

## Preparation And Spectral Characterization of New Azo imidazole Ligand 2-[1-(2,4-Dichloro phenyl)Azo]- $\alpha$ -Amino-1H-imidazole-4-Propionic Acid And Its Complexes With Co(II), Ni(II), Cu(II), Pd(II) And Ag(I) Ions

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### Abstract:

The preparation and spectral characterization of complexes for Co(II) Ni (II) Cu(II) Pd(II) and Ag (I) ions with new organic heterocyclic azo dye as ligand 2-[1-(2,4-Dichloro phenyl)Azo ]- $\alpha$ -Amino-1H-imidazole -4-Propionic Acid (DCIPAHs) were prepared by reacting a dizonium salt solution of 2,4-dichloro aniline with L-Histidine in alkaline ethanolic solution. The isolated complexes are found to have the general formula  $[\text{CoL}_2\text{Cl}_2]\cdot\text{H}_2\text{O}$ ,  $[\text{NiL}_2\text{Cl}_2]$ ,  $[\text{CuL}_2\text{Cl}_2]\cdot\text{H}_2\text{O}$ ,  $[\text{PdLCl}_2]$  and  $[\text{AgL}_2]\cdot\text{NO}_3$  were reacting from azo imidazole ligand and metal chloride (nitrate for Ag (I) in 1:1 molar ratio (metal :ligand) for Pd (II) ion and 1:2 for the rest metal ions. These complexes were characterized spectroscopically by infrared and electronic spectra and along with elemental analysis, molar conductance and susceptibility measurements. The data show that the ligand a bidantate and coordinates to the metal ion via the nitrogen atom of azo and with imidazole N<sub>3</sub> atom. Octahedral environment is suggested for Co (II) Ni (II) and Cu (II) metal complexes but square planer for Pd (II) complex and tetrahedral for Ag (I) complex.

### 1-Introduction :-

Azo imidazole derivatives are very important class of chemical compounds receiving attention scientific research<sup>(1,2)</sup> They are highly colored and have been used as dyes and pigments for along time.<sup>(3,4)</sup> They are important in drugs<sup>(5)</sup>, cosmetics<sup>(6)</sup>, biological activities including antibacterial<sup>(7)</sup>, coordination capacity<sup>(8)</sup> and participate in azo coupling reactions.<sup>(9)</sup> The coupling of diazonium salt occurs in position 2 of imidazole ring in alkaline medium to give shining azo imidazole dyes.<sup>(10,11)</sup> Azo imidazole molecule being the azo imine group ( $-\text{N}=\text{N}-\text{C}=\text{N}-$ ), which is  $\pi$ -acidic and stabilized low valant metal redox state.<sup>(12)</sup> The azo imidazole reagents does not have the same interst in research and investigation because of the rarity in the preparation of this kind of reagents although the imidazole was known before 150 years.<sup>(13)</sup> A number of these azo dyes have been used as chelating ligands<sup>(4,8,14)</sup> in addition of the uses as reagents in analytical chemistry.<sup>(9,15,16)</sup> The present study reports the preparation and spectral characterization of new azo imidazole ligand (DCIPAHs) and some of its metal complexes.

**Key words:-** Preparation, azo imidazole ligand ,metal complex, characterization

### **2-Experimental**

### 2.1-Apparatus and material

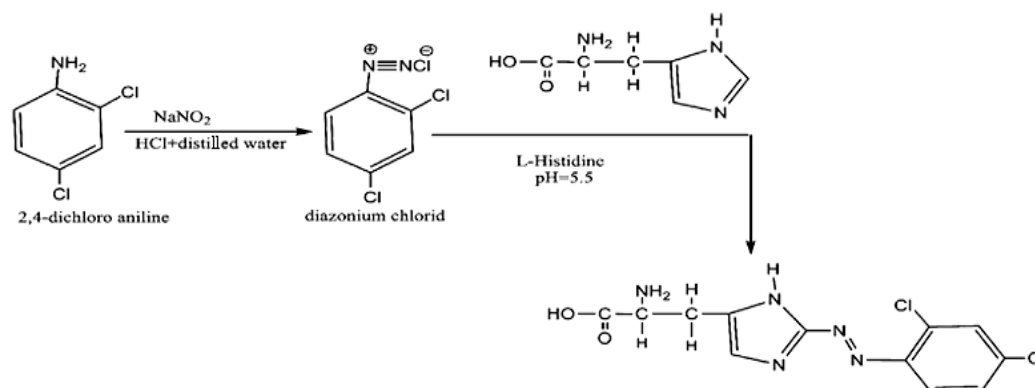
All chemicals and solvents were highest purity obtained from Fluk, Merck and BDH. The melting points were determined on a Electro thermal, melting point 9300. Elemental analysis(C.H.N) were obtained using 1108 C.H.N elemental analyzer. IR spectra were recorded using KBr discs in the range (4000-400)  $\text{cm}^{-1}$  on FTIR Teast scan Shimaduz model 8400S .while the UV-Vis. Spectra recorded in absolut ethanol on Shimaduz model 1650PC. Molar conductance measurements were determined in DMF ( $10^{-3}$  M) at room temperature by using conductivity bridge model 31A and the pH measurements were carried out using aphilips pw 9421 pH meter(  $\text{pH} \pm 0.001$ ). The metal contents of the complexes was measured by using atomic absorption technique by shimadzu AA-160. The chloride ion was estimated by Mohr method.<sup>(21)</sup> Magnetic susceptibilities were measured by using Faraday method blance magnetic MSB-MKI was used for this purpose and diamagnetic corrections for the ligand were calculated using pascal's constant.<sup>(22)</sup>

### 2.2-Preparation of the ligand (DCIPAHs)

The hetero cyclic azo ligand was prepared according to the following general procedure as described for 2-(aryl azo)-imidazoles.<sup>(23)</sup> A diazonium solution was prepared by dissolving (1.62gm, 0.01 mol) of 2,4-dichloro aniline in 6ml of concentrated hydrochloric acid and 30ml distilled water. To this mixture a solution of (0.75gm, 0.01mol) of sodium nitrate in 15ml of distilled water was added dropwise at (0-5)  $^{\circ}\text{C}$  and left to stand 35min. This diazonium solution was added dropwise into a 800ml beaker containing (1.93gm, 0.01mol) of L-Histidine dissolved in 200ml of alkaline ethanol and 30ml of 10% sodium hydroxide at (0-5)  $^{\circ}\text{C}$ , the mixture was stirred for additional 3hrs in ice-bath and allowed to stand over night and acidified with dilute hydrochloric acid to  $\text{pH}=5.5$ . The precipitate was filtered off, washed with distilled water and recrystallized twice from hot ethanol and dried in oven at 60  $^{\circ}\text{C}$  for 24hour. yield was 81% of redish brown crystals the procedure was seen in scheme1.

### 2.2-Preparation of complexes

The metal complexes were prepared by dissolved (0.656gm, 0.002 mol )from ligand in hot ethanol (100ml) and added dropwise with stirring to a stoichiometric



**Scheme(1) :-Preparation of the ligand (DCIPAHs)**

amounts of 1:2 (metal:ligand) molar ratio of Co(II),Ni(II) and Cu(II) chlorides salts and Ag(I) nitrate(0.001mol) or 1:1 ratio

of Pd(II) chloride(0.328gm,0.01 from ligand ) dissolving in 30ml buffer solution (ammonium acetate) at optimal pH for each metal ions. The mixture solution was stirred under reflux for 40 min. The solid product thus formed was filtered off from the ice-cooled reaction mixture, washed with 10ml hot ethanol to remove the remaining unreacted substances and dried at 70°C over night

### 3-Result and discussion

The reaction of heterocyclic azo ligand(DCIPAHs) with the metal ions mentioned above different color crystals depending on the nature of metal ion. The complexes are stable in air and insoluble in water but soluble in most organic solvents. The analytical and physical data of the ligand and it`s complexes are given in Table1 they are consistent with the calculated results from empirical formula of each compound.

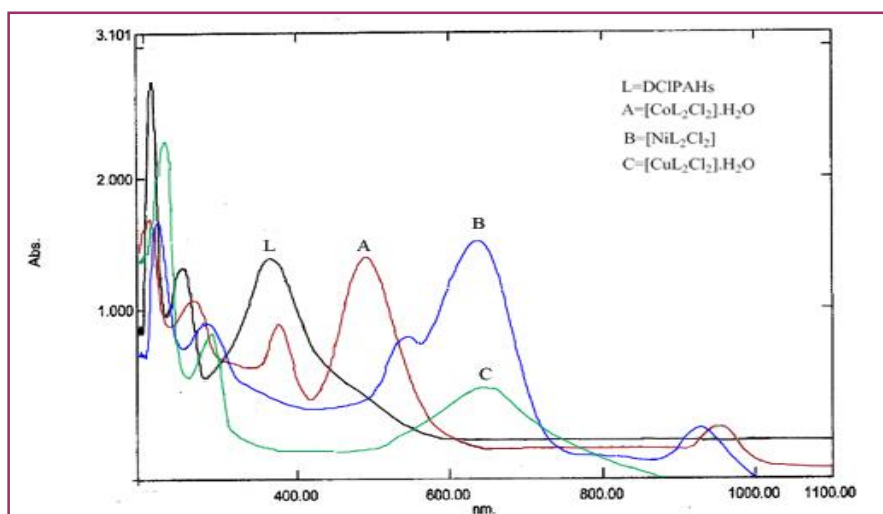
**Tabil(1):- Analytical data and physical properties of the ligand (DCIPAHs) and it`s complexes.**

No	Compound	Optimal pH	Color	m.P °C	Yield %	Molecular formula (Mol.Wt)	Found (Calc.)%			
							C	H	N	M
1	L=(DCIPAHs)	5.5	Redish brown	151	81	C <sub>12</sub> H <sub>11</sub> N <sub>5</sub> O <sub>2</sub> Cl <sub>2</sub> (328.16)	43.78 (43.92)	3.79 (3.38)	21.28 (21.34)	—
2	[CoL <sub>2</sub> Cl <sub>2</sub> ].H <sub>2</sub> O	7.0	Dark orange	163	67	C <sub>24</sub> H <sub>24</sub> N <sub>10</sub> O <sub>5</sub> Cl <sub>6</sub> Co (804.17)	35.68 (35.85)	2.92 (3.01)	17.23 (17.42)	6.97 (7.33)
3	[Ni L <sub>2</sub> Cl <sub>2</sub> ]	7.5	Dark green	204	73	C <sub>24</sub> H <sub>22</sub> N <sub>10</sub> O <sub>4</sub> Cl <sub>6</sub> Ni (785.91)	36.81 (36.68)	2.94 (2.82)	17.97 (17.82)	7.19 (7.47)
4	[Cu L <sub>2</sub> Cl <sub>2</sub> ].H <sub>2</sub> O	6.0	green	223 d.	62	C <sub>24</sub> H <sub>24</sub> N <sub>10</sub> O <sub>5</sub> Cl <sub>6</sub> Cu (808.78)	35.85 (35.64)	2.89 (2.99)	17.48 (17.32)	7.62 (7.86)
5	[Pd L Cl <sub>2</sub> ]	6.5	Dark brown	214 d.	68	C <sub>12</sub> H <sub>11</sub> N <sub>5</sub> O <sub>2</sub> Cl <sub>4</sub> P d (505.48)	28.27 (28.51)	2.08 (2.19)	13.67 (13.85)	21.29 (21.05)
6	[Ag L <sub>2</sub> ] NO <sub>3</sub>	7.0	Redish Purple	187	65	C <sub>24</sub> H <sub>22</sub> N <sub>11</sub> O <sub>7</sub> Cl <sub>4</sub> Ag (826.18)	34.71 (34.89)	2.59 (2.68)	18.44 (18.65)	12.79 (13.06)

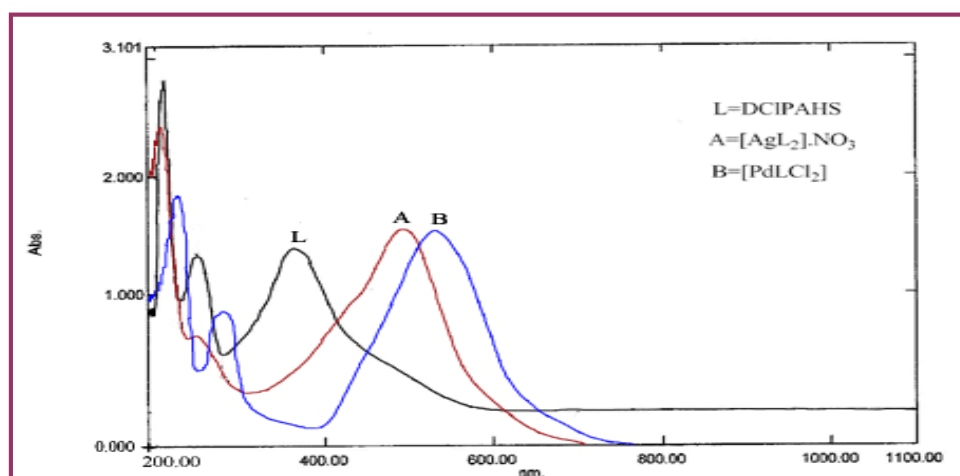
d=decompos

#### 3.1:-Absorption spectra

The absorption spectra in aqueous ethanolic solution 50% (V/V) were studied for the prepared complexes showed a bathochromic shift ranging between (170-284)nm depending on the metal ion the absorption spectra of the Co(II),Ni(II),Cu(II),Pd(II) and Ag(I) chelat complexes are shown in Figs.1and2



**Figure(1):-The absorbance spectra of free ligand (L)and their complexes in a suitable pH;con.  $(1.25-1.75) \times 10^{-5}$  M In aqueous ethanolic solution ;(L=DCLPAHs)**

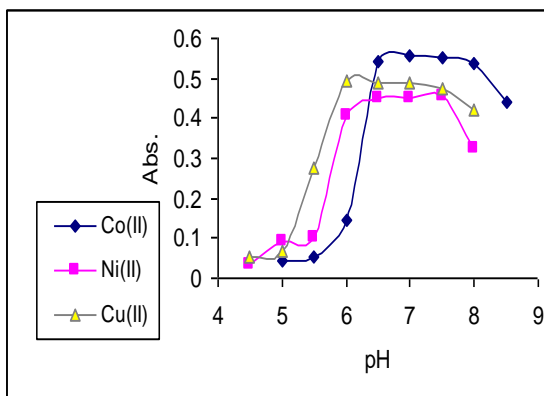


**Figure(2):-The absorbance spectra of free ligand (L)and their complexes in a suitable pH;con.  $(1.25-1.75) \times 10^{-5}$  M In aqueous ethanolic solution ;(L=DCLPAHs)**

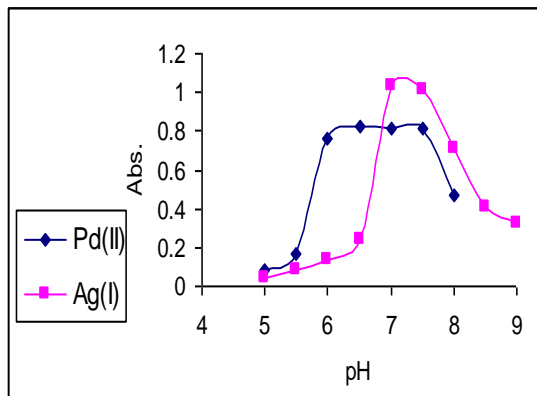
### 3.2-Effect of pH and Time

To optimal pH values on the absorbance for metal complexes solution were studied in the 50%(v/v) ethanolic as shown in Figs.3 and 4.The ligand (DCIPAHs) formed a very stable complexes with metal ions Co(II) ,Ni(II),Cu(II),Pd(II) at pH(6.0-7.5) except Ag(I) 7 .This result with the fact of the lower basicity of the nucleus,will lead to shift of reaction for the more acidic region.<sup>(4,14)</sup> Also the reaction is complete

in 10 min at room temperature and remains stable for about 24 hour. This shows the ligand (DCIPAHs) strong coordination with all metal ions. The results are shown in Figs. 5 and 6.



Figure(3):-The absorbance spectra of DCIPAHs - metal chelates (1.25-1.75) × 10<sup>-5</sup>M in aqueous ethanolic



Figure(4):-The absorbance spectra of DCIPAHs - metal chelates (1.25-1.5) × 10<sup>-5</sup>M in aqueous ethanolic

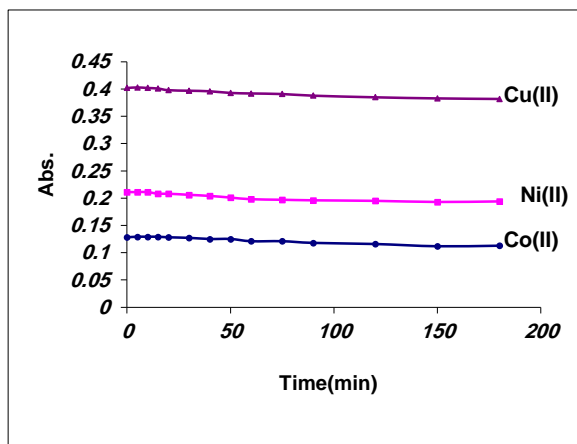


Fig (5):-Effect of time on the absorbance of metal complexes ;at room temp. M=Co (n), Ni(n) and Cu(n).

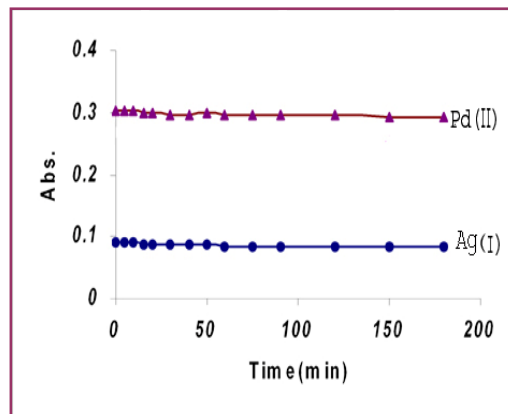
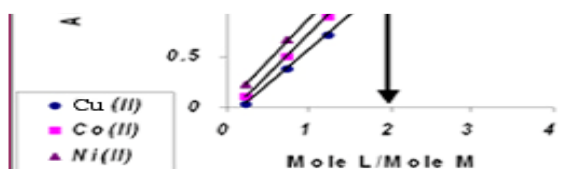


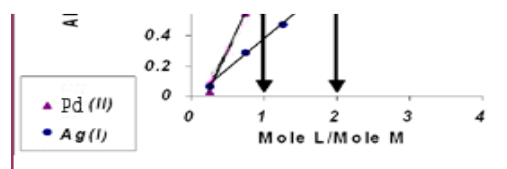
Fig (6):-Effect of time on the absorbance of metal complexes ;at room temp. M=Pd (n), Ag(I)

Composition of chelate complexes were investigated by mole ratio method at fixed concentration of metal ion and increasing concentration of ligand at optimum pH and  $\lambda_{\text{max}}$ . This method indicated that. The more probable structure of complex was 1:1 for Pd(II) ion and 1:2 for the Co(II), Ni(II), Cu(II) and Ag(I) ions as shown in Figs 7 and 8. The results are given in Table 2.

**Fig.(7):-Molar ratio method (M:L)  
DCIPAHs-metal chelates  
at optimal pH and concentration**



**Fig.(8):- Molar ratio method (M:L)  
DCIPAHs-metal chelates  
at optimal pH and concentration**



### 3.4-Determination of the metal complexes stability constants

Stability constant ( $\beta$ ) values are obtained spectrophotometrically by measuring the absorbance of a mixture of ligand and metal solution at fixed wavelength ( $\lambda_{\text{max}}$ ) and optimum pH values. The degree of formation of the complexes are obtained from the relationship<sup>(24)</sup>,  $\beta=(1-\alpha/4\alpha^3c^2)$  for 1:2 metal complexes and  $\beta=(1-\alpha/\alpha^2c)$  for 1:1 metal chelate and  $\alpha=A_m-A_s/A_m$  where  $A_s$  and  $A_m$  are the absorbance of the partially and fully formed complex respectively at optimum concentration. The calculated  $\beta$  and  $\log \beta$  values for the prepared complexes are given in Table 2.

### 3.5-Molar conductivity

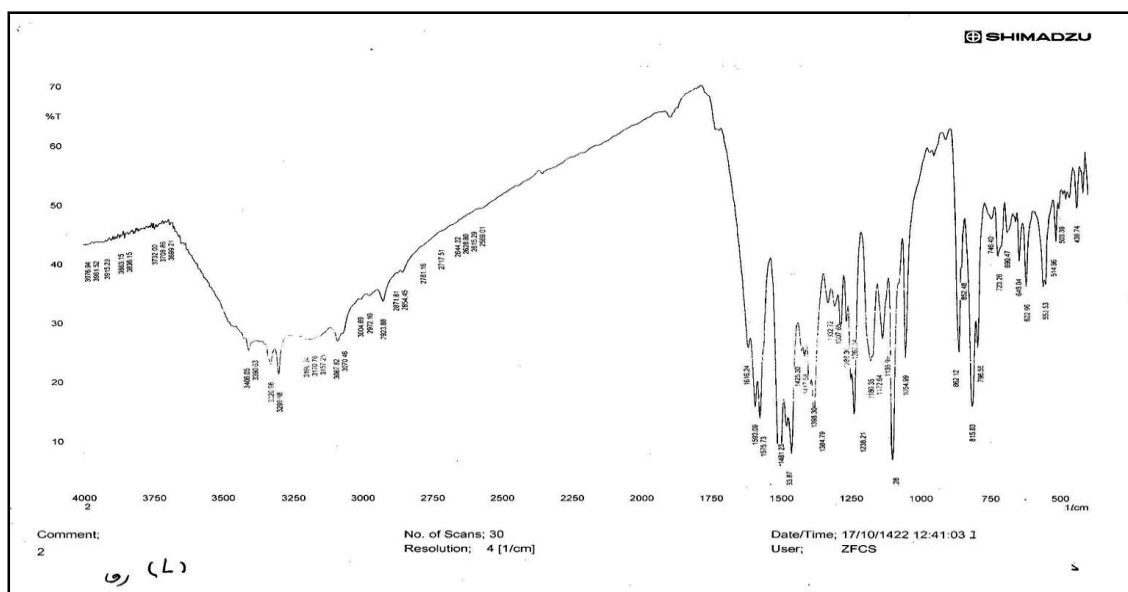
The data obtained from the measurement of molar conductance of the complexes are shown in table 2 were carried out in DMF( $10^{-3}\text{M}$ ) at room temperature. The values indicate that the chelate complexes of Co(II), Ni(II), Cu(II) and Pd(II) ions are non-electrolytes nature, where the values suggest that no anions outside the coordination spheres.<sup>(25,26)</sup> But the high value of molar conductivity ( $63.17\text{S.cm}^2\text{mol}^{-1}$ ) for the Ag(I) complex indicating that this complex is 1:1 electrolyte and suggest that  $\text{NO}_3^-$  anion present outside the coordination spheres<sup>(27)</sup>.

**Table (2) :- metal :ligand stability constant values molar conductivity  
optimal concentration and wave length with molar absorptivity ( $\epsilon$ )  
of chelate complexes**

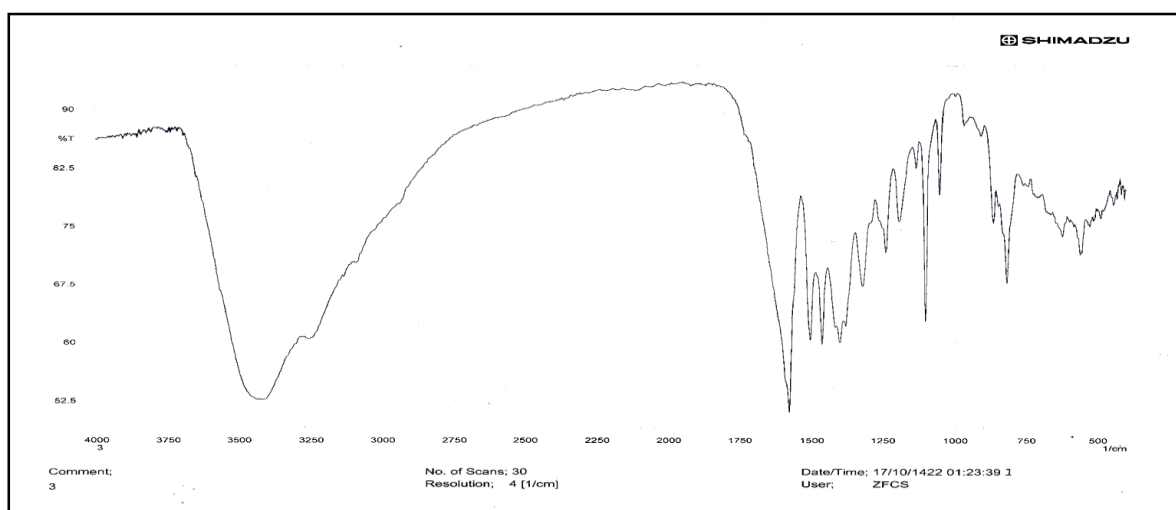
Ligand	Metal Ions	Metal : ligand	Optimal molar conc. x 10 <sup>-5</sup> M	Optimal wave length ( $\lambda_{max}$ )nm	Molar absorptivity ( $\epsilon$ )x10 <sup>4</sup> L.mol <sup>-1</sup> .cm <sup>-1</sup>	$\beta$ L <sup>2</sup> .mol <sup>-2</sup>	Log $\beta$	Molar conductivity s.mol <sup>-1</sup> .cm <sup>2</sup>
DCIPAHs, $\lambda_{max}$ =364 nm $\epsilon=13.9 \times 10^4$ L.mol <sup>-1</sup> .cm <sup>-1</sup>	Co(II)	1:2	1.25	478	11.28	9.65x10 <sup>9</sup>	9.91	11.32
	Ni(II)	1:2	1.75	648	9.31	7.65x10 <sup>9</sup>	9.88	14.06
	Cu(II)	1:2	1.75	632	3.43	1.30x10 <sup>10</sup>	10.1	8.31
	Pd (II)	1:1	1.50	527	10.73	6x10 <sup>6</sup>	6.77	9.19
	Ag(I)	1:2	1.25	485	12.96	1.5x10 <sup>12</sup>	12.1	63.17

### 3.6-Infrared spectra

Infrared spectra data (KBr disk) of ligand (DCIPAHs) and its complexes are summarized in table 3. The comparison between spectrum of the ligand with those of the coordination complexes have revealed certain characteristic differences. Azo ligand spectrum show two weak bands at 3391cm<sup>-1</sup> and 3327 cm<sup>-1</sup> due to  $\nu$ (OH) and  $\nu$ (NH<sub>2</sub>) groups<sup>(28)</sup> These bands are remained in the same region in free ligand and in chelate complexes. Thus the remaining of hydroxyl group (OH) and amine group  $\nu$ (NH<sub>2</sub>) indicates its not involvement in coordination with metal ions.<sup>(29)</sup> The medium band at 3300cm<sup>-1</sup> in the spectrum of the ligand may be attributed to the  $\nu$ (NH) of imidazole ring.<sup>(30)</sup> The unchanged of this band in all complexes means that the  $\nu$ (NH) group dose not participate in coordination.<sup>(31)</sup> Spectrum of ligand shows two weak bands at 3088cm<sup>-1</sup> and 2924 cm<sup>-1</sup> due to  $\nu$ (CH) aromatic and aliphatic respectively. These bands are stable in position and intensity in both ligand and its metal complexes. The free ligand shows a strong band at 1593cm<sup>-1</sup> due to  $\nu$ (C=O) of carboxylic group.<sup>(32)</sup> This band is stable in position in both ligand and complex. Another strong band appear at 1576cm<sup>-1</sup> in the ligand spectram which is due to  $\nu$ (C=N).<sup>(33)</sup> In this spectra of complexes this band was shifted to a higher frequencies at (1585-1560)cm<sup>-1</sup> with a little change in shape. These differences suggest a coordination of the metal ions with nitrogen atom N<sub>3</sub> of imidazole ring.<sup>(34)</sup> The  $\nu$ (N=N) stretching vibration appears band at 1481cm<sup>-1</sup> in the free ligand spectrum. This band appearing at (1475-1435)cm<sup>-1</sup> with different in shape and reduced in intensity in prepared complexes spectra. Both bands shifted and reduced intensity dueto complex formation.<sup>(35)</sup> Some other new bands appeared in the region of (510-440) cm<sup>-1</sup> in the complexes spectra which are not present in the spectrum of the ligand may attributed to the  $\nu$ (M-N) band.<sup>(36)</sup> Thus the above IR spectra data lead to suggest that ligand behaves as a bidentate chelating agent and the coordination sites are the nitrogen atom of azo group nearest to phenyl ring and N<sub>3</sub> atom of the imidazole ring to give five-membered chelat ring. Representative example for their spectra are given in Figs. 9,10 and 11.

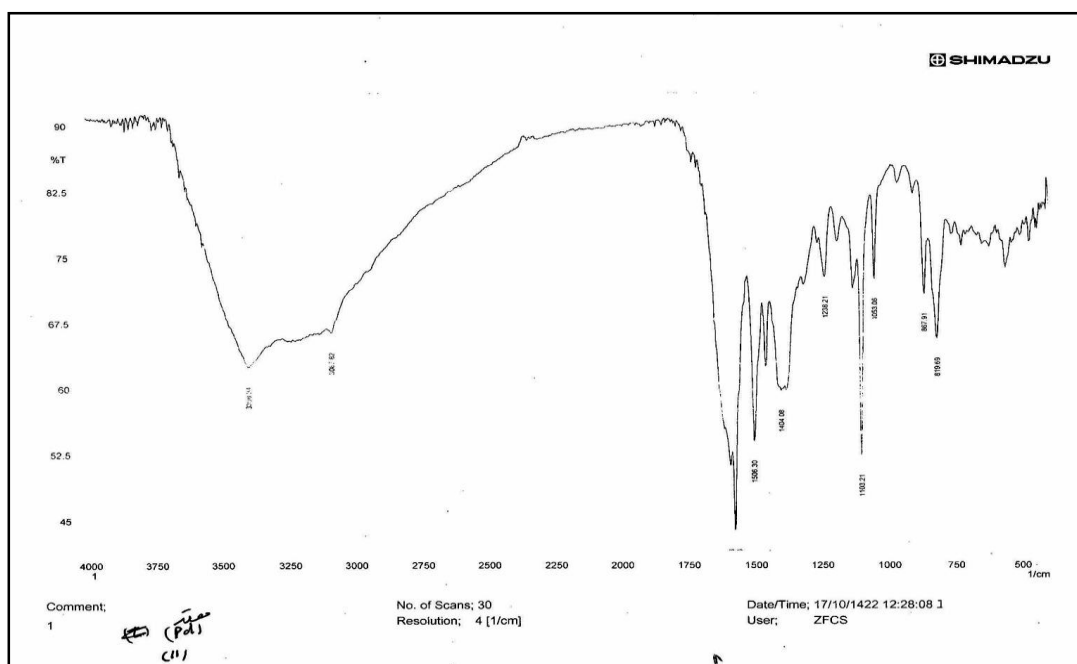


Figure(9):- IR spectrum of the ligand (DCIPAHs=L)



Figure(10): IR spectrum of the complex  
[Co (L)<sub>2</sub>Cl<sub>2</sub>].H<sub>2</sub>O





**Figure( 11): IR spectrum of the complex [PdLCl<sub>2</sub>]**

**Table(3) :-Characteristic IR absorption bands of the ligand (DCIPAHs) and its complexes in cm<sup>-1</sup> units (KBr disk)**

No.	Compound	$\nu(\text{O-H})$	$\nu(\text{NH}_2)$	$\nu(\text{N-H})$ imidazole	$\nu(\text{C=O})$ Asym.	$\nu(\text{C=O})$ sym.	$\nu(\text{C=N})$	$\nu(\text{N=N})$	Imid.r.de	$\nu$ (M-N)
1	L=(DCIPAHs)	3391w	3327m	3300m	1593s	1463s	1576s	1481s	1054s	—
2	[CoL <sub>2</sub> Cl <sub>2</sub> ] .H <sub>2</sub> O	3405br.	3335w	3315w	1590s	1425.s	1585s	1475s	1085s	485w
3	[Ni L <sub>2</sub> Cl <sub>2</sub> ]	3406wbr.	3332m	3310w	1594s	1490m	1578s	1435m	1105s	505w
4	[Cu L <sub>2</sub> Cl <sub>2</sub> ] .H <sub>2</sub> O	3395w	3335m	3305w	1598s	1435s	1580m	1455m	1065m	465w
5	[Pd L Cl <sub>2</sub> ]	3398w	3328w	3310w	1595s	1506s	1568s	1470s	1103s	510w
6	[Ag L <sub>2</sub> ] NO <sub>3</sub>	3403w	3325w	3308w	1597s	1430s	1560m	1475m	1105s	440w

W=weak; s=strong; br.=brod; m=medium; Asym=Asymetry; sym=symmetry.

### 3.7-Electronic spectra and magnetic properties

The electronic spectra data and the magnetic moment of prepared complexes are listed in table 4. The ligand is characterized by three absorption bands in UV-visible. These bands are appearing at the position 214nm ( $46729\text{cm}^{-1}$ ) and 244nm ( $40984\text{cm}^{-1}$ ) the first one can be attributed to a  $\pi \rightarrow \pi^*$  transition with in hetrocyclic imidazole ring<sup>(37)</sup> while the second UV band observed at a longer wavelength can be ascribed to the excitation of the  $\pi$ -electrons of the phenylsystem.<sup>(37)</sup> The characteristion third visible band occurred at 364nm ( $27472\text{cm}^{-1}$ ) may by due to a  $\pi \rightarrow \pi^*$  charge transfer transition

mainly from the aryl moiety to the imidazole ring. <sup>(38,39)</sup> This band showed at a red shift on coordination with a metal ions. <sup>(4,18,20)</sup>

#### **Cobalt(II) complexes**

The magnetic moment for the Co(II)- complexes has been found to be 5.07 B.M which is with range of distorted (z-out) octahedral high spin( hybridization,  $sp^3d^2$ ) geometry. <sup>(40,4)</sup> The electronic spectrum of this complex show three absorption bands at 962 nm( $10395 \text{ cm}^{-1}$ ), 478 nm( $20921 \text{ cm}^{-1}$ ) and 380 nm( $26316 \text{ cm}^{-1}$ ) there are assigned to  $^4T_{1g(F)} \rightarrow ^4T_{2g(F)} (\nu_1)$  ;  $^4T_{1g(F)} \rightarrow ^4A_{2g(F)} (\nu_2)$  and  $^4T_{1g(F)} \rightarrow ^4T_{1g(P)} (\nu_3)$  transitions respectively, which are characteristic of octahedral stereochemistry. <sup>(4,40,41)</sup>

#### **Nickel (II) complexex**

The value magnetic moment for the Ni(II)- complexes is found to be 3.61B.M wich may suggest an octahedral high spin (hybridization , $sp^3d^2$ ) structure. The d-d transitions electronic spectrum of this complex shows three bands at 974nm( $10267 \text{ cm}^{-1}$ ), 648nm ( $15432 \text{ cm}^{-1}$ ) and 562nm( $17794 \text{ cm}^{-1}$ ) wich are suggesting the existence of  $^3A_{2g} \rightarrow ^3T_{2g(F)} (\nu_1)$  ;  $^3A_{2g} \rightarrow ^3T_{1g(F)} (\nu_2)$  and  $^3A_{2g(F)} \rightarrow ^3T_{1g(P)} (\nu_3)$  transitions respectively with an octahedral configuration. <sup>(40,42)</sup>

#### **Copper(II) complexes**

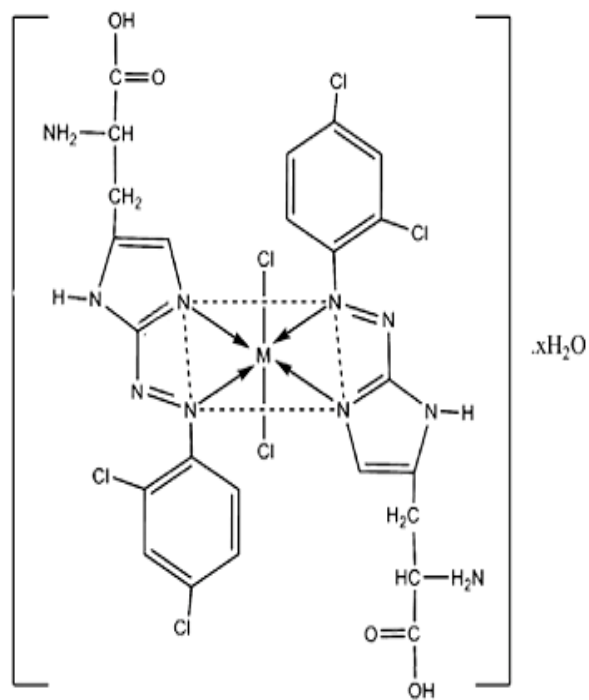
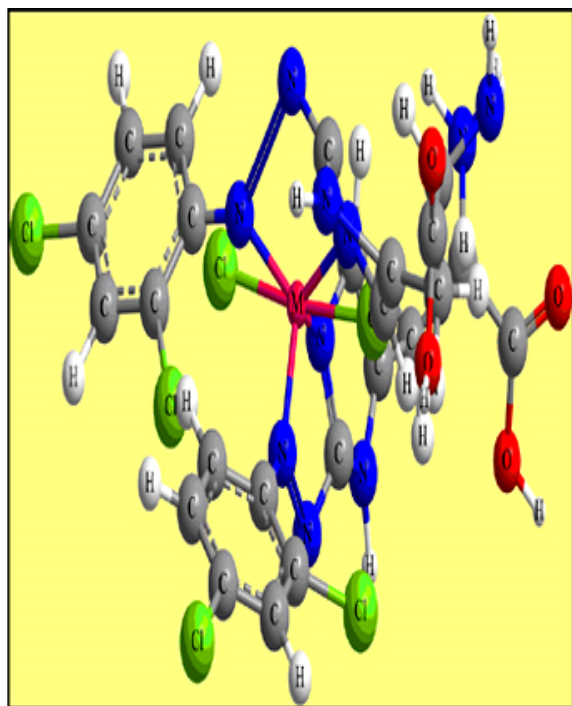
The magnetic moment for Cu(II)- complexes found to be 1.82 B.M due to presence of one unpaired electron in this complex. The electronic absorption spectrum of this complex shows abroad band around 632nm( $15823 \text{ cm}^{-1}$ ). This band is assigned to the transition  $^2E_g \rightarrow ^2T_{2g}$ . It is reasonable to assign distorted octahedral structure (z-out or z-in) and hybridization  $sp^3d^2$  geometry. <sup>(4,18,40,42)</sup>

#### **Palladium(II) complexes**

The zero magnetic value of Pd(II)-complex indicate a square planer geometry (hybridization,  $dsp^2$ ) which is the stereochemistry for this complex a tetra coordinate. The electronic spectrum of this complex show absorption band at the position 527nm( $18975 \text{ cm}^{-1}$ ) which is attributed to  $^1A_{1g} \rightarrow ^1B_{1g}$  transition in a square planer symmetry <sup>(39,43)</sup>

#### **Silver (I)complex**

The UV-vis spectrum of Ag(I)-complex with ligand (DCIPAHs) do not show any d-d transition bands. The magnetic susceptibility moment for ion Ag(I) ( $d^{10}$ ) which is characteristic of teterhedral stereo chemistry at 1:2 (M:L) and hybridization  $sp^3$  geometry. <sup>(20,39)</sup>

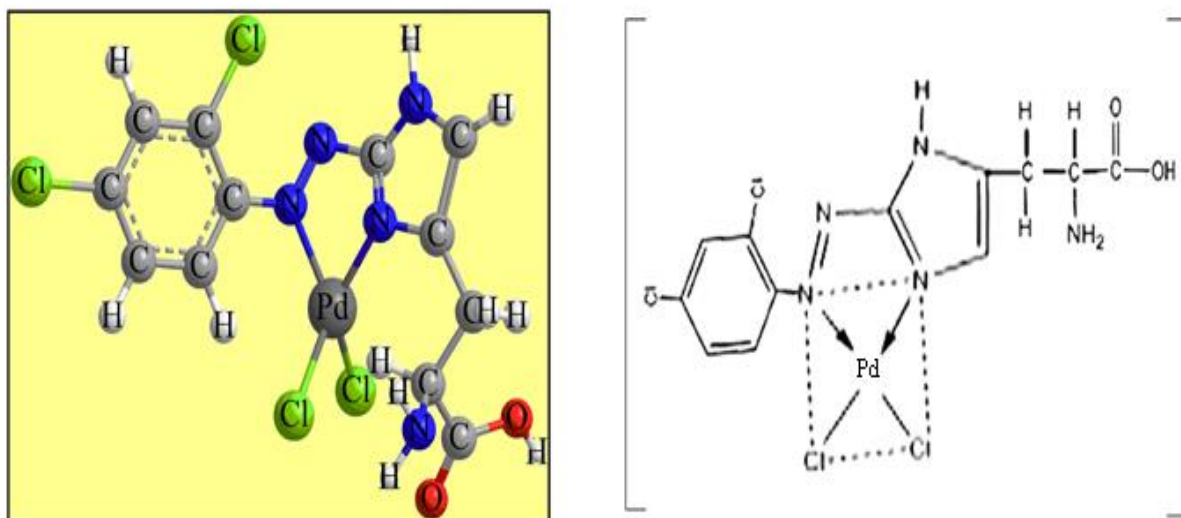


Fig( 12) :- The suggested structural formula of complexes  
M=Ni(II) ; x=0 ,Co(II) and Cu(II) ;x=1

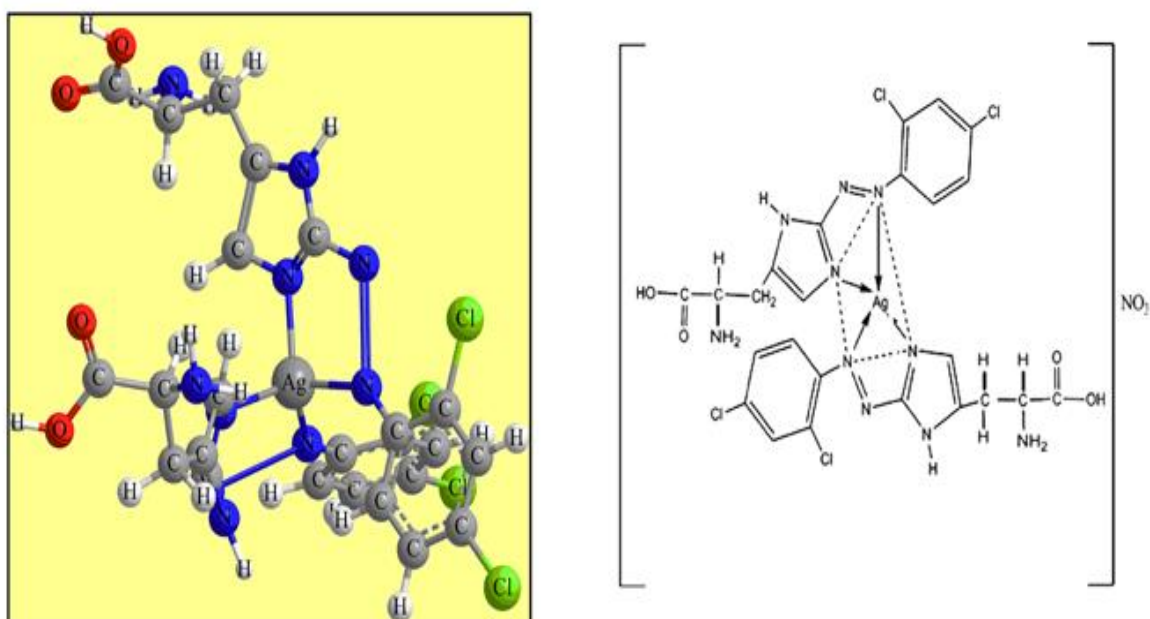
**Table(4):- Electronic spectra and magnetic moments values of complexes**

No.	Complexes	$\lambda_{\max}$ nm	Absorption bands $\nu$ cm <sup>-1</sup>	Transition	$\mu_{\text{eff}}$ (B.M)
1	[CoL <sub>2</sub> Cl <sub>2</sub> ] .H <sub>2</sub> O	962	10395	$\nu_1$ ${}^4T_{1g(F)} \rightarrow {}^4T_{2g(F)}$	5.07
		478	20921	$\nu_2$ ${}^4T_{1g(F)} \rightarrow {}^4A_{2g(F)}$	
		380	26316	$\nu_3$ ${}^4T_{1g(F)} \rightarrow {}^4T_{1g(P)}$	
2	[Ni L <sub>2</sub> Cl <sub>2</sub> ]	974	10267	$\nu_1$ ${}^3A_{2g} \rightarrow {}^3T_{2g(F)}$	3.61
		648	15432	$\nu_2$ ${}^3A_{2g} \rightarrow {}^3T_{1g(F)}$	
		562	17794	$\nu_3$ ${}^3A_{2g} \rightarrow {}^3T_{1g(P)}$	
3	[Cu L <sub>2</sub> Cl <sub>2</sub> ] .H <sub>2</sub> O	632	15823	${}^2E_g \rightarrow {}^2T_{2g}$	1.82
4	[Pd L Cl <sub>2</sub> ]	527	18975	${}^1A_{1g} \rightarrow {}^1B_{1g}$	dia
5	[Ag L <sub>2</sub> ] NO <sub>3</sub>	485	—	—	dia

Accoding to these results the structural of these complexes may by proposed in figs.12,13 and 14.



Fig( 13):- The proposed structural formula of Pd(II) –complexes



Fig(14):- The proposed structural formula of Ag(I) –complexes

In this present study we report the preparation characterization and spectroscopy study of new azo ligand derived from imidazole and its complexes with Co(II),Ni(II),Cu(II) Pd(II) and Ag(I) metal ions. The isolated complexes were characterized by available techniques. The aryl azo imidazole ligand (DCIPAHs) behaves as a bidentate chelating agent and coordinating through the N<sub>3</sub> atom of imidazole and another nitrogen atom of azo group which is the farthest of imidazole ring to form five-membered metalo ring. The coordination of the metal ions Co(II),Ni(II) and Cu(II) with ligand (DCIPAHs) are to give hexa coordinated show octahedral stereochemistry but Pd(II) and Ag(I) complexes are a tetra coordination to give a square planer and tetrahedral symmetry respectively.

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## التحضير والتشخيص الطيفي لليكاند أزو جديدة 2-1-1-2 (4، 2) ثنائي كلورو فنيل (أزو) - $\alpha$ - أمينو - H1 - أميدازول - 4 - حامض البروبانويك ومعقداته الفلزية مع أيونات Co(II) و Ni(II) و Cu(II) و Pd(II) و Ag(I)

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### الخلاصة:-

تحضير وتشخيص طيفي لمعقدات لا يونات الكوبلت (II) والنيكل (II) والنحاس (II) والبلاديوم (II) والفضة (I) مع صبغة الأزو العضوية الغير متجانسه الحلقة الجديده 2-1-1-2 (4، 2) ثنائي كلورو فنيل (أزو) - $\alpha$  - أمينو - H1 - أميدازول - 4 - حامض البروبانويك (DCIPAHs) والتي حضرت بمفاعلة محلول ملح الديازونيوم للمركب 4، 2 - ثنائي كلورو انلين مع محلول الهستدين في محلول قاعدي كحولي. تم تحديد الصيغ العامه للمعقدات الصلبه وكانت  $[CoL_2Cl_2].H_2O$  و  $[PdLCl_2]$  و  $[CuL_2Cl_2].H_2O$  و  $[NiL_2Cl_2]$  و  $[AgL_2].NO_3$  وذلك من تفاعل ليكاند الأزو أميدازول مع كلوريدات الأيونات الفلزية (والنترات للفضه (I)) وقد بلغت النسبه المولييه (فلز: الليكاند) 1:1 لمعقد البلاديوم فيما بلغت النسبه 2:1 لبقية الأيونات الفلزية كما شخص المعقدات الصلبه طيفياً باستخدام الأشعه تحت الاحمرء والأطياف الالكترونية بالاضافه الى التحليل الدقيق للعناصر والتوصيليه المولاريه والحساسيه المغناطيسيه واستناداً الى تلك المعطيات التحليليه فقد تبين أن الليكاند ثنائي السن ويرتبط مع الأيون الفلزي من خلال احدى ذرتي نيتروجتتين مجموعه الأزو وذرة النيتروجين ( $N_3$ ) للاميدازول . تم اقتراح الشكل ثماني السطوح للمعقدات الفلزية لا يونات الكوبلت (II) والنيكل (II) والنحاس (I) والمربع المستوي لمعقد البلاديوم (II) و رباعي السطوح لمعقد الفضة (I)