

Preparation and Spectral Characterization of New Azo Imidazole Ligand 2-[(2'-Cyano Phenyl) Azo]-4,5-Diphenyl Imidazole and its Complexes with Co(II), Ni(II), Cu(II), Zn(II), Cd(II) and Hg (II) Ions

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Abstract:

The preparation and spectral characterization of complexes for Co(II), Ni(II), Cu(II), Cd(II), Zn(II) and Hg(II) ions with new organic heterocyclic azo imidazole dye as ligand 2-[(2'-cyano phenyl) azo]-4,5-diphenyl imidazole (2-CyBAI) were prepared by reacting a dizonium salt solution of 2-cyano aniline with 4,5-diphenyl imidazole in alkaline ethanolic solution. These complexes were characterized spectroscopically by infrared and electronic spectra along with elemental analysis, molar conductance and magnetic susceptibility measurements. The data show that the ligand behaves a bidentate and coordinates to the metal ion via nitrogen atom of azo and with imidazole N₃ atom. Octahedral environment is suggested for all metal complexes.

Key words: Spectral, Characterization, Imidazole Ligand .

Introduction:

Imidazole is ubiquitous in biology and chemistry[1]. This has encouraged the design of molecules with imidazole as one of the ligand platforms. In an effort towards the design of an imidazole containing azo system, we have synthesized arylazoimidazoles[2]. These ligands bear a pacidic azoimine (-N=N-C=N-) function and have been utilized for the isolation of transition metal complexes of lower oxidation states[3-7]. The p-acidity of the chelating function is largely dependent on the nature of the heterocyclic, the ring size, number of hetero atoms and substitutions in the aryl group[8].

The present study reports the preparation and spectral characterization of new azo imidazole ligand (2-CyBAI) and some of its metal complexes.

Material and Methods:

1-Apparatus and material

All chemicals and solvents were highest purity obtained from Fluka, 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) cm⁻¹ on FTIR Teast scan Shimaduz model 8400S. while the UV-Vis. Spectra recorded in absolute ethanol on Shimaduz model 1650PC. The ¹H NMR spectrophotometer (solvent DMSO-d⁶) were recorded on Bruker DMX-500 spectrophotometer-300 MHz spectrophotometer with TMS and the ¹³C NMR spectrophotometer (solvent DMSO-d⁶) were recorded on Bruker

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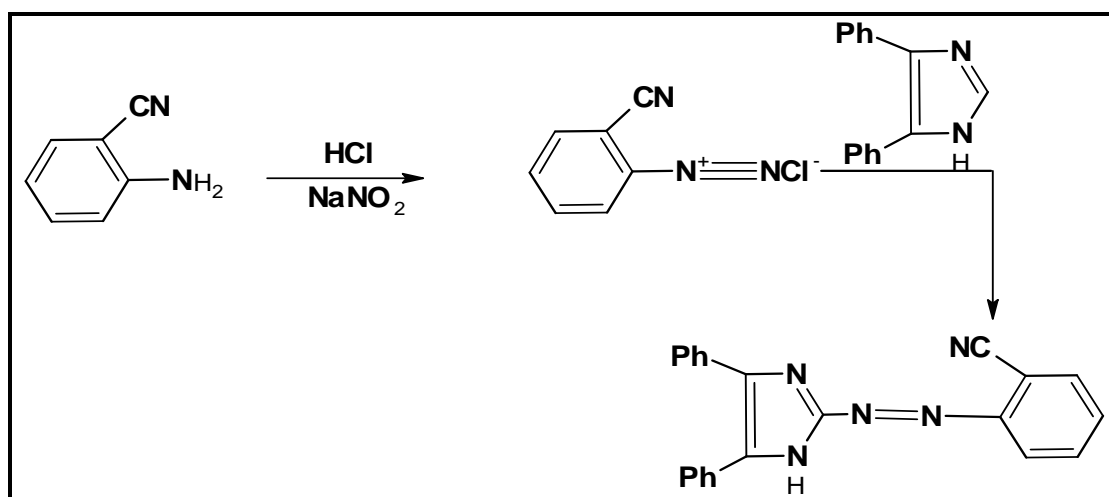
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DMX-500 spectrophotometer -300 MHz spectrophotometer. Mass spectrophotometer agilent technologies 5975 at 70C and MSD energy. Molar conductance measurements were determined in ethanol at room temperature by using conductivity bridge model 31A and the 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. Magnetic susceptibilities were measured by using Faraday method balance magnetic MSB-MKI was used for this purpose and diamagnetic corrections for the ligand were calculated using pascal's constant.

2-Preparation of the ligand (2-CyBAI)

The hetero cyclic azo ligand was prepared according to the general

method [9] by dissolving (3.49gm, 0.01 mol) of 2-Aminobenzonitrile in 2ml of concentrated hydrochloric acid, 10ml ethanol and 10ml distilled water. To this mixture a solution of 10% of sodium nitrate in dissolved distilled water was added dropwise at (0 to -5) °c and left to stand 15min. This diazonium solution was added dropwise into a 1000ml beaker containing (2.2gm, 0.01mol) of 4,5-diphenyl imidazole dissolved in (150ml) ethanol and (50ml) sodium hydroxide (10%) solution at (0-5) °c, the mixture was stirred in ice-bath and allowed to stand over night and acidified with dilute hydrochloric acid to $\text{pH} = 6$. The precipitate was filtered off, washed with distilled water and recrystallized from hot ethanol and dried in oven at 60 °c for 24 hour. The yield was 69% of reddish orange crystals the procedure was seen in scheme1.



Scheme(1) :-Preparation of the ligand (2-CyBAI)

3-Preparation of complexes

The metal complexes were prepared by dissolved (0.698gm, 0.002 mol) from ligand in ethanol (5ml) and added dropwise with stirring to (0.001mol) of 1:2 (metal:ligand) molar ratio of Cu(II), Co(II), Ni(II), Zn(II), Cd(II) and Hg(II) chlorides salts dissolving in buffer solution

(ammonium acetate) at optimal pH for each metal ions. 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 left to dried at room temperature.

Result and Discussion:

The reaction of heterocyclic azo ligand(2-CyBAI) with the metal ions mentioned above different color crystals depending on the nature of

metal ion. The complexes insoluble in water but soluble in most organic solvents. The analytical and physical data of the ligand and it`s complexes are given in table (1) .

Table (1): Analytical data and physical properties of the ligand (2-CyBAI) and it`s complexes.

No.	Compound	M.wt	Optimal pH	Color	m.P °C	Yield %	Metal analysis %		%Element analysis Calc. (Found)%		
							Calculate	Found	C	H	N
1	L-(2-CyBAI)	349	6	Reddish orange	188-190	69	—	—	75.69 (77.86)	4.29 (4.7)	20.00 (19.47)
2	[CuL ₂ Cl ₂].H ₂ O		5.5	Dark violate	160-162	86	7.47	7.22	—	—	—
3	[Co L ₂ Cl ₂].H ₂ O		7	Dark brown	156-158	80.5	6.96	7.12	—	—	—
4	[Ni L ₂ Cl ₂].H ₂ O		8	Bright reed	188-190	71	6.94	6.68	—	—	—
5	[Zn L ₂ Cl ₂].H ₂ O		7.5	Dark brown	202-204	70	7.59	7.40	—	—	—
6	[Cd L ₂ Cl ₂].H ₂ O		6.5 9.5	Bright orange	204-206	77	12.38	12.06	—	—	—
7	[Hg L ₂ Cl ₂].H ₂ O		5.5	Bright reed	198-200	78.5	—	—	—	—	—

3.1- Mass, ¹HNMR and ¹³CNMR spectrum of new ligand (2-CyBAI) :

The mass spectrum of (2-CyBAI) a number group of peaks, figure(1) and scheme (2) , centered at (m/z) 320 and 116 for these peaks appears to be corresponds with C₂₂H₁₅N₃⁺ and C₇H₄N₂⁺ respectively , while ¹HNMR

and ¹³CNMR spectrum, figures (2) and (3), showed the following data (7.0-8.2(m,15H,aromatic proton and NH) and (118-138(C=C, aromatic carbons), 153and 150(C≡N, C=N, HN=C-Ph)) respectively.

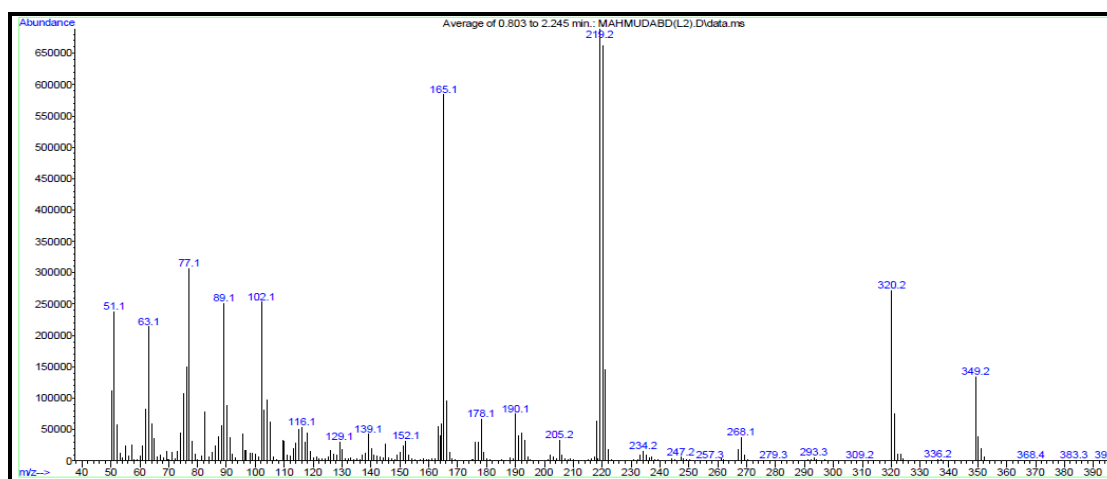
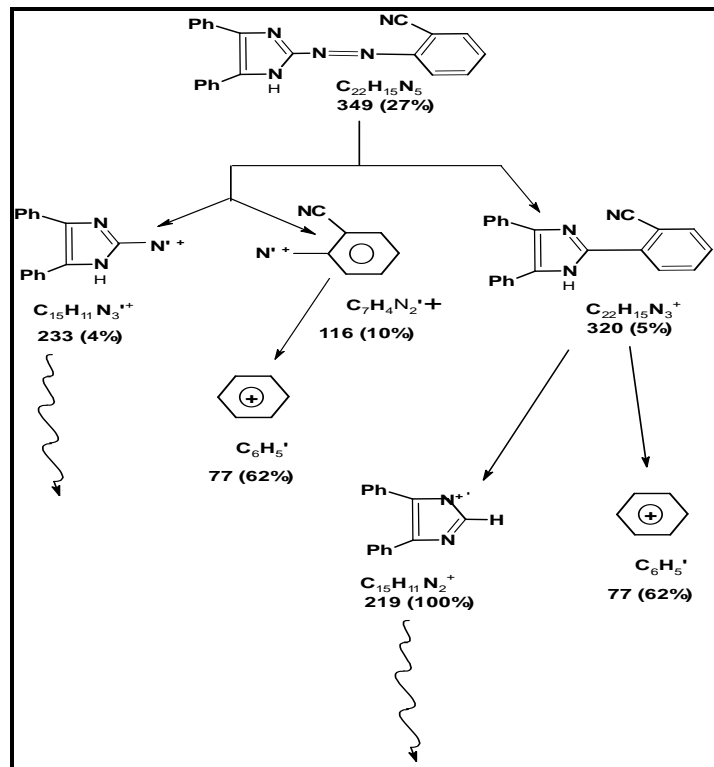


Fig. (1): Mass spectrum of new ligand (2-CyBAI).



Scheme(2): Fragmentation pattern of ligand(2-CyBAI).

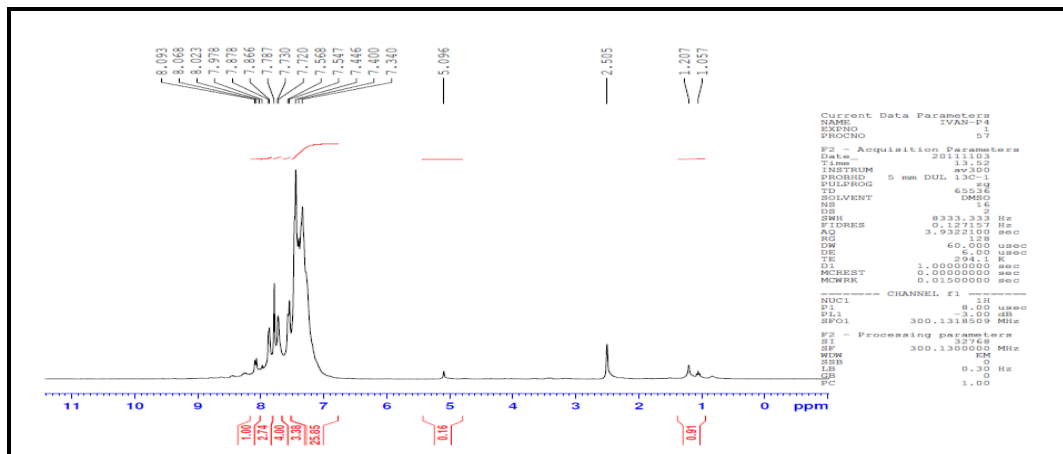


Fig.(2): The ¹H NMR spectrum of ligand (2-CyBAI).

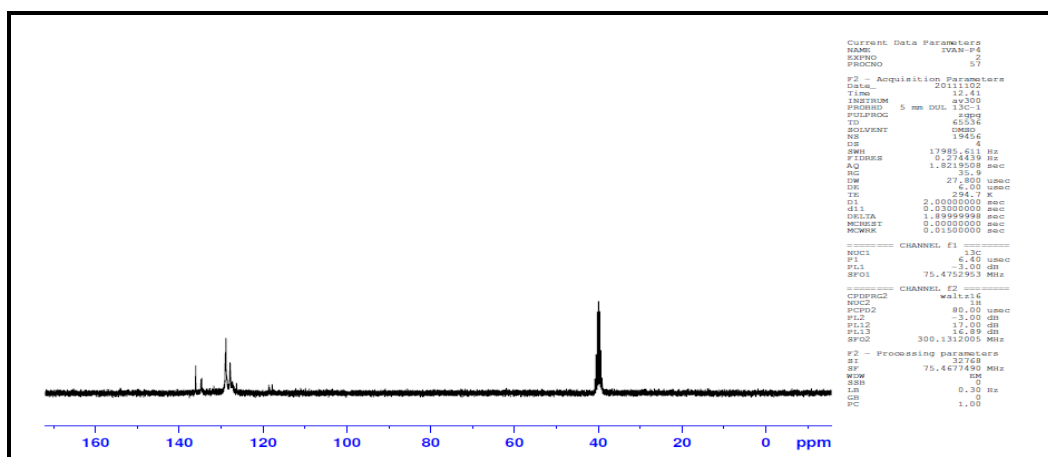


Fig.(3): The ¹³C NMR of ligand (2-CyBAI).

3.2- Effect of pH and concentration:

The studied molar concentration of the prepared solution were within the range 10^{-3} – 10^{-6} molar , while the pH range was between 4 to 11. These concentrations are not all suitable in

regard to the spectroscopic measurements.

The molar concentration that obey Lambert-Beer's law and showed a clear intense color was 1×10^{-5} M, while the optimum pH values, figures (4), have been studied in buffer solution.

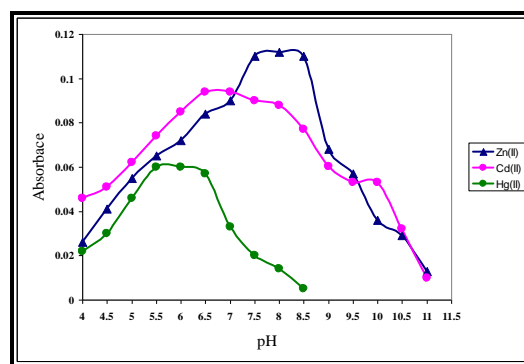
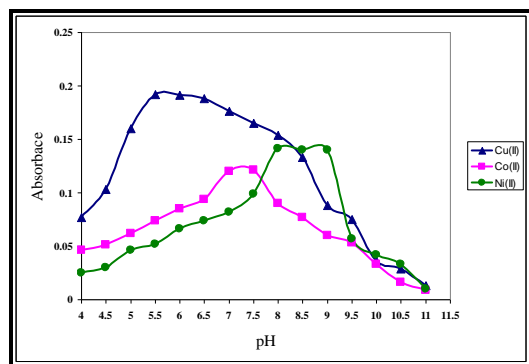


Fig.(4): Effect of pH on absorbance at (λ_{max}) for (2-CyBAI) complexes at optimum concentration.

3-Metal:ligand ratios

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 λ_{mex} . This method indicated that. The more probable structure of complex was 1:2 for all complexes as shown in figures 5 – 10.

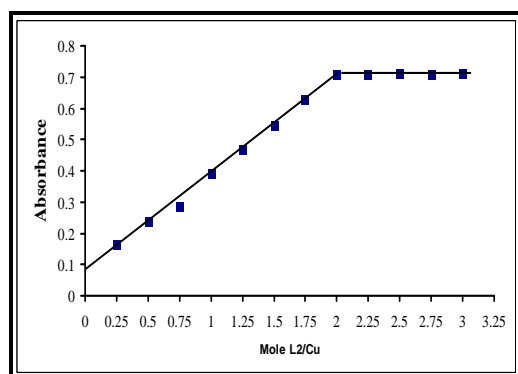


Fig.(5): Mole ratio plot for ligand Cu complex solution.

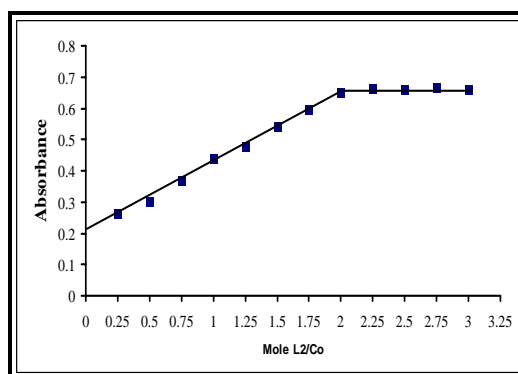


Fig.e(6): Mole ratio plot for ligand Co complex solution.

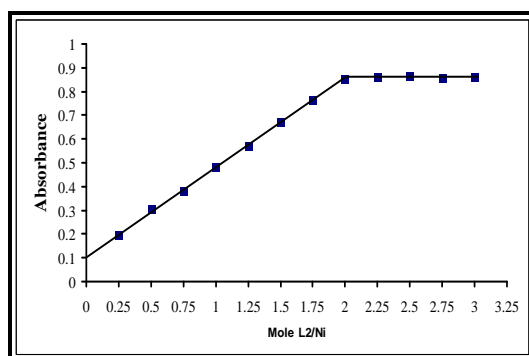


Fig.(7): Mole ratio plot for ligand Ni complex solution.

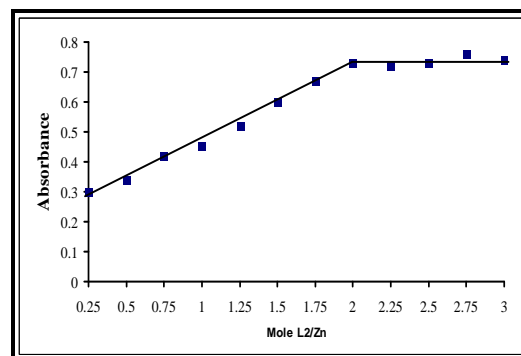


Fig.(8): Mole ratio plot for ligand Zn complex solution.

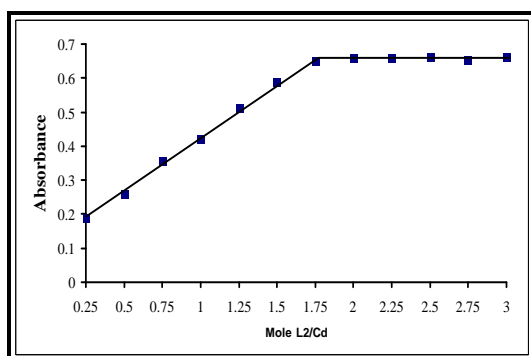


Fig.(9): Mole ratio plot for ligand Cd complex solution.

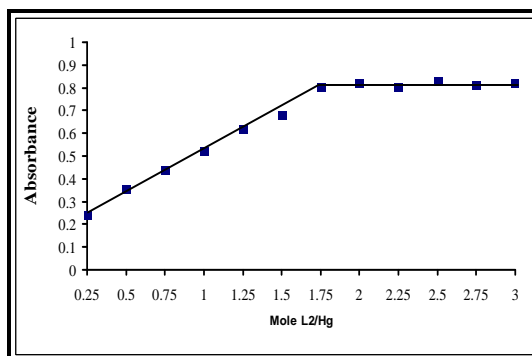


Fig.(10): Mole ratio plot for ligand Hg complex solution.

4-Determination of the metal complexes stability constants

Stability constant (β) values are obtained spectrophotometrically by measuring the absorbance of a mixture of ligand and metal solution at fixed wavelength (λ_{\max}) and optimum pH values. The degree of formation of the complexes are obtained from the relationship [10], $\beta = (1 - \alpha / 4\alpha^3 c^2)$ for 1:2 metal complexes and $\beta = (1 - \alpha / \alpha^2 c)$ 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 β and $\log \beta$ values for the prepared complexes are given in table(2).

5-Molar conductivity

The data obtained from the measurement of molar conductance of the complexes are shown in table (2) were carried out in ethanol ($10^{-3}M$) 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. [2]

Table (2) : metal :ligand stability constant values molar conductivity optimal concentration and wavelength with (ϵ) of chelate complexes.

Complexes	(λ_{\max}) nm	(ϵ) $\times 10^4$ L.mol ⁻¹ .cm ⁻¹	β L ² .mol ⁻²	Log β	Molar conductivity s.mol ⁻¹ .cm ²
CuL	467	8.6300	3.314×10^{16}	16.520	1.92
CoL	518	4.7900	1.387×10^{15}	15.142	0.88
NiL	476	7.7900	2.174×10^{15}	15.337	1.98
ZnL	473	5.2700	9.99×10^{14}	14.999	1.46
CdL	460	7.5600	5.335×10^{14}	14.727	7
HgL	469	8.4000	3.2980×10^{14}	14.518	1.75

6-FT-IR spectra

Infrared spectra data (KBr disk) of ligand (2-CyBAI) and its complexes are summarized in table (3). The comparison between spectrum of the ligand with those of the coordination complexes have, table (3), figures (11-17) revealed certain characteristic differences. The most significant information on the geometry of these

complexes comes from the analysis of the C=N group of imidazole, the azo bridge absorption regions.

1. The FT-IR spectra of the ligand 2-CyBAI show bands in the range (3226) cm^{-1} corresponding to $\nu(\text{OH})$. This band showed, sometimes, a remarkable change in the intensity and broadening upon complexation.

2. The spectra also show weak bands located in the regions (3056 and 2989) cm^{-1} which were assigned to the aromatic and aliphatic (C-H) stretching vibrations, respectively.

3. Bands were observed within the range (1582) cm^{-1} , this band was attributed to $\nu(\text{C}=\text{N})$ spectra. On complexation a small shift with change in shape were observed for this band. That changed may be a result of coordination of metal ions through the nitrogen of imidazole (C=N) group.

4. Bands characteristic of the azo bridge vibrations have been attributed to the positions [(1400), (1442) and (1456)] cm^{-1} , 1180 cm^{-1} and [(831) and (881)] cm^{-1} . The first three group band positions were assigned to the $\nu(\text{N}=\text{N})$ while the second group represents the vibrations of $\nu(\text{C}-\text{N}=\text{N}-\text{C}) + \nu(\text{N}=\text{N})$, while the third group band positions represents $\nu(\text{C}-\text{N}=\text{N}-\text{C}) + \nu(\text{C}=\text{N})$. On

complexation, a small shift were observed for the $\nu(\text{N}=\text{N})$ stretching vibrations, while shifting or splitting was recommended for the bands represents the $\nu(\text{C}-\text{N}=\text{N}-\text{C}) + \nu(\text{N}=\text{N})$.

5. Significant changes were also observed for the third bands $\nu(\text{C}-\text{N}=\text{N}-\text{C}) + \nu(\text{C}=\text{N})$, indicating the engagement of those groups in the coordination with the metal ions.

6. A group of bands located at (1099) cm^{-1} and [(732), (752) and (765)] cm^{-1} assigned to the Benz.R.Deff. and Imi.R.Deff. frequency respectively. Those bands effected on complexation through splitting, shifted or changing in their shapes.

7. New band assigned to $\nu(\text{M}-\text{N})$ in the range (474-486) cm^{-1} appeared on complexation, which proved the coordination of metal ions with ligands through nitrogen atom.

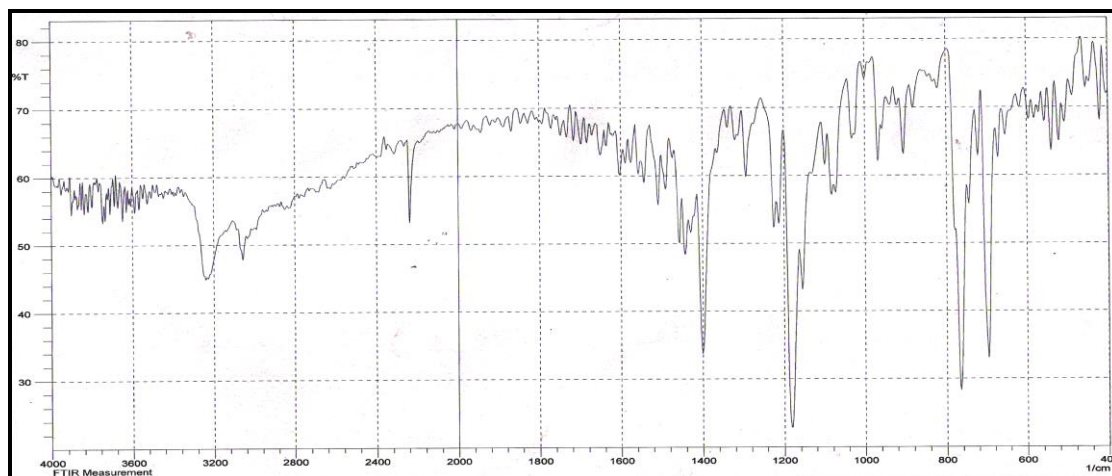


Fig. (11): IR- spectrum of ligand (2-CyBAI) .

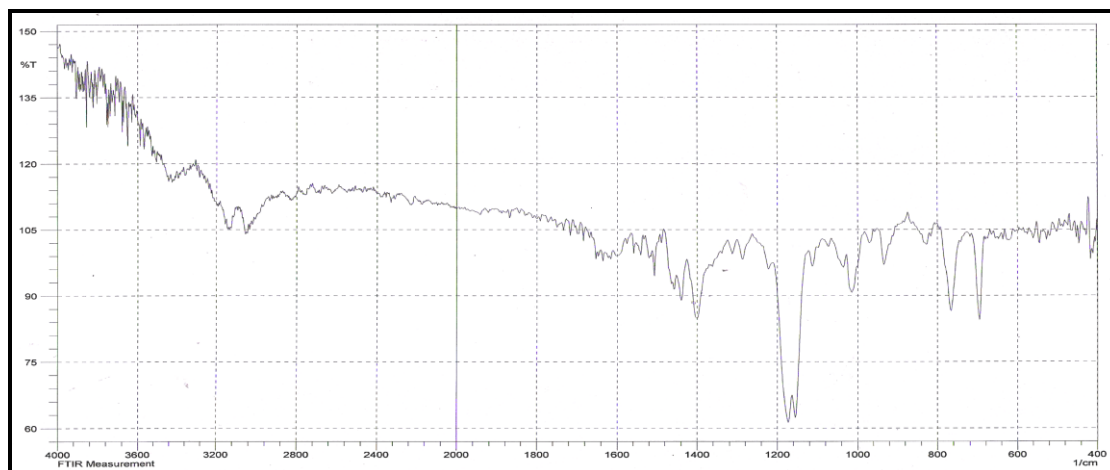


Fig.(12): IR- spectrum of [Cu (2-CyBAI)₂ Cl₂] .

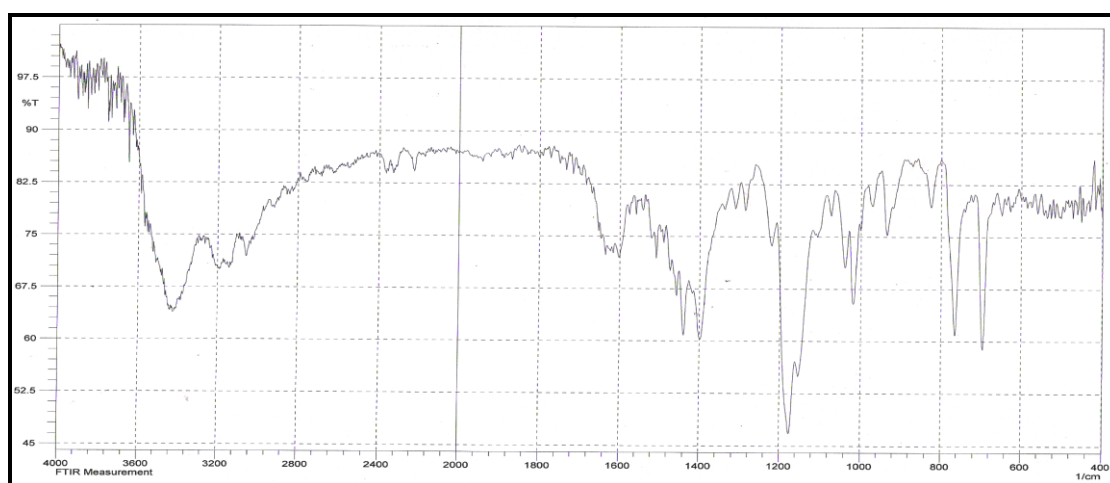


Fig.(13): IR- spectrum of [Co (2-CyBAI)₂ Cl₂] .

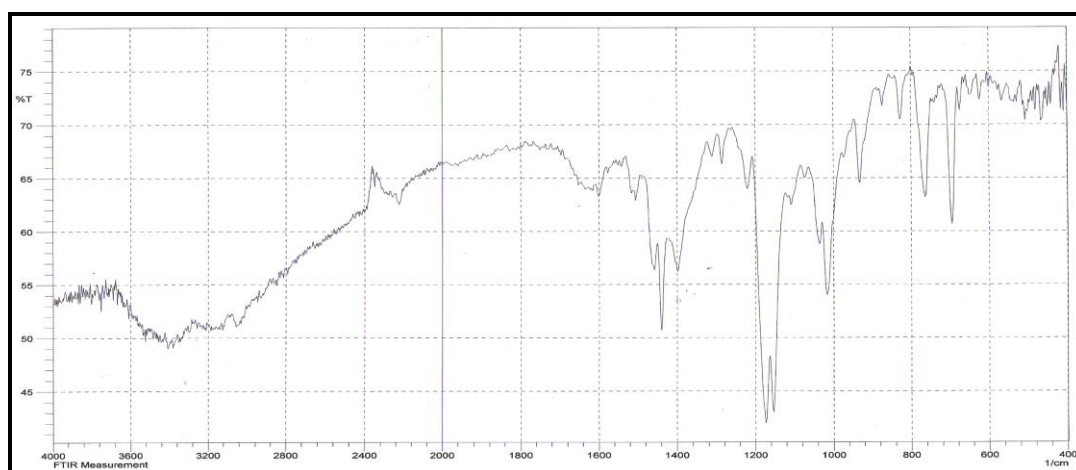


Fig.(14): IR- spectrum of [Ni (2-CyBAI)₂ Cl₂] .

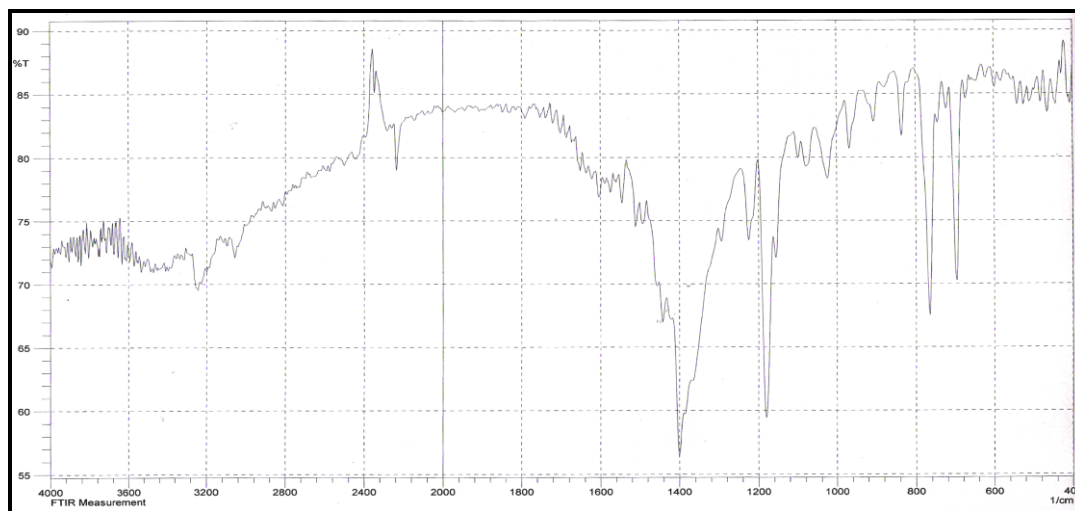


Fig.(15): IR- spectrum of [Zn (2-CyBAI)₂ Cl₂] .

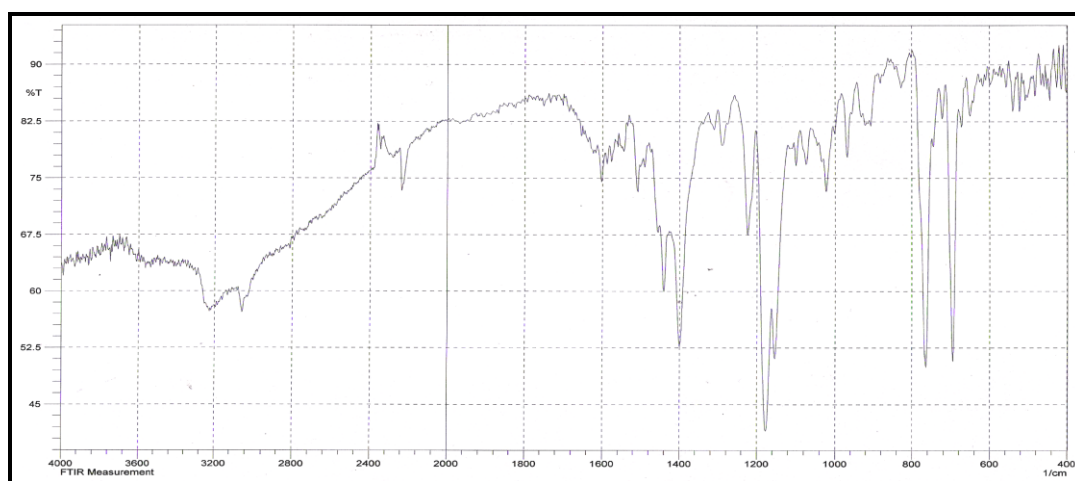


Fig.(16): IR- spectrum of [Cd (2-CyBAI)₂ Cl₂] .

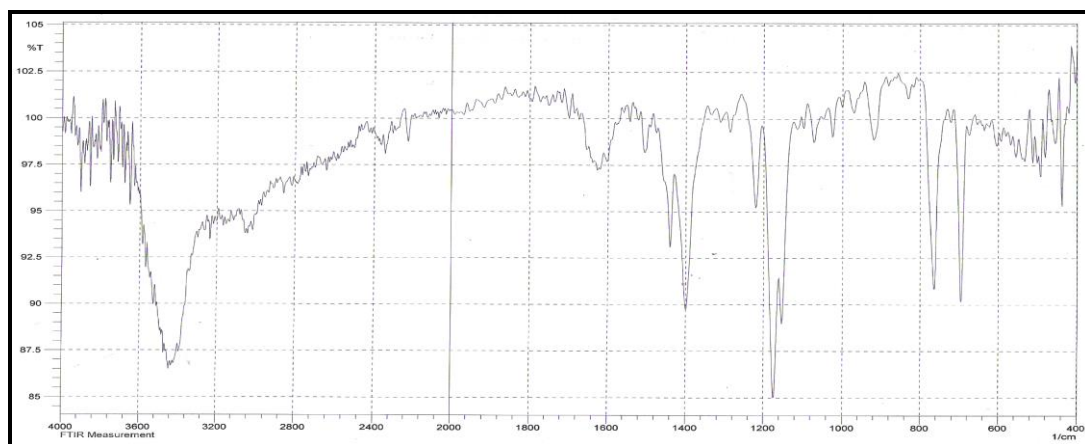


Fig.(17): IR- spectrum of [Hg (2-CyBAI)₂ Cl₂] .

Table(3): Characteristic IR absorption bands of the ligand (2-CyBAL) and its complexes in cm^{-1} units (KBr disk).

No.	Compound	ν_{OH}	ν_{NH}	$\nu_{\text{C-H}}$ aliph.	$\nu_{\text{C-H arom.}}$	$\nu_{\text{N=N}}$	$\nu_{\text{C=N}}$	$\nu_{\text{C-N/C}}$ + $\nu_{\text{C=N}}$	$\nu_{\text{C-N/C}}$ $\nu_{\text{N=N}}$	ν (A.T.N)	$\nu_{\text{Barr. R}}$ Def.	$\nu_{\text{Imid. R}}$ Def.
1	L=(2-CyBAL)	3226	—	2989	3056	1400 1442 1456	1582	831 881	1180	—	1099	732 752 765
2	[CoL ₂ Cl ₂]	3136	—	2989	3055	1400 1438 1458	1573	827 883	1155 1172	480	1040 1060	727 746 765
3	[CoL ₂ Cl ₂]	3448	—	2987	3056	1398 1438 1460	1575	825 885	1123 1176	483	1039 1072	727 744 765
4	[NiL ₂ Cl ₂]	3407	—	2985	3056	1398 1438 1458	1590	827 873	1143 1172	474	1035 1080	728 732 763
5	[ZnL ₂ Cl ₂]	3244	—	2988	3058	1400 1440 1456	1578	835 878	1125 1180	484	1080	730 748 763
6	[CdL ₂ Cl ₂]	3218	—	2985	3058	1400 1440 1468	1585	821 880	1125 1176	483	1077 1099	730 746 763
7	[HgL ₂ Cl ₂]	3444	3230	2988	3057	1400 1440 1465	1600	838 885	1143 1174	486	1072	725 740 765

7-Electronic spectra and magnetic properties

The electronic spectra data and the magnetic moment of prepared complexes, figures (18-24), the ligand is characterized by three absorption bands in UV-visible. These bands are appearing at the position 203nm, 281 nm and 449nm. The first one can be attributed to a $\pi \rightarrow \pi^*$ transition with in hetrocyclic imidazole ring [11] while the second UV band observed at a

longer wavelength can be ascribed to the excitation of the π -electrons of the phenyl system [12]. The third peak may be attributed to the $n \rightarrow \pi^*$ transition resulted from the presence of groups containing double bond, in addition to the presence of hetero atom carrying a lone pair of electrons such as (>C=N-) in addition to intermolecular charge-transfer taken place from benzene ring to the hetro

imidazole ring through the azo group ($-N=N-$). [13] This band showed at a red shift on coordination with a metal ions. [14]

The magnetic susceptibility measurements show that :

1. The magnetic values of Cu(II) complexes were (1.8)B.M., which indicated the paramagnetic properties of single electron for these complexes that have octahedral configuration. These result were comparable to the theoretical value of spin moment (1.73)B.M., which confirm the absence of spin-orbit coupling with tetrahedral configuration of Cu(II) complexes.

2. The Co(II) complexes give magnetic values (4.23) B.M., those values were consistent with the

theoretical spin moment (4.1-5.2)B.M. of high spin octahedral complexes ($t_{2g}^5 e_g^2$) which indicated spin-orbit coupling in other hand there is no change in cobalt oxidation state from Co(II) to Co(III).

3. The magnetic susceptibility measurements of Ni(II) complexes were (3.1)B.M., which belong to the two unpaired electrons of Ni(II), the excess in magnetic values attributed to distorted octahedral configuration.

4. All the magnetic values of group(IIB) divalent complexes of (Zn, Cd and Hg) behave as diamagnetic complexes which confirm there is no change in mercury oxidation state.

According to these results the structural of these complexes may be proposed in this figure :

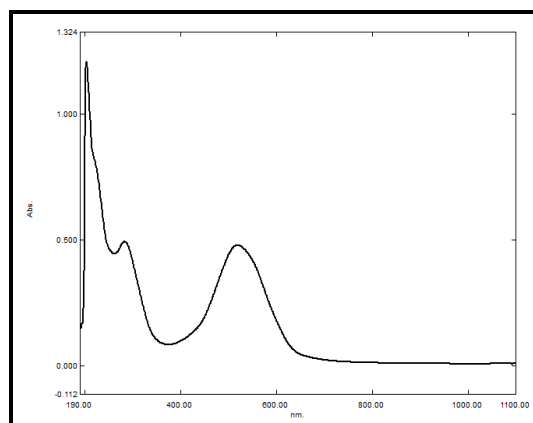
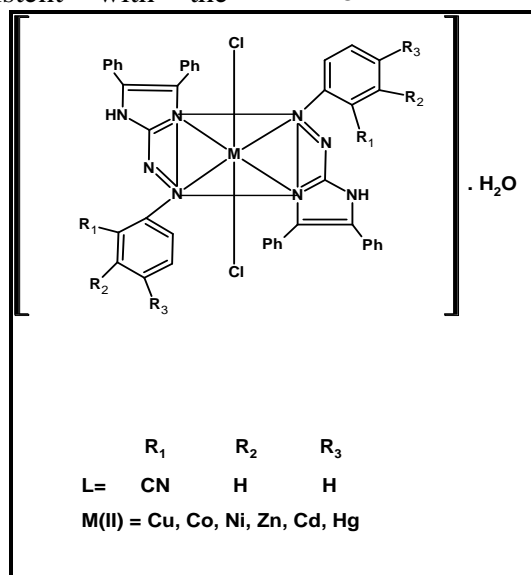


Fig.(18): UV-Vis spectrum of [Cu (4-SuBAI)₂ Cl₂].

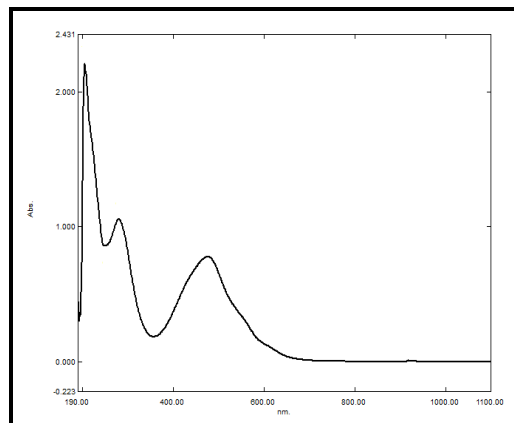


Fig.(19): UV-Vis spectrum of [Co (4-SuBAI)₂ Cl₂].

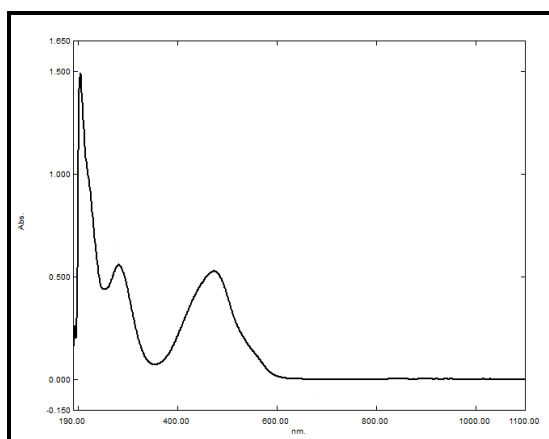


Fig.(20): UV-Vis spectrum of [Ni (4-SuBAI)₂ Cl₂].

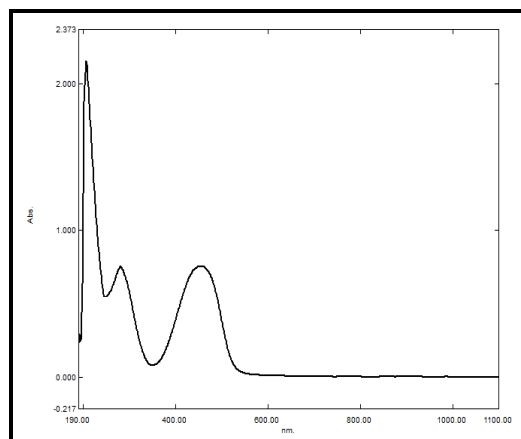


Fig.(21): UV-Vis spectrum of [Zn (4-SuBAI)₂ Cl₂].

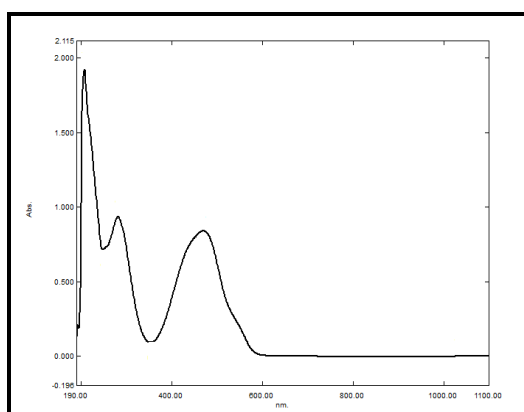


Fig.(22): UV-Vis spectrum of [Cd (4-SuBAI)₂ Cl₂].

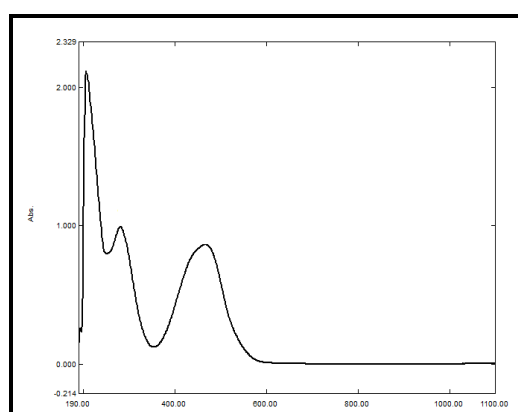


Fig.(23): UV-Vis spectrum of [Hg (4-SuBAI)₂ Cl₂].

Conclusions:

We have synthesized and structurally characterized complexes of Cu(II), Cu(II), Ni(II), Zn(II), Cd(II) and Hg(II) metal chloride with aryl azo imidazole ligand (2-CyBAI) p-acidic ligand.

The spectroscopy analysis and other techniques show that the coordination of all metal ions with (2-CyBAI) ligand are octahedral structural through the N₃ atom of imidazole and another nitrogen atom of azo group.

References:

- 1- Liu C., Zhou A., Wang S. and Chena Z. 2008. Bis[4,5-dimethyl-2-(2-pyridyl)-1H-imidazole-K²N²,N³] (1H-imidazole-KN³) copper (II) bis (perchlorate). Acta Crystallogr Sect E, 1(64):914-915.
- 2- Banerjee D., Raya U.S., Wub J.S., Lub T.H. and Sinha C. 2006. Naphthylazoimidazole complexes of cobalt(II): Synthesis structure and electrochemistry. Polyhedron, 25(16): 3077-83.
- 3- Senapati S., Jasimuddin S., Mostafa G., Lu T.H., Sinha C. 2006. Coupling of arylamine with coordinated arylazopyrimidine in platinum(II) complexes. Single crystal X-ray structure, spectra and electrochemistry. Polyhedron, 25:1571-1578.
- 4- Datta P., Gayen P. and Sinha C. 2006. Naphthylazoimidazole complexes of tetracarbonyl chromium and molybdenum: Synthesis, spectra, electrochemistry and photophysical studies. Polyhedron 25: 3435-40.

- 5- Mondal T.K., Dinda J., Slawin A. M.Z., Woollins J. D. and Sinha C. 2007. Osmium-carbonyl complexes of naphthylazoimidazoles. Single crystal X-ray structure of [Os(H)(CO)(PPh₃)₂(a-NaiEt)](PF₆){a-NaiEt = 1-ethyl-2-(naphthyl-a-azo)imidazole}. *Polyhedron* 26:600–606.
- 6- Saha G., Sarkar K.K. , Datta P. , Raghavaiah P. and Sinha C. 2010. Synthesis, spectroscopic properties, structural characterization and electrochemistry of mixed ligand complexes of copper(I) halide with PPh₃ and naphthylazoimidazole. *Polyhedron* 29 : 2098–2104.
- 7- Mondal T.K., Wu J. S, Lu T.H., Jasimuddin S. and Sinha C.2009. Syntheses, structures, spectroscopic, electrochemical properties and DFT calculation of Ru(II)–thioarylazoimidazole complexes. *Journal of Organometallic Chemistry* 694 : 3518–25.
- 8- AL-Dheimy, M.H.S. 2007. Synthesis and spectral analysis of some Lanthanide complexes with the new Antipyrine –azo ligands, Ph.D. Thesis, Univ. of Baghdad.
- 9- Shibata S., Furukawa M. and Nakashima R.1976.Syntheses of azo dyes containing 4,5-diphenylimidazole and their evaluation as analytical reagents. *Anal. Chem. Acta.*; 81:131
- 10- Witwit A. N. K. 2004. Synthesis and spectral, study of group (IIB) metal ions complexes with new organic reagent 2- (2 , 4 Dinitro phenyl azo) 4,5 – diphenyl imidazole; M.Sc.thesis College Education for Women , University of AL-Kufa.
- 11- Figgis B.N., and Lewis. 1960. "Modern coordination chemistry" Interscience,New York.
- 12- Jasimuddin S., Mostafa G. and Sinha C. 2004. Mixed ligand complexes of osmium(II)-2,20-bipyridine: synthesis, spectral characterization and electrochemical properties of bis-chelated- arylazoimidazole-bipyridine-osmium(II) and X-ray crystal structure of [(2,20-bipyridine)- bis- {1-methyl-2-(p-tolylazo) imidazole} osmium(II) hexafluorophosphate. *Inorganica Chimica Acta* 357:1975–1984
- 13- Mathur T., Jasimuddin S., Milton H., Woollins J.D. and Sinha C. 2004. First example of mixed azoheterocycles: structural studies of metallo-macrocycle Ag(I) versus tetrahedral Cd(II) complexes of pyridyl-azo-imidazole. *Inorganica Chimica Acta* 357 :3503–09.
- 14- Skooge A., West M. and James F. 1997. "Fundamentals Analytical Chemistry,7th Ed. New York.

تحضير وتشخيص طيفي لليكاند الأزو الجديد 2-[(2'-سيانو فنيل)ازو 4,5-ثنائي فنيل اميدازول
ومعداته الفلزية مع ايونات Cu(II)، Co(II)، Ni(II)، Zn(II)، Cd(II) و Hg(II)

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الخلاصة:

التحضير والتشخيص الطيفي لمعدتات ايونات النحاس (II)، الكوبالت (II)، النيكل(II)، الخارصين(II)، الكادميوم(II) والزنك(II) مع صبغة الأزو العضوية غير متجانسه الحلقة الجديده 2-[(2'-سيانو فنيل)ازو 4,5-ثنائي فنيل اميدازول] (2-CyBAI) والتي حضرت بمفاعلة محلول ملح الديازونيوم للمركب 2-سيانو انيلين مع 4,5-ثنائي فنيل انيلين في محلول قاعدي كحولي .
شخصت المعدتات الصلبه طيفياً باستخدام الاشعه تحت الاحمرء والأطياف الالكترونية فضلا عن التحليل الدقيق للعناصر والتوصيليه المولاريه والحساسيه المغناطيسيه واستناداً الى تلك المعطيات التحليليه فقد تبين أن الليكاند ثنائي السن ويرتبط مع الايون الفلزي من خلال احدى ذرتي نيتروجتتين مجموعه الازو وذرة النيتروجين (N₃) للاميدازول . تم اقتراح الشكل ثماني السطوح لجميع المعدتات الفلزيه .