

# Synthesis and Characterization of Ligand Type $N_2S_2$ and its Various Metal Ions Complexes $Zn^{+2}$ , $Co^{+2}$ and $Cu^{+2}$

Saleh Abdulkarem Hassan<sup>(1)</sup>

Basima Gattea Salman<sup>(2)</sup>

1- Department of Dentistry, the university college of humanities.

2- Department of Medical Lab. Science and Technology, Al-Yarmouk University

## Abstract:

The present work concerned with the synthesis and characterization of ligand  $N_2S_2$  donor atoms, since this ligand considered to be anticancer, antitumor and antibacterial agents, the ligand was prepared by the condensation reaction between one mole of benzoyal acetone and two mole of thiosemicarbazide. The complexes of this ligand were formed from the direct reaction of divalent metal ions such as  $Co^{+2}$ ,  $Cu^{+2}$  and  $Zn^{+2}$  with ligand.

The ligand and their complexes were characterized by FT-IR, UV-Vis, and C.H.N microanalysis methods. The melting point and molar conductivity measurements were carried out as well as the solubility in different solvents. The spectroscopic studies and molar conductivity measurements suggested that the complexes have a geometry around the metal ions is distorted tetrahedral.

E-mail: [chemistrysalman@yahoo.com](mailto:chemistrysalman@yahoo.com)

## **Introduction:-**

The chemistry of coordination complexes of metallic elements formed a great significance and took a great deal of attention, especially those complexes containing sulfur and nitrogen-giving system  $N_2S_2^{(1,2)}$  and demonstrated the importance of these complexes through their use in medical fields (diagnosis and treatment) in certain types of diseases and cancers that afflict the body<sup>(3)</sup>. meanwhile some of these complexes that containing ligand type  $N_2S_2$  models have been used in some enzymatic reactions as mimic or coenzymes as nickel and copper complexes<sup>(4, 5)</sup> furthermore, these complexes formed a huge importance in different sites of life and especially in industry and as a source for many studies in this regard<sup>(6,7)</sup> the most important stereo chemical models in transition metal

Coordination chemistry. Moreover, it has been proved that azomethine linkage ( $C=N$ ) of Schiff base provides the opportunity for the stupendous biological activities such as antitumor, antibacterial, antifungal and herbicidal activities<sup>(8, 9)</sup>. Among the research progress in Schiff base complexes, the development of new drugs and Catalysts have obtained special concern for the past few years. Because

The coordination complexes derived from transition metals with Schiff base ligands play a significant role in many catalytic reactions like oxidations, asymmetric cyclo-propanation and polymerization<sup>(10, 12, 13)</sup>. Ketimines (ligand type  $N_2S_2$ ) produce from the condensation reactions of ketones with primary amines and contain azomethenes ( $C = N$ ) which known in chemistry as Schiff bases<sup>(14, 15)</sup>.

## **Materials and Method**

All chemicals were purchased from Fluka and BDH chemical company, and were used without further purification. Melting points were measured on Stuart melting point Apparatus. IR Spectra of the ligand and their metal complexes were recorded using KBr discs with FTIR-8400 [Fourier transform infrared spectrophotometer Shimadzu] covering the range ( $4000-400\text{ cm}^{-1}$ ). Electronic Spectra of prepared compounds were measured in the region (800-200) nm for  $10^{-3}$  Molar solution in DMF at  $25^\circ\text{C}$  using Shimadzu 160 spectrophotometer with  $1.000 \pm 0.001\text{cm}$  matched quartz cell. Electrical conductivity

measurements of the complexes were recorded at 25° C for  $10^{-3}$ M solution of the sample in DMF using Capacitor Analyzer and Resistance bridge type CRB<sub>3</sub>. Elemental analysis (C.H.N) was obtained using Perkin Elmer 240 B Elemental Analy

### **A- Synthesis of Schiff base [L]**

In a 50 ml round bottomed flask, 1g ( $6.165 \times 10^{-3}$  mole) of benzoyl acetone was placed. It was dissolved in (15ml) of ethanol. To the solution 1.12g (0.012mole) of thiosemicarbazide was added gradually with stirring. The mixture was stirred for ten minutes then heated under reflux for 150 minutes. The color of the mixture was turned to yellow. The mixture was cooled down and filtered. The solid product was washed with cold ethanol. The filtrate was allowed to evaporate at room temperature, a yellow crystals was obtained, The weight of the obtained crystals was 1.5g ( $0.48 \times 10^{-2}$  mole) and percentage of yield 83% recorded the melting point which was in the range 93° - 94° C.

### **B- Synthesis of [ZnL]**

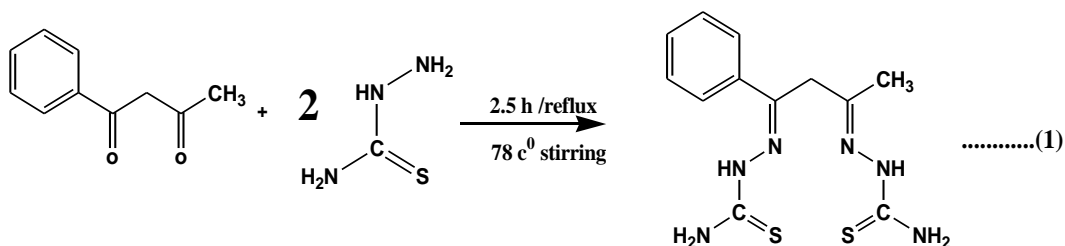
In a 50 ml round bottomed flask, 1g ( $3.2 \times 10^{-4}$  mole) of [L] was placed. It was dissolved in (15ml) of methanol. To the solution 4.4g ( $3.3 \times 10^{-3}$  mole) of zinc chloride was added gradually with stirring. The mixture was stirred for ten minutes then heated under reflux for 150 minutes. The color of the mixture was turned to white. The mixture was cooled down and filtered. The solid product was washed with cold methanol. The filtrate was allowed to evaporate at room temperature, a white crystals was obtained, The weight of the obtained crystals was 0.03g and percentage of yield 54% then recorded the melting point which was in the range 178° - 179° C.

Table (1): Physical data of the prepared complexes

Salt used	Wight Salt	Wight of ligand	product	%	color	mp C°
CoCl <sub>2</sub>	0.094	0.1 g	0.09g	81%	Red- brownish	143-144
CuCl <sub>2</sub>	0.055	0.1 g	0.07g	52%	Light- green	161-162

## Results and Discussion:-

**A - Schiff base [N<sub>2</sub>S<sub>2</sub>] ligand** was prepared by using one equivalent benzoyl acetone with two equivalent of Thiosemicarbazide, using ethanol as a solvent by the equation below:-



The prepared compounds have been characterized by FTIR, UV-Visible spectroscopies, the microanalysis of elements (C.H.N), melting point, solubility with various solvents and the electrical conductivity.

## B- Infrared spectrum

### Infrared spectrum of ligand [L]

The infrared spectrum of the starting material Benzoyl Acetone showed in figure (1) special band at the wave length ( $3100\text{ cm}^{-1}$ ) belong to stretch  $\nu(\text{C-H})$  bond for the aromatic rang, and showed the stretch  $\nu(\text{C=O})$  for the carbonyl wide band in the range ( $1610, 1600\text{ cm}^{-1}$ ), the reason in appear these band at that way could be due to present two different carbonyl croups, one of them neighbored the methyl group ( $-\text{CH}_3$ ) and the other neighbored the vinyl ring ( $\text{Ph-}$ )<sup>(16)</sup> Figure (2) showed special infrared spectrum bands of the substrate (thiosemi carbazide): one of them at the wave length ( $3377\text{ cm}^{-1}$ ) belong to stretch of  $\nu(\text{N-H})$  and other double band at wave length ( $3280, 3263, \text{ cm}^{-1}$ ) belong to amine group  $\nu_{\text{asymm}}$  and  $\nu_{\text{symm}}$  ( $\text{N-H}_2$ ). While the band at frequency ( $1648\text{ cm}^{-1}$ ) was belong to the Tutomerism of ( $\text{C=S}$ ) and ( $\text{C=N}$ ) bonds between the amine group neighbored ( $\text{C=S}$ ) group. The band ( $1622\text{ cm}^{-1}$ ) was belong to bent  $\delta$  ( $\text{N-H}$ ) bond, meanwhile ( $\text{C=S}$ ) bond showed two different bands: at wave length ( $1535\text{ cm}^{-1}$ ) belong to bent ( $\text{C=S}$ ) bond, and the other at ( $1317, 1000\text{ cm}^{-1}$ ) were belong to  $\nu(\text{C=S})$  stretch.

In figure (3); special bands were disappear from the infrared spectrum of the ligand [L] which were  $\nu(1610, 1600\text{ cm}^{-1})$  that belong to stretch substrate's carbonyl group, in addition to band ( $1648\text{ cm}^{-1}$ ) that was belong to Tutomrism between ( $\text{C=S}$ ) and neighbored ( $\text{N-H}$ ). In the same figure new band was appear at ( $1683\text{ cm}^{-1}$ ) which belong to asomethene group  $\nu(\text{C=N})$  and this considered as an evidence to the formation of Schiff base in the product, meanwhile the bands ( $3300-1215\text{ cm}^{-1}$ ) could be refer to stretch of  $\nu(-\text{NH}_2, -\text{NH})$  respectively<sup>(17)</sup>. As well as the stretch of  $\nu(\text{C=S})$  bond could be notice at wave length ( $1283, 1000\text{ cm}^{-1}$ ).

## Infrared spectra of ligands $[\text{Zn}(\text{L})]^{+2}$ , $[\text{Co}(\text{L})]^{+2}$ , $[\text{Cu}(\text{L})]^{+2}$

The infrared spectrum of zinc, cobalt, and copper complexes showed gradient shift at the wave length ( $1683\text{ cm}^{-1}$ ) which belong to stretch frequency of  $\nu(\text{C}=\text{N})$  bond, in the free ligand its easily notice the shift to lower frequency ( $1645, 1666, 1676\text{ cm}^{-1}$ ) for  $(\text{Cu}^{+2}, \text{Co}^{+2}, \text{Zn}^{+2})$  ions respectively and that due to the delocalization of negative charge between metal ion and Isomethene group that belong to transition from HOMO→LUMO:-

**HOMO: - Highest Occupied Molecular Orbital**

**LUMO: - Lowest Unoccupied Molecular Orbital**

In addition to the shifts in  $(\text{C}=\text{S})$  bond (bent and stretch) that happen due to the coordination of the metal ion with sulfur and nitrogen electron peers, meanwhile new bands were appear belong to these complexes (ligands) at different range: ( $570\text{-}520\text{ cm}^{-1}$ ) and ( $472\text{-}450\text{ cm}^{-1}$ ) which were belong to stretch of M-N and M-S respectively<sup>(18)</sup> as in figures (4, 5, and 6).

## C- UV-VIS. Spectra Spectra of ligand [L]

The electronic spectra of ligand is presented at figure (7) displays two characteristic at ( $350\text{ nm}$ ) ( $32786.8\text{ cm}^{-1}$ ) ( $952\text{ L.mole}^{-1}\text{ cm}^{-1}$ ) and ( $411\text{ nm}$ ) ( $24330.1\text{ cm}^{-1}$ ) ( $1098\text{ L.mole}^{-1}\text{ cm}^{-1}$ ) which belong to a  $(\pi\rightarrow\pi^*)$ ,  $(n\rightarrow\pi^*)$  respectively. The electronic spectra of zinc ion complex is presented figure (8) it showed the charge transfer and ligand field as well as d - d<sup>\*</sup> transition<sup>(19)</sup> at the wave length ( $312\text{ nm}$ ) ( $32051.8\text{ cm}^{-1}$ ) ( $157\text{ L.mole}^{-1}\text{ cm}^{-1}$ ), the spectra of cobalt and copper ion complexes are presented at figure (10,11) respectively appeared the charge transfer and ligand field as well as d - d<sup>\*</sup> transition<sup>(19)</sup> at the wave length ( $299\text{ nm}$ ) ( $33448.1\text{ cm}^{-1}$ ) ( $784\text{ L.mole}^{-1}\text{ cm}^{-1}$ ) belongs to charge transfer, weak peak at ( $301\text{ nm}$ ) ( $33222.5\text{ cm}^{-1}$ ) ( $675\text{ L.mole}^{-1}\text{ cm}^{-1}$ ) and weak peak in rang between ( $545\text{-}618\text{ nm}$ ) refer to the d - d<sup>\*</sup> transition type ( $^4\text{A}_{2\rightarrow}^4\text{T}_2$ )<sup>(20)</sup> and ( $^2\text{E}\rightarrow^2\text{T}_2$ )<sup>(21)</sup> indicating the geometry of zinc ,cobalt and copper at figures(9,10, and 11) shows these peaks.

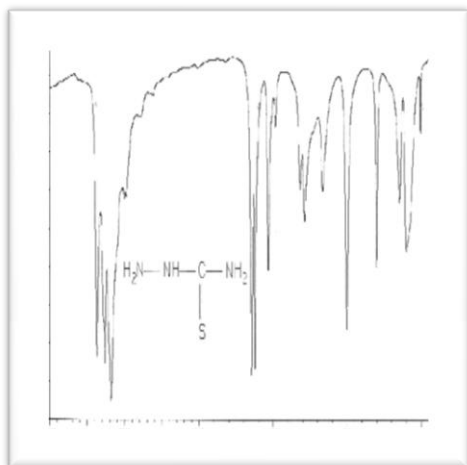


Fig.(2)spectrum IR of thiosemicarbazid

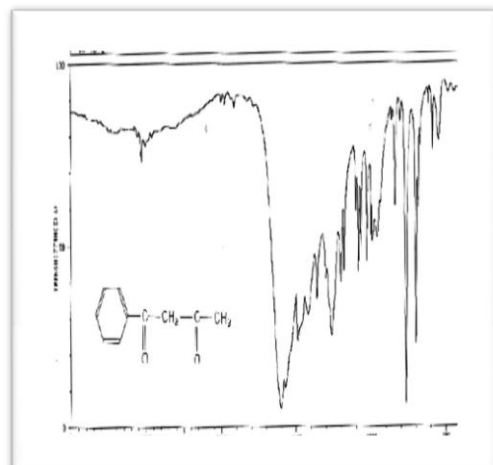


Fig.(1)spectrum IR of Beanzoyl Acetone

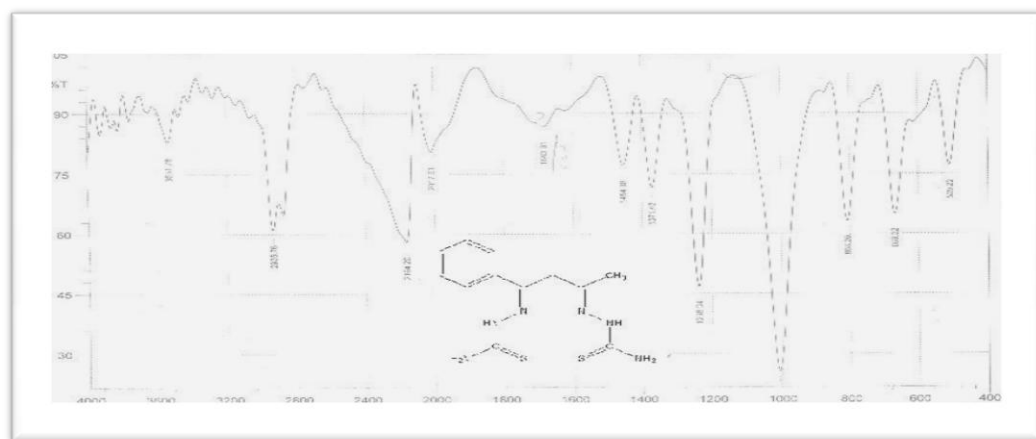


Fig. (3) Spectrum IR of complex [L]

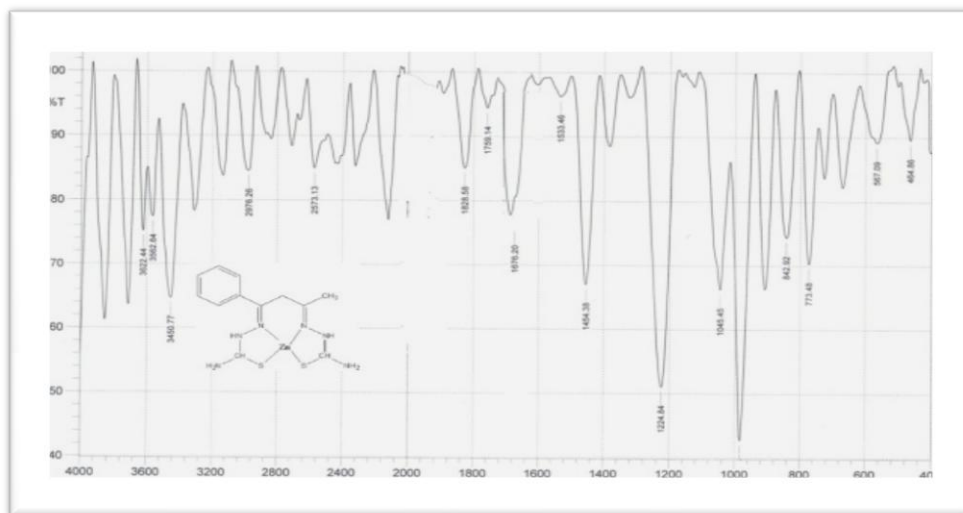


Fig.(4)spectrum IR of complex  $[ZnL]^{+2}$

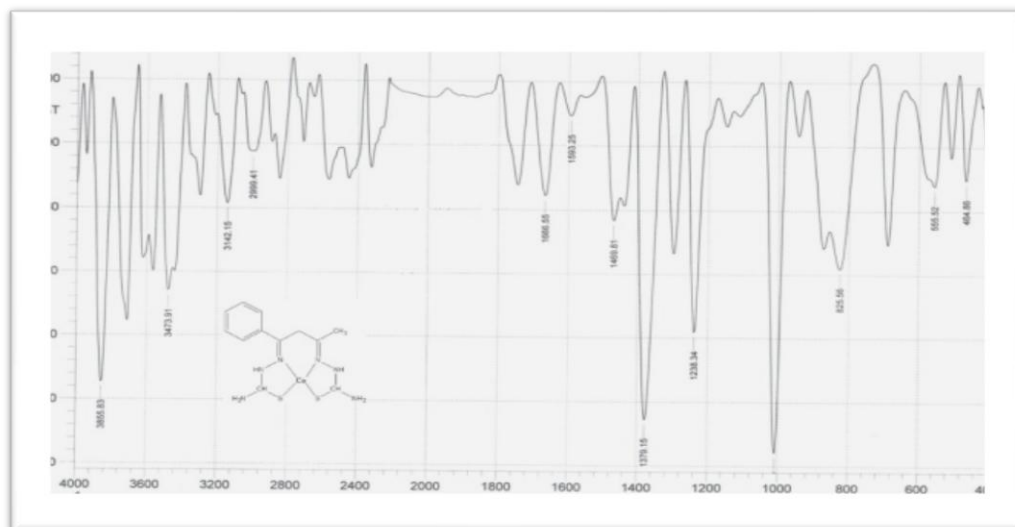


Fig.(5)spectrum IR of complex  $[CoL]^{+2}$



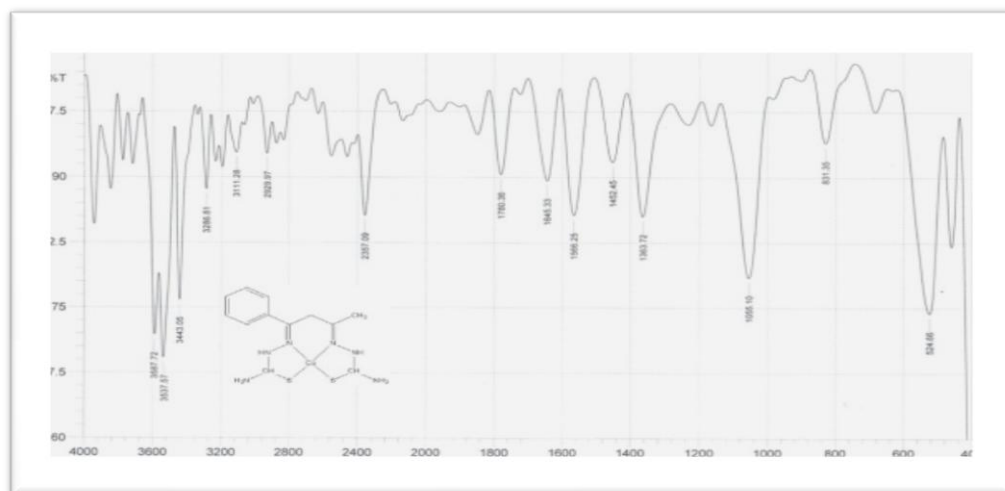


Fig.(6)spectrum IR of complex  $[CuL]^{+2}$

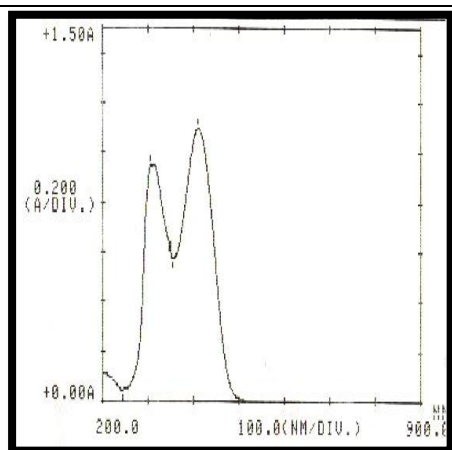


Fig.(7)spectra uv-vis of [L]

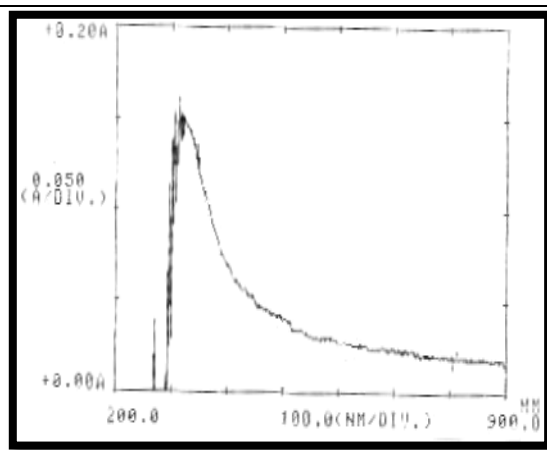


Fig.(8)spectra uv-vis of [ZnL]<sup>+2</sup>

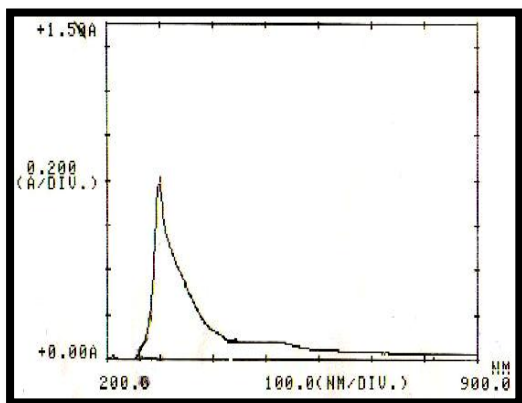


Fig.(9)spectra uv- vis of [CoL]<sup>+2</sup>

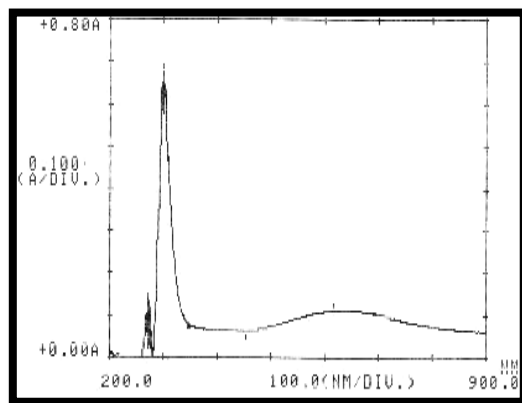


Fig.(10)spectra uv-vis of [CuL]<sup>+2</sup>

D- Geometry of prepared complexes  $[\text{Zn}(\text{L})]^{+2}$ ,  $[\text{Co}(\text{L})]^{+2}$ ,  $[\text{Cu}(\text{L})]^{+2}$

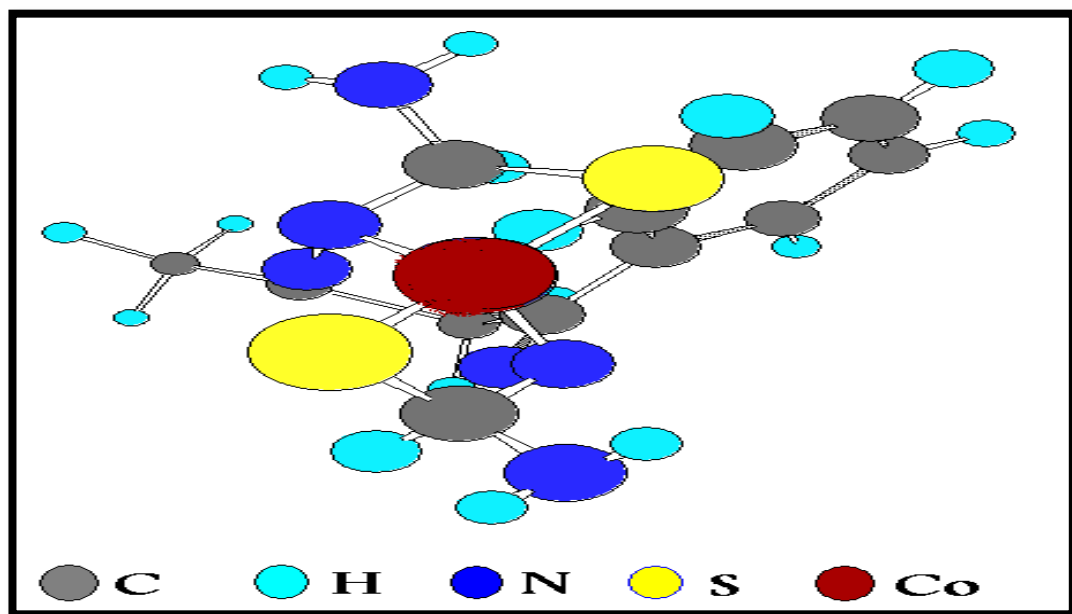
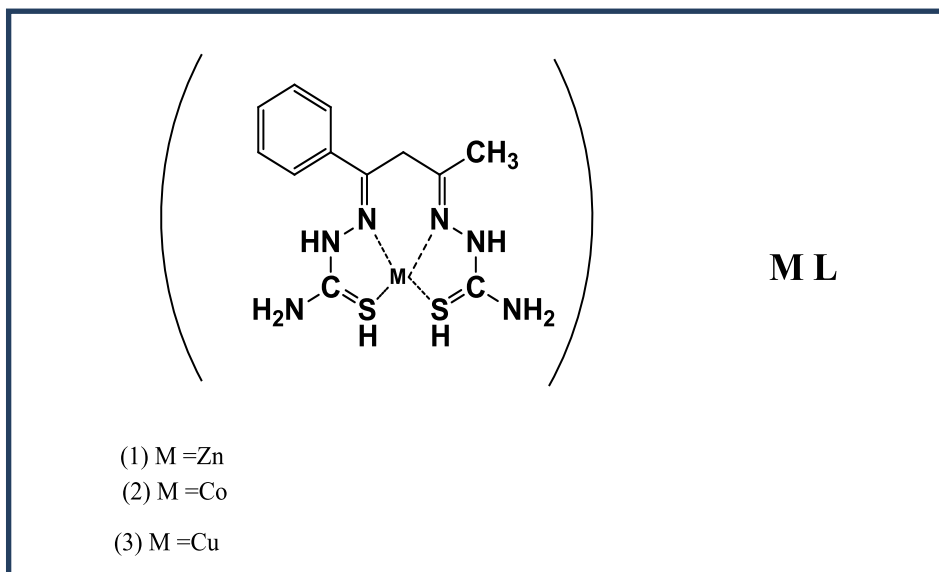


Figure (11-a): coordination of prepared complexes

## References:

1. M. N. Hughes; "The Inorganic Chemistry of Biological Processes"; 2<sup>nd</sup>. Ed.; John Wiley and sons, (1988).
2. F.A. cotton, G. willinson, "Advanced Inorganic Chemistry ", 4<sup>th</sup> Ed. Wilegintre Sciences; (1980).
3. S. Z. lever, H. D. Burns, T. M. Kervitsky, H. W. Goldfart, D.V. Wong, L. A. Epps, A. V. Karmer, and H. N. Wagner, JR. J. Nucl. Med, 26, 1287(1985).
4. K. E. Baidoo and S. Z. lever; Bio conjugate chem., 1, 132, (1990).
5. K. E. Baidoo and S. Z. lever; cancer Res. (supll), 50, 7995 (1990).
6. S. Z. lever, S. Y. Sun, F. kaltovich, U. Scheff, 1, H.Goldfart, A. Mahmood, K. E Baidoo and H.N. Wagner; J. Nucl. Med, 29, 789 (1988).
7. **J. P. O'Neil, S.R. Wilson and J. A. Katazenellenbogen; Inorgani Chemistry, vol. 33 No (1994).** 8. S. Rekha, K.R. Nagasundara, Indian J. Chem. a 4 2421(2006).
9. N. Raman, A. Selvan, S. Sudharsan, Spectrochim. Acta A 79 (2011) 873.
10. A. Golcu, M. Tumer, H. Demirelli, R.A. Wheatley, Inorg. Chime. Acta 358 (2005) 1785.

11. A.A.A. Aziz, A.N.M. Salem, M.A. Sayed, M.M. Aboaly, J. Mol. Struct. 1010 (2012) 130.
12. C. Jiang, Z. Ming, Q. Tan, D. Qian, T. You, Enantiomer 7 287. (2002)
13. S. J. Gruber, C. M. Harris and E. Sinn, J. Inorg. Nucl. Chem., 301805, (1986).
14. Prakash A, Adhikari D. Application of Schiff bases and their meta complexes areview. Int J Chem Tech Res; 3:1891e6(2011)
15. A. H. Dawood, M.Sc. Thesis, University of Baghdad, College of Education (Ibn- Al-Haitham) (2002)
16. A. H. Dawood, Ph.D. Thesis , University of Baghdad, College of Education (Ibn- Al-Haitham) (2006).
17. Gh. M. Abd M.sc. Thesis, University of Baghdad, College of sciences, (2008).
18. N. N. Green Wood and A. Earnshaw “ Chemistry of the Elements “J. Wiley and Sons . Inc. New York (1998).
19. A. B. P. Lever, “Inorganic Electronic Spectroscopy 2<sup>nd</sup> Edition “,New York (1984).
20. J. C. Bailer and J. R. Urban “comprehensive Inorganic chemistry “First Edition, Pergamon Press Oxford, (1975).
21. M. A. Ali, and S. G. Teoh, J. Inorg. Nucl. Chem. 40. 451, (1978).

## تحضير وتشخيص $N_2S_2$ ومعقداته مع ايونات عناصر فلزية ثنائية التكافؤ ليكند من نوع



د. صالح عبد الكريم حسن<sup>1</sup> باسمة كاطع سلمان<sup>2</sup>

1- استاذ مساعد كلية الدراسات الانسانية الاهلية / قسم طب الاسنان

2- كلية اليرموك الجامعة الاهلية / قسم التحليلات المرضية.

### الخلاصة :-

تضمن البحث تخليق وتشخيص ليكند جديد من نوع  $N_2S_2$  كذرات واهبة لما لهذه الليكندات من اهمية لاستخدامها كمضادات للاورام السرطانية والاورام وكمضادات بكتيرية .

حضر الليكند من تفاعل التكتيف لمول واحد من البنزويل اسيتون مع مولين من الثايوسيبي كاربازايد .

وحضرت معقدات لهذا الليكند مع ايونات فلزية ثنائية التكافؤ  $Co^{+2}$ ،  $Cu^{+2}$  و  $Zn^{+2}$  بمفاعله مباشرة مع املاح تلك لايونات .

شخص الليكند ومعقداته بوساطة مطيافية الاشعة تحت الحمراء FTIR، الاشعة فوق البنفسجية والمرئية UV-Vis والتحليل الكمي الدقيق (C.H.N) وكذلك قيست درجات الانصهار، التوصيلية المولارية وقابلية ذوبانها في مذيبات مختلفة ومن الدراسات الطيفية والتوصيلية المولارية توصلنا الى الشكل الهندسي لهذه المعقدات وهو رباعي السطوح المشوه .

