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**Computational and theoretical studies on some  
thiosemicarbazide derivatives and their Ni (II) complexes**

**A graduation research project**

**By**

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**Under supervision**

**OF**

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# Computational and theoretical studies on some thiosemicarbazide derivatives and their Ni(II) complexes

## Abstract

Four new nickel (II) complexes of some thiosemicarbazides have been synthesized and spectrochemically characterized. The thiosemicarbazides are prepared by the addition of 4-(2-pyridyl)-3-thiosemicarbazide to phenyl isothiocyanate (H<sub>2</sub>PPS), benzoyl isothiocyanate (H<sub>2</sub>PBO), phenyl isocyanate (H<sub>2</sub>APO) and 2-pyridyl isothiocyanate (H<sub>2</sub>PPY). Theoretical calculations have been performed to obtain IR spectra of ligand and its complexes using AM1, MM, Zindo/1, MM+ and PM3, methods. Satisfactory theoretical-experimental agreements were achieved by MM method for the ligand and PM3 for its complexes. The calculated IR vibrations of the metal complexes, using the PM3 method was the nearest method for the experimental data, and it could be used for all complexes. Also, valuable information are obtained from calculation of molecular parameters for all compounds carried out by the previous methods of calculation (electronegativity of the coordination sites, net dipole moment of the metal complexes, values of heat of formation and binding energy) which approved that the complexes are more stable than ligand. The low value of  $\Delta E$  could be expected to indicate thiosemicarbazid molecules have high inclination to bind with the metal ions.

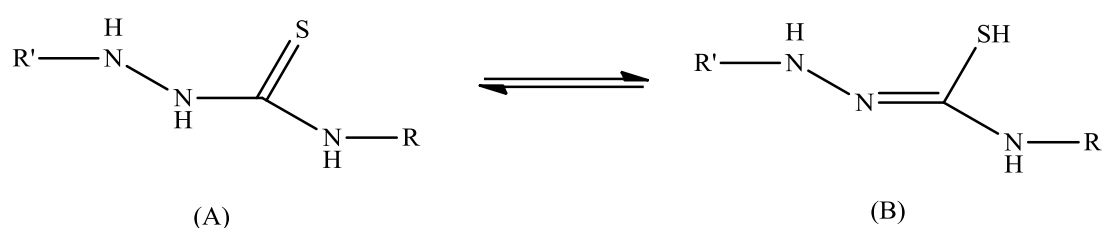
## Introduction

Metal complex formation is among the most prominent interaction in nature [1, 2]. Binding by metal ions and proteins can influence the biological action of medicinal agents. Of particular importance in pharmacy and medicine is the relation between complexation and the absorption and distribution of a drug in body and also the way in which complexation affects the onset and duration of drug action [3].

Sulfur incorporating compounds and their metal complexes seem to have antimicrobial activity [4,5], antifungal [6], antibacterial [7,8], anticarcinogenic [9-11] and insulin mimetic properties [12]. The antitumor activity may be due to an inhibition

of DNA synthesis produced by the modification in the reductive conversion of ribucleotide to deoxyribnucleotide [13].

The biological activity of thiosemicarbazide ligands is mainly due to their strong ability to form chelates with the essential metal ions, in which the fungus needs in its metabolism. Thiosemicarbazides have also been used as reagents for analysis of metals [14–16], device applications relative to telecommunications and optical storage [17,18]. They exist in tautomeric thione (A) and thiol (B) forms [19]. The existence of tautomeric forms as an equilibrium mixture in solution is essential for their versatile chelating behavior.



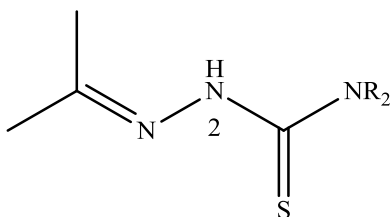
Structure 1: Thione-thiol tautomers of thiosemicarbazides

A number of reports concerning thiosemicarbazides and their metal complexes were established owing to their chemical and biological activities [20-24]. Really, an important number of thiosemicarbazides being NNS tridentate donors possess carciovostatic efficacy [25] and substantial *in vivo* activity against various human tumor lines [26,27] but structural variations on some thiosemicarbazides with regard to the chelating ability may destroy or reduce its medicinal values [28].

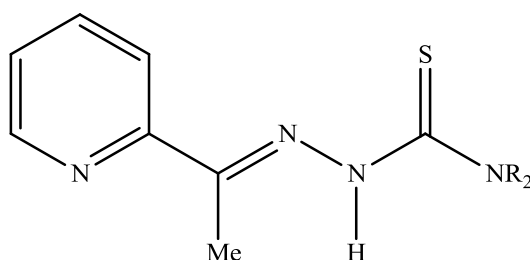
## 1.1. Literature Survey on Hydrazone Complexes

Thiosemicarbazone moiety (Structure 2) without substituents attached to the thione sulfur coordinates as either a neutral or anionic NS bidentate ligand, depending on the method of complex preparation [29]; a third coordinating atom often gives ONS (e.g. 2-hydroxybenzaldehyde thiosemicarbazones) [30] or NNS (e.g. 2-acetylpyridine thiosemicarbazones, Structure 3) tridentate ligands. A few examples of higher denticity involving one or more thiosemicarbazone moieties, as well as monodentate coordination, have been reported [31]. When an additional coordinating functionality is present in the proximity of the donating centers, the ligands bond in a

tridentate manner. This occurs with either the neutral molecule [32] or the monobasic anion upon loss of hydrogen from N<sup>2</sup> [31]. If the additional functionality can also lose a proton (e.g. phenolic group), anions of greater negative charge are formed. There are instances reported, however, where the heterocyclic atom and the azomethine nitrogen are involved in bidentate coordination [33], and the sulfur atom is considered not to be coordinated, weakly coordinated to the same metal center, or coordinated to an adjacent metal center [31].

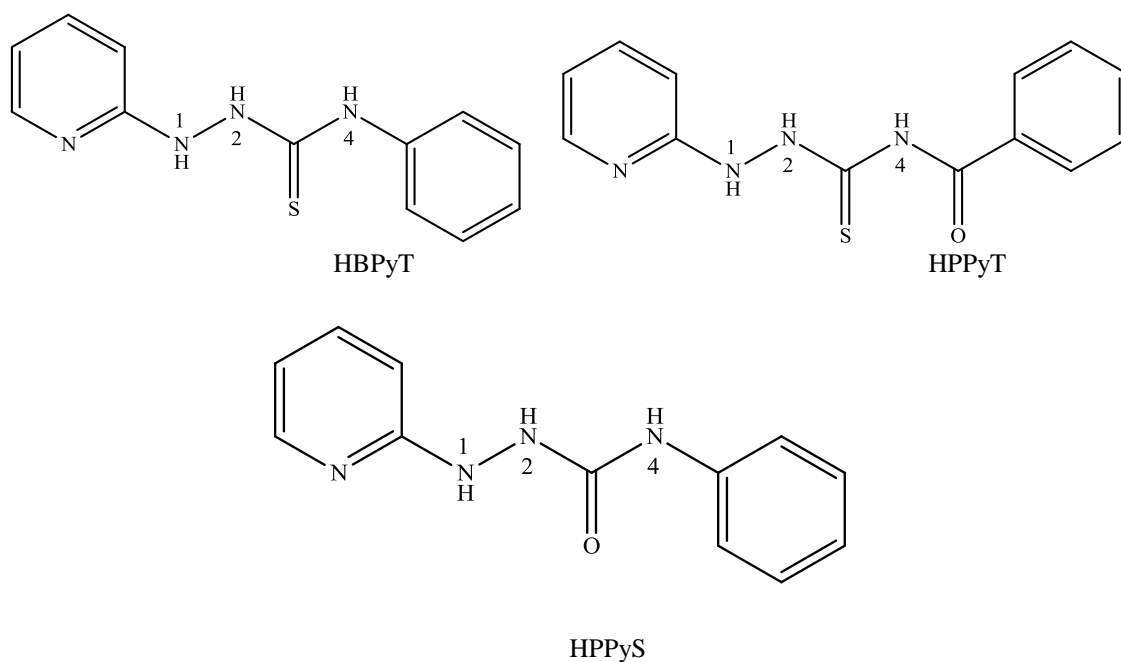


Structure 2: Thiosemicarbazone moiety

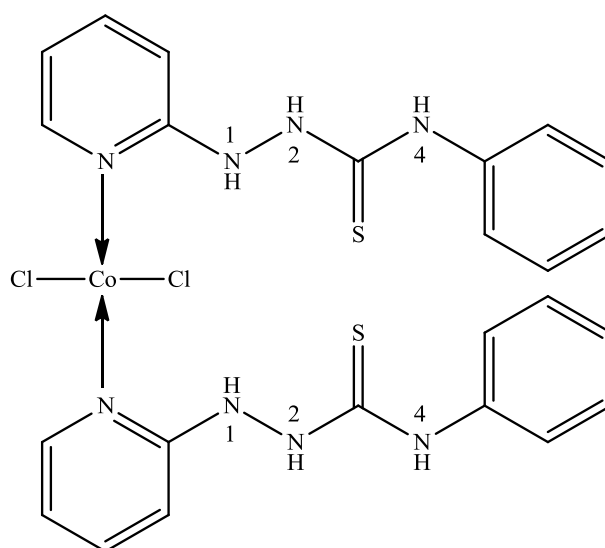


Structure 3: Structure of 2-acetylpyridine thiosemicarbazone

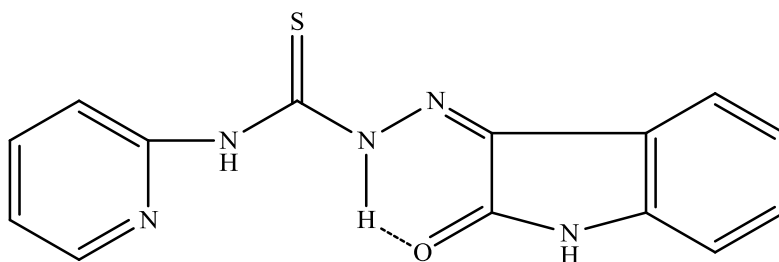
The synthesis and characterization of Co(II), Ni(II), Cu(II) and Cu(I) complexes of 4-benzoyl-1-(2-pyridyl)-S-thiosemicarbazide (HBP<sub>2</sub>T), 4-phenyl-1-(2-pyridyl)-3-thiosemicarbazide (HPP<sub>2</sub>T) and 4-phenyl-1-(2-pyridyl)-3-semicarbazide (HPP<sub>2</sub>S) (structure 4) are reported [34]. Elemental analyses, molar conductivities, magnetic and spectral (visible, IR) measurements have been used to characterize the complexes. The IR spectral data showed that the ligands behaved as monodentate through (C=N) of the pyridine group as in [Co(HBP<sub>2</sub>T)<sub>2</sub>Cl<sub>2</sub>] (Structure 5) complex and/or bidentate ligands *via* (C=N) of the pyridine group and N<sup>2</sup>H or *via* N<sup>1</sup>H and enolized carbonyl group (=C-OH) with displacement of a hydrogen atom from the latter group. HPP<sub>2</sub>T behaved as a reducing agent towards Cu(II). Different stereochemistries were proposed for the Co(II), Ni(II) and Cu(II) on the basis of spectral and magnetic studies.



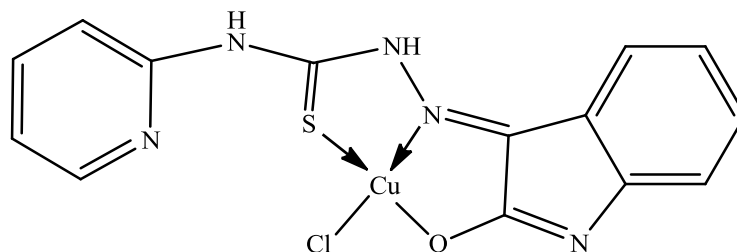
Structure 4: Structure of HBPyT, HPPyT and HPPyS



Co(II), Ni(II), Cu(II), Zn(II), Cd(II) and  $\text{UO}_2^{2+}$  complexes of isatin-4-(2-pyridyl)-3-thiosemicarbazone,  $\text{H}_2\text{IPT}$  (structure 6) have been synthesized and characterized by elemental analysis, molar conductance, spectral (IR, visible and  $^1\text{H}$ NMR) and magnetic moment measurements [35]. IR spectra showed that  $\text{H}_2\text{IPT}$  behaves as ON or SN bidentate and ONS tridentate in a neutral or anionic form. An octahedral structure was proposed for Co(II), Ni(II) and  $\text{Cu}(\text{H}_2\text{IPT})_2(\text{OAc})_2$  complexes and square-planar structure for the  $\text{Cu}(\text{HIPT})\text{Cl}\cdot 2\text{H}_2\text{O}$  complex (Structure 7) on the basis of spectral and magnetic studies.

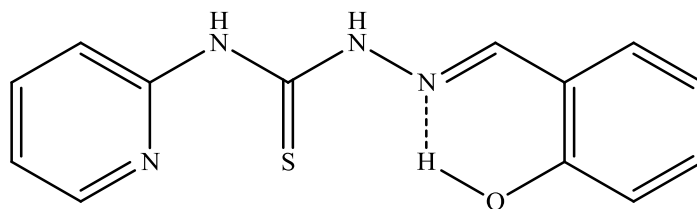


Structure 6: Structure of the ligand (H<sub>2</sub>IPT)

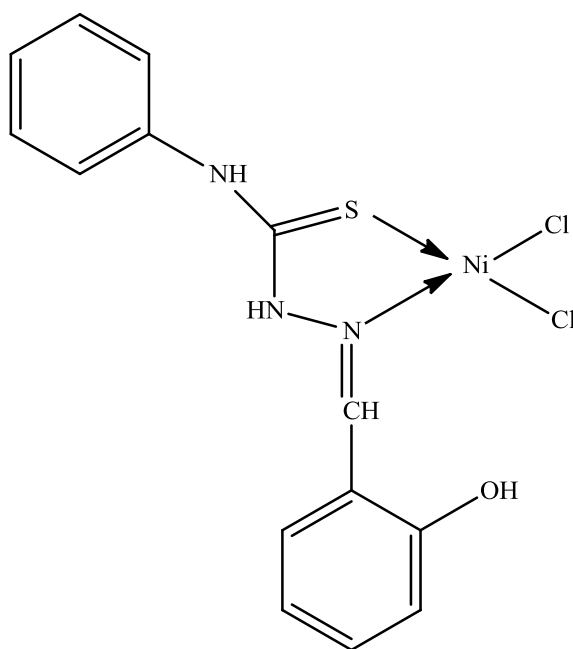


Structure 7: Structure of Cu(HIPT)Cl.2H<sub>2</sub>O

El-Ayaan et al [36] have synthesized Cr(III), Mn(II), Fe(III), Co(II), Ni(II), Cu(II), Zn(II), Cd(II), Hg(II), Pd(II) and dioxouranium(VI), (UO<sub>2</sub><sup>2+</sup>), complexes of 4-(2-pyridyl)-1-salicyladyhyde-3-thiosemicarbazone (H<sub>2</sub>SBT) (structure 8). The isolated complexes were characterized by elemental analysis, molar conductance, spectral (IR, visible and <sup>1</sup>HNMR) and magnetic moment measurements. IR spectral data showed that the ligand behaves in a bi, tri, and/or tetradentate manner. An octahedral structure was proposed for Cr(HSBT)<sub>2</sub>Cl(H<sub>2</sub>O), Mn(HSBT)<sub>2</sub>, Fe(HSBT)Cl<sub>2</sub>.H<sub>2</sub>O, Ni(SBT).2H<sub>2</sub>O and Co(HSBT)<sub>2</sub>Cl.H<sub>2</sub>O, while a square-planar structure was assigned for Ni(H<sub>2</sub>SBT)<sub>2</sub>Cl<sub>2</sub>.H<sub>2</sub>O (structure 9), Pd(HSBT)<sub>2</sub>, Cu<sub>3</sub>(HSBT)<sub>2</sub>Cl<sub>4</sub>.H<sub>2</sub>O and Cu<sub>2</sub>(SBT)(OAc)<sub>2</sub>.2H<sub>2</sub>O complexes.

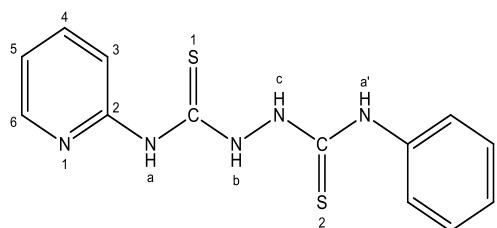


Structure 8: Structure of the ligand (H<sub>2</sub>SPT)



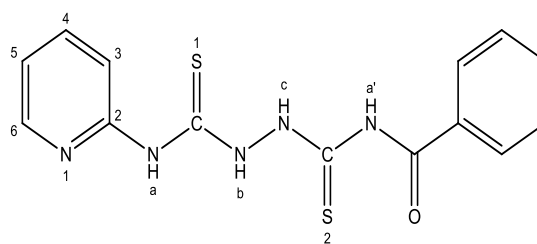
Structure 9: Structure of Ni(H<sub>2</sub>SBT)<sub>2</sub>Cl<sub>2</sub>.H<sub>2</sub>O complex

Yousef et al [37] have prepared four new cobalt (II) complexes of some thiosemicarbazides obtained by the addition of 4-(2-pyridyl)-3-thiosemicarbazide to phenyl isothiocyanate (H<sub>2</sub>PPS), benzoyl isothiocyanate (H<sub>2</sub>PBO), phenyl isocyanate (H<sub>2</sub>APO) and 2-pyridyl isothiocyanate (H<sub>2</sub>PPY) (Structure 10). The complexes were of two types octahedral complexes such as [Co(PPS)(H<sub>2</sub>O)<sub>2</sub>].H<sub>2</sub>O and [Co(HAPO)Cl(H<sub>2</sub>O)<sub>2</sub>].H<sub>2</sub>O (Structure 11) and tetrahedral complexes such as [Co(PBO)(H<sub>2</sub>O)](H<sub>2</sub>O)<sub>2</sub> and [Co(HPPY)Cl(H<sub>2</sub>O)].H<sub>2</sub>O (Structure 12). In the octahedral complexes, H<sub>2</sub>PPS acted as dianionic tetradentate SSNN and H<sub>2</sub>APO acted as mono-anionic tridentate NON. In the tetrahedral complexes, H<sub>2</sub>PBO acted as dianionic tridentate NSO and H<sub>2</sub>PPY acted as mono-anionic bidentate NS. The modeling studies confirmed the geometry of the ligands and their investigated complexes. From TG and DTA studies, kinetic parameters are determined using Coats–Redfern and Horowitz–Metzger methods.



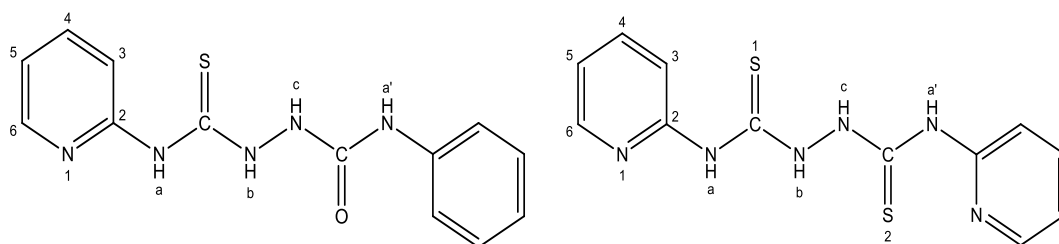
*N*<sup>1</sup>-phenyl-*N*<sup>2</sup>-(pyridin-2-yl)hydrazine-1,2-bis(carbothioamide)

(H<sub>2</sub>PPS)



*N*-phenyl-2-(2-(pyridin-2-ylcarbamoithioyl)hydrazinyl)-2-thioacetamide

(H<sub>2</sub>PBO)

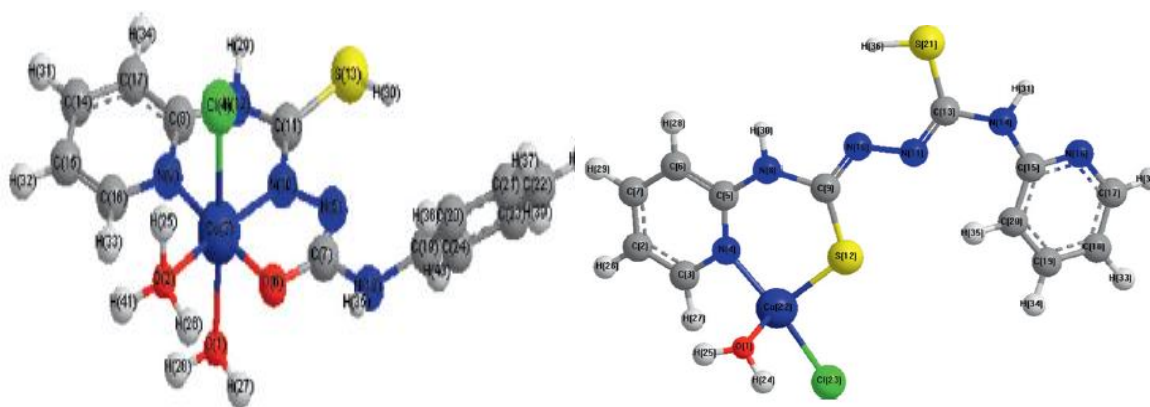


*N*-phenyl-2-(pyridin-2-ylcarbamothioyl)hydrazinecarboxamide 1-(amino-*N*-(pyridin-2-yl)methanethio)-4-(pyridin-2-yl)thiosemicarbazide

(H<sub>2</sub>APO)

(H<sub>2</sub>PPY)

Structure 10: structure of H<sub>2</sub>PPS, H<sub>2</sub>PBO, H<sub>2</sub>APO and H<sub>2</sub>PPY.



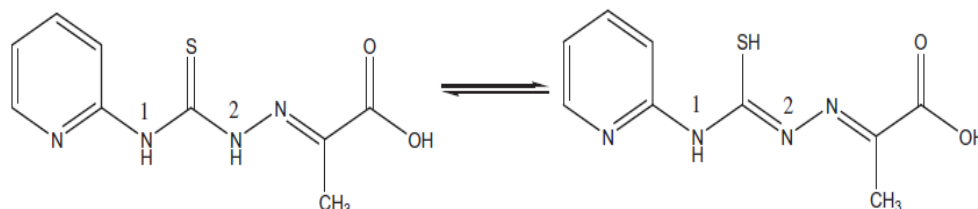
Structure 11: Molecular modeling of [Co(HAPO)Cl(H<sub>2</sub>O)<sub>2</sub>](H<sub>2</sub>O) complex

Structure 12: Molecular modeling of [Co(HPPY)Cl(H<sub>2</sub>O)](H<sub>2</sub>O) complex

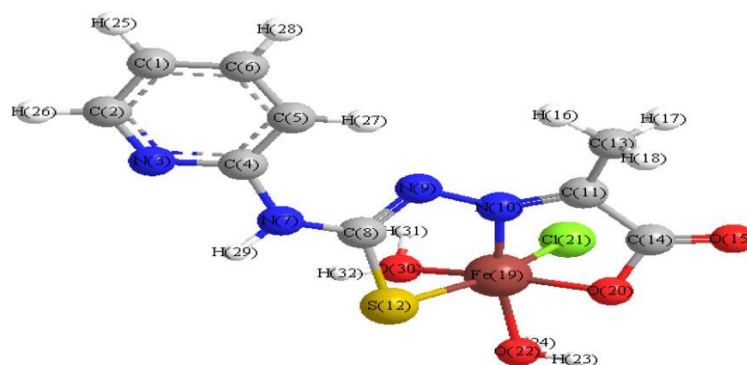
Yousef et al [38] have prepared [Co(HPTP)Cl(H<sub>2</sub>O)<sub>2</sub>], [Cu(HPTP)Cl], [Cd(HPTP)Cl](H<sub>2</sub>O)<sub>4</sub>, [Fe(PTP)Cl(H<sub>2</sub>O)<sub>2</sub>](H<sub>2</sub>O), [UO<sub>2</sub>(HPTP) (OAc)(H<sub>2</sub>O)<sub>2</sub>] complexes of Schiff-bases derived from 4-(2-pyridyl)-3-thiosemicarbazide and pyruvic acid (H<sub>2</sub>PTP) (Structure 13). Schiff-base exhibit thiol–thione tautomerism wherein sulfur plays an important role in the coordination. The coordination possibility of the Schiff-bases towards metal ions have been proposed in the light of elemental analyses, spectral (IR, UV–vis, <sup>1</sup>H NMR, <sup>13</sup>C NMR and ESR), magnetic and thermal studies. IR spectra show that H<sub>2</sub>PTP is coordinated to the metal ions in a mono or binate tridentate manner. An octahedral structure was proposed for Co(II) and [Fe(PTP)Cl(H<sub>2</sub>O)<sub>2</sub>](H<sub>2</sub>O) (Structure 14) complexes and square-planar structure for the [Cu(HPTP)Cl] complex (Structure 15) on the basis of spectral and magnetic studies. The molecular parameters: total energy, binding energy, isolated atomic energy, electronic energy, heat of formation, dipole moment, HOMO and LUMO were calculated for the ligand and its complexes. Furthermore, the kinetic and thermodynamic parameters for the different decomposition steps were calculated



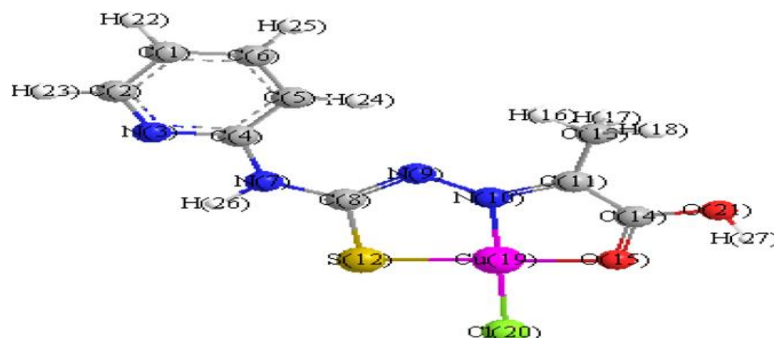
using the Coats–Redfern and Horowitz–Metzger methods. The synthesized ligand, in comparison to its metal complexes is screened for its antibacterial activity against bacterial species, *Bacillus thuringiensis*, *Staphylococcus aureus*, *Pseudomonas aeruginosa* and *Escherichia coli*.



Structure 13: Structure of the free ligand ( $H_2PTP$ ): thione–thiol tautomerism.



Structure 14: Molecular modeling of  $[Fe(PTP)Cl(H_2O)_2](H_2O)$ .



Structure 15: Molecular modeling of  $[Cu(HPTP)Cl]$ .

## 2. Experimental

### 2.1. Physical measurements

All the chemicals were purchased from Aldrich and Fluka and used without further purification. Elemental analyses (C, H) were performed with a Perkin-Elmer 2400 series II analyzer. IR spectra ( $4000 - 400 \text{ cm}^{-1}$ ) for KBr discs were recorded on a Mattson 5000 FTIR spectrophotometer. Electronic spectra were recorded on a

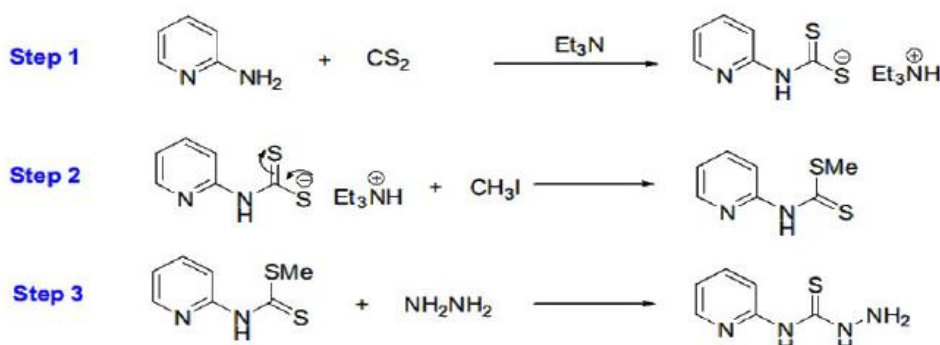
Unicam UV-Vis spectrophotometer UV2. Magnetic susceptibilities were measured with a Sherwood scientific magnetic susceptibility balance at 298 K.  $^1\text{H}$ NMR measurements in  $d_6$ -DMSO at room temperature were carried out on a Varian Gemini WM-300 MHz spectrometer.

## 2.1. Synthesis of ligands and their Ni(II) complexes

### 2.1.1. Synthesis of ligands

#### 2.1.1.1 Synthesis of 4-(2-pyridyl)-3-thiosemicarbazide (PTC)

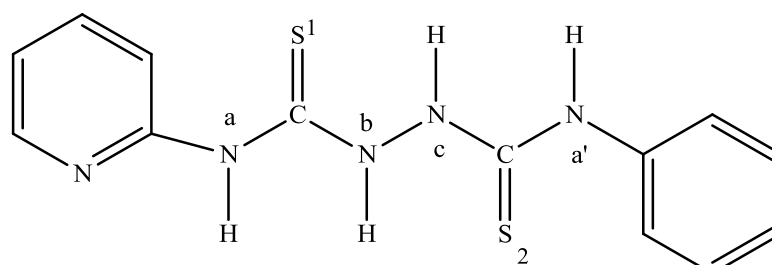
4-(2-pyridyl)-3-thiosemicarbazide was synthesized according to the general literature method [39].



Preparation of 4-(2-pyridyl)-3-thiosemicarbazide (PTC).

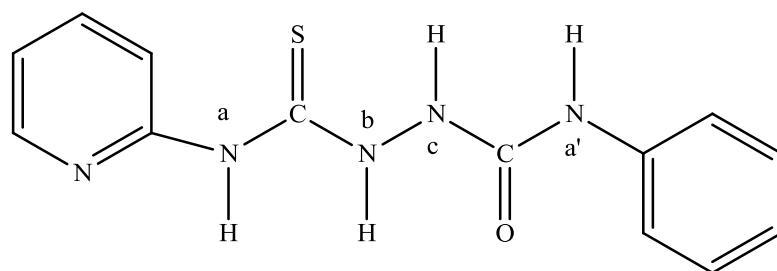
#### 2.1.1.2 Synthesis of ( $\text{H}_2\text{PPS}$ , $\text{H}_2\text{PBO}$ , $\text{H}_2\text{APO}$ and $\text{H}_2\text{PPY}$ ) Ligands

An equimolar of 4-(2-pyridyl)-3-thiosemicarbazide (1.6g, 100 mmol) and each of the compounds phenyl isothiocyanate, benzoyl isothiocyanate, phenyl isocyanate and methyl-2-pyridyldithiocarbamate was heated under reflux for 2-4 hrs. After cooling, the obtained solids were filtered, dried and recrystallized. The organic ligands used in the present investigation are represented by the following structural formulae:



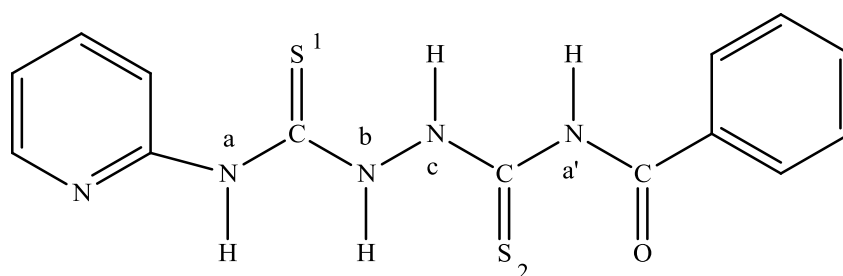
1-(aminoN-phenylmethanethio)-4-(pyridine-2-yl)thiosemicarbazide

(H<sub>2</sub>PPS)



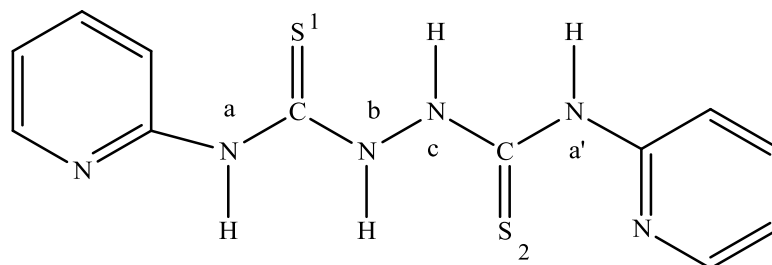
N-phenyl-2-(pyridine-2-ylcarbamothioyl) hydrazinecarboxamide

(H<sub>2</sub>PBO)



1-(amino(thioformyl)-N-phenylform)-4-(pyridine-2-yl)thiosemicarbazide

(H<sub>2</sub>APO)



1-(aminoN-(pyridine-3-yl)methanethio)-4-(pyridine-yl)thiosemicarbazide

(H<sub>2</sub>PPY)

## 2.2 Synthesis of Ni(II) complexes

All complexes were prepared by refluxing equimolar amounts of the ligands and NiCl<sub>2</sub> · (H<sub>2</sub>O)<sub>6</sub> in 30 ml ethanol or aqueous ethanol (15:15 ml) for 2-3 hrs. The method was applied for the preparation of all complexes. The precipitate was filtered off, washed with hot ethanol and finally dried in a vacuum desiccator over anhydrous CaCl<sub>2</sub> (Table 1).

### 3. Results and discussion

#### 3.1. SPECTRAL (IR, VISIBLE AND <sup>1</sup>HNMR) AND MAGNETIC DATA OF LIGANDS AND ITS METAL COMPLEXES

##### 3.2.1 Infrared and <sup>1</sup>HNMR spectra of ligands:

The most important IR bands of ligands are recorded in Table 2. The spectra exhibit three bands between 3234-3100 cm<sup>-1</sup> due to  $\nu(\text{NH})$  groups. The  $\nu/\delta$  modes of (CN) group of pyridyl ring are found at  $\approx 1560$  and 620-635 cm<sup>-1</sup>.

An inspection on the Table 2 describing the IR spectra of H<sub>2</sub>PPS, H<sub>2</sub>PBO, and H<sub>2</sub>PPY indicates that the appearance of strong bands assigned to  $\nu(\text{C}=\text{N})$  (azomethine),  $\nu(\text{C}-\text{S})$  and  $\nu(\text{SH})$  as well as (C=S) modes suggested that these ligands exist in thione-thiol form. As these ligands contain two C=S groups, (C=S)<sup>1</sup> and (C=S)<sup>2</sup>, we proposed that (C=S)<sup>1</sup> is in thione form and (C=S)<sup>2</sup> in thiol form. This assumption is confirmed by the absence of bands due to  $\nu(\text{C}=\text{N})$  (azomethine),  $\nu(\text{C}-\text{S})$  and  $\nu(\text{SH})$  vibrational modes in the IR spectrum of the start (4-pyridyl thiosemicarbazide) [40] and the missing of SH signal in the <sup>1</sup>HNMR spectrum of H<sub>2</sub>APO.

In the IR spectrum of H<sub>2</sub>PPY the band due to  $\nu(\text{C}=\text{N})$  mode was difficult to recognize because it is overlapped with  $\nu(\text{C}=\text{C})$  of pyridyl ring. Also, the appearance of  $\nu(\text{C}-\text{S})$  at higher wavenumber, 683 cm<sup>-1</sup> than that of other ligands may be due to the presence of pyridyl groups at the extremes of H<sub>2</sub>PPY structure which act as electron withdrawing groups.

The IR spectrum of H<sub>2</sub>APO exhibits a sharp band at 3521 cm<sup>-1</sup> due to  $\nu(\text{OH})$  in addition to the  $\nu(\text{CO})$  band at 1675 cm<sup>-1</sup> suggested the keto – enol tautomerism .

The  $^1\text{H}$ NMR spectra of  $\text{H}_2\text{PPS}$ ,  $\text{H}_2\text{PBO}$  and  $\text{H}_2\text{PPY}$  derivatives in  $\text{DMSO-d}_6$  show two signals at approximately  $\delta$  11.10 and 15.4 ppm relative to TMS that disappear upon adding  $\text{D}_2\text{O}$ . These signals are attributed to the amide ( $\text{NH}_{\text{a,a}'}$ ) and thiol ( $\text{SH}$ ) protons. The signal at  $\delta$  8.29 ppm is due to the ( $\text{NH}_{\text{b}}$ ), while the multiplets at 7.00 - 7.86 ppm are characteristic to the pyridine ring protons [41]. The appearance of signal at  $\delta$  15.4 ppm in the spectrum of  $\text{H}_2\text{PPY}$  due to  $\text{SH}$  proton and a signal at  $\delta$  12.57 ppm due to  $\text{OH}$  group in the spectrum of  $\text{H}_2\text{APO}$  confirm the thiol - enol tautomerism in solution.

### 3.2.2. Nickel complexes

#### (i) Infrared Spectra:

A careful comparison of the IR spectra of ligands and its  $\text{Ni(II)}$  complexes in Table 2 gave a good insight on the mode of bonding and the nature of metal-ligand bond. The IR spectra of the investigated  $\text{Ni(II)}$  Complexes showed that the ligand  $\text{H}_2\text{PPS}$  acts as binegative NSSN tetradentate *via* ( $\text{C}=\text{N}$ ), two ( $\text{C}=\text{S}$ ) in thiol form with loss of both protons and new ( $\text{C}=\text{N}$ )\* groups.  $\text{H}_2\text{PBO}$  behaves as binegative tetradentate coordinating through the ( $\text{C}=\text{N}$ )<sub>py</sub>, one ( $\text{C}=\text{S}$ ) group in thione form, the second one in thiol form and enolized ( $\text{C}=\text{O}$ ) groups.  $\text{H}_2\text{APO}$  acts as mononegative tridentate *via* the ( $\text{C}=\text{N}$ )<sub>py</sub>, enolized ( $\text{C}=\text{O}$ ) and ( $\text{NH}_{\text{b}}$ ) groups while  $\text{H}_2\text{PPY}$  acts as a binegative pentadentate *via* the two ( $\text{C}=\text{N}$ )<sub>py</sub>, new ( $\text{C}=\text{N}$ )\* and two ( $\text{C}=\text{S}$ ) groups both in thiol form.

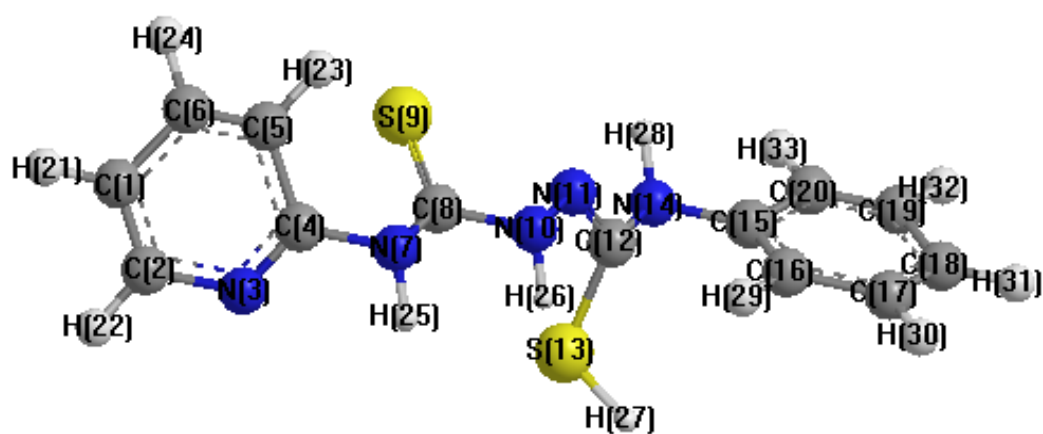


Fig. 1. Molecular modeling of  $\text{H}_2\text{PPS}$

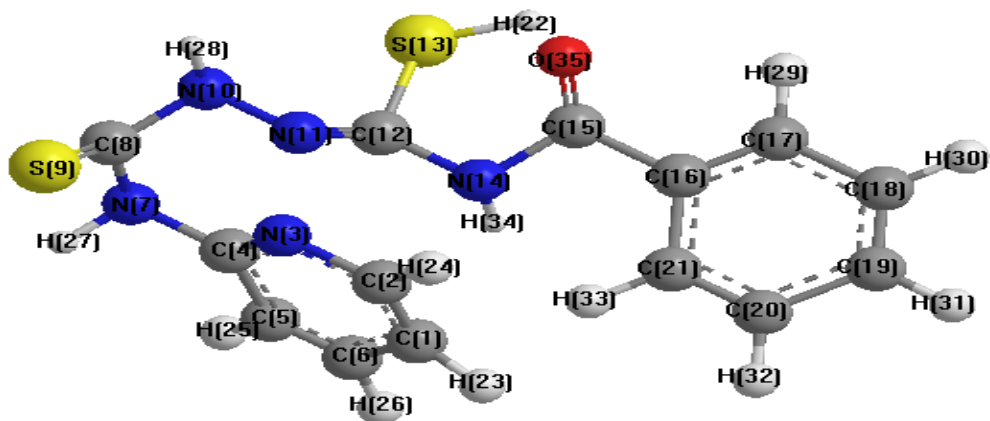


Fig. 2. Molecular modeling of H<sub>2</sub>PBO

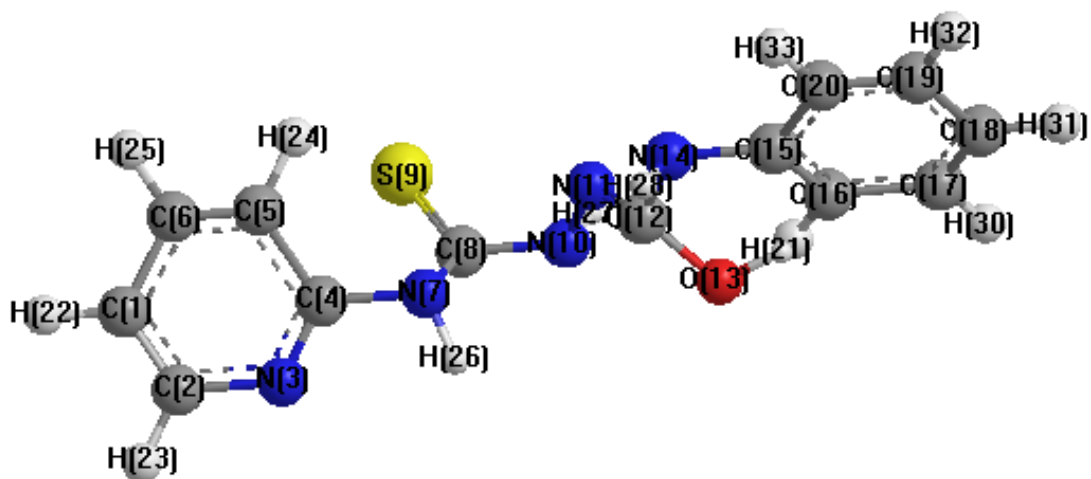


Fig. 3. Molecular modeling of H<sub>2</sub>APO

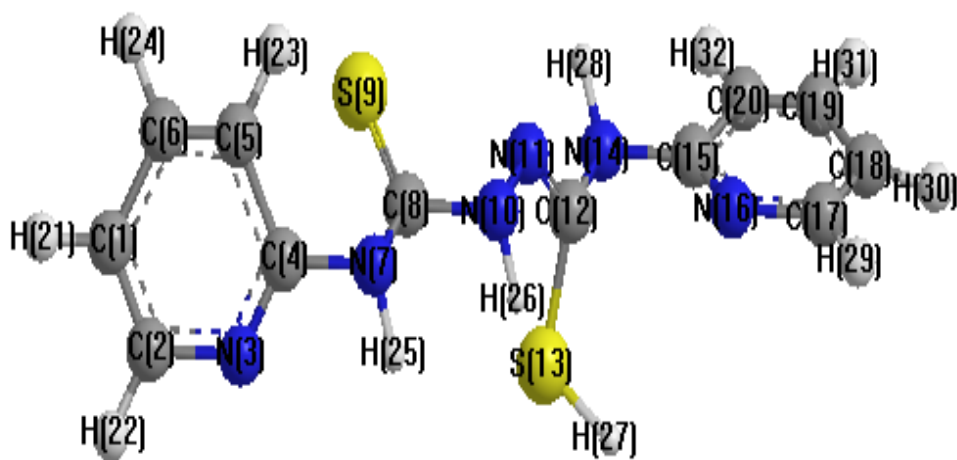


Fig. 4. Molecular modeling of H<sub>2</sub>PPY

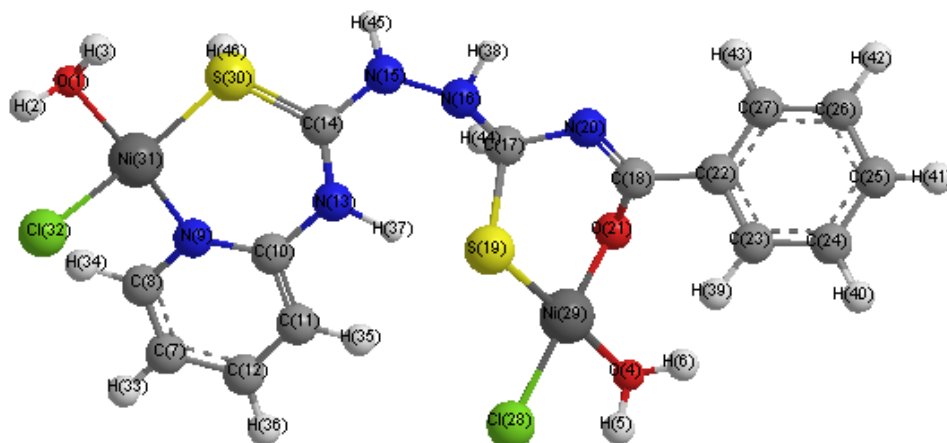


Fig. 5. Molecular modeling of  $[\text{Ni}_2(\text{PBO})\text{Cl}_2(\text{H}_2\text{O})_2]$  complex

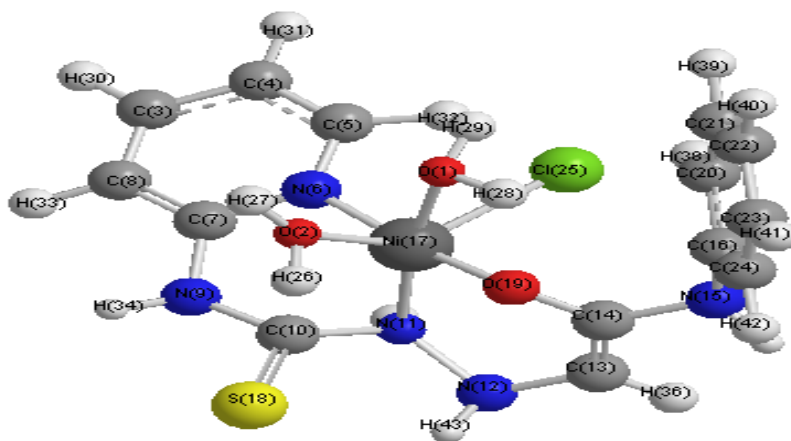


Fig. 6. Molecular modeling of  $[\text{Ni}(\text{HAPO})\text{Cl}(\text{H}_2\text{O})_2](\text{H}_2\text{O})$  complex

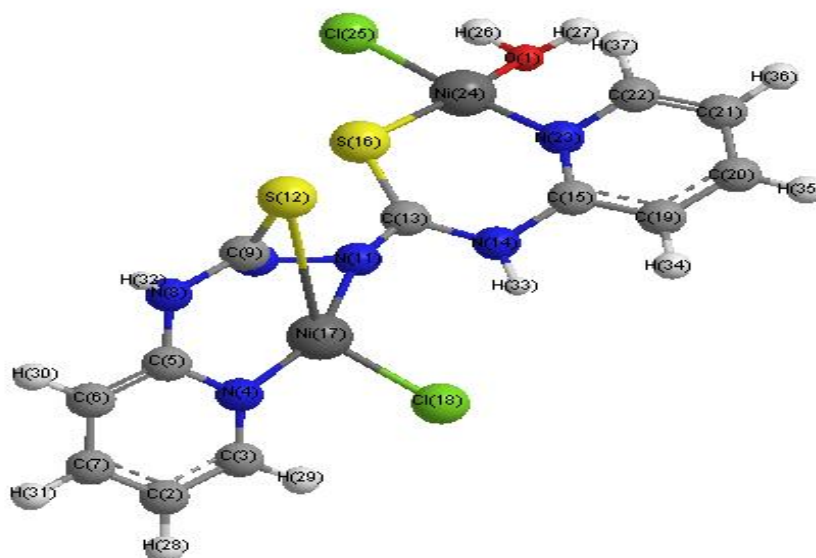


Fig. 7. Molecular modeling of  $[\text{Ni}_2(\text{PPY})\text{Cl}_2(\text{H}_2\text{O})](\text{H}_2\text{O})$  complex

This is supported by the following:

(i) Disappearance of bands due to  $\nu(\text{NH})^b$  and (C=S) modes with appearance of new bands at 1543 and 1614  $\text{cm}^{-1}$  due to (C=N-N=C) and 622-727  $\text{cm}^{-1}$  assignable to (C-S) vibrations in the IR spectra of  $[\text{Ni}(\text{PPS})(\text{H}_2\text{O})_2]$  and  $[\text{Ni}_2(\text{PBO})\text{Cl}_2(\text{H}_2\text{O})_2]$  complexes, respectively.

(ii) The presence of the imine  $\nu(\text{CN})$  band at 1646  $\text{cm}^{-1}$  in the spectrum of  $\text{H}_2\text{PPS}$  and at 1616  $\text{cm}^{-1}$  in the IR spectrum of  $[\text{Ni}(\text{PPS})(\text{H}_2\text{O})_2]$  complex support coordination of the azomethine nitrogen.

(iii) Shift of  $\nu(\text{N-N})$  band to higher wavenumber.

(iv) Shift of deformation mode of pyridine ring either to lower or higher wavenumber is an indication of coordination of the metal ion to pyridine nitrogen.

(v) The disappearance of  $\nu(\text{C-OH})$  band in the IR spectra of  $[\text{Ni}_2(\text{PBO})\text{Cl}_2(\text{H}_2\text{O})_2]$  and  $[\text{Ni}(\text{HAPO})\text{Cl}(\text{H}_2\text{O})_2](\text{H}_2\text{O})$  complexes suggests its coordination with displacement of proton. Also, the shift of  $\nu(\text{C-O})$  to higher wavenumber confirmed this behavior for these ligands. Moreover, the bands at 540 and 553  $\text{cm}^{-1}$ , respectively due to  $\nu(\text{M-O})$  reveal this coordination.

In all the above complexes, the appearance of band in the region 453-480  $\text{cm}^{-1}$  assigned to  $\nu(\text{M-N})$  supports the proposed mode of coordination. Water of coordination is indicated by the broad bands at  $\approx 3396\text{-}3430$   $\text{cm}^{-1}$ , 846-875  $\text{cm}^{-1}$  and  $\approx 513\text{-}523$  regions in the IR spectra of the studied complexes are referred to  $\nu(\text{OH})$ ,  $\Delta(\text{H}_2\text{O})$ ,  $\rho_r(\text{H}_2\text{O})$  and  $\rho_w(\text{H}_2\text{O})$  vibrations. On the other hand, water of crystallization in complexes is indicated by a broad band at 3478-3490  $\text{cm}^{-1}$  in the IR spectra. To verify between the coordinated water and crystallized water, TGA studies were done.

## **(ii) Electronic spectra and magnetic moments:**

The electronic spectra of thiosemicarbazides under study and their Ni(II) complexes are displayed in DMF and Nujol mull. Magnetic moments, band positions and ligand field parameters values of the investigated complexes are recorded in Table 3. The electronic spectra of  $[\text{Ni}(\text{PPS})(\text{H}_2\text{O})_2]_n$  and  $[\text{Ni}(\text{HAPO})\text{Cl}(\text{H}_2\text{O})_2](\text{H}_2\text{O})$  complexes exhibited two bands in the 14409 and 21097  $\text{cm}^{-1}$  for the first and at 15060



and 19084 cm<sup>-1</sup> regions for the second assignable to the  ${}^3A_{2g} \rightarrow {}^3T_{1g}(F)(v_2)$  and  ${}^3A_{2g} \rightarrow {}^4T_{1g}(P)(v_3)$  transitions, respectively characteristic for Ni(II) octahedral complexes [42]. The subnormal magnetic moment value of the first complex (2.5 B.M.) may be attributed to the polymeric structure.

The complexes,  $[Ni_2(PBO)Cl_2(H_2O)_2]$  and  $[Ni_2(PPY)Cl_2(H_2O)](H_2O)$  have a magnetic moment values (3.68 and 3.58 B.M.), respectively which are lower than the measured value per one nickel atom which are in turn less than that reported for d<sup>8</sup>-octahedral and /or tetrahedral complexes and higher than diamagnetic square-planar complexes. The values may suggest the existence of the complexes in a mixed stereochemistry [43]. Such assumption is also confirmed by two bands at 18050 and 18138 cm<sup>-1</sup> for the two complexes assignable to  ${}^3T_1 \rightarrow {}^3T_1(P)$  transition consistent with a tetrahedral configuration in addition to another two bands at 22510 and 22833 cm<sup>-1</sup>, respectively referring to a square planar geometry [44].

### 3.3 Molecular Modeling:

#### 3.3.1. Molecular Modeling of the ligands:

The molecular numbering of each ligand is shown in Figs. (1 - 4). Some parameters like total energy, binding energy, electronic energy, heat of formation, dipole moment, highest occupied molecular orbitals (HOMO) and lowest unoccupied molecular orbitals (LUMO) of each ligand and its complexes have been calculated. The lower HOMO energy values show that molecules donating electron ability is the weaker. On contrary, the higher HOMO energy implies that the molecule is a good electron donor. LUMO energy presents the ability of a molecule receiving electron [45].

Analysis of the data in Tables (4 – 10) for bond length and bond angle of each bond in the ligand molecule, one can conclude the following remarks:

1- All bond lengths of the C-N bonds are nearly similar, except N(11)-C(12) which are smaller than the rest due to the double bond character in case of all ligands.

2-All bond lengths of the C-S bonds are nearly similar, except C(8)-S(9) which are smaller than the rest due to the double bond character in case of all ligands.

3-The N-N bond lengths are nearly similar, except for H<sub>2</sub>PPY which is larger than the rest.

### 3.3.5 Molecular Modeling of Nickel complexes:

The molecular structure along with atom numbering of ligands and its Ni(II) complex are shown in Figs. (5 – 7).

Analysis of the data in Tables (11 - 16) calculated for the bond lengths and angles for the bond, one can conclude the following remarks:

1- The bond angles of the thiosemicarbazide moiety are altered somewhat upon coordination; the largest change affects N(3)-C(4)-N(7), N(7)-C(8)-N(10) and N(10)-N(11)-C(12) angles which are reduced from 111.5°, 114° and 124° on ligand to 125.5°, 120.4 and 112.8° in case of [Ni<sub>2</sub>(PBO)Cl<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>] complex, C(4)-N(7)-C(8) and N(10)-N(11)-C(12) from 126.7° and 122.5° on ligand to 118.5° and 112.9° in case of [Ni(HAPO)Cl(H<sub>2</sub>O)<sub>2</sub>](H<sub>2</sub>O) and C(8)-N(10)-N(11) from 116° on ligand to 132° in case of [Ni<sub>2</sub>(PPY)Cl<sub>2</sub>(H<sub>2</sub>O)](H<sub>2</sub>O) as a consequence of bonding.

2- All the active groups taking part in coordination have bonds longer than that already exist in the ligand (like C=S, N-H, (C=N)<sub>py</sub> and C=O). Short bond lengths are observed in all complexes.

Table 1. Analytical and physical data of H<sub>2</sub>PPS, H<sub>2</sub>PBO, H<sub>2</sub>APO and H<sub>2</sub>PPY and their Ni(II) complexes

Compound		Color	M.p. (°C)	Found (Calcd.) %				Yield (%)
Empirical formula, (F. Wt)	M			Cl	C	H		
H <sub>2</sub> PPS C <sub>13</sub> H <sub>13</sub> N <sub>5</sub> S <sub>2</sub> (303.41)	yellow	270	-	-	51.33 (51.46)	4.19 (4.32)	93	
[Ni(PPS)(H <sub>2</sub> O) <sub>2</sub> ] C <sub>13</sub> H <sub>15</sub> NiN <sub>5</sub> S <sub>2</sub> (396.12)	Pale brown	>300	14.53 (14.8)	-	39.88 (39.42)	3.99 (3.82)	82	
H <sub>2</sub> PBO C <sub>14</sub> H <sub>13</sub> N <sub>5</sub> OS <sub>2</sub> (331.42)	yellow	270	-	-	50.81 (50.74)	3.88 (3.95)	90	
[Ni <sub>2</sub> (PBO)Cl <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ](H <sub>2</sub> O) C <sub>14</sub> H <sub>17</sub> Ni <sub>2</sub> N <sub>5</sub> O <sub>4</sub> S <sub>2</sub> Cl <sub>2</sub> (572.74)	Pale brown	>300	20.31 (20.5)	12.11 (12.4)	29.21 (29.36)	2.86 (2.99)	87	
H <sub>2</sub> APO C <sub>13</sub> H <sub>13</sub> N <sub>5</sub> OS (287.27)	White	182	-	-	54.51 (54.35)	4.43 (4.56)	90	
[Ni(HAPO)Cl(H <sub>2</sub> O) <sub>2</sub> ](H <sub>2</sub> O) C <sub>13</sub> H <sub>18</sub> NiN <sub>5</sub> O <sub>4</sub> SCl (434.45)	Dark yellow	>300	13.78 (13.5)	8.33 (8.16)	35.88 (35.94)	3.96 (4.18)	89	
H <sub>2</sub> PPY C <sub>12</sub> H <sub>12</sub> N <sub>6</sub> S <sub>2</sub> (304.35)	yellow	310	-	-	47.47 (47.31)	4.55 (3.97)	93	
[Ni <sub>2</sub> (PPY)Cl <sub>2</sub> (H <sub>2</sub> O)](H <sub>2</sub> O) C <sub>12</sub> H <sub>14</sub> Ni <sub>2</sub> N <sub>6</sub> O <sub>2</sub> S <sub>2</sub> Cl <sub>2</sub> (527.67)	brown	>300	21.8 (22.2)	13.1 (13.4)	27.21 (27.37)	2.62 (2.67)	83	

Table 2. Assignments of IR spectral bands of H<sub>2</sub>PPS, H<sub>2</sub>PBO, H<sub>2</sub>APO and H<sub>2</sub>PPY and their Ni(II) complexes

Compound	$\nu(\text{NH})^{\text{a}}$	$\nu(\text{NH})^{\text{b,c}}$	$\nu(\text{C}=\text{N})_{\text{py}}$	$\nu(\text{C}=\text{N})^*$	$\nu(\text{C}=\text{S})$	$\nu(\text{C}=\text{N})$	$\delta(\text{C}=\text{N})_{\text{py}}$	$\nu(\text{N}-\text{N})$	$\nu(\text{C}=\text{O})$	$\nu(\text{C}-\text{O})$	$\nu(\text{OH})$	$\nu(\text{C}-\text{S})$
H <sub>2</sub> PPS	3160,3099	3220	1562	-	860	1646	624	971	-	-	-	660
[Ni(PPS)(H <sub>2</sub> O) <sub>2</sub> ]	3197	3270	1562	1543	-	1616	614	993	-	-	-	727
H <sub>2</sub> PBO	3118	3228	1562	-	861	1641	630	990	1672	1164	3337	660
[Ni <sub>2</sub> (PBO)Cl <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ](H <sub>2</sub> O)	-	3280	1544	1614	846	1634	638	1030	-	1192	-	709
H <sub>2</sub> APO	3158	3239	1542	-	865	-	634	1008	1675	1243	3363	-
[Ni(HAPO)Cl(H <sub>2</sub> O) <sub>2</sub> ](H <sub>2</sub> O)	-	-	1562	-	870	1616	606	1034	-	1232	-	-
H <sub>2</sub> PPY	3174	3234	1562	-	861	-	625	1000	-	-	-	683
[Ni <sub>2</sub> (PPY)Cl <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ](H <sub>2</sub> O)	3326	-	1565	-	-	1617	602	1045	-	-	-	622

Compound	Solvent	Band position (cm <sup>-1</sup> )	Dq	B	β	μ <sub>eff</sub> (B.M.)
H <sub>2</sub> PPS	DMF	35211 31847 29069	-	-	-	-
	Nujol	-	-	-	-	-
[Ni(PPS)(H <sub>2</sub> O) <sub>2</sub> ]		35211 31847 29069				
	DMF	25252 24390 21097	858.5	876	0.85	
		16891 14409				2.5
	Nujol	23697 21739 20661 14451	834.2	851.2	0.83	
H <sub>2</sub> PBO	DMF	35461 32680 29070	-	-	-	-
	Nujol	-	-	-	-	-
[Ni <sub>2</sub> (PBO)Cl <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ]		35211 31645 28409				
	DMF	22510 18056	-	-	-	3.68
	Nujol	25773 23041 17422	-	-	-	
H <sub>2</sub> APO	DMF	35211 32051	-	-	-	-
	Nujol	-	-	-	-	-
[Ni(HAPO)Cl(H <sub>2</sub> O) <sub>2</sub> ](H <sub>2</sub> O)		35211 32467 27624				
	DMF	19084 16835 15060	922	941	0.91	3.01
	Nujol	24876 22624 16722	876	894	0.87	
H <sub>2</sub> PPY	DMF	35211 30120 18050	-	-	-	-

	Nujol	-	-	-	-
		35211	31847	29585	
	DMF	26178	22833	-	-
[Ni <sub>2</sub> (PPY)Cl <sub>2</sub> (H <sub>2</sub> O)](H <sub>2</sub> O)		18138			3.56
	Nujol	24390	20661	16892	

Table 4. Bond length of H<sub>2</sub>PPS

Bond	Length (Å)	Bond	Length (Å)
C(4)-N(7)	1.34	C(12)-N(14)	1.45
N(7)-C(8)	1.40	N(14)-C(15)	1.46
C(8)-S(9)	1.64	C(12)-S(13)	1.78
C(8)-N(10)	1.44	N(11)-C(12)	1.31
N(10)-N(11)	1.39	C(4)-N(3)	1.37

Table 5. Bond angles of H<sub>2</sub>PPS

Angle	Degree(°)	Angle	Degree (°)
C(4)-N(7)-C(8)	127.58	N(7)-C(8)-N(10)	109.56
C(8)-N(10)-N(11)	116.80	N(10)-N(11)-C(12)	123.27
N(11)-C(12)-N(14)	112.65	C(12)-N(14)-C(15)	116.90

Bond	Length (Å)	Bond	Length (Å)
C(4)-N(7)	1.43	N(7)-C(8)	1.38
C(8)-S(9)	1.66	C(8)-N(10)	1.45
N(10)-N(11)	1.39	N(11)-C(12)	1.31
C(12)-N(14)	1.45	C(12)-S(13)	1.77
N(14)-C(15)	1.44	C(15)-O(35)	1.22
C(15)-C(16)	1.49	C(4)-N(3)	1.37

Table 7. Bond angles of H<sub>2</sub>PBO

Angle	Degree(°)	Angle	Degree (°)
C(4)-N(7)-C(8)	126.6	N(7)-C(8)-N(10)	113.97
C(8)-N(10)-N(11)	117.50	N(10)-N(11)-C(12)	124.00
N(11)-C(12)-N(14)	111.85	C(12)-N(14)-C(15)	121.43
N(14)-C(15)-C(16)	116.58	N(14)-C(15)-O(35)	119.29

Table 8. Bond length of H<sub>2</sub>APO

Bond	Length (Å)	Bond	Length (Å)
C(4)-N(7)	1.43	N(7)-C(8)	1.38
C(8)-S(9)	1.66	C(8)-N(10)	1.44
N(10)-N(11)	1.41	N(11)-C(12)	1.31
C(12)-O(13)	1.36	C(12)-N(14)	1.44
N(14)-C(15)	1.45	C(4)-N(3)	1.37

Table 3.3.1.10 Bond angles of H<sub>2</sub>APO

Angle	Degree(°)	Angle	Degree (°)
C(4)-N(7)-C(8)	126.73	N(7)-C(8)-N(10)	114.18
C(8)-N(10)-N(11)	116.74	N(10)-N(11)-C(12)	122.49
N(11)-C(12)-O(13)	120.26	N(11)-C(12)-N(14)	119.30
C(12)-N(14)-C(15)	118.43	N(7)-C(8)-S(9)	128.82

Table 9. Bond length of H<sub>2</sub>PPY

Bond	Length (Å)	Bond	Length (Å)
C(4)-N(7)	1.43	N(7)-C(8)	1.40
C(8)-S(9)	1.64	C(8)-N(10)	1.44
N(10)-N(11)	1.39	N(11)-C(12)	1.31
C(12)-S(13)	1.77	C(12)-N(14)	1.44
N(14)-C(15)	1.42	C(4)-N(3)	1.37

Table 10. Bond angles of H<sub>2</sub>PPY

Angle	Degree(°)	Angle	Degree (°)
C(4)-N(7)-C(8)	127.58	N(7)-C(8)-N(10)	109.42
C(8)-N(10)-N(11)	117.34	N(10)-N(11)-C(12)	123.12
N(11)-C(12)-N(14)	108.89	C(12)-N(14)-C(15)	123.73



Table 11. Bond length of  $[\text{Ni}_2(\text{PBO})\text{Cl}_2(\text{H}_2\text{O})_2]$ 

Bond	Length (Å)	Bond	Length (Å)
Cl(28)-Ni(29)	2.21	N(13)-C(14)	1.37
O(4)-Ni(29)	1.89	N(15)-C(14)	1.39
O(21)-Ni(29)	1.83	C(18)-O(21)	1.35
S(19)-Ni(29)	2.20	N(15)-N(16)	1.46
S(30)-Ni(31)	2.22	N(16)-C(17)	1.49
O(1)-Ni(31)	1.88	C(17)-S(19)	1.92
Cl(32)-Ni(31)	2.22	C(17)-N(20)	1.46
N(9)-Ni(31)	1.82	N(20)-C(18)	1.33
S(30)-C(14)	1.79		

Table 12. Bond angles of  $[\text{Ni}_2(\text{PBO})\text{Cl}_2(\text{H}_2\text{O})_2]$ 

Angle	Degree(°)	Angle	Degree (°)
N(9)-Ni(31)-S(30)	91.36	N(20)-C(18)-O(21)	125.47
N(9)-Ni(31)-Cl(32)	96.36	C(18)-O(21)-Ni(29)	113.82
Cl(32)-Ni(31)-O(1)	81.88	O(21)-Ni(29)-O(4)	87.53
S(30)-Ni(31)-O(1)	91.44	O(4)-Ni(29)-Cl(28)	86.50
Ni(31)-S(30)-C(14)	108.53	Cl(28)-Ni(29)-S(19)	91.77
S(30)-C(14)-N(13)	125.54	S(19)-Ni(29)-O(21)	93.95
C(14)-N(15)-N(16)	123.18	C(17)-N(20)-C(18)	116.36
N(15)-N(16)-C(17)	112.83	S(19)-C(17)-N(20)	109.21

Table 13. Bond length of [Ni(HAPO)Cl(H<sub>2</sub>O)<sub>2</sub>](H<sub>2</sub>O)

Bond	Length (Å)	Bond	Length (Å)
N(11)-Ni(16)	1.85	C(10)-S(17)	1.66
O(18)-Ni(16)	1.86	C(10)-N(11)	1.47
Cl(24)-Ni(16)	2.57	N(11)-N(12)	1.49
O(1)-Ni(16)	1.92	N(12)-C(13)	1.45
O(2)-Ni(16)	2.02	C(13)-O(18)	1.27
N(6)-Ni(16)	1.84	C(13)-N(14)	1.38
C(7)-N(9)	1.44	N(14)-C(15)	1.45
N(9)-C(10)	1.44		

Table 14. Bond angles of [Ni(HAPO)Cl(H<sub>2</sub>O)<sub>2</sub>](H<sub>2</sub>O)

Angle	Degree(°)	Angle	Degree (°)
Cl(24)-Ni(16)-O(18)	83.45	N(12)-C(13)-N(14)	119.43
O(1)-Ni(16)-N(6)	89.61	C(13)-N(14)-C(15)	121.29
O(2)-Ni(16)-N(6)	95.32	N(11)-N(12)-C(13)	113.39
O(2)-Ni(16)-N(11)	121.78	C(10)-N(11)-N(12)	119.06
O(18)-Ni(16)-N(11)	90.03	N(9)-C(10)-N(11)	111.49
O(1)-Ni(16)-Cl(24)	68.18	C(7)-N(9)-C(10)	120.93

Table 15 Bond length of  $[\text{Ni}_2(\text{PPY})\text{Cl}_2(\text{H}_2\text{O})](\text{H}_2\text{O})$ 

Bond	Length (Å)	Bond	Length (Å)
N(23)-Ni(24)	1.83	N(10)-C(9)	1.44
S(16)-Ni(24)	2.19	C(9)-N(8)	1.46
Cl(25)-Ni(24)	2.19	N(8)-C(5)	1.43
O(1)-Ni(24)	1.90	C(9)-S(12)	1.65
C(15)-N(14)	1.44	S(12)-Ni(17)	3.58
N(14)-C(13)	1.45	N(4)-Ni(17)	1.80
C(13)-N(11)	1.32	N(11)-Ni(17)	1.87
N(11)-N(10)	1.54	Cl(18)-Ni(17)	2.21

Table 16. Bond angles of  $[\text{Ni}_2(\text{PPY})\text{Cl}_2(\text{H}_2\text{O})](\text{H}_2\text{O})$ 

Angle	Degree(°)	Angle	Degree (°)
O(1)-Ni(24)-N(23)	98.37	Cl(18)-Ni(17)-N(11)	107.54
O(1)-Ni(24)-Cl(25)	81.21	Cl(18)-Ni(17)-N(4)	95.13
S(16)-Ni(24)-Cl(25)	88.26	S(12)-Ni(17)-N(4)	102.66
S(16)-Ni(24)-N(23)	93.13	S(12)-Ni(17)-N(11)	66.80
C(15)-N(14)-C(13)	118.28	N(14)-C(13)-N(11)	112.81
C(13)-N(11)-N(10)	131.99	N(11)-N(10)-C(9)	112.36
N(10)-C(9)-N(8)	109.06	C(9)-N(8)-C(5)	123.83

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