



Manganese(II) catalyzed synthesis of *bis*(*N*-cyclohexylthiourea) derived from thiosemicarbazide: Structural characterization, fluorescence, cyclic voltammetry, Hirshfeld surface analysis and DFT calculation

S. Jaiswal^a, M.K. Gond^a, M.K. Bharty^{a,*}, B. Maiti^a, S. Krishnamoorthi^a, R.J. Butcher^b

^a Department of Chemistry, Banaras Hindu University, Varanasi 221005, India

^b Department of Chemistry, Howard University, 525 College Street NW, Washington, DC 20059, USA

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ABSTRACT

A new compound *bis*(*N*-cyclohexylthiourea) (H_2chth) has been synthesized and characterized with the aid of elemental analyses, IR, NMR and single crystal X-ray diffraction data. Compound H_2chth crystallizes in triclinic system with space group P-1. During the course of reaction, the cyclohexyl isothiocyanate moiety of the substituted thiosemicarbazide undergoes tautomerization and rearrangement into the corresponding carbothioamide moiety in the presence of manganese(II) acetate. The interaction of H_2chth with different metal ions in methanol solution is studied and it shows interesting red shifts with Mn^{2+} , Co^{2+} , Ni^{2+} , Cu^{2+} , Zn^{2+} and Cd^{2+} ions which suggests that compound H_2chth may be a useful probe for sensing of these metal ions. Cyclic voltammetric studies of H_2chth and its interaction with different metal ions exhibit complete irreversible redox behavior. Compound H_2chth exhibits emission at 27322 cm^{-1} upon excitation at 37037 cm^{-1} . The emission spectra of different metal ions with H_2chth exhibit less intense emissions as compared to the free H_2chth . The structure of compound H_2chth is stabilized via intermolecular N-H...S and C-H...S hydrogen bonding. The geometry of the compound H_2chth has been optimized using the B3LYP density functional theory method and the results are compared with the X-ray diffraction data. The calculated geometrical parameters corroborate with the experimental data. Frontier molecular orbital analysis suggests that compound H_2chth is soft and highly reactive. Hirshfeld surface map and 2D finger print plot were used to explore the intermolecular interactions of H_2chth .

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1. Introduction

Nitrogen-sulfur containing ligands have been of great interest to researchers and play an important role in the synthesis of biologically active compounds [1-6]. This is due to their potential biological activities viz. anticancer, antibacterial, antifungal, antiamoebic and insecticidal and also for their therapeutic uses [7-16]. A variety of nitrogen and sulphur containing ligands are known which include thiourea, thiosemicarbazide, thiosemicarbozones and *N*-acyl-*N'*-thioaroylhydrazides. A number of thiosemicarbazides and their derivatives have been synthesized and characterized by various physicochemical techniques and used as intermediate for the syntheses of five membered nitrogen-sulfur or nitrogen-oxygen heterocyclic compounds [17,18]. Thiourea and *N*, *N'*-disubstituted

thiourea are important compounds which possess biological activity, act as corrosion inhibitors, antioxidant and are the main component of the polymers [19]. They are used as analytical reagents, especially for the determination of metal ions in the presence of various metal ions [20,21]. Acyl/aryl thiourea derivatives are well known for a wide range of biological activities such as bactericidal, fungicidal, insecticidal and possess regulating activity for plant growth [22-24]. Due to the presence of S, N and O donor atoms, the versatility and interesting behaviour of thiourea as building blocks in polydentate ligands for metals have become a research topic of interest in the last few years. It has been reported that acylthiourea ligands behave as monodentate or bidentate bonding through sulphur and oxygen donor atoms [25]. These hard and soft donor atoms provide a multitude of bonding possibilities [26,27]. A number of thiourea derivatives have been reported to form complexes with 3d metal ions [28]. In view of the above, we have synthesized a new compound *bis*(*N*-cyclohexylthiourea) (H_2chth) and characterized by various physicochemical techniques and single crystal X-ray diffraction data.

* Corresponding author.

E-mail addresses: mkbharty@bhu.ac.in, manoj_vns2005@yahoo.co.in (M.K. Bharty).

2. Experimental

2.1. Chemicals and starting materials

Commercial reagents were used without further purification. Cyclohexyl isothiocyanate was purchased from Sigma Aldrich. Other chemicals were of reagent grade and used as received without further purification. All the synthetic manipulations were carried out in open atmosphere and at room temperature. The solvents were dried and distilled before use following the standard procedure.

2.2. Physical measurements

The carbon, hydrogen and nitrogen contents were determined on an Elementar Vario EL III Carlo Erba 1108 instrument. Infrared spectra were recorded in the 400–4000 cm^{-1} region as KBr pellets on a Varian Excalibur 3100 FT-IR spectrophotometer. ^1H and ^{13}C NMR spectra were recorded in $\text{DMSO}-d_6$ on a JEOL JNM-EZ500R/S1 FT-NMR spectrometer using TMS as an internal reference. Electronic spectra were recorded at 10^{-4} M solution in MeOH on a SIMADZU 1700 UV-Vis spectrophotometer. The fluorescent data were collected at room temperature on “Agilent Technologies Cary Eclipse” Fluorescence Spectrophotometer in MeOH. Electro chemical studies were performed on Metrohm (Netherlands) Instrument (Autolab PGSTAT204) attached with NOVA 1.11 software at room temperature under N_2 atmosphere. A three electrode, one compartment cell with solid Pt electrode as a working electrode, platinum wire as counter electrode and Ag/AgCl as reference electrode was used. Thermogravimetric analysis (TG-DTA) of H_2chth was done using a Perkin Elmer-STA 6000 thermal analyzer, TA instruments under a nitrogen atmosphere with heating rate of $10^\circ\text{C min}^{-1}$.

2.3. Crystal structure determination

Crystals suitable for X-ray analysis of *bis*(*N*-cyclohexylthiourea) (H_2chth) was grown at room temperature. The Crystal data were collected on an oxford Gemini diffractometer equipped with a CryAlis CCD software using a graphite mono-chromated $\text{Mo K}\alpha$ ($\lambda = 0.71073\text{\AA}$) radiation source at 293 K. A multi scan absorption correction was solved by direct methods (SHELXL-08) and refined

against all data by full matrix least-square on F^2 using anisotropic displacement parameters for all non-hydrogen atoms. All of the hydrogen atoms were included in the refinement at geometrically ideal positions and refined with riding model [29]. The MERCURY package and ORTEP-3 for windows program were used for generating the structures [30,31].

2.4. Quantum Chemical Calculation

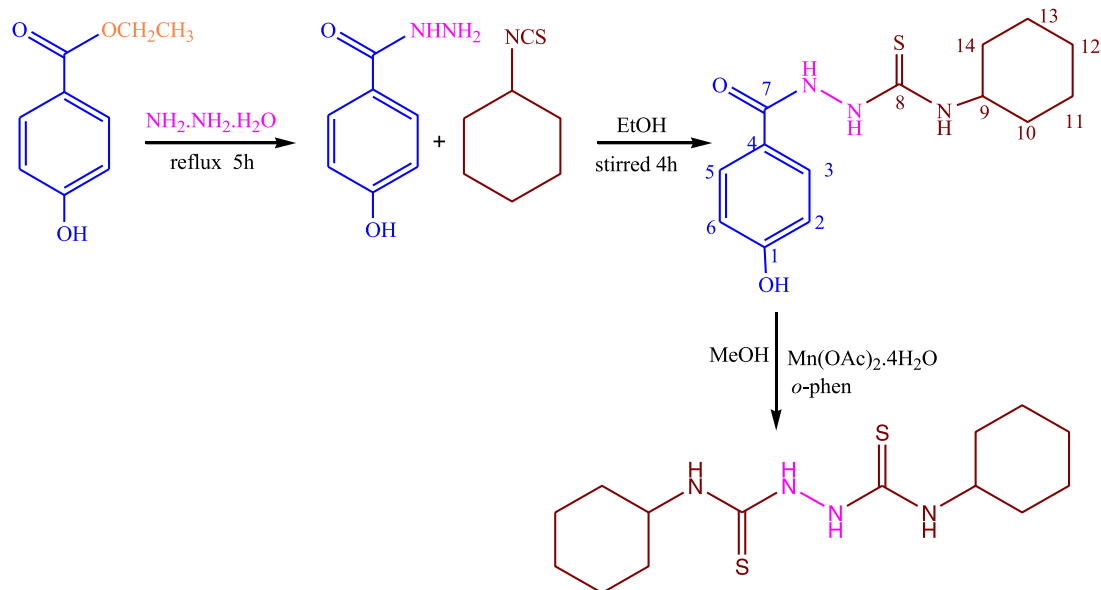
Density Functional Theory (DFT) calculations were performed using the B3LYP functional [32]. The 6-31G** basis set was used for all atoms. The geometry optimization and frequency calculation (to verify genuine minimum energy structures) were performed using Gaussian 09 program package [33].

2.5. Synthesis of 1-hydroxy benzoyl-4-cyclohexyl-3-thiosemicarbazide (H_2hbchth)

4-Hydroxy benzoic acid hydrazide was prepared by refluxing ethyl-4-hydroxybenzoate (3.0 g, 20 mmol) and hydrazine hydrate (1.2 mL, 20 mmol) for 5 h at 80°C . White solid obtained after cooling the reaction mixture was washed with ether and dried in *vacuo*. To the ethanol suspension of 4-hydroxy benzoic acid hydrazide, cyclohexyl isothiocyanate (2.54 mL, 20 mmol) added dropwise and the reaction mixture was stirred for 4 h. The light yellow solid of 1-hydroxy benzoyl-4-cyclohexyl-3-thiosemicarbazide obtained upon cooling was filtered off, washed with ether and dried in *vacuo*. Yield: 72%. M.p. 195°C . Anal. Calc. for $\text{C}_{14}\text{H}_{19}\text{N}_3\text{O}_2\text{S}$ (293.00): C, 57.3; H, 6.48; N, 14.33. Found: C, 56.01; H, 6.19; N, 15.32. IR (KBr, cm^{-1}): $\nu(\text{-OH})$ 3420, $\nu(\text{-NH})$ 3212, 3112, $\nu(\text{-CH aromatic ring})$ 3007, $\nu(\text{-CH cyclohexyl ring})$ 3112, $\nu(\text{-C=O})$ 1673, $\nu(\text{-N-N})$ 1169, $\nu(\text{-C=S})$ 984. ^1H NMR ($\text{DMSO}-d_6$, 500 MHz; δ ppm) 10.30, 9.35 (2H, -NH), 7.77–7.80 (4H, aromatic protons), 4.25 (1H, OH), 1.22–1.28 (cyclohexyl protons). ^{13}C NMR ($\text{DMSO}-d_6$, 500 MHz; δ ppm) 180.89 (C=S), 162.04 (C=O), 114.91–131.49 (aromatic ring carbons), 14.40–32.60 (cyclohexyl ring carbons).

2.6. Synthesis of bis(*N*-cyclohexylthiourea) (H_2chth)

A methanol solution (20 mL) of $\text{Mn}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ (0.122 g, 0.5 mmol) was added to the methanol suspension of 1-hydroxy



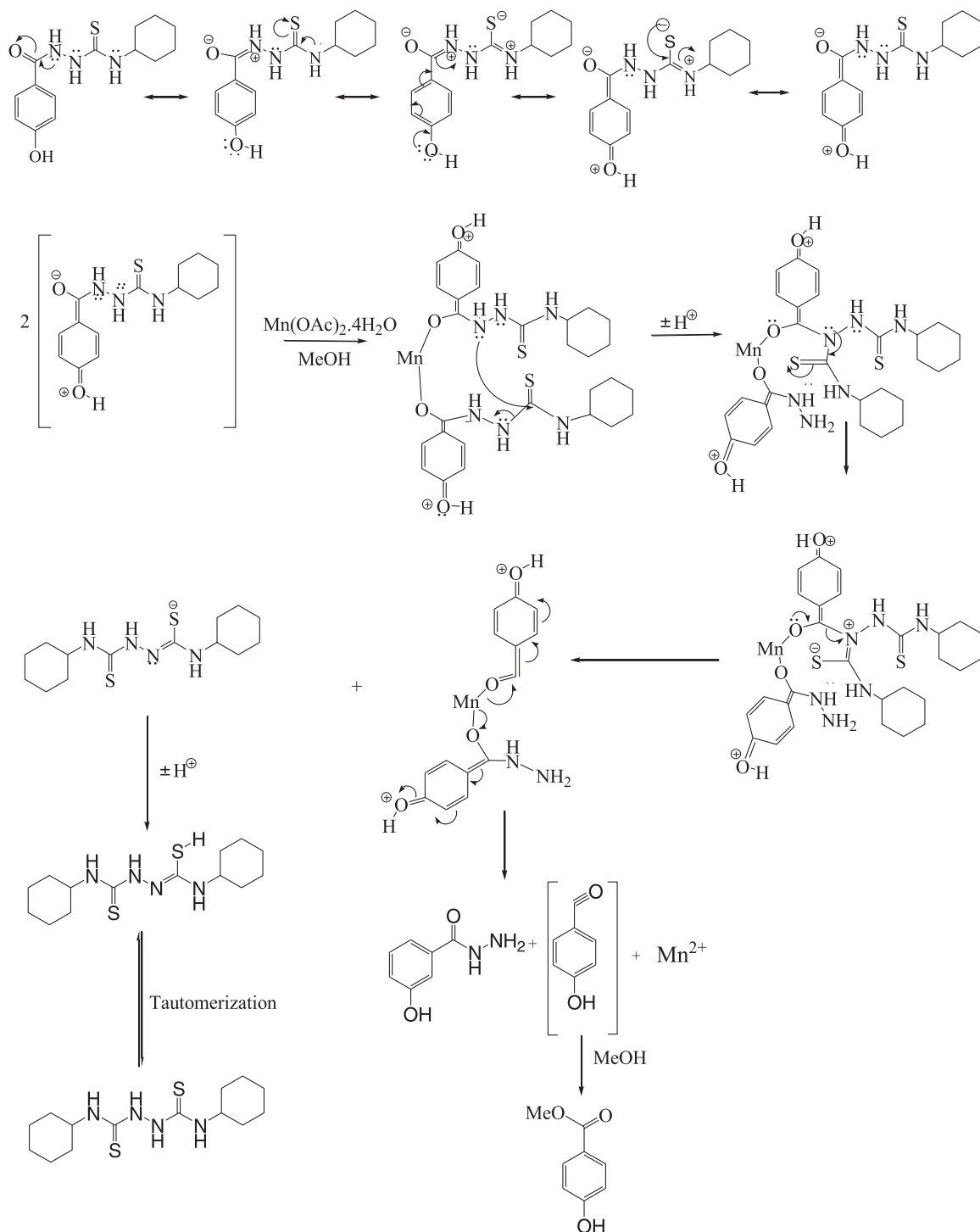
Scheme 1. Synthesis of *bis*(*N*-cyclohexylthiourea) (H_2chth)

benzoyl-4-cyclohexyl-3-thiosemicarbazide (0.293 g, 1 mmol) and stirred for 4 h. White solid was obtained, filtered off and washed with ether. A methanol solution of *o*-phen (0.099 g, 0.5 mmol) was added to methanol suspension of above solid and stirred for 1 h. A clear solution was obtained, filtered off and kept for crystallization. White crystals of H₂chth, suitable for X-ray analysis, were obtained by slow evaporation of the above solution over a period of 10 days. Yield 60 %. M.p. 220°C. Anal. Found: C, 53.80; H, 7.90; N, 17.40 %. Anal. Calc. for C₁₄H₂₆N₄S₂ (314.51): C, 53.50; H, 8.2; N, 17.83 %. IR (KBr, ν , cm⁻¹): 3245, 3144 ν (NH), 1446 ν (C-N), 1168 ν (N-N); 984 ν (C=S). ¹H NMR (DMSO-*d*₆, 500 MHz; δ ppm): 10.30, 8.87 (s, 4H,

NH), 1.23-1.33 (cyclohexyl protons). ¹³C NMR ((DMSO-*d*₆, 500 MHz; δ ppm): 165.36 (C=S), 23.52-38.83 (cyclohexyl ring carbons).

3. Result and discussion

The intermediate 1-hydroxy benzoyl-4-cyclohexyl-3-thiosemicarbazide (H₂hbchth) reacts with Mn(OAc)₂•4H₂O and forms white precipitate in methanol solution. The above precipitate was dissolved in methanol solution of *o*-phen to yield bis(N-cyclohexylthiourea) (H₂chth). We have synthesized H₂chth from 1-hydroxy benzoyl-4-cyclohexyl-3-thiosemicarbazide



Scheme 2. Plausible mechanism for synthesis of the bis(N-cyclohexylthiourea)

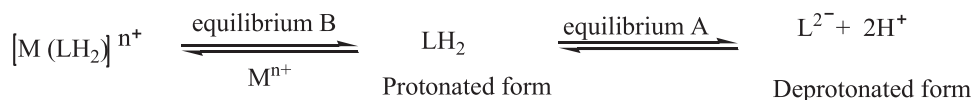
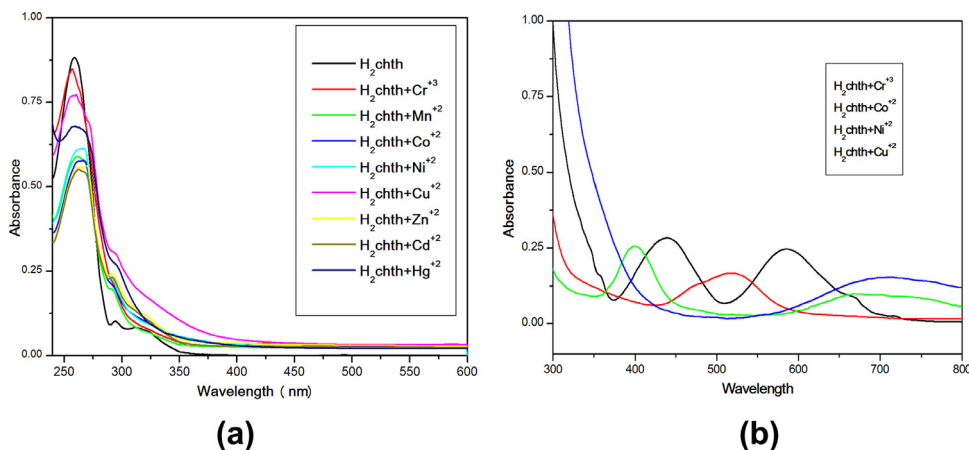
Scheme 3. Protonated and deprotonated form of bis(N-cyclohexylthiourea) (H₂chth)

Fig. 1. A: UV-vis. absorption spectra of H₂chth and interaction with various metal ions at 10⁻⁴ M (A) B: UV-vis. absorption spectra of H₂chth and interaction with metal ions shows d-d transitions

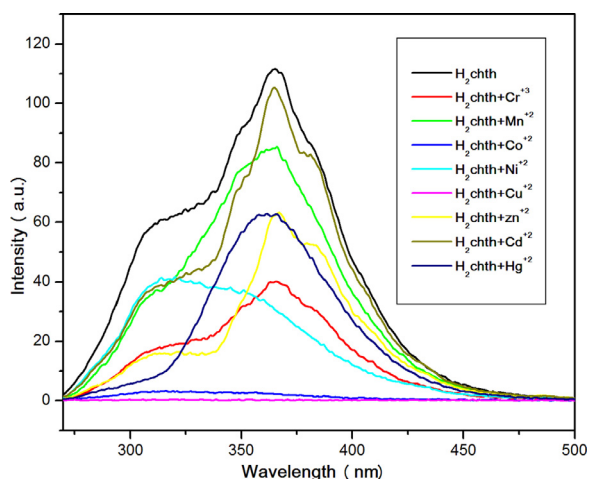


Fig. 2. Emission spectra of H₂chth with various metal ions in MeOH solution at room temperature

(H₂hbchth) assisted by Mn(II) acetate at room temperature with the product yield of 60%. During the course of reaction, the cyclohexyl isothiocyanate moiety of the intermediate undergoes tautomerization and rearrangement into the corresponding carbothioamide moiety in the presence of manganese(II) acetate. This method is different from the reported earlier synthesis of other similar bis(N-acylthiourea) [34]. The schemes 1 and 2 depict the formation of compound H₂chth and its plausible mechanism, respectively. The compound H₂chth is air stable, non-hygroscopic crystalline solid. It is soluble in common organic solvents and can be kept at room temperature over a prolonged period without any sign of decomposition. The present route is relatively safer involving less hazardous chemicals that can be easily handled. The compound H₂chth melts at 220 °C. Thus, the new route employed for the synthesis of above compound does not only impart good yield but is also adequate for growing their single crystals.

3.1. IR spectra

The IR spectrum of the intermediate 1-hydroxy benzoyl-4-cyclohexyl-3-thiosemicarbazide (H₂hbchth) shows absorption band

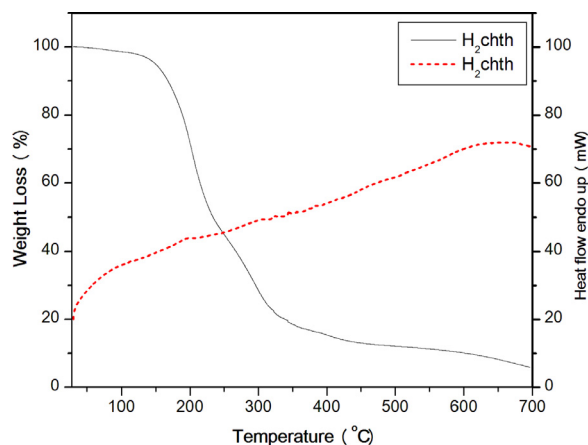


Fig. 3. Thermogram of bis(N-cyclohexylthiourea) (H₂chth)

due to the stretching modes (cm⁻¹) of OH (3420), NH (3212, 3112), C=O (1673), N-N (1169) and C=S (984). Two bands observed at 3007 and 2939 cm⁻¹ due to CH stretching vibrations of aromatic and cyclohexyl rings. The IR spectrum of H₂chth shows absorption due to stretching modes of NH (3245, 3144), C-N (1446), N-N (1168) and C=S (984). The absence of ν(C=N) band together with the appearance of one new band for ν(C-N) at 1446 cm⁻¹ in the IR spectrum of the H₂chth suggests the conversion of thiosemicarbazide to bis(N-cyclohexylthiourea). Thus, it is clear from the IR data that the intermediate 1-hydroxy benzoyl-4-cyclohexyl-3-thiosemicarbazide converted to the corresponding bis(N-cyclohexylthiourea). A band observed at 3007 cm⁻¹ due to CH stretching vibrations of aromatic ring in intermediate H₂hbchth which is absent in the spectrum H₂chth. Compound H₂chth showed two absorptions bands at 2853 and 2931 cm⁻¹ due to CH stretching vibrations of cyclohexyl ring. The HCH scissoring vibrations observed in the region 1534–1446 cm⁻¹ are due to cyclohexyl ring.

3.2. NMR spectra

The ¹H NMR spectrum of intermediate 1-hydroxy benzoyl-4-cyclohexyl-3-thiosemicarbazide (H₂hbchth) exhibits three signals

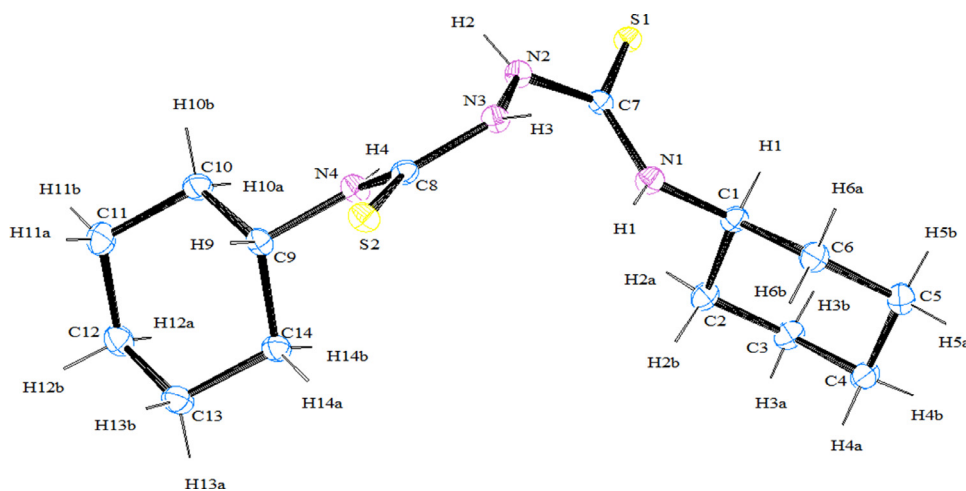


Fig. 4. ORTEP diagram of *bis*(*N*-cyclohexylthiourea) (H_2chth) with atomic numbering scheme

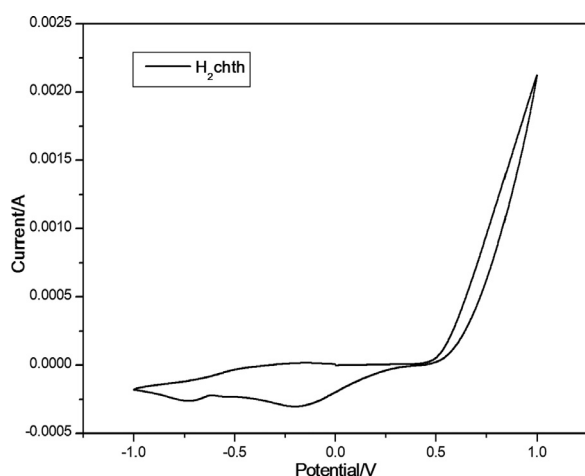


Fig. 5. Showing cyclic voltammogram of *bis*(*N*-cyclohexylthiourea) (H_2chth)

at δ 10.30, 9.95 and 9.35 ppm for the amide, thioamide and NH protons attached with cyclohexyl ring, respectively. Aromatic protons appear as multiplet between δ 6.82–7.80 ppm. One signal observed at 4.23 ppm due to OH proton. Cyclohexyl ring protons appear in the region of 1.22–1.28 ppm. The ^{13}C NMR spectrum of $H_2hbchth$ shows several signals for various carbon atoms out of which the signals at δ 180.89 and 162.04 ppm are due to $>C=S$ and $>C=O$, carbons, respectively. The signals appearing between δ 114.91–131.49 ppm are due to aromatic carbons. Cyclohexyl ring carbons appear in the region of 14.40–32.60 ppm. The 1H NMR spectrum of H_2chth shows two signals at 10.30 and 8.87 ppm due to the thioamide NH protons and one NH proton attached to the cyclohexyl ring, respectively. Cyclohexyl ring protons appear in the region of 1.23–1.33 ppm. The ^{13}C NMR spectrum of H_2chth shows a signal at δ 165.6 ppm due to $C=S$ carbon. The cyclohexyl ring carbons appear in the range δ 14.40–32.60 ppm. Disappearance of $C=O$ signal in ^{13}C NMR spectrum of H_2chth (present at 162.04 ppm in the intermediate $H_2hbchth$) suggests the conversion of thiosemicarbazide moiety to the corresponding *N*-acylthiourea moiety.

3.3. Electronic absorption and Emission spectra

The electronic spectra of H_2chth and interaction with different metal ions are recorded in methanol of 10^{-4} M solution. Compound H_2chth displays one high intensity band at 38610 cm^{-1}

($\epsilon = 8750\text{ L M}^{-1}\text{ cm}^{-1}$) may be assigned to $n \rightarrow \pi^*$ transition which is attributed to the HNCS moiety. The electronic spectra of H_2chth with different metal ions show two bands in the range of $38910\text{--}37735\text{ cm}^{-1}$ which may be assigned to the intraligand/charge transfer transitions (Fig. 1A & 1B). Upon excitation at 37037 cm^{-1} , compound H_2chth exhibits maximum emission at 27322 cm^{-1} (Fig. 2). Emission spectra of Cr^{3+} , Mn^{2+} , Co^{2+} , Ni^{2+} , Cu^{2+} , Zn^{2+} , Cd^{2+} and Hg^{2+} ions with H_2chth exhibit a slightly lower luminescent property as compared to the free H_2chth with respect to intensity and energy. Metal ions Cr^{3+} , Mn^{2+} , Co^{2+} , Ni^{2+} , Cu^{2+} , Zn^{2+} , Cd^{2+} and Hg^{2+} with H_2chth , upon excitation at 37037 cm^{-1} , exhibit emission maxima at 27397, 27322, 31152, 31847, 31250, 27247, 27472 and 27322 cm^{-1} , respectively. Thus compound H_2chth and its interaction with different metal ions show Stokes shift of 9640, 9715, 5885, 5190, 5787, 9790, 9565 and 9715 cm^{-1} , respectively and emit blue light. The emission spectra suggest that metal ions with H_2chth exhibit less intense emission as compared to free H_2chth . The compound H_2chth possesses two dissociable protons and is supposed to furnish its deprotonated form with higher extent of conjugation and thereby high extent of luminescence. Upon the addition of a particular metal ion to the H_2chth solution the same is expected to compete for the lone pairs of the H_2chth . Consequently, the complex species is expected to get formed in the solution. This phenomenon might be diminishing the extent of equilibrium A and prospective the same towards left hand side i.e. equilibrium B (scheme 3). In other words, upon the addition of metal ions the prospective of equilibrium A is diminished and is favoured towards the left hand side i.e. equilibrium B which ultimately leads to decrease in luminescence behaviour of LH_2 (protonated form of compound).

3.4. Cation Interaction Behaviour

UV-Vis absorption spectra were recorded in 10^{-4} M methanol solution. The absorption spectral band observed for compound H_2chth at 38610 cm^{-1} may be assigned to $n \rightarrow \pi^*$ transition due to the presence of HNCS moiety (Fig. 1A). Addition of 1.0 equivalent each of Cr^{3+} , Mn^{2+} , Co^{2+} , Ni^{2+} , Cu^{2+} , Zn^{2+} , Cd^{2+} and Hg^{2+} metal ion as their acetate salts respectively to the 10^{-4} M solution of H_2chth produced UV-vis. spectral changes. We detected the colour change and new *d-d* absorption bands upon addition of different metal(II) acetates due to coordination between metal ion and thioamide sulfur atom (Fig. 1B). The above observation clearly proves the sensitivity of H_2chth towards the above mentioned transition metal ions via coordination between metals and

thioamide sulfur atom. Upon addition of chromium acetate solution the colour changed to light green and two new bands were observed at 17123 and 22727 cm^{-1} due to d-d transitions whereas upon addition of manganese(II) acetate solution, the ions did not show any significant colour change and an absorption band was observed at 38314 cm^{-1} (Fig. 1B). These values are close to the absorption maxima reported in their metal complexes with similar ligands [35]. Cobalt, nickel, copper and mercury acetate gave light pink, light green, light blue and light yellow colour, respectively in methanol solution of H_2chth , while zinc and cadmium acetate did not show any significant colour change in the solution. Upon addition of cobalt acetate solution the colour changed to light pink and a new band was observed at 19230 cm^{-1} . This band can be assigned to the $^4T_{1g}(F) \rightarrow ^4A_{2g}(F) (\nu_2)$ transition, suggesting a distorted octahedral geometry for the complex (Fig. 1B). Nickel- H_2chth solution gives two absorption bands at 25000 and

15015 cm^{-1} , and it is the characteristic of octahedral Ni(II) complex assigned to the $^3A_{2g} \rightarrow ^3T_{1g}(P)$ and $^3T_{1g}(P) (\nu_2)$ transitions [35] (Fig. 1B), respectively. Upon addition of copper(II) acetate solution the colour changed to light blue and absorption band at 14100 cm^{-1} for Cu- H_2chth may be assigned to the envelope of the $^2T_{2g} \rightarrow ^2E_g$ transitions indicating an octahedral geometry for the Cu(II) complex [35, 36]. This study suggests that Co^{2+} , Cu^{2+} , Mn^{2+} and Ni^{2+} ions showed significant red shift in UV-visible spectra, hence compound H_2chth may be a good probe for sensing these metal ions in the solution. The high energy absorption maxima in the range of 38910-33898 cm^{-1} can be attributed to the HNCS moiety. It is noteworthy that free H_2chth showed one band at 38610 cm^{-1} due to the presence of HNCS moiety while upon addition of metal ions the former band either disappeared or its intensity decreased. It also suggests the interaction of metal ions with HNCS moiety present in the H_2chth .

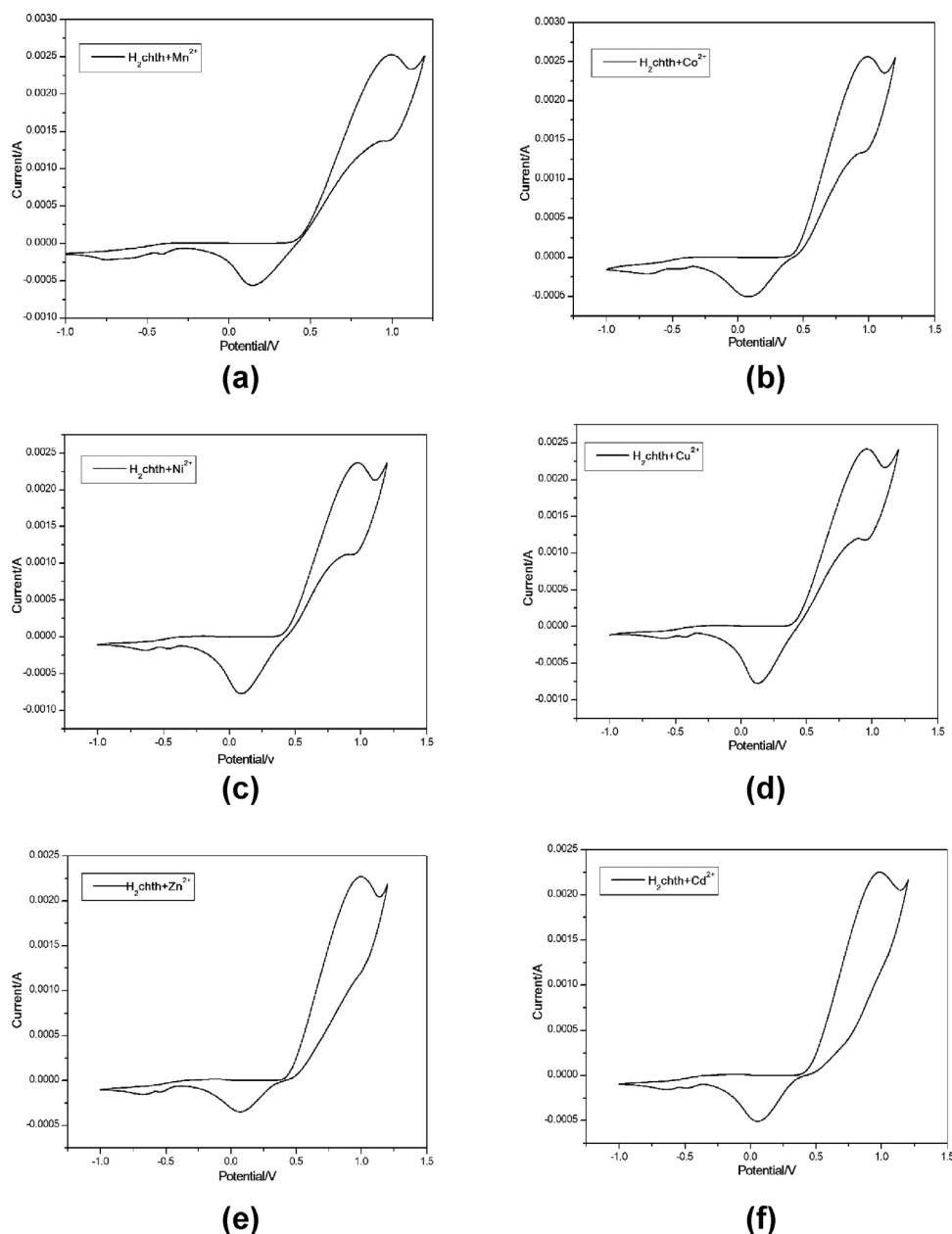


Fig. 6. A: Cyclic voltammogram of Mn- H_2chth at 140 mVs^{-1} scan rate B: Cyclic voltammogram of Co- H_2chth at 140 mVs^{-1} scan rate C: Cyclic voltammogram of Ni- H_2chth at 140 mVs^{-1} scan rate D: Cyclic voltammogram of Cu- H_2chth at 140 mVs^{-1} scan rate E: Cyclic voltammogram of Zn- H_2chth at 140 mVs^{-1} scan rate F: Cyclic voltammogram of Cd- H_2chth at 140 mVs^{-1} scan rate

Table 1
Crystallographic data, structure solution and refinement for H₂chth.

Parameters	H ₂ chth
Empirical formula	C ₁₄ H ₂₆ N ₄ S ₂
Formula weight	314.51
Crystal system	Triclinic
Space group	P-1
T (K)	100(2)
λ, Mo Kα (Å)	0.71073
a (Å)	6.1344(3)
b (Å)	10.0305(5)
c (Å)	13.7249(6)
α (°)	85.736(2)
β (°)	80.569(2)
γ (°)	89.352(2)
V, (Å ³)	831.88(7)
Z	2
ρ _{calcd} (g/cm ³)	1.256
μ (mm ⁻¹)	0.317
F(000)	340
Crystal size(mm ³)	? x ? x ?
θ range for data collections(°)	2.442 to 28.318
Index ranges	-8 ≤ h ≤ 8, -10 ≤ k ≤ 13, -18 ≤ l ≤ 18
No. of reflections collected	10194
No. of independent reflections(R _{int})	4087
No. of data/restraints/parameters	4087 / 0 / 189
Goodness-of-fit on F ²	1.101
R ₁ ^a , wR ₂ ^b [(1>2σ(I))]	0.0898, 0.2451
R ₁ ^a , wR ₂ ^b (all data)	0.1024, 0.3287
Largest difference in peak /hole (e.Å ⁻³)	2.362, -0.994

^a R₁ = Σ||F_o| - |F_c||Σ|F_o|.^b R₂ = [Σw(|F_o| - |F_c|)²/Σw|F_o|²]^{1/2}

3.5. Thermal analysis of bis(N-cyclohexylthiourea) (H₂chth)

The thermal property of compound H₂chth was studied by TGA in the temperature range 30–700°C under the nitrogen atmosphere. The thermogravimetric analysis of H₂chth shows that it starts decomposing at 150°C and thermogram exhibits two distinct decompositions step in the range of 140–340 and 340–600°C (Fig. 3). The major weight loss of 52.86 % (obs.50.76 %) in the temperature range of 140–340°C due to loss of two molecules of cyclohexyl ring. The second minor weight loss may be due to the loss of two molecules of HNCS moiety (Calcd. weight loss 37.57%; obs. 32.85%). At higher temperature remaining organic moiety finally converted into the gaseous products. The corresponding endothermic peak in the DTA was obtained at 194°C. This study suggests that H₂chth is almost stable upto its melting temperature of 220 °C and starts decomposing thereafter.

3.6. Crystal structure description of bis(N-cyclohexylthiourea) (H₂chth)

The molecular structure of compound H₂chth has been determined by single crystal X-ray diffraction data. The details of data collection, structure solution and refinement are listed in Table 1. ORTEP diagram for H₂chth with atom numbering scheme have shown in Fig. 4. Selected bond lengths and angles are given in Table 2. Weak intermolecular hydrogen bonding interactions are listed in Table 3. The compound H₂chth crystallizes in triclinic system with space group P-1 but discrete molecules are located on the twofold axes, out of the symmetry centres. Therefore, H₂chth has lower C₂ symmetry as shown in Fig. 4. The dihedral angle between two cyclohexyl ring is found to be 49.37° indicating that rings are tilted with respect to each other. The C7-S1 bond length is shorter [1.695(3) Å] in H₂chth molecule than other reported compounds [1.753(5) Å] [37–39], but similar to that in other re-

Table 2
Bond length (Å) and angles (°) for H₂chth

Bond length (Å)	Cal	Bond angle (°)	Cal
S(1)-C(7)	1.695(3)	C(7)-N(1)-C(1)	124.8(2)
S(2)-C(8)	1.695(3)	N(1)-C(7)-S(1)	124.7 (2)
N(1)-C(7)	1.323(3)	S(1)-C(7)-N(2)	118.03(19)
N(1)-C(1)	1.467(3)	N(3)-N(2)-C(7)	119.5(2)
N(2)-C(7)	1.374(3)	N(4)-C(8)-N(3)	117.2(2)
N(2)-N(3)	1.396(3)	C(8)-N(4)-C(9)	125.2 (2)
N(3)-C(8)	1.369(3)	C(10)-C(9)-N(4)	111.8(2)
N(4)-C(8)	1.327(3)	C(2)-C(1)-N(1)	111.8(2)

Table 3
Hydrogen bonds parameter for H₂chth (Å and °)

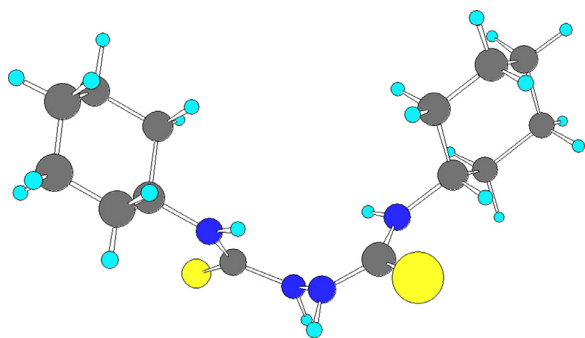
D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(2)-H(2C)...S(1)#1	0.87(4)	2.51(4)	3.371(2)	174(3)
N(3)-H(3N)...S(2)#2	0.93(3)	2.41(3)	2.336(2)	174(3)
C(2)-H(2A)...S(2)#3	0.99	2.89	3.727(3)	142.6
C(10)-H(10A)...S(1)#4	0.99	2.87	3.701(3)	142.2
N(2)-H(2C)...S(1)#1	0.87(4)	2.51(4)	3.371(2)	174(3)
N(3)-H(3N)...S(2)#2	0.93(3)	2.41(3)	2.336(2)	174(3)
C(2)-H(2A)...S(2)#3	0.99	2.89	3.727(3)	142.6
C(10)-H(10A)...S(1)#4	0.99	2.87	3.701(3)	142.2

Symmetry transformations used to generate equivalent atoms: #1 -x,-y,-z+1 #2 -x,-y+1,-z+1 #3 -x+1,-y+1,-z+1 #4 -x+1,-y,-z+1

ported phenyl thiosemicarbazide [1.685(5) Å] and phenylthiourea derivatives [40,41]. Thus, the carbon sulfur bond length has a double bond character [37,42]. The C7-N2 and C7-N1 bond length in the thiourea moiety are 1.374(3) and 1.323 (3) Å, respectively. These values differ from the thiosemicarbazide moiety 1.326(2) and 1.316(3) Å but are very similar to other reported thiosemicarbazide compounds 1.373(3), 1.320(3) Å [43,44]. In the solid state, the structure of the compound H₂chth is stabilized by N-H...S intermolecular hydrogen bonding (N2-H2C...S1 & N3-H3N...S2) occurring between the NH hydrogen of thioamide group and sulfur atoms of other unit of the thioamide group leading to the formation of a supramolecular architecture (supplementary figure 3). In addition, the structure is further stabilized by C-H...S hydrogen bonding (C2-H2A...S2 & C10-H10A...S1) between the CH hydrogen of cyclohexyl rings and sulfur atoms of thioamide group (supplementary figure 3).

3.7. Electrochemical characterization

The electrochemical behavior of the compound H₂chth was studied using cyclic voltammetry and is depicted in Fig. 5. The cyclic voltammograms were recorded in 10⁻³ M H₂chth solution in CH₃CN at a platinum electrode using 0.1M TBAP as supporting electrolyte. Compound H₂chth exhibited only one cathodic peak at 0.190 V (scan rate 0.140 V.s⁻¹) due to the reduction of carbon sulfur double bond (thione form) into carbon sulfur single bond (thiol form). Upon addition of metal ions to the acetonitrile solution of H₂chth, the cathodic peak shifted to the positive potential due to the complexation (Fig. 6A–6F). Various transition metal ions such Mn²⁺, Co²⁺, Ni²⁺, Cu²⁺, Zn²⁺ and Cd²⁺ with H₂chth exhibit anodic and cathodic peaks at 0.998 and 0.143 V for Mn²⁺, 0.994 and 0.084 V for Co²⁺, 0.989 and 0.094 V for Ni²⁺, 0.958 and 0.129 V for Cu²⁺, 0.994 and 0.070 V for Zn²⁺ and at 0.989 and 0.050 V for Cd²⁺ ions (scan rate 0.140 V.s⁻¹), respectively. All anodic peaks observed in the cyclic voltammograms of the metal ions with H₂chth might be assigned to the irreversible oxidation of metal ions (M²⁺ to M³⁺). Similarly, all the cathodic peaks might be assigned to the irreversible reduction of thione to thiol form as discussed earlier. The slight positive shift observed in the presence of metal ions may be due to the complexation. On scanning with higher scan

Fig. 7. Optimized structure of H₂chth

rates the cathodic peak potential slightly shifted and anodic peak current increased which indicates that the process is completely irreversible [45–47]. We have also performed the cyclic voltammetric studies of Cr³⁺ and Hg²⁺ ions with compound H₂chth which show no significant changes in to the cathodic peak of H₂chth and no anodic peak is observed in the interaction of metal ions with compound (Supplementary figures 1 & 2).

3.8. DFT calculation

3.8.1. Geometry optimization

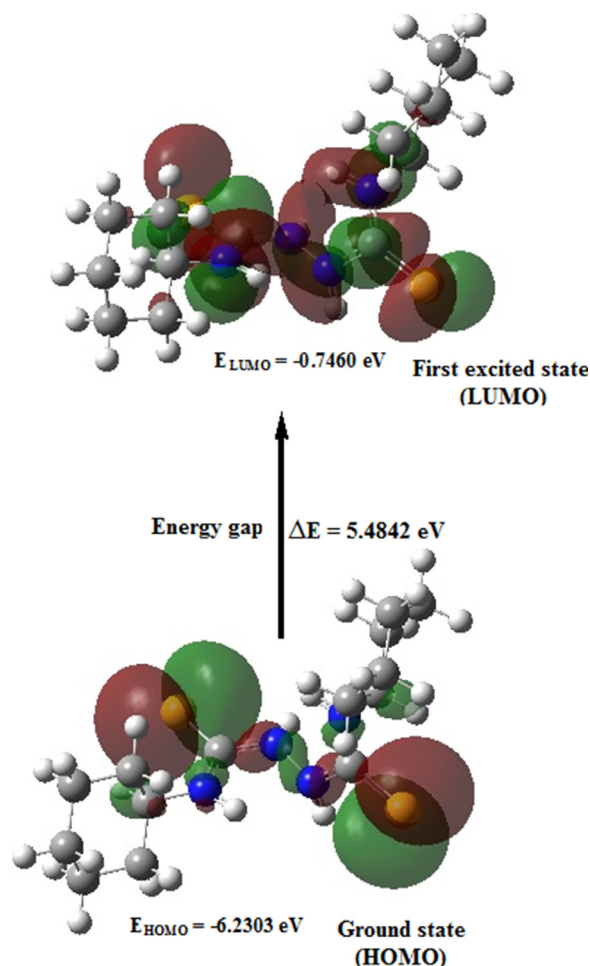
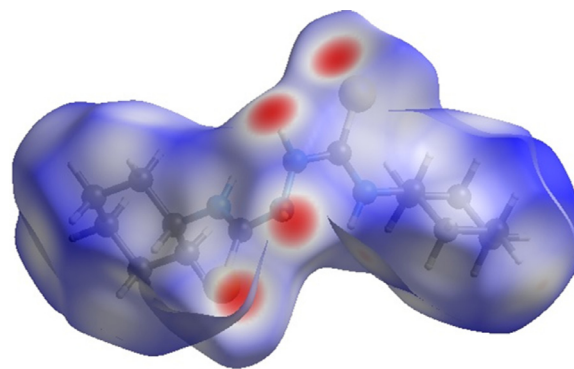
The geometry optimization of compound H₂chth has been carried out to understand bonding. The structure obtained from geometry optimization confirms the formation of H₂chth as determined by X-ray diffraction analysis. Structure of H₂chth optimized by DFT is shown in Fig. 7 and calculated bond lengths and angles from DFT are given in Table 2. The slight disagreement in the bond lengths is due to the fact that the DFT calculations are done for an isolated molecule in gaseous phase while the X-ray crystallographic data were obtained from crystal lattice of complex molecules. The computed geometrical parameters using DFT (specifically, B3LYP) corroborates X-ray crystallography data as can be seen from Table 2.

3.8.2. Frontier molecular orbital analysis

The most important frontier molecular orbitals (FMOs) such as highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) analysis of a molecule is very useful. HOMO and LUMO analysis determines reactivity, optical polarizability, chemical hardness-softness and also determines the charge transfer capability of a molecule. A molecule with smaller energy gap between HOMO and LUMO orbitals is more reactive, highly polarizable or soft [48]. The shapes and energy levels of the HOMO and LUMO of H₂chth are displayed in Fig. 8. It indicates that HOMO of H₂chth is having dominant electron density on the S atoms of the thioamide group while LUMO is more likely on both the nitrogen and sulphur atoms of the H₂chth. HOMO is of π -type and LUMO is of π^* type. Hence, for H₂chth HOMO-LUMO transition is going to be of $\pi \rightarrow \pi^*$ transition. The energy gap between HOMO and LUMO for H₂chth is 5.4842 eV [49,50]. The small energy gap indicates that this compound is soft and highly reactive and can serve as better target for photophysical studies and electronics applications [51,52].

3.8.3. Hirshfeld surface analysis

Hirshfeld surfaces showing weak intermolecular interactions present in crystal structure are plotted over d_{norm} (Fig. 9) for H₂chth from its crystal structure (cif file). To compute Hirshfeld surface we have used Crystal Explorer 17.5 suits of program [53]. From the Fig. 10, it is discernible that there two types of H-bonding interactions N-H...S and S...H-C through red spot over the d_{norm}

Fig. 8. Frontier molecular orbitals of H₂chthFig. 9. Hirshfeld surface of H₂chth showing weak intermolecular interactions plotted over d_{norm}

surface. Two middle red spots represent hydrogen bond N-H...S with donor S atom from neighbouring molecule and H atom as acceptor (H→S type). On the other hand, extreme two red spots represent S...H-C interactions with S donor atom to neighbouring H atom as acceptor (S→H type). 2D fingerprint plot of the Hirshfeld surface is depicted in Fig. 10 a-d. The S...H interactions appeared as scattered spikes in the 2D fingerprint plots with overall Hirshfeld surfaces of 9.6 % (H→S) + 13.9% (S→H) = 23.5%.

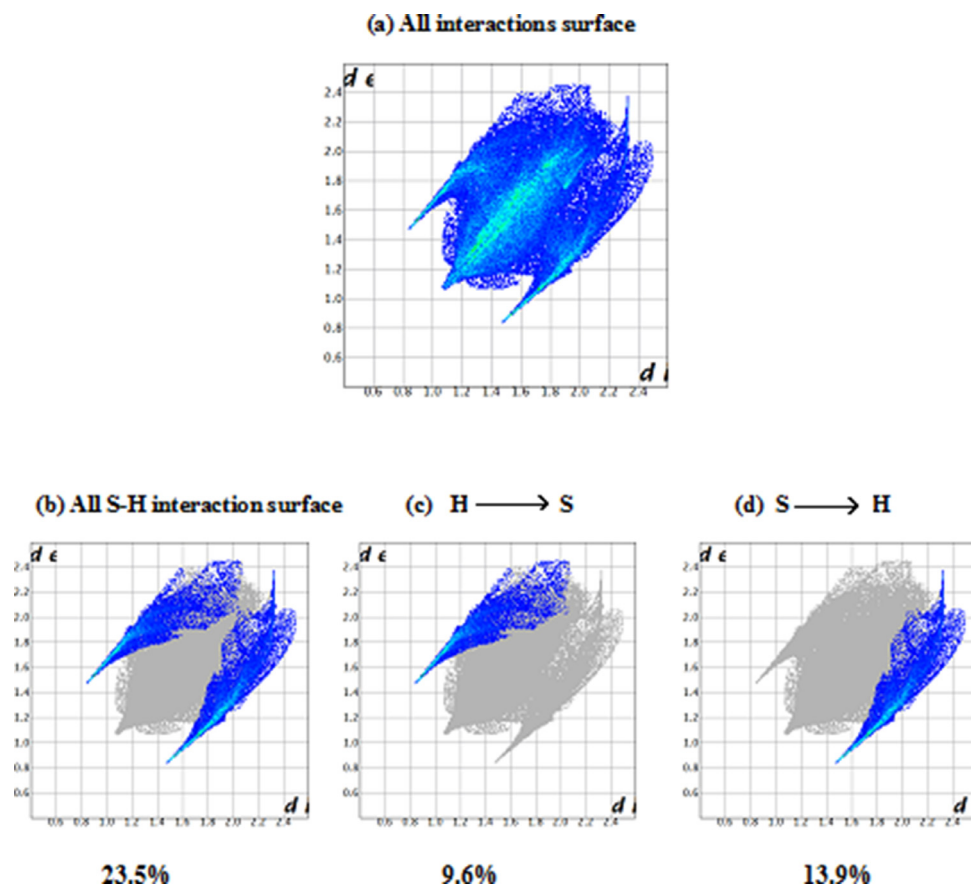


Fig. 10. Atom-atom interactions and their contribution to the Hirshfeld surface: (a) all interactions surface (b) all S...H interaction surface (c) contribution from H...S and (d) contribution from S...H

4. Conclusions

In this paper we report the synthesis, structure, fluorescence and electrochemical behaviour of a compound *bis*(N-cyclohexylthiourea) (H_2chth). The compound was synthesized using 1-hydroxy benzoyl-4-cyclohexyl-3-thiosemicarbazide, $Mn(OAc)_2 \cdot 4H_2O$ and *o*-phen in two steps. The compound is characterised by various physicochemical methods. During the course of reaction, the cyclohexyl isothiocyanate moiety of the intermediate substituted thiosemicarbazide undergoes tautomerization and rearrangement into the corresponding carbothioamide in the presence of manganese(II) acetate. In the UV-Vis absorption spectrum of the compound a band observed at 38610 cm^{-1} which may be assigned to $n \rightarrow \pi^*$ transition due to the presence of HNCS moiety. Upon excitation at 37037 cm^{-1} , the H_2chth exhibits maximum emission at 27322 cm^{-1} which indicates that the compound may be used as fluorescent active material. The sensing behaviour of the compound with different metal ions in methanol solution are studied and it showed interesting red shifts with Co^{2+} , Cu^{2+} , Ni^{2+} and Mn^{2+} ions which suggested that H_2chth may be useful in the sensing of these metal ions in solution. The emission spectra of metal ions with H_2chth exhibit less intense emission as compared to free H_2chth . Cyclic voltammetric analysis of the H_2chth and its interaction with different metal ions ($H_2chth-M$) exhibit complete irreversible redox behaviour. The thermal degradation of the compound, as analysed by TG-DTA method, showed that compound H_2chth is almost stable upto $220\text{ }^\circ\text{C}$ and starts decomposing thereafter and finally remaining organic moiety converted into the gaseous products at higher temperature. The structure of H_2chth is stabilized *via* intermolecular N-H...S

and C-H...S hydrogen bonding. Frontier molecular orbitals analysis reveals that compound H_2chth is soft and highly reactive.

Credit author statement

Shubham Jaiswal: Development and design of methodology, writing the original draft, and Data curation.

Mannu Kumar Gond: Data curation, Writing – review, and editing.

Biswajit Maiti: Data curation, Software (DFT calculation).

S. Krishnamoorthi: Data curation, Writing – review, and editing.

Ray J Butcher: Data curation, Software (X-ray single-crystal analysis).

Manoj Kumar Bharty: Conceptualization, Formal analysis, Funding acquisition, Investigation, Resources, Software, Supervision, Validation, Roles/ writing original draft, Writing – review and editing.

Declaration of Competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.molstruc.2021.131060.

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