CHAPTER
TWO

Synthesis and characterization of thiosemicarbazone ligands

2.1. Introduction

The coordinating ability of thiosemicarbazones to both transition and main group metallic cations is attributed to the extended delocalization of electron density over the thiosemicarbazone skeleton, which is enhanced by substitution at N(4)-position. Condensation of thiosemicarbazides with aldehydes or ketones extends the electron delocalization along azomethine bond. 2-hydroxybenzaldehyde N(4)-substituted thiosemicarbazones, as well as heterocyclic thiosemicarbazones, which derives from the presence of several potential donor atoms, their flexibility, and their ability to coordinate in either neutral or deprotonated forms, have been the subject of extensive investigations [1], because of their ability to strongly coordinate metal ions as tridentate ligands and their wide spectrum of biological applications [2]. Due to their good complexing properties, biological activity, and analytical application, semi-/thiosemi-/isothiosemicarbazides and their Schiff bases of different denticity, as well as their metal complexes, have been the subject of many studies. Apparently, the most numerous among them are the complexes with tridentate salicylaldehyde semi-/thiosemi-/isothiosemicarbazones [3].

Thiosemicarbazone of salicylaldehyde [4, 5] and its derivatives are a class of versatile tridentate ONS donors capable of stabilizing both higher and lower oxidation states of transition metal ions [6-8]. Although capable of deprotonation at

both the phenol and thioamide functions to give a dianionic ligand, they can also act as monoanionic chelating ligands, coordinating to a metal centre through the deprotonated phenolic oxygen, the thione sulfur and azomethine nitrogen [6]. The dianionic form of the ligand is favored at higher pH, whereas the monoanionic form is promoted at low pH. However, the coordination chemistry of substituted or unsubstituted thiosemicarbazones of salicylaldehyde is quite unexplored with a few previous reports [9-12]. This prompted our study into the synthesis and characterization of substituted thiosemicarbazones using aromatic aldehydes and its metal complexes. Here we have synthesized the following four new ligands using benzaldehyde, 2-hydroxybenzaldehyde, 4-methoxybenzaldehyde, 3-hexamethyleneiminyl thiosemicarbazide and 3-tetramethyleneiminyl thiosemicarbazide.

- Benzaldehyde 3-hexamethyleneiminylthiosemicarbazone [HL^1]
- 2-Hydroxybenzaldehyde 3-hexamethyleneiminylthiosemicarbazone [H_2L^2]
- 4-Methoxybenzaldehyde 3-hexamethyleneiminylthiosemicarbazone [HL^3]
- 2-Hydroxybenzaldehyde 3-tetramethyleneiminylthiosemicarbazone [H_2L^4]

This chapter deals with the synthesis and spectral characterization of thiosemicarbazone ligands. It also deals with X-ray diffraction studies of H_2L^2. The IUPAC numbering scheme is not very appropriate for describing the structural data of thiosemicarbazones because the numbering of C and N atoms on the thiosemicarbazone chain does not run into the numbering of substituted groups. This is probably why a variety of different numbering schemes have been used in the literature. In this chapter, the following numbering scheme is used for the four ligands, except in X-ray diffraction studies. The structure and numbering schemes are given in Figure 2.1

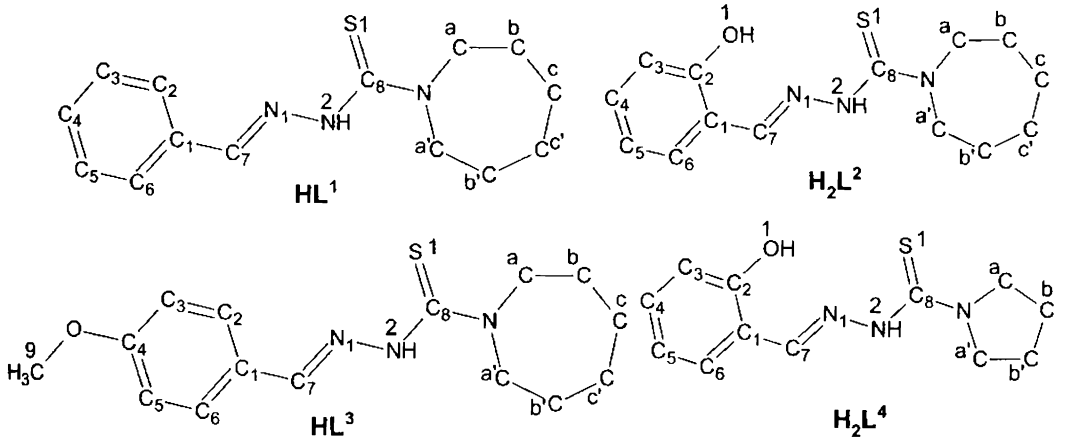


Figure 2.1. Structures and numbering schemes of the thiosemicarbazones

2.2. Experimental

2.2.1 Materials

The reagent grade benzaldehyde (Merck), 4-methoxybenzaldehyde (SRL chemicals), 2-hydroxybenzaldehyde (SRL chemicals), carbon disulfide (Merck), N-methylaniline (Merck), sodium chloroacetate (Merck) and hydrazine hydrate 98% (Glaxo–Fine Chemicals) were used as received. Hexamethyleneimine (Fluka) and tetramethyleneimine (Fluka) were used as received. The solvents were purified and dried by using standard methods and procedures.

2.2.2 Synthesis of ligand precursors

Step 1:-

Preparation of carboxy methyl-N-methyl-N-phenyl dithiocarbamate

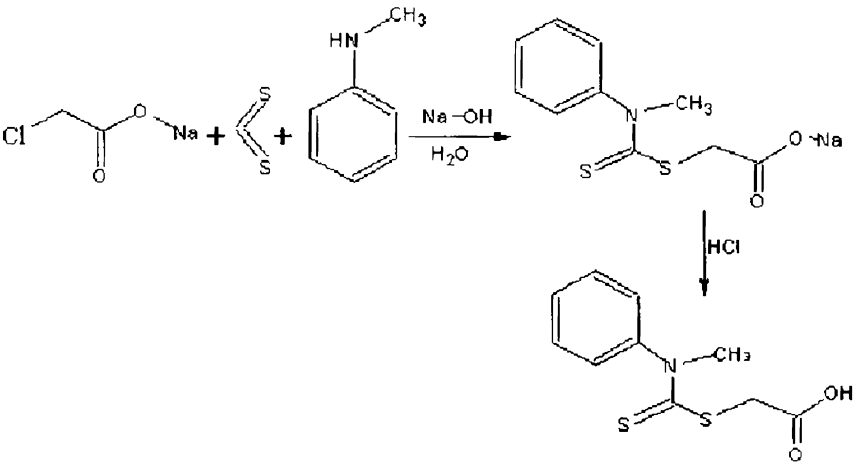
A mixture consisting of 12 ml CS_2 (15.2 g, 0.2 mol) and 21.6 ml (21.2 g, 0.2 mol) of N-methylaniline were stirred with a solution of 8.4 g (0.21 mol) of NaOH in 250 ml water for 4 h. When the organic layer had disappeared, the straw-colored solution was treated with 23.2 g of sodium chloroacetate and allowed to stand

overnight (17 h). The solution was acidified with conc. HCl (25 ml) and the solid that separated was washed with water, filtered and dried. This afforded 39.7 g (82%) of the pale buff colored carboxymethyl-N-methyl-N-phenyl dithiocarbamate (m.p 197-198 °C). (Scheme 2.1).

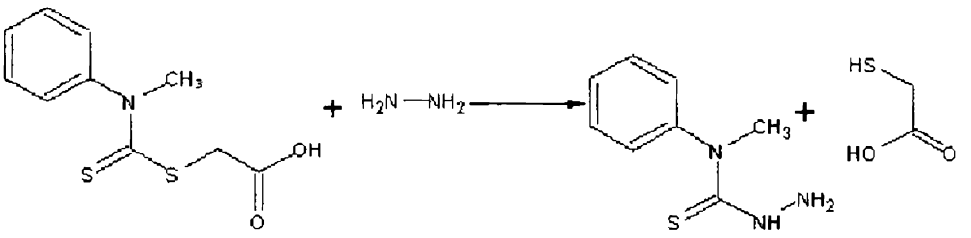
Step 2:-

Preparation of N-methyl-N-phenyl-3-thiosemicarbazide

A mixture of 17.8 g of carboxymethyl-N-methyl-N-phenyl dithiocarbamate, 20 ml of hydrazine hydrate and 10 ml of water was heated on the rings of the water bath for 22 minutes. The compound separated was filtered, washed with water, dried and recrystallized from 2:1 alcohol. Yield 78%. m.p. 124-125 °C (Scheme 2.2) [13].



Scheme 2.1

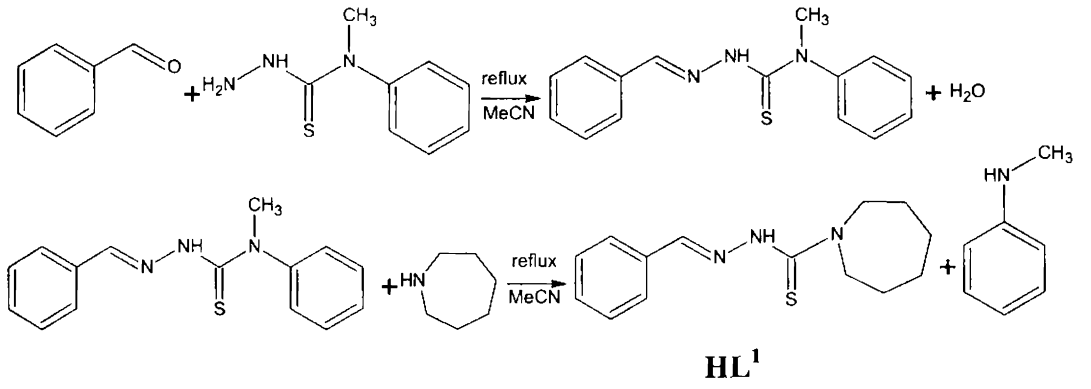


Scheme 2.2

2.2.3 Synthesis of ligands

i) Benzaldehyde 3-hexamethyleneiminyl thiosemicarbazone [HL^1]

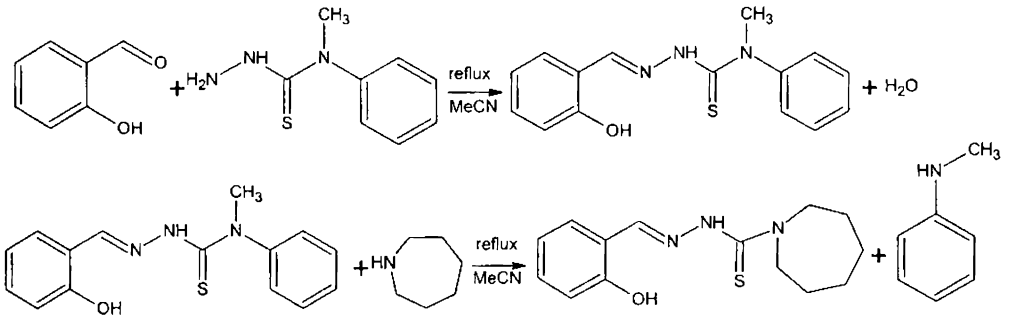
A solution of 1 g (5.52 mmol) of 4-methyl-4- phenyl-3-thiosemicarbazide in 5 ml acetonitrile was treated with 0.586 g (5.52 mmol) of benzaldehyde and 0.547 g (5.52 mmol) of hexamethyleneimine and refluxed for 40 minutes. The solution was chilled (overnight) and fine colorless needles of the compound separated out. The solution was filtered, washed well with cold acetonitrile. The compound was recrystallized from ethanol and dried *in vacuo* over P_4O_{10} (Scheme 2.3) [14].



Scheme 2.3

ii) 2-Hydroxybenzaldehyde 3-hexamethyleneiminyl thiosemicarbazone [H_2L^2]

A solution of 1 g (5.52 mmol) of 4-methyl-4- phenyl-3-thiosemicarbazide in 5 ml acetonitrile was treated with 0.674 g (5.52 mmol) of 2-hydroxybenzaldehyde and 0.547 g (5.52 mmol) of hexamethyleneimine and refluxed for 40 minutes. The solution was chilled (overnight) and the crystals that separated were filtered and washed well with cold acetonitrile. The compound was recrystallized from ethanol and dried *in vacuo* over P_4O_{10} (Scheme 2.4).

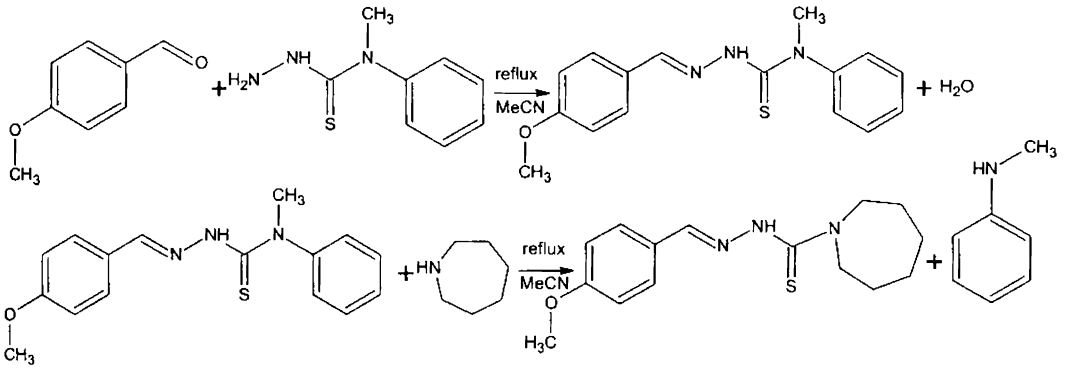


H_2L^2

Scheme 2.4

iii) 4-Methoxybenzaldehyde 3-hexamethyleneiminyl thiosemicarbazone [HL^3]

A solution of 1 g (5.52 mmol) of 4-methyl-4- phenyl-3-thiosemicarbazide in 5 ml acetonitrile was treated with 0.752 g (5.52 mmol) of 4-methoxybenzaldehyde and 0.547 g (5.52 mmol) of hexamethyleneimine and refluxed for 40 minutes. The solution was chilled (overnight) and colorless needles of the compound separated out. The solution was filtered, washed well with cold acetonitrile. The compound was recrystallized from ethanol and dried *in vacuo* over P_4O_{10} (Scheme 2.5).

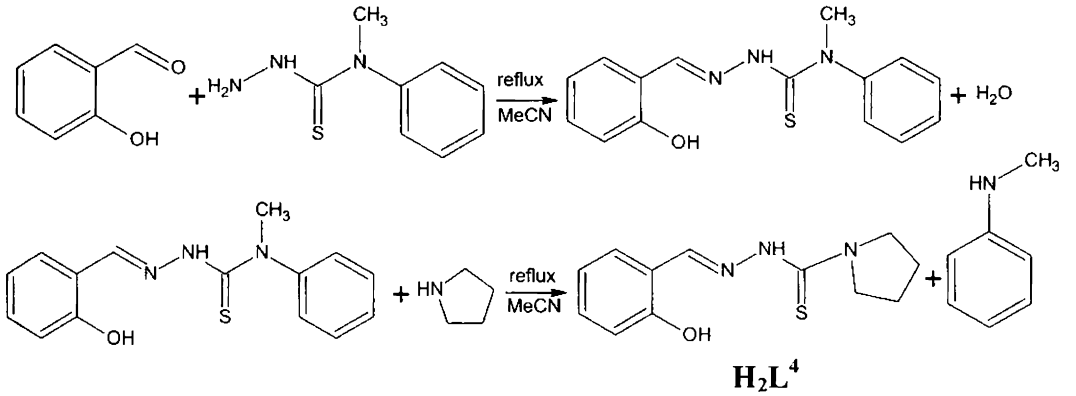


HL^3

Scheme 2.5

iii) 2-Hydroxybenzaldehyde 3-tetramethyleneiminyl thiosemicarbazone [H_2L^4]

A solution of 1 g (5.52 mmol) of 4-methyl-4- phenyl-3-thiosemicarbazide in 5 ml acetonitrile was treated with 0.674 g (5.52 mmol) of 2-hydroxybenzaldehyde and 0.393 g (5.52 mmol) of pyrrolidine and refluxed for 40 minutes. The solution was chilled (overnight) and fine colorless needles of the compound separated out. The solution was filtered, washed well with cold acetonitrile. The compound was recrystallized from ethanol and dried *in vacuo* over P_4O_{10} (Scheme 2.6).



H_2L^4

Scheme 2.6

2.3. Characterization techniques

The ligands were characterized by using partial elemental analyses, IR spectra, electronic spectra, ^1H NMR spectra and single crystal X-ray diffraction. The details regarding these techniques are given in Chapter 1.

2.3.1. X-ray crystallography

The colorless block crystals of H_2L^2, suitable for X-ray diffraction studies were obtained by slow evaporation of its solution in ethanol. A crystal having approximate dimensions 0.35 x 0.30 x 0.25 mm^3 was sealed in a glass capillary and intensity data was measured at room temperature (293 K). The crystal structure data and structure refinement parameters for the compound are given in Table 2.1.

The X-ray diffraction data was measured at room temperature and data acquisition and cell refinement was done using the Argus (Nonius, MACH3 software) [15]. The Maxus (Nonius software) were used for data reduction [16]. The structure was solved by direct methods with the program SHELXS-97 and refined by full matrix least squares on F^2 using SHELXL-97 [17]. The graphical tool used was DIAMOND version 3.1d [18] and PLATON [19]. All C-bound H atoms were positioned geometrically and treated riding on their parent C atoms, with C–H distances of 0.93 and 0.97 Å). All non-hydrogen atoms were refined anisotropically, atom H1O1 {on O1} atom H2N (on N2) were located from different maps and were refined with isotropic displacement parameters.

Table 2.1. Crystal data and structure refinement parameters for H_2L^2

Empirical formula	$C_{14}H_{19}N_{30}S$
Formula weight	277.38
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	$P2_1/n$
Unit cell dimensions	a = 6.448 (11) Å α = 90°
	b = 14.099(2) Å β = 94.617(12)°
	c = 15.924(2) Å γ = 90°
Volume	1443.0(4) $Å^3$
Z	4
Density (calculated)	1.277 g/cm^3
Absorption coefficient	0.221 mm^{-1}
F(000)	592
Crystal size	0.35 x 0.30 x 0.25 mm^3
θ range for data collection	1.93 to 24.98 °
Index ranges	$-7 \leq h \leq 0, -16 \leq k \leq 0, -18 \leq l \leq 18$
Reflections collected	2764
Independent reflections	2524 [R(int) = 0.0203]
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2524 / 0 /180
Goodness-of-fit on F^2	0.981
Final R indices [I>2σ(I)]	$R_1 = 0.0444$, $wR_2 = 0.0892$
R indices (all data)	$R_1 = 0.1402$, $wR_2 = 0.1106$
Largest diff. peak and hole	0.144 and -0.162 $e.A^{-3}$

2.4. Results and discussion

The preparation of the thiosemicarbazones from 4-methyl-4-phenyl thiosemicarbazide in a single step involves a simultaneous occurrence of condensation between aromatic aldehyde and NH_2 of the thiosemicarbazide moiety and transamination in which the N-methylaniline from 4-methyl-4-phenyl thiosemicarbazide is replaced by the amine present in the solution. Since, the reaction depends on the strength of the bases, and hence N-methylaniline acts as a good leaving group in the reaction. The solvent also plays an important role in the reaction. Here, acetonitrile is used as solvent and mild refluxing condition is adopted. The ligand HL^1, HL^3 and H_2L^4 are pale yellow in color and H_2L^2 is colorless. The analytical data of the ligands are presented in Table 2.2.

Table 2.2. Analytical data

Compound	Empirical formula	Found (Calcd.) %		
		C	H	N
HL^1	$C_{14}H_{19}N_3S$	64.14 (64.33)	7.69 (7.33)	16.01 (16.08)
H_2L^2	$C_{14}H_{19}N_3OS$	60.25 (60.62)	7.37 (6.90)	15.09 (15.15)
HL^3	$C_{15}H_{21}N_3S$	61.69 (61.82)	7.49 (7.26)	14.34 (14.42)
H_2L^4	$C_{12}H_{15}N_3OS$	57.69 (57.81)	6.29 (6.06)	16.89 (16.85)

2.4.1. Crystal structure of H_2L^2

The molecular structure of H_2L^2 along with the atom numbering scheme is given in Figure 2.2. Selected bond lengths and bond angles are listed in Table 2.3. H_2L^2 crystallizes with one molecule per asymmetric unit into triclinic crystal system with a space group of $P2_1/n$. It adopts an *E* configuration about the N2–C8 and C7–N1 bonds relative to the N1–N2 bond. The N1–N2–C8–S1 torsion angle of −6.0(3)° indicates that the thione S1 and hydrazine N1 atoms are in the *Z* configuration with respect to the C8–N2 bond, similar to 2-pyridineformamide 3-

hexamethyleneiminyl thiosemicarbazone [20] but in contrast to the parent salicylaldehyde thiosemicarbazone [21], where an *E* configuration exists. The *Z* configuration eliminates the possibility of any steric repulsion between the bulky rings. As a result, atom N1 lies trans to N3, with an N1–N2–C8–N3 torsion angle of 174.1 (2)°. The C8–S1 and C8–N2 bond distances are similar to the C=S double and C–N single bonds in thiosemicarbazones [21-23] and suggest the thione form for H_2L^2. It is implicit from the literature that the delocalization of electron density along the thiosemicarbazide moiety is a characteristic of thiosemicarbazones. For instance, the C–S distance is always an intermediate between a C–S single and a C=S double bond (1.82 and 1.56 Å, respectively) [24]. It was pointed out that apparently the parent aldehyde or ketone moiety has a strong influence on the C–S bond distance [24]. The C8–S1 bond length H_2L^2 is in agreement with values in salicylaldehyde thiosemicarbazone [21] and does not differ significantly from the corresponding lengths in the thiosemicarbazones of some different aldehydes and ketones [25-31]. The presence of electron density delocalization is again confirmed by the N1–N2, N2–C8 and C8–N3 bond lengths. Of the two C8–N bonds, C8–N3 is significantly shorter than C8–N2, suggesting greater double-bond character for the former bond and indicating increased electron localization at this substituted end. This is confirmed by the typical double-bond nature [1.269(3) Å] of the C7=N1 bond.

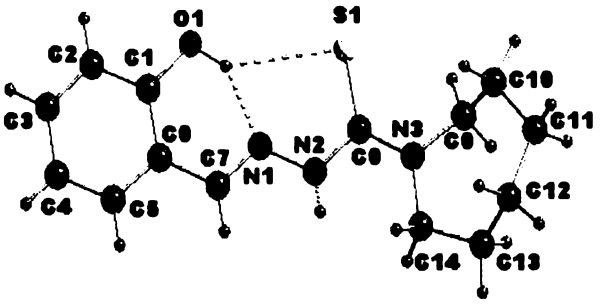


Figure 2.2. Molecular structure of H_2L^2. Intramolecular hydrogen bonding interactions are shown as dashed lines

The salicylaldehyde thiosemicarbazone moiety, excluding atom N3, is almost planar, with a maximum deviation from the mean plane of 0.151(1) Å for atom S1. The hexamethyleneiminyl ring adopts a chair conformation [the puckering parameters [32] are Q_T=0.799(3) Å, θ_2=38.4(3)°, ψ_2=45.6(3)° and ψ_3=73.95(3)°]. The Cg(1) plane [comprising atoms C1–C6, with a maximum deviation of 0.003(2) Å for atom C5] makes an angle of 40.59(13)° with a mean plane through the hexamethyleneiminyl ring (atoms N3/C9–C14).

Table 2.3. Selected bond lengths (Å) and bond angles (°) for the ligand (H_2L^2)

Bond lengths (Å)		Bond angles (°)	
S1–C8	1.684(3)	C8–N2–N1	119.3(3)
N2–C8	1.362(3)	C8–N2–H2N	121.1(17)
N2–N1	1.356(3)	N1–N2–H2N	119.4(17)
N2–H2N	0.78(2)	C8–N3–C9	120.0(2)
N3–C8	1.336(3)	N1–C7–C6	119.4(2)
N3–C9	1.454(3)	C1–O1–H1O1	110(2)
C7–N1	1.269(3)	C7–N1–N2	120.0(2)
C7–C6	1.442(3)	N3–C8–N2	115.4(2)
O1–C1	1.344(3)		
O1–H1O1	0.92(3)		

There are two intramolecular and two intermolecular hydrogen bonds (Table 2.4 and Figure 2.3) in H_2L^2. The packing of the molecules in the crystal lattice is given in Figure 2.4. The intramolecular N1···H1O1–O1 hydrogen bond is

very strong, as indicated by the bond length of 1.76(3) Å, which is shorter than the value of 1.96(3) Å seen in salicylaldehyde thiosemicarbazone [20] and similar to the values in some hydrazones [33, 34]. Simultaneously, atom H1O1 is involved in a weaker hydrogen bond with atom S1, forming a five-membered ring, N1/H1O1/S1/C8/N2. The intermolecular hydrogen bonds involving atoms H5 and H7 with atoms $O1^{i}$ and $S1^{i}$ [symmetry code: (i) x+1, y, z], respectively, form infinite one-dimensional chains of molecules along the *a* axis. The strengths of these four hydrogen bonds have a direct influence on the angles subtended at atoms C1 and C8 (Table 2.4). The weak C9–H9B···π interaction with Cg(1) reinforces the packing stability along *c* axis.

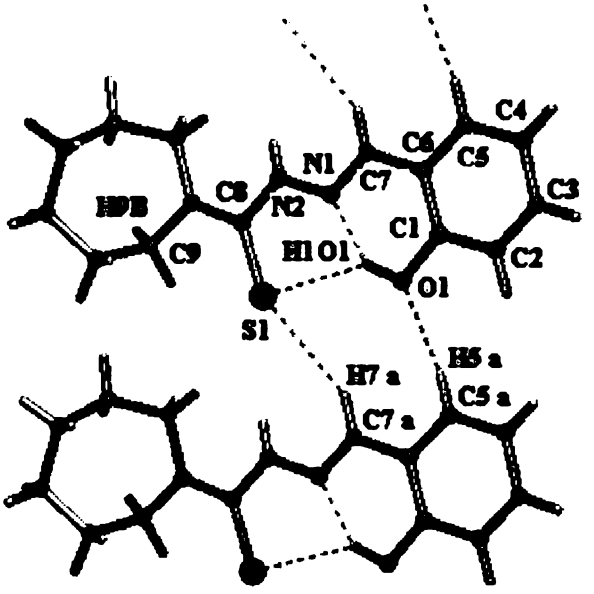


Figure 2.3. Intra and intermolecular hydrogen bonding interactions of H_2L^2

Table 2.4. Hydrogen-bond geometry (Å,°)

D–H···A	D–H	H···A	D···A	D–H···A
O1–H1O1···N1^{i}	0.92(3)	1.76(3)	2.562(3)	144(3)
O1–H1O1···S1^{i}	0.92(3)	2.82(3)	3.600(3)	143(3)
C5–H5···O1^{ii}	0.93	2.42	3.239(4)	147
C7–H7···S1^{ii}	0.93	2.87	3.706(6)	150
C9–H9B···Cg(1)^{iii}	0.97	2.96	3.758(1)	141

Symmetry Codes: (i) x, y, z; (ii) x+1, y, z; (iii) −x+1, −y+1, −z.
Cg(1)= C1, C2, C3, C4, C5, C6

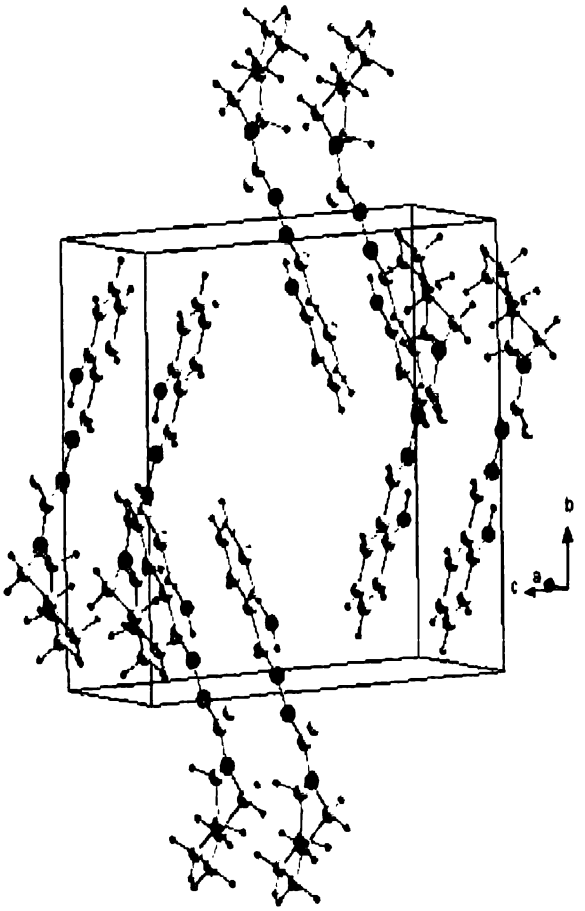


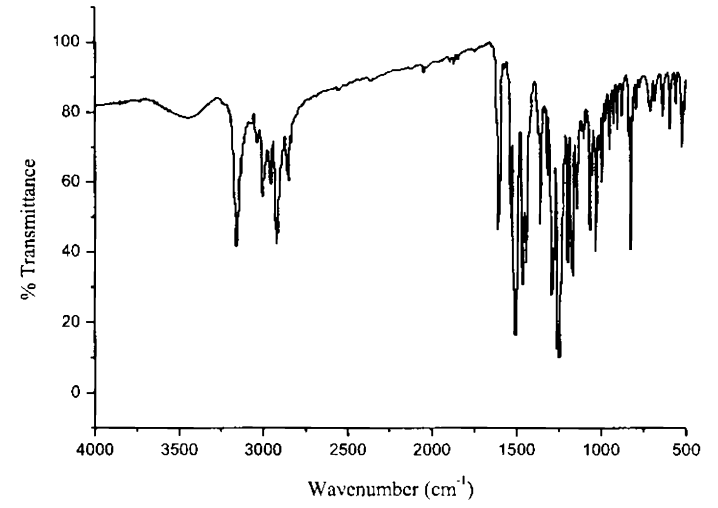
Figure 2.4. Unit cell packing diagram of H_2L^2

2.4.2. IR spectra

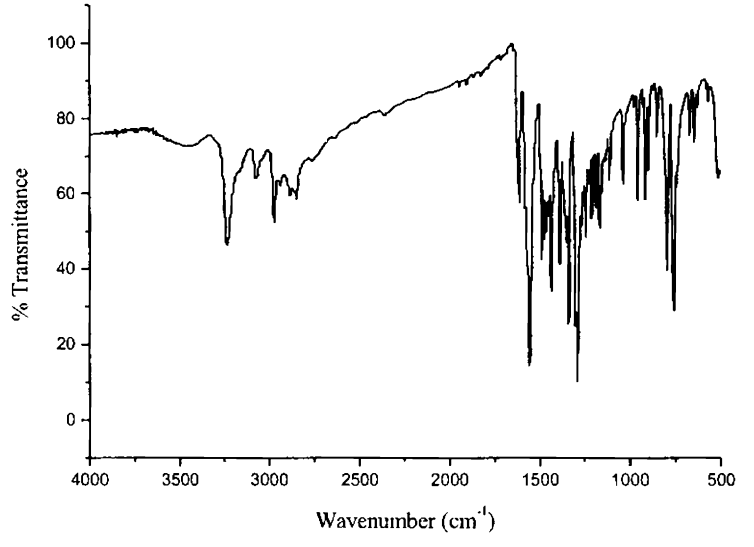
The characteristic IR bands for the ligands (HL^1, H_2L^2, HL^3 and H_2L^4) provide significant indications regarding the geometry are listed in Table 2.5. IR spectra of H_2L^2 and H_2L^4 show bands at 3315 and 3232 cm^{-1} region due to intermolecular hydrogen bonded phenolic −OH groups. All the ligands have bands in the range of 3050–3160 cm^{-1} due to −NH groups present in the molecule. Absence of any bands in the range 2500-2800 cm^{-1} points towards the lack of −SH stretching absorptions in the molecule. It reveals the presence of only the thione tautomer in the solid state. The azomethine stretching vibrations, $C=N_{azo}$, characteristics of a Schiff base, are observed at ~ 1615 cm^{-1} [35-37]. The thiocarbonyl group shows stretching and bending vibrations at ~ 1320 and 840 cm^{-1}, while additional bands in the broad region of 1500−700 cm^{-1} are due to vibrations involving interactions between C=S stretching and C−N stretching of the C=S group attached to a nitrogen atom [38]. Medium bands observed in the range 1030–1070 cm^{-1} are assigned to hydrazinic N–N bonds [39]. The 1600-1400 cm^{-1} region of the spectra is complicated by the presence of thioamide bands and ring breathing vibrations of the phenyl rings. IR spectra of the ligands HL^3 and H_2L^4 are presented in Figure 2.5.

Table 2.5. Selected IR bands (cm^{-1}) of the ligands (HL^1, H_2L^2, HL^3 and H_2L^4)

Ligands	ν(O−H)	ν(N−H)	ν(C=N)	ν(N−N)	ν/δ(C=S)	ν(C−O)	ν(C−C−O)
HL^1	...	3091	1624	1064	1334, 837	...	...
H_2L^2	3315	3050	1612	1037	1324, 861	1271	1100
HL^3		3154	1607	1064	1312, 821		
H_2L^4	3232	3072	1622	1034	1338, 839	1288	1108



HL^3



H_2L^4

Figure 2.5. IR spectra of the ligands HL^3 and H_2L^4

2.4.3. Electronic spectra

In contrast to the infrared spectrum, the electronic spectrum is not used primarily for the identification of individual functional groups, but rather to show the relationship between functional groups, chiefly conjugation [40]. The electronic spectral data of the ligands HL^1, H_2L^2, HL^3 and H_2L^4 in DMF solution are presented in Table 2.6. The $\pi \rightarrow \pi^*$ transitions of the phenyl ring are observed in the 35300-36500 cm^{-1} region. The $n \rightarrow \pi^*$ transitions of the imine function of the thiosemicarbazone moiety are observed in the region of 28700-31200 cm^{-1} [41, 42]. Electronic spectra of the ligands are presented in Figure 2.6.

Table 2.6. Electronic spectral assignments for the ligands

Ligands	π - π*	n - π*
HL^1	32150	28730
H_2L^2	36110	29500
HL^3	35340	31150
H_2L^4	36490	30210

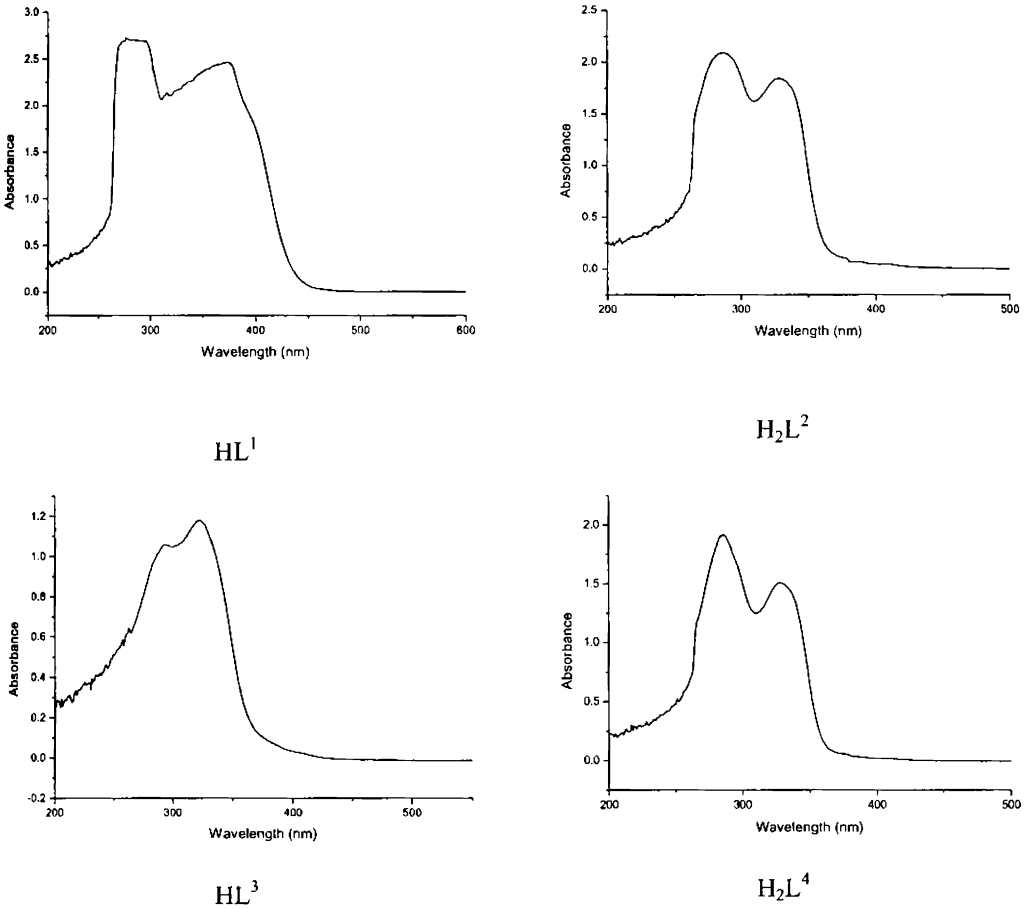


Figure 2.6. Electronic spectra of the ligands

2.4.4. ^1H NMR spectra

Proton Magnetic Resonance spectroscopy is a helpful tool for the preparation of organic compounds in conjugation with other spectrometric informations. The ^{1}H NMR spectra of the ligands recorded in $CDCl_3$ are given in Table 2.7. The ligands do not show any peak attributable to –SH proton but they show peaks assignable to the secondary N–H protons.

In the spectra of HL^1 and HL^3, sharp singlets at δ = 7.96 (HL^1) and 8.25 ppm (HL^3) corresponds to ^{7}CH= proton. Absence of any coupling interactions by

^{2}NH due to the unavailability of protons on neighboring atoms render singlet peak for the imine proton at δ=8.77 (HL^{1}) and 8.66 ppm (HL^{3}) are assigned to the ^{2}NH protons. The $^{a}CH_2$ protons adjacent to the ring nitrogen produces a triplet at δ=4.02 (HL^{1}) and 4.01 ppm (HL^{3}) due to coupling with nearby $^{b}CH_2$ protons. The $^{b}CH_2$ protons due to coupling with $^{a}CH_2$ and $^{c}CH_2$ protons resonate as the multiplet observed at δ=1.94 (HL^{1}) and 1.93 ppm (HL^{3}). $^{c}CH_2$ protons also resonate as the multiplet at δ=1.64 (HL^{1}) and 1.62 ppm (HL^{3}). In the case of HL^{1}, the *ortho* protons of the phenyl ring *viz.* ^{2}CH and ^{6}CH are observed at δ=7.28 ppm. The *meta* positioned protons of the aromatic ring ^{3}CH and ^{5}CH are observed at δ=7.57 ppm. The *para* positioned proton ^{4}CH resonate as triplet at δ=7.65 ppm. For HL^{3}, the phenyl group is disubstituted and the *ortho* protons of the phenyl ring *viz.* ^{2}CH and ^{6}CH are observed at δ=7.53 ppm and the *meta* positioned protons ^{3}CH and ^{5}CH resonate at 6.92 ppm. The $-OCH_3$ protons in HL^{3} appear as a singlet at δ=3.83 ppm.

The spectra of diprotic ligands (H_2L) show sharp singlets, which integrates as one hydrogen at δ ~ 10.08 ppm is assigned to the proton attached to the oxygen atom. The downfield shift of this proton is assigned to its intra and intermolecular hydrogen-bonding interactions. The hydrogen bonding decreases the electron density around the proton, and thus moves the proton absorption to a lower field [36]. Absence of any coupling interactions by ^{2}NH due to the unavailability of protons on neighboring atoms render singlet peak for the imine proton at δ=8.89 (H_2L^{2}) and 8.58 ppm (H_2L^{4}). The presence of electron withdrawing azomethine group near to the ^{7}CH proton leads to its resonance as a singlet at δ=7.99 (H_2L^{4}) and 8.00 ppm (H_2L^{4}). Aromatic protons ^{4}CH, ^{6}CH, ^{3}CH, ^{5}CH appear as a multiplet in the range of 6.67-7.30 ppm [12]. Aliphatic protons of hexamethyleneiminyl and tetramethyleneiminyl rings were observed as three signals at δ ~ 3.60, 1.70 and 1.52

ppm assigned to positions a, b and c respectively. NMR assignments are in agreement with values already reported [41, 43-45]. ^{1}H NMR spectra of the ligands are presented in Figures 2.7-2.10.

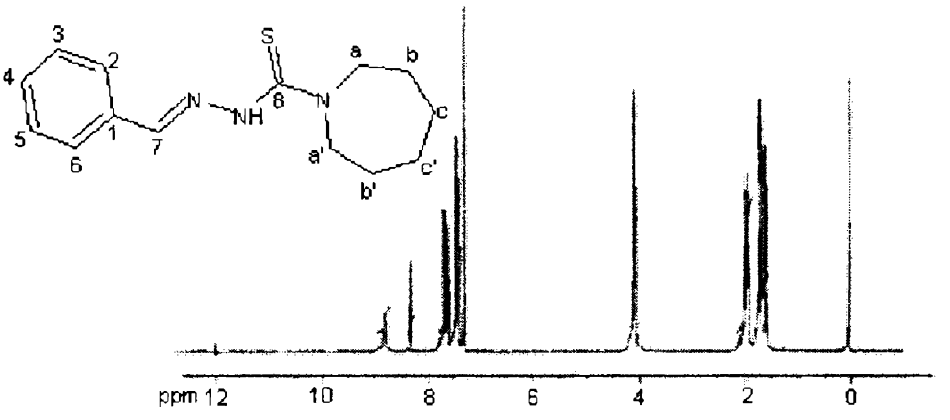


Figure 2.7. ^{1}H NMR spectrum of HL^1

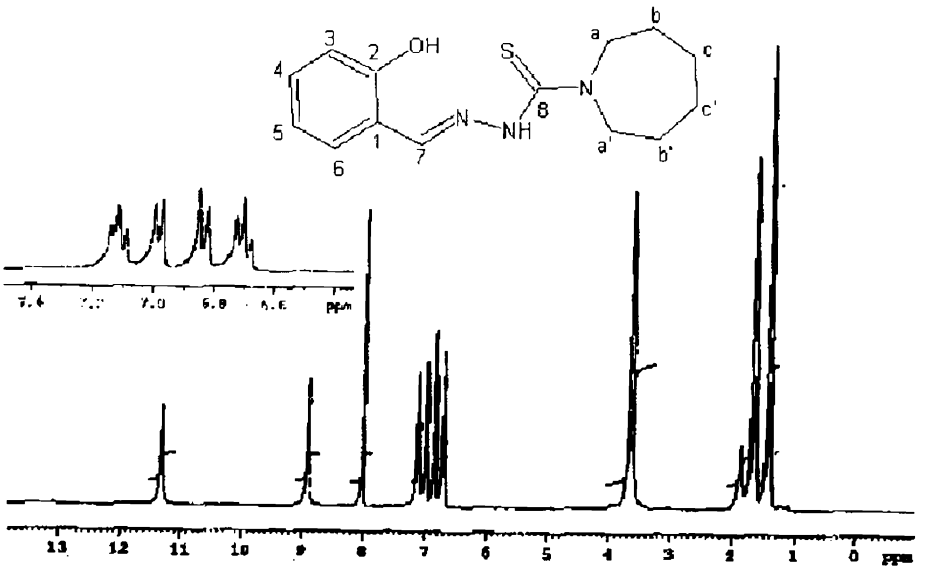


Figure 2.8. ^{1}H NMR spectrum of H_2L^2

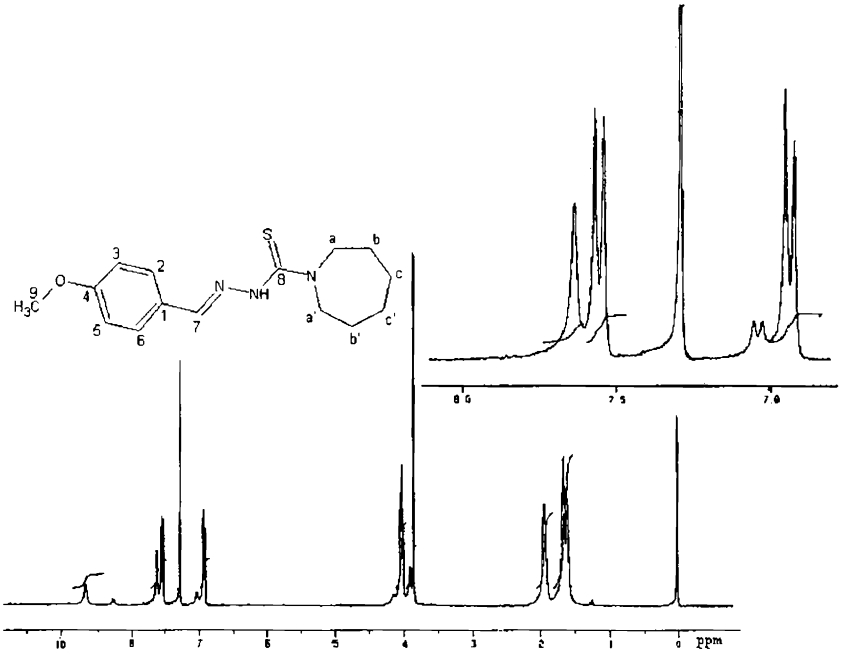


Figure 2.9. ^{1}H NMR spectrum of HL^{3}

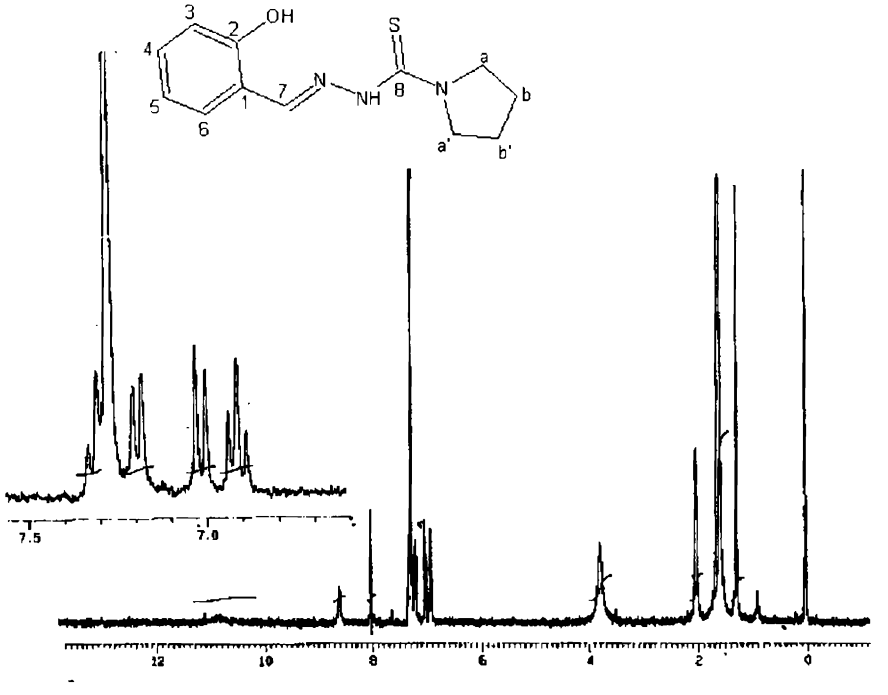


Figure 2.10. ^{1}H NMR spectrum of H_2L^{4}

Table 2.7. ^{1}H NMR ($CDCl_3$) assignments of the ligands (δ in ppm)

Compound	OH	Aromatic Protons					^{2}NH	^{7}CH=	$^{a}CH_2$	$^{b}CH_2$	$^{c}CH_2$
		H^2 Ph	H^3 Ph	H^4 Ph	H^5 Ph	H^6 Ph					
HL^1	----	7.63	7.57	7.28	7.57	7.63	8.77	7.96	4.02	1.94	1.64
H_2L^2	11.3	----	6.80	6.97	6.67	7.09	8.89	7.99	3.63	1.66	1.42
HL^3	----	7.53	6.92	----	6.92	7.53	8.66	8.25	4.01	1.93	1.62
H_2L^4	10.3	----	6.99	7.21	6.90	7.29	8.58	8.00	3.59	1.73	----

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