

**Preparation And Spectral Characterization Of Some Transition Metal Complexes With New Azo Imidazole Ligand And Study Some Industrial Application**

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**Abstract:-**

New organic heterocyclic azo dye as ligand 2-[1-(4-Bromo phenyl)azo]-imidazol (4-BrPAIm) has been prepared by coupling reaction of the diazonium salt of 4-Bromo aniline with imidazole in alkaline ethanolic solution. The azo dye ligand has been characterized and depending upon spectral data of IR, UV-visible and <sup>1</sup>HNMR. Metal complexes of this ligand with Ni(II), Pd(II), Pt(IV), Cu(II), Ag(I) and Au(III) salts were prepared with a metal:ligand ratio (M:L) of (1:1) for Pd(II) and Au(III) while it is 1:2 ratio for rest metal ions. The isolated solid complexes are found to have the general formula [NiL<sub>2</sub>Cl<sub>2</sub>].H<sub>2</sub>O, [PdLCl<sub>2</sub>], [PtL<sub>2</sub>Cl<sub>2</sub>]Cl<sub>2</sub>.H<sub>2</sub>O, [CuL<sub>2</sub>Cl<sub>2</sub>].H<sub>2</sub>O, [AgL<sub>2</sub>]NO<sub>3</sub> and [AuLCl<sub>2</sub>]Cl.H<sub>2</sub>O. The chelate complexes were characterized and their stereo chemical structures and geometries were suggested depending upon data of elemental analysis, molar conductivity, atomic absorption, magnetic susceptibility measurements, IR and electronic spectra. The data show that the ligand is bidentate and coordinates to the metal ion via the nitrogen atom of azo group and with imidazole N<sub>3</sub> atom. Octahedral configuration is suggested for Ni(II), Pt(IV) and Cu(II) metal complexes but square planar for Pd(II) and Au(III) complexes and tetrahedral for Ag(I) complex. Conductivity measurements of prepared complexes showed electrolyte for Pt(IV), Au(III) and Ag(I) complexes and non electrolyte for rest complexes. In dimethyl sulphoxide (DMSO) solution have been evaluated by agar plate diffusion technique against four human pathogenic bacterial *Staphylococcus aureus* (Gram Positive Bacteria), *Pseudomonas aeruginosa*, *Escherichia coli* and *Ribrio cholerae* (Gram negative Bacteria). The ligand and some of the complexes were found exhibit good bacterial activities. In addition the dyeing performance of the prepared ligand and its complexes was assessed. The dye were tested for light and detergent fastness. The fixed color have the feature of stability to wards light, wash and friction.

**Key words:-Preparation, New azo imidazole ligand, Metal complexes, Characterization Biological activities and dyeing.**

**A part of M.Sc. Thesis**

## 1-Introduction

The imidazole compound and its derivatives are used in different directions. The azo imidazole dyes are highly colored and have been used as dyeing nylon<sup>(1)</sup> and polyester<sup>(2)</sup>. This compound is important in drugs<sup>(3)</sup>, cosmetics<sup>(4)</sup>, biological activities including antibacterial<sup>(5)</sup>, and preparation of azo dyes<sup>(6,7)</sup>. Researchers in the field of analytical and inorganic chemistry pay more attention to prepare, isolate and estimate of this kind of ligand and their chelated complexes which were known by their colors with advancing of knowledge improve this sensitivity<sup>(8)</sup> and selectivity<sup>(9)</sup> in determination of trace amount of metal elements in living tissue in mice live after the injection of mice with the ligand<sup>(10,11)</sup>. In the field of spectra determination<sup>(12)</sup> it has a distinguished role in spectra evaluation of very small concentration of elements using UV-visible<sup>(13,14)</sup> because it gives colored solution when reacts with metal ions. Azo imidazole molecule being the azo imine group (-N=N-C=N-) which is acidic and stabilizes low valent metal redox state<sup>(15)</sup>. The chemical study of imidazole shows that it is a mixture of pyridine and pyrrole characteristics. Imidazole forms many polarizational salts and as a base, it is stronger than pyridine<sup>(16)</sup>. The coupling of diazonium salt occurs in position (2) of imidazole ring in alkaline medium to give shining azo imidazole dyes<sup>(17,18)</sup>. In the present study reports the preparation and spectral characterization of new azo imidazole ligand (4-BrPAIm) and chelated complexes with some transition metals including Ni(II), Pd(II), Pt(IV), Cu(II), Ag(I) and Au(III). The probable structures of the isolated metal complexes have been determined using several techniques. The biological activity of the ligand and its complexes has been investigated to show as antibacterial. The ligand and its complexes had been used as dyes and it showed it is stable dyes towards sun light, washing, detergents and friction.

## 2-Experimental

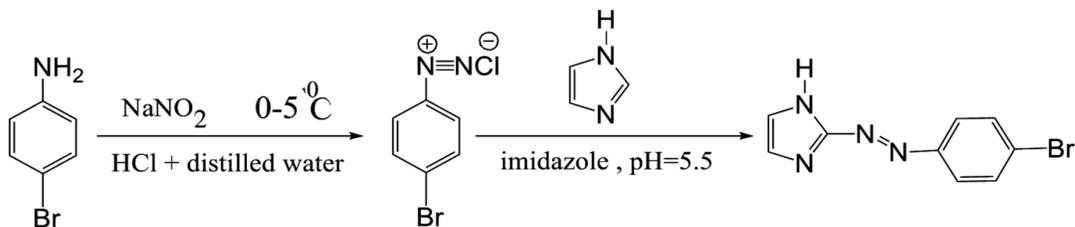
### 2.1- Materials and measurements

All chemicals and solvents were of highest purity from commercial suppliers such as BDH, Fluka and Aldrich. Elemental analysis (C,H,N) were obtained using 1108 C.H.N elemental analyzer. FT-IR spectra of the ligand as well as the complexes were recorded as KBr discs in the range (400-4000)cm<sup>-1</sup> on a FT-IR Teast scan Shimadzu model 8400S. Electronic spectra were recorded on a UV-vis. Shimadzu model 1650PC for 10<sup>-5</sup>M solution of the ligand and its complexes in absolute ethanol at 25°C using 1cm quartz cell. Proton Nuclear Magnetic Resonance (<sup>1</sup>H-NMR) for the prepared ligand was carried out using NMR-Unter suchunges auftrag AVS-300 in Jordan with CD<sub>3</sub>OD as solvent. The molar conductance measurements were carried out in ethanol and DMF solvents (10<sup>-3</sup>M) at room temperature by using conductivity bridge model 31A and the pH measurements were carried out using Philips PW 9421 pH meter (pH±0.001). The magnetic moment measurements of complexes were measured by using magnetic susceptibility (Faraday method) with balance magnetic MSB-MKI apparatus. The metal percentage in the complexes was measured by using Shimadzu flame atomic absorption model; AA-160. Melting point were measured by Electro thermal melting point 9300. The chloride ion was estimated by Mohr method.<sup>(19)</sup>

### 2.2-Preparation of the ligand (4-BrPAIm)

The azo imidazole ligand (4-BrPAIm) was prepared according to the following general procedure as described for 2-(aryl azo)-imidazoles with some modification.<sup>(20)</sup> A diazonium solution was prepared by dissolving (1.79g, 0.01 mol) of 4-bromo aniline in 5ml of concentrated hydrochloric acid and 25ml

distilled water. To this mixture a solution of (0.75gm, 0.01mol) of sodium nitrate in 20ml of distilled water was added dropwise at (0-5) °C and left to stand 30min. This diazonium solution was added dropwise into a 800ml beaker containing (0.68gm, 0.01mol) of imidazole dissolved in 200ml of alkaline ethanol and 30ml of 10% sodium hydroxide at (0-5) °C, the mixture was stirred for additional 2hrs in ice-bath and allowed to stand over night and acidified with dilute hydrochloric acid to pH=5.5. The precipitate was filtered off, washed with distilled water and recrystallized twice from hot ethanol and dried in a vacuum desicator. The yield was 81.46% of dark yellow crystals. The procedure was seen in scheme 1.



4-bromo aniline

diazonium chloride

2-[1-(4-Bromo phenyl)azo ]-imidazole: (4-BrPAIm)

**Scheme(1) :-Preparation of the ligand 2-[1-(4-Bromo phenyl)azo ]-imidazole; (4-BrPAIm)**

### 2-3-Preparation of metal complexes

#### A-Ni(II),Pd(II),Pt(IV);Cu(II)andAg(I) complexes:

These complexes were prepared by dissolved (0.502gm,0.002mol) from ligand in hot ethanol (50ml) and added dropwise with stirring to a stoichiometric amounts of 1:2 (metal:ligand) molar ratio of NiCl<sub>2</sub>,PtCl<sub>4</sub>,CuCl<sub>2</sub> and AgNO<sub>3</sub> ,and 1:1 for the PdCl<sub>2</sub> (0.251gm,0.001mol of ligand) which were dissolved in 25ml of suitable buffer solution (ammonium acetate ) for each metal ions. The mixture was stirred at (70-80)°C for 40min and left overnight. The precipitate which was formed was filtered, washed with 10ml hot ethanol to remove the remaining unreacted substances and dried in a desiccator over anhydrous calcium chloride.

#### B-Au(III)complex<sup>(21)</sup>:

This complex was prepared by dissolving (0.251gm,0.001mol)of ligand in 40ml hot ethanol and mixed with solution of NaAuCl<sub>4</sub>.2H<sub>2</sub>O (0.595gm,0.001mol)in 30ml of hot ethanol (metal:ligand=1:1).To this mixture 10ml of buffer solution (pH=6.5) was added slowly with stirring .The mixture was then heated to 70°C for 50mints,and left over night. The dark red solid mass obtainend was filtered washed with 10 ml hot ethanol and dried in a desiccatore over anhydrous calcium chloride .

### 3-Results and Discussion

### 3.1-Characterization of ligand (4-BrPAIm) and its complexes

The hetrocyclic azo dye ligand was dark yellow crystals ,but the chelat complexes of this ligand gives different color crystals.The ligand and its complexes are stable to words air and insoluble in water but soluble in organic solvents ,including methanol, ethanol,acetone ,DMSO and DMF.The azo ligand showed acid-base indicator properties.Red color in strongly acidic solution ( $\text{pH} \geq 2.5$ )and greensh blue in strongly alkaline solution( $\text{pH} \geq 12$ ).The physical properties and elemental analysis are in agreement with the formulae of the ligand and its chelat complexes are summarized in Table1.

**Table(1):Elemental analyses and some physical properties of azo ligand (4-BrPAIm) and its complexes**

No.	Compound	pH	Color	m.P °C	Yield %	Molecular formula (Mol.Wt)	Found (Calc.)%			
							C	H	N	M
1	4-BrPAIm=L	5.5	Dark yellow	159	81.46	C <sub>9</sub> H <sub>7</sub> N <sub>4</sub> Br (251.08)	(43.05) 43.37	(2.81) 2.71	(22.31) 22.14	—
2	[NiL <sub>2</sub> Cl <sub>2</sub> ] H <sub>2</sub> O	8.0	brown	181	78.32	C <sub>18</sub> H <sub>16</sub> N <sub>8</sub> Br <sub>2</sub> Cl <sub>2</sub> ONi (649.76)	(33.27) 33.77	(2.84) 2.27	(17.24) 17.44	(9.03) 8.90
3	[PdLCl <sub>2</sub> ]	7.5	Dark brown	196	64.12	C <sub>9</sub> H <sub>7</sub> N <sub>4</sub> BrCl <sub>2</sub> Pd (428.40)	(25.23) 25.73	(1.65) 1.45	(13.08) 13.18	(24.84) 24.89
4	[PtL <sub>2</sub> Cl <sub>2</sub> ] Cl <sub>2</sub> .H <sub>2</sub> O	8.0	Dark purple	220	69.37	C <sub>18</sub> H <sub>16</sub> N <sub>8</sub> Br <sub>2</sub> Cl <sub>4</sub> OPt (855.43)	(25.23) 25.68	(1.88) 1.59	(13.07) 13.27	(22.76) 22.78
5	[CuL <sub>2</sub> Cl <sub>2</sub> ] .H <sub>2</sub> O	6.0	green	175	71.05	C <sub>18</sub> H <sub>16</sub> N <sub>8</sub> Br <sub>2</sub> Cl <sub>2</sub> OCu (654.62)	(33.02) 33.32	(2.46) 2.63	(17.12) 16.61	(9.71) 9.47
6	[AgL <sub>2</sub> ] NO <sub>3</sub>	7.0	Redish Purple	203	78.66	C <sub>18</sub> H <sub>16</sub> N <sub>9</sub> Br <sub>2</sub> O <sub>3</sub> Ag (672.26)	(32.17) 31.79	(2.10) 2.24	(18.76) 18.46	(16.05) 15.90
7	[AuLCl <sub>2</sub> ] Cl.H <sub>2</sub> O	6.5	Dark Red	213	67.87	C <sub>9</sub> H <sub>9</sub> N <sub>4</sub> BrCl <sub>3</sub> OAu (572.41)	(18.88) 18.57	(1.58) 1.76	(9.79) 10.21	(34.41) 34.53

### 3.2-<sup>1</sup>H-NMR Spectrum of ligand <sup>(22,23)</sup>

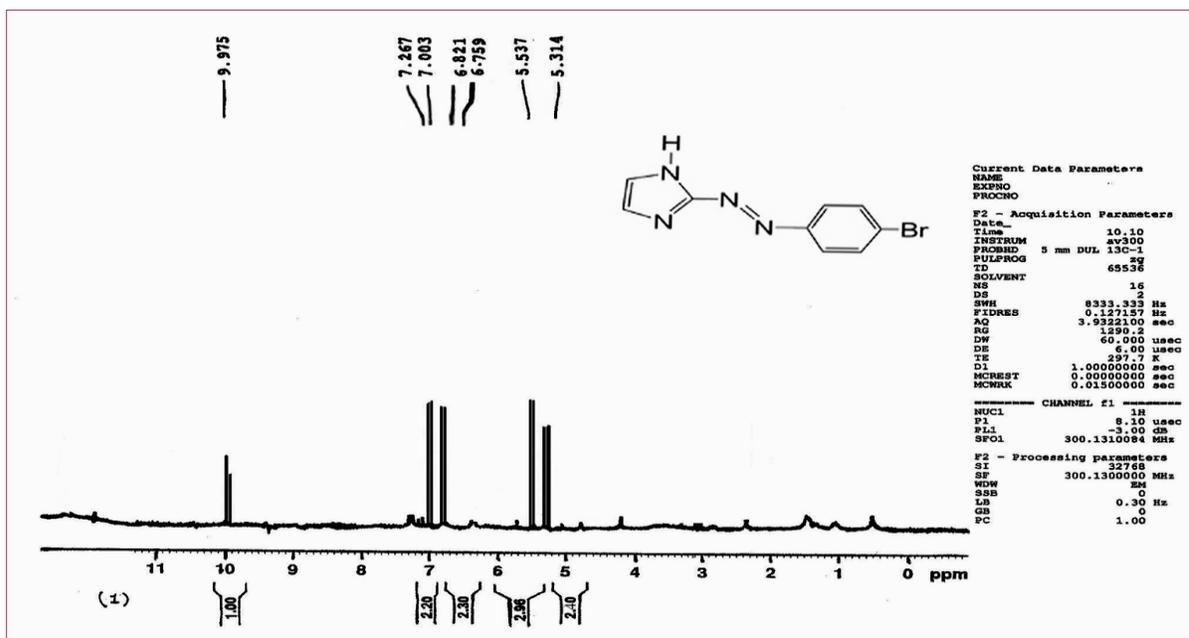
The  $^1\text{H-NMR}$  spectrum of the free ligand (4-BrPAIm) was carried out using  $\text{CD}_3\text{OD}$  as a solvent and the following peak were detected (Fig.1)

A-Single peak at  $\delta = 9.975$  ppm for NH of imidazole ring

B.Tetra peaks at  $\delta = (7.267-6.759)$ ppm for CH adjacent to four proton [H(2,3,5,6)]of the aromatic ring

C.Dblate peaks at  $\delta = 5.537$ ppm for H(4) proton of the imidazole ring

D.Dblate peak at  $\delta = 5.314$ ppm which is related to the H(5)proton of the imidazole ring



### 3-3-Absorption spectra

The absorption spectra in aqueous ethanolic solution 50%(V\V) were studied for the prepared complexes showed a bathochromic shift ranging between (72-233)nm depending on the metal ion. The absorption spectra of the Ni(II), Pd(II), Pt(IV), Cu(II) and Ag(I) chelat complexes are shown in figures.2 and 3.

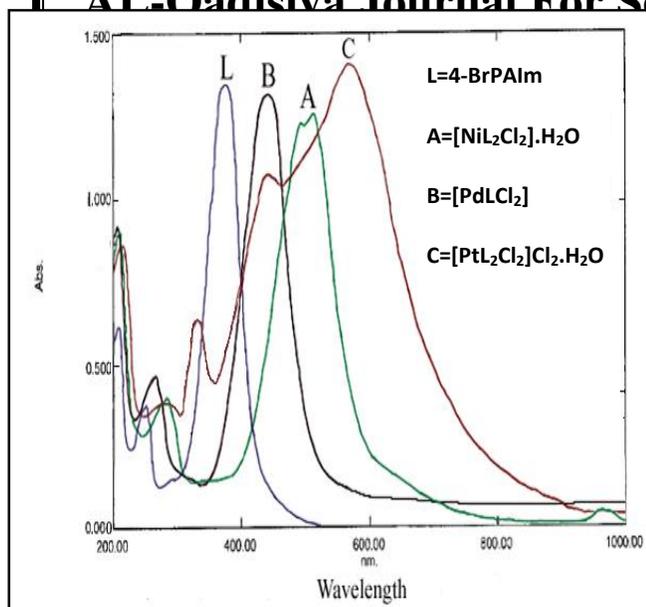


Fig.(2):-UV-vis. spectra of 4-BrPAIm–metal complexes;(  $1.75-2.25 \times 10^{-5} \text{M}$  in aqueous solution 50% (V/V);

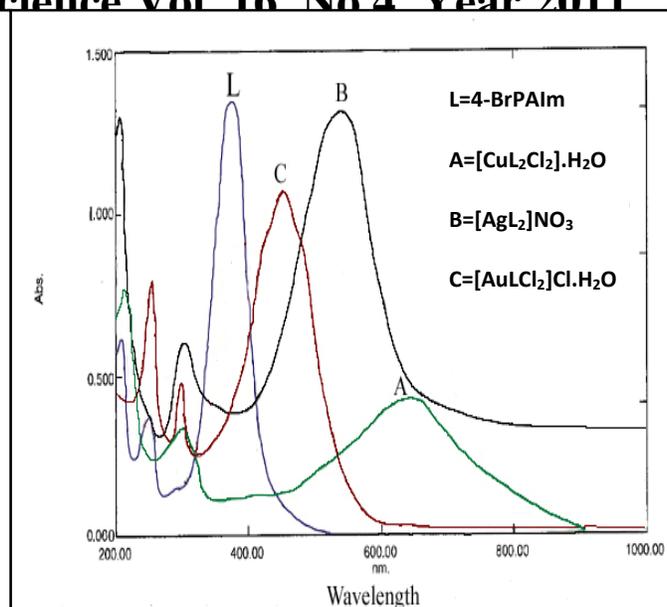


Fig.(3):- UV-vis. spectra of 4-BrPAIm–metal complexes; (  $2.0-2.25 \times 10^{-5} \text{M}$  in aqueous solution 50% (V/V);

### 3.4-Infrared spectra:

The infrared spectra of the ligand (4-BrPAIm) and its complexes are summarized in Table2. The careful comparison between spectra of the ligand and chelat complexes have revealed certain characteristic differences. The spectra are complicated owing to the extensive overlap of a number of bands arising from O-H, N-H, C=N and N=N groups in addition of other bonds originated from phenyl and imidazole rings which appeared in the region  $(400-4000) \text{cm}^{-1}$ . The shifts in the positions and intensity for both ligand and chelat complexes of these bands suggest the probable modes of bonding the free ligand with metal ions. Some of these main shifts and conclusion are given below.

The spectrum of free ligand showed a medium intensity band at  $3320 \text{cm}^{-1}$  may be attributed to the  $\nu(\text{NH})$  group of imidazole ring<sup>(24)</sup>. This band unchanged in the spectra of all complexes indicates its non involvement in coordination of the ligand to the metal ions. A broad and medium band in the range of  $(3520-3570) \text{cm}^{-1}$  due to the presence of water molecules in the spectra of the Ni(II), Pt(IV), Cu(II) and Au(III) complexes.<sup>(25,26)</sup> A weak band observed at  $3085 \text{cm}^{-1}$  in the free ligand spectrum which is due to  $\nu(\text{C-H})$  aromatic. This band is stable in position and intensity in both ligand and chelat complexes. The strong and sharp band at  $1570 \text{cm}^{-1}$  in the ligand spectrum is considered to be  $\nu(\text{C=N})$  of imidazole ring<sup>(27)</sup>. The changing of this group to higher frequency at  $(1578-1595) \text{cm}^{-1}$  indicates the affected of this group by complexation<sup>(28)</sup>. The Vibration band assigned to the azo group  $\nu(\text{N=N})$  which appears at  $1460 \text{cm}^{-1}$  in the free ligand spectrum. The shifting and changing in shape of this band to lower frequency in the spectra of the chelat complexes in the range of  $(1456-1467) \text{cm}^{-1}$ , suggest the participation of azo group (N=N) in chelation and complex formation.<sup>(28-30)</sup> New bands in the range of  $(415-560) \text{cm}^{-1}$  in the complexes spectra which are not present in the free ligand are due to  $\nu(\text{M-N})$  vibrations.<sup>(11,26,30)</sup> Depend on IR spectra data lead to suggest that ligand behaves as a bidentate chelating ligand coordinating through the position of nitrogen of azo group nearest to a phenyl ring and  $\text{N}_3$  atom of the imidazole ring to give five-membered chelat ring<sup>(6,11,25,30)</sup>. Representative example for their spectra are given in figures 4, 5 and 6.

**Table (2);-Selected IR absorption bands of the ligand and its complexes in cm<sup>-1</sup> unit (KBr disc)**

Assignment	4-BrPAIm	Ni <sup>+2</sup> pH=8	Pd <sup>+2</sup> pH=7.5	Pt <sup>+4</sup> pH=8	Cu <sup>+2</sup> pH=6	Ag <sup>+1</sup> pH=7	Au <sup>+3</sup> pH=6.5
<b>v(O-H)</b>	—	3520	—	3540 m.br.	3530 m.br.	—	3570 m.br.
<b>v(N-H)</b> <b>imidazole</b>	3320 m.	3325 m.	3325 w.	3320 w.	3320 w.	3325 m.	3332 w.
<b>v(C=N)</b> <b>imidazole</b>	1570 s.	1578 s.	1595 m.	1582 m.	1575 s.	1574 m.	1595 m.
<b>v(N=N)</b>	1460 s.	1456 s.	1458 s.	1667 m.br.	1462 s.	1460 s.	1465 s.br.
<b>v (C-N=N-C)</b>	1364 m	1394 w	1393 m	1365 m	1394 m	1392 m.sh.	1396 m.sh.
<b>v(C=C)</b>	1359 s.	1360 Vs.	1359 s.	1467 m.br.	1462 s.	1354 s.br.	1358 s.
<b>Imid.r.d.e.</b>	1101 s.	1066 Vs.	1068 s.	1068 s.	1068 s.	1067 s.	1067 s.
<b>Phenyl ring</b>	829s. 790s.	831s. 792m.	830m. 790m.	831m. 790m.br.	835s. 796s.	831m. 790s.	831s. 792m.
<b>v (M-N)</b>	—	560 w.	535 w.	520 w.	516 w.	525 w.	520 w.

**W=weak , S=stronge ,m= medium , br=broad , sh= shoulder**

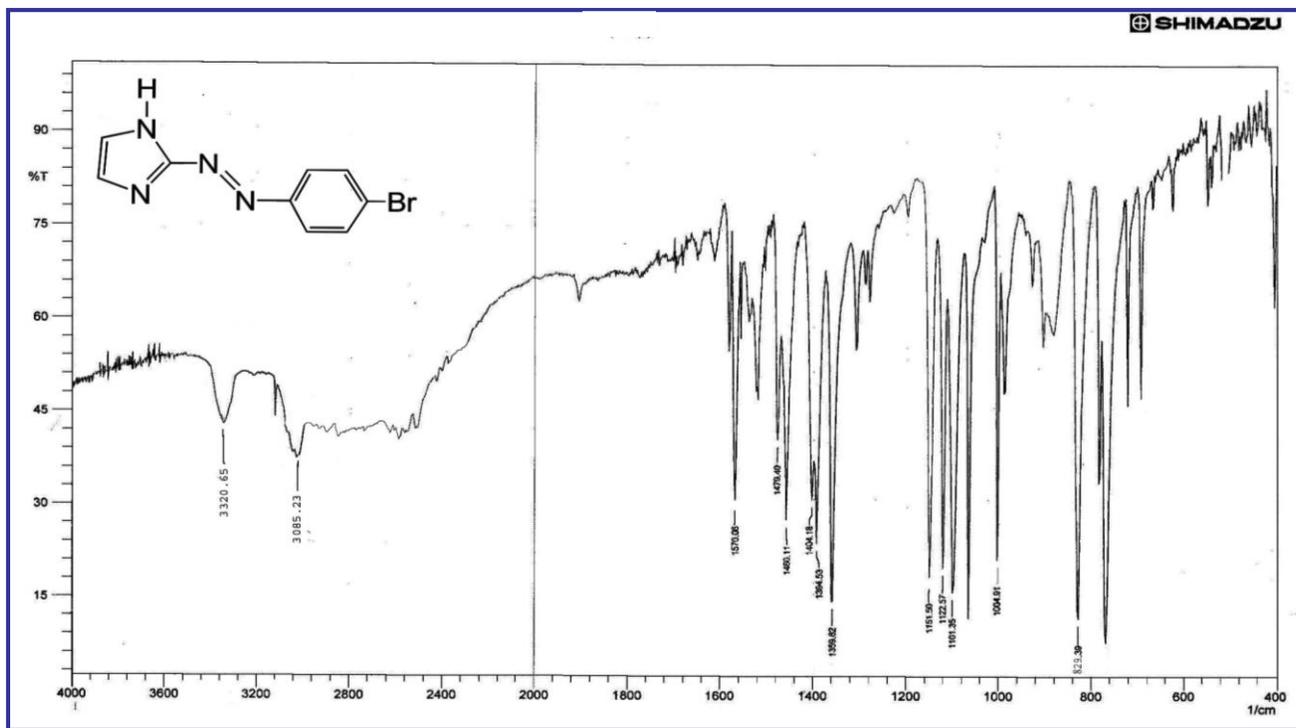


Fig.(4):-FT-IR Spectrum of the free ligand (4-BrPAlm)

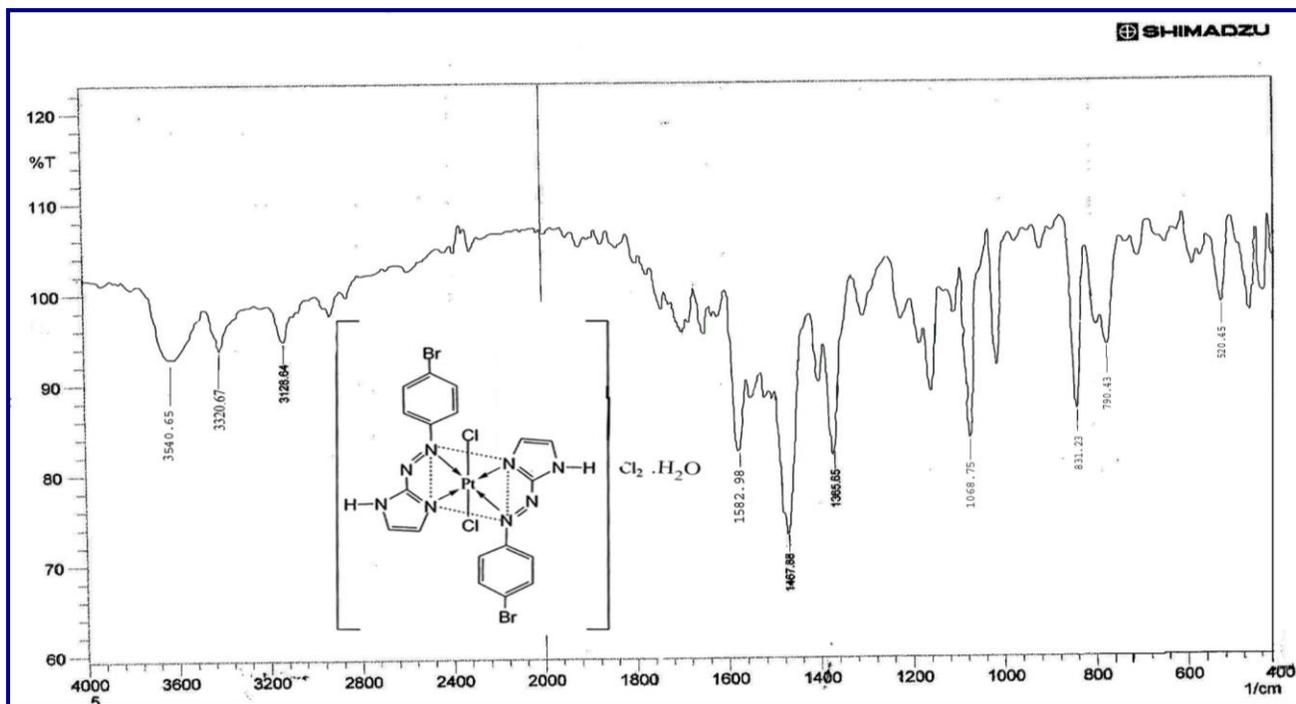


Fig.(4):-FT-IR Spectrum of the complex  $[Pt(4-BrPAlm)_2 Cl_2] Cl_2 .H_2O$

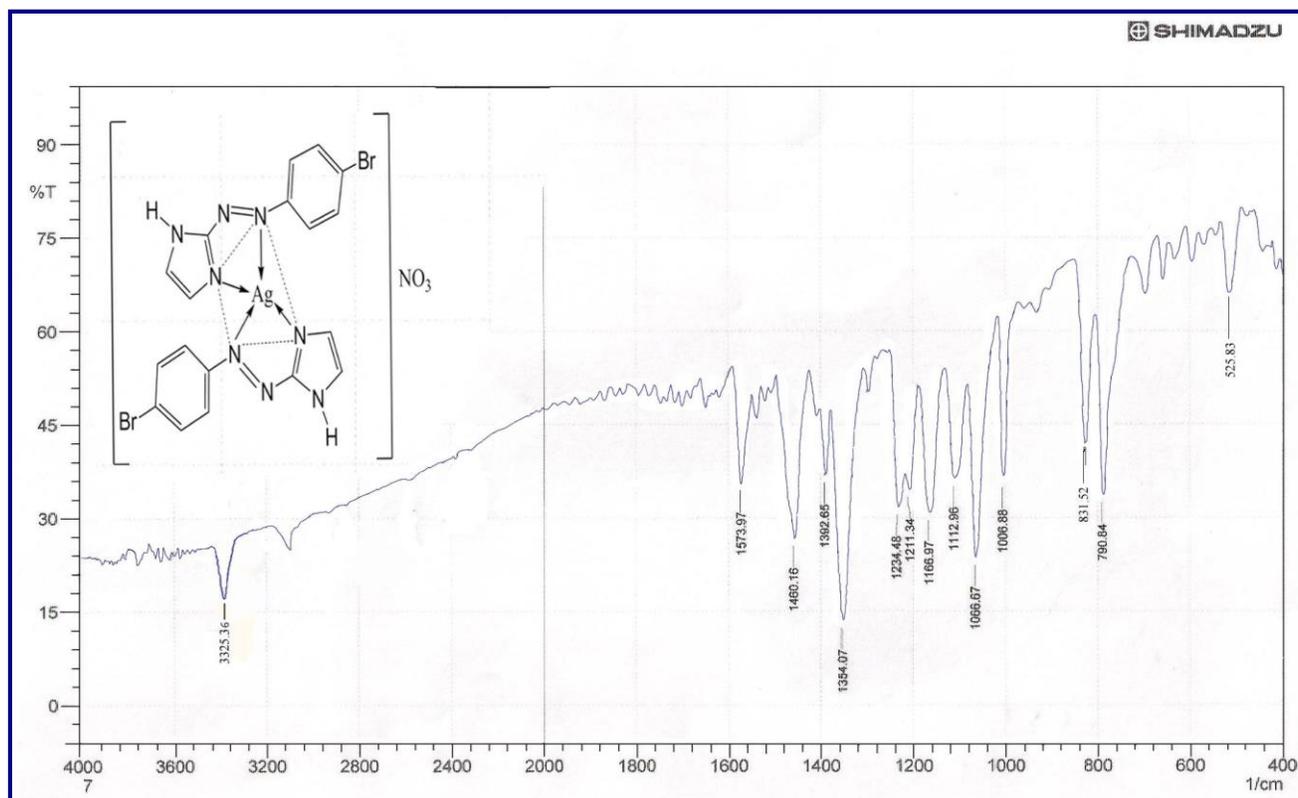


Fig.(4):-FT-IR Spectrum of the complex  $[Ag(4-BrPAIm)_2] NO_3$

### 3-5-Electronic spectra and magnetic moments

The magnetic moment values measured at room temperature and electronic spectra of the azo dye ligand and its complexes were recorded in absolute ethanol and their assignments are given in table 3. The free ligand (4-BrPAIm) showed three bands. The first band located at 222nm ( $45045\text{cm}^{-1}$ ) for ( $\pi \rightarrow \pi^*$ ) transition within heterocyclic imidazole ring<sup>(31)</sup>, while the second band observed at 276nm ( $36232\text{cm}^{-1}$ ) to the excitation of the  $\pi$ -electrons of (C=C) group of aromatic ring<sup>(32)</sup>. The third band at 377nm ( $26525\text{cm}^{-1}$ ) for ( $n \rightarrow \pi^*$ ) of the azo group (N=N). The latter showed a red shift on coordination with a metal ion. These observations represent a further indication for the coordination of the azo ligand to the metal ion.<sup>(8,11,26,30)</sup> For the spectra of chelate complexes the following results were obtained.

#### Ni(II)-Complex

The electronic spectrum of this complex shows three absorption bands at 963nm ( $10384\text{cm}^{-1}$ ), 578nm ( $17301\text{cm}^{-1}$ ) and 469nm ( $21322\text{cm}^{-1}$ ) there are assigned to  ${}^3A_{2g} \rightarrow {}^3T_{2g(F)} (v_1)$ ;  ${}^3A_{2g} \rightarrow {}^3T_{1g(F)} (v_2)$  and  ${}^3A_{2g} \rightarrow {}^3T_{1g(P)} (v_3)$  transition respectively with an octahedral configuration.<sup>(11,30,33)</sup> The magnetic moment for the Ni(II) complex has been found to be 2.830 B.M which may suggest an octahedral high spin with hybridization  $sp^3d^2$  structure.

**Pd(II) –Complex**

The d-d transitions electron spectrum of this complex shows one absorption band at the position 449nm (22272 cm<sup>-1</sup>) which is attributed to <sup>1</sup>A<sub>1g</sub>→<sup>1</sup>B<sub>1g</sub> transition in a square planer symmetry.<sup>(34,35)</sup> The magnetic susceptibility for Pd(II)-complex gave  $\mu_{\text{eff}}=0.0\text{B.M}$  (dia magnetic) because of location of palladium is second round (d<sup>8</sup>-low spin) and indicate a square planer geometry (hybridization dsp<sup>2</sup>) which is the stereo chemistry for this complex a tetra coordinate.

**Pt(IV)-Complex**

The electronic absorption spectrum of Pt(IV)-complex showed three bands at 576nm (17361cm<sup>-1</sup>) of <sup>1</sup>A<sub>1g</sub>→<sup>1</sup>T<sub>1g(F)</sub>(v<sub>1</sub>), 420nm(23809cm<sup>-1</sup>) of <sup>1</sup>A<sub>1g</sub>→<sup>2</sup>T<sub>2g(F)</sub>(v<sub>2</sub>) and 347nm (28818cm<sup>-1</sup>) of <sup>1</sup>A<sub>1g</sub>→<sup>1</sup>E<sub>g</sub>(v<sub>3</sub>) transitions.<sup>(36)</sup> The magnetic moment for this complex found to be diamagnetic character ( $\mu_{\text{eff}}=0.0\text{B.M}$ ). suggest a low spin octahedral geometry.<sup>(36)</sup> The hybridization of this complex is d<sup>2</sup>sp<sup>3</sup> because of location of the platinum in third round (d<sup>6</sup>-low spin).

**Cu(II) –Complex**

Copper(II) –complex showed a broad band at around 610nm (16393 cm<sup>-1</sup>) due to <sup>2</sup>E<sub>g</sub>→<sup>2</sup>T<sub>2g</sub> transition. The magnetic moment for this complex found to be 1.813 B.M because of presence of one unpaired electron in Cu(II)-complex. These results suggest distorted octahedral structure (d<sup>9</sup>, Z-out or Z-in) and hybridization sp<sup>3</sup>d<sup>2</sup> geometry.<sup>(11,26,30)</sup>

**Ag(I)-Complex**

No d-d transition bands of this complex exhibit high intense a charge transfer transition in visible region 541nm (18484 cm<sup>-1</sup>) which are due to (M→L,CT).<sup>(21,30)</sup> The magnetic susceptibility for Ag(I)-complex due the electronic configuration d<sup>10</sup> to be diamagnetic character ( $\mu_{\text{eff}}=0.0\text{B.M}$ ) which is characteristic of tetrahedral geometry at 1:2(M:L) and hybridization sp<sup>3</sup> symmetry.

**Au(III)-Complex**

For Au(III) azo dye complex, the spectrum shows one band at 482nm (20747cm<sup>-1</sup>) due to <sup>1</sup>A<sub>1g</sub>→<sup>1</sup>B<sub>1g</sub>(v<sub>1</sub>) transition. It is reasonable to suggest square planer configuration and hybridization dsp<sup>2</sup> (d<sup>8</sup>-low spin). The zero magnetic value of this complex ( $\mu_{\text{eff}}=0.0\text{B.M}$ ) indicate square planer geometry which is the common stereo chemistry for tetra coordinate Au(III)-complex<sup>(21,38)</sup>.

**3.6-Molar conductivity measurements**

The molar conductance measurements of the prepared complexes were carried out in ethanol and DMF solvents with the concentration of 10<sup>-3</sup> M at room temperature. The chelate complexes of Pt(IV), Ag(I) and Au(III) ions are a good electrolyte with ionic nature (table 3) indicate that these complexes are 1:1 electrolyte for Ag(I) and Au(III) complexes, and 1:2 electrolyte for Pt(IV) complex. But showed very weak conductance for the rest chelate complexes (Ni(II), Pd(II) and Cu(II)) which means a non-electrolyte with non ionic nature.

**Table(3):- Electronic Spectra, magnetic moments and molar conductivity of chelate complexes**

Complexes	$\lambda_{max}$ nm	Absorption bands (cm <sup>-1</sup> )	Transition	$\mu_{eff}$ B.M	Conductivity S.cm <sup>2</sup> .mol <sup>-1</sup>	
					EtOH	DMF
[NiL <sub>2</sub> Cl <sub>2</sub> ] H <sub>2</sub> O	963	10384	<sup>3</sup> A <sub>2g</sub> → <sup>3</sup> T <sub>2g(F)</sub> (v <sub>1</sub> )	2.830	6.78	8.92
	578	17301	<sup>3</sup> A <sub>2g</sub> → <sup>3</sup> T <sub>1g(F)</sub> (v <sub>2</sub> )			
	469	21322	<sup>3</sup> A <sub>2g</sub> → <sup>3</sup> T <sub>1g(P)</sub> (v <sub>3</sub> )			
[PdLCl <sub>2</sub> ]	449	22272	<sup>1</sup> A <sub>1g</sub> → <sup>1</sup> B <sub>1g</sub>	dia	7.54	10.37
[PtL <sub>2</sub> Cl <sub>2</sub> ] Cl <sub>2</sub> .H <sub>2</sub> O	576	17361	<sup>1</sup> A <sub>1g</sub> → <sup>1</sup> T <sub>1g(F)</sub> (v <sub>1</sub> )	dia	87.31	158.29
	420	23809	<sup>1</sup> A <sub>1g</sub> → <sup>1</sup> T <sub>2g(F)</sub> (v <sub>2</sub> )			
	347	28818	<sup>1</sup> A <sub>1g</sub> → <sup>1</sup> E <sub>g</sub> (v <sub>3</sub> )			
[CuL <sub>2</sub> Cl <sub>2</sub> ] .H <sub>2</sub> O	610	16393	<sup>2</sup> E <sub>g</sub> → <sup>2</sup> T <sub>2g</sub>	1.813	10.76	13.08
[AgL <sub>2</sub> ] NO <sub>3</sub>	541	18484	M→L,CT	dia	42.59	78.34
[AuLCl <sub>2</sub> ] Cl.H <sub>2</sub> O	482	20747	<sup>1</sup> A <sub>1g</sub> → <sup>1</sup> B <sub>1g</sub>	dia	47.25	86.77

### 3.7-Metal:Ligand ratio

The metal:Ligand ratio (M:L) of chelate complexes were determined by molar ratio method at fixed concentration and optimal pH at wavelength of maximum absorption .The ligand was found to form 1:1 complexes with Pd(II) and Au(III) metal ions and 1:2 chelate complexes with Ni(II),Pt(IV),Cu(II) and Ag(I) metal ions .This results are in agreement with the values reported for some phenyl azo imidazole complexes. <sup>(6,8,11,26,30)</sup> The results are given in table 4 shown in figures 7 and 8.

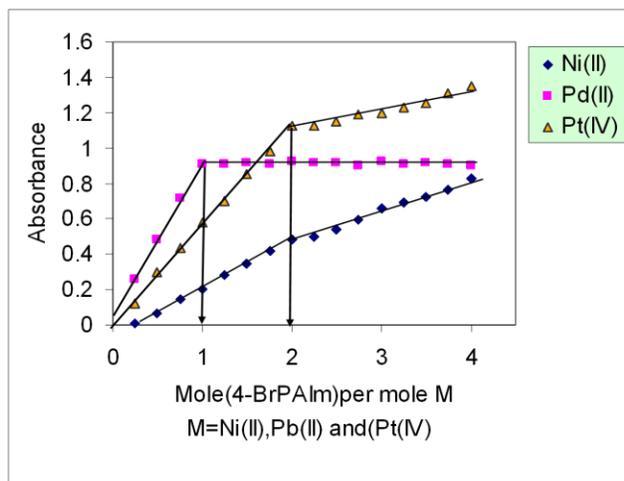


Fig (7):-Molar ratio method 4-BrPAIm –metal chelates at optimal pH and concentration

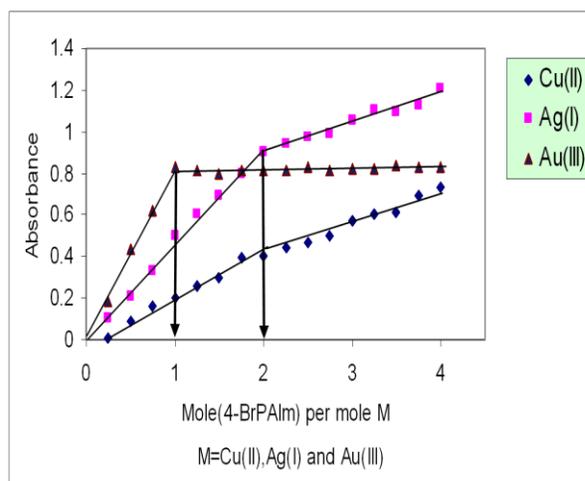


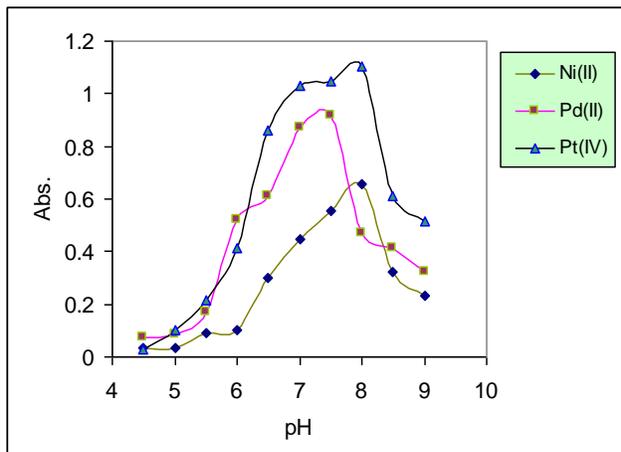
Fig (8):-Molar ratio method 4-BrPAIm –metal chelates at optimal pH and concentration

### 3.8-Calculation of the chelate complexes stability constants

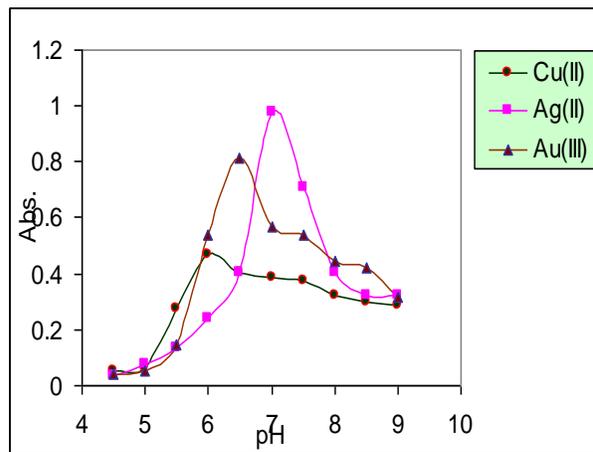
stability constants for chelate complexes are obtained spectrophotometrically by measuring the absorbance of solutions of ligand and metal ions at fixed wavelength ( $\lambda_{max}$ ) and pH values. The degree of formation of the chelate complexes are obtained from the relationship  $\beta = (1 - \alpha / \alpha^2 C^2)$  for 1:2 (M:L) metal complexes and  $\beta = (1 - \alpha / \alpha^2 C)$  for 1:1 (M:L) metal chrlates<sup>(39)</sup>. The  $\alpha$  values were obtained from the relationship  $\alpha = A_m - A_s / A_m$ , where  $A_m$  and  $A_s$  are the absorbances of the fully and partially formed complex respectively at optimum concentration. The calculated  $\beta$  and  $\log \beta$  values for the prepared complexes are listed in table 4.

### 3.9-Effect of pH and Time

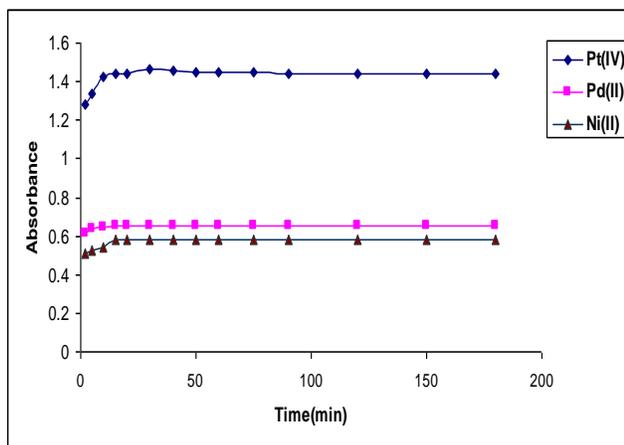
The effect of pH were studied in aqueous ethanolic solution (50% V/V). The absorption of  $M^{+n}$ -(4-BrPAIm) solution of all complexes a very stable complexes with metal ions at pH =6.0-8.0. The reaction between ligand and metal ions are complete in 10 mints .at room temperature and remains stable for about 24 hour. The result are shown in figures 9-12



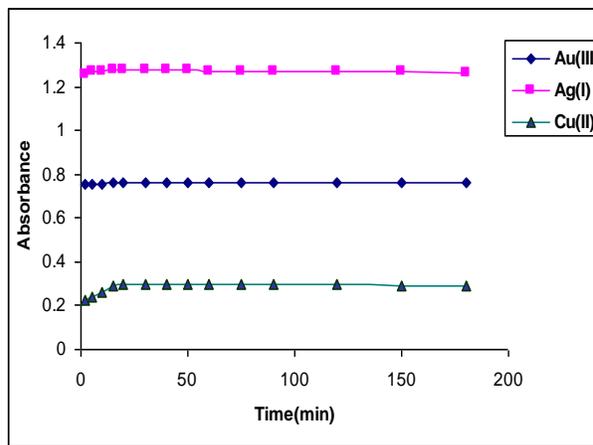
**Fig. (9):- Effect of pH on complex formation of 4-BrPAIm -metal chelats  $(1.75-2.25) \times 10^{-5} M$  in aqueous ethanol solution**



**Fig. (10):- Effect of pH on complex formation of 4-BrPAIm -metal chelats  $(2.00-2.25) \times 10^{-4} M$  in**



**Fig.(11):-Effect of time on the absorbance of metal complexes at room temperature.**

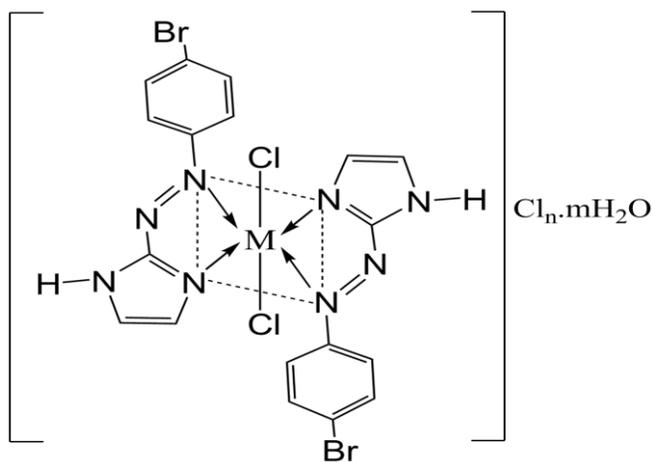
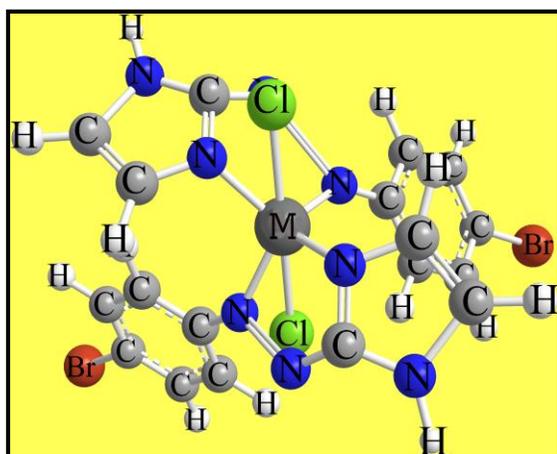


**Fig.(12):-Effect of time on the absorbance of metal complexes at room temperature.**

**Table (4) :- Metal :ligand, stability constants values, molar conductivity; optimal concentration and wavelength with molar absorptivity ( $\epsilon$ ) of chelate complexes**

NO.	Complexes	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 $\beta$	Ligand
1	[NiL <sub>2</sub> Cl <sub>2</sub> ] H <sub>2</sub> O	1:2	1.75	578	3.74	1.31x10 <sup>10</sup>	10.12	4-BrPAIm , $\lambda_{max}= 377$ nm $\epsilon=10.9 \times 10^3$ L .mol <sup>-1</sup> .cm <sup>-1</sup> Conc.=1.25x10 <sup>-4</sup>
2	[PdLCl <sub>2</sub> ]	1:1	2.25	449	4.53	1.54x10 <sup>10</sup>	10.18	
3	[PtL <sub>2</sub> Cl <sub>2</sub> ] Cl <sub>2</sub> .H <sub>2</sub> O	1:2	2.00	579	10.22	1.075x10 <sup>11</sup>	11.03	
4	[CuL <sub>2</sub> Cl <sub>2</sub> ] .H <sub>2</sub> O	1:2	2.00	610	1.19	1.08x10 <sup>10</sup>	10.03	
5	[AgL <sub>2</sub> ] NO <sub>3</sub>	1:2	2.25	541	5.88	2.17x10 <sup>10</sup>	10.33	
6	[AuLCl <sub>2</sub> ] Cl.H <sub>2</sub> O	1:1	2.25	482	7.72	4.44x10 <sup>10</sup>	10.64	

From the previous chemical and spectral analysis data we can suggest the following geometrical structures for the prepared metal complexes, figures 13, 14 and 15



**Fig.(13):-The proposed chemical structure formula of the metal complexes when:-**

**M= Ni (II) and Cu (II); n=0, m=1**

**M= Pt (IV); n=2, m=1**

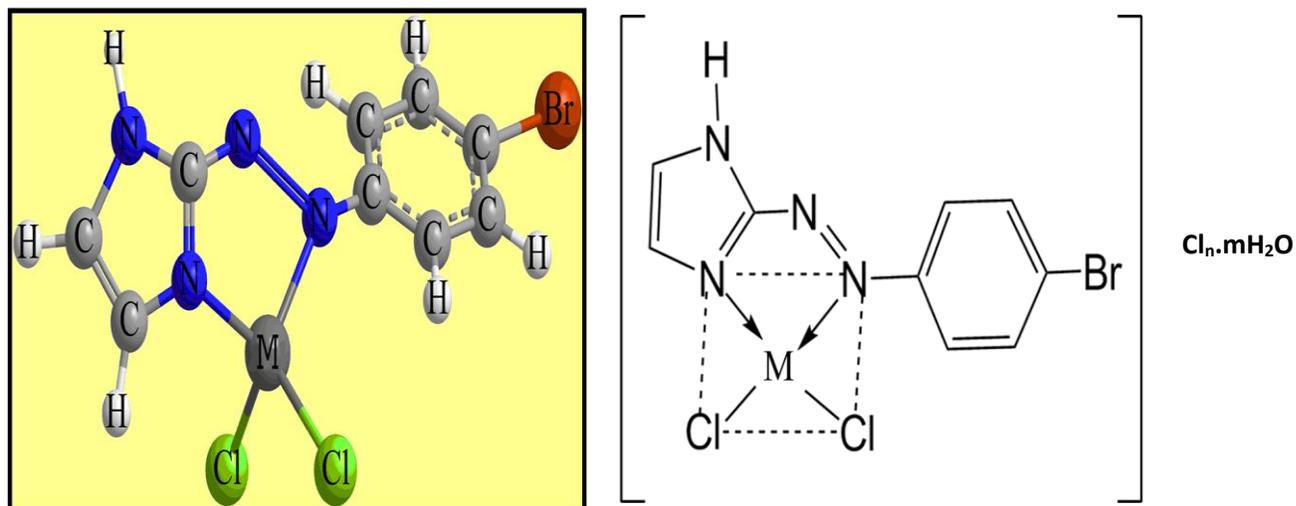


Fig.(14):-The proposed chemical structure formula of the metal complexes when:-

M= Pd (II); n=0, m=0

M= Au (III); n=1, m=1

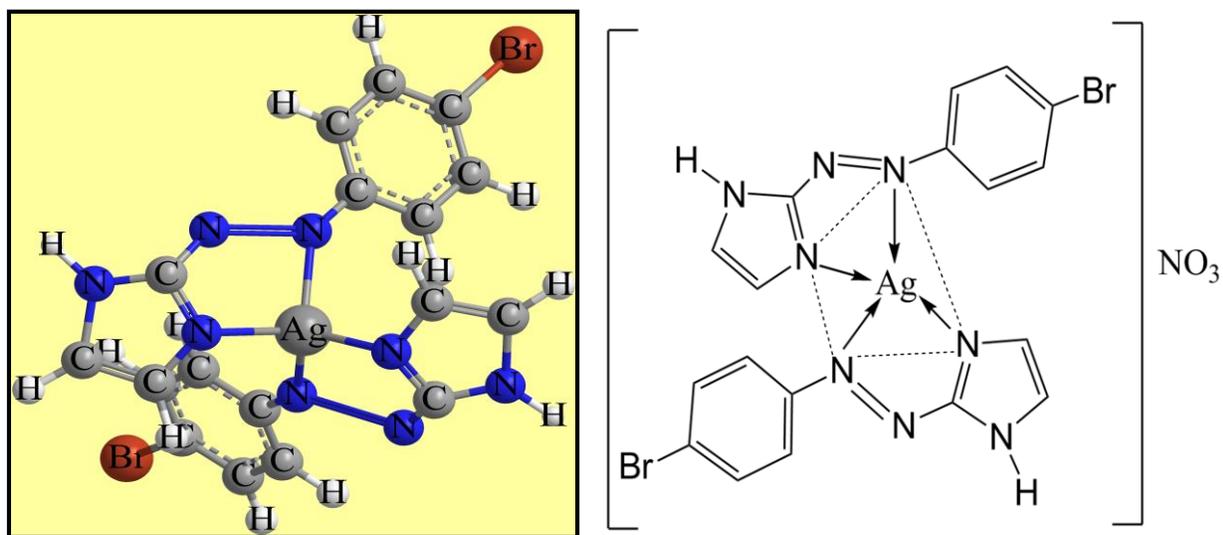


Fig.(15):-The proposed chemical structure formula of Ag(I)-complex

### 3.10-Antibacterial Activity

The biological activity of prepared ligand (4-BrPAIm) and their complexes have been studied by using Muller Hinton agar by inoculating 50 ml of fresh culture broth (18 hrs) the tested bacteria (gram positive bacteria: staphylococcus Aureus) and (gram negative bacteria: Escherichia coli , Pseudomonas and Ribrio cholera) for 24 hr. at 37 °C and inhibition zones were measured table 5. The ligand and its complexes the results demonstrate that Escherichia coli and Pseudomonas Aeruginosa was sensitive to ligand and its complexes. The staphylococcus Aureus was sensitive to all complexes while resistance to ligand where Ribrio cholera was sensitive to Ni(II), Pt(IV), Cu(II), Ag(I) and Au(III) complexes while resistance to ligand and Pd(II) complex. Figures 16 showed that the antibacterial activity of the ligand and its complexes.

**Table(5):-Antibacterial activity of ligand (4-BrPAIm) and its complexes**

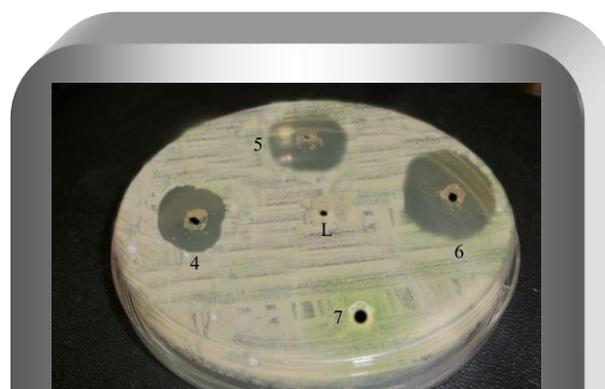
No.	Compounds	zone of Inhibition			
		Staphylococcus Aureus	Escherichia Coli	Pseudomonas Aeruginosa	Ribrio Cholerae
1	4-BrPAIm=L	-	++	+	-
2	[Ni L <sub>2</sub> Cl <sub>2</sub> ].H <sub>2</sub> O	++	++	+	+++
3	[Pd L Cl <sub>2</sub> ]	+++	+++	++	-
4	[PtL <sub>2</sub> Cl <sub>2</sub> ]Cl <sub>2</sub> . H <sub>2</sub> O	+++	+++	+++	+++
5	[CuL <sub>2</sub> Cl <sub>2</sub> ].H <sub>2</sub> O	++	+++	++	+++
6	[AgL <sub>2</sub> ].NO <sub>3</sub>	+++	+	++	+
7	[AuLCl <sub>2</sub> ]Cl.H <sub>2</sub> O	+++	++	++	+++

(+++)**High active-Inhibition zone >12mm** , (++) **Moderate active-Inhibition zone=9-12mm.**

(+) **Slightly active-Inhibition zone=6-9mm** , (-) **Inactive <6mm.**



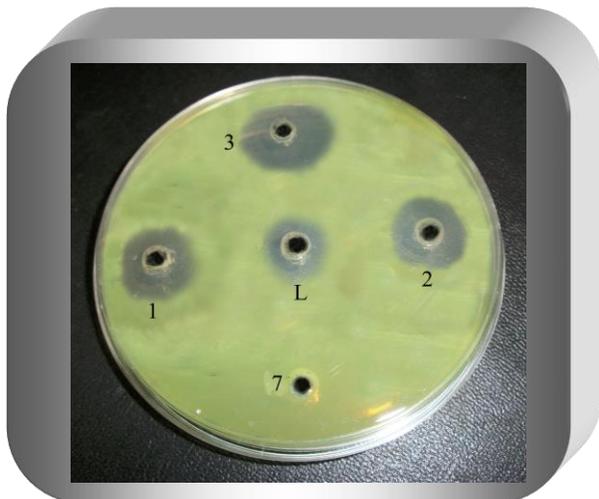
109





**(C) Escherichia coli**  
 L= 4-BrPAIm  
 1=  $[\text{NiL}_2\text{Cl}_2] \cdot \text{H}_2\text{O}$   
 2=  $[\text{Pd LCl}_2]$   
 3=  $[\text{Pt L}_2\text{Cl}_2] \text{Cl}_2 \cdot \text{H}_2\text{O}$   
 7= DMSO

L= 4-BrPAIm  
 4=  $[\text{CuL}_2\text{Cl}_2] \cdot \text{H}_2\text{O}$   
 5=  $[\text{AgL}_2] \cdot \text{NO}_3$   
 6=  $[\text{AuLCl}_2] \text{Cl} \cdot \text{H}_2\text{O}$   
 7= DMSO



**(D) Pseudomonas aeruginosa**  
 L= 4-BrPAIm  
 1=  $[\text{NiL}_2\text{Cl}_2] \cdot \text{H}_2\text{O}$   
 2=  $[\text{Pd LCl}_2]$   
 3=  $[\text{Pt L}_2\text{Cl}_2] \text{Cl}_2 \cdot \text{H}_2\text{O}$   
 7= DMSO

L= 4-BrPAIm  
 4=  $[\text{CuL}_2\text{Cl}_2] \cdot \text{H}_2\text{O}$   
 5=  $[\text{AgL}_2] \cdot \text{NO}_3$   
 6=  $[\text{AuLCl}_2] \text{Cl} \cdot \text{H}_2\text{O}$   
 7= DMSO

Fig.(16):- Antibacterial activity of ligand and its complexes

3.11- Dyein<sub>6</sub>

Dyes either chemically manufactured or extracted it must have the feature of giving color equally and homogeneously to the dyed material, also it must have the feature of stability to wards light, wash and friction and this depends on the type of dyed texture and its origin, type of used solvent and the media which dye operation done either acid or base<sup>(40)</sup>. Sample dyed with prepared dyes submitted to many tests after application on cotton textures for the purpose of evaluation. And the most important of these tests is the domain of resistance to wards sun light, friction, washing, detergent materials, stability of color and its intensity and also the sweating tests with both types acidic and basic where it gave good results. Finally the dyes were tested for light and detergent fastness, fixed yellow, orange brown, red, dark purple and green colour were obtained figure 17.



Fig.(17):-The colors of samples dyed by using the ligand (4-BrPAIm) and its complexes

## Conclusion

In this work we report the preparation, identification, dyeing and antibacterial activity of bidentate heterocyclic azo ligand derived from imidazole and its complexes with Ni(II), Pd(II), Pt(IV), Cu(II), Ag(I) and Au(III) metal ions. The ligand (4-BrPAIm) coordinates through the N<sub>3</sub> atom of the imidazole ring and another nitrogen atom of the azo group. The geometry is proposed for all complexes: octahedral stereochemistry for Ni(II), Pt(II) and Cu(II) complexes and square planar stereochemistry for Pd(II) and Au(III) complexes, while the Ag(I) complex shows tetrahedral stereochemistry.

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التحضير والتشخيص الطيفي لمعقدات بعض العناصر الانتقالية مع ليكاند أزو أميدازول الجديده ودراسة  
بعض تطبيقاتها الصناعية

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**الخلاصة :-**

حضرت صبغة أزو عضويه غير متجانسه الحلقة الجديده 2- [1- (4- برومو فنييل) أزو ] -أميدازول (4-BPAIm) وذلك من أزواج ملح الديازونيوم للمركب 4-برومو أنيلين مع الاميدازول في وسط قاعدي كحولي. شخصت ليكاند صبغة الأزو بالأعتماد على التحليل الطيفيه وهي طيف الأشعه تحت الحمراء (IR) وطيف الأشعه المرئيه-فوق البنفسجية (UV-visible) وطيف بروتون الرنين النووي المغناطيسي ( $^1\text{H-NMR}$ ). حضرت المعقدات الفلزيه لهذا الليكاند مع أيونات النيكل (II) والبلاديوم (II) والنحاس (IV) والفضه (I) والذهب (III) حيث بلغت النسبه الموليه (الفلز: الليكاند) 1:1 لمعقد بلاديوم (II) والذهب (III) فيما بلغت النسبه 2:1 لبقية الأيونات الفلزيه. تم تحديد الصيغه العامه للمعقدات الصلبه المعزوله وكانت  $[\text{NiL}_2\text{Cl}_2] \cdot \text{H}_2\text{O}$  و  $[\text{PdLCl}_2]$  و  $[\text{PtL}_2\text{Cl}_2]\text{Cl}_2 \cdot \text{H}_2\text{O}$  و  $[\text{CuL}_2\text{Cl}_2] \cdot \text{H}_2\text{O}$  و  $[\text{AuLCl}_2]\text{Cl} \cdot \text{H}_2\text{O}$ .  $[\text{AgL}_2]\text{NO}_3$  شخصت المعقدات الكليتيه المحضره وتم التوصل الى تراكيبيها الكيمائيه وأشكالها الهندسيه أعتماً على دراسات التحليل الدقيق للعناصر والتوصيليه المولاريه والامتصاص الذري اللهي وقياسات الحساسيه المغناطيسيه وطيفياً باستخدام الأشعه تحت الحمراء (IR) والاطياف الالكترونييه (UV-visible). واستناداً الى تلك الدراسات فقد تبين ان الليكاند ثنائي السن ويرتبط مع الأيون الفلزي من خلال احدى ذرتي نيتروجين مجموعه الأزو الجسريه وذرة النيتروجين ( $\text{N}_3$ ) للاميدازول. تم اقتراح الشكل ثماني السطوح للمعقدات الفلزيه لايونات النيكل (II) والبلاتين (II) والنحاس (II) والمربع المستوي لمعقدات البلاديوم (II) والذهب (III) ورباعي السطوح لمعقد الفضة (I) وقد دلت قياسات التوصيله المولاريه ان معقدات البلاتين والذهب والفضه ذات طبيعه الكتروليتيه فيما اظهرت المعقدات الاخرى على انها غير الكتروليتيه. في محلول ثنائي مثيل اوكسيد الكبريت (DMSO) استخدمت أربعه انواع من الجراثيم البشريه المرضيه باستخدام تقنيه الانتشار على وسط الاكار كمضادات للبكتريا وهي *Staphylococcus Aureus* ممثله عن البكتريا الموجبه لصبغة كرام وبكتريا *Ribrio cholerae* و *Pseudomonas Aeruginosa* و *Escherichia Coli* ممثله عن البكتريا السالبة لصبغة كرام. وقد اثبتت الدراسات في الوسط الزراعي ان الليكاند وبعض معقداته الفلزيه لها فعاليه كمضادات لبعض الجراثيم. استخدم الليكاند ومعقداته الفلزيه كاصباغ لصبغة الانسجه القطنيه نظراً لماتميز به من ألوان زاهيه وقد تبين ان الوانها ثابتة وذات مقاومه عاليه للغسل والمنظفات وضوء الشمس والاحتكاك.

البحث جزء من رسالة الماجستير للطالب هيثم كاظم دخيل 2011