Synthesis, characterisation and biological application of polymeric complexes of copper(I) with aromatic thiosemicarbazone

FOR

Master of Science (Hons) in chemistry
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Gitanshi

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CHAPTER-1

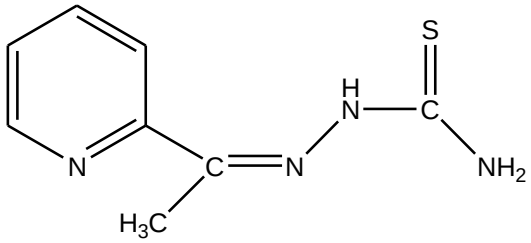
Introduction

A Thiosemicarbazone [$RCHN(NH)(C=S)NH_2$] is known as derivative of imines produced by the condensation reaction between a aldehyde or ketone and with semicarbazide. These are generally classified as an imine derivatives because they were produced by the reaction of a ketone or aldehyde with a terminal -NH_2 group of a semicarbazide, which acts very uniformly as primary amines [1]. They contains very important class of a N, S- donour ligands and their coordination chemistry were came during the early sixties [2].

Importance of thiosemicarbazone in various fields:

Thiosemicarbazones have various analytical and biological application like anti cancer , antifungal, antiviral, anti tumour, antibacterial [4-5]. Cancer is the major killer disorder throughout the human beings history. Cancer does not contain only one disease but a huge number of diseases arises due to the unrestricted growth and spread of abnormal cells [6]. Heterocyclic molecules are familiar to play an crucial role in life sciences and also in pharmaceutical drug design [3]. Currently a number of heterocyclic compounds are acessable as anticancer drugs and great efforts still have to be done to generate some miracle type of drugs. Metals thiosemicarbazones complexes mainly used for chemotherapeutic agents. Some thiosemicarbazones even use to expand their antitumour activity with their ability to forming a chelates with some particular type of metal ions . It is disclosed that the anticancer activitity of thiosemicarbazones is nearly related to parent ketone or aldehyde group, metal chelation ability. Between these, the parent ketone or aldeyhde group is considered very criticizing to shown the anticancer activity [6-7]. The biological activity shown by thiosemicarbazones depend mainly upon the existence of bulky group at the terminal nitrogen to increases the activity. The existence of the bulky groups at the N position of thiosemicarbazone moiety ahead with additional binding site is set up to significantly effects the biological activity. In modern years, the medicinal and biological properties of transition metal complexes of the thiosemicarbazones, like Pd (II) and Pt (II) complexes of 5-chlorosemicarbazones has been studied. The results of the compound mainly shows antimicrobial properties and metal chelates exhibits better

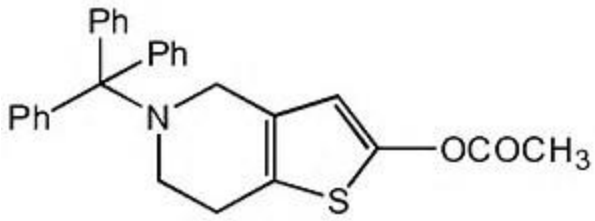
consequences as compared to the parent ligands. Pt (II) complexes of 2-acetylpyridine thiosemicarbazone **(I)** was formed in which the intramolecular hydrogen bond, pi-pi and weak Pt-Pt and Pt-π contacts which conducts to form the aggregation. These complexes shows completely lethal effect (cause death) on a Gram positive bacteria [6].



2-acetylpyridine (I)

Importance of thiosemicarbazones as analytical reagents:

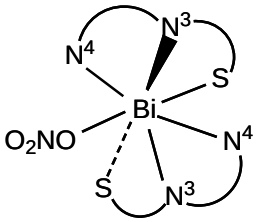
Thiosemicarbazones mainly formed coloured complexes with transition metal ions. In sensitive and selective determinations of metal ions mainly these are the complexes which could be used as an analytical reagents. Ferrocene type of derivatives involves mainly thiosemicarbazide side chain which has been calculated and explore using cyclic voltammetry method [7]. Metals like Co (II), Fe (II) and Cu (II) are used mainly in pharmaceutical preparations which could be determined using the proces called pre-column derivitization and also can be determined using solvent extraction technique by taking the help of 2-acetylpyridine-4-phenyl-3-thiosemicarbazone **(II)** mainly as complexing agent [7].



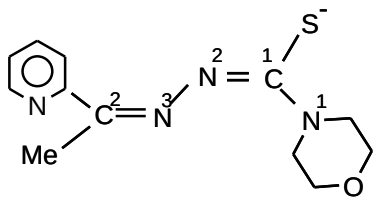
(II)

Thiosemicarbazones also find significance for determining the trace metals in biological and pharmaceutical samples consumed for the extraction of metals, and also for the inhibition of

corrosion etc. Generally, the chelates could be formed and extracted from the suitable solvents [8]. **Chart 1** shows some thiosemicarbazones mainly used as analytical reagents [8-10].



(A)



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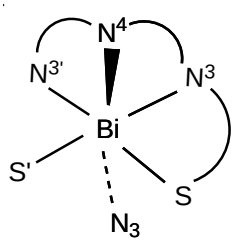

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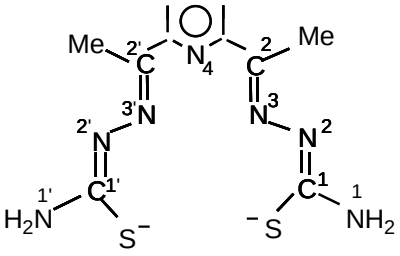

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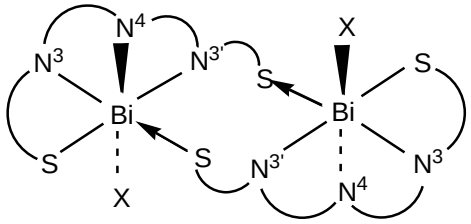
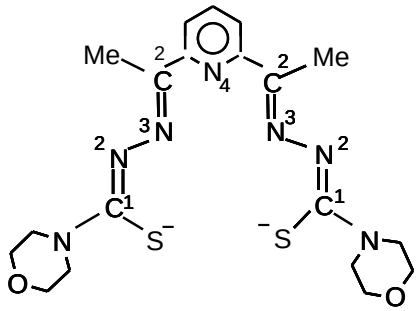


(E) (X = ONO_2)

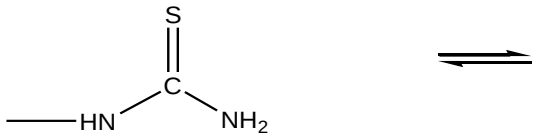


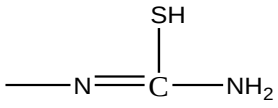
(F)

chart 1

Stereochemistry of thiosemicarbazones and metal complexes:

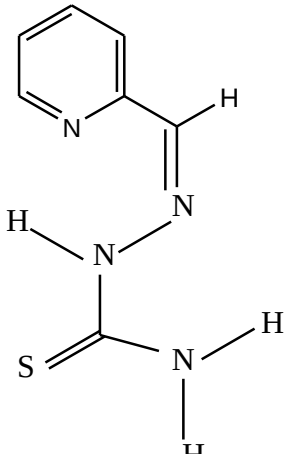
The Stereochemistry of thiosemicarbazone, metal complexes and adducts depends upon the charge on the ligand and also depends upon the additional coordination site on the ligand. The charge on the ligand mainly depends on the thione **(III)** ↔ thiol **(IV)** equilibrium [12]. Thiosemicarbazone majourly exist as two stereoisomers E **(V)** and Z **(VI)** due to = N bond . The crystal structure that is of pyridine-2-carbaldehyde N(4)-phenylthiosemicarbazone indicates E and Z configuration ie., trans configurations which is observed between both azomethine and hydrazinic bonds [13-14].



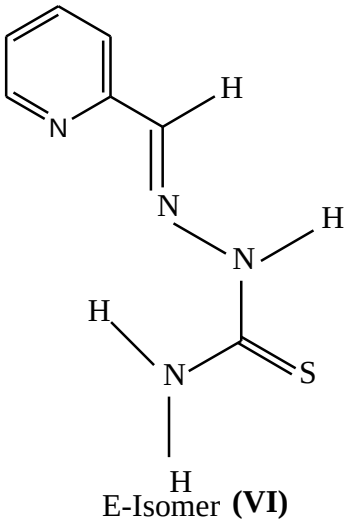


THIONE FORM **(III)**

THIOL FORM **(IV)**



Z-Isomer **(V)**



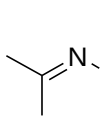
E-Isomer **(VI)**

Thiosemicarbazones organize as bidentate ligand over azomethine nitrogen and thione/thiolate sulphur. The Stereochemistry shown by metal complexes of thiosemicarbazones mainly depends upon the oxidation state of the metal. The oxidation state of the metal controls the degree of softness . The degree of hardness and softness mainly regulates the stability of a metal complex. The Low spin d^{10} and d^{8} type of metal ions can form stable complexes with thiosemicarbazone ligands. Mainly metal complexes of thiosemicarbazones have square planer and octahedral in geometry [12]. Octahedral geometry is very common in thiosemicarbazone type complexes of Fe (III), Mn (II), Co (III) with a general formula $[ML_2]^{n+}$. The geometry of complexes di-2-pyridyl ketone N(4), N(4) – dimethyl thiosemicarbazone are generally tetrahedral .Copper complexes commonly show square planer geometry. The stereochemistry shown by copper atom in a complex of schiffs bases of 5-benzyldithiocarbazate and 3-benzoyl pyridine is intermediate among trigonal bipyramidal and square pyramidal geometries [14]. In First row transition metals they have an capacity to form complexes in which square-coplanar, octahedral,

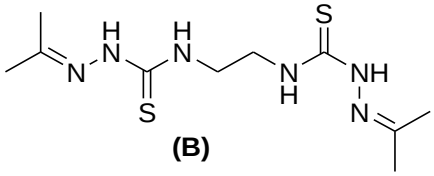
tetrahedral, and other stereochemistries may predominate. Cu (II) ion is unique to form coordination complexes with different types of geometries [15].

Literature survey

There are many thiosemicarbazones complexes reported. Mainly complexes formed are mononuclear or dinuclear, and only few complexes are of higher nuclearity. There are only rare polymeric species. Thiosemicarbazones could be classified majourly into three main groups: (i) monothiosemicarbazones **(A)**, (ii) dithiosemicarbazones **(B)**, (iii) bis(thiosemicarbazones) **(C)**. Monothiosemicarbazones, as its name proposed, there is only one thiosemicarbazone moiety, while bis(thiosemicarbazones) involves two moieties linked through their imine nitrogens to an organic spacer. Dithiosemicarbazones also contain two thiosemicarbazone moieties, where, they are directly linked to an organic spacer through its amine nitrogen atoms [16].



(A)



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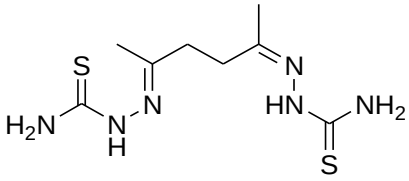
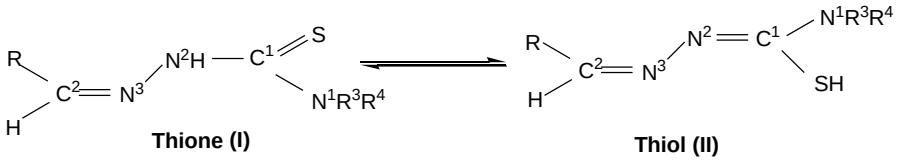
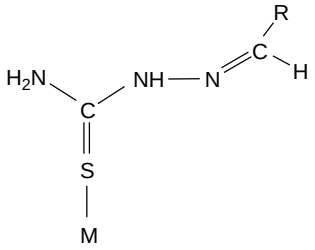


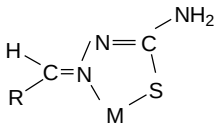
(C)

There is an interesting feature of thiosemicarbazones is about its thione **(I)** and thiol **(II)** form. In solid form, they mainly come in thione **(I)** form, whereas in solution form they may exist in both the forms thione as well as thiol **(II)** and also can be bind to a metal centre in neutral **(III)**, or in anionic form **(IV)**. The anionic form can be generated after the loss of H atom from N^2H **(I)** or H from SH **(IV)** [17].





(III)



(IV)

Many types of bonding modes have been detected for thiosemicarbazones in their neutral or anionic forms. In a neutral form, mainly the binding occurs with the help of only S atom in η^1-S **(V)**, μ_2-S **(VI)**, η^2-N^3, S- chelation **(VII)**, η^3-N^3, S- chelation and also S- bridging **(VIII)** modes. However, if the substituent at C^2 contains a donor atom and also includes in bonding, then the additional bonding modes can be observed which are, η^3-X, N^3, S-chelation **(IX)**, η^4-X, N^3, S-chelation and S-brigging **(X)**, and η^4-X, N^3, S-chelation and X-bridging **(XI)**, (Chart 2) [18].

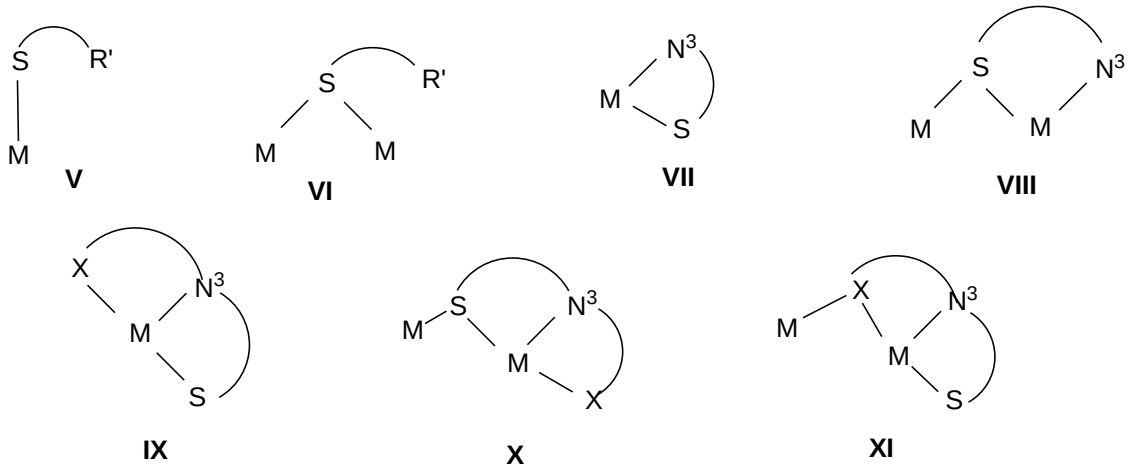


Chart 2

The modes shown above from **(IV to XI)** by neutral ligands are also presented by anionic type of ligands, viz. η^1 –S, μ_2-S, η^2 -N^3, S –chelation, η^2 –N^3, S –chelation and S – bridging, η^3-X, N^3, S –chelation, η^3-X, N^3, S –chelation- cum- S bridging, η^3 –X, N^3, S-chelation and X-bridging [19-20]. In adding, η^2 –N^2, S **(XII)** and N^2, S-bridging and S-bridging modes **(XIII)** are identified (Chart 3) [21-22]. A uncommon example of pentacoordination **(XIV)** by a thiosemicarbazone ligand have been described [23].

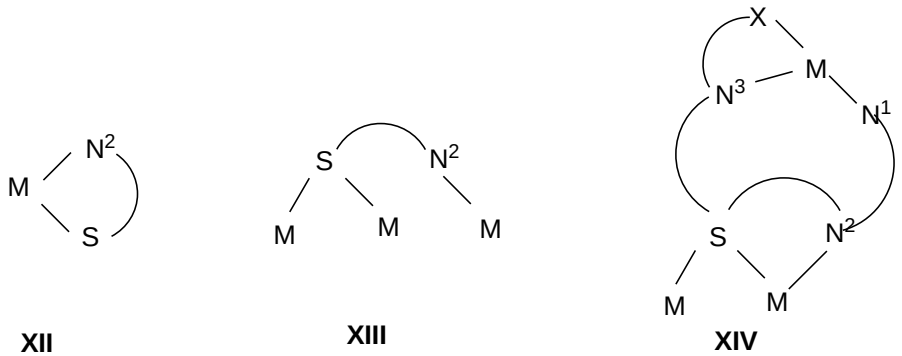
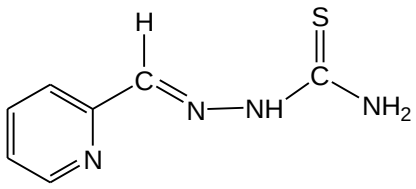


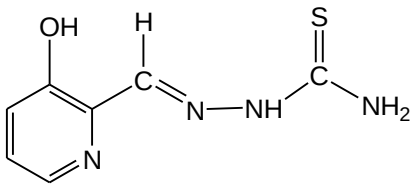
Chart 3

Thiosemicarbazone established considerable attention due to their vast potential pharmacological advantages [24-26]. For example, N-heterocyclic 2-formylpyridine **(XV)** and 3-

hydroxy-2-formylpyridine **(XVI)** type of thiosemicarbazones show anticancer properties. A conjugated N,N,S – system helps to increase the activity [28].



XV



XVI

COPPER

Copper is an transition element with a symbol of **Cu** (from the latin word: *cuprum*) and with atomic number 29. Its electronic configuration is [Ar] $3d^{10}$ $4s^{1}$. Copper is present in group 11, period 4 of periodic table. Copper mainly forms a huge variety of compounds**,** commonly with oxidation states +1 and +2, which are normally called as cuprous and cupric, respectively. Copper is generally a soft, malleable, and a ductile metal with a high thermal and electrical conductivity. Copper is commonly used to conduct heat and electricity, as a building material, and also as a essential part of various metal alloys, such as gold and silver mainly used in jewelry, also used to form marine hardware and coins. Copper compounds are commonly utilized as bacteriostatic agents, fungicides, and sometimes as a wood preservatives [31]. Copper is very crucial for all living organisms as a trace dietry mineral because it is the important constituent of respiratory enzyme complex i.e. cytochrome c oxidase. In human beings, it is mainly present in liver, muscle, and bone [30]. Copper ions form an stable complexes with the wide range of ligands; undoubtedly, the blue colour commonly seen in copper salts is due to the copper ions complexing with water. The coordination number most commonly seen is 6 but can be 4 also for some ligands [29].

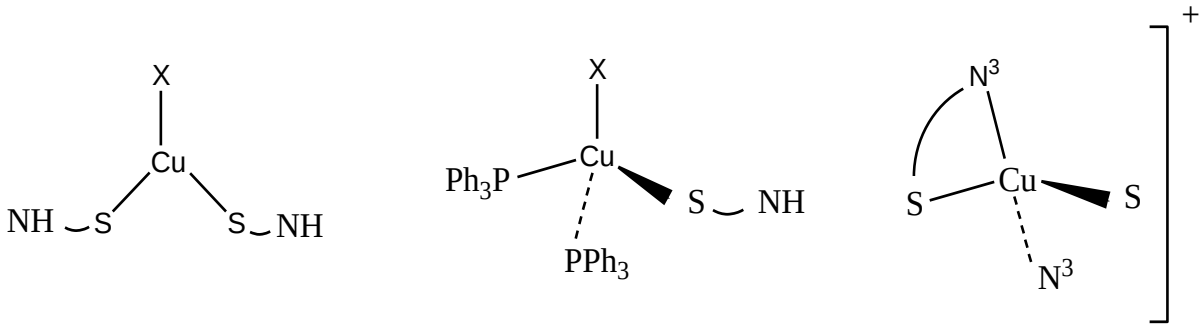
Literature Survey:-

Copper complexes with different types of nuclearity occur with both Cu^{I} and Cu^{II} oxidation states. Copper(I) may contains monomeric, dimeric, tetrameric, and hexameric type of complexes, and likewise, copper(II) also forms monomers, tetramers, dimers and polymers type

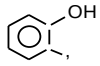
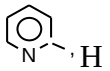
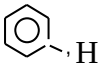
of complexes. Cu center have coordination number from 3 to 6, and the geometries shown are square planar, octahedral, square pyramid, distorted trigonal planar, or tetrahedral.

Copper(I) monomers :

Copper(I) halide contains mononuclear complexes, [Cu(η^1-S-HL)$_2$X] {X = Cl, **6** [36]; I, **7** [37]}(**7**), [CuX(η^1-S-HL)(Ph_3P)$_2$] {**8–9** [41, 37–40, 42, 43, 44] **(16)**, and [Cu(HL)$_2$]Cl 23 [18]. Neutral thiosemicarbazone ligands generally coordinates with the help of a S donor atom in complexes as shown in **6-22**. Complexes may have both trigonal planar **(6, 7)** or distorted tetrahedral geometry **(8–24)**. The geometry shown by N^3, S-chelated complex **23** is found to be more distorted.



R^1R^2C=N-NH-C(=S)NH_2

R^1, R^2	Ph, Ph	 H	 H	 H	 H	Ph, Ph	Me, Me
X	I	I, Br	Br	I, Br, Cl	I, Br	Br, Cl	-
	7 [42]	**8, 9** [38]	**10** [38]	**15-17** [41]	**18, 19** [41]	**21, 22** [42]	**23** [45]

R=N-NH-C(=S)NH_2

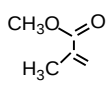
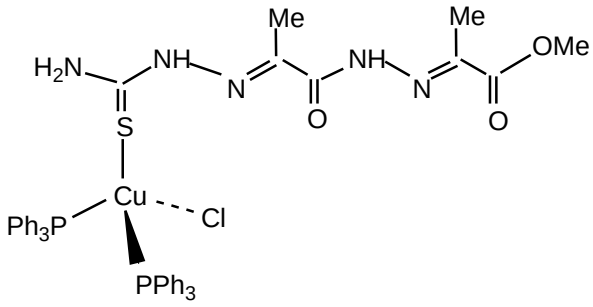
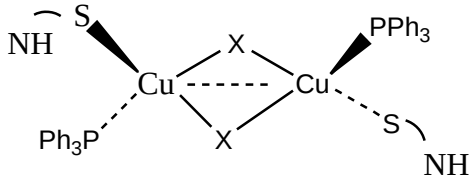
R			
X	Cl	I, Br, Cl	I
	6 [36]	**12–14**[40, 46]	**7** [44]

Chart 4

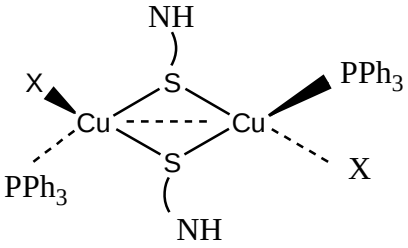


11, [39]

Many of dimeric complexes are observed with two types of central cores, Cu(μ-X)$_2$Cu **(24–33)**, [47, 41,48,49], or Cu(μ-S)$_2$Cu core **(33–37),** (37; 21**,** 33) [41, 46] from (Chart 5). Sulfur-bridging is not favouring theoretically and stabilization needs hydrogen bonding between halogen atom and water, or solvent of crystallization **(33–37**) [41, 46].



25-33

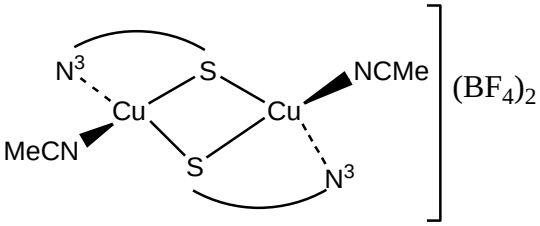


34-37

R^1R^2C=N-NH-C(=S)NH_2

R^1					CH_3	CH_3				
R^2	H	H	H	CH_3	CH_3	H	H	H	H	H
X	I	I	I	Br, Cl	I	Br, I	Br	Br, Cl	Br, Cl	Cl
	24 [12]	**25**	**26** [13]	**27, 28** [14]	**29**	**30, 31** [15]	**32** [13]	**33, 34** [13]	**35, 36** [13]	**37**

Chart-5



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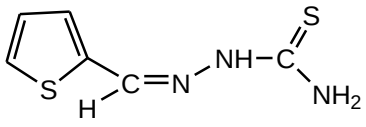
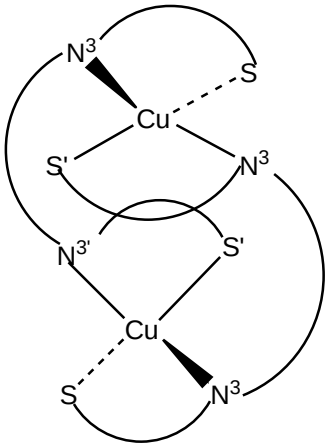


38,[50]



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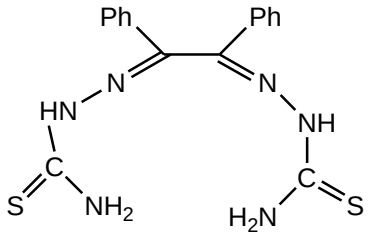


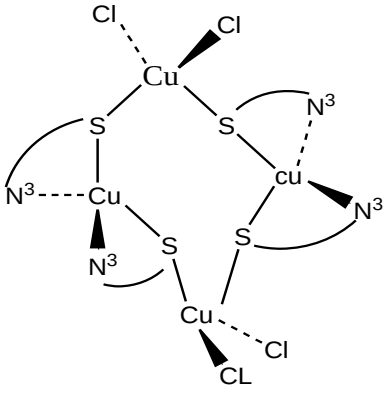
39,[51]

The dinuclear complex as shown by $[Cu_2(\mu_2\text{-N, S-HL})_2(CH_3CN)_2]\cdot 2BF_4$ **(38)** has N^3, S-chelation-and-S-bridging [50], where as in complex i.e. $[Cu_2L_2](PF_6)_2$ **(39)** [52], the bis-thiosemicarbazone ligands works as bidentate N, S- donors and also copper atom is in respective distorted tetrahedral N_2S_2 type of environment.

The ^{31}P spectra shown by mononuclear complex i.e. $[CuX(HL)(Ph_3P)_2]$, **15, 18** and **19,** dinuclear complex which is hydogen beidged , $[Cu_2(\mu\text{-X})_2(HL)_2(Ph_3P)_2]$ **25** and **32** and sulfur-bridged dinuclear , $[Cu_2(\mu\text{-S-HL})_2(HL)_2(Ph_3P)_2]$ **34** complexes exhibits that there is no any variation in their respective solid state structures which is in solution state [41]. Although, the complexes **35** and **36**, shows conversion of S-bridged dimer into monomers and the complex, **26** shows isomerization of iodo-bridged dimer into an S-bridged dimer which is in a solution state [41].

Polynuclear Complexes:

Mainly there are two tetranuclear and one hexanuclear compounds recognized. The Tetranuclear Cu^I complexes are $[Cu_2(HL)_2Cl_2]_2$ **42** [53], and $[Cu_4L_4]$ **43** [54]. In Complex **42** there are two main types of tetrahedral copper centers having CuN_2S_2 and CuS_2Cl_2 cores, and two copper(I) centers which are bridged using sulfur atoms to form a eight membered rings. In complex **43**, the ligand shown is deprotonated, and every copper contains CuS_2N coordination core. In this Two Copper atoms are bridged using S atoms by making a four-membered ring, and two of these rings are interconnected with N^2-donor atom which fallouts in the formation of a tetranuclear complex.



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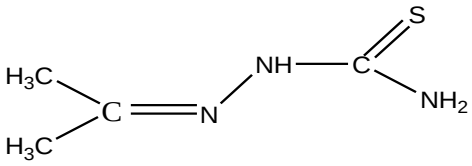
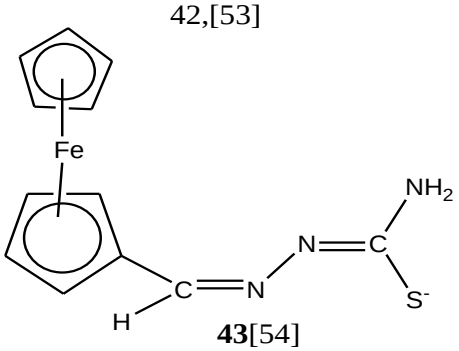
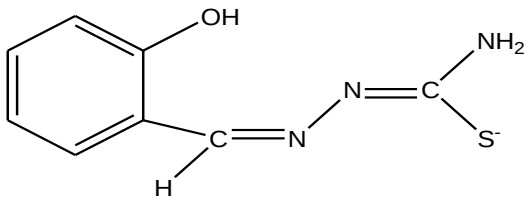


42,[53]



43[54]



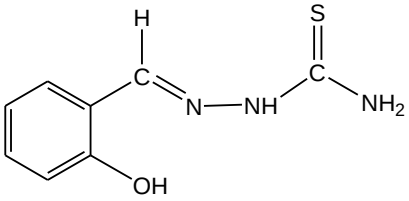
44,[54]

The structure of $[Cu_6L_6]$ **44** which is an hexanuclear complwex has been given. Its preparation was done by reacting salicylaldehyde thiosemicarbazone (H_2L) with $[Cu(MeCN)_4]\cdot PF_6$ in DMF in the presence of triethylamine base [55]. The complex include, three Cu zatoms and three S atoms with the help of three deprotonated ligand moieties which results into a six membered Cu_3S_3 ring, and these two types of rings are interconnected by N^2 nitrogen of the ligand which resulting into an hexanuclear complex. The geometry shown by every Cu center is trigonal planar.

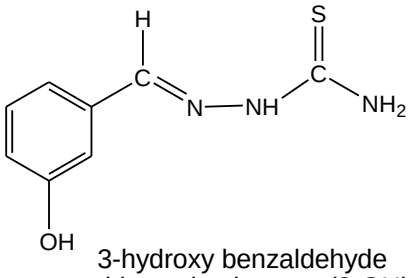
Objective of the report:

From above literature survey, it is clear that although a number of complexes of thiosemicarbazone with Cu(I) are known, but very few are polymeric in nature. The main objective of this research project is to explore Cu(I) polymeric complexes of thiosemicarbazones. Keeping theses points in mind the current research project is aimed to the following objectives:

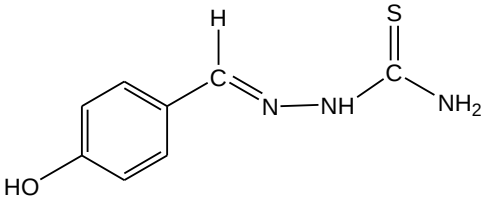
1. Synthesis of 2-hydroxybenzaldehyde thiosemicarbazone (2-OHbtsc), 3-hydroxybenzaldehyde thiosemicarbazone (3-OHbtsc) and 4-hydroxybenzaldehyde thiosemicarbazones (4-OHbtsc) (Scheme 1).
2. Characterization of synthesized ligands using IR, ^{1}H NMR and UV spectroscopy.
3. Synthesis of Polymeric Cu(I) thiosemicarbazone complexes.
4. Characterization of synthesized polymeric Cu(I) thiosemicarbazone complex using IR, ^{1}H NMR, UV spectroscopy.
5. Biological application of synthesized ligands and complexes.



2-hydroxy benzaldehyde thiosemicarbazone (2-OHbtsc)



3-hydroxy benzaldehyde thiosemicarbazone (3-OHbtsc)



4-hydroxy benzaldehyde thiosemicarbazone (4-OHbtsc)

Scheme 1

CHAPTER- 2

MATERIALS AND METHODS

Material

Acetonitrile, diethyl ether, p-hydroxy benzaldehyde, N,N-dimethylformamide, silver nitrate, hydrazine hydrate, nickel acetate tetra hydrate and thiosemicarbazide are purchased from

Qualikems Fine Chem Pvt Ltd. Hexaflurophosphric acid and ammounium hexafluorophosphate are purchased from Sigma Aldrich. All the reagents used are of analytical grade.

METHODOLOGY

Instrumentation:

Melting point:

The melting point of synthesized ligands was determined with the help of a lab fitted electrically heated apparatus.

Infrarred spectroscopy

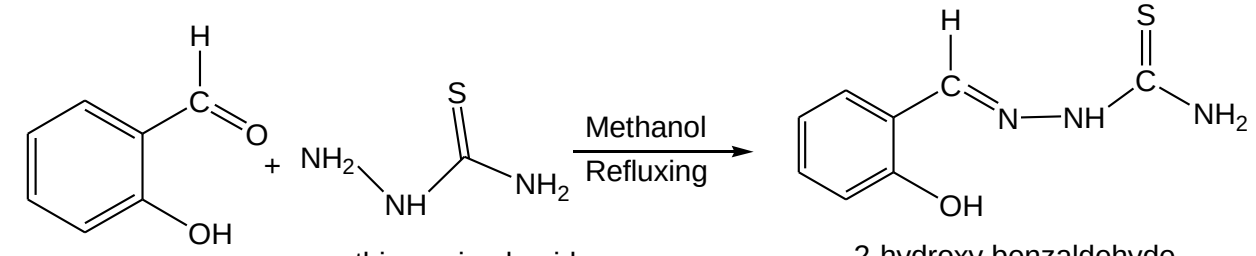
Infrared (IR) spectra of synthesized ligand was recorded using KBr pellets by SHIMADZU FTIR 8400S, Fourier Transform, Infrared spectrophotometer from (Department of Chemistry, Lovely Professional University).

Experimental

Synthesis of ligands :

(i) Synthesis of 2-hydroxy benzaldehyde thiosemicarbazone (2-OHbtsc):

To a solution of thiosemicarbazide (1g, 21.94 mmol) in 50-60 ml of methanol was added 2-hydroxy benzaldehyde (1.33 g, 21.96 mmol). The mixture was refluxed for 5-6 hours. Transparent solution is formed and was filtered carefully and kept for crystallization. After two-three days, transparent crystals were formed. Crystals were filtered properly and dried them in vacuum.



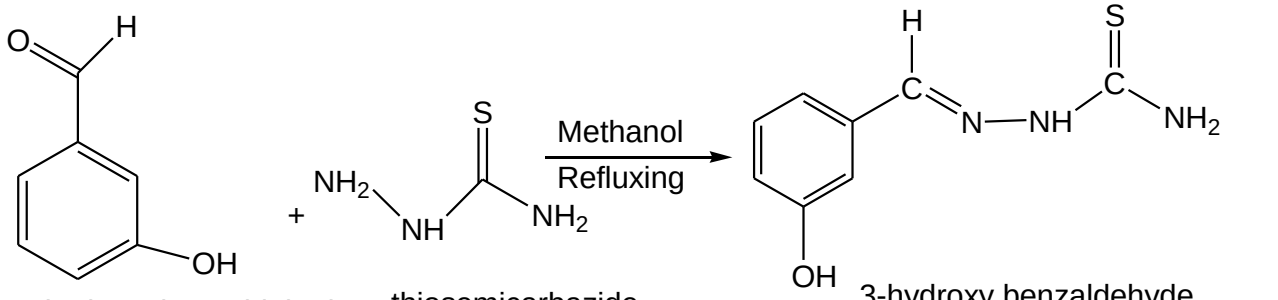
2-hydroxy benzaldehyde thiosemicarbazide 2-hydroxy benzaldehyde thiosemicarbazone (2-OHbtsc)

Characterization:

Melting Point	120-122°C
Solubility	Soluble: chloroform, DCM, methanol Insoluble: Hexane
IR (in KBr cm^{-1})	ν(O-H), 3414; ν(N-H), 3254; ν(-N-H), 3155; ν(C=C), 1643; ν(C=N), 1518; ν(NH_2), 1465; ν(C=S), 868.

(ii) Synthesis of 3-hydroxy benzaldehyde thiosemicarbazone (3-OHbtsc):

To a Solution of thiosemicarbazide (1g, 21.94 mmol) in 50-60 ml of methanol was added 3-hydroxy benzaldehyde (1.33 g, 21.96 mmol). The mixture was refluxed continuous for 5-6 hours. Light yellow coloured solution is formed and was filtered carefully and kept for crystallization. After two-three days, light yellow coloured crystals were formed. Crystal were filtered properly and dried them in vaccum.



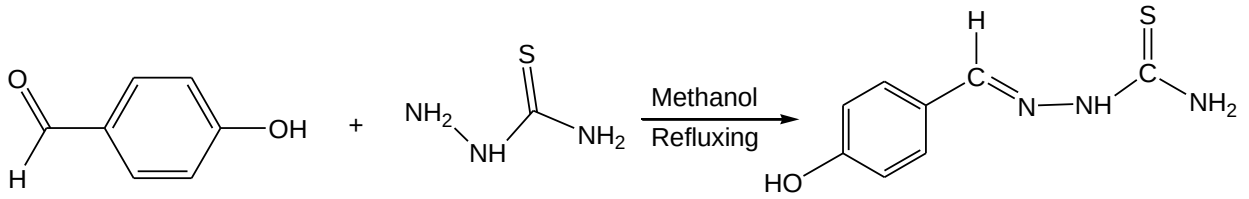
3-hydroxy benzaldehyde thiosemicarbazide 3-hydroxy benzaldehyde thiosemicarbazone (3-OHbtsc)

Characterization:

Melting Point	100-102°C
Solubility	Soluble - methanol, chloroform (partially soluble). Insoluble - DCM, Hexane
IR (in KBr cm^{-1})	ν(O-H),3435; ν(N-H),3281; ν(-N-H),3163; ν(C=C),1590; ν(C=N),1523; ν(NH_2),1465; ν(C=S),815

(iii) Synthesis of 4-hydroxy benzaldehyde thiosemicarbazone (4-OHbtsc):

To a Solution of thiosemicarbazide (1g, 21.94 mmol) in 50- 60 ml of methanol was added 4-hydroxy benzaldehyde (1.33 g, 21.96 mmol). The mixture was refluxed continous for 5-6 hours. Light orange coloured solution is formed and was filtered carefully and kept it for crystallization. After two-three days, light orange coloured crystals were formed. Crystal were filtered properly and dried them under vaccum.



4-hydroxy benzaldehyde | thiosemicarbazide | 4-hydroxy benzaldehyde thiosemicarbazone (4-OHbtsc)

Characterization:

Melting Point	100-102°C
Solubility	Soluble:-Methanol, DCM, chloroform Insoluble:-Hexane
IR (in KBr cm^{-1})	ν(O-H),3311; ν(N-H),3169; ν(-N-H),2906; ν(C=C),1627; ν(C=N),1581; ν(NH_2),1504; ν(C=S),815

Synthesis of Cu_2O:

Solid $CuSO_4.5H_2O$, 2g is dissolved in 400ml of distilled water. To it dropwise add 25ml of 1 M Sodium hydroxide solution was added. The colour of the solution change from blue to green colour, which indicate the formation of $Cu(OH)_2$. The solution is stirred for 30 minutes to complete the formation of $Cu(OH)_2$. To this solution add around 60ml of 1M glucose solution and the mixture is heated at moderate temperature. The colur of mixture changes and become yellow this shows the reduction of $Cu(OH)_2$ to Cu_2O (Figure A). The colloidal particles should settle down for around 2 hours to complete the nucleation process. The precipitates is washed three times with water and then with ethanol and then dry them properly.

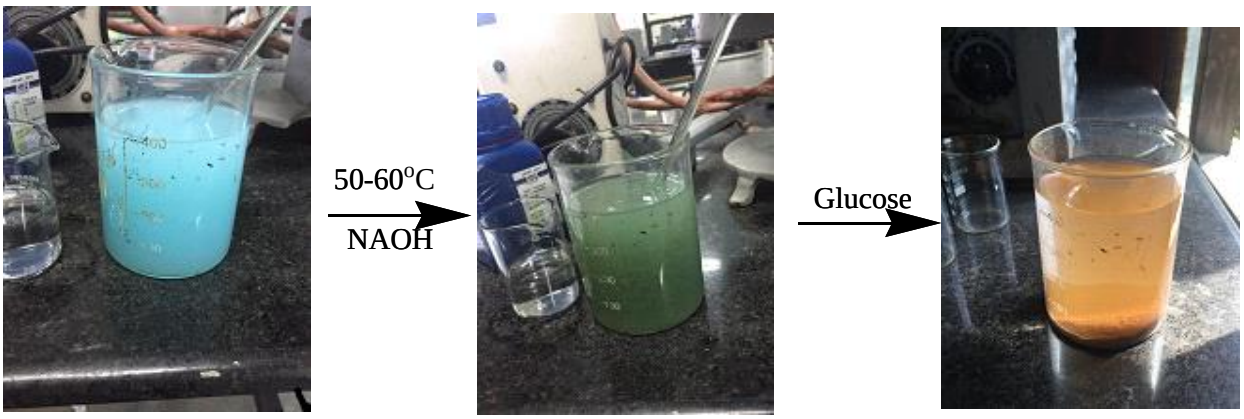
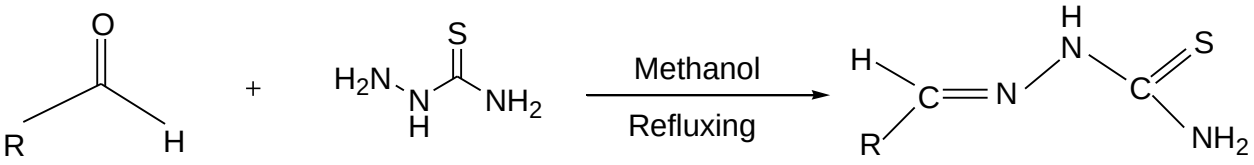


Figure A. Formation of Cu_2O

CHAPTER-3

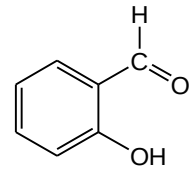
RESULTS AND DISSCUSSION:-

The ligands 2-OH Benzaldehyde thiosemicarbazone (2-OHbtsc), 3-OH Benzaldehyde thiosemicarbazone (3-OHbtsc) and 4-OH Benzaldehyde thiosemicarbazone (4-OHbtsc) was prepared by reacting them with thiosemicarbazide (Scheme 2). Scheme 3 represents the mechanism of condensation.

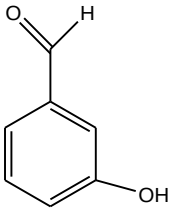


thiosemicarbazide Thiosemicarbazone

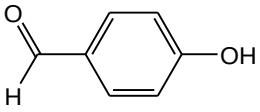
Where R=



2-hydroxy benzaldehyde



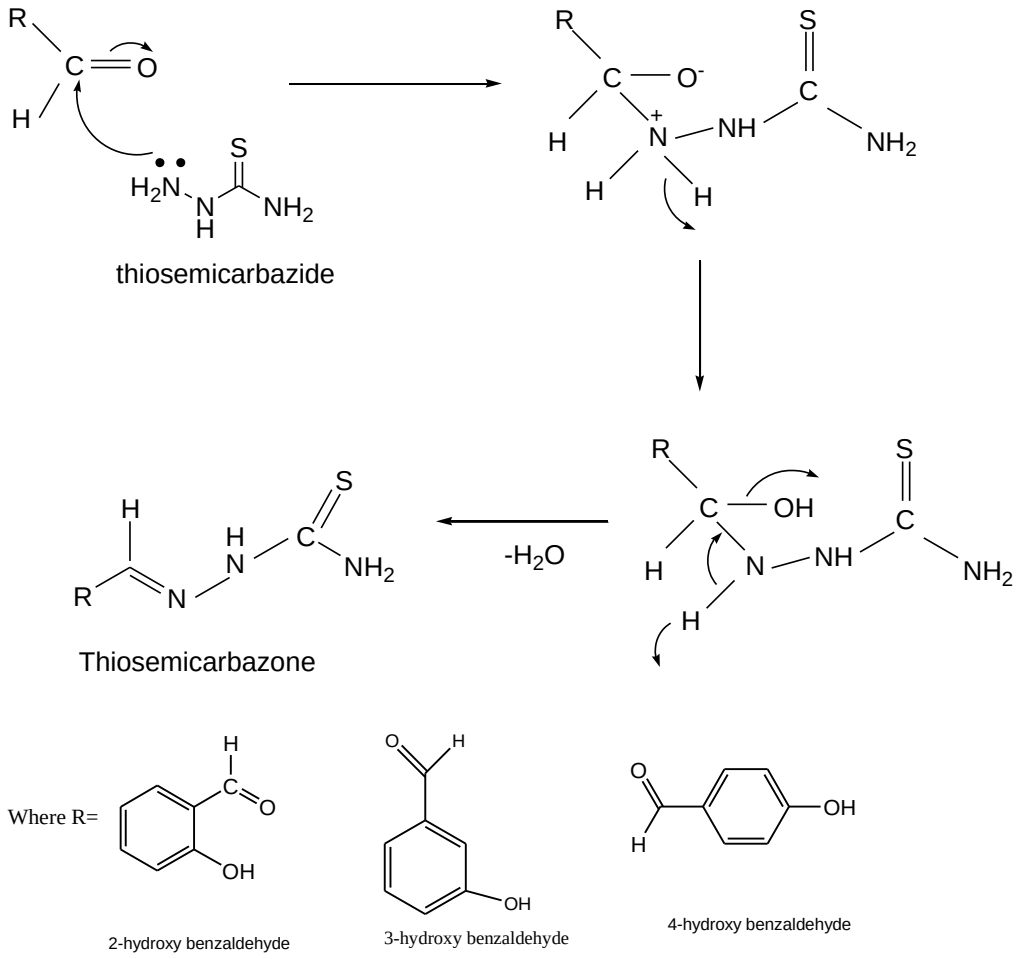
3-hydroxy benzaldehyde



4-hydroxy benzaldehyde

Scheme-2

Mechanism of the reaction:



Scheme-3

Discussion on IR

Important IR peaks of ligands 2-OH benzaldehyde thiosemicarbazone (2-OHbtsc), 3-OH benzaldehyde thiosemicarbazone (3-OHbtsc), 4-OH benzaldehyde thiosemicarbazone (4-OHbtsc) are listed in Table 1. The ν(C=O) peak in 3-hydroxybenzaldehyde and 4-hydroxybenzaldehyde appeared at 1673 cm^{-1} and 1690 cm^{-1} respectively (Figures 1 and 2). Disappearance of ν(C=O) peak and appearance of ν(C=N) peak at 1510-1600 cm^{-1} support the condensation. The ν(O-H) peaks of thiosemicarbazones appeared in the range, 3310-3450 cm^{-1}. The ν(N-H) peaks of thiosemicarbazone ligands are divided into two groups: i) Peaks due to amino group (-NH_2): appeared in the range, 3150-3300 cm^{-1} ii) Peaks due to ν(-NH-) of amide group: appeared in the range, 2900-3150 cm^{-1} in a ligands H^1L-H^3L. The characteristic peak of ν(C=S) appeared at 868 cm^{-1} (H^1L), 815 cm-1(H^2L) and 815 cm^{-1} (H^3L) under the range 800-880 cm^{-1} . Appearance of all of these peaks ensures the formation of ligands.

Table 1- Important IR Peaks of ligands (H^1L-H^3L, cm^{-1})

Ligand	ν(O-H)	ν(N-H)	ν(-NH-)	ν(C=C)+ν(C=N) +δ(NH_2)	ν(C=S)
2-OHbtsc (H^1L)	3414	3254	3155	1643, 1518, 1465	868
3-OHbtsc (H^2L)	3435	3281	3163	1590, 1523, 1465	815
4-OHbtsc (H^3L)	-	3311	3169	1627, 1581, 1504	815

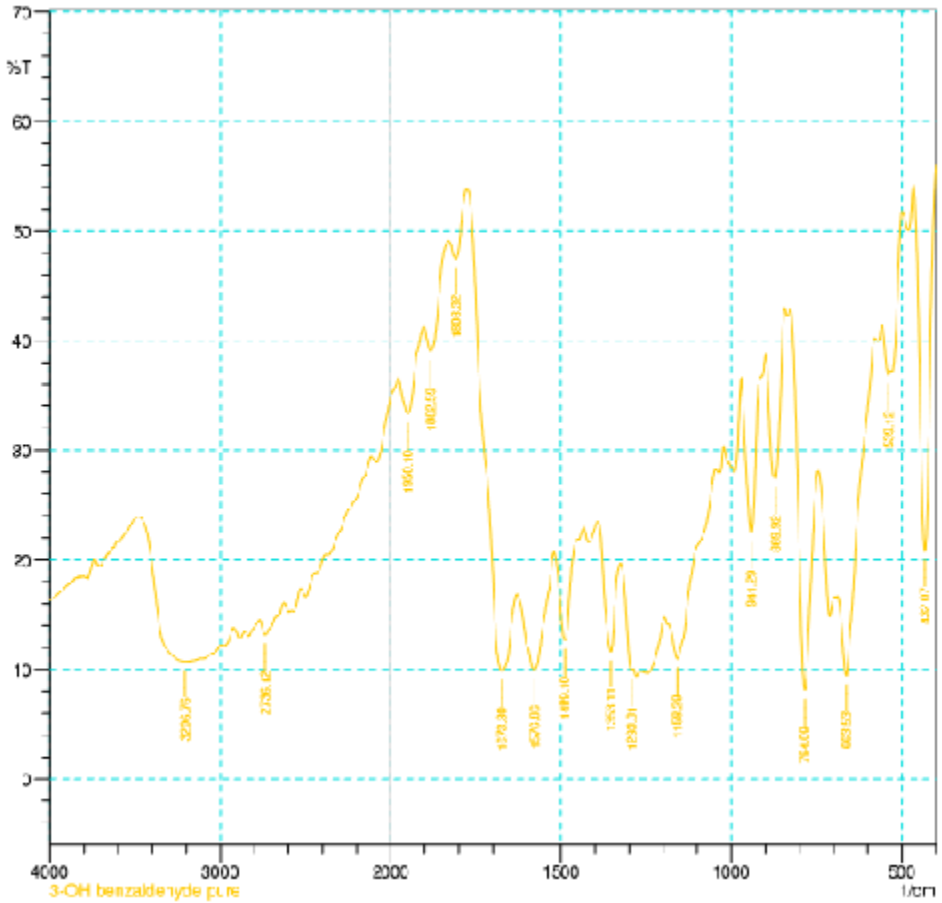


Figure 1: IR spectrum of 3-OH Benzaldehyde

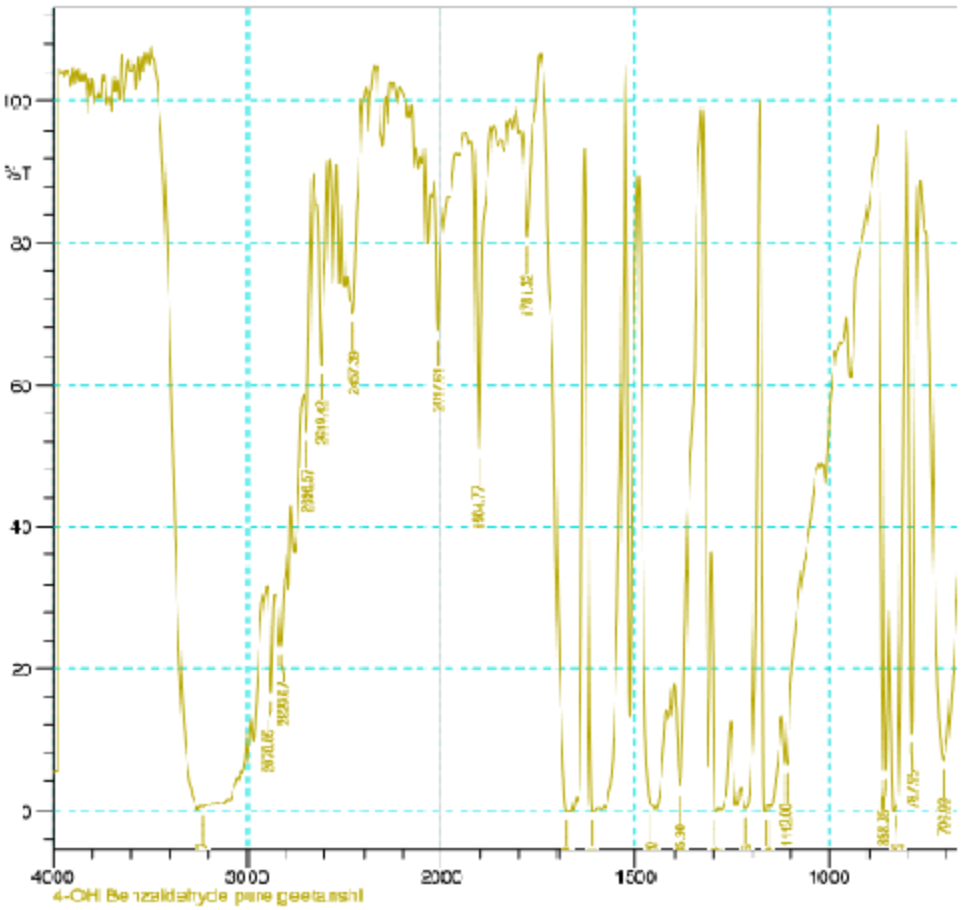


Figure 2: IR spectrum of 4-OH Benzaldehyde

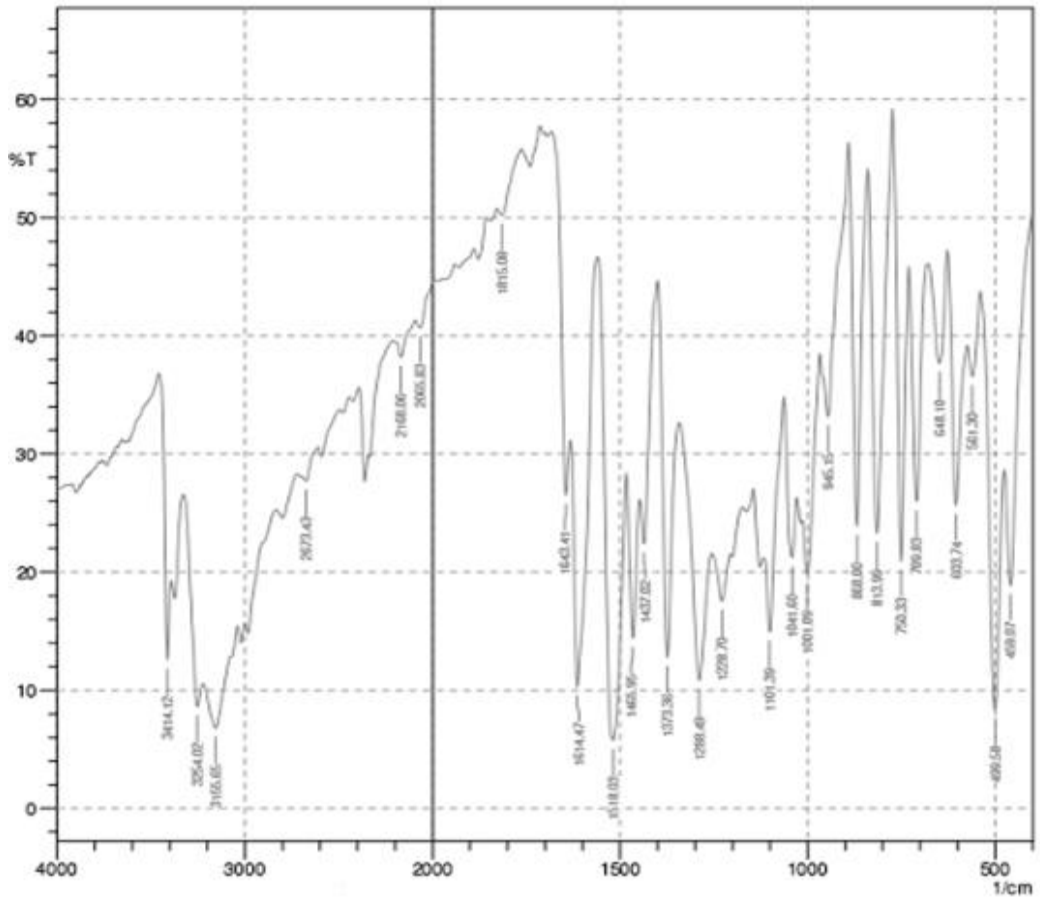


Figure 4: IR spectrum of 2-OH Benzaldehyde thiosemicarbazone

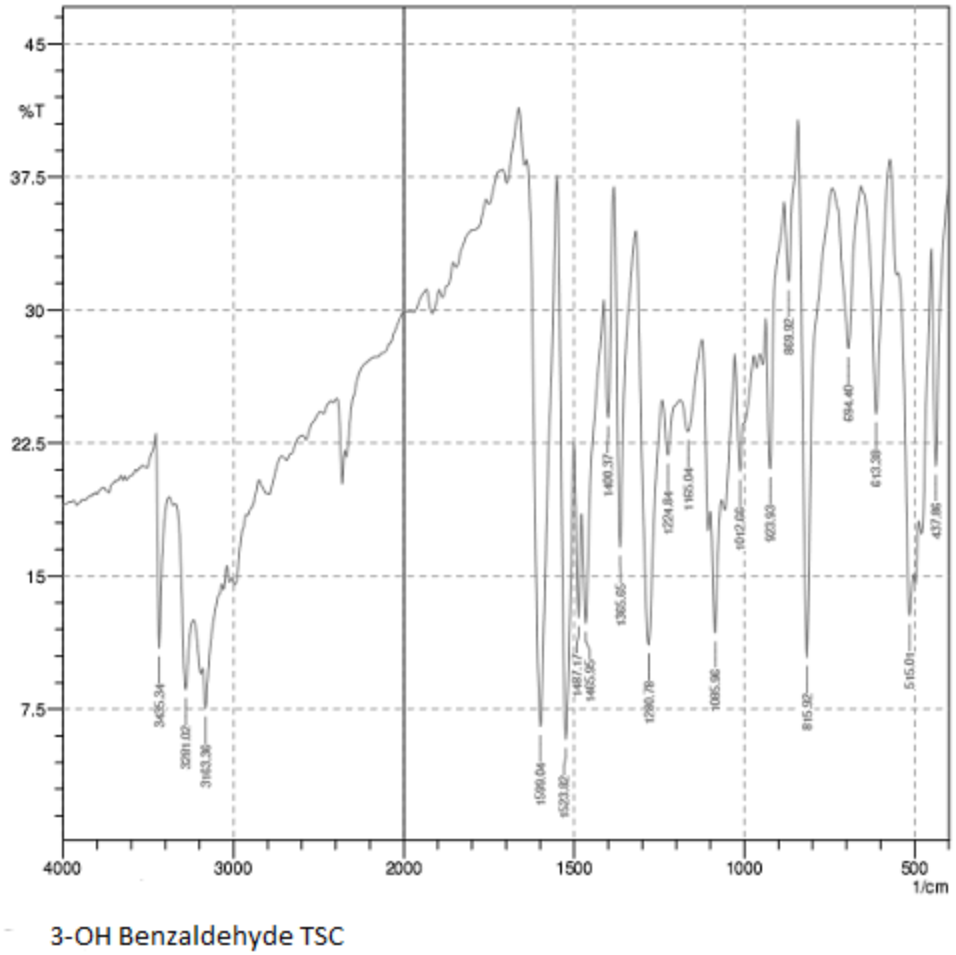


Figure 5: IR spectrum of 3-OH Benzaldehyde thiosemicarbazone

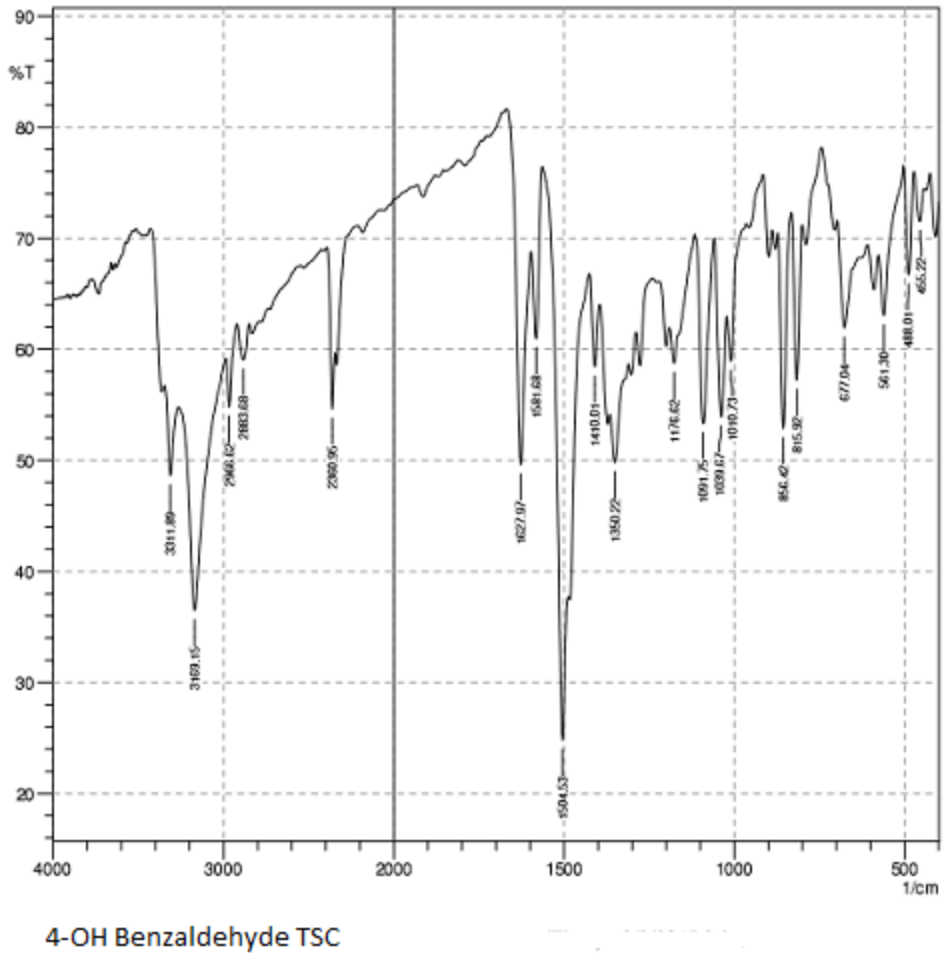


Figure 6: IR spectrum of 4-OH Benzaldehyde thiosemicarbazone

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