



---

## A DESCRIPTIVE ANALYSIS AND BIOLOGICAL STUDIES OF SOME METAL COMPLEXES OF THIOSEMICARBAZIDE

---

**Mr. Kotilingaiah Nalamada**

*Ph.D. Research Scholar,  
Department of Chemistry,  
Shri. J.J.T. University, Rajasthan, India*

**Dr. Rakesh Kumar**

*Professor & Ph.D. Research Guide  
Department of Chemistry,  
Shri. J.J.T. University, Rajasthan, India*

---

### ABSTRACT:

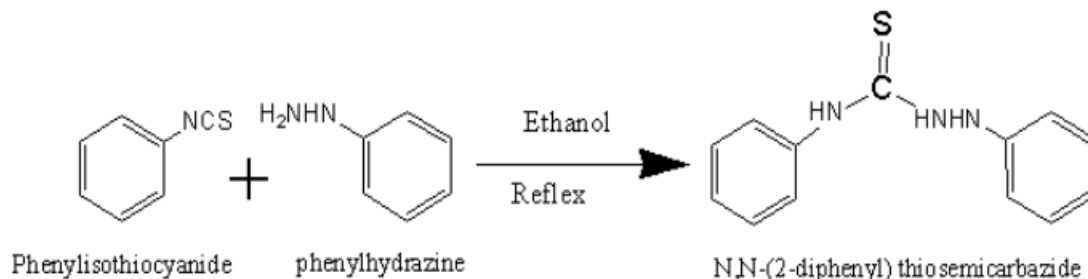
As a result of the interaction between phenyl isothiocyanate and phenylhydrazine, a ligand known as N,-(2-diphenyl) Thiosemicarbazide (L) may be produced. Metallic complexes of the forms  $[M(L)_2Cl_2]$  (M= Cu(II) square planer) and (Hg(II) and Zn(II), Cd(II) tetrahedral) were produced by the mixing reaction of the ligand (L) with metal salts  $MCl_2$ , where M= Cu(II), Hg(II), Zn(II), and Cd(II). The melting point, micro-elemental analysis, infrared, ultraviolet-visible spectroscopy,  $^1H$  NMR,  $^{13}C$  NMR, conductivity, and magnetic susceptibility measurements were all used to characterise each and every complex that was synthesised. The well-diffusion technique was used to investigate the biological activity of the ligand (L) and its metal complexes on gram-negative bacteria *Klebsiella pneumonia* and *Escherichia coli* as well as gram-positive bacteria *Staphylococcus aureus*. It was discovered that the ligands and complexes were sensitive.

***Key Words: Thiosemicarbazide derivative, transition metal complexes, biological activity.***

### INTRODUCTION:

Thiosemicarbazones of aromatic and heterocyclic aldehydes [1] and their complexes with many binuclear transition elements is well explored [2]. In addition, it has been discovered that they possess a wide variety of biological activities, and they are now well established as an important class of sulfur/nitrogen donor ligands [3] because of their ability to exhibit diverse biological activities [4]. Antimicrobial characteristics are included among these activities, in addition to other activities that are relevant to industry [5].

In this study, we generated a thiosemicarbazide by reacting phenylisothiocyanate with phenylhydrazine. Additionally, a variety of metal complexes of copper (II), mercury (II), cadmium (II), and zinc (II) were synthesised, described, and tested for their biological activities.



### REAGENTS AND STARTING MATERIALS:

The phenylisothiocyanate and KBr that were used in this experiment were obtained from Fluka AG. ZnCl<sub>2</sub> and acetone were manufactured by Merk. Methanol, as well as the chemicals CuCl<sub>2</sub>·2H<sub>2</sub>O, HgCl<sub>2</sub>·6H<sub>2</sub>O, and CdCl<sub>2</sub>·4H<sub>2</sub>O, are provided by BDH. Riedel was the vendor for the acquisition of DMSO and phenylhydrazine.

#### ***Preparation The Ligand:***

In order to produce the thiosemicarbazides, phenylisothiocyanate (25 mmol) was combined with phenylhydrazine (25 mmol) while the mixture was being carried out in the presence of ethanol (20 mL). At room temperature, the reaction mixture was stirred continuously for one hour while it was held. After obtaining the solid, it was filtered, and then was washed with ice-cold ethanol [5].

#### ***General Procedure for Preparation of Metal Complexes:***

The warm ethanolic solution of the ligand and the solution of the metal salts were combined in the stoichiometric proportion of 1:2, which is the ratio of metal to ligand for all divalent metal ions. After the formation of the precipitate, the solution combination was allowed to cool in an ice bath to ensure full precipitation. After being filtered, washed with ethanol and diethyl ether, dried in an oven, and finally chilled in a desiccator over CaCl<sub>2</sub>, the product was obtained. (You will get 85% of it).

***Biological Activity:***

The biological activity of the ligand, denoted by "L," as well as the metal complexes of the ligand were investigated and quantified. The well-diffusion approach was used for the in vitro antibacterial screening that was carried out [6]. During the screening process, the gram-negative bacteria *Klebsiella pneumonia* and *Escherichia coli* as well as the gram-positive bacteria *Staphylococcus aureus* were used as bacterial species [7].

***Physical Measurements:***

The (stuart digital melting) point instrument was used to conduct the melting point measurements. A (T60 UV/Vis) spectrophotometer was used to detect the electronic spectra of the ligand as well as the complexes while they were dissolved in DMSO. On a (Shimadzu) infrared spectrophotometer, the FT-Infrared spectra of the ligands and complexes were recorded in the (400-4000)  $\text{cm}^{-1}$  range. Utilizing a Perkin Elmer-2400 CHNS analyzer, elemental analysis was performed. The conductivities of the complexes were measured using a conductometer type (Cond. 720) conductivity metre while they were dissolved in DMSO. The magnetic data were acquired using a Guoy technique auto magnetic susceptibility balance.

***Infrared Spectroscopy:***

A unique absorption band can be seen in the FT-IR spectra of the ligand (L) (Fig. 1) at 3167 (N-H) stretching, 1542 (N-H) bending, 1198 (C-N) stretching, and 1070 (C=S)  $\text{cm}^{-1}$  [8]. The infrared spectra of the Cu(II) (Fig. 2), Hg(II), and Cd(II) complexes reveal bands at 3225, 3210, and 3220  $\text{cm}^{-1}$  respectively. These bands have been pushed to higher frequencies, which is indicative of the creation of a link between the metal and the nitrogen atom in the hydrazinic group. As a direct result of this, the frequency of the bending of the N-H bond and the stretching of the C-N bond increased. While the complex of Zn(II) shows a band at 1002  $\text{cm}^{-1}$  that is ascribed to (C=S), its shift to lower frequencies is detected, and this shift is given to a bond with an atom of sulphur. Despite the fact that the new bond at (493- 491), (392- 376), and (432)  $\text{cm}^{-1}$  for (M-N), (M-Cl), and (M-S) respectively [9-15]. The IR data of the newly synthesised ligand as well as its metal complexes may be found in table below (1).

**Table1: Selected IR bands and electronic data of the ligand and its metal complexes (cm-1).**

No.	Compound	Band absorption		Assignment	$\mu_{\text{eff}}$ (B.M)	$\nu(\text{N-H})$	$\nu(\text{N-H})$ Bend.	$\nu(\text{C=S})$	$\nu(\text{C-N})$ Stretch.	Additional peaks
		cm <sup>-1</sup>	nm							
	Ligand (L)	4000 0	250			3167	1542	1070	1198	
1	[Cu(L) <sub>2</sub> Cl <sub>2</sub> ]	3508 7 2739 0	285 460	Intraligand C.T.	1.82	3225	1555	1066	1191	$\nu(\text{M-N})$ 491 $\nu(\text{M-Cl})$ 392
2	[Hg(L) <sub>2</sub> Cl <sub>2</sub> ]	3508 7	285	C.T.	0	3210	1562	1072	1207	$\nu(\text{M-N})$ 490 $\nu(\text{M-Cl})$ 383
3	[Zn(L) <sub>2</sub> Cl <sub>2</sub> ]	4081 6	245	C.T.	0	3173	1541	1002	1197	$\nu(\text{M-S})$ 432 $\nu(\text{M-Cl})$ 394
4	[Cd(L) <sub>2</sub> Cl <sub>2</sub> ]	3367 0	297	C.T.	0	3220	1555	1072	1209	$\nu(\text{M-N})$ 493 $\nu(\text{M-Cl})$ 376

**ELEMENTAL ANALYSIS:**

The results of elemental analysis performed on the artificially produced ligand and its metal complexes are shown in (table 2). They are compatible with the stoichiometries that have been proposed, and the findings were found to be in a good agreement with the estimated values, in addition to the spectroscopic techniques (IR), (UV-Vis), and (1H, 13C) NMR. In addition, the colour of the synthesised ligand as well as the melting temperatures of its metal complexes are presented in (table 2).

**Table 2: Color, melting point, elemental analysis and conductivity data for the synthesized thiosemicarbazide metal complexes**

No.	Compound	Yield%	Color M.P (C°)	Found (Calculated)%				$\frac{m \Lambda}{(\Omega^{-1} \cdot \text{cm}^2 \cdot \text{mol}^{-1})}$
				C %	H %	N %	S %	
	Ligand (L)	85	White (182)	46.54 (46.70)	3.43 (3.62)	21.58 (20.95)	9.27 (9.59)	
1	[Cu(L) <sub>2</sub> Cl <sub>2</sub> ]	72	Dark- green (193)	39.10 (38.95)	2.73 (3.02)	17.93 (17.48)	8.20 (7.98)	14.6
2	[Hg(L) <sub>2</sub> Cl <sub>2</sub> ]	69	White (170)	33.36 (33.19)	2.36 (2.57)	14.68 (14.90)	6.35 (6.80)	9.5
3	[Zn(L) <sub>2</sub> Cl <sub>2</sub> ]	82	Brown (295)	30.24 (30.16)	1.95 (2.34)	13.37 (13.5)	6.10 (6.19)	12.6
4	[Cd(L) <sub>2</sub> Cl <sub>2</sub> ]	68	Brown (106)	39.00 (38.89)	2.97 (2.76)	17.30 (17.44)	8.24 (7.99)	9.7

***Molar Conductivities:***

The molecular conductivities of all of the synthetic complexes are given in (table 2). When these observed values are compared with known molar conductivities [16], it reveals that they are not electrolytes, and it also demonstrates that the suggested formula for them [17] is accurate.

***Magnetic Susceptibility:***

Because the magnetic susceptibility of the Cu(II) complex is 1.73 B.M., a square planer shape may be inferred around Cu(II) [18]. The magnetic susceptibility of Hg(II), Zn(II), and Cd(II) complexes are all zero, which indicates that they are diamagnetic as predicted. It is also plausible that these complexes have tetrahedral structures and have tetrahedral arrangements around their metal centres [19].

**BIOLOGICAL ACTIVITY:**

The biological activities that were assessed for the ligand (L) and its metal complexes are presented in this order. There is no evidence that *Klebsiella pneumonia* can survive in the presence of the ligand (L) or any of the metal complexes [20]. Complexes 1 and 4 are the only ones that are susceptible to the *Escherichia coli* bacteria, whereas the other complexes are immune to it. Complexes 1 and 3 are the only ones that are susceptible to the *Staphylococcus aureus* bacteria, while the other complexes are resistant. On the basis of the Overtone idea and chelation theory [21], one may explain how the metal complexes were able to exhibit such an enhanced level of activity. According to the overtone concept of cell permeability, when a metal ion is chelated, the polarity of the metal ion is significantly reduced as a result of the overlap of the ligand orbital and the partial sharing of the positive charge of the metal ion with donor groups. This results in an increase in the delocalization of electrons over the entirety of the chelate ring, which in turn improves the complex's lipophilicity. As a consequence of this, the complex is able to more easily penetrate the lipid membrane of the microbe, and it is able to block the metal binding sites on the enzymes of the microorganism [22].

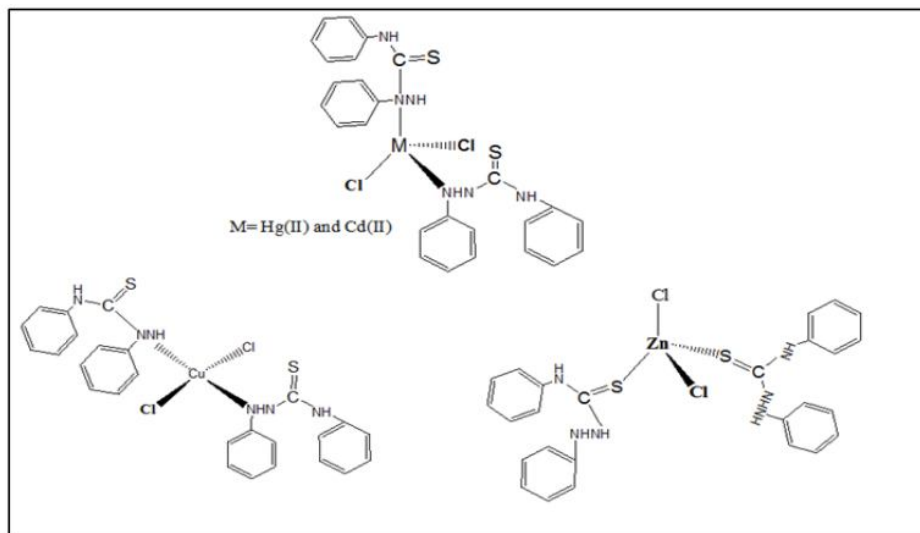
**CONCLUSION:**

Figure 1: Proposed chemical structure of ligand-metal complexes (L).

The following structures are postulated for the synthesised metal complexes based on the results of elemental analysis, infrared and ultraviolet-visible spectroscopy, conductivity, and magnetic susceptibility measurements. These structures are shown in figure 1.

**REFERENCES:**

- [1]. Tetiana Panchenko, Maria Evseeva and Anatoliy Ranskiy, copper(II) and nickel(II) with N,N'-bis(salicylidene)thiosemicarbazide heterometal complex compounds, *Chemistry & Chemical Technology*, 8(3), 243- 244, (2014).
- [2]. Mohamad J. Al-Jeboori and Ashour Hamoad Dawood, Synthesis and Structural Studies of Novel 2,6-Diformyl-p- Cresol Bis-(thiosemicarbazone) Ligand and Their Binuclear Complexes with Ni<sup>2+</sup>, Pd<sup>2+</sup>, Zn<sup>2+</sup>, Cd<sup>2+</sup> and Hg<sup>2+</sup> Metal Ions, *Journal of Kerbala University*, 6(1) Scientific, 133- 143, (2008).
- [3]. Monika Tyagi and Sulekh Chandra, Synthesis, characterization and biocidal properties of platinum metal complexes derived from 2,6-diacetylpyridine (bis thiosemicarbazone), *Open Journal of Inorganic Chemistry*, 2, 41- 48, (2012).
- [4]. A. Castiñeiras, E. Bermejo, J. Valdes-Martinez, G. Espinosa-Pérez, D.X. West, Structural study of two N(3)-substituted thiosemicarbazide copper(II) complexes, *Journal of Molecular Structure*, 522, 271–278, (2000).

- [5]. Camilla Moretto dos Reis, Danilo Sousa Pereira, Rojane de Oliveira Paiva Lucimar Ferreira Kneipp and Aurea Echevarria, Microwave-Assisted Synthesis of New N1, N4-Substituted Thiosemicarbazones, *Molecules*, 16, 10668-10684, (2011).
- [6]. Rahman A. MuhameedMurad and Tahir A. Tahir, Synthesis, characterization and biological studies of metal complexes of m- amino benzoic acid, *Diyala J. of pure science* 10(4), 65 – 66, (2014).
- [7]. Bauer AW, Kirby WM, Sherris JC, Turck M., Synthesis and Characterization of 1,3,4- oxadiazole derivatives with some new transition metal complexes, *Am. J. Clin. Pathol.*, 45, 493- 496, (1966).
- [8]. Omima M.I. Adly , Synthesis, molecular modeling, thermal and spectral studies of metal complexes of hydrazone derived from 5-acetyl-4-hydroxy-2H-1,3-thiazine2,6(3H)-dione and thiosemicarbazide, *Spectrochimica Acta Part A*, 79, 1295– 1303 (2011).
- [9]. Safa IbtahimKhadir, Synthesis, structural characterization, and biological activity of a silver (I) thiosemicarbazides complex and new ligands of thiadiazole, triazole and oxadiazole derived from isonicotinoyl Chloride, *Journal Of College Of Education*, 6, 344 - 365, (2011).
- [10]. B. Prathima, Y. Subba Rao, P.V. Chalapathi, Y. P. Reddy And A. Varada Reddy, spectral, structural and biological analysis of Cr(III) complex with benzyloxybenzaldehyde-4-phenyl-3-thiosemicarbazone , *international journal of pharmacy and pharmaceutical sciences*, 4(3), 167-174, (2012).
- [11]. RejaneLúcia de Lima, Letícia Regina de Souza Teixeira, Tania M. Gomes Carneiro, and Heloisa, Nickel(II), Copper(I) and Copper(II) Complexes of Bidentate Heterocyclic Thiosemicarbazones, *J. Braz. Chem. Soc.*, 10(3), 184-188, (1999).
- [12]. Vukadin M. Leovac ,Sladana B. Novakovic, Goran A. Bogdanovic, Milan D. Joksovic, Katalin MészárosSzécsényi and Valerija I. Cesšljevic, Transition metal complexes with thiosemicarbazide-based ligands. Part LVI: Nickel(II) complex with 1,3-diphenylpyrazole-4-carboxaldehyde thiosemicarbazone and unusually deformed coordination geometry, *Polyhedron*, 26, 3783–3792, (2007).
- [13]. M.V. Angelusiu, G.L. Almăjan, D.C. Ilies T. Rosu and M. Negoiu, Cu(II) Complexes with Nitrogen-Oxygen Donor Ligands: Synthesis and Biological Activity, *Chem. Bull. "POLITEHNICA" Univ. (Timisoara)*, 53(67), 78-82, (2008).

- [14]. Hakan Arslan, Ulrich Flörke, and NevzatKülcü, Spectral, magnetic and biological studies of 1,4-dibenzoyl-3- thiosemicarbazide complexes with some first row transition metal ions, *Acta Chim. Slov.*, 51, 787-792, (2004).
- [15]. K.B. Vyas, K.S. Nimavat, G.R. Jani, and M.V. Hathi, Synthesis, structural and spectral characterization of Zn(II) complexes, derived from thiourea and thiosemicarbazide, *Journal of Sciences, Islamic Republic of Iran*, 20(2), 111-114, (2009).
- [16]. Kazuo Nakamoto, "Infrared and Raman Spectra of Inorganic and Coordination Compounds", Part B: Applications in Coordination, Organometallic, and Bioinorganic Chemistry 2009 by John Wiley.
- [17]. Nand K . Singh, Saty B. Singh, AnuraagShrivastav and Sukh M. Singh, Proc. Spectral, magnetic and biological studies of 1,4-dibenzoyl-3- thiosemicarbazidecomplexes with some first row transition metal ions, *Indian Acad. Sci. (Chem. Sci.)*, 113(4), 257–273 , (2001).
- [18]. S.I. Orysyk, V.V. Bon, O.O. Obolentseva, Yu.L. Zborovskii, V.V. Orysyk, V.I. Pekhnyo, V.I. Staninets, V.M. Vovk, Synthesis, structural and spectral characterization of Zn(II) complexes, derived from thiourea and thiosemicarbazide, *InorganicaChimica Acta* 382, 127–138, (2012).
- [19]. Abdul-Ghany M. Al-Daher Ibraheem A. Al-Qassar, Synthesis and Characterization of Co(II), Ni(II), Cu(II), and Zn(II) Complexes with 2 Furaldehyde-2- Thenoylhydrazone, *Raf. J. Sci.*, 22(4), 109-120, (2011)
- [20]. Hikmat A. Mohamad, Synthesis and characterization of Phenyl bis-hydrazone complexes with Pd (II), Mn (II), Ni (II) and Fe(III) ions, *WasiitJournall for Science&Mediicine*, 2(1), 209 – 226, (2009).
- [21]. Magdy Shebl, M.A. Ibrahim, Saied M.E. Khalil, S.L. Stefan, H. Habib, Binary and ternary copper(II) complexes of a tridentate ONS ligand derived from 2- aminochromone-3 carboxaldehyde and thiosemicarbazide: Synthesis, spectral studies and antimicrobial activity, *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*, 115, 399–408, (2013).
- [22]. Mohammed M. Al-Ne'aimi, Synthesis and Characterization of Bis acylhydrazone Derivatives as Tetradentate Ligands and Their DinuclearMetal(II) Complexes, *Iraqi National Journal of Chemistry*, 47, 355-369, (2012).