

Synthesis and Characterization of Nickel (II), Cobalt (II), Copper (II) and Zinc (II) Complexes with 5-Chloropyridine-2-Carbaldehydethiosemicarbazone

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Authors' contributions

This work was carried out in collaboration among all authors. All authors read and approved the final manuscript.

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ABSTRACT

5-chloropyridine-2-carbaldehydethiosemicarbazone (HL1) and its nickel(II), cobalt(II), Zinc(II) and copper(II) complexes: $[\text{Ni}(\text{HL}1)_2]$, $[\text{Co}(\text{HL}1)_2]$, $[\text{Zn}(\text{HL}1)_2]$, $[\text{Cu}(\text{HL}1)_2]$, $[\text{Cu}(\text{HL}1)]$, were synthesized and characterized. The ligand has been characterized by elemental analyses, IR, ^1H NMR and Mass spectroscopy. The dentate nature of the ligand is evident from the spectral obtained data and literature.

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1. INTRODUCTION

“Heterocyclic thiosemicarbazone and their metal complexes are among the most widely studied compounds of thiosemicarbazone that containing important hetero atoms like sulphur and nitrogen. Heterocyclic thiosemicarbazone possess Structural simplicity, easy synthetic procedure, shorter course of reaction and wide pharmacological profile make them a class extensively studied and explored. They offer a wide spectrum of pharmacological activities like analgesic and anti-inflammatory [1], anti-viral [2], antibacterial [3], anticonvulsant [4], anti-HIV [5], anti leishmania [6], antifungal [7], anti-malaria [8], anticancer [9], neurotropic [10], anti trypanosomal [11], antitubercular [12], insulin like [13], and human and rat cholinesterase [14] activities”. “Metal complexes of thiosemicarbazones have also been found to be useful in radio pharmacy for therapeutic as well as diagnostic purposes” [15]. “Anti-cancer

properties of these derivatives have been studied widely. Recently, there have been frequent studies of metal complexes of heterocyclic thiosemicarbazones [16] Many of these have featured either 2-formylpyridine [17-20] or 2-acetylpyridine [21-24] thiosemicarbazones; of 2-benzoylpyridine thiosemicarbazone” [25]. “Synthesis, Characterization and Antimicrobial Activities of Co (III) and Fe (III) Complexes of Imino-*N*-heterocyclic Carbenes Ligands [26] and 3D Series Metal Complexes Containing Schiff Base Ligand with 2,2'-Bipyridine: Synthesis, Characterization and Assessment of Antifungal Activity [27] were recently studied”. To our knowledge, studies of the metal complexes of the of chloride substituents at C5 carbon of pyridine-2-carbaldehydethiosemicarbazone and its complexes was not investigated enough. The present communication reports the synthesis, characterization of Ni(II), Co(II) and Cu(II) complexes with 5-chloropyridine-2-carbaldehydethiosemicarbazone.

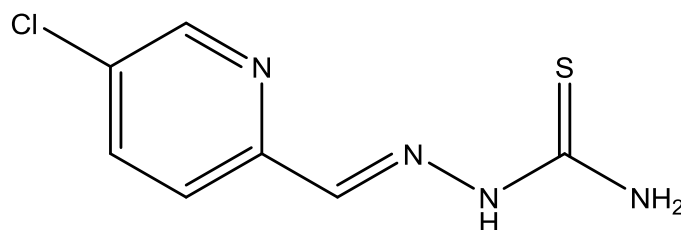


Fig. 1. The structure of 5-Chloro-2-pyridinecarboxaldehyde thiosemicarbazone((E)-2-((5-chloropyridin-2-yl)methylene)hydrazine-1-carbothioamide

2. MATERIALS AND METHODS

2.1 Materials

5-chloropyridine-2-carbaldehyde (Merck) and thiosemicarbazide (Aldrich) were used as received. The metal salts $\text{CoCl}_2 \cdot \text{H}_2\text{O}$, $\text{NiCl}_2 \cdot 4\text{H}_2\text{O}$, $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (Merck) were used as supplied. Solvents used for the reactions were used as received. The ligand has been prepared by the method reported earlier [13]. As an example some characteristics of the ligand are summarized below.

2.2 Preparation of the Ligand (HL1)

5-Chloro-2-pyridinecarboxaldehyde (0.283 g, 0.002mol) in ethanol (10 cm³) was added to thiosemicarbazide (0.182 g, 0.002 mol) in ethanol-water solution (V/V 1 : 1, 80 cm³) followed by the addition of drops of glacial acetic acid. The reaction mixture was refluxed for 3 hours. The obtained precipitate (5-Chloropyridine-2-carbaldehyde thiosemicarbazone) (HL1) was filtered off, washed with water and ethanol and recrystallized from ethanol, and then was dried in vacuum.

2.3 Preparation of the Complexes

General procedure for the preparation of the metal complexes (1–5)

Complexes 1–5 were prepared by direct reaction between the ligand and the corresponding metal salts.

2.3.1 Synthesis of [Co (HL1)2]

To a solution of Cobalt (II) Chloride $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ (0.0005 mol, 0.1189 g) in 5 ml of methanol was added a solution of ligand 5-Chloropyridine-2-carbaldehyde thiosemicarbazone (0.001 mol, 0.215 g) in 25 ml of methanol. The mixture was refluxed for 2 hours (70-80 °C) and then stirred for 12 hours then filtered. The volume of filtrate was left for slow evaporation at room temperature. After two days large of dark brown colored crystals was obtained.

2.3.2 Synthesis of [Ni (HL1)2]

The hexahydrated nickel chloride, $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ (0.0005 mmol, 0.119 g), was dissolved in 30 ml distilled water. An ethanolic solution of 5-Chloropyridine-2-carbaldehyde thiosemicarbazone (0.001 mmol; 0.215 g, 10 ml) was added slowly while stirring. The mixture was refluxed for 3 h. After cooling at room temperature, a green precipitate appeared. It was filtered, washed with small amounts of absolute ethanol and finally dried in vacuum over silicagel (light brown). All the compounds were washed and dried in the same way.

2.3.3 Synthesis of [Zn(HL1)2]

0.136 g, 0.001 mol ZnCl_2 was dissolved in 20 ml warm absolute ethanol with stirring. To a solution containing 0.429 g, 0.002 mol 5-Chloro-2-pyridine-2-carboxaldehydethiosemicarbazone dissolved in 20 ml of absolute ethanol drop wise of NaOH (1M) was added. The mixture was refluxed for two hours. The separated brown powder was filtered washed with ethanol and to dry in air.

2.3.4 Synthesis of [Cu (HL1)2]

A quantity of 5-Chloro-2-pyridine -2-carboxaldehydethiosemicarbazone (0.430 g, 0.002 mol) was dissolved in warm 20 mL ethanol with stirring and to this solution was added slowly a solution of (0.134 g 0.001 mol) of the metal salts $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ dissolved in 20 mL ethanol,

then added drops of NaOH (1M). Although the complex appeared instantaneously the mixture was reflux on water bath for two hours. The separated green solid was left to dry in air after filtered and washed with ethanol.

2.3.5 Synthesis of [Cu(HL1)]

A quantity of 5-Chloro-2-pyridine -2-carboxaldehydethiosemicarbazone (0.215 g, 0.001 mol) was dissolved in warm 20 mL ethanol with stirring and to this solution was added slowly a solution of (0.134 g 0.001 mol) of the metal salts $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ dissolved in 20 mL ethanol, then added drops of NaOH (1M). Although the complex appeared instantaneously the mixture was reflux on water bath for two hours. The separated green solid was left to dry in air after filtered and washed with ethanol.

2.4 Physical Measurements

- **Elemental analyses** for (C, H, N and S) were performed using a Heraeus Carlo Erba 1108 elemental analyzer.

- **Melting points** were determined with a digital melting point apparatus using capillary technique.

- **Mass spectra** were recorded with a Micromass LCT electrospray (Qtof Micro YA263) mass spectrometer.

- **NMR spectra** were recorded in DMSO-d6 solution on a Bruker Avance DPX 300 NMR spectrometer.

- **IR spectra** were obtained on a Perkin Elmer Spectrum Two IR spectrometer with samples prepared as KBr pellets.

3. RESULTS AND DISCUSSION

3.1 Synthesis and Physical Properties of the Complexes

Firstly the ligands (HL1) was prepared from the reaction between 5-Chloro-2-pyridinecarboxaldehyde and thiosemicarbazide in alcoholic medium as indicated in Fig. (2) followed by the addition of drop of glacial acetic acid.

The melting point of (HL1) = 201°C. The elemental analytical calculation for the ligand was found C, 39.25, H, 3.26; N, 26.1; S, 17.0%, it's quite agreed with literature (C, 39.13, H, 3.25; N, 26.9; S, 17.65%).

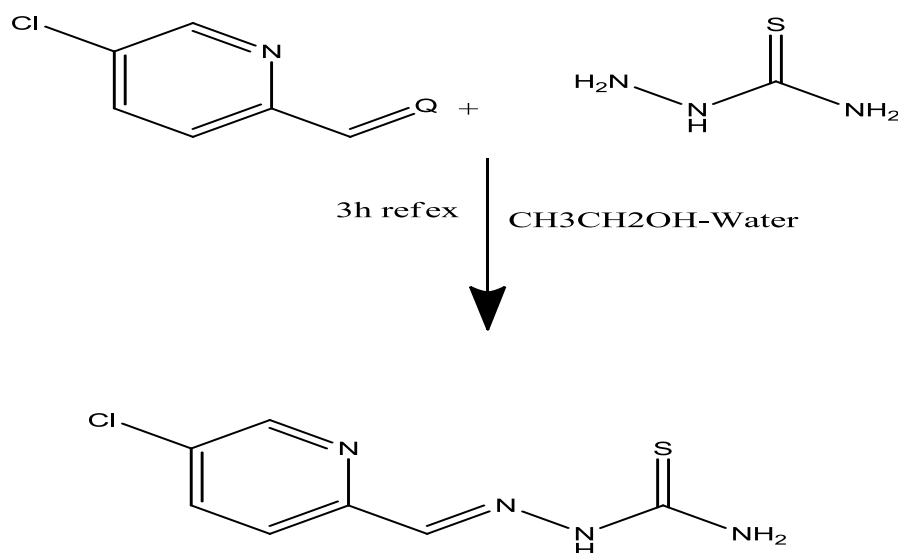


Fig. 2. Preparation of the ligand HL1 (5-Chloro-2-pyridinecarboxaldehyde thiosemicarbazone((E)-2-((5-chloropyridin-2-yl)methylene)hydrazine-1-carbothioamide)

After that the preparative reactions for the complexes can be represented by the following equations (1)-(5):

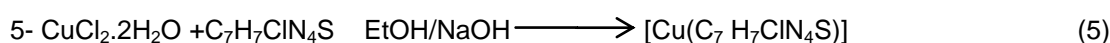
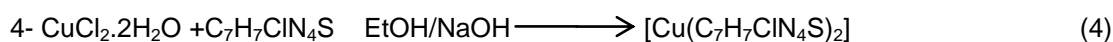
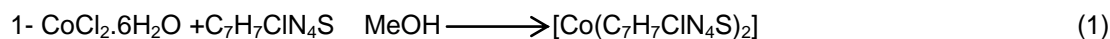


Table 1. Color, M.p and elemental analysis of the ligand 5-chloropyridine-2-carbaldehydethiosemicarbazone alone and its Ni, Co, Cu and Zn complexes

Compound	Color	M.p(^o c)	Elemental analysis found (Cal)			
			C (%)	H (%)	N (%)	S(%)
5CIPTSC	Brown	154	39.13(39.25)	3.25(3.26)	26.9(26.10)	17.65(15.02)
[Ni (C ₇ H ₇ ClN ₄ S) ₂]	green	226	28.66(27.7)	2.83(2.3)	18.83(18.42)	7.81(10.5)
[Co (C ₇ H ₇ ClN ₄ S)]	Blue	244	30.50(30.16)	2.63(2.51)	19.65(20.11)	8.03(11.49)
[Cu (C ₇ H ₇ ClN ₄ S) ₂]	Dark green	237	30.74(29.86)	2.63(2.48)	20.8(19.90)	11.5(11.37)
[Zn (C ₇ H ₇ ClN ₄ S)]	Brown	216	23.99(23.95)	2.36(2.00)	16.71(16.00)	6.41(7.90)
[Cu (C ₇ H ₇ ClN ₄ S)]	Dark green	233	23.61(24.00)	2.09(2.00)	15.7(16.04)	10.13(9.00)

Note that all these reaction needed areflux for certain time as metioned in the above procedure (2.3.1-2.3.5).

All the complexes are microcrystalline or amorphous powder, stable in the normal laboratory atmosphere, and slightly soluble in

common organic solvent but completely soluble in DMF and DMSO.

The results of color, M.p and elemental analysis of the ligand 5-chloropyridine-2-carbaldehydethiosemicarbazone alone and its Ni,

Co, Cu and Zn complexes were shown in Table (1).

3.2 IR Spectra

The IR spectral data, Table (2) 5-Chloro-2-pyridinecarboxaldehyde thiosemicarbazone, shows bands at 3419cm^{-1} which is assigned to $\nu(\text{NH}_2)$ sym.str.vib. The band at 1606cm^{-1} is assigned to $\nu(\text{C}=\text{N})$ sym.str.vib, and $\nu(\text{C}=\text{S})$ sym.str.vib shows band at 825cm^{-1} . The band at 3157 is assigned to $\nu(\text{NH})$ sym.str.vib.

The Infra-red spectral data of Ni (II) complex with the ligand HL¹ is shown in Table (2). The band at 1606cm^{-1} assigned to $\nu(\text{C}=\text{N})$ in the free ligand is shifted to 1616cm^{-1} in the spectrum of the complex. This indicates complexation of ligand through the azomethine nitrogen to the Ni (II) ion. The band at 825cm^{-1} assigned to $\nu(\text{C}=\text{S})$ in the free ligand is shifted to 833cm^{-1} . This suggests coordination of the ligand via the $\nu(\text{C}=\text{S})$ sulfur.

The Infra-red spectral data of cobalt(II) complex with the ligand is shown in Table (2). The band at 1606cm^{-1} assigned to $\nu(\text{C}=\text{N})$ in the free ligand is shifted to higher frequency, (1618cm^{-1}), in the spectrum of the complex. This indicates complexation of the ligand through the azomethine nitrogen to the cobalt (II). The band at 825cm^{-1} assigned to $\nu(\text{C}=\text{S})$ in the free ligand is shifted to 877cm^{-1} . This suggest coordination of the ligand via the $\nu(\text{C}=\text{S})$ sulfur. The Infra-red spectral data of zinc(II) complex with the ligand is shown in Table (2). The band at 1587cm^{-1} assigned to $\nu(\text{C}=\text{N})$ in the free ligand is shifted to 1606cm^{-1} in the spectrum of the complex. This indicates complexation of the ligand through the azomethine nitrogen to the zinc(II) ion. The band at 838cm^{-1} assigned to $\nu(\text{C}=\text{S})$ in the free ligand is disappeared in the complex spectrum. This may be due to deprotonation of the thiol sulfur atom.

The copper ligands complexes IR spectral data can be explain in the same way which mentioned

above for Ni, Co and Zn complexes with slightly different in the position of absorption band between the two Cu complexes as its clear from Table (2) the different band in Cu(HL)₂ complexes were shifted to lower frequency in Cu(HL) and this is attributed to lowering of the force constant and dipole moment in the second complexes.

3.3 NMR and Mass Spectra

“The ¹H NMR spectrum of (5CIPTSC), shows a singlet at 11.6 ppm due to the NH group next to C=S, while the signal of the proton on C=N double bond appears at 7.50 ppm. It is interesting to note the presence of two broad singlets for the two NH₂ protons, respectively at 7.78 and 8.15 ppm: it means that the free rotation around the C=N bond is blocked because of its partial double bond character” [10]. The spectra of the complexes [CoCl₂(5CIPTSC)₂] and [CuCl₂(5CIPTSC)] show no differences as compared to that of the free ligand. This enhances the hypothesis

It's clear from Fig. (4) that M.wt of the ligand appeared approximately at m/z 214 which agreed with calculated data, the mass for Ni, Co ligand complexes gives molecular ions in high relative abundance indicating the cleavage of uni ligand from the bidentate structure followed by atom rearrangement such as nitrogen migration.

“As all thiosemicarbazones, our ligand can exhibit thione-thiol tautomerism, since it contains a thioamide –NH–C=S functional group” [21]. “There is no IR band at 2500–2600 cm in the spectrum of the free ligand, and this indicates the absence of S–H grouping in the free ligand. However, there are bands in the regions of 855 and 3150 cm⁻¹, characteristic of $\nu(\text{C}=\text{S})$ and $\nu(\text{N}-\text{H})$, respectively, indicating that the ligand remains as the thione tautomer. This is

Table 2. Main IR spectral vibrations (cm⁻¹) of the ligand 5CIPTSC and its Ni, Co, Cu and Zn complexes

Compound	$\nu(\text{NH}_2)$	$\nu(\text{C}=\text{S})$	$\nu(\text{C}=\text{N})$	$\nu(\text{M}-\text{N})$	$\nu(\text{M}-\text{S})$
5CIPTSC	3419	825	1606	511	411
[Ni (C ₇ H ₇ ClN ₄ S) ₂]	3267	833	1616	453	432
[Co (C ₇ H ₇ ClN ₄ S) ₂]	3269	877	16018	531	430
[Cu (C ₇ H ₇ ClN ₄ S) ₂]	3461	784	1595	491	441
[Zn (C ₇ H ₇ ClN ₄ S)]	3276	705	1631	522	422
[Cu (C ₇ H ₇ ClN ₄ S)]	3361	686	1625	426	407

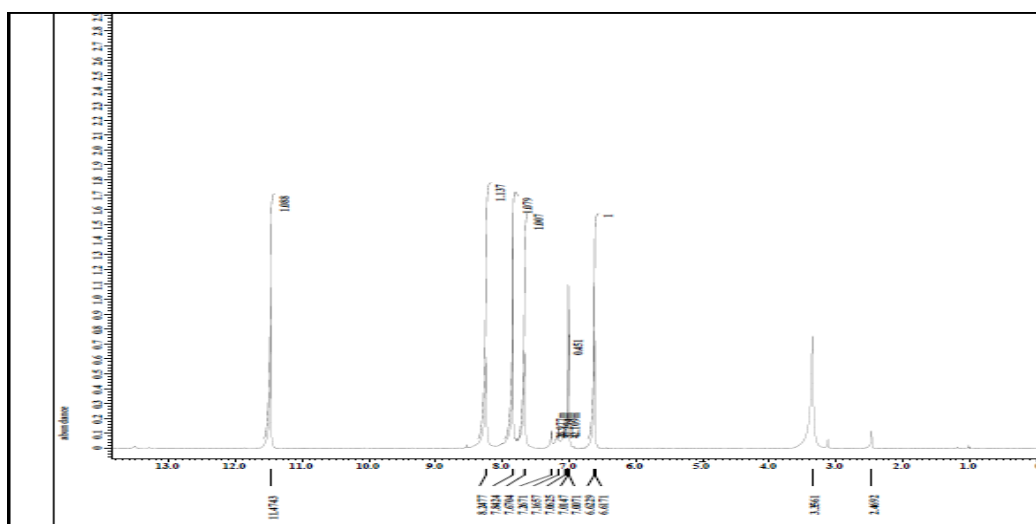


Fig. 3. The ^1H NMR spectrum of (5CIPTSC)

supported by the H NMR spectrum which does not show any peak at 4 ppm attributable to the S–H proton, but it shows a singular peak at 11.3 ppm relative to the NH next to C=S. The bands appearing around 1345 and 785 cm^{-1} in the spectrum of the ligand are either weakened or shifted to higher wave numbers in all the complexes [22,23], and this shift can be assigned to $\nu(\text{C}=\text{S})$ vibration. On the other hand, the bands in the region 3440–3270 cm^{-1} attributed to symmetrical and asymmetrical stretching mode $\nu(\text{NH})_2$ in the spectra of the ligand, undergo appreciable change in the spectra of the

complexes". "This is due to the coordination of sulfur from the $\text{C}=\text{S}(\text{NH})$ group as reported earlier". [24]. "This coordination is confirmed by the presence of a new band at 380–395 cm^{-1} [5,25] which is assigned to $\nu(\text{M}-\text{S})$ for all the complexes. In ligand spectra, the strong band observed at 1600 cm^{-1} corresponds to $\nu(\text{C}=\text{N})$ vibration band" [24]. "This band shifts to a higher region [22,24] in the spectra of Ni–nickel complexes and this indicates the coordination of nitrogen of the azomethine group in coordination" [5,25].

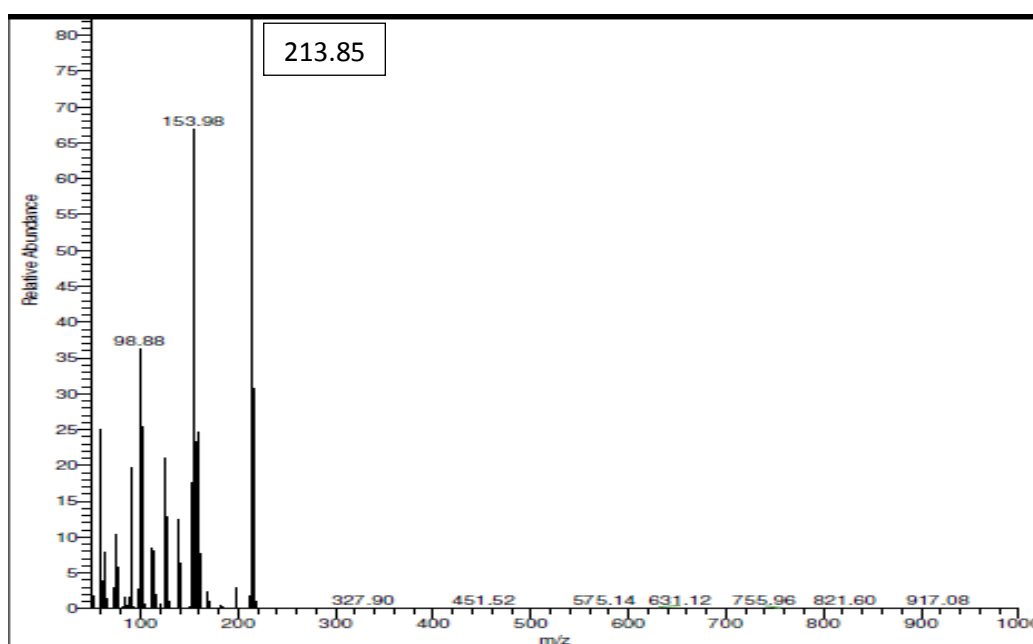


Fig. 4. Mass spectrum of 5-Chloro-2-pyridinecarboxaldehyde thiosemicarbazone

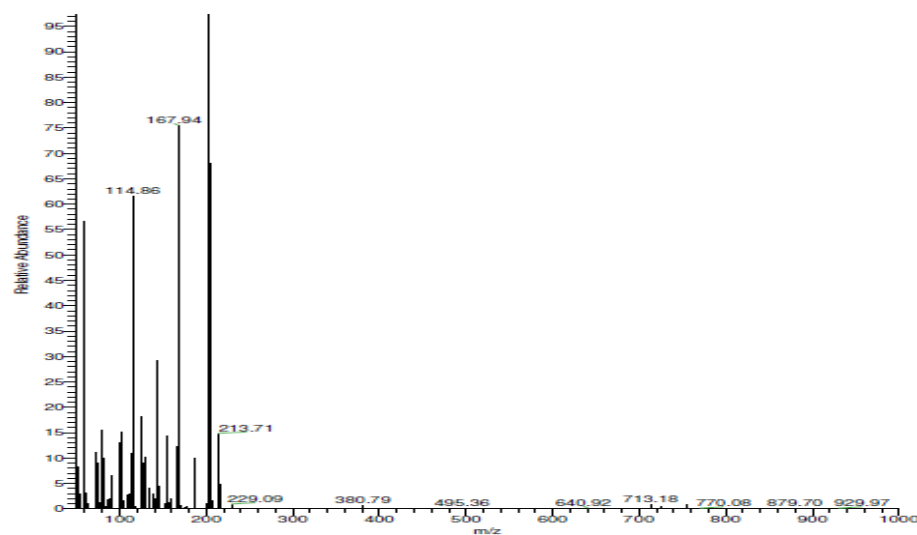


Fig. 5. Mass spectrum of [Ni(HL1)₂]

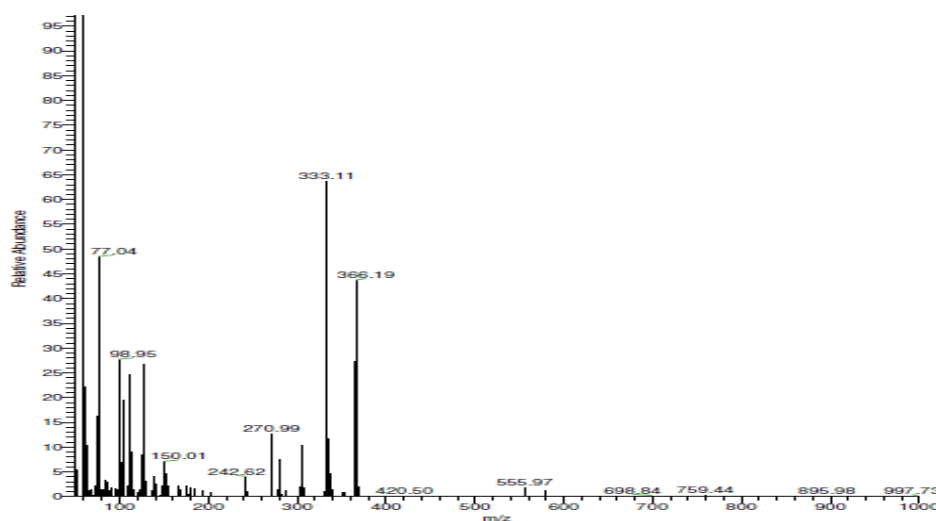


Fig. 6. Mass spectrum of [Co(HL1)₂]

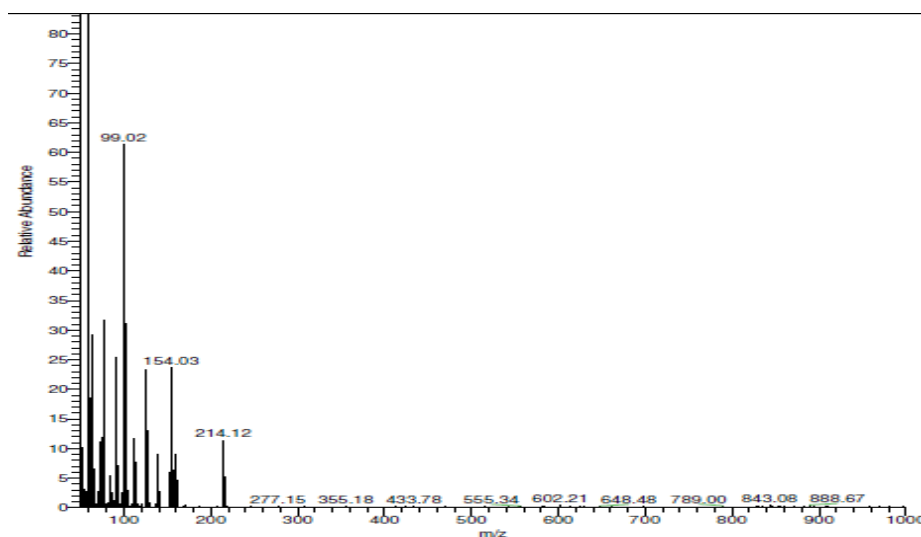


Fig. 7. Mass spectrum of [Zn(HL1)₂]

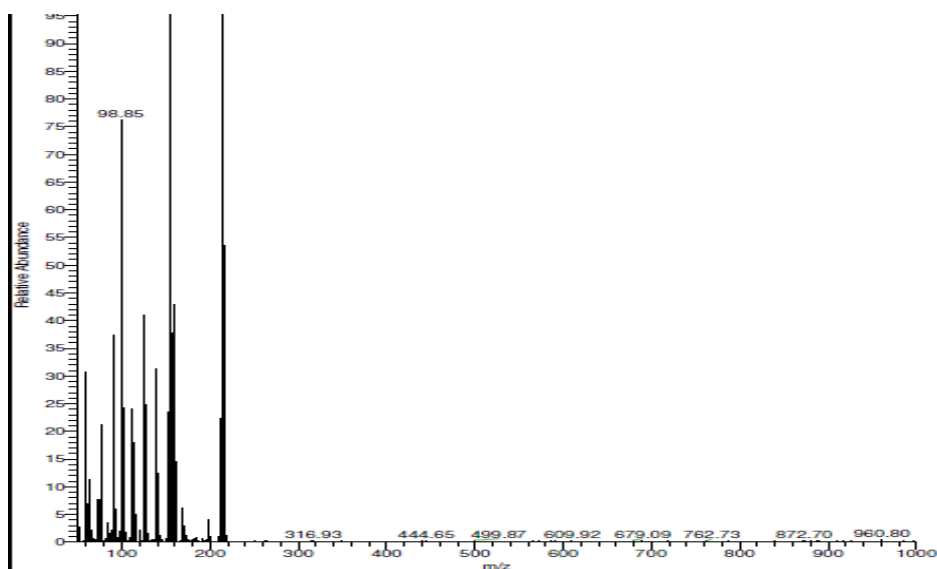


Fig. 8. Mass spectrum of [Cu(HL1)]

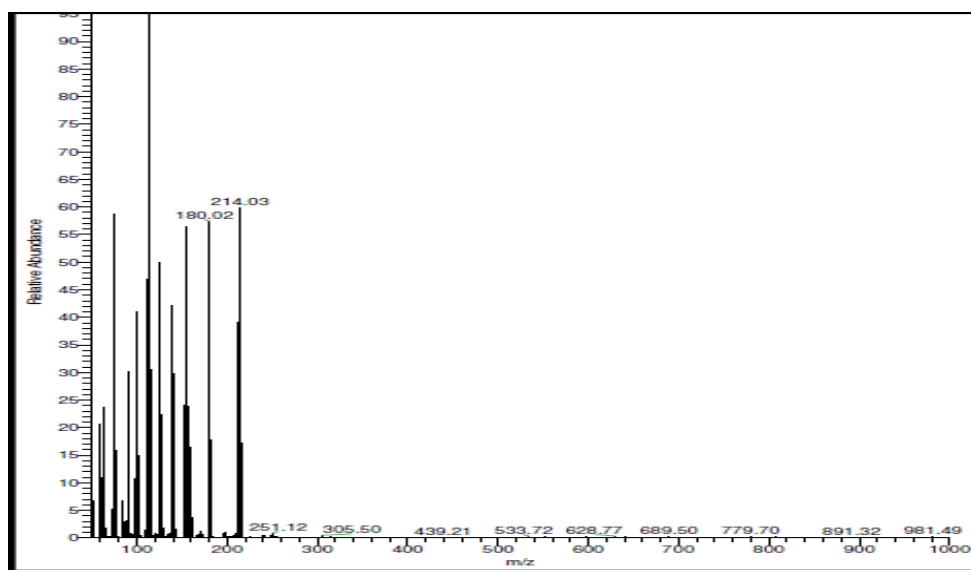


Fig. 9. Mass spectrum of [Cu(HL1)₂]

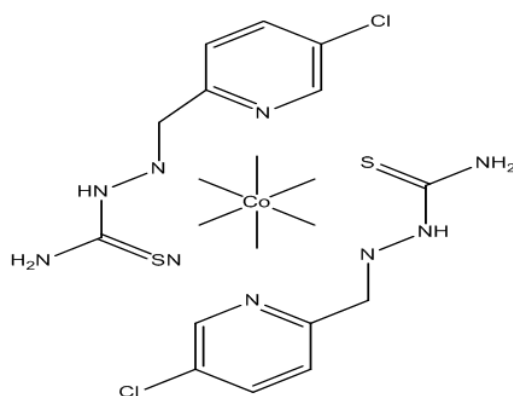


Fig.10. The probable structure of complex [Co (HL1)₂]

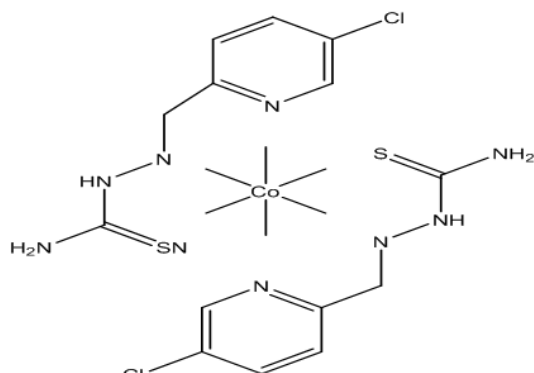


Fig. 11. The probable structure of complex [Ni (HL1)2]

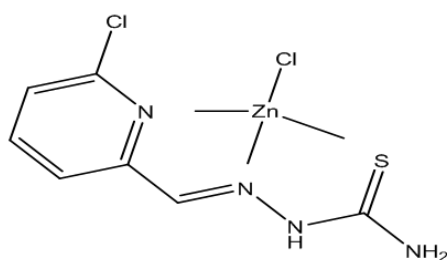


Fig. 12. The probable structure of complex [Zn (HL1)2]

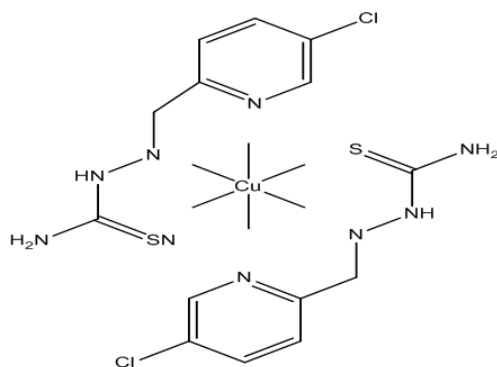


Fig. 13. The probable structure of complex [Cu (HL1)2]

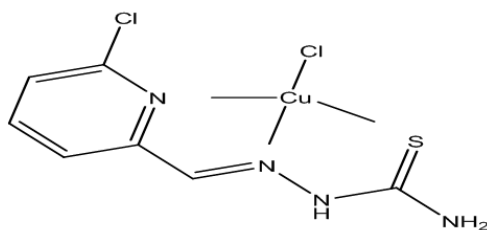


Fig. 14. The probable structure of complex [Cu (HL1)]

Figs. (5) to (9) showed the mass spectrum of the ligand and metal (Co, Ni, Zn and Cu) complexes all the expected fragmentations and the molecular ion peak and m/z peaks appeared successfully.

The proposed structure for the different complexes and after our previous discussion of the spectral data obtained for the ligands and its metal complexes were shown below in

Figs. (9-12) This may suggest a tetrahedral geometry for the complexes (Suni.V et al., 2007).

In the complex of cobalt(II) with the ligand 5-Chloro-2-furaldehyde thiosemicarbazone (HL²), the band at 1587 cm⁻¹ assigned to ν (C=N) is shifted to 1622 cm⁻¹, indicating coordination of the ligand through the azomethine nitrogen. The band assigned to ν (C=S) is shifted from 838 cm⁻¹ to 831 cm⁻¹ indicating the involvement of sulfur in complexation.

The [Cu (HL)₂]Cl₂ complex shows bands at 46082 cm⁻¹ (217 nm), 28169 cm⁻¹ (255 nm) and 13850 cm⁻¹ (534 nm). The observed magnetic moment is 1.86 BM, this suggest distorted square planar geometry of the copper center.(Amna Qasem Ali et al ; 2014). For Zn the complex is square planar from the obtained spectral data (Mihail Revenco, et al; 2014).

4. CONCLUSIONS

Synthesis and characterization of metal ligand complexes was very important field because these compounds found wide applications, in this study the synthesis and characterization of nickel(II), cobalt(II) and Zinc(II) complexes with 5-chloropyridine-2-carbaldehydethiosemicarbazone had been studied. The complexes were synthesized successfully and the structure of them were indicated from the obtained spectral data, the research goes further in antimicrobial investigation which did not shown here because the results were not complete till now and we will published it in our next coming paper.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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