Dalton Transactions

Cite this: *Dalton Trans.*, 2011, **40**, 2837

www.rsc.org/dalton

PAPER

Oxidative cyclization of thiosemicarbazone: an optical and turn-on fluorescent chemodosimeter for Cu(II)†

Arghya Basu and Gopal Das*

Received 7th November 2010, Accepted 12th January 2011
DOI: 10.1039/c0dt01549k

A weakly fluorescent thiosemicabazone ($\mathbf{L_1H}$) was found to be a selective optical and "turn-on" fluorescent chemodosimeter for Cu^{2+} ion in aqueous medium. A significant fluorescence enhancement along with change in color was only observed for Cu^{2+} ion; among the other tested metal ions (*viz.* Na^+, K^+, Mg^{2+}, Ca^{2+}, Cr^{3+}, Zn^{2+}, Cd^{2+}, Hg^{2+}, Pb^{2+}, Ag^+, Ni^{2+}, Co^{2+}, Fe^{3+} and Mn^{2+}). The Cu^{2+} selectivity resulted from an oxidative cyclization of the weak fluorescent $\mathbf{L_1H}$ into highly fluorescent rigid 4,5-dihydro-5,5-dimethyl-4-(naphthalen-5-yl)-1,2,4-triazole-3-thione ($\mathbf{L_2}$). The signaling mechanism has been confirmed by independent synthesis with detail characterization of $\mathbf{L_2}$.

Introduction

Thiosemicarbazones are a class of compounds very promising in the treatment of many diseases, cancer in particular, and their development is still in progress.[1] In addition, they continue to draw attention not only as multifunctional ligands,[2] but also because they can undergo ring closure processes by the action of bases, acids or oxidants.[3] Although these cyclizations are well described in the literature, especially those involving Cu^{2+} or Fe^{3+} cations, their mechanism is still not clearly resolved.[4]

The development of sensitive and selective fluorescent chemosensors for biologically important metal ions is of intense current interest because these metal ions play important roles in living and environmental systems.[5] The third most abundant (after Fe^{2+} and Zn^{2+}) transition metal ion Cu^{2+} is an essential trace element present in the human body and plays a vital role in a variety of fundamental physiological processes in organisms ranging from bacteria to mammals but can often be toxic to certain biological systems when the levels of Cu^{2+} exceed cellular needs. It is also associated with neurodegenerative diseases such as Alzheimer's and Parkinson's and is also suspected to cause amyloidal precipitation and toxicity.[6] For most of the reported fluorescent sensors of Cu^{2+}, binding of the metal ion causes a quenching of the fluorescence emission[7] due to its paramagnetic nature.[8] Only a few sensors in which the binding of Cu^{2+} ion causes an increase in the fluorescence intensity have been reported.[9]

Department of Chemistry, Indian Institute of Technology Guwahati, Guwahati, 781039, Assam, India. E-mail: gdas@iitg.ernet.in; Fax: +91 0361 2582349; Tel: +91 361 258231

† Electronic supplementary information (ESI) available: Crystallographic CIF, ^1H and ^{13}C NMR, UV-visible spectra, FT-IR, X-ray tables, and figures. CCDC reference numbers 777755–777758. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c0dt01549k

Recently, there has been immense interest in chemodosimeter-based chemical sensing through a specific irreversible chemical reaction between dosimetric molecules and the target species, leading to a fluorescent/color change in the receptor.[10] It should be pointed out that there have been several nice Cu^{2+} chemodosimeters with enhanced fluorescence signal outputs, which however follow hydrolysis[11] or rearrangement reactions.[12] Moreover, reports on the single-crystal X-ray crystallographic characterization of chemodosimetric sensing are very rare.[13]

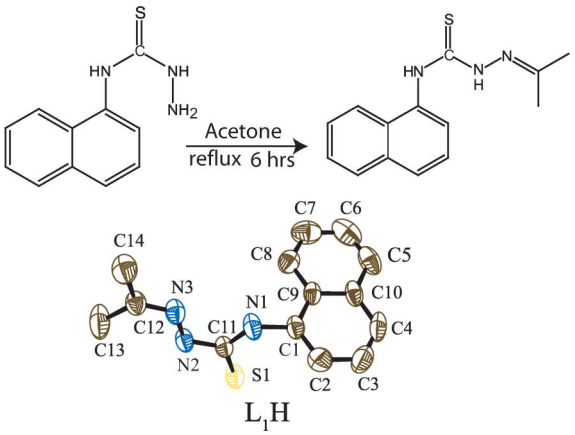
Herein we report our successful development of a chemodosimetric fluorescent chemosensor selective for Cu^{2+}. Detailed experiments allowed us to ascertain that the enhanced fluorescence was due to an oxidative cyclization by Cu^{2+} of the comparatively less fluorescent thiosemicarbazone ligand ($\mathbf{L_1H}$) into highly fluorescent rigid 4,5-dihydro-5,5-dimethyl-4-(napthalen-5-yl)-1,2,4-triazole-3-thione ($\mathbf{L_2}$). The ligand $\mathbf{L_1H}$ therefore shown to be a kind of redox based "turn-on" fluorescent chemodosimeter for Cu^{2+}.

Results and discussion

The synthesized thiosemicarbazone ligand $\mathbf{L_1H}$ (Scheme 1) shows remarkable selectivity towards Cu^{2+} by both UV-Vis and fluorescence spectroscopic methods. A beautiful yellowish orange color is formed with dramatic enhancement of fluorescence intensity when equivalent amount of Cu^{2+} ions was added to the colorless aqueous ethanolic solution of $\mathbf{L_1H}$, whereas other tested metal ions produce insignificant or minor changes.

Photophysical studies

The photophysical properties of the ligand $\mathbf{L_1H}$ with several metal cations (Na^+, K^+, Mg^{2+}, Ca^{2+}, Cu^{2+}, Cr^{3+}, Zn^{2+}, Cd^{2+}, Hg^{2+}, Pb^{2+}, Ag^+, Ni^{2+}, Co^{2+}, Fe^{3+} and Mn^{2+}) using their perchlorate



Scheme 1 Synthesis of ligand $\mathbf{L_1H}$ and molecular structure of $\mathbf{L_1H}$ with thermal ellipsoids set to the 50% probability level.

or chloride salts in H_2O–EtOH (90 : 10, v/v) are investigated by UV-Vis and fluorescence measurements and titration studies that are conducted at pH 7.2 (buffered by 10 mM Tris-HCl). However perchlorate salt of Cu^{2+} has been used through out all photophysical studies.

UV-Vis absorption studies

The absorption spectrum of the ligand $\mathbf{L_1H}$ ($c = 1.33 \times 10^{-5}$ M) in H_2O–EtOH (90 : 10, v/v) exhibits λ_{max} at 267 nm with molar absorption coefficient 1.93×10^4 M^{-1} cm^{-1} indicative of the (π–π^*) transition character.[14] However during titration with Cu^{2+} ($c = 5 \times 10^{-4}$ M) ions the absorption intensity decreases at 267 nm with increasing intensity concomitantly at 328 nm and 242 nm. Two isosbestic points were observed at 288 nm and 251 nm (Fig. 1b) which indicates the formation of new species by the influence Cu^{2+} ion over $\mathbf{L_1H}$. The red shift in absorption spectra could be applied to detect the sensing process by the naked eye. A beautiful yellowish orange color is formed when equivalent amount of Cu^{2+} ions was added to the colorless aqueous ethanolic solution of $\mathbf{L_1H}$ (Fig. 3b). The addition of other metal ions such as Na^+, K^+, Mg^{2+}, Ca^{2+}, Cr^{3+}, Zn^{2+}, Cd^{2+}, Hg^{2+}, Pb^{2+}, Ag^+, Ni^{2+}, Co^{2+}, Fe^{3+} and Mn^{2+} produces insignificant or minor changes in absorption spectra (Fig. 1a).

Fluorescence studies

Fluorescence emission spectra at RT of the receptor $\mathbf{L_1H}$ ($c = 1.33 \times 10^{-5}$ M) in H_2O–EtOH (90 : 10, v/v) are recorded upon excitation at 270 nm to understand the nature of interactions in the excited state. In the presence of Cu^{2+} however, an instant response was observed by a dramatic enhancement of up to 10-fold, despite the well known quenching character of Cu^{2+}. A sharp increase in the fluorescence intensity with a red-shifted emission maxima at 363 nm to 390 nm is observed reaching its limit value after adding ~15 μM Cu^{2+}. This is probably due to instant formation highly fluorescent rigid cyclic product $\mathbf{L_2}$. Thus the ligand $\mathbf{L_1H}$ behaves as an "*off-on*" type of fluorescence probe towards Cu^{2+}. Whereas other metal ions did not induce any discernible spectral changes (Fig. 2a). The unexpected spectral change and the high selectivity for Cu^{2+} therefore could not be simply attributed to Cu^{2+} coordination to $\mathbf{L_1H}$.

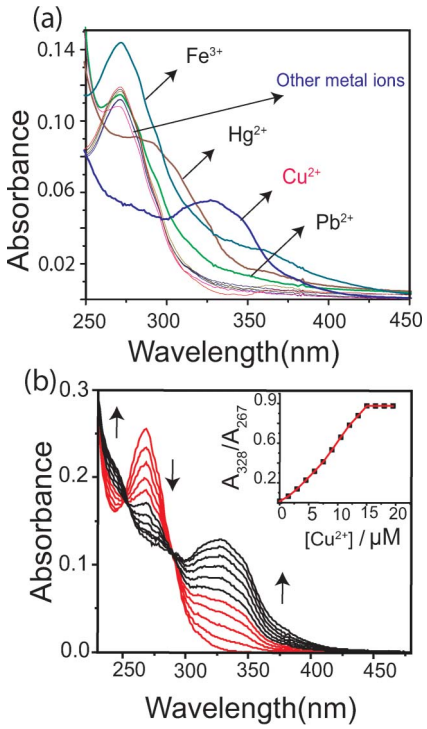


Fig. 1 (a) UV-Vis spectra of 5×10^{-6} M solutions of $\mathbf{L_1H}$ with 30 equiv. of various metal ions in water–ethanol (90 : 10). (b) UV-Vis titration spectra of $\mathbf{L_1H}$ upon addition of Cu^{2+} ion in water–ethanol (90 : 10). Inset shows quotient of absorbance at 328 and at 267 nm as a function of Cu^{2+} concentration. Aqueous solutions are buffered by 10 mM Tris-HCl at pH 7.2.

Rationalization of photophysical studies

The fluorescence emission of a ligand can be not only affected by metal ion coordination, but by a metal ion mediated reaction as well.[15] It was well reported that thiosemicarbazone undergoes oxidative cyclization by several oxidants.[3] Thus we assume that the unexpected spectral change (both by UV-Vis and fluorescence) and the high selectivity for Cu^{2+} therefore could not be simply attributed to Cu^{2+} coordination to $\mathbf{L_1H}$; therefore it is probably due to the oxidative cyclization of $\mathbf{L_1H}$. The most decisive evidence supporting this assumption was obtained from the independent synthesis of 4,5-dihydro-5,5-dimethyl-4-(napthalen-5-yl)-1,2,4-triazole-3-thione ($\mathbf{L_2}$; Fig. 3a). The oxidative cyclization product $\mathbf{L_2}$ was fully characterized by ESIMS, ^{1}H NMR, ^{13}C NMR and single-crystal X-ray crystallographic characterization. Fluorescence emission and UV-Vis spectra of the synthesized oxidative cyclization product $\mathbf{L_2}$ was found almost identical to $\mathbf{L_1H}$ in the presence of 1.0 equivalent of Cu^{2+}. Interestingly, the UV-Vis titration of $\mathbf{L_1H}$ with Cu^{2+} results in a new band arises centered at 328 nm which is almost identical to absorption spectrum of pure $\mathbf{L_2}$ situated at the same wavelength under the same experimental conditions (ESI, Fig. S18†). Hence, it is quite logical to believe that Cu^{2+} induced formation of the new band at 328 nm in the

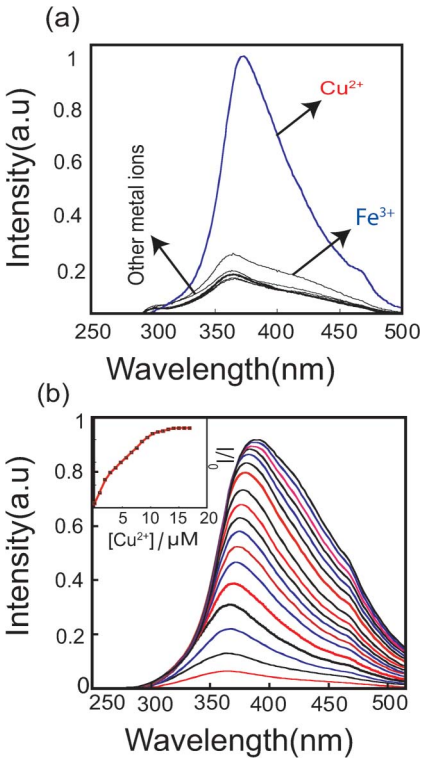


Fig. 2 (a) Fluorescence spectra (λ_{ex} = 270 nm) of $\mathbf{L_1H}$ (13 μM) measured in water–ethanol (90 : 10) respective metal cations (30 equiv.). (b) Fluorescence spectra of $\mathbf{L_1H}$ ($c = 1.33 \times 10^{-5}$ M) in the absence and presence of Cu^{2+} in water–ethanol (90 : 10). Aqueous solutions are buffered by 10 mM Tris-HCl at pH 7.2.

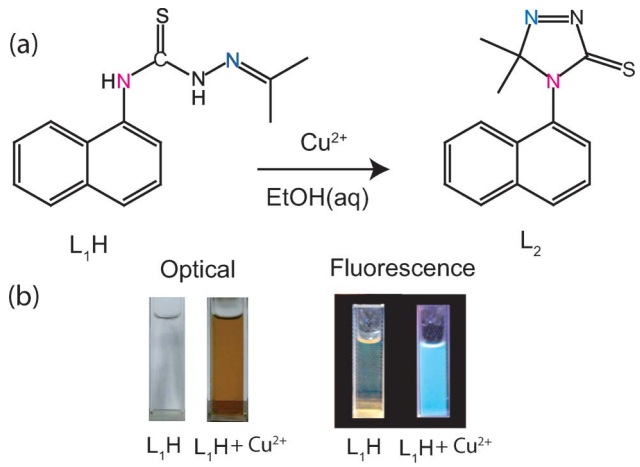


Fig. 3 (a) Synthesis of cyclic product $\mathbf{L_2}$. (b) Digital photographs of $\mathbf{L_1H}$ (~10^{-3} M) and $\mathbf{L_1H}$ (~10^{-3} M) in presence of equivalent amount of Cu^{2+} under normal light (left) and under UV irradiation (right).

UV-Vis spectra of $\mathbf{L_1H}$ is not due to Cu^{2+} coordination; therefore it is due to the formation of cyclized product $\mathbf{L_2}$.

EPR study

To assure the role of Cu^{2+} during cyclization reaction EPR experiment in CH_3CN at RT was carried out in which the Cu^{2+} concentration was kept constant while the $\mathbf{L_1H}$ concentration varied.[16] It was found that the intensity of EPR signal of Cu^{2+} was continuously decreases with increasing $\mathbf{L_1H}$ concentration (Fig. 4). It was therefore suggested that conversion of paramagnetic Cu^{2+} into diamagnetic Cu^{+} which is stabilized through CH_3CN coordination.

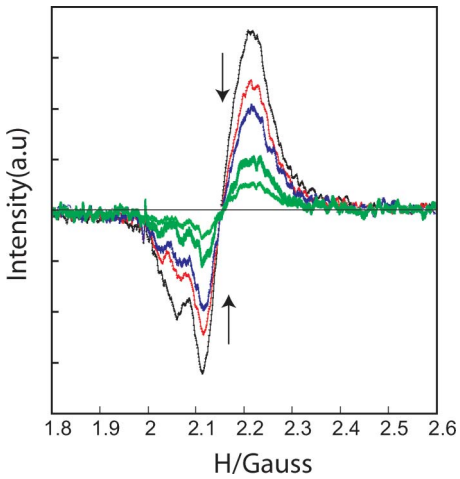
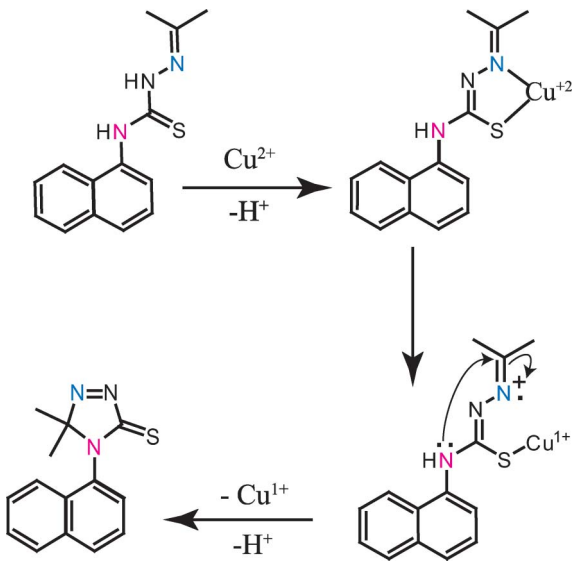


Fig. 4 EPR spectrum Cu^{2+} with increasing concentration of $\mathbf{L_1H}$ (taken at RT, 298 K).

In addition to the EPR study we have also confirmed the reduction process of Cu^{2+} to Cu^{+} during cyclization by UV-Vis spectroscopic analysis in CH_3CN.[16] Similar to EPR study here also Cu^{2+} concentration maintained constant while the $\mathbf{L_1H}$ concentration varied. It was found that the absorbance of the d-d transition band of Cu^{2+} situated at 760 nm decreases with increasing concentration of $\mathbf{L_1H}$ thus it was suggested the conversion of Cu^{2+} (d^9) to Cu^{+} (d^{10}) where d-d transition is not possible (ESI, Fig. S15†). Thus a plausible mechanism of the oxidative cyclization by Cu^{2+} was therefore suggested (Scheme 2). Hence, both the experiments convincingly ascertain that the selective Cu^{2+} sensing is due to oxidative cyclization of $\mathbf{L_1H}$.



Scheme 2 Proposed oxidative cyclization mechanism of $\mathbf{L_1H}$ by Cu^{2+}.

The formation of stable metal complexes with Zn^{2+} and Ni^{2+} with no significant spectral changes also supports our assumption

that the Cu^{2+} selective spectral changes of $\mathbf{L_1H}$ are not due to simple metal ligand coordination therefore, due to the formation of rigid cyclic product $\mathbf{L_2}$.

Crystal structure

The structure of $\mathbf{L_1H}$ has been established unambiguously by X-ray diffraction of single crystals. Crystals of $\mathbf{L_1H}$ were obtained by slow-driven crystallization from dilute solution of ethanol. $\mathbf{L_1H}$ crystallized in the space group $P\bar{1}$. The structure determination of $\mathbf{L_1H}$ shows (Fig. 5) that in the solid state the thiosemicarbazone exists in the thione form, supported by the presence of hydrazinic hydrogens and a C–S distance of 1.674(3) Å, which is much shorter than a single C–S bond. The sulfur atom S(1) and the hydrazone nitrogen N(3) are in the *E* position with respect to the C(11)–N(2) bond. This configuration is probably due to the formation of centrosymmetric dimer through N(2)–H···S(1) hydrogen bond interaction. The N(2)–N(3) (1.386(4) Å) and N(2)–C(11) (1.355(4) Å) bond distances in $\mathbf{L_1H}$ are intermediate between ideal values of corresponding single [N–N, 1.45 Å; C–N, 1.47 Å] and double bonds [N═N, 1.25 Å, C═N, 1.28 Å], giving evidence for an extended π-delocalization along the semicarbazone chain. The solid state packing of the ligand is mainly governed by the different C–H···π interactions.

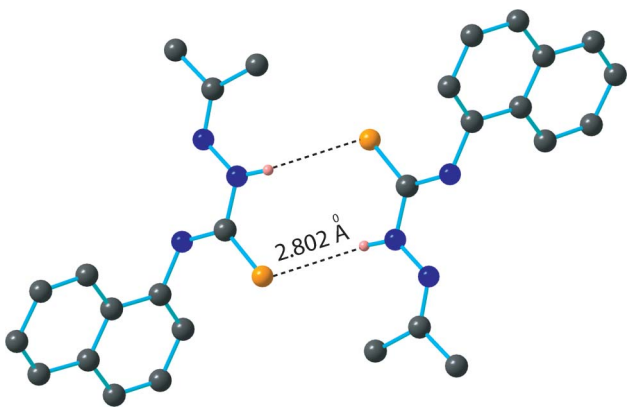


Fig. 5 Inter molecular dimeric hydrogen bonding interaction between two ligands ($\mathbf{L_1H}$).

The single crystals of $\mathbf{L_2}$ were obtained by slow-driven crystallization from dilute solution of acetonitrile. $\mathbf{L_2}$ crystallized in the space group $P2_12_12_1$ with $Z = 4$. Molecular structure of $\mathbf{L_2}$ along with atom numbering is shown in Fig. 6. In the crystal structure $\mathbf{L_2}$ the two rings are perpendicular to each other. The significant change in bond lengths N2–N3 1.386 Å to 1.235 Å and N3–C12 1.272 Å to 1.476 Å in $\mathbf{L_2}$ compared to $\mathbf{L_1H}$ reveals that the double bond was shifted between N3–C12 to N2–N3 in $\mathbf{L_2}$. In addition, from crystallographic data it is apparent that removal two N–H protons of thiourea moiety in $\mathbf{L_1H}$ occurs during the cyclization procedure.

Single crystals of $\mathbf{Ni(L_1)_2}$ were grown by vapor diffusion of Et_2O into a 2 : 1 $CHCl_3$–DMF solution. The complex crystallized into a monoclinic space group *C*2/*c*. An ORTEP plot along with the atom numbering scheme of $\mathbf{Ni(L_1)_2}$ is shown in Fig. 7a. The crystallographic data reveals that the complex species $\mathbf{Ni(L_1)_2}$ is centrosymmetric where the nickel atom at the centre of symmetry. The coordination results in a square-planar geometry involving

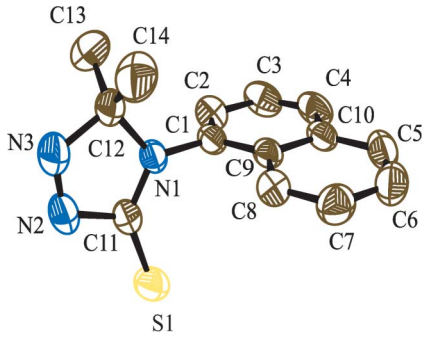


Fig. 6 Molecular structure of $\mathbf{L_2}$ with thermal ellipsoids set to the 50% probability level.

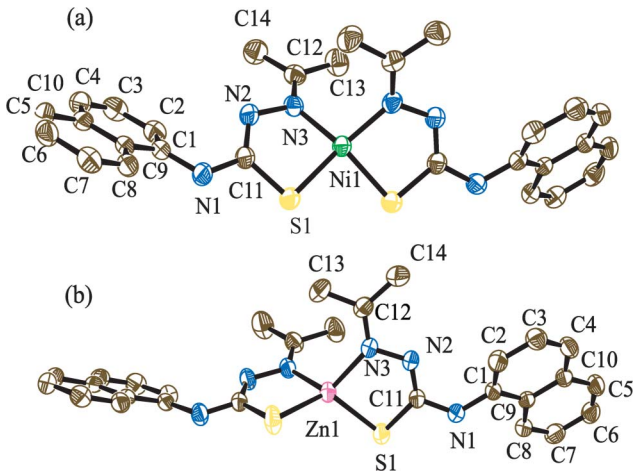


Fig. 7 ORTEP plot of (a) nickel and (b) zinc complexes with $\mathbf{L_1H}$. Thermal ellipsoids set to the 50% probability level.

two deprotonated S,N-bidentate ligands chelate the nickel atom in its iminothiolate form *via* the thiolate sulfur atom and the azomethine nitrogen atom in a *Z* configuration around the C(1)–N(2) bond. The negative charge of the deprotonated ligand is fully delocalized along the thiosemicarbazone moiety. The solid state packing of the complex is mainly governed by the different C–H···π and N–H···π interactions.

Single crystals of $\mathbf{Zn(L_1)_2}$ were grown by vapor diffusion of Et_2O into a 2 : 1 $CHCl_3$–DMF solution. An ORTEP plot of the $\mathbf{Zn(L_1)_2}$ is shown in Fig. 7b along with the atom numbering scheme. The complex crystallized into a monoclinic space group *C*2/*c*. The crystallographic data reveals that two deprotonated S,N-bidentate ligands chelate the zinc atom in its iminothiolate form *via* the thiolate sulfur atom, the azomethine nitrogen atom, giving rise to a distorted tetrahedral coordination polyhedron with S(1)–Zn(1)–N(3) angle is 86.65°. While coordinating in their iminothiolate forms, the negative charges generated by deprotonation are well delocalized in the C–N–N–C system as shown by the intermediate C(12)–N(3) [1.299 Å], N(3)–N(2) [1.399 Å] and N(2)–C(11) [1.297 Å] bond distances. The N(3) atom is in Z configuration around the C(11)–N(2) bond. Here also the three dimensional solid state packing is mainly controled by the different C–H···π and N–H···π interactions.

Conclusions

In conclusion we have developed a simple thiosemicarbazone ligand $\mathbf{L_1H}$ for selective colorimetric and fluorometric detection of Cu^{2+} by a chemodosimetric approach. Isolation of oxidative cyclized product and detection Cu^{2+} to Cu^{+} reduction process during cyclization allowed us to establish that the enhanced fluorescence was due to an oxidative cyclization by Cu^{2+} of the comparatively less fluorescent thiosemicarbazone ligand ($\mathbf{L_1H}$) into highly fluorescent rigid 4,5-dihydro-5,5-dimethyl-4-(napthalen-5-yl)-1,2,4-triazole-3-thione ($\mathbf{L_2}$). The cyclized compound $\mathbf{L_2}$ has been characterized by both structurally and spectroscopically. The selective sensing process and the formation of cyclized product $\mathbf{L_2}$ also been observed in CH_3CN as well. Formation of stable metal complexes with other metal ions such as Ni^{2+} and Zn^{2+} also convincingly supports that the sensing process is not simply due to the metal ligand coordination; therefore it is due to the oxidative cyclization of the thiosemicarbazone ligand. The chemodosimetric reaction, in combination with selective metal ion-induced catalysis, may be a promising approach to develop selective detection methods toward various metal ions.

Experimental

Materials and methods

All reagents were obtained from commercial sources and used as received. Solvents were distilled freshly following standard procedures.

Instrumentation

The IR spectra were recorded on a Perkin Elmer-Spectrum One FT-IR spectrometer with KBr disks in the range 4000–400 cm^{-1}. UV-Vis and Fluorescence spectra were recorded with Perkin–Elmer Lambda-25 UV-Visible spectrophotometer and Carry eclipse spectrofluorometer respectively. NMR spectra were recorded on a Varian FT-400 MHz instrument. The chemical shifts were recorded in parts per million (ppm) on the scale using tetramethylsilane (TMS) as a reference. ESIMS spectra were recorded in WATERS LC-MS/MS system, Q-Tof Premier in the Central Instrument Facility (CIF) of IIT Guwahati.

Synthesis of compounds

Designing aspect of thiosemicarbazone ligand $\mathbf{L_1H}$. For chemodosimetric detection of particular metal ion the ligand should be design such a way that the ligand undergoes some irreversible change in presence of a particular metal ion. The designing principles of $\mathbf{L_1H}$ are as follows: (1) The ligand $\mathbf{L_1H}$ composed with various multidented donor atoms in suitable position for both metal complexation and self cyclization process. (2) The metal induce oxidative cyclization of thiosemicarbazone ligand are well established in the literature.[3] (3) The naphthalene fluorophore unit presence in $\mathbf{L_1H}$ is responsible for signal transduction during spectroscopic studies.

Synthesis of $\mathbf{L_1H}$. The ligand $\mathbf{L_1H}$ was facilely synthesized[17] by refluxing 4-(1-naphthyl)-3-thiosemicarbazide 0.217 g (1 mmol) in 50 ml acetone, followed by removal of excess solvent under reduced pressure. White solid was obtained after drying the residue in vacuum (yield 80%). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 9.45(s, 1H–N1) 8.7(s, 1H–N2), 7.94(d, 1H), 7.88(m, 2H), 7.53(m, 3H), 7.81(d, 1H), 2.107(s, 3H) and 1.997(s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 17.05, 25.52, 122.07, 125.11, 125.50, 126.34, 126.71, 127.58, 128.68, 129.78, 133.91, 134.33, 150.21, and 178.13 ESI mass spectrometry: calcd for 258.10. [M + H^+]; found 258.10 [M + H^+].

Synthesis of $\mathbf{L_2}$. A aqueous ethanolic solution of $\mathbf{L_1H}$ (0.257 gm 1 mmol) was mixed with $Cu(ClO_4)_2$ (1.1 g, 3 mmol, 15 ml). The whole solution became yellowish orange after few minutes. The mixture was stirred at room temperature for 6 h and then evaporated *in vacuo*. Aqueous NaCl solution was added and the solution was then extracted by ethyl acetate (3 × 25 ml). The organic layer was dried over anhydrous Na_2SO_4, and concentrated under vacuum, then purified by column chromatography on silica gel with ethyl acetate hexane (1 : 4) as eluent. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.81(m, 2H), 7.55(m, 3H), 7.41(d, 1H), 7.27(d, 1H), 1.803(s, 3H) and 1.59(s, 5H,(CH_3 + H_2O)). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 22.80, 23.19, 111.22, 122.89, 125.75, 126.01, 127.24, 127.68, 128.94, 129.26, 130.76, 131.33, 135.02 and 188.03. ESI mass spectrometry: calcd for 256.09. [M + H^+]; found 256.09 [M + H^+].

Synthesis of $[Ni(L_1)_2]$. $NiCl_2$ (0.24 g; 1 mmol 10 ml) was added to the ethanolic solution of $\mathbf{L_1H}$ (0.64 g; 2.5 mmol; 25 ml) under refluxing condition. An aqueous solution of sodium hydroxide was added drop wise to reach pH in the range of 6–7. The reflux was maintained for 5 h. The complexes were removed by filtration, washed with EtOH and finally dried in vacuum over silica gel. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.90(d, 2H), 7.83(d, 1H), 7.46(m, 4H), 6.736(s, 1H–N1), 2.89(s, 3H) and 2.47(s, 3H). ESI mass spectrometry: calcd for 571.12. [M + H^+]; found 571.06 [M + H^+].

Synthesis of $[Zn(L_1)_2]$. $ZnCl_2$ (0.27 g; 2 mmol; 10 ml) was added to the ethanolic solution of $\mathbf{L_1H}$ (1.156 g; 2.5 mmol; 25 ml) under refluxing condition. An aqueous solution of sodium hydroxide was added drop wise to reach pH in the range of 6–7. The reflux was maintained for 5 h. The complexes were removed by filtration, washed with EtOH and finally dried in vacuum over silica gel. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.43(d, 1H), 8.0(d, 1H), 7.84(d, 1H), 7.6(d, 1H), 7.495(m, 3H), 7.132(s, 1H–N1), 2.193(s, 3H) and 2.164(s 3H). ESI mass spectrometry: calcd for 577.12. [M + H^+]; found 577.05 [M + H^+].

X-Ray crystallography

The intensity data were collected using a Bruker SMART APEX-II CCD diffractometer, equipped with a fine focus 1.75 kW sealed tube Mo-Kα radiation (λ) 0.71073 Å) at 298 K, with increasing ω (width of 0.3° per frame) at a scan speed of 5 s per frame. The SMART software was used for data acquisition. Data integration and reduction were undertaken with SAINT and XPREP software[18] Multiscan empirical absorption corrections were applied to the data using the program SADABS.[19] Structures were solved by direct methods using SHELXS-97 and refined with full-matrix least-squares on F^2 using SHELXL-97.[20] All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were located from the difference Fourier maps and refined.

Structural illustrations have been drawn with ORTEP-3 for Windows.[21]

Crystal data for L_1H. Formula = $C_{14}H_{15}N_3S$, formula weight = 257.36, crystal system = triclinic, space group = $P\bar{1}$, a/Å = 8.8572(9), b/Å = 8.9640(9), c/Å = 9.6791(10), α (°) = 98.898(7), β (°) = 99.319(7), γ (°) = 113.365(5), Volume/Å^3 = 675.52(12), Z = 2, T/K = 298(2), μ/cm^{-1} = 0.227, d_{cal}/g cm^{-3} = 1.270, crystal dimensions/mm^3 = 0.34 × 0.30 × 0.25, no. of reflns collected = 5694, no. of unique reflns = 5284, no. of params = 174, R_1, w$R_2(I > 2\sigma(I))$ = 0.0828, 0.1368, R_{int} = 0.0795, GOF(F^2) = 1.062, CCDC No. = 777756.

Crystal data for L_2. Formula = $C_{14}H_{13}N_3S$, formula weight = 255.34, crystal system = orthorhombic, space group = $P2_12_12_1$, a/Å = 7.2254(3), b/Å = 8.4194(4), c/Å = 21.4719(10), α (°) = 90, β (°) = 90, γ (°) = 90, Volume/Å^3 = 1306.21(10), Z = 4, T/K = 298(2), μ/cm^{-1} = 0.235, d_{cal}/g cm^{-3} = 1.305, crystal dimensions/mm^3 = 0.31 × 0.27 × 0.21, no. of reflns collected = 1854, no. of unique reflns = 1645, no. of params = 166, R_1, w$R_2(I > 2\sigma(I))$ = 0.0368, 0.0557, R_{int} = 0.0874, GOF(F^2) = 1.035, CCDC No. = 777755.

Crystal data for $Ni(L_1)_2$. Formula = $C_{28}H_{28}N_6S_2Ni$, formula weight = 571.39, crystal system = monoclinic, space group = $C2/c$, a/Å = 25.9620(10), b/Å = 7.7407(3), c/Å = 13.1235(5), α (°) = 90, β (°) = 96.079(4), γ (°) = 90, Volume/Å^3 = 2622.52(17), Z = 4, T/K = 298(2), μ/cm^{-1} = 0.929, d_{cal}/g cm^{-3} = 1.447, crystal dimensions/mm^3 = 0.34 × 0.31 × 0.28, no. of reflns collected = 3275, no. of unique reflns = 2473, no. of params = 175, R_1; w$R_2(I > 2\sigma(I))$ = 0.0348, 0.0493, R_{int} = 0.0993, GOF(F^2) = 0.978, CCDC No. = 777757.

Crystal data for $Zn(L_1)_2$. Formula = $C_{28}H_{28}N_6S_2Zn$, formula weight = 578.09, crystal system = monoclinic, space group = $C2/c$, a/Å = 26.8575(10), b/Å = 7.4489(3), c/Å = 13.6206(4), α (°) = 90, β (°) = 98.572(4), γ (°) = 90, volume/Å^3 = 2694.48(17), Z = 4, T/K = 298(2), μ/cm^{-1} = 1.096, d_{cal}/g cm^{-3} = 1.425, crystal dimensions/mm^3 = 0.34 × 0.29 × 0.25, no. of reflns collected = 3321, no. of unique reflns = 2079, no. of params = 175, R_1; w$R_2(I > 2\sigma(I))$ = 0.0441, 0.0717, R_{int} = 0.0789, GOF(F^2) = 0.890, CCDC No. = 777758.

Acknowledgements

GD acknowledges DST (SR/S1/IC-01/2008) and CSIR (01-2235/08/EMR-II), New Delhi India for financial support, CIF and IIT Guwahati for providing instrument facility and DST-FIST for single crystal X-ray diffraction facility. A.B thanks IIT Guwahati for fellowship.

Notes and references

1 (*a*) D. R. Richardson, *Crit. Rev. Oncol. Hematol.*, 2002, **42**, 267; (*b*) P. Jutten, W. Schumann, A. Hartl, L. Heinisch, U. Grafe, W. Werner and H. Ulbricht, *Bioorg. Med. Chem. Lett.*, 2002, **12**, 1339.
2 (*a*) J. S. Casas, M. S. Garcıa-Tasende and J. Sordo, *Coord. Chem. Rev.*, 2000, **209**, 197–261; (*b*) T. S. Lobana, R. Sharma, G. Bawa and S. Khanna, *Coord. Chem. Rev.*, 2009, **253**, 977–1055.
3 (*a*) R. Noto, F. Buccheri, G. Cusmano, M. Gruttadauria and G. J. Werber, *J. Heterocycl. Chem.*, 1991, **28**, 1421–1427.
4 (*a*) R. Noto, P. Lo Meo, M. Gruttadauria and G. Werber, *J. Heterocycl. Chem.*, 1999, **36**, 667–674; (*b*) S. Buscemi and M. Gruttadauria, *Tetrahedron*, 2000, **56**, 999–1004; (*c*) M. H. Shih and C. L. Wu, *Tetrahedron*, 2005, **61**, 10917–10925; (*d*) A. Foroumadi, S. Pournourmohammadi, F. Soltani, M. Asgharian-Rezaee, S. Dabiri, A. Kharazmi and A. Shafiee, *Bioorg. Med. Chem. Lett.*, 2005, **15**, 1983–1985; (*e*) A. Foroumadi, Z. Kiani and F. Soltani, *Farmaco*, 2003, **58**, 1073–1076; (*f*) J. P. Kilburn, J. Lau and R. C. F. Jones, *Tetrahedron Lett.*, 2003, **44**, 7825–7828; (*g*) R. Severinsen, J. P. Kilburn and J. F. Lau, *Tetrahedron*, 2005, **61**, 5565–5575; (*h*) E. Lopez-Torres, A. R. Cowley and J. R. Dilworth, *Dalton Trans.*, 2007, 1194–1196.
5 (*a*) A. P. de Silva, H. Q. N. Gunaratne, T. A. Gunnlaugsson, J. M. Huxley, C. P. McCoy, J. T. Rademacher and T. E. Rice, *Chem. Rev.*, 1997, **97**, 1515–1566; (*b*) B. Valeur and I. Leray, *Coord. Chem. Rev.*, 2000, **205**, 3–40; (*c*) J. S. Kimand and D. T. Quang, *Chem. Rev.*, 2007, **107**, 3780–3799.
6 (*a*) G. Muthaup, A. Schlicksupp, L. Hess, D. Beher, T. Ruppert, C. L. Masters and K. Beyreuther, *Science*, 1996, **271**, 1406–1409; (*b*) R. A. Løvstad, *BioMetals*, 2004, **17**, 111–113; (*c*) K. J. Barnham, C. L. Masters and A. I. Bush, *Nat. Rev. Drug Discovery*, 2004, **3**, 205–214; (*d*) D. R. Brown and H. Kozlowski, *Dalton Trans.*, 2004, 1907–1917; (*e*) G. L. Millhauser, *Acc. Chem. Res.*, 2004, **37**, 79–85; (*f*) E. Gaggelli, H. Kozlowski, D. Valensin and G. Valensin, *Chem. Rev.*, 2006, **106**, 1995–2044.
7 (*a*) Y. Zheng, J. Orbulescu, X. Ji, F. M. Andreopoulos, S. M. Pham and R. M. Leblanc, *J. Am. Chem. Soc.*, 2003, **125**, 2680–2686; (*b*) Y. Xiang and A. Tong, *Luminescence*, 2008, **23**, 28–31; (*c*) H. J. Kim, S. Y. Park, S. Yoon and J. S. Kim, *Tetrahedron*, 2008, **64**, 1294–1230; (*d*) H. J. Kim, J. Hong, A. Hong, S. Ham, J. H. Lee and J. S. Kim, *Org. Lett.*, 2008, **10**, 1963–1966; (*e*) W. Lin, L. Yuan, W. Tan, J. Feng and L. Long, *Chem.–Eur. J.*, 2009, **15**, 1030–1035; (*f*) D. Y. Sasaki, D. R. Shnek, D. W. Pack and F. H. Arnold, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 905–907; (*g*) J. Yoon, N. E. Ohler, D. H. Vance, W. D. Aumiller and W. Czarnik, *Tetrahedron Lett.*, 1997, **38**, 3845–3848; (*h*) B. Bodenant, T. Weil, M. Businelli-Pourcel, F. Fages, B. Barbe, I. Pianet and M. Laguerre, *J. Org. Chem.*, 1999, **64**, 7034–7039; (*i*) Y. Zheng, K. M. Gatta's-Asfura, V. Konka and R. M. Leblanc, *Chem. Commun.*, 2002, 2350–2351.
8 (*a*) A. V. Varnes, R. B. Dodson and E. L. Whery, *J. Am. Chem. Soc.*, 1972, **94**, 946–950; (*b*) K. Rurack, U. Resch, M. Senoner and S. Daehne, *J. Fluoresc.*, 1993, **3**, 141–143; (*c*) H. Mu, Rui. Gong, Q. Ma, Y. Sun and E. Fu, *Tetrahedron Lett.*, 2007, **48**, 5525–5529; (*d*) S. Goswami and R. Chakraborty, *Tetrahedron Lett.*, 2009, **50**, 2911–2914.
9 (*a*) P. Ghosh and P. K. Bharadwaj, *J. Am. Chem. Soc.*, 1996, **118**, 1553–1554; (*b*) B. Ramachandram and A. Samanta, *Chem. Commun.*, 1997, 1037–1038; (*c*) K. Rurack, M. Kollmannsberger, U. Resch-Genger and J. Daub, *J. Am. Chem. Soc.*, 2000, **122**, 968–969; (*d*) J. S. Yang, C. S. Lin and C. Y. Hwang, *Org. Lett.*, 2001, **3**, 889–892; (*e*) Z. C. Weng, R. Yang, H. He and Y. B. Jiang, *Chem. Commun.*, 2006, 106–108; (*f*) H. Yang, Z. Q. Liu, Z. G. Zhou, E. X. Shi, F. Y. Li, Y.-K. Du, T. Yi and C. H. Huang, *Tetrahedron Lett.*, 2006, **47**, 2911–2914.
10 (*a*) M. Suresh, S. K. Mishra, S. Mishra and A. Das, *Chem. Commun.*, 2009, 2496–2498; (*b*) M. H. Lee, T. V. Giap, S. H. Kim, Y. H. Lee, C. Kang and J. S. Kim, *Chem. Commun.*, 2010, **46**, 1407–1409; (*c*) A. F. Li, H. He, Y. B. Ruan, Z. C. Wen, J. S. Zhao, Q. J. Jiang and Y. B. Jiang, *Org. Biomol. Chem.*, 2009, **7**, 193–200; (*d*) B. N. Ahamed, M. Arunachalam and P. Ghosh, *Inorg. Chem.*, 2010, **49**, 4447–4457; (*e*) J. Du, J. Fan, X. Peng, P. Sun, J. Wang, H. Li and S. Sun, *Org. Lett.*, 2010, **12**, 476–479; (*f*) F. Song, S. Watanabe, P. E. Floreancig and K. Koide, *J. Am. Chem. Soc.*, 2008, **130**, 16460–16461; (*g*) J. V. Ros-Lis, M. D. Marcos, R. Matinez-Manez, K. Rurack and J. Soto, *Angew. Chem., Int. Ed.*, 2005, **44**, 4405–4407; (*h*) X. Zhang, Y. Xiao and X. Qian, *Angew. Chem., Int. Ed.*, 2008, **47**, 8025–8029; (*i*) Y. K. Yang, K. J. Yook and J. Tae, *J. Am. Chem. Soc.*, 2005, **127**, 16760–16761; (*j*) J.-S. Wu, I. C. Hwang, K. S. Kim and J. S. Kim, *Org. Lett.*, 2007, **9**, 907–910; (*k*) M. Y. Chae and A. W. Czarnik, *J. Am. Chem. Soc.*, 1992, **114**, 9704–9705; (*l*) J. Huang, Y. Xu and X. Qian, *J. Org. Chem.*, 2009, **74**, 2167–2170; (*m*) M. Suresh, A. Shrivastav, S. Mishra, E. Suresh and A. Das, *Org. Lett.*, 2008, **10**, 3013–3016; (*n*) Y.-K. Yang, K.-J. Yook and J. Tae, *J. Am. Chem. Soc.*, 2005, **127**, 16760–16761; (*o*) K. C. Song, J. S. Kim, S. M. Park, K.-C. Chung, S. Ahn and S.-K. Chang, *Org. Lett.*, 2006, **8**, 3413–3416.
11 (*a*) V. Dujols, F. Ford and A. W. Czarnik, *J. Am. Chem. Soc.*, 1997, **119**, 7386–7387; (*b*) R. M. Kierat and R. Kramer, *Bioorg. Med. Chem. Lett.*, 2005, **15**, 4824–4827; (*c*) J. Kovacs, T. Rodler and A. Mokhir, *Angew. Chem., Int. Ed.*, 2006, **45**, 7815–7817; (*d*) J. Kovacs, T. Rodler and A. Mokhir, *Angew. Chem.*, 2006, **118**, 7979–7981; (*e*) X. Qi, E. J. Jun, L. Xu, S.-J. Kim, J. S. J. Hong, Y. J. Yoon and J. Yoon, *J. Org. Chem.*, 2006, **71**, 2881–2884; (*f*) J. Kovacs and A. Mokhir, *Inorg. Chem.*, 2008, **47**, 1880–1882.

12 J. L. Bricks, K. Rurack, R. Radeglia, G. Reck, B. Schulz, H. Sonnenschein and U. Resch-Genger, *J. Chem. Soc., Perkin Trans. 2*, 2000, 1209–1214.
13 (*a*) X. Chen, S.-W. Nam, M. J. Jou, Y. Kim, S.-J. Kim, S. Park and J. Yoon, *Org. Lett.*, 2008, **10**, 5235–5238; (*b*) Y. Zhao, Z. Lin, C. He, H. Wu and C. Duan, *Inorg. Chem.*, 2006, **45**, 10013–10015; (*c*) M. H. Lee, S. W. Lee, S. H. Kim, C. Kang and J. S. Kim, *Org. Lett.*, 2009, **11**, 2101–2104; (*d*) W. Huang, X. Zhu, D. Wua, C. He, X. Hu and C. Duan, *Dalton Trans.*, 2009, 10457–10465.
14 (*a*) E. López-Torres, M. A. Mendiola, J. Rodríguez-Procopio, M. T. Sevilla, E. Colacio, J. M. Moreno and I Sobrados, *Inorg. Chim. Acta*, 2001, **323**, 130–138; (*b*) A. J. M. Al-Karawi, W. Clegg, R. W. Harrington and Richard A. Henderson, *Dalton Trans.*, 2009, 564–570.
15 A. Mokhir and R. Käamer, *Chem. Commun.*, 2005, 2244–2246.
16 M. Sarma, A. Kalita, P. Kumar, Amardeep Singh and Biplab Mondal, *J. Am. Chem. Soc.*, 2010, **132**, 7846–7847.
17 Z. Li, Y. Xiang and A. Tong, *Anal. Chim. Acta*, 2008, **619**, 75–80.
18 *SMART, SAINT and XPREP*, Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA, 1995.
19 G. M. Sheldrick, *SADABS: Software for Empirical Absorption Correction*, University of Gottingen, Institute fur Anorganische Chemieder Universitat, Gottingen, Germany, 1999–2003.
20 G. M. Sheldrick, *SHELXS-97*, University of Gottingen:, Germany, 1997.
21 L. J. Farrugia, *J. Appl. Crystallogr.*, 1997, **30**, 565.