



ELSEVIER

Contents lists available at SciVerse ScienceDirect

## Journal of Luminescence

journal homepage: [www.elsevier.com/locate/jlumin](http://www.elsevier.com/locate/jlumin)

# Thiosemicarbazone based fluorescent chemosensor for transition metal ions in aqueous medium

Duraisamy Udhayakumari, Sivalingam Suganya, Sivan Velmathi\*

Organic and Polymer Synthesis Laboratory, Department of Chemistry, National Institute of Technology, Tiruchirappalli 620 015, India

## ARTICLE INFO

### Article history:

Received 16 October 2012

Received in revised form

8 March 2013

Accepted 15 March 2013

Available online 26 March 2013

### Keywords:

Thiosemicarbazone

Transition metals

Fluorescence spectroscopy

PET

## ABSTRACT

Highly efficient fluorescent chemosensors for metal ions have been synthesized by using thiosemicarbazide and aromatic aldehydes. Detection of transition metal ions was performed via UV–vis and fluorescence spectroscopic methods. This is the first report on thiosemicarbazone based sensor capable of detecting transition metal ions in aqueous medium. The binding constant, stoichiometry of the complex were confirmed by using B–H plot and Job's plot method. The fluorescence enhancement of thiosemicarbazones on binding with  $\text{Hg}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$  and  $\text{Sn}^{2+}$  ions is due to the inhibition of photoinduced electron transfer mechanism whereas, quenching of fluorescence is attributed to the photoinduced electron transfer mechanism in case of  $\text{Cu}^{2+}$  and  $\text{Mn}^{2+}$  ions.

© 2013 Elsevier B.V. All rights reserved.

## 1. Introduction

The development of artificial receptors for monitoring heavy and transition metal ions has received considerable attention owing to the wide application in environmental and analytical chemistry [1–3]. Fluorescent chemosensor supplies high sensitivity towards a practical application in biological and cell imaging field and can be directly used as chemosensors with fiber optic systems [4,5]. Copper is the third most abundant metal existing in human cells, tissues and especially in liver [6–8]. A high concentration of copper in neuronal cytoplasm may contribute to the etiology of Alzheimer's disease [9,10]. Cyanocobalamin, a natural organometallic compound which plays a vital role in the metabolism contains cobalt as the central metal atom. Its deficiency in human body may lead to pathological conditions and acts also a significant environmental pollutant [11–15]. Nickel is a very important element among various heavy metals; it is used in many industries, catalytic process and present in various effluents. Nickel (II) ion can cause disorders of central nervous system and cancer in the nasal cavity and lungs. In 1990 the International Agency for Research on Cancer (IARC) classified nickel compounds as group I carcinogenic to humans [16–20].

Mercury is one of the toxic and heavy metals that are present in the earth crust in 0.08 ppm. In the environment mercury exists in three forms, elemental, organic and inorganic. High concentration of mercury causes lot of human health problems [21–23]. Zinc is the second most abundant transition metal ion in the human biological system. Zinc (II) is present in approximately 300 enzymes, either for a structural purpose or as a part of a catalytic site. Zinc is also

known to have a role in neurological disorders, such as Alzheimer's disease, Epileptic seizures and Parkinson's disease [24–28]. Zinc and cadmium both have similar chemical properties. Therefore,  $\text{Zn}^{2+}$  and  $\text{Cd}^{2+}$  cause alike spectral changes when coordinated with a fluorosensor. Thus, it is necessary to develop a sensor that selectively senses  $\text{Zn}^{2+}$  in the presence of  $\text{Cd}^{2+}$  [29–31]. Developing fluorescent sensor that can detect different kinds of toxic metal cations in manner of simplicity, high sensitivity and time is of considerable interest [32]. Here, we report the thiosemicarbazone based compounds derived from the condensation of thiosemicarbazide and substituted aldehydes as fluorescent and optical sensors for transition metal ions, whose synthesis procedure is well documented [33,34]. Thiosemicarbazones are a class of compounds showing promise in the treatment of many diseases, cancer in particular, and their development is still in progress. The chemistry of thiosemicarbazone ligands has been receiving considerable attention primarily because of their bioinorganic relevance. Though thiosemicarbazones are widely used in the field of medicinal chemistry, their application as sensors has not been explored in detail. These sulfur and/or nitrogen heterocyclic azo dyes provide strong binding affinity prompted us to use thiosemicarbazone based dyes as chemosensors. To the best of our knowledge, this is the first report on **R1**, **R2** and **R3** as a fluorescent and optical sensor for transition metal ions.

## 2. Experimental

### 2.1. Chemicals and spectroscopic measurements

Thiosemicarbazide, salicylaldehyde, 5-nitrosalicylaldehyde, 2,4-dihydroxybenzaldehyde, iron (III) chloride, cobalt (II) chloride,

\* Corresponding author. Tel.: +91 431 2503640, +91 431 2500133;

fax: +91 431 2500133.

E-mail addresses: [velmathis@nitt.edu](mailto:velmathis@nitt.edu), [svelmathi@hotmail.com](mailto:svelmathi@hotmail.com) (S. Velmathi).

nickel (II) chloride, copper (II) chloride, zinc (II) acetate, cadmium (II) acetate, tin (II) chloride, lead (II) acetate, manganese (II) acetate, chromium (II) chloride, mercury (II) nitrate and analytical grade solvents such as acetonitrile (CH<sub>3</sub>CN) and ethanol (EtOH) were purchased from Sigma Aldrich and used as such. Proton NMR spectra were obtained using a Bruker 400 MHz spectrometer using Tetramethylsilane (TMS) as an internal standard, IR spectra was recorded in pellet mode on a Perkin-Elmer Spectrum One FTIR spectrometer. Shimadzu UV-2600 UV–vis spectrophotometer was used to record UV–visible spectra using quartz cell with 1 cm path length. Fluorescence emission spectra were recorded in a Shimadzu RF-5301 PC spectrofluorophotometer at a scan rate of 500 nm/slit width Ex: 10 nm; Em: 10 nm. Excitation wavelength was set at 360 nm.  $2.5 \times 10^{-5}$  M solution of the receptors in CH<sub>3</sub>CN and  $1.5 \times 10^{-3}$  M aq. solutions of the cations were prepared. UV titrations were carried out by the incremental addition of 0.2 eq. (10  $\mu$ L)–2 eq. (100  $\mu$ L) guest solutions to 3 ml of receptors in the UV cuvette. The same solutions were used for fluorescent titrations also. The receptors and cation solutions were prepared as  $2.5 \times 10^{-5}$  M in CH<sub>3</sub>CN for Job's plot.

## 2.2. Synthesis and characterization of sensors R1–R3

All the sensors were well characterized by <sup>1</sup>H NMR, FT-IR and UV–vis spectroscopic techniques. A hot ethanolic solution of thiosemicarbazide was slowly added to a solution of substituted salicylaldehyde in ethanol. The reaction mixture was reflux at 75–80 °C for 3 h, yielding the precipitate of **R1–R3** (Fig. 1). After evaporating the solvent in vacuum, the residue was filtered and recrystallized with ethanol.

**R1**: yield: 80%; m.p. 220 °C; IR (KBr, cm<sup>-1</sup>)  $\nu$ : (C=S) 949, (C=N) 1608, (N–H) 3122, (OH) 3424. <sup>1</sup>H NMR (DMSO-d<sub>6</sub>  $\delta_{ppm}$ ) 6.78–6.86 m (aromatic H), 7.18–7.22 m (aromatic), 7.91 m (aromatic), 8.09 s (NH<sub>2</sub>), 8.35 s (HC=N), 9.87 s (NH), 11.36 s (OH).

**R2**: Yield: 83%; m.p. 224 °C; IR (KBr, cm<sup>-1</sup>)  $\nu$ : (C=S) 943, (C=N) 1603, (N–H) 3122, (OH) 3415. <sup>1</sup>H NMR (DMSO-d<sub>6</sub>  $\delta_{ppm}$ ) 7.02–7.04 m (aromatic H), 8.08–8.11 m (aromatic), 8.19 m (aromatic), 8.25 s (NH<sub>2</sub>), 8.36 s (HC=N), 8.83 s (NH), 11.49 s (OH).

**R3**: yield: 75%; m.p. 192 °C; IR (KBr, cm<sup>-1</sup>)  $\nu$ : (C=S) 967, (C=N) 1620, (N–H) 3167, (OH) 3466. <sup>1</sup>H NMR (DMSO-d<sub>6</sub>  $\delta_{ppm}$ ) 6.24–6.26 m (aromatic H), 6.28–6.29 m (aromatic), 7.64–7.66 m (aromatic), 7.72 s (NH<sub>2</sub>), 7.92 s (OH) 8.23 s (HC=N), 9.74 s (NH), 11.15 s (OH). (For <sup>1</sup>H NMR, FT-IR spectra see supporting information).

## 3. Results and discussion

### 3.1. UV–vis spectroscopic studies

Thiosemicarbazide with three different substituted aldehydes capitulate three sensors **R1–R3** in good yield. The reason for choosing NO<sub>2</sub> as substituent (R2) is mainly because of its electron withdrawing nature. It will enhance the acidity of the hydroxyl proton present in the receptor 2 and form a strong bond with the

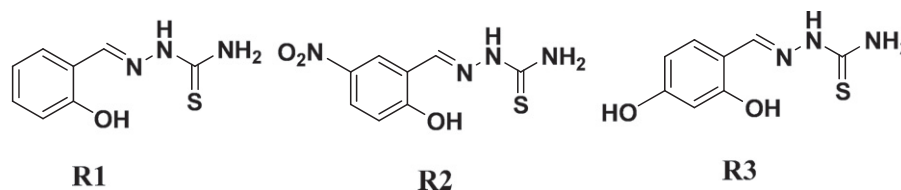
cations. By increasing the electron withdrawing properties, we can be able to get strong complexes with higher binding constants. And in R3 –OH group acts as an auxochrome. It has both n and  $\pi$  e-s, so that these show  $n \rightarrow \pi^*$  transition in addition to  $\pi \rightarrow \pi^*$  transitions. Because of these reasons we expect the binding affinity of receptor with metal cations is increasing. The binding action of receptors with metal ions was investigated using UV–vis spectroscopic titration method. The titrations were carried out with receptors ( $2.5 \times 10^{-5}$  M) in organic medium and cations in aqueous medium ( $1.5 \times 10^{-3}$  M). Electronic spectra of **R1**, **R2** and **R3** displayed three different transitions and the  $\lambda_{max}$  values are listed in Table 1. Fig. 2a conceals the electronic spectrum of **R1** with different metal cations. In the gradual addition of Zn<sup>2+</sup> into **R1**, the band at 330 nm decreases and the band at 235 nm increases with the appearance of new band around 400 nm (Fig. 2b). A similar trend was observed upon the incremental addition of Co<sup>2+</sup>, Ni<sup>2+</sup> and Cu<sup>2+</sup> (see supporting information). But, other guest solutions such as Fe<sup>3+</sup>, Cd<sup>2+</sup>, Sn<sup>2+</sup>, Mn<sup>2+</sup>, Pb<sup>2+</sup>, Hg<sup>2+</sup> and Cr<sup>2+</sup> showed zero effect with receptors' solutions. Interestingly, selective colorimetric response towards Hg<sup>2+</sup> and Sn<sup>2+</sup> was observed in case of **R2**. The color change was visualized by direct eye experiments, visual inspection of the **R2** showed the color turn-off from green to colorless by adding 200  $\mu$ L of Hg<sup>2+</sup> (Fig. 2c inset) and Sn<sup>2+</sup> ions (Fig. S10 inset). The color change can be attributed to the complex formation. During the incremental addition of Hg<sup>2+</sup> into **R2**, the absorbance band at 210 nm was getting intensified and the band at 310 nm and 450 nm were being diminished (Fig. 2c). Similar spectra were observed upon increasing the concentration of Sn<sup>2+</sup> into **R2** (see supporting information). There are no optical changes observed upon the excess addition of other metal cations into **R2**. Fig. 2d accentuates the absorbance changes of different metal ions into **R3**. With the continuing addition of Mn<sup>2+</sup> into **R3**, the band at 400 nm got amplified and the bands at 230 and 330 nm got reduced (Fig. 2e). The red shift in the absorption band can be attributed to the ligand to metal charge transfer (LMCT) complex formation. But no optical change was observed when other metal ions were added to **R3**. So **R3** was selectively sensing Mn<sup>2+</sup> in the presence of other metal ions. Fig. 2(f) and (g) shows the relative absorbance of **R1** and **R3** with metal ions. As we expected, three receptors show their own selectivity in sensing transition metal ions due to the difference in the ring substitution.

### 3.2. Binding constant and Jobs plot studies

The binding constants ( $K_{app}$ ) of metal ions with receptors were calculated using B–H plot method. From the non-linear least square

**Table 1**  
Electronic spectra of **R1**, **R2** and **R3**.

S. no.	Receptor	$\lambda_{max}$ (nm)
1	<b>R1</b>	235, 300, 330
2	<b>R2</b>	235, 300, 330, 450
3	<b>R3</b>	240, 300, 330



**Fig. 1.** Structure of receptors **R1**, **R2** and **R3**.

Download English Version:

<https://daneshyari.com/en/article/5400640>

Download Persian Version:

<https://daneshyari.com/article/5400640>

[Daneshyari.com](https://daneshyari.com)