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Research Article

SYNTHESIS AND SPECTRAL STUDIES OF 3-AZACYCLOTHIOSEMICARBAZONES

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ABSTRACT

3-Azacyclothiosemicarbazones of benzaldehyde and 4-methoxy benzaldehyde have been prepared and physico-chemically characterized. IR, NMR and electronic spectra of the ligand have been obtained. IR spectra suggest thiocarbonyl group 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. ^{1}HNMR spectra of the ligands show signals 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. On the basis of spectral and analytical studies, the ligands behave as monobasic bidentate NS donors. The complexes were given the formulae HL^1 (**1**) and HL^2 (**2**).

Keywords: Benzaldehyde, 4-Methoxybenzaldehyde, 3-Azacyclothiosemicarbazone

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, 3]. 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 [4].

Thiosemicarbazone of salicylaldehyde [5, 6] and its derivatives are a class of versatile tridentate ONS donors capable of stabilizing both higher and lower oxidation states of transition metal ions [7-9]. 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 [7]. 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 [10-13]. This prompted our study into the synthesis and characterization of substituted thiosemicarbazones using aromatic aldehydes and its metal complexes. We have already reported Cu(II) [14], Zn(II) [15], Ni(II) [16,17] and Cd(II) [18] complexes using 3-azacyclothiosemicarbaones. Here we report the synthesis and characterization of benzaldehyde and 4-methoxybenzaldehyde 3-azacyclothiosemicarbazone ligands using infrared, electronic and ^{1}H NMR studies.

- Benzaldehyde 3-azacyclothiosemicarbazone [HL^1]
- 4-Methoxybenzaldehyde 3-azacyclothiosemicarbazone [HL^2].

2. EXPERIMENTAL

2.1. Materials

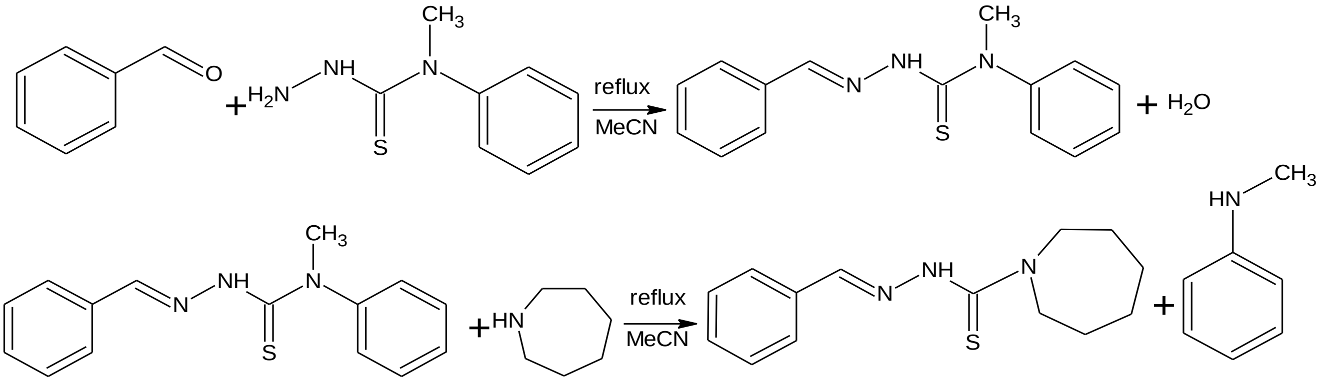
The reagent grade benzaldehyde (Merck), 4-methoxybenzaldehyde (SRL chemicals), carbon disulfide (Merck), N-methylaniline (Merck), sodium chloroacetate (Merck) and hydrazine hydrate 98% (Glaxo–Fine Chemicals) were used as received. Hexamethyleneimine (Fluka) were used as received. The solvents were purified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

2.2. Synthesis of ligands

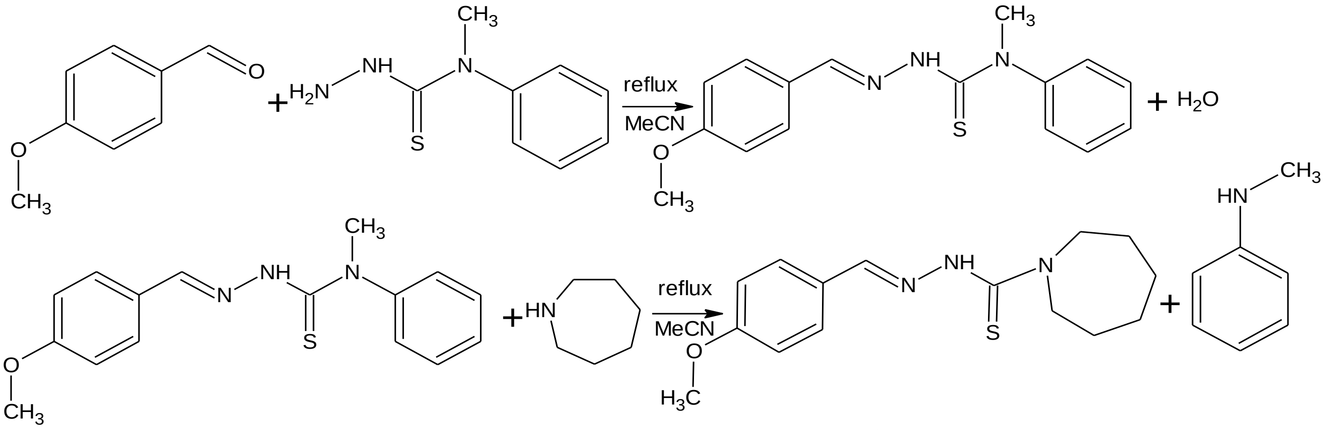
4-methyl-4-phenyl thiosemicarbazide was prepared as described by Scovill [19].

2.2.1. Synthesis of Benzaldehyde 3-azacyclothiosemicarbazone [HL^1] (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} [20]. The synthesis route of the ligand is given in Scheme 1.



Scheme 1: Synthesis route of HL^1



Scheme 2: Synthesis route of HL^2

2.2.2. Synthesis of 4-Methoxybenzaldehyde 3-azacyclo thiosemicarbazone [HL^2] (2)

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} The synthesis route of the ligand is given in Scheme 2. The colors and analytical data of the ligands are presented in Table 1.

Table 1: Colors and partial elemental analysis of the ligands

Compound	Empirical formula	Found (Calcd.) %		
		C	H	N
HL^1 (**1**)	$C_{14}H_{19}N_3S$	64.14 (64.33)	7.69 (7.33)	16.01 (16.08)
HL^2 (**2**)	$C_{15}H_{21}N_3S$	61.69 (61.82)	7.49 (7.26)	14.34 (14.42)

2.3. Physical Measurements

Elemental analyses were carried out using a Vario EL III CHN analyzer at SAIF, Kochi, India. The FT-IR spectra were recorded on a Thermo Nicolet AVATAR 370 DTGS FTIR spectrometer using KBr pellets in the range 400-4000 cm^{-1} at SAIF, Cochin University of Science and Technology, Kochi 22, India. Electronic spectra were recorded on a UVD-3500 UV-VIS-Double beam Spectrophotometer from solutions in DMF. ^{1}HNMR spectra were recorded on a Bruker AMX 300 in $CDCl_3$ with TMS as internal standard.

3. 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 ligands 1 and 2 are pale yellow in color.

3.1. Infrared spectra

The characteristic IR bands for the ligands **1** and **2** provide significant indications regarding the geometry are listed in Table 2.

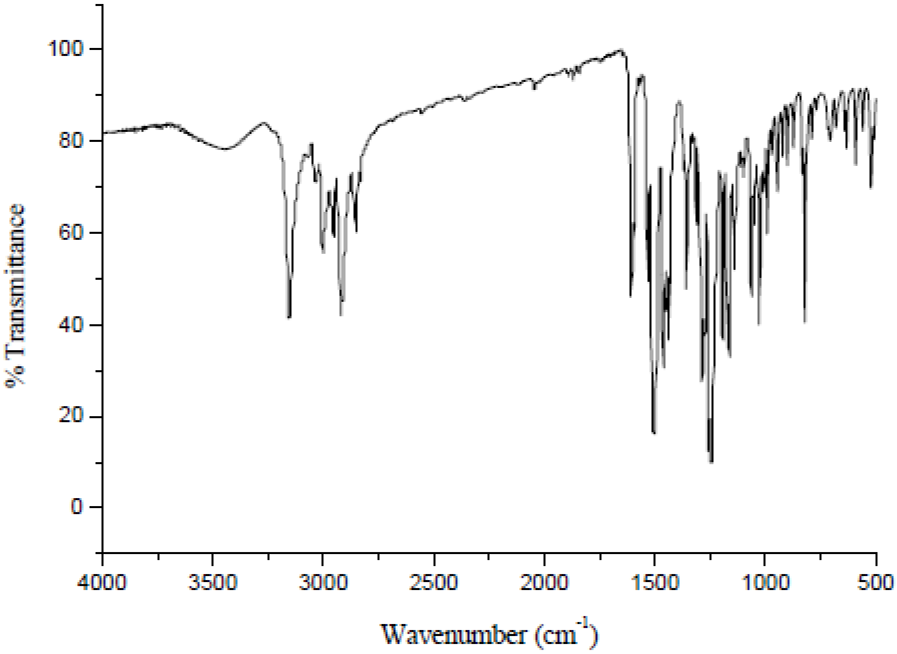


Fig. 1: IR spectrum of compound 2

All the ligands have bands in the range of 3050-3160 cm^{-1} due to -NH groups present in the molecule and these signals play an important role in evaluating the nature of the bonding in the complexes. 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} [21-23]. 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 [24]. Medium bands observed in the range 1030–1070 cm^{-1} are assigned to hydrazinic N-N bonds [25]. 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 2 is given in Fig.1.

The IR spectral bands most useful for the determination of the mode of coordination are given in Table 2.

Table 2: Selected IR bands (cm^{-1}) with tentative assignments of the ligands

Ligands	ν(N-H)	ν(C=N)	ν(N−N)	ν/δ(C=S)
HL^1 (**1**)	3091	1624	1064	1334, 837
HL^2 (**2**)	3154	1607	1064	1312, 821

3.2. 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 [26]. The electronic spectral data of the ligands **1** and **2** in DMF solution are presented in Table 3. The π→π* transitions of the phenyl ring are observed in the 35300-36500 cm^{-1} region. The *n*→π* transitions of the imine function of the thiosemicarbazone moiety are observed in the region of 28700-31200 cm^{-1} [27]. Electronic spectra of 1 **is** given in Fig. 2.

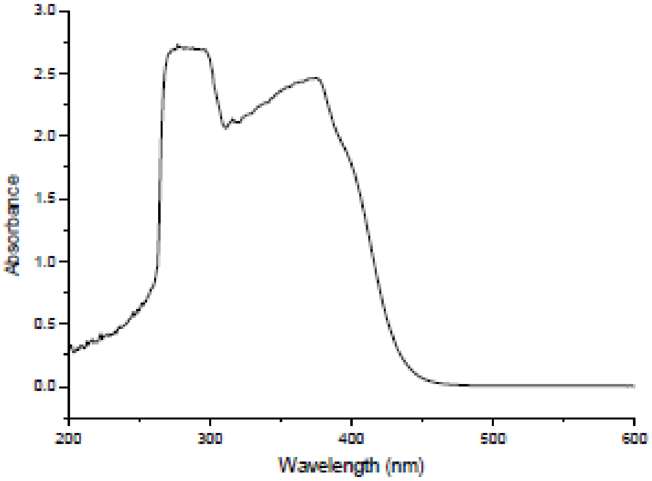


Fig. 2: Electronic spectrum of compound 1

Table 3: Electronic spectral assignments for the ligands (cm^{-1})

Ligands	π - π*	n - π*
HL^1(**1**)	32150	28730
HL^2(**2**)	35340	31150

3.3. ^{1}H 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 4. 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 the ligands **1** and **2**, sharp singlets at δ = 7.96 (**1**) and 8.25 ppm (**2**) 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 (**1**) and 8.66 ppm (**2**) are assigned to the ^{2}NH protons. The $^aCH_2$ protons adjacent to the ring nitrogen produces a triplet at δ=4.02 (**1**) and 4.01 ppm (**2**) due to coupling with nearby $^bCH_2$ protons. The $^bCH_2$ protons due to coupling with $^aCH_2$ and $^cCH_2$ protons resonate as the multiplet observed at δ=1.94 (**1**) and 1.93 ppm (**2**). $^cCH_2$ protons also resonate as the multiplet at δ=1.64 (**1**) and 1.62 ppm (**2**). In the case of compound **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 compound **2**, 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 **2** appear as a singlet at δ=3.83 ppm. ^{1}H NMR spectra of **2** is given in Fig. 3.

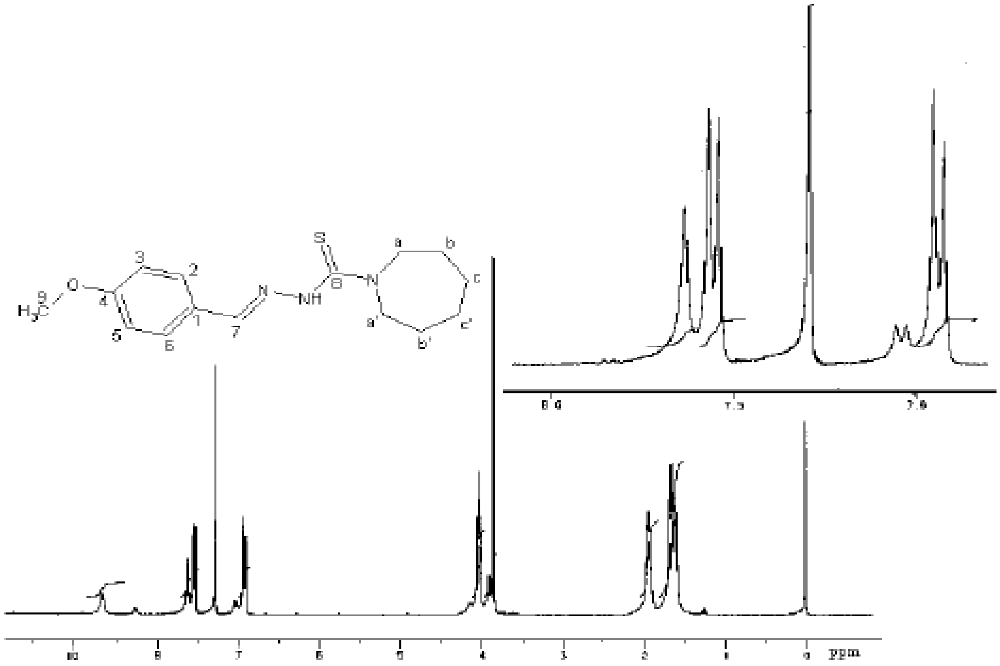


Fig. 3: ^{1}H NMR spectrum of compound 2

Table 4: ^{1}H NMR ($CDCl_3$) assignments of the ligands (δ in ppm)

Compound	Aromatic protons	^{7}CH=	^{a}CH$_2$	^{b}CH$_2$	^{c}CH$_2$
HL^1 (**1**)	7.26 - 7.65	7.96	4.02	1.94	1.64
[HL^2] (**2**)	6.89 – 7.60	8.12	3.83	1.93	1.62

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