Chemistry and Materials Research
ISSN 2224- 3224 (Print) ISSN 2225- 0956 (Online)
Vol.9 No.1, 2017

# Synthesis, Structure, and Spectral Characterization of Cu(II) Complexes of Thiocarbohydrazide and Derivates

Shaza GHALI[1] Faez hyzwany[2]
1. Master of inorganic Chemistry - Faculty of Sciences, Al-Baath University,Homs, Syria
2. Dr.Prof in inorganic chemistry: Chemistry Department- Faculty of Sciences, University of Al-Baath, Homs,Syria

## Abstract

The synthesis and structure of thiocarbohydrazide and metal complexes of thiocarbohydrazone ligand are described. The ligand was obtained by condensation of N,N`-thiocarbohydrazide with salicylaldehyde. The Cu(II)complex have been synthesized by reacting $CuCl_2.2H_2O$ and Ligand by molar ratio 2:1(M:L),while the Cu(II) complex of thiocarbohydrazide have been synthesized by reacting $CuCl_2.2H_2O$ and TCH by molar ratio 1:2(M:L) These complexes are soluble only to a larger extent in DMF and DMSO .The bonding sites are the azomethine nitrogen atom, phenolic oxygen atom and thiol sulfur atom. The metal complexes exhibit square planner and octahedral structure. Characterization and structure elucidation of the synthesized compounds were achieved by spectral (IR, electronic,$^1H$ and $^{13}C$ NMR) as well as molar conductivities.

**Keywords**: Thiocarbohydrazide, Thiocarbohydrazone ligand, Cu(II) Complexes, $^1H$ and $^{13}C$ NMR.

## 1. Introduction

Thiocarbohydrazide (TCH) one of the simplest hydrazine derivatives of thiocarbonicacide ,is an important chemical intermediate in organic synthesis and is used in the industrial production of insecticides, fungicides and various agricultural chemicals as well as in chemical laboratories as a chemical reagent[1,2] . Thiocarbohydrazide constitute an important class of N, S donor ligands possessing interesting chemical, biological and medicinal properties[3,4].Thiocarbohydrazide derivatives have attracted much attention in recent years due to their applications in the synthesis of heterocyclic compounds [5,6] synthesis of 1,2,4-triazole[7-9], synthesis of transition metal complexes, [10] and in pharmacological studies [11].Both hydrazine groups of thiocarbohydrazide are very reactive and predominantly form bis derivatives with aldehydes and ketones [12]. Hydrazone-based Schiff bases are versatile ligands capable of generating a variety of molecular architectures, coordination compounds, and polymerization catalysts [13]Metal complexes of thiocarbohydrazones have attracted much attention due to their biological activity [14,15].

The aim of the present work is to study preparation of thiocarbohydrazide and the chelating behavior of TCH and the thiocarbohydrazone ligand towards transition metal copper(II),The structures of the ligand and metal complexes were characterized by FT-IR, $^1H$ and $^{13}C$ NMR and electronic spectra as well as conductivity measurements at room temperature.

## 2. Experimental:

**2.1. Materials:**copper(II)was used as chloride salt and was SCP, hydrazine hydrate , potassium hydroxide and salicylaldehyde were Sigma Aldrich, carbon disulfide was Riedel-deHaen , Organic solvents (ethanol, ,methanol, diethyl ether and dimethylformamide (DMF) )were Euro lab and were used without further purification.

**2.2. Measurements:**FT–IR spectra were recorded on a Jasco-Japan 410 spectrometer (4000–400 cm$^{-1}$) in KBr pellets .Electronic spectra were recorded at room temperature on a Hitache UV/Vis spectrophotometer as DMF solutions. The $^1H$ and $^{13}C$ NMR spectra, as solutions in DMSO-d6, were recorded on a Bruker 400 MHz spectrometer at room temperature using TMS as an internal, Molar conductivities of $10^{-3}$ M solutions of the solid complexes in DMF were measured on the Corning conductivity meter NY 14831 model 441.

**2.3.Synthesis of thiocarbohydrazide**: A specified quantity (1.5mol) of 50- 60 % aqueous hydrazine hydrate was placed in the flask. The temperature was lowered to 10°C and the stirring rate was controlled to 800 rpm , 30.15 ml of $CS_2$(0.5mol)were added dropwise over about one hour while maintaining the temperature below 15°C.after addition the reaction mixture continued to be agitated for 30 min at room temperature .the resultant mixture was refluxed at 70°C for 6h,The reaction mixture was cooled to room temperature and the crystalline precipitate separated from liquid by filtration then Recrystallization by water, the TCH crystals was dried at 110°C .m.p172-174°C.

**2.4.Synthesis of thiocarbohydrazone ligand $H_3L$**: A mixture of 2-hydroxy-1-benzaldehyde, (3.27 gr, 19 mmol) and thiocarbohydrazide (1 gr, 9.43 mmol) in absolute ethanol was refluxed for 3 h. where a yellow precipitate was formed on hot ,then allowed to cool slowly and collected by filtration, washed with ethanol then diethyl ether , air-dried and recrystallized from ethanol. The crystalline ligand was kept in a desiccators until used .The analytical and physical data for the $H_3L$ ligand and its metal complexes are listed in Table (2,3).

**2.5. Synthesis of Cu(II) complex of thiocarbohydrazide:** To a hot methanolic solution (20 mL) of TCH(8 mmol,0.85 gr) was added $CuCl_2.2H_2O$ (4 mmol, 0.68 g) and the mixture was refluxed for 3 h till it became homogeneous. A few drops of triethylamine were then added to became PH=8 and cause precipitation and the refluxing was continued for additional 2 h. The solvent was removed by filtration, which afforded dark green precipitate. It was washed with methanol and dried in vacuum.

**2.6. Synthesis of the [$Cu_2$(SATCH)$Cl_4$]**:Potassium hydroxide, KOH (0.142 gr,3.38 mmol) in the least amount of methanol (10 mL) was added gradually with constant stirring to the solution of the ligand, $H_3L$,(0.7 gr, 1.69 mmol) in ethanol (30 mL), in molar ratio 2:1(KOH:$H_3L$). Cupper chloride Dihydrate, $CuCl_2.2H_2O$ (0.457 g,1.69mmol) in ethanol (30 mL) was added gradually with constant stirring to the above mixture. The resulting mixture was refluxed for 3 h. A greenish black precipitate was formed, filtered off and washed several times with small amounts of methanol, ethanol then diethyl ether and finally air-dried. The yield was 0.8 g m.p. > 340°C.

## 3. Results and discussion

### 3.1. Characterization of the TCH:

The characteristic peaks at 1530-1488 cm$^{-1}$ are assigned to coupled modes consisting principally of N-H wagging and C-N stretching vibrations .The C=S stretching vibration contributes to the two peaks 1184-756 cm$^{-1}$. The H-N-H stretching vibration contributes to the two peaks 3273-3203 cm$^{-1}$.

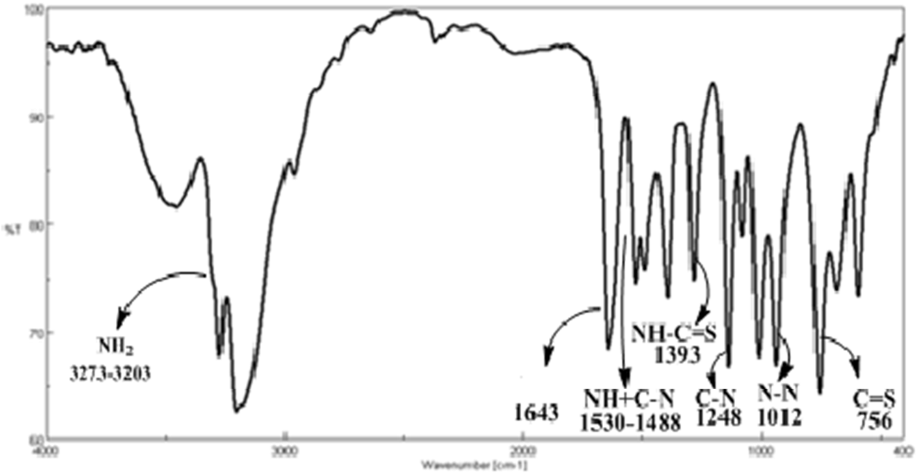


Figure.1. FT-IR spectral of TCH

The electronic spectrum of the TCH in DMF showed one band at 305 nm. This band may be assigned to $\pi \longrightarrow \pi^*$ and $(n \longrightarrow \pi^*)$ transitions of (C=S) groups. $^1$H and $^{13}$C NMR spectral data ($\delta$ppm) of the TCH relative to TMS (0 ppm) in DMSO-d6,The signal observed at 4.47 ppm may be due to H-N-H protons(4H).The signals observed at 8.68 ppm may be due to the NH protons(2H).This is supported by the $^{13}$C NMR spectrum that showed one signal at 181.79 ppm that may be assigned to C=S.

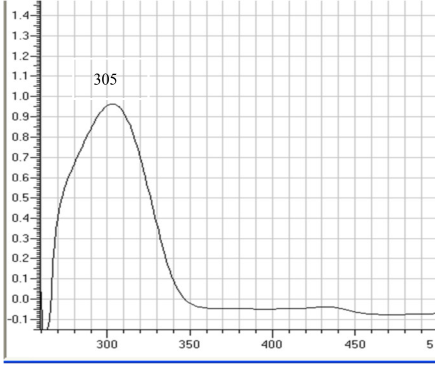


Figure.2.UV spectral of TCH

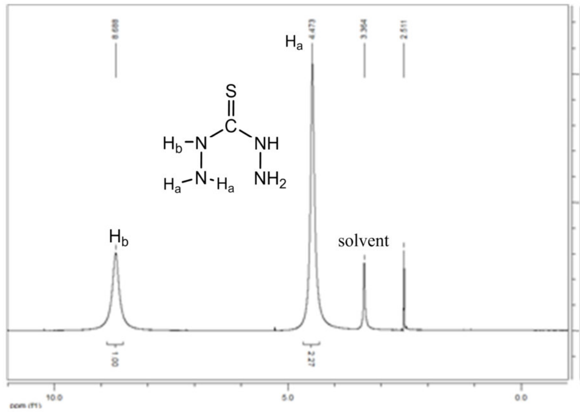


Figure.3. $^1H$ NMR of TCH

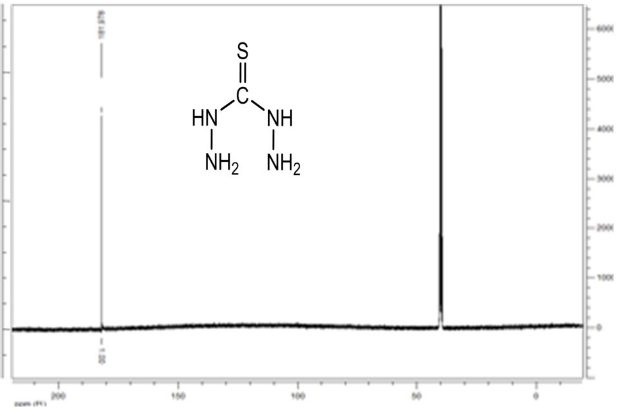


Figure.4. $^{13}C$ NMR of TCH

### 3.2. Characterization of the Thiocarbohydrazone ($H_3L$):

The structure of the ligand was elucidated by IR, electronic and $^1H$ and $^{13}C$ NMR spectra .The IR spectrum of the ligand showed bands at 3425, 3228, 1620 and 1284 cm$^{-1}$ that may be assigned to $\nu$(OH), $\nu$ (NH), $\nu$ (C=N) and $\nu$ (C-O) phenolic, respectively. The appearance of the bands characteristic to $\nu$ (C=S) in addition to the absence of an IR band around 2600 cm$^{-1}$ due to $\nu$ (SH)support the thione nature of the ligand in the solid state .The electronic spectrum of the ligand in DMF showed two bands at 345 and 400 nm. The first bands may be assigned to $\pi \longrightarrow \pi^*$ transitions of the aromatic benzene ring and the (C=N) and (C=S) groups while the last band may be assigned to transitions of $(n \longrightarrow \pi^*)$ to the (C=N) and (C=S) groups. $^1H$ and $^{13}C$ NMR spectral data ($\delta$ppm) of the ligand relative to TMS (0 ppm) in DMSO-d6 , lend further support of the suggested structure of the ligand. The signals observed at 9.86 ppm may be due to the phenolic OH protons.The signals observed at 9.74 ppm may be due to the NH protons. Also, signals observed at 8.32 ppm may be due to protons of the HC=N groups. The aromatic protons showed signals in the range 6.8–7.99 pm. This is supported by the $^{13}C$- NMR spectrum that showed signals at 176, 156 and 139.88 ppm that may be assigned to C=S, C-O and C=N groups, respectively.

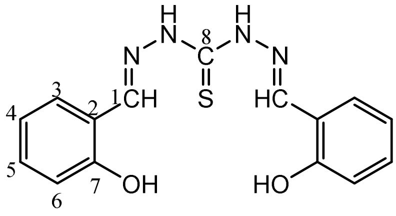


Figure.5. structureof $H_3L$

**Table 1.**13C NMR spectral data (ppm) for $H_3L$ ligand (DMSO-d6):

| Group | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 |
|---|---|---|---|---|---|---|---|---|
| **Chemical shift** | **139.88 ppm** | **120.72 ppm** | **127.618 ppm** | **116.39 ppm** | **119.68 ppm** | **131.208 ppm** | **156.75 ppm** | **176.67 ppm** |

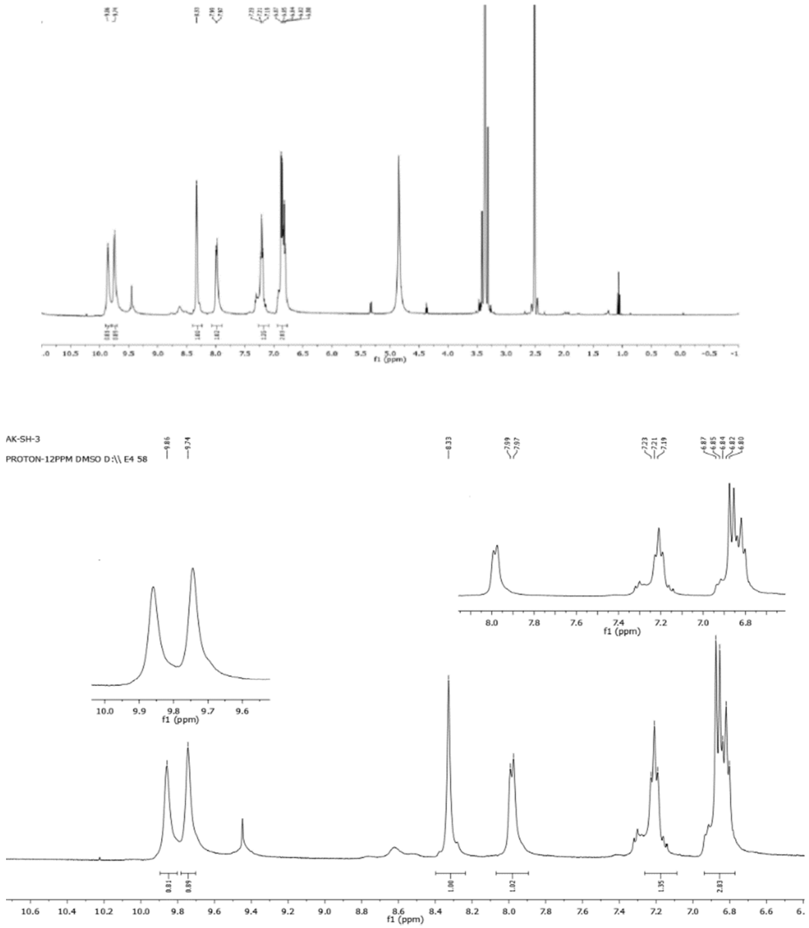


Figure.6. $^1$H NMR of $H_3L$

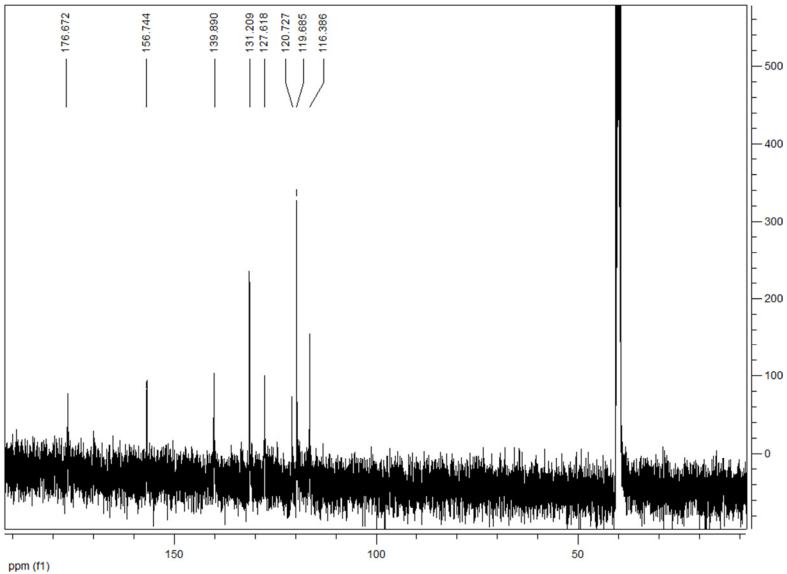


Figure.7. $^{13}$C NMR of $H_3L$

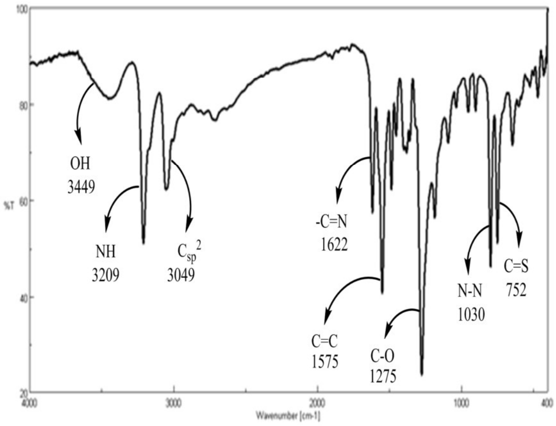


Figure.8.IR spectral of $H_3L$

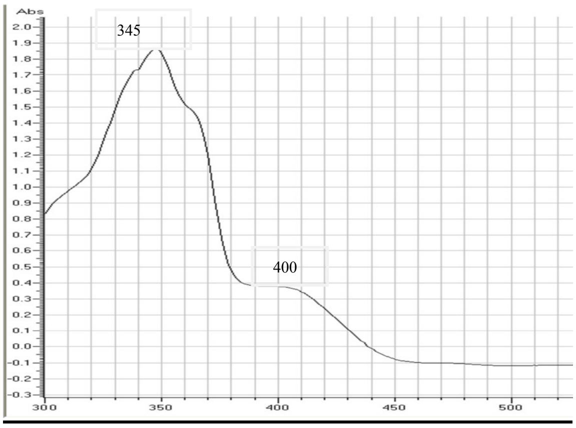


Figure.9.UV spectral of $H_3L$

### 3.2. Characterization of complexes:

### 3.2. 1.Characterization of copper complex with Thiocarbohydrazide[Cu(tch)$_2$]:

**- IR spectra:**

The IR spectral data of the complexes are listed in Table 2. Comparison of the IR spectra of the metal complex with that of the TCH revealed that complex showed bands in the range 3273–3203 cm$^{-1}$ which can be assigned to υ(NH2) of the amine group of the TCH was shifted to lower frequencies (3254-3163) . Although there are five donor sites, the TCH acts as a tridentate ligand. On moving from free TCH to[ Cu(tch)$_2$] the ν(N–H) is blue shifted (Table 2) .The ν(C= S) of TCH was shifted to high frequencies (770 cm$^{-1}$) A new band at 1620 cm$^{-1}$ assigned to (C=N). We have observed a strong band at 1505 cm−1 that is intermediate between ν(C–N) and ν(C= N) indicating

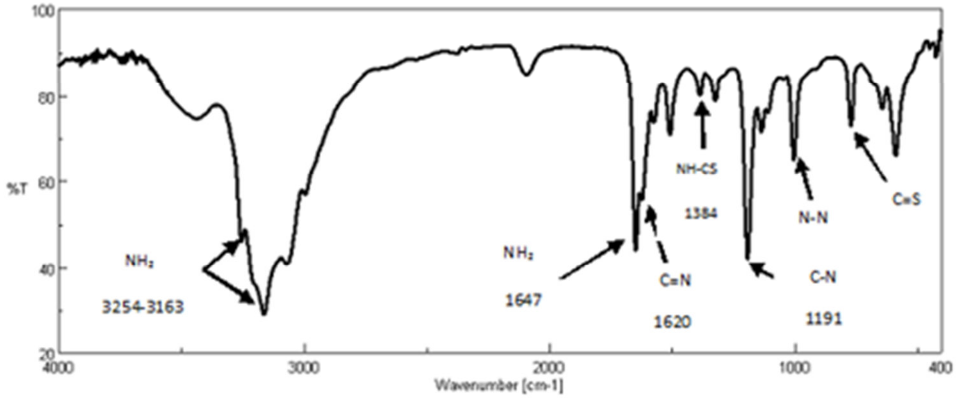
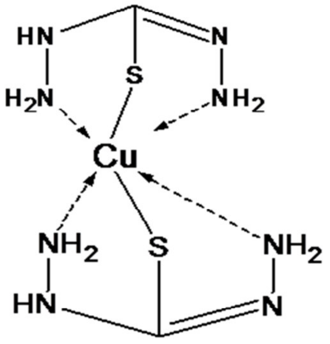


Figure.10.IR spectral of [Cu(tch)$_2$]

**- Electronic spectral data and Conductivity measurements :**

The electronic spectra of the [Cu(tch)$_2$] in DMF has one band at (430)nm. These band may beassigned to the transitionsd-d.The molar conductance values of the complex in DMF ($10^{-3}$ M solutions) were measured at room temperature and the results are listed in Table 3. The values show that the complex has non-electrolytic nature. this data refers that this complex has octahedral geometry.



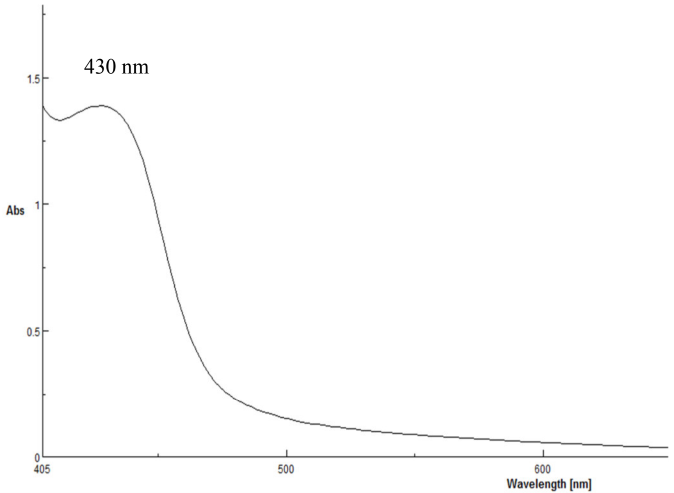


Fig.9.Suggested structure of $Cu(tch)_2$

Fig.10.UV Spectral of $[Cu(tch)_2]$

**3.2.2. Characterization of copper complex with SATCH $[Cu_2(SATCH)Cl_4]$:**

**FT- IR spectra:**

The IR spectral data of the complexes are listed in Table 2. Comparison of the IR spectra of the metal complex with that of the free ligand revealed that the band at 3449 $cm^{-1}$ assigned to υ(OH) in the free ligand was shifted to lower frequencies (3435 $cm^{-1}$) in the complex,. Also, the band at 1622 $cm^{-1}$ assigned to υ(C=N) in the free ligand was shifted to lower frequencies (1603) in the complex, indicating the participation of the azomethine nitrogen in chelation .The υ(C-O)phenolic of the free ligand at 1275 $cm^{-1}$ was shifted to lower frequencies (1248 $cm^{-1}$) in the complex , suggesting the participation of the phenolic –OH group in chelation .The bands assigned to υ(C=S) in the free ligand remained unchanged or shifted to higher frequencies in the complex, indicating the nonparticipationof the (C=S) group inchelation.

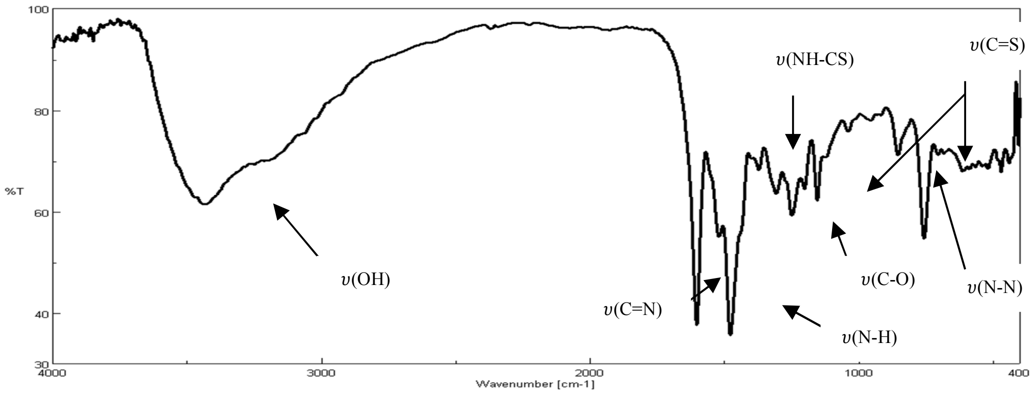


Figure.10.IR spectral of $[Cu_2(SATCH)Cl_4]$

**- Electronic spectral data and Conductivity measurements:**

The data of the electronic spectra of the ligand and its complexes are given in Table 4. The spectrum of thiocarbohydrazone ($H_3L$) presented two bands in the UV interval at 348nm assigned to ($\pi \rightarrow \pi^*$), 400 nm assigned to ($n \rightarrow \pi^*$) transitions respectively.

The electronic spectra of the $[\mathbf{Cu_2(SATCH)Cl_4}]$ in DMF has two bands at (338)nm. These bands may be assigned to the transitions ($\pi \rightarrow \pi^*$),410 nm assigned to the transitions ($n \rightarrow \pi^*$) and that have high intensity Comparison of the electronic spectra of the ligand ,that refer to $L \longrightarrow M$ .The values of Conductivity measurementsshow that the complexhas non-electrolytic nature.

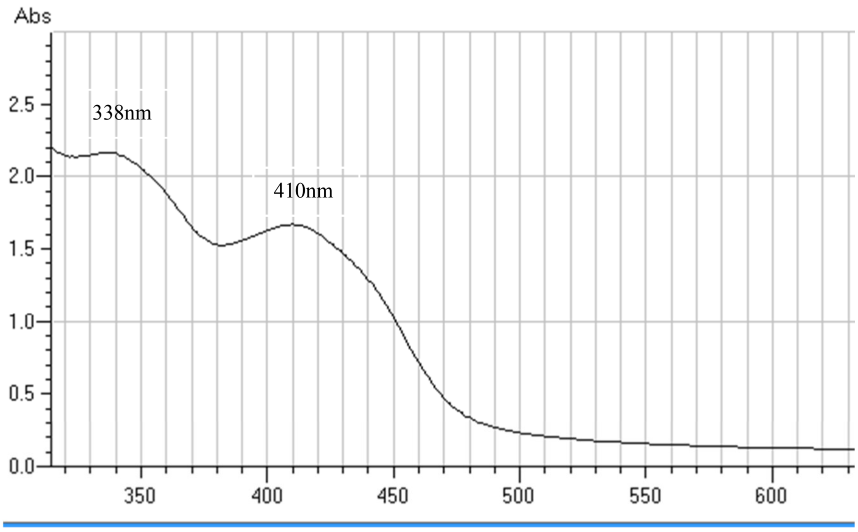


Fig.10.UV Spectralof [$Cu_2$(SATCH)$Cl_2$]

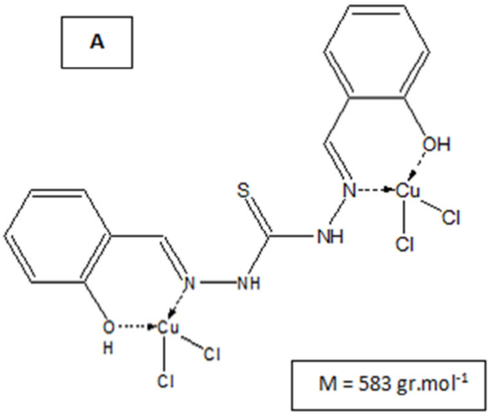
**- Determination molar ratio of (M: L) by furnace :**

Analyse of metal ions followed dissolution of the solid complex (0.0513 gr) in hot concentrated nitric acid, $HNO_3$, then these sample were sintered at 900 °C for 1 h in a furnace (Carbolite Furnace, CWF 1200) and then cooled at room temperature in desiccators, after that we notice that the formed compound is CuO(Black color) (0.0134 gr).

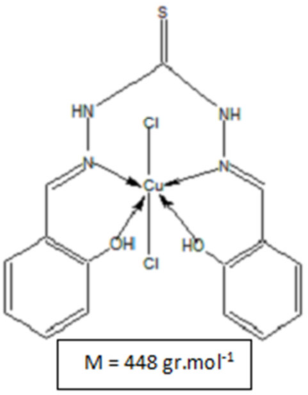
$$\left.\begin{array}{ccc} Cu & \longleftarrow & CuO \\ 64\text{ gr} & & 80\text{ gr} \\ Xgr & & 0.0134\ gr \end{array}\right\} \boxed{X = 0.01072\text{ gr}}$$

So the complex contain (0.01072 gr ) of copper metal , we suggest two structure of this complex and account the amount of copper in each of them and compare it with The practical value to determine the correct structure.

**A**



**B**



$$\left.\begin{array}{l} \underline{\textbf{Compound A :}}\text{ molecular weight 592 gr contain 128 gr of copper metal} \\ \text{Weight of disjointed sample 0.0513 gr contain y gr of copper metal} \end{array}\right\} \Longrightarrow \boxed{Y = 0.01126\text{ gr}}$$

$$\left.\begin{array}{l} \underline{\textbf{Compound B:}}\text{ molecular weight 448 gr contain 64 gr of copper metal} \\ \text{Weight of disjointed sample 0.0513 gr contain Z gr of copper metal} \end{array}\right\} \Longrightarrow \boxed{Z = 0.0073\text{ gr}}$$

When we compare between X,Y,Z, we notice that X ≅ Y , So the complex has a dinuclear structure [A]

$$\boldsymbol{yeild = \frac{X}{Y} = \frac{0.01072}{0.01126} = 95.2\%}$$

Tabel-2- Characteristic infrared absorption frequencies (cm$^{-1}$) of the ligand and complexes.

| complexes | $\nu(NH_2)_{St}$ | $\nu(NH_2)_w$ | $\nu(N-H)_{St}$ | $\nu(C=N)$ | $\nu(NH-CS)$ | $\nu(C=S)$ | $\nu(C_{SP}{}^2-H)$ | $\nu(C-O)$ | $\nu(OH)$ | $\nu(M-N)$ |
|---|---|---|---|---|---|---|---|---|---|---|
| **TCH** | **3273-3203** | **1643** | **3180** | **-** | **1393** | **756**<br>**1184** | **-** | **-** | **-** | **-** |
| **Cu(TCH)$_2$** | **3254-3163** | **1647** | **3069** | **1620** | **1384** | **770**<br>**1191** | **-** | **-** | **-** | **423** |
| **SATCH** | **-** | **-** | **3209** | **1622** | **1375** | **2** | **3049** | **1275** | **3449** | **--** |
| **[Cu$_2$(SATCH)Cl$_2$]** | **-** | **-** | **3189** | **1603** | **1372** | **756**<br>**1155** | **3030** | **1248** | **3435** | **469** |

Table -3- Molecular weight and melting point of the ligand and complexes

| Compounds | Mol.Weight | Colour | Yeild | M.P.(℃) |
|---|---|---|---|---|
| **Thiocarbohydrazide** | **106** | **White needles** | **70%** | **172-174** |
| **[Cu(tch)$_2$]** | **275.4** | **Greenish black** | **45%** | $< 350$ |
| **SATCH** | **314** | **yellow** | **75%** | **192-195** |
| **[Cu$_2$(SATCH)Cl$_4$]** | **592** | **Dark green** | **35%** | $< 350$ |

Table 4. Electronic spectral data , molar conductance and geometries of ligand and complexes

| compounds | Electronic spectra (nm) | Assignment | geometry | Conductance $^a$ µS/cm |
|---|---|---|---|---|
| **Thiocarbohydrazide** | **305** | $n \rightarrow \pi^*$ | **-** | **-** |
| **[Cu(tch)$_2$]** | **430** | **d-d** | **octahedral** | **20** |
| **SATCH** | **345**<br>**400** | $\pi \rightarrow \pi^*$<br>$n \rightarrow \pi^*$ | **-** | **-** |
| **[Cu$_2$(SATCH)Cl$_4$]** | **338**<br>**410** | $\pi \rightarrow \pi^*$<br>$n \rightarrow \pi^*$ | **Square planner** | **30** |

a: Solutions in DMF (10$^{-3}$ M) , at room temperature 25 °C

## Conclusions

In this research the preparation, isolation, and characterization of a new five-dentate Schiff basederived from thiocarbohydrazide and its complexes with Cu(II) have been carried out. It have beenproposed that the Schiff base ligand coordinates through the nitrogen of the azomethine group and the phenolic oxygen atom, while TCH coordinate through the amine group and sulfur atom forming a stable chelate complexes.

In the light of the above discussion, square planner geometry have been proposed for Cu(II) complexewith SATCH in molar ratio (1:2) (L:M), Whereas Cu(II) formed octahedral with TCH in (1:2) molar ratio(M:L) .

## Acknowledgement

The authors express their thanks to central laboratory in department of chemistry, AL BaathUniversity, faculty of sciences, for their assistance during the work.

## Refrence

1. Zhou.J,Wu.D,Guo.D ,Optimization of the production of thiocarbohydrazide using the taguchimethod,Wiely Online Library,Vol85.1402-1406 (2010).
2. AudriethLF,ScottES,and Kippur PS,Hydrazine derivatives of the carbonic and thiocarbonic acids.1.The preparation and properties of thiocarbohydrazide.J Org Chem 19:733-741(1954).
3. Siddiqi.K.S, Khan.S,Nami.Sh.A.A,Elajaily.M.M, Polynuclear transition metal complexes with thiocarbohydrazide and dithiocarbamates, Spectrochimica Acta,Vol67,PP.995-1002, (2007).
4. O.D. Fox, M.G.B. Drew, E.G.S. Wilkinson, P.D. Beer, Chem. Commun. (2000) 319
5. SINGH.D, KUMAR1.K, KUMAR ,and SINGH.J,(2010)- Template synthesis and characterization of biologically active transition metal complexes comprising 14-membered tetraazamacrocyclicligand,Journal Of The Serbian Chemical Society,Vol75(2),PP.217-228.
6. Singh.D.P,andKumar.R,(2006)- Template synthesis, spectroscopic studies and biological screening of macrocycliccomplexes derived from thiocarbohydrazide and benzyl, Transition Metal

Chemistry,Vol(31),PP.970-973.

7. Kaymakcioglu.K.B, Celen.O.A, Tabanca.N,Ali.A, Khan.I.SH,Khan.A.I and Wedge.E.D,(2013)- Synthesis and Biological Activity of Substituted Urea andThiourea Derivatives Containing 1,2,4-Triazole Moieties,Molecules,Vol(18),PP.3562-3576.
8. BERCEAN.N.V,CREANGA.A.A,BADEA.V,DELEANU.C,and CSUNDERILIK.C,(2011)- 5-Substituted-4*H*-4-amino-3-mercapto-1,2,4-triazoles with Increased Complexing Capabilities, REV. CHIM. (Bucharest),Vol(62),PP.47-50.
9. Manjula.S.P,Sarojini.K.B,andDarshanRaj.G.C,(2015)-Antibactirial and in vitro Antioxidant Activities Of Some-4-amino-1.2.4-Triazole-5(4H)ThioneDerivatives,Journal of Fundamental And Applied Sciences,Vol7(3),PP.394-407.
10. Bacchi.A, Carcelli.M, Pelagatti.P, Pelizzi.C, Pelizzi.G, Zani.F,(1999)- Antimicrobial and mutagenic activity of some carbon and thiocarbonohydrazone ligands and their copper(II), iron(II) and zinc(II) complexes, Journal of Inorganic Biochemistry, Vol75,123–133..
11. Gangarapu.K, Manda.S, Jallapally.A, Thota.S, Karki.S, Balzarini.J, De Clercq.E,andTokuda.H,(2013)- Synthesis of thiocarbohydrazide and carbohydrazide derivatives as possible biologically active agents, MEDICINAL CHEMISTRY RESEARCH,
12. Gangarapu.K, Manda.S, Jallapally.A, Thota.S, Karki.S, Balzarini.J, De Clercq.E,andTokuda.H,(2013)- Synthesis of thiocarbohydrazide and carbohydrazide derivatives as possible biologically active agents, MEDICINAL CHEMISTRY RESEARCH
13. CHANDR.A. and SHARMA.A.K,(2009)- Biological and spectral studies of transition metal complexes with a quinquedentate Schiff base, 2,6-diacetylpyridine bis(thiocarbohydrazone), Journal of Coordination Chemistry, Vol. 62, No. 22,PP. 3688–3700.
14. Shebl.M,Khalil.E.M,Al-Ghani.S.F,(2010)- Preparation, spectral characterization and antimicrobial activity of binaryand ternary Fe(III), Co(II), Ni(II), Cu(II), Zn(II), Ce(III) and UO2(VI) complexes Of a thiocarbohydrazone ligand , Journal of Molecular Structure ,Vol(980),PP.78-87.
15. Bacchi.A, Carcelli.M, Pelagatti.P, Pelizzi.C, Pelizzi.G, Zani.F,(1999)- Antimicrobial and mutagenic activity of some carbon and thiocarbonohydrazone ligands and their copper(II), iron(II) and zinc(II) complexes, Journal of Inorganic Biochemistry, Vol75,123–133.