

Preparation , characterization and molecular models of a ligand derivative of the 1,3,4-thiadiazole and some transition metal complexes.

تحضير وتشخيص و أشكال الجزيئات لمشتقات اللكند ل(١,٣,٤-ثياديازول) و بعض فلزات العناصر الانتقالية.

.Waleed Muhsen Sarhan, Chemistry Department, college of science, Kufa university

Abstract:

That thiadiazoles derivative are biologically active as antimicrobial agent⁽¹⁾ . therefore, the derivative of the 1,3,4-thiadiazole has prepared along with series of their metal complexes. The reaction of ligand; 2-amino-5-[[diethylamino]carbonothioyl]dithio}1,3,4-thiadiazole with Cu(II) , Fe (II) , Ni (II) ions yield the following complexes [Cu(ligand)₂Cl₂], [Fe(ligand)₂(H₂O)₂]SO₄ , [Ni(ligand)₂Cl₂] . The ligand and their metal complexes were characterized using the appropriate techniques, which included melting point, IR, and UV-visible .According to the data obtained, the structural formula with three dimensions of our complexes were suggested.

الخلاصة:

من المعروف إن عدد من مشتقات الثيادايازول تمتلك فعالية بيولوجية كعوامل مضادة للميكروبات^(١) لذلك تم تحضير مركب جديد مشتق من حلقة ١,٣,٤-ثيادايازول و اختيرت لتحضير سلسله من المعقدات الفلزية الجديدة. إن تفاعل اللكند : ٢-امينو-٥-[[داي اثل امينو]كاربونوثايول]داي ثايو }١,٣,٤-ثيادايازول مع الايونات التالية : Ni (II) , Cu (II) , Fe (II) وقد أعطت المعقدات التالية : [Cu(ligand)₂Cl₂] ، [Fe(ligand)₂(H₂O)₂]SO₄ ، [Ni(ligand)₂Cl₂] . ان اللكند المحضر قد شخص باستخدام التقنيات المناسبة و التي شملت كل من : درجات الانصهار ، و أطيف الاشعه تحت الحمراء و المرئية – فوق البنفسجية ، و بالاعتماد على النتائج المستحصلة من هذه القياسات تم اقترحت أصيغه التركيبية و الشكل ذو الأبعاد الثلاثة للمعقدات الجديدة.

Introduction

A glance at the standard references show that most of the studies has been carried out on the 1,3,4-thiadiazole-containing compounds which are synthesized and tested for their antimicrobial activity⁽²⁻³⁾, these compounds had received more attention during the last decade. It has found that the substituted thiadiazole to display fungicidal⁽⁴⁻⁵⁾, neumatocidal⁽⁶⁾, and antitubercular⁽⁷⁾ activities.

1,3,4-thiadiazole derivatives⁽⁸⁾ are associated with a number of biological activities probably due to the presence of the -N=C-S groups⁽⁹⁾. substituted thiadiazole have been reported to display diverse applications as oxidation inhibitor, cyanine dyes, and metal complexing agents too⁽¹⁰⁾.

The main role for the disulfide bonds is the stabilize the three dimensional structure of molecule⁽¹¹⁾, by Pryor had suggested that bivalent sulfur bond is nearly pure p orbital. The bond angle for two atoms attached to sulfur was about 105⁰ . the four electrons that still left on a sulfur atom were assigned as two to the s orbital and two to the third p orbital. In disulfide bond, the pairs of the non-

bonded p electrons on adjacent atoms were considered to repel each other, so that ,to minimized repulsion, R groups of R-S-S-R take the dihedral angle of about 90° . As a result of this situation, the molecule creates a barrier for rotation around the disulfide bond⁽¹²⁾.

Experimental part

Apparatus

1) Infrared spectroscopy

I.R. spectra of the prepared compounds (KBr disc) recorded using Pye Unicam SP3-100 and perkin-Elmer 1130 infrared spectrophotometer (4000-600 cm^{-1} range)

2) Electronic absorption spectra

The electronic spectra of the complexes were obtained using shimadzu uv-vis-160A ultra-violet spectrophotometer at room temperature using silica cells of 1.0cm length

Purification of starting material

1- thiosemicarbazide was purified by recrystallization from hot distilled water. This process produced pale yellow crystal.

2- carbon disulfide was purified by extraction from isobutanol. thioacetic acid was purified by adding equal amount of sodium bicarbonate to convert the acid to salt and then extracted from aqueous layer. This product was used as such in the preparation of ligand

Preparation of ligand

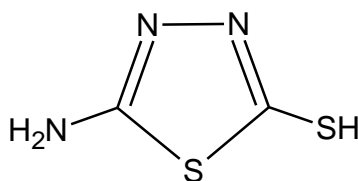


Figure (1): 5-amino-1,3,4- thiadiazol -2-thiol compound

5-amino-1,3,4- thiadiazol -2-thiol compound fig.(1) was prepared by the method adopted by Petrow and co-workers⁽¹³⁾ as follows:

Thiosemicarbazide (0.3 mole, 27.3 g) was suspended in absolute ethanol (105 ml), anhydrous sodium carbonate (15.9 g) and carbon disulfide (0.36 mole, 27.6 g) were then added and the mixture was refluxed with stirring for 6 hrs. The reaction mixture was then allowed to cool at room temperature and filtered. The filtrate was evaporated to dryness under reduced pressure and the residue was dissolved in distilled water (600 ml) and acidified to pH 6 with concentrated HCl to give

an orange precipitate. The crude product was filtered, washed excessively with distilled water and recrystallized from hot water to give compound as yellow needles.

Preparation of bis(5-amino-1,3,4- thiadiazol-2-yl) disulfide

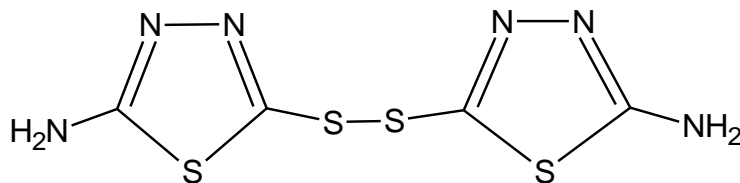


Figure (2): bis(5-amino-1,3,4- thiadiazol-2-yl) disulfide

This compound fig.(2) was prepared by oxidation of compound (5-amino-1,3,4- thiadiazol -2-thiol) using hydrogen peroxide ⁽¹⁴⁾.

Hydrogen peroxide (31 ml, 3% w/v) was added drop wise to a solution of 5-amino-1,3,4-thiadiazol -2-thiol (45.8 m mole, 6g) in ethanol (50 ml) with continuous stirring for 1 hr at room temperature'. A yellow precipitate was formed, and this was collected by filtration, washed with distilled water and dried in oven at 70°C to provide compound .

Preparation of 2-amino-5-[[[(diethylamino)carbonothioyl]dithio]1,3,4-thiadiazole :

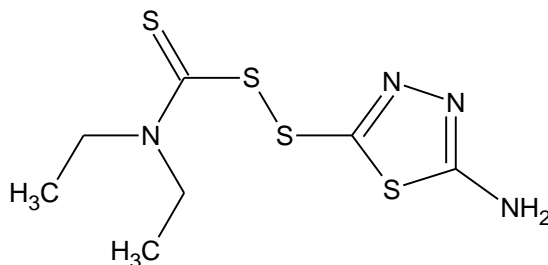


Figure (3) 2-amino-5-[[[(diethylamino)carbonothioyl]dithio]-1,3,4-thiadiazole

This compound fig. (3) was prepared by the general procedure of thiol-disulfide interchange method⁽¹⁴⁾.

An aqueous solution (30 ml) containing sodium diethyldithiocarbonate (2.12 g) was added to the yellowish compound of bis(5-amino-1,3,4- thiadiazol-2-yl) disulfide (3.5 g). The reaction mixture was stirred continuously for 1 hr at room temperature. A straw yellow precipitate was formed, and this was filtered, washed with distilled water and dried in an oven at 70°C.

Preparation of Metal Complexes:

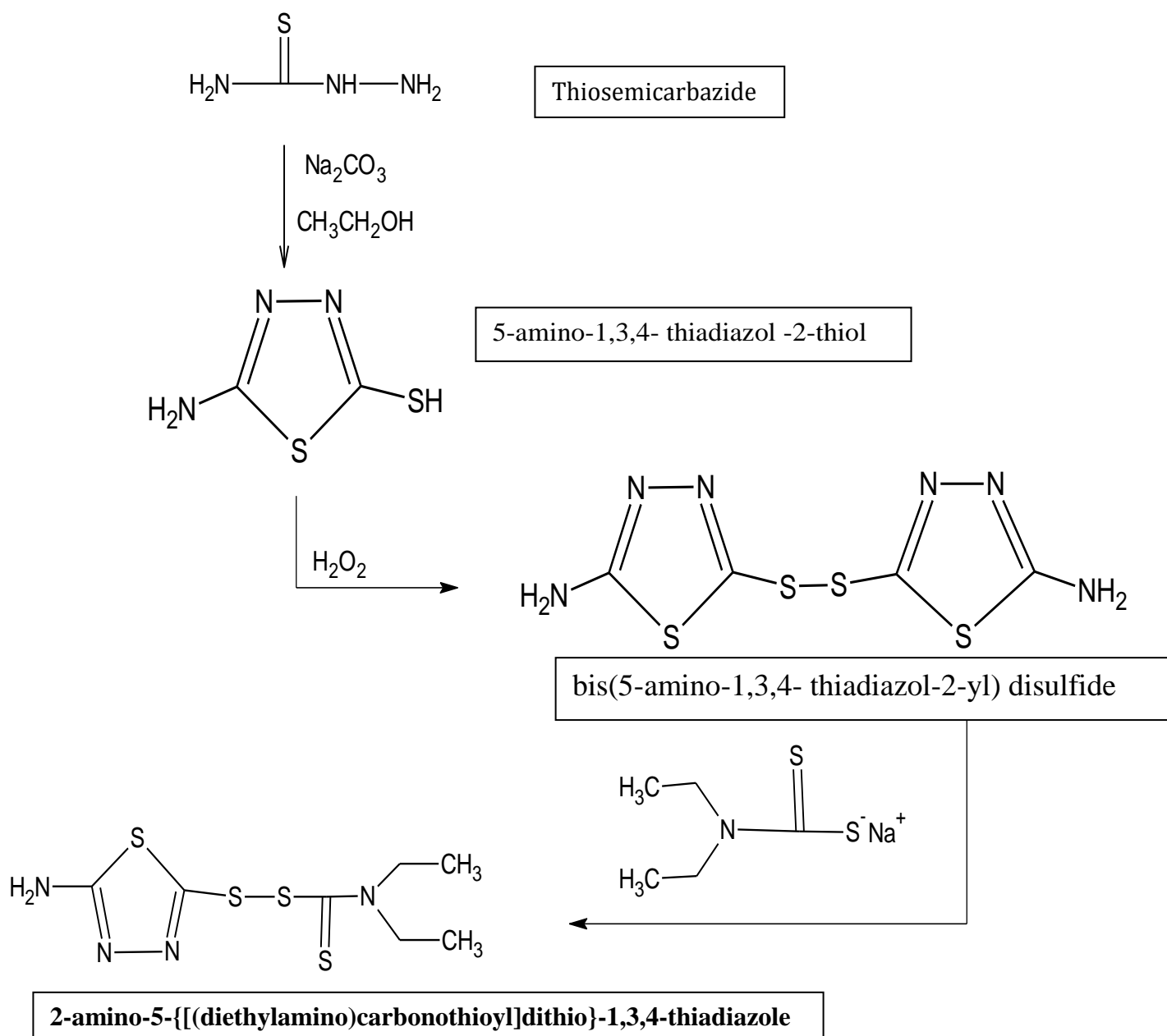
Each individual metals ion was prepared by a general procedure ⁽¹⁵⁾ as follows:

to 1 mmole of metals ions {which are; Cu²⁺ , Ni²⁺ ions used as chloride salts except Fe²⁺ ions as sulfate } dissolved in distilled water and add 2 mmole of the ligand to the aqueous solution of the ion . the complexes produced were washed with distilled water, filtered and dried in an oven at 70°C.

Results and Discussion;

Preparation, Mechanism, And Identification Of Thiadiazole Derivative:

The thiadiazole derivative was prepared according to the general scheme (1) outlined below: -



Scheme (1) Mechanism Of the Thiadiazole Derivative

Good yield, and purer product was produced in this work by introducing some changes on the method of preparation.

Compound was prepared according to the method described by Petrow⁽¹³⁾, through the reaction of thiosemicarbazide with carbon disulfide in the presence of anhydrous sodium carbonate in absolute ethanol. The structure of compound was confirmed by its melting point, I.R and U.V. spectrum which showed λ_{max} at 326 nm that is consistent with the reported data⁽¹⁶⁾.

FT-IR of the ligand

The FT-IR spectrum of ligand , Fig. (4), shows the following bands :-

The two strong - sharp bands appeared at $(3259) \text{ cm}^{-1}$ and $(3270) \text{ cm}^{-1}$ may correspond to symmetric stretching vibrations and asymmetric of (NH_2) , respectively, $(\text{C}=\text{N})$ appeared at $(1645) \text{ cm}^{-1}$. The weak band appeared at $\nu (450) \text{ cm}^{-1}$ could be attributed to the $\nu (\text{S}-\text{S})$ bond. The weak band at $(630) \text{ cm}^{-1}$ could be attributed to $(\text{S}=\text{C})$ stretching vibration group⁽¹⁷⁾.

FT-IR of the Cu(II) complex

The FT-IR spectrum of Cu(II) complex is shown in figure (5), which shows the following features :-

The medium band appears at $(625) \text{ cm}^{-1}$, which correspond to $\nu (\text{C}=\text{S})$ of the ligand⁽¹⁷⁾, was shifted by 22 cm^{-1} compared to that of the uncomplexed (free) ligand, this indicate the coordination of copper (II) ion with the ligand through the sulfur of $\text{C}=\text{S}$ group. A further evidences for the formation of Cu-N band came from the appearance of weak broad band at $(480) \text{ cm}^{-1}$ as a shoulder which correspond to $\nu (\text{Cu}-\text{N})$ ⁽¹⁸⁾.

FT-IR of the Ni(II) complex :

The FT-IR spectrum of Ni(II) complex is shown in figure (6) , which show the following common features : a weak band appeared at $(645) \text{ cm}^{-1}$ which correspond to $\nu (\text{C}=\text{S})$ of the ligand was shafted by $(15) \text{ cm}^{-1}$ compared to that of the uncomplexed (free) ligand, indicating the bonding of nickel ion with the ligand through the sulfur of $\nu (\text{C}=\text{S})$ group, the band corresponding to , another weak band appears at $(475) \text{ cm}^{-1}$ which give further evidences for the formation of $(\text{Cu}-\text{N})$ band.⁽¹⁸⁾

FT-IR Fe(II) ligand complex:-

The FT-IR spectrum of Fe(II) complex is shown in figure (7), which shows of the following bands : the weak band appeared at ν (652) cm^{-1} which correspond to (C=S) of the ligand which came (22) cm^{-1} higher than that of the free ligand, this indicate the bonding of Fe(II) ion with the ligand through the sulfur of (C=S) group. As further evidences for the formation of (Fe-N) band came from the appearance of weak band at (470) cm^{-1} as a shoulder⁽¹⁷⁾⁽¹⁸⁾

Electronic spectra :

The electronic spectra is based on the electronic interaction of the metal d-orbitals and orbitals of the ligand. In our study, the spectra were recorded in the range of (200-1100) nm using solvent - system of 10% ethanol in DMSO:

Below, simple explanations for the electronic spectra of the ligand and their respective complexes.

The ligand has two characteristics bands in the u.v. region, which correspond to the thiadiazole ring at (359) nm and the disulfide bond at (230)nm⁽¹⁹⁾. These two bands were assigned to ($\pi \rightarrow \pi^*$) transitions of the aromatic ring and ($n \rightarrow \pi^*$) transition of the lone-pair of electrons of disulfide bond.

The Cu(II) complex spectra showed one broad band at 825 nm which is an indication for the (${}^2E_g \rightarrow {}^2T_{2g}$) transitions of octahedral geometry figure (8), as expected. These transitions are weak because they are forbidden. The band is an indication for the distortion expected by d^9 complexes (Jahn-Teller distortion)⁽¹⁹⁾.

The electronic spectra for Fe(II) complex showed one absorption band at (380) nm refers to (${}^5T_{2g} \rightarrow {}^5E_g$) transition of the 5D state of d^6 complexes. As suggested, the structure of Fe (II) is octahedral figure (9).

The Ni (II) complex spectra showed two weak bands at; (390) nm, and (432)nm which may be referred to the 3F state of the transition; (${}^3A_{2g} \rightarrow {}^3T_{1g}$) (P), (${}^3A_{2g} \rightarrow {}^3T_{1g}$) (F), the third transition (${}^3A_{2g} \rightarrow {}^3T_{2g}$) of the d^8 system of octahedral figure (10).⁽¹⁹⁾

Formation constant :

The composition of complex was studied by mole-ratio method ⁽²⁰⁾ and this method indicate that the ratio of metal ion to ligand (M:L) was (1:2) for Cu(II), Fe(II) and Ni(II) fig (12, 13, 14) respectively.

The formation constants calculated by applied procedure and was found :

$$\text{Cu(II)} = 0.66 * 10^{14}$$

$$\text{Fe(II)} = 0.23 * 10^{10}$$

$$\text{Ni(II)} = 0.76 * 10^{13}$$

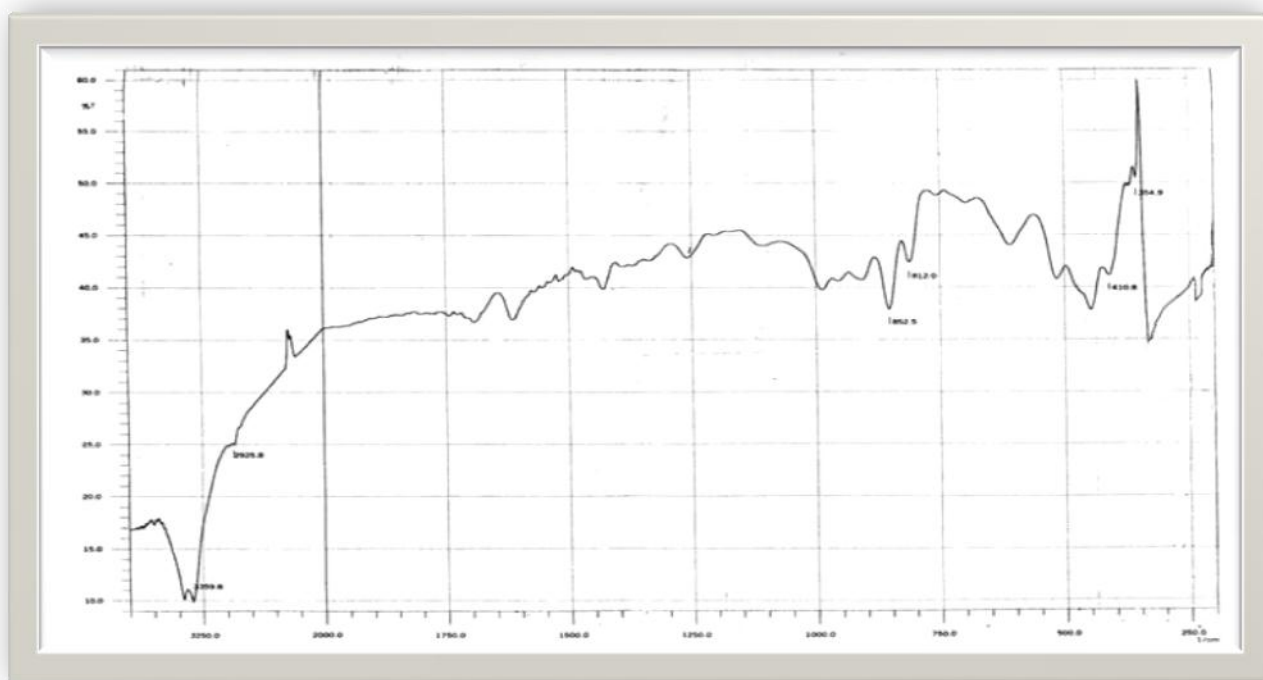


Fig. (4) :- FT-IR spectrum of the ligand

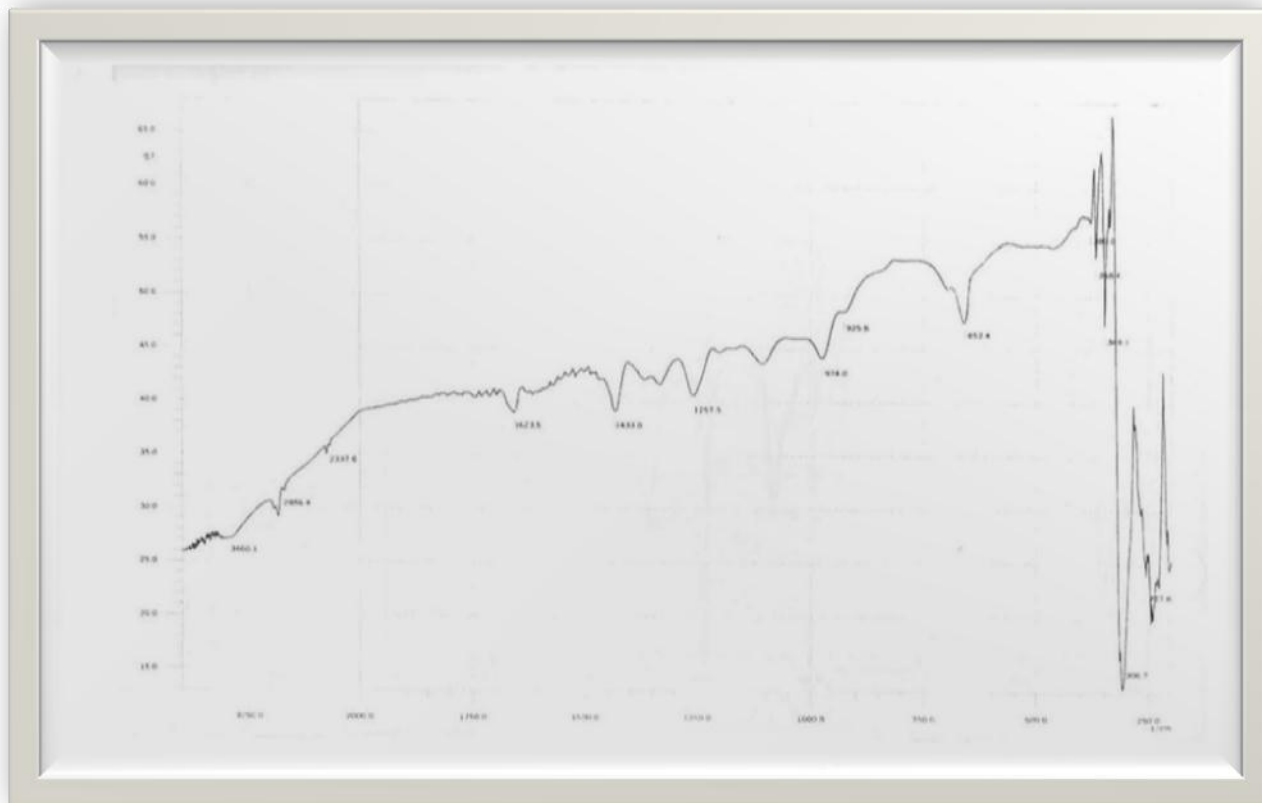


Fig. (5) :- FT-IR spectrum of the Cu(II) complex

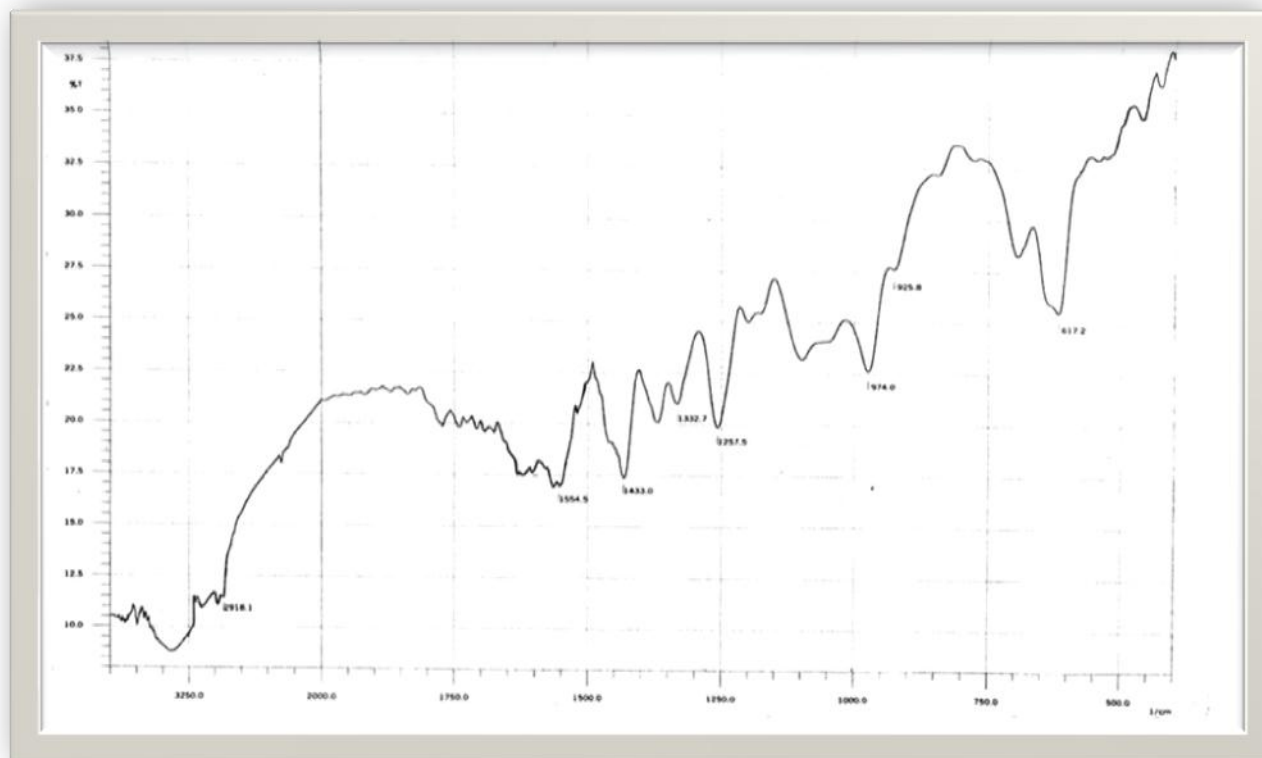


Fig. (6) :- FT-IR spectrum of the Ni(II) complex

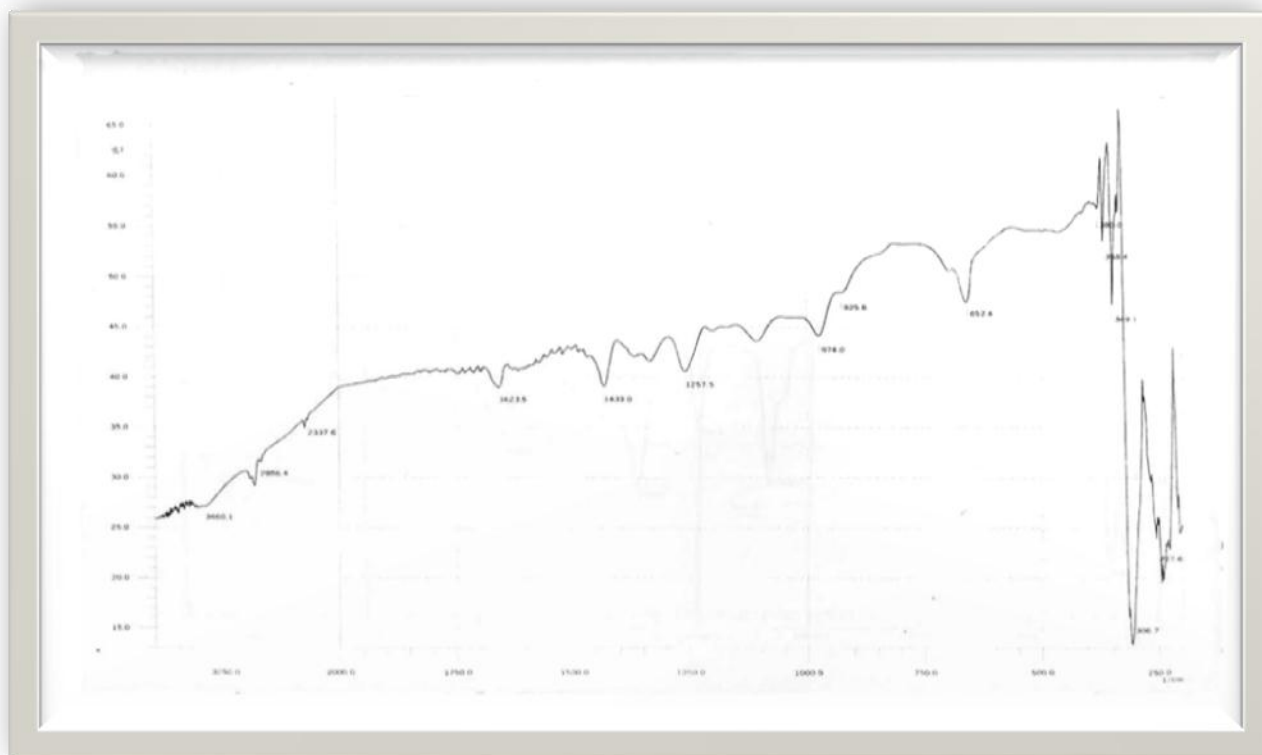


Fig. (7) :- FT-IR spectrum of the Fe(II) complex

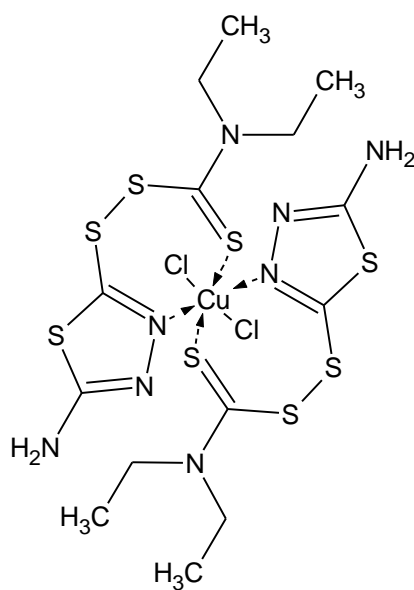


Figure (8) Cu (II) complex

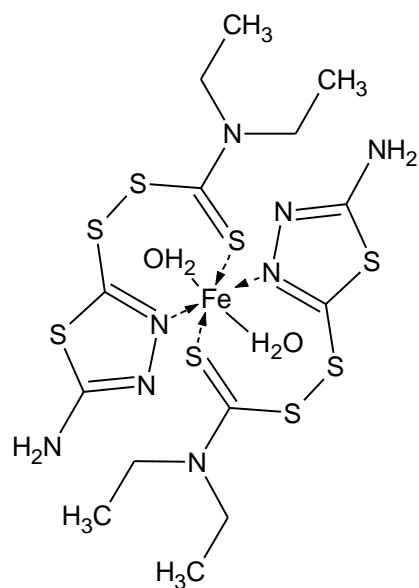


Figure (9) Fe(II) complex

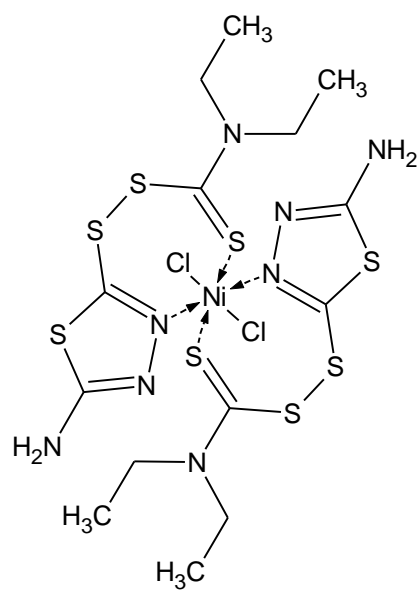


Figure (10) Ni(II) complex

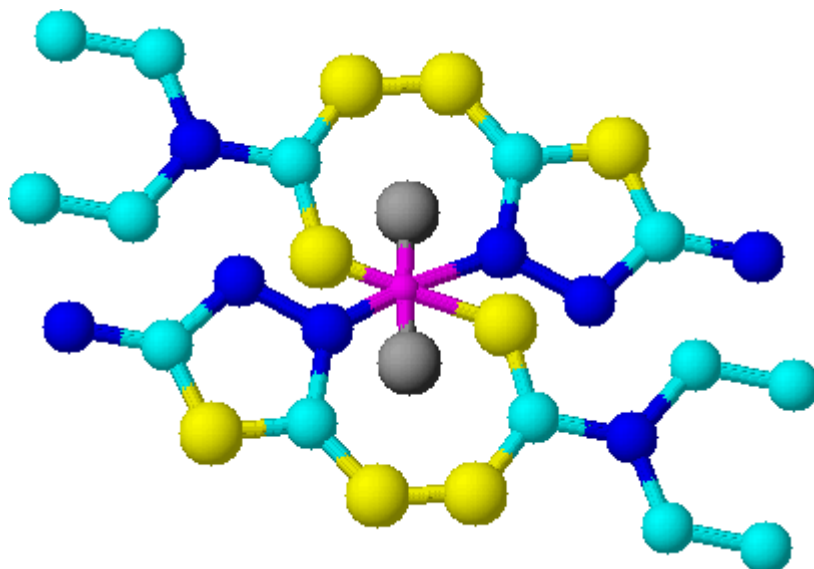


Figure (11) the 3D structure of three complexes

Sample	color	M.P C°
ligand	straw yellow	205-207
Cu(II) complex	blue	242-244
Fe (II) complex	brown	۲۸۳-۲۸۱
Ni (II)complex	Pale blue	۲۷۴-۲۷۳

Table (1) :physical data for the ligand and complexes

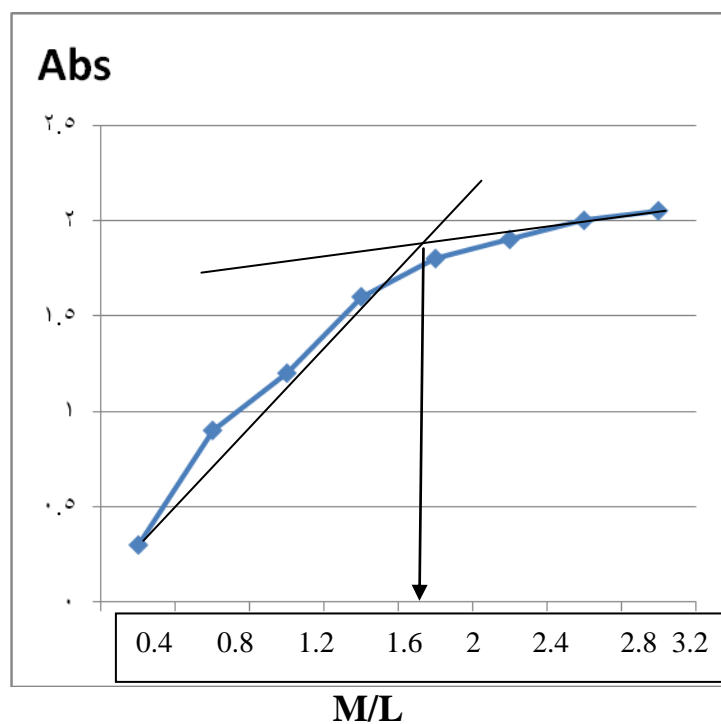
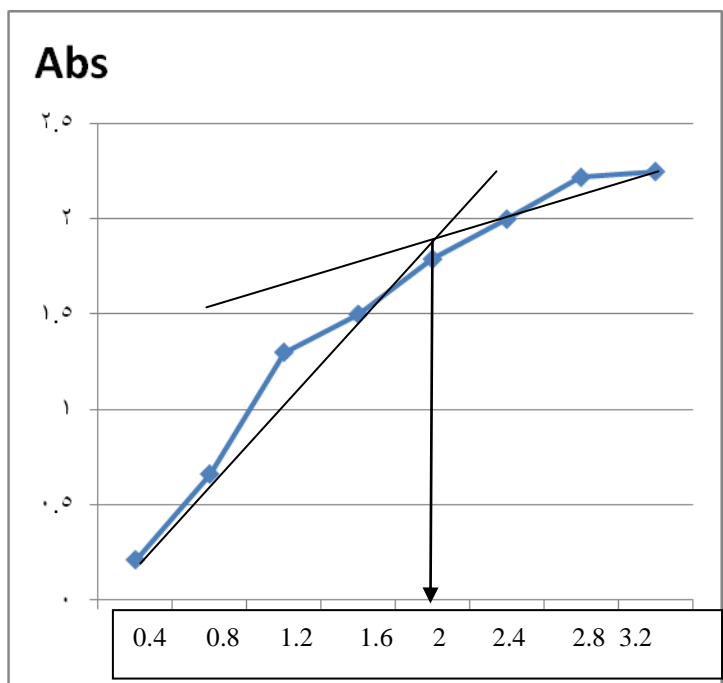


Fig (12) mole ratio of Cu(II) complex

M/L

Fig (13) mole ratio of Fe(II) complex

0.4	0.8	1.2	1.6	2	2.4	2.8	3.2
-----	-----	-----	-----	---	-----	-----	-----



M/L

Fig (14) mole ratio of Ni(II) complex

References

- (1) Wilson & Gisvold's : "Text Book of Organic Medical and Pharmaceutical Chemistry", Tenth Edition : pp.255, 1998.
- (2) Auzzi G. et al: Ibid, 45(11): pp.1 193-1203, 1990.
- (3)Habib N. S., Abdel-Hamid S., El-Hawash M. : Ibid, 44(12): .1225-1232, 1989.
- (4) Auzzi G., Branif et al : Farmco. Ed. Sc., 41 :pp. 666-675 , 1986
- (5) Suman S. P., and Bahl S. C. : J. Indian Chem. Soc, 65 : pp. 374, 1979.
- (6) Santus M. : Acta-Pol-Pharm : 45(3): pp.219-224, 1988.
- (7) Mayer W., Boner B. and Dawes D. : Der. Ofeen, 1974, 2, 418; Chem. 82, 1975, 31328K.
- (8) Gawande N. G. and Shingare M. S.: Indian J. Chem., 26B, 387, 1987.
- (9) Lalezari I., Shaafiee A., Badaly A., Salimi M. M., Makay et al : J. of Pharm. Sc., 64-1252, 1975.
- (10) A. S., M.S GThesis, Saddam University, Iraq, 1997
- (11) Cecil R. in Neutrath H. (Editor) "The Proteins" volJ.2, 2nd ed., Academic Press, New York, pp379, 1963.
- (12) Pryor W. A, "Mechanism of Sulfur reaction", McGraw-Hill, New York, pp 16-70, 1962.
- (13) Petrow V, Stephanson O, Thomas A. J. amd Will A. M.; J Chem. Soc, 1508, 1958.
- (14) Gula A.; J. Amer. Chem. Soc, 44, 1502, 1922.
- (15) El-Shazly R. M.; Chem. Pharm Bull, 47(11), 1614-1617, 1999.
- (16) Barnabas L. L. ;" Five membered Heterocyclic compounds with Nitrogen and Sulfur,Sulfur and Oxygen (except thiazole), Interscience Publishers, New York, pp. 152, 1952.
- (17) Silverstein R.M.; G. Clayton Bassler, and T.C. Morrill: "Spectrometric identification of organic compounds ", Fourth edition, Jhon Wiley and Sons, New York, (1981).
- (18) Nakamoto, B.K. Infra red spectra of inorganic and coordination commpounds. Johnwiely, (1997).
- (19) Mohammed, M. H. M.Sc. Thesis, Baghdad University, Iraq, 1997.
- (20) Harvey A.E and Manning D.L, J.Am , Chem.. Soc. ,72,4488, (1950)