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Novel thiosemicarbazone based sensors for transition metals†

Repale Anil Vithal,[a] Ram Kishore,[b] Dongare Suvarna Janardan,[c]
N. S. Chundawat,[a] Nitin Srivastava*[b] and Girdhar Pal Singh*[a]

A novel and efficient thiosemicarbazone based chemosensor for the detection of transition metals through UV-visible fluorescence has been reported in this research. Dibenzyl thiosemicarbazones can bind with the transition metal ions and lead to the enhancement of the fluorescence. The reported dibenzyl thiosemicarbazone can detect Zn^{2+}, Co^{2+}, Ni^{2+} and Hg^{2+} appreciably due to inhibition of electron transfer while quenching of fluorescence occurs in Mn^{2+} and Cu^{2+} due to photoinduced electron transfer.

Introduction

Heavy metals are widely distributed in nature and in some cases harmful to living beings if they are disposed of in a discretionary manner. Sustainable development necessitates the detection and estimation of metal pollutants in the environment around us. Detection of heavy transition metals is desired in analytical and environmental chemistry to estimate the contamination in the environment around us.[1–3] Sensors for the detection of transition metals may be very useful and need to be explored for specificity and efficiency. Fluorescence chemosensors have relevance in studies of biological species and studies of drug action in various parts of the body.[4–6] It has been reported that the onset of Alzheimer's disease can be detected with the presence of a high concentration of copper in the cytoplasm of neurons.[7,8] Metal cobalt is contained in vitamin C and causes certain diseases in the body, but it is also responsible for environmental pollution.[9–13] Nickel, which is used in industrial processes as a catalyst, is a significant cause of water and soil pollution and is highly carcinogenic.[14–18]

Mercury, a toxic heavy metal present in the environment, poses a severe threat to mankind and damages the nervous system, liver, kidneys, and the immune system.[19–21] It is present in the elemental form, or in organic or inorganic compounds. Similarly, zinc is one of the most prominent metals that is present in biological systems and is an integral part of the catalytic sites in the enzymes. Zinc is responsible for neurological problems like Parkinson's disease, epilepsy, and Alzheimer's disease.[22–25] Since zinc shows similar spectral properties to cadmium, the development of sensors to detect zinc in the presence of cadmium would be helpful in the detection of heavy metals like zinc and cadmium in the environment and the diagnosis of neurological disorders. This justifies the exploration of the field for the designing of novel sensors for application in the environmental sciences and in the medical field to study cells, their functioning and malignancy. A hybrid material has been reported for the detection and absorption of Cu^{2+} ions from the environment.[26] Arene-based sensors containing multiple BODIPY units were designed and synthesized and found to exhibit selectivity and sensitivity to Hg^{2+} and Sn^{2+}.[27] Biosorbent materials with mesoporous structures reportedly exhibited sorption of highly toxic Cr^{6+}.[28] Since the reported methods in the literature are mostly for the detection of one or two ions, we tried to explore thiosemicarbazone derivatives as sensors for the large number of transition metals based on the electron donating atoms in them. We have been constantly working on the synthesis and screening of biologically potent scaffolds having electron donating N and S atoms and exploring their applications in various fields.[29–36] This led us to further explore the synthesis of thiosemicarbazone derivatives and their anticancer activities.[37] Thiosemicarbazones have been found to possess sensor activities for transition metals.[38] Here we are reporting the novel synthesis and characterization of novel thiosemicarbazones employing microwave irradiation and their properties as fluorescence and optical sensors for transition metal ions like Zn^{2+}, Mn^{2+}, Co^{2+}, Ni^{2+}, Hg^{2+}, and Sn^{2+}. These thiosemicarbazones contain S and N atoms, which may act as donor atoms for making complexes with the transition metals like Zn^{2+}, Co^{2+}, Ni^{2+}, Hg^{2+}, Mn^{2+}, Sn^{2+}, Cu^{2+}, *etc.* Fluorescence studies of the transition metal complexes with thiosemicarbazones have resulted in sensing the presence of these metals.

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[a] *Department of Chemistry, Bhupal Nobles' University, Udaipur, Rajasthan, India. E-mail: girdharpal@gmail.com*
[b] *Department of Chemistry, Amity University Uttar Pradesh, Lucknow Campus, India. E-mail: nitinsriv5@gmail.com*
[c] *Abeda Inamdar Senior College of Arts, Science & Commerce, Pune, India*

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Experimental

Chemicals and instruments

All chemicals used in this research were purchased from Merck, Alfa Aesar, and Sigma Aldrich. The ^{1}H NMR and ^{13}C NMR spectra of the synthesized compounds were obtained with a Bruker Advance spectrophotometer at frequencies of 400 MHz and 100 MHz and the peaks were obtained with respect to standard tetramethylsilane. LCMS was conducted on a Waters mass spectrometer. UV-visible spectra of the compounds were obtained on a Shimadzu UV-2600 spectrophotometer. Fluorescence emission was studied on a Shimadzu RF5301 PC spectrofluorophotometer.

General protocol for the synthesis of thiosemicarbazones

An empty RB flask was charged with 10 mL of DMSO and 1 mmol of isothiocyanate was added with constant stirring for 10 minutes. 1 mmol of hydrazine hydrate was further added and stirred at room temperature for another 10 minutes with further addition of 2 mmol of Triton-B. Finally, 1 mmol of biphenyl-4-carbaldehyde was added to the mixture and treated with MW irradiation (Discover 2.0 by CEM Corporation, 25 W, 50 °C) for 10 minutes. A thin layer chromatographic (TLC) plate was used to monitor the progress of the reaction. After cooling the reaction, 5 mL of water was added and the synthesized compound was extracted with ethyl acetate (3 × 20 mL). The extract was dried over Na_2SO_4 and filtered, and the organic layer was concentrated with a rotary evaporator. The pure sample was obtained by column chromatography (silica gel, hexane–ethyl ethanoate, 5 : 1).

Characterization of the synthesized thiosemicarbazones

(*E*)-1-(4-Phenylbenzylidene)-4-(2-chlorophenyl) thiosemicarbazide (TSC1)

White solid, m.p. = 200–202 °C. Elemental analysis of $C_{20}H_{16}ClN_3S$ calcd. (found) %: C, 65.64 (65.82); H, 4.39 (4.32); Cl, 9.70 (9.83); N, 11.50 (11.57); S, 8.77 (8.79). ^{1}H NMR: δ 9.846 (bs, 1H), 9.681 (bs, 1H), 8.720 (t, J = 6.9 Hz, 1H), 7.944 (s, 1H), 7.785 (d, J = 7.9 Hz, 2H), 7.675 (d, J = 7.9 Hz, 2H), 7.640 (d, J = 6.8 Hz, 2H), 7.491–7.454 (m, 3H), 7.410–7.341 (m, 2H), 7.196–7.174 (m, 1H). ^{13}C NMR: 127.4, 129.0, 136.6, 138.9, 127.5, 129.5, 130.1, 154.6, 192.2, 125.9, 126.7, 126.9, 129.2, 130.6, 139.8; IR (cm^{-1}): 3378, 3201, 3042, 1606, 1438, 1200; MS (ESI): *m*/*z* (M)$^-$ calculated for $C_{20}H_{16}ClN_3S$: 365.08, found (M + 1)$^+$: 366.13.

(*E*)-1-(4-Phenylbenzylidene)-4-(2,3-dichlorophenyl) thiosemicarbazide (TSC2)

White solid, m.p. = 178–180 °C. Elemental analysis of $C_{20}H_{15}Cl_2N_3S$ calcd. (found) %: C, 59.88 (60.12); H, 3.80 (3.78); Cl, 17.68 (17.72); N, 10.48 (10.45); S, 7.98 (8.02). ^{1}H NMR 400 MHz ($CDCl_3$): δ 9.920 (bs, 1H), 9.142 (bs, 1H), 8.733–8.708 (m, 1H), 7.946–7.883 (m, 2H), 7.796–7.649 (m, 5H), 7.477–7.319 (m, 5H). ^{13}C NMR: 127.2, 127.4, 128.8, 133.5, 139.2, 127.2, 129.5, 130.3, 139.2, 143.3, 177.2, 127.4, 128.1, 128.7, 130.3, 139.8, 133.5; IR (cm^{-1}): 3386, 3195, 3020, 1602, 1432, 1225; MS (ESI): *m*/*z* (M)$^-$ calculated for $C_{20}H_{15}Cl_2N_3S$: 399.04, found (M + 1)$^+$: 400.07.

(*E*)-1-(4-Phenylbenzylidene)-4-(2,4-dichlorophenyl) thiosemicarbazide (TSC3)

White solid, m.p. = 179–181 °C. Elemental analysis of $C_{20}H_{15}Cl_2N_3S$ calcd. (found) %: C, 59.98 (60.18); H, 3.78 (3.72); Cl, 17.69 (17.81); N, 10.47 (10.32); S, 7.99 (8.02). ^{1}H NMR 400 MHz ($CDCl_3$): δ 9.798 (bs, 1H), 9.080 (bs, 1H), 8.750–8.729 (m, 1H), 7.948–7.929 (m, 1H), 7.867 (s, 1H), 7.787–7.768 (m, 2H), 7.716–7.676 (m, 2H), 7.642–7.623 (m, 2H), 7.520–7.459 (m, 2H), 7.143–7.381 (m, 1H), 7.335–7.312 (m, 1H); ^{13}C NMR: 127.1, 127.7, 129.0, 136.4, 129.5, 130.1, 139.8, 177.2, 127.4, 128.1, 129.5, 136.2, 132.4, 139.8; IR (cm^{-1}): 3390, 3198, 3050 1600, 1430, 1220; MS (ESI): *m*/*z* (M)$^-$ calculated for $C_{20}H_{15}Cl_2N_3S$: 399.04, found (M + 1)$^+$: 400.07.

Results and discussion

Synthesis

The model reaction was designed and carried out by mixing 2-chlorophenyl isothiocyanate, hydrazine hydrate and biphenyl-4-carbaldehyde in the presence of DMSO and irradiating with MW irradiation. The progress of the reaction was monitored periodically with the help of a thin layer chromatographic (TLC) plate. After cooling the reaction, 5 mL of water was added and the synthesized compound was extracted with ethyl acetate (3 × 20 mL). The extract was dried over Na_2SO_4 and filtered, and the organic layer was concentrated with a rotary evaporator. The pure sample was obtained by column chromatography (silica gel, hexane–ethyl ethanoate, 5 : 1). The product structure was confirmed by the spectrometric and analytical results, all of which were consistent with the proposed structure (see the Experimental section). The reaction was optimized for phase transfer catalysts (PTCs) (Table 1), employing a variety of PTCs like tetra-*n*-butylammonium chloride (TBAC), tetramethylammonium bromide (TMAB), tetra-*n*-butylammonium bromide (TBAB), tetra-*n*-butylammonium iodide (TBAI), tetra-*n*-butylammonium hydrogen carbonate (TBAHC), tetra-*n*-butylammonium hydrogen sulphate (TBAHS), Triton-B, and crown ether (18-crown-6). The best results were obtained with Triton-B (86% yield in 10 min).

After optimizing the reaction for PTCs, we explored the reaction for the microwave energy for the maximum yield, and we found that the irradiation of the reaction with 25 MW for just 10 minutes served the purpose of obtaining the highest yield of the reaction. We explored various solvents like DMSO, DMF, chloroform, dichloromethane, methanol, benzene, toluene, *n*-hexane, and *n*-heptane. We found that excellent yield was obtained in DMSO (Table 2).

Table 1 Effects of phase transfer catalysts on time and yield in the preparation of **TSC1**

Entry	Phase transfer catalyst	Time in min	% yield
1	TBAHS	30	65
2	**Triton-B**	**10**	**86**
3	TBAHC	40	60
4	TBAB	25	65
5	Crown ether (18-crown-6)	60	50
6	TMAB	48	70
7	TBAC	50	50

Reaction conditions: substituted benzaldehyde (1 mmol), hydrazine hydrate (1 mmol) and 3-phenyl isothiocyanate (1 mmol), MW irradiation (25 W, 50 °C) for 10 min in the presence of 2.0 mmol (0.35 mL) of PTC.

Table 2 Effects of solvents on the time and yield of the reaction

Entry	Solvent	Time, min	% yield
1	Dimethylformamide (DMF)	20	72
2	**Dimethyl sulfoxide (DMSO)**	**10**	**86**
4	Chloroform	30	50
5	Dichloromethane	35	56
6	Methanol	50	28
7	Benzene	40	40
8	Toluene	45	45
9	*n*-Hexane	60	50
10	*n*-Heptane	60	50

After optimizing the process for the synthesis of thiosemicarbazones in terms of the phase transfer catalysts, solvents, and microwave energy radiation, three different thiosemicarbazones were synthesized for their further exploration and application in fluorescence and optical sensors for metals like Zn, Mn Co, Ni, Hg, and Sn (Table 3).

UV-visible spectroscopic analysis

The chloro-substituted benzaldehydes were chosen as they are good electron donating species to the metal ions. The chloro group attached to the benzaldehyde acts as an auxochrome and gives rise to both n → π* and π → π* transitions, suggesting the better interaction of the ligand with the metals, which was experimentally verified with the help of a UV-visible spectroscopic titration method using ligands and metal cations in organic and aqueous media. The transitions and λ_{max} values of the electronic spectra of the three compounds are shown in Table 4.

Table 3 Synthesis of thiosemicarbazones

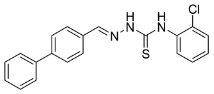
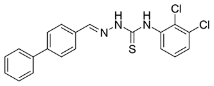
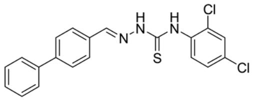
Entry	Structure	Time (min)	% yield
TSC1		10	86
TSC2		10	85
TSC3		10	82

Table 4 Absorption maximum (λ_{max}) values in electronic spectra of compounds

S. No	Ligand	λ_{max} (nm)
1	**TSC1**	230, 320, 340
2	**TSC2**	240, 320, 340, 480
3	**TSC3**	240, 320, 340

Fig. 1a presents the electronic spectra of **TSC1** with some metals. In Fig. 1b, we find that by increasing the

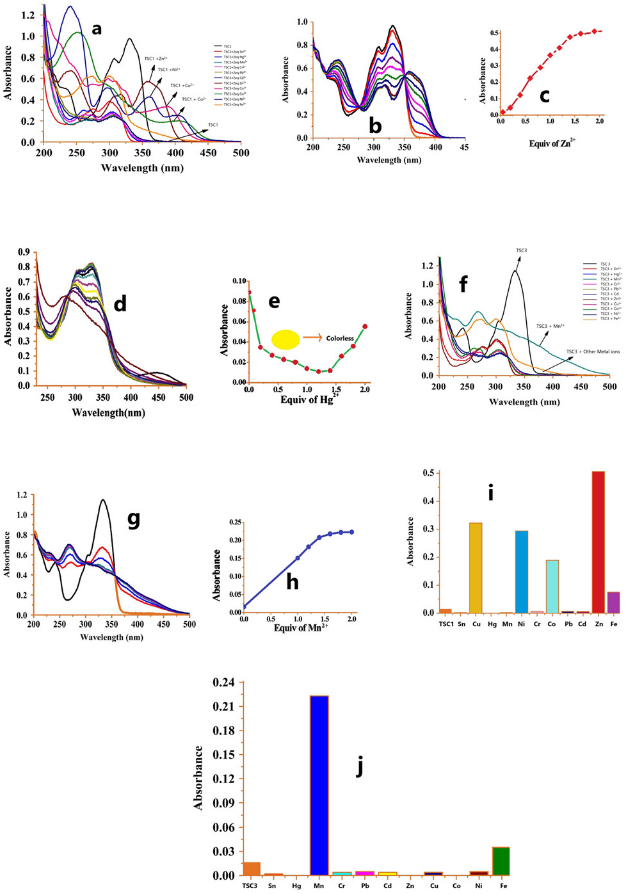


Fig. 1 (a) Absorption of 2.5 × 10^{-5} M **TSC1** in CH_3CN on the addition of different metal ions (aq. 1.5 × 10^{-5} M). (b) Changes in the UV-visible spectra of **TSC1** (2.5 × 10^{-5} M in CH_3CN) on the gradual addition of aq. 1.5 × 10^{-5} M solution of Zn^{2+}. (c) Changes of the absorbance at 375 nm. (d) UV-visible absorption spectra of 2.5 × 10^{-5} M **TSC2** in CH_3CN on the addition of Hg^{2+} ions (aq. 1.5 × 10^{-5} M). (e) Changes in the absorption on the addition of Hg^{2+} ions at 450 nm. (f) UV-visible absorption spectra of 2.5 × 10^{-5} M **TSC3** in CH_3CN on the addition of different metal ions (aq. 1.5 × 10^{-5} M). (g) UV-visible absorption spectra of 2.5 × 10^{-5} M **TSC3** in CH_3CN on the addition of Mn^{2+} ions (aq. 1.5 × 10^{-5} M); (h) Changes in the absorption on the addition of Mn^{2+} ions at 450 nm. (i) Relative absorbance of 2.5 × 10^{-5} M **TSC1** at 450 nm with 2 eq. of different metal ions. (j) Relative absorbance of 2.5 × 10^{-5} M **TSC3** at 450 nm with 2 eq. of different metal ions.

concentration of Zn^{2+} in **TSC1**, there is an increase in the band at 240 nm with the formation of a new band at 400 nm and a decrease in the band at 340 nm. The addition of other metals like Co^{2+}, Ni^{2+}, and Cu^{2+} also presented the same trend, while metals like Cr^{2+}, Hg^{2+}, Pb^{2+}, Mn^{2+}, Sn^{2+}, Cd^{2+}, and Fe^{3+} did not show any effect in the solution of **TSC1**. The second thiosemicarbazone **TSC2** exhibited absorption with Sn^{2+} and Hg^{2+}. As shown in Fig. 1d, the addition of 200 μL of Sn^{2+} and Hg^{2+} changed the colour from green to colourless, which was assumed to be due to the formation of a complex. As shown in Fig. 1d, the absorbance band at 220 nm was becoming more intense while the bands at 320 nm and 480 nm were diminishing. We obtained similar results on increasing the Sn^{2+} concentration in **TSC2**. Fig. 1f presents the absorption spectra of the addition of different metals in **TSC3**. In the case of the addition of Mn^{2+} in **TSC3**, the bands at 240 and 340 nm became weaker while the band at 410 nm intensified (Fig. 1f). The bathochromic shift in the absorption band suggests charge transfer complex formation in the metal. In the case of **TSC3**, no change in the absorption bands was observed on the addition of other metals. Hence, we may draw an inference that in the presence of several metal ions, **TSC3** selectively senses Mn^{2+}. Fig. 1i and j present the relative absorbance of **TSC1** and **TSC3** with different metal ions. We proposed that the three thiosemicarbazones are selective in sensing transition metal ions, which may be due to the different ring substitutions in the thiosemicarbazones.

The binding of the synthesized thiosemicarbazones as ligands and the metal ions has also been examined with the help of B–H plots (refer to the ESI†). The binding constants of **TSC1** with Co^{2+}, Ni^{2+}, Cu^{2+}, and Zn^{2+} as observed in the nonlinear least squares fitting plots were 1.2×10^4, 1.30×10^4, 1.2×10^4 and 1.6×10^4, respectively. For ligand **TSC2**, the binding constants with Sn^{2+} and Hg^{2+} were 1.50×10^4 and 2.3×10^4, respectively. In the case of **TSC3**, the binding constant with Mn^{2+} was found to be 3.2×10^4. The observation of the plots suggested the stoichiometric ratio of the ligand and the metal ions. In the case of **TSC1**, the complexation with the metals Co^{2+}, Ni^{2+}, Cu^{2+}, and Zn^{2+} occurred in the ratio of 2 : 1 between the ligand and the metal ions. However, the complexation of ligand **TSC2** and metal ions Hg^{2+} and Sn^{2+} took place in the ratio of 1 : 1. Complexation of **TSC3** with metal ion Mn^{2+} occurred in the ratio of 1 : 1. The formation of the complexes with the metal ions was proposed, as shown in Fig. 2.

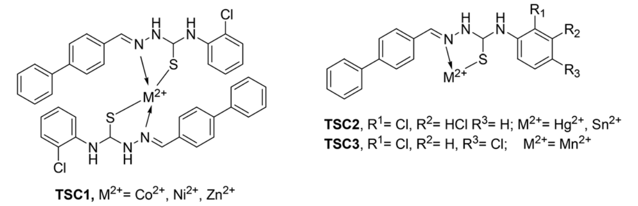


Fig. 2 Proposed binding with the synthesized thiosemicarbazones and metal ions.

Conclusions

To summarize, we may say that the synthesis, characterization, and UV-vis absorption of thiosemicarbazones **TSC1**, **TSC2**, and **TSC3** have been done in this research. It was found that thiosemicarbazone **TSC3** acts as a highly selective sensor for Mn^{2+} ions in the presence of other transition metal ions. Another result that may be concluded from this research is that **TSC1** undergoes complexation with Zn^{2+}, Ni^{2+}, and Co^{2+} and exhibited fluorescence change by inhibiting the charge transfer mechanism. Similarly, **TSC2** undergoes complexation with Hg^{2+} and Sn^{2+} and exhibits enhanced fluorescence due to inhibition of charge transfer.

Data availability

The data supporting this article have been included as part of the ESI.†

Author contributions

Conceptualization: Dr. Nitin Srivastava. Data curation: Dr. Girdhar Pal Singh. Formal analysis: Dr. Ram Kishore. Investigation: Repale Anil Vithal and Dongare Suvarna Janardhan. Methodology: Dr. N. S. Chundawat.

Conflicts of interest

The authors affirm that there are no conflicts to declare.

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