3+}, Al^{3+}, Cr^{3+} or Cu^{2+}each is buffered in phosphate buffer solution pH 7.0 and at 25^0C

Among the studied complexes, copper and chromium seem to form stable complexes, which can be explained by the high electronic density of the hydroxyl and iminic groups, which in turn increase the nucleophilicity of the sensor ligand towards both centers, consolidating the Cu^{2+}/sensor and Cr^{3+}/sensor links and stabilizing the complexes formed.

The complexation constants of the inclusion complexes formed were displayed in Table (1).

The results in Table (1) were consistent with the fluorescence emission enhancement shown in Fig (1).

The trend of the formation constants M^{n+}/sensor complexes follows the order: Cu^{2+}/Sensor > Cr^{3+}/sensor > M^{n+}/sensor, M^{n+} = Al^{3+}, Fe^{3+}, Co^{2+}, K^{+} and Na^{+}, respectively.

Table (1) The formation constants for the inclusion complexes of the sensor (SBS) with the metal ions studied, in ethanol : water (1:1 v/v) buffered system pH = 7 *of I* = 20 mM phosphate solution and at at 25 °C.

Inclusion complex, M^{n+}/SBS	Formation constant, M^{-2}
Na^{+}/ SBS	2.20×10^{11}
K^{2+}/ SBS	2.45×10^{11}
Co^{2+}/ SBS	2.80×10^{11}
Fe^{3+}/ SBS	3.20×10^{11}
Al^{3+}/ SBS	3.80×10^{11}
Cr^{3+}/ SBS	8.00×10^{12}
Cu^{2+}/ SBS	10.30×10^{12}

The Schiff base (SBS) designed in the present research work, exhibited a powerful selectivity for both copper and chromium metal ions in aqueous media.

The SBS sensor has the imine and hydroxyl centers as the binding moieties in the sensor. The SBS sensor under study was fluorescently silent in the absence of examined metal ion but upon coordination with target analyte exhibited a significant chelation-enhanced fluorescence effect at λ_{em} 345 nm.

Conclusions

In summary, a very simple fluorescence sensor, SBS was synthesized and used as a fluorescence sensor for ion recognition.

The sensor exhibited its sensing behavior towards some metal ions: Na^{+}, K^{+}, Co^{2+}, Fe^{3+}, Al^{3+}, $Cr^{3+}$and Cu^{2+}. It exhibited a sensitive, selective determination for both Cu^{2+} and Cr^{3+} ions over all other studied metal ions in aqueous samples.

A 2:1 stoichiometry between SBS sensor and the metal ion studied was demonstrated by Job's plot (based on fluorescence emission data).

The SBS sensor is suggested to show coordination with the metal ions through the hydroxyl and imine groups embedded onto the SBS molecules.

Among the metal ions studied, both Cu^{2+} and Cr^{3+} were able to enhance the fluorescence of sensor SBS, remarkably. It demonstrated high selectivity for Cu^{2+} and Cr^{3+} ions among all other studied metal ions. The selectivity was attributed due to chelation abilities of these ions towards the donor atoms embedded onto SBS sensor molecules.

Finally, the complex formation constant, K_f were determined through recording fluorescence emission spectra at $\lambda em=345\ nm$ and applying modified Benesi-Hildebrand equation.

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