

## Synthesis and Characterization Studies of new Heterocyclic Azo Compound 2-[2-(4,5-Dimethyl thiazolyl azo)]-5-Amino Anilin with some Complexes Metal Ions

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**Abstract:** This work included the preparation of a new ligand of heterogeneous azo ligands derived from thiazole 2- [2-(4,5-Dimethyl thiazolyl azo)]-5-Amino Anilin (DMeTAAA) and some of its metallic complexes were diagnosed by means of the infrared spectrum, mass spectrum, nuclear magnetic resonance proton spectra, ultraviolet-visible spectrum, thermogravimetric analysis, and in addition to the careful analysis of the elements. Eight metal complexes were prepared by reaction the prepared ligand with Chromium (III), Iron (II), Cobalt (III), Nickel (II), Copper (II), Zinc (II), mercury (II) and silver (I). The effect of the solvent on ligand has been studied and the results have indicated that all the obtained complexes possess high stability. The percentage of metallic ions in the prepared complexes was obtained by the flame atomic absorption spectrometer. A careful analysis of the elements showed a great compatibility between the theoretically calculated and practically obtained ratios. The results of magnetic sensitivity showed that Cr(III),Ni(II) and Cu(II)-complexes possessed magnetic para qualities while the other complexes possessed magnetic dia qualities, as well as the molar conductivity of the prepared complexes was studied and the results showed that all complexes possess the ionic Based on the results obtained, the synthetic formulas of chelated complexes were proposed revealing that the investigated thiazolele azo ligand behaves as a triple ligand.

**keywords:** heterogeneous azo, metal complexes, TGA and mass spectrum

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### 1. Introduction

Cyclic organic compounds whose composition contains one or more atoms different from the carbon atom and the most common different atoms are [S,O,N] [1]. The heterocyclic compounds may be saturated or aromatic in nature depending on their chemical composition, this type of compounds is the most used and relatively new if we compare it with

homogeneous cyclic compounds [2]. The rings of these compounds may be compensated with acid or base aggregates in different positions [3-5].When the compensated aggregates are in the ortho position of the azo group, the complexes will be more stable [6]. including the preparation of Stable complexes as in the compound 4,2 (pyridylazo) resorcinol with the formula shown below used in the formation of

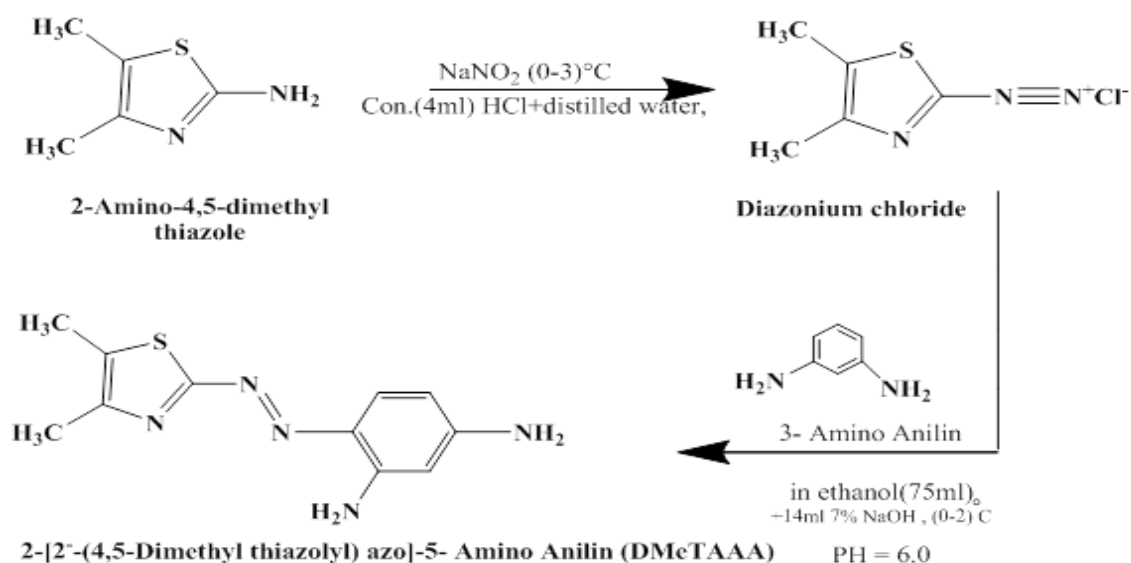
stable complexes with ions of some transition elements such as cadmium, superoxide dismutase, copper, nickel, iron and manganese [7,8].

## EXPERIMENTAL

### Preparation of Ligand 2-[2<sup>-</sup>-(4,5-Dimethyl thiazolyl azo)]-5-Amino Anilin (DMeTAAA)

The above ligand was prepared based on the based on method described in the literature with some modifications to the method, where 1.28 g (0.01) Mol of 2 - amino 5,4 Dimethyl thiazole was dissolved in a mixture of 4 ml of concentrated hydrochloric acid and 30 ml of Water, then the mixture was cooled to a temperature of (2-0) C° And then a solution of sodium nitrite (0.012 mol, 0.83 g) dissolved in 25 ml water was added drop by drop with constant and cooling for 15 minutes. , noting

that the temperature was kept below 5 °C, leave the solution was allowed to settle for 30 minutes to complete, Then diazonium chloride solution was added drop by drop with constant stirring and cooling to a solution of 1.20 g (0.01) Mol of 3-amino aniline dissolved in a mixture of 75 ml ethanol and 14 ml of 7% sodium hydroxide solution cooled to a temperature of 0 °C, and after completion the addition process, the mixture left for 60 Minutes, then the precipitate was filtered and washed several times with cold distilled water and recrystallized using absolute ethanol, the formation of an orange precipitate was observed and described in the chemical reaction scheme for the preparation of Ligand (DMeTAAA) in the two steps of azotation (Diazotization and coupling)[9-11] shown in the scheme (1) below:



Scheme (1):- preparation of new azo ligand ( $L_1$ )

### Synthesis of Metal Complexes

Solid metal complexes of chromium (III), Iron (II), cobalt (II), nickel (II), Copper (II), Mercury (II) and silver nitrate were prepared depending on the optimal conditions of concentration and molar ratio, Table 1 shows some of the physical properties of these complexes, the complexes were prepared with a molar ratio of 2: 1 , [L:M]by the addition of 0.247 gm (0.002) Mol of ligand dissolved in 20 ml of absolute ethanol gradually with continuous stirring to 0.230 gm (0.001) Mol of chromium (II) hexahydrate chloride, 0.230 gm (0.001) Mol of Iron(II) hexahydrate chloride, 0.273 gm (0.001)Mol of cobalt chloride(III) hexahydrate, 0.238 gm (0.001) mol of nickel chloride (II) hexahydrate 0.234 gm (0.001) Mol of copper chloride (II) hexahydrate, 0.136 gm (0.001)Mol of zinc chloride (II), 0.152 gm (0.001) Mol of silver nitrate, and 0.271 gm (0.001) Mol of Mercury chloride (II), the solute dissolved in 20 ml of the regulated solution at the function acid pH=7.0, where the color changed at the moment of mixing, after heating the reaction mixture for 40 minutes at a temperature of 60 C°, the formation of a precipitate was observed, the precipitate was filtered, washed several times with distilled water, then with a small amount of ethanol, and recrystallized with absolute ethanol, then the

percentage and melting point was calculate [12-17].

**Table (1):** Some physical properties of ligand and its metal complexes.

molecular formula	color	m.P °C	Yield %
Ligand=L	Orange	132	68
[Cr (L) <sub>2</sub> ] Cl <sub>2</sub>	Brown	155	60
[Fe(L) <sub>2</sub> ] Cl <sub>3</sub>	Reddish brown	186	73
[Co(L) <sub>2</sub> ] Cl <sub>3</sub>	purple	174	80
[Ni(L) <sub>2</sub> ] Cl <sub>2</sub>	blue	180	78
[Cu(L) <sub>2</sub> ] Cl <sub>2</sub>	dark purple	170	80
[Zn(L) <sub>2</sub> ] Cl <sub>2</sub>	dark red	176	65
[Ag (L) <sub>2</sub> NO <sub>2</sub> ]	red	170	76
[Hg(L) <sub>2</sub> ] Cl <sub>2</sub>	Brown	190	71

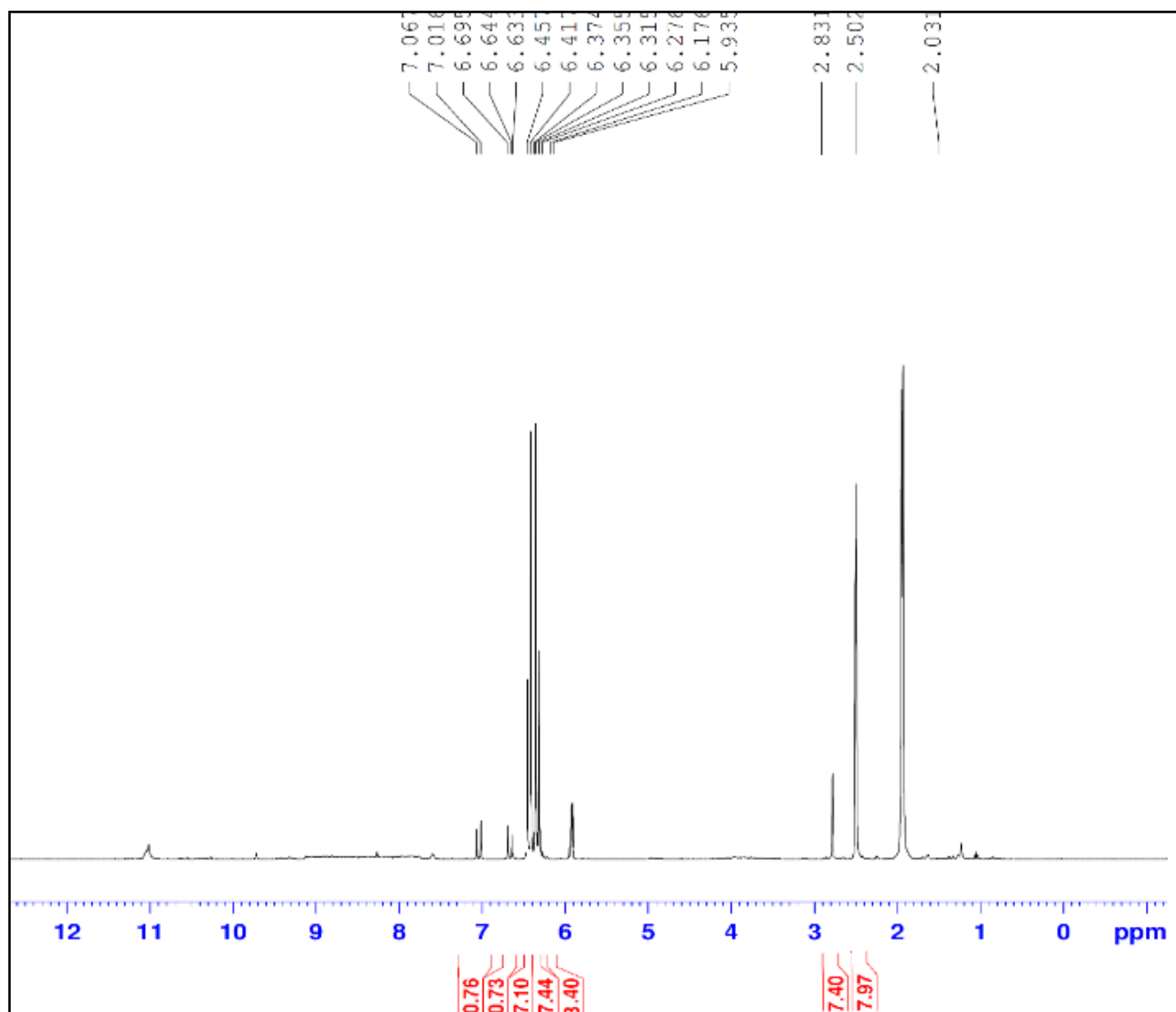
### 3-Result and Discussion

#### <sup>1</sup>H-NMR Spectra

The <sup>1</sup>H-NMR Proton spectrum of ligand was studied and analyzed based on what is mentioned in the literature [18-20], we were able to explain the appearance of the following beams: a single beam at a chemical shift of 5.935 ppm belongs to the Proton of the amine group (NH<sub>2</sub>) in the aniline ring .a single peak at

a chemical shift of 2.502 ppm belongs to the protons of the group (CH<sub>3</sub>) in the thiazole ring adjacent to the sulfur atom. A single beam at a chemical shift of 2.831 ppm belongs to the protons of the (CH<sub>3</sub>) group in the thiazole ring adjacent to the nitrogen atom. signals with overlapping peaks at a chemical shift of 6.176-

ppm 7.067, which are due to hydrogen protons belonging to the benzene ring a single peak at a chemical shift of ppm 200, IT belongs to DMSO-d<sup>6</sup>, which was used as a solvent in the measurement process.



**Figure (1):** <sup>1</sup>H-NMR proton magnetic resonance spectrum of ligand (DMeTAAA) in DMSO solvent.

### Mass spectra

The mass spectrum of the ligand was recorded and it gave a set of peaks and the proposed mass fractions of ligand were shown in Figure (2), which are as follows [21-23]:

The main peak at  $m+/e$ , 247 is due to the ion  $C_{11}H_{13}N_5S$  and is similar to the molecular weight of ligand, a peak of 233  $m+/e$  with a relative abundance (10.63%) is due to  $C_{10}H_{11}N_5S$ , a peak at 218,  $m+/e$  with a relative abundance (25.53%) is due to the ion  $C_{10}H_{10}N_4S$ , peak at 202,  $m+/e$  with a relative abundance (34%) and belonging to the ion  $C_{10}H_8N_3S$ , the cause of which is the loss of the  $C_6H_3O$  group (phenol ring), a peak at 232,  $m+/e$  with a relative abundance (61.70%) is due to the loss of one carbon atom of the ion  $C_{10}H_{10}N_5S$ . We also note the appearance of a peak at 217,  $m+/e$  and a relative abundance (87.23%) of  $C_{10}H_9N_4S$ .

The mass spectrum of ligand also showed a peak at the region 126,  $m+/e$  and a relative abundance (100%) of the ion  $C_9H_7N_3S$ . The mass spectrum of ligand also showed a peak at the region 189  $m+/e$  and a relative abundance (46.80%) of the ion  $C_4H_4N_3S$  as for the peak at

the region 98,  $m+/e$  with a relative abundance (46.80%) of the  $C_4H_4NS$  ion.

The mass spectrum of ligand also showed a peak at the region 78,  $m+ / e$  and a relative abundance (46.80%) of the ion  $C_6H_6$ .

**Table (2):** ligand mass fractionation products (DMeTAAA).

Fargment	Exact mass (m/z)
$C_{11}H_{13}N_5S$	247
$C_{10}H_{11}N_5S$	233
$C_{10}H_{10}N_4S$	218
$C_{10}H_8N_3S$	202
$C_{10}H_{10}N_5S$	232
$C_{10}H_9N_4S$	217
$C_9H_7N_3S$	126
$C_4H_4N_3S$	189
$C_4H^4NS$	98
$C_6H_6$	78

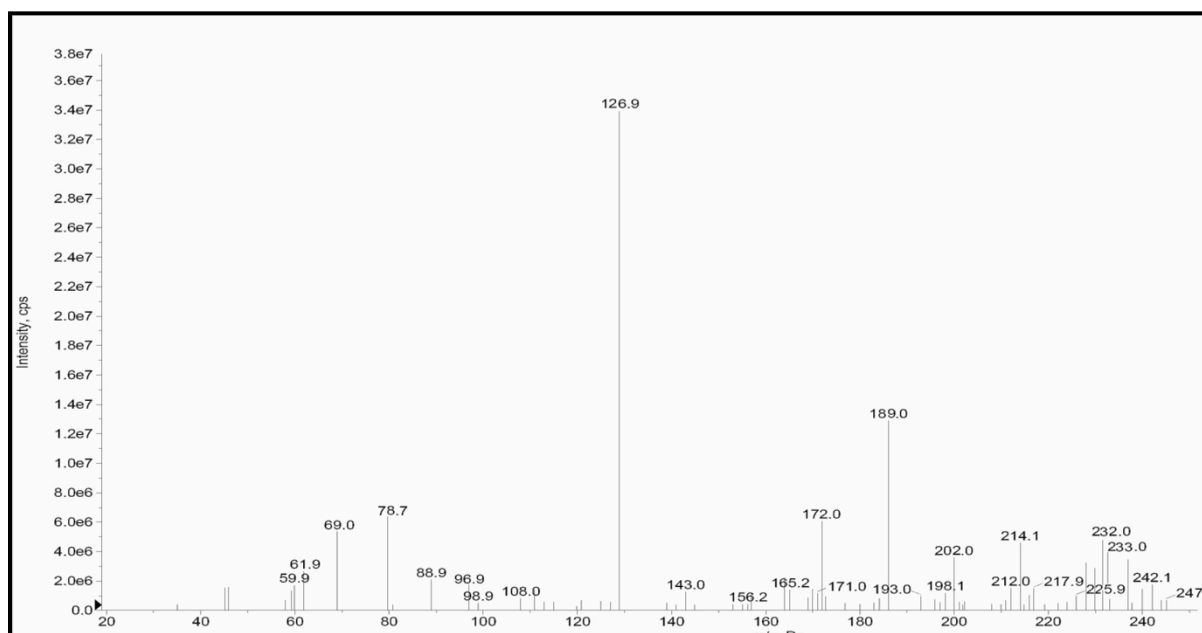
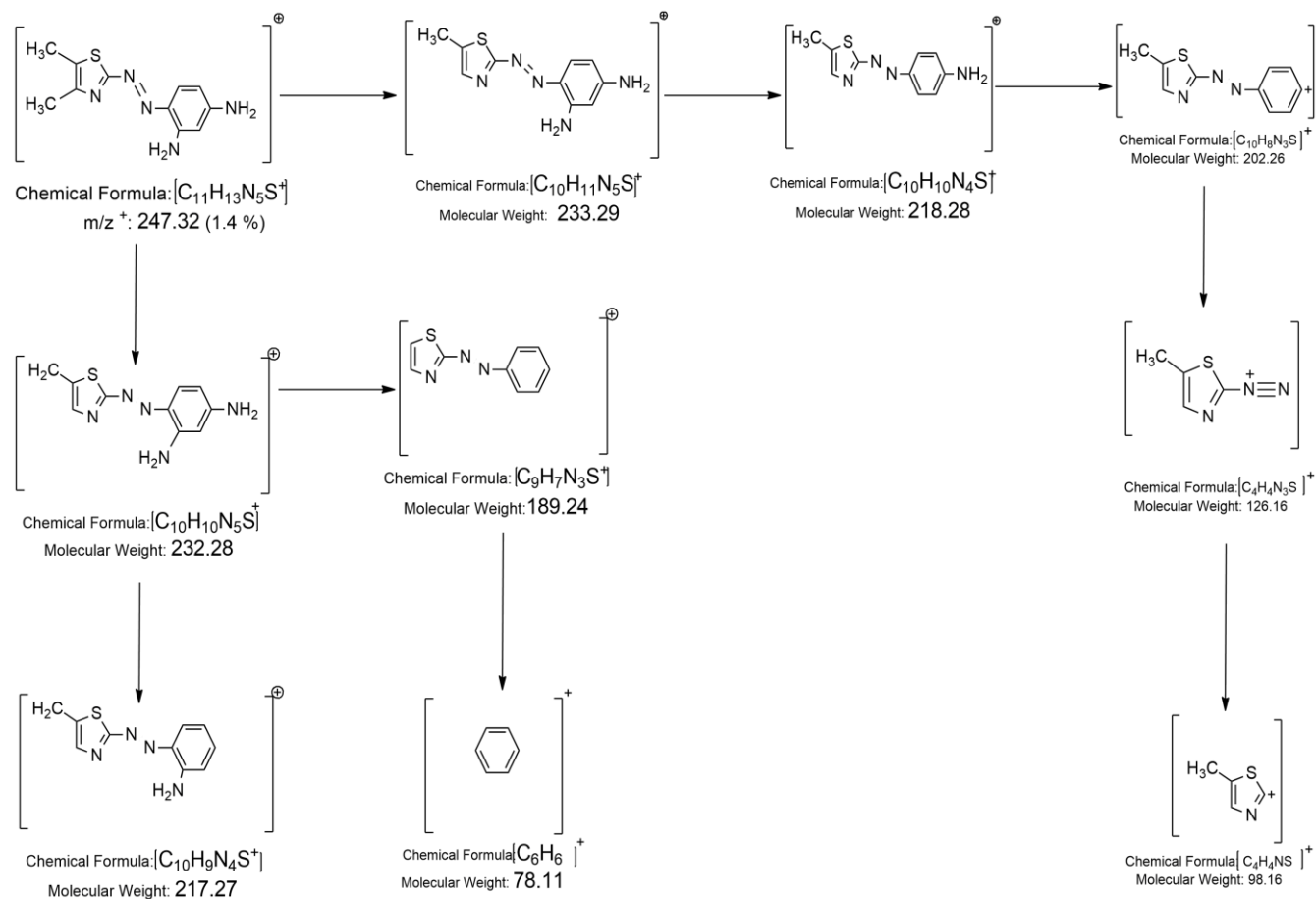


Figure (2): ligand mass spectrum (DMETAAA).



Scheme (2): Proposed block fragmentation pathways for ligand (DMETAAA).

**Infrared spectra of azo-schiff base ligand and their metal complexes**

The ligand spectrum showed an absorption beam of medium intensity at the frequency 1600  $\text{cm}^{-1}$  due to the elastic frequency of the band (C=N) of the thiazole ring, and the spectra of the prepared complexes showed a noticeable change in the location and intensity of this beam, due to the participation of the non-tastrict electronic double of the nitrogen atom of the thiazole ring in the harmonization process. The ligand spectrum showed two absorption beams at the frequency of 1454 and 1508  $\text{cm}^{-1}$  due to the conjugate C=C and the azo-bridge group N=N, respectively. The absorption beam at the frequency of 1242  $\text{cm}^{-1}$  is due to the elastic frequency of the bond C-N=N-C. These beams have undergone changes in position, intensity and shape. The reason for the redshift of these beams are due to the coordination process between the metal ion and the nitrogen atom of the azo bridge group far from the thiazole ring. The beams located in the range of 844  $\text{cm}^{-1}$  are due to the deformation of the thiazole ring, these beams have suffered changes in intensity, shape, and location, and have been displaced towards lower or higher frequencies by the limits of 20

$\text{cm}^{-1}$  in the spectra of metal complexes, and this confirms their influence as a result of the binding of the metal ion to the ligand. The beams of metal-ligand bonds do not usually appear in the spectrum of free ligand but appear in the form of new beams in the spectrum of the complex. This type of collimation is characterized by weak.

beams indicative of it and that these beams may not appear due to the possibility of interference with neighboring absorbers in the spectrum, especially in compounds containing aromatic rings; metal - nitrogen bonds interfere with the absorbers that occur because of distortions outside the plane of the rings and inside them, resulting in a change in the dipole moment. And the spectra of complexes the metal ligands under study have multiple beams within the frequency range 540-416  $\text{cm}^{-1}$ , the intensity of which ranged from medium to weak. These vibrations may be due to the metal - nitrogen bonds of the symmetry of the metal ion with the nitrogen of the azo Bridge Group far from the thiazole ring and the nitrogen of the thiazole ring. It was diagnosed according to the literature [24-27]. The several changes mentioned are shown in Table 3.

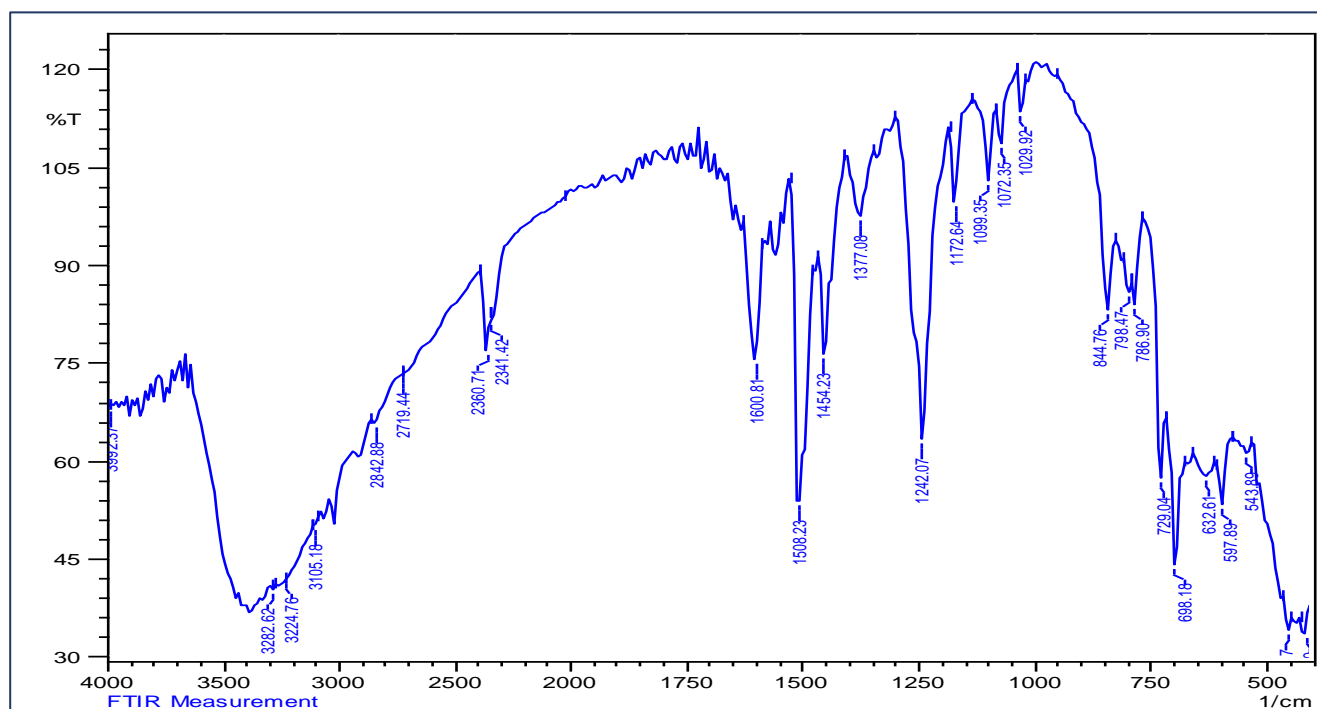


Figure (3): Infrared spectrum of ligand in KBr

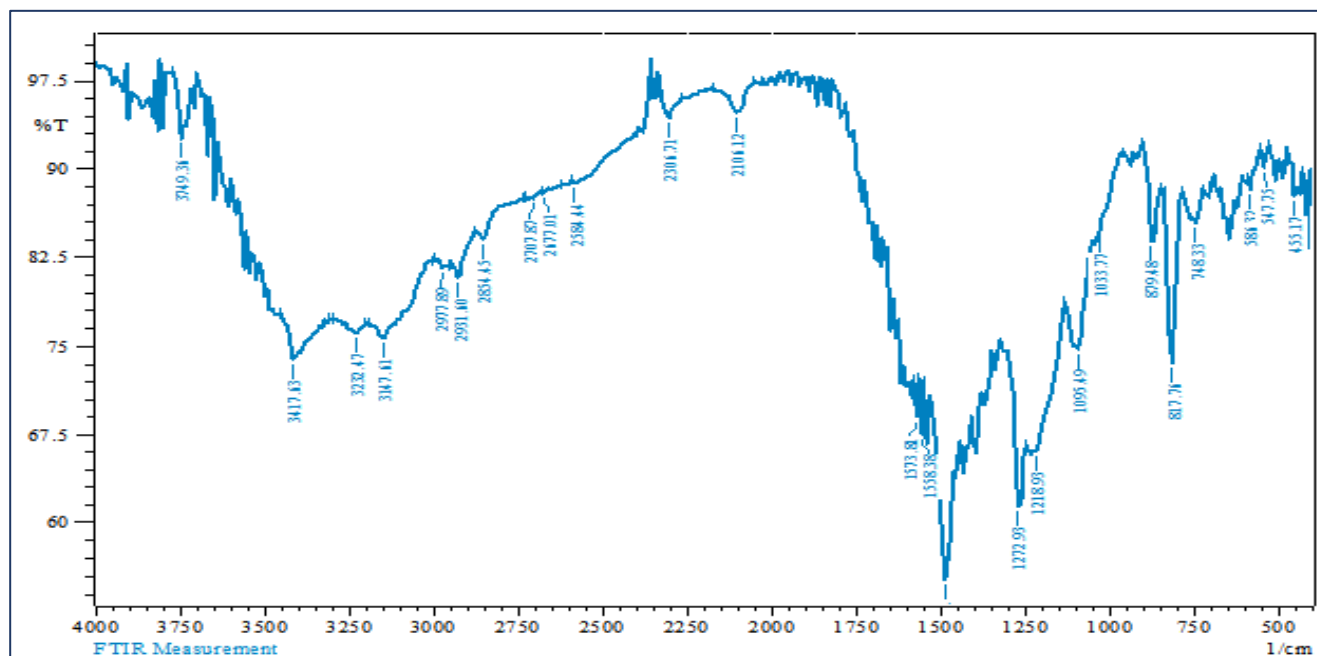


Figure (4): Infrared spectrum of  $[Cr(L)_2]Cl_2$  in KBr.



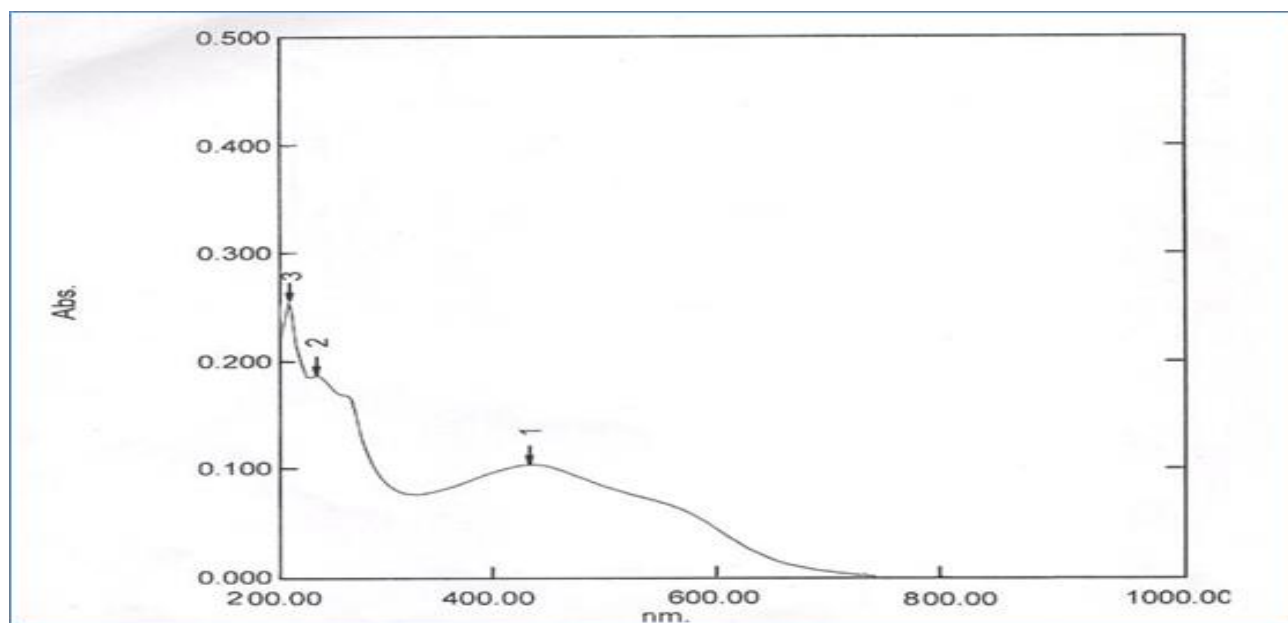
**Table: (3):** Infrared frequencies ( $\text{cm}^{-1}$ ) of ligand and its complex.

Assignment	L	[Cr(L)]Cl <sub>2</sub>	[Fe(L) <sub>2</sub> ]Cl <sub>2</sub>	[Co(L) <sub>2</sub> ]Cl <sub>3</sub>	[Ni(L) <sub>2</sub> ]Cl <sub>2</sub>	[Cu(L) <sub>2</sub> ]Cl <sub>2</sub>	[Zn(L) <sub>2</sub> ]Cl <sub>2</sub>	[Ag(L) <sub>2</sub> ]NO <sub>2</sub>	[Hg(L) <sub>2</sub> ]Cl <sub>2</sub>
(N-H)	3301 w.br.	3417 m.br.	3224w.br.	3247 w	3332 w.br.	3331m.br.	3443w.br.	3409 m.br	3241 m.br
$\nu$ (C-H)	3105 m.br	3147m. br	3147 w.	3147 m.br	3124 m.br	3133m.br	3101 w.	3155 m.br	3155 m.br
$\nu$ (C=N)	1600 m.	1573w.	1573m.	1588 w	1601 s	1604 w.	1607 m.	1589 m	571 w
$\nu$ (N=N)	1508m.	1500.s.	1498s.	1491 s	1512 s.	1512.s.	1441 m.	1491. s	1493. s
$\nu$ (C=C)	1454s.	1363m.	1396 m	1404 m	1442 s.	1438 s.	1334 v.s	1344 .m	1404. m
$\nu$ (C-N=N-C)	1242 s.br	1280 s.	1326.93 s.	1226.m	1288 s.br	1280 s.	1326.93 s.	1272.m	1272. w
$\nu$ (C-S)	1172 s.	1218m.	1226 m	1272 m	1233 s. 779 s.	1238. s. 1110 s.	1212. s	1226 .m	1218 .m
$\nu$ (M-N)	—	586 w.	574 w.	547 w	—	531 w.	517w.	533. w	563.w

### Magnetic susceptibility and electronic spectra measurements

The free ligand spectrum gave three peaks, the first at 430 nm ( $23255 \text{ cm}^{-1}$ ), belonging to the electron transition ( $\pi \rightarrow \pi^*$ ) of the azo group (N=N). As for the

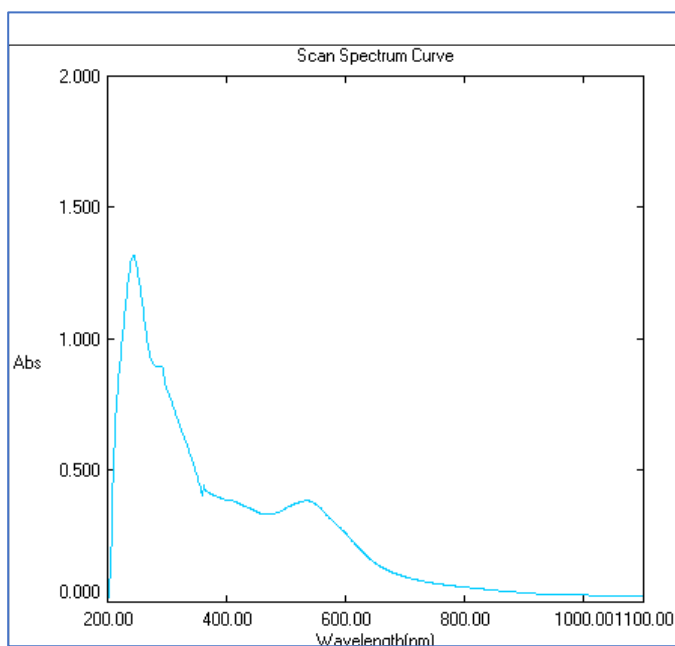
second peak, it appeared at 240 nm ( $41666 \text{ cm}^{-1}$ ) (dependent on the electron transition ( $\pi \rightarrow \pi^*$ ) of the bond (C=C) in thiazole and the aromatic ring ((111, as for the third peak at 221 Nm  $45248 \text{ cm}^{-1}$  dependent on the electron transition ( $n \rightarrow \pi^*$ ) of the amine group as well as the thiazole ring



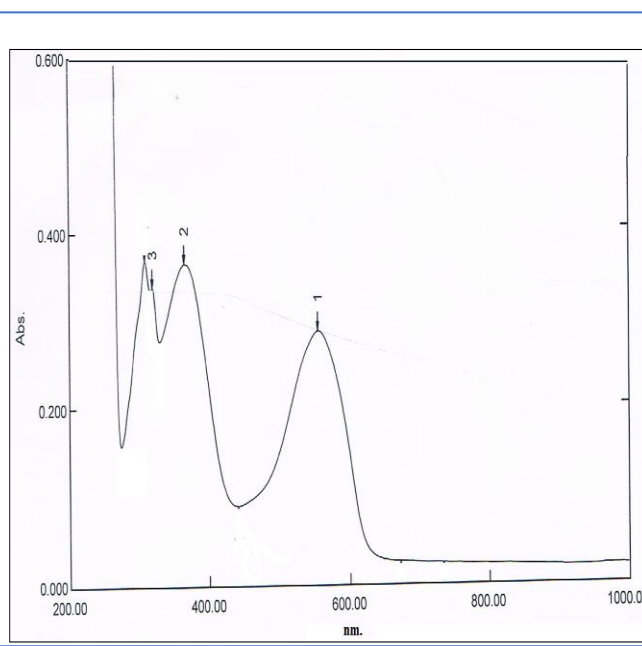
**Figure (5):** UV– visible spectrum of free ligand in ethanol.

The electron spectrum of the cobalt complex gave two absorption peaks, one at 541 nm ( $19455 \text{ cm}^{-1}$ ) (and the other at 418 nm ( $23923 \text{ cm}^{-1}$ )) (which are due to the allowed electron transitions ( ${}^1A_{2g} \rightarrow {}^1t_{1g}$ ) (F) and ( ${}^1A_{2g} \rightarrow {}^1t_{2g}$ ), respectively. The nickel complex showed three absorption peaks at 964 nm ( $10373 \text{ cm}^{-1}$ ) (and 613 nm ( $16313 \text{ cm}^{-1}$ )) (and 578 nm ( $15301 \text{ cm}^{-1}$ )) belonging to the electron transitions ( ${}^3A_{2g} \rightarrow {}^3t_{2g}$ ) (F) and ( ${}^3A_{2g} \rightarrow {}^3t_{1g}$ ) (F) and

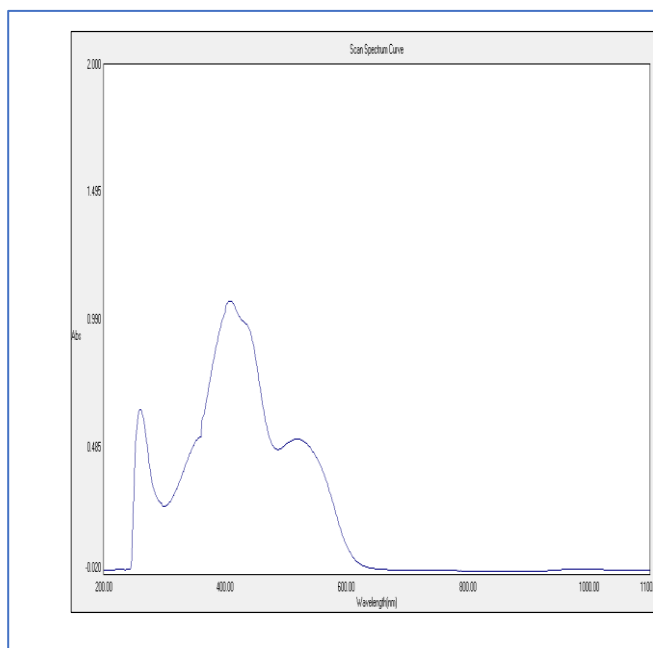
${}^3A_{2g} \rightarrow {}^3T_{1g}$  (p) respectively. While the copper-tip complex gives a broad absorption at 571 nm ( $14903 \text{ cm}^{-1}$ ), it is a follower of the electron transition ( ${}^2E_g \rightarrow {}^2t_{2g}$ ). The spectra of mercury and silver complexes were studied and the spectra of these complexes do not give d-d transitions because they have ( $d^{10}$ ) in their outer valence shell, but they gave absorption peaks at 501 nm ( $19960 \text{ cm}^{-1}$ ) and 498 nm ( $20080 \text{ cm}^{-1}$ ) and 501 nm ( $19960 \text{ cm}^{-1}$ ), respectively, and they belong to the transitions (M $\rightarrow$ L, CT) [28-32].



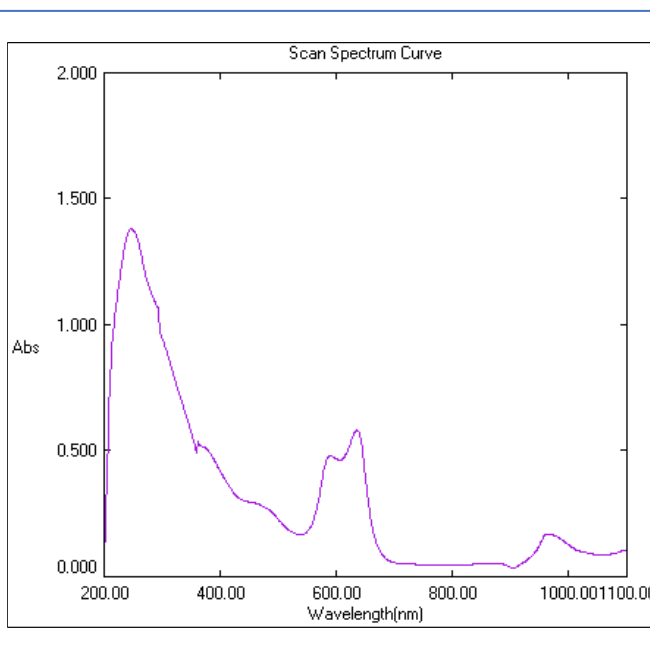
**Figure(6):** Uv-visible spectrum of Cu(II)-complex in ethanol.



**Figure 7:** Uv-visible spectrum of Fe(II)-complex in ethanol.



**Figure(8):** Uv-visible spectrum of Cr(III)-complex in ethanol.



**Figure(9):** Uv-visible spectrum of Ni(II)-complex in ethanol.

**Table (4):** electron Spectra and magnetometry of the metal complexes of ligand under study at Laboratory temperature.

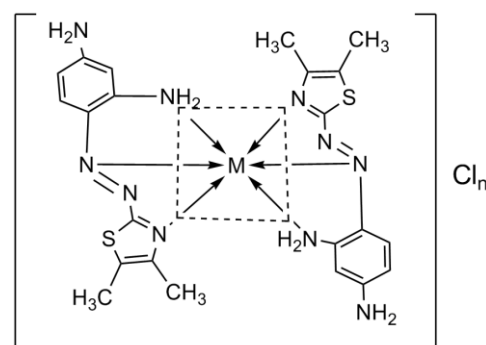
Complexes	$\lambda_{\max}$ ( nm)	Absorption bands ( $\text{cm}^{-1}$ )	Transition	$\mu_{\text{eff}}$ (B.M)
Ligand	430	23255	$\pi \rightarrow \pi^*$	-----
	240	41666	$\pi \rightarrow \pi^*$	
	221	45248	$n \rightarrow \pi^*$	
[Co(L) <sub>2</sub> ]Cl <sub>3</sub>	514	19455	$^1A_{2g} \rightarrow ^1T_{1g(F)} (\nu_1)$	Dia
	418	23923	$^1A_{2g} \rightarrow ^1T_{2g(F)} (\nu_2)$	
	964	10373	$^3A_{2g} \rightarrow ^3T_{2g(F)}$	2.71
[Ni(L) <sub>2</sub> ]. H <sub>2</sub> O	613	16313	$^3A_{2g} \rightarrow ^3T_{1g(F)}$	
	578	17301	$^3A_{2g} \rightarrow ^3T_{1g(p)}$	
[Cu(L) <sub>2</sub> ]Cl <sub>2</sub>	671	14903	$^2E_g \rightarrow ^2T_{2g}$	1.65
[Zn(L) <sub>2</sub> ]	501	19960	M→L, CT	Dia
[Ag (L)]NO <sub>3</sub>	498	20080	M→L, CT	Dia
[Hg(L) <sub>2</sub> ] Cl <sub>2</sub>	50	199607	M→L, CT	Dia
[Fe(L) <sub>2</sub> ]Cl <sub>2</sub>	560	17857	$^2A_{2g} \rightarrow ^4T_{1g(F)}$	Día
	380	26315	$^2A_{2g} \rightarrow ^4T_{1g(p)}$	
[Cr(L <sub>2</sub> )Cl <sub>3</sub>	519	19267	$^4A_{2g} \rightarrow ^4T_{1g(F)}$	2.91

The study of the visible ultraviolet (UV-Vis) Spectra has shown.) Solid complexes dissolved in ethanol show absorption at the maximum wavelength max higher than in the free ligand and these results are consistent with what is stated in the literature [33-36] about the occurrence of redshift in the complexes of this type of compounds.

### Thermal analysis

The thermal-weight analysis technique is a distinct technique; it is used to study the thermal behavior and to verify the proportions of organic and inorganic components in the complexes, as the thermal of the complexes has been studied and its good thermal stability has been observed and the metal complexes have been characterized by not being affected by air and moisture, which indicates high thermal stability and purity , In addition, their high melting points, which give another proof of the stability of the prepared metal complexes, were studied thermal stability of ligand and some using the technique of thermal decomposition of weight and differential thermal decomposition calorimetric starting at normal temperatures to a degree of 644 C° in an inert atmosphere of nitrogen gas with an average temperature of (10) C° as. The curve of the thermal decomposition of

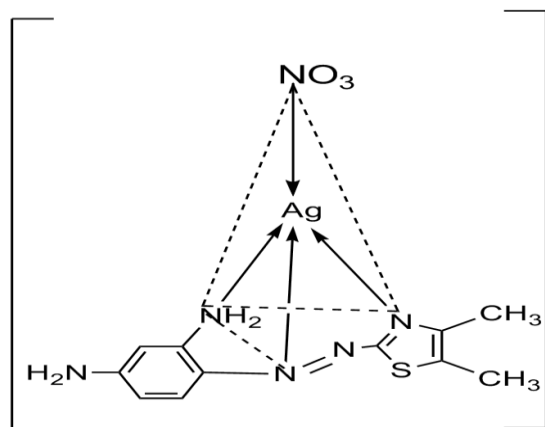
ligand and its complexes showed two stages of weight loss, the first stage, which is within the thermal range (100-395) and during this stage the process of losing adsorbent water and volatile substances such as gases, carbon dioxide and moisture [37], or the second stage, which is at a range of temperatures ranging from (300-644) C°. During this stage, the highest amount of weight loss was found, and the reason for this loss is due to ligand thermal dissociation and loss of functional aggregates [38-40]. The remaining potentially formed substances after the completion of the thermal decomposition of the complexes are metal oxides, table 5 shows the thermal decomposition of ligand and some of its prepared metal complexes. Based on the results of the obtained diagnostic measurements, we can formulate the proposed formulas for the complexes under study (Fig. 10 and Fig.11).



**Figure (10):** the form of metal ion complexes M= Ni(II), Zn(II), Fe(II), Cu(II) Hg(II) n=2 M= Cr(III) , Co(III) n=3.

**Table (5):** thermal-weight decomposition of ligand and some of its metal complexes under study.

Compound		TGA Reang °C	The missing mass %	The missing	Formation	DSC
ligand	30-113	8.24941	Volatile substances and moisture, Loss of benzamidazole group, The loss of the azo group Editing by CH <sub>4</sub> and N <sub>2</sub> O	Release of gases and loss of solids	180	Endothermic(+)
	113-395	25.6352			210	Endothermic(+)
	395-644	46.2158			537	Endothermic(+)
[Cu(L) <sub>2</sub> ]Cl <sub>2</sub>	30-193	8.15547	Volatile substances and moisture	CuO	122	Endothermic(+)
	193-643	46.2158	Loss of ligand molecules and composition CuO		520	Endothermic(+)
[Ni(L) <sub>2</sub> ].H <sub>2</sub> O	30-172	4.82	Volatile substances and moisture	NiO	100	Endothermic(+)
	172-408	12.126	Loss of ligand molecules and composition NiO		210	Endothermic(+)
	408-643	32.132			530	Endothermic(+)



**Figure (11):** the form of the Ag(I) Complex.

#### 4-Conclusion

A new azo ligand was prepared, which is characterized by high stability against high thermal stability under inert conditions, as well as a very high selectivity for the detection of nickel and copper dioxide

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