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Baghdad Science Journal **Vol.12(3)2015**

Preparation and Characterization of Some Metal Complexes with Heterocyclic Azo Ligand (4-SuBAI)

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Received 7, November, 2013
Accepted 5, January, 2014

Abstract:

The preparation and characterization of the Cu (II), Co(II), Ni(II), Zn(II), Cd(II), and Hg(II) metal complexes of heterocyclic azo ligand 2-[(4`-sulphamide phenyl) azo] -4,5-diphenyl imidazole (4-SuBAI) have been studied by elemental analysis, FT-IR and UV-Vis Spectroscopic, magnetic moment and molar conductance methods. The analytical data showed that all chelate complexes were prepared with (metal-ligand) ratio of (1:2).

The general formula of these complexes was $[ML_2X_2]$. nH_2O [were L=2-[(4`-sulphamide phenyl) azo]-4,5-diphenyl imidazole and X=Cl, and the octahedral geometry were suggested for these complexes .

Key words: Characterization, Metal Complexes, Heterocyclic, Azo, Ligand.

Introduction:

Azo imidazole derivatives are very important class of chemical compounds receiving attention scientific research[1]. They are highly colored and have been used as dyes and pigments for along time.[2,3]. They are important in drugs[4], cosmeties[5], biological activities including antibacterial[6], coordination capacity[7] and participate in azo coupling reactions[8]. Azo imidazole molecule being the azo imine group (─N═N─C═N─), which is π-acidic and stabilized low valant metal redox state[9] .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[10]. Anumber of these azo dyes have been used as chelating ligands[3,7,11]in addition of the uses as reagents in analytical chemistry[8,12].

The present study reports the preparation and spectral characterize-ation of new azo imidazole ligand (4-SuBAI) and some of its metal complexes.

Material and Methods:

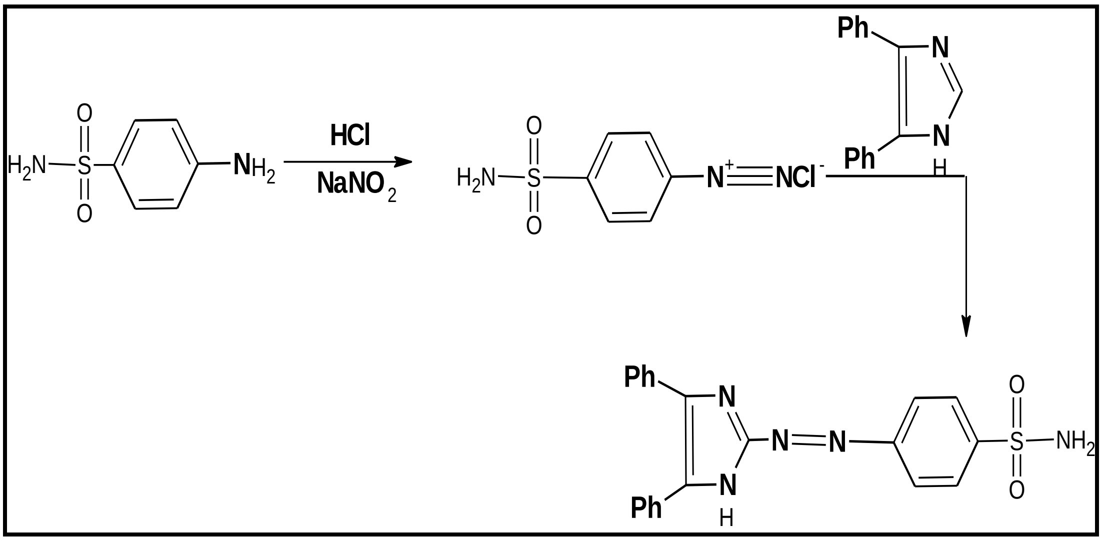
1-Apparatus and material

All chemicals and solvents used and were of highest purity obtained from Fluka, Merck and BDH. The melting points of the compounds were determined on a Electro thermal, meltaing point 9300. Elemental analysis(C.H.N) were obtained using 1108 C.H.N elemental analyzer. IR speatra 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 absolut ethanol on Shimaduz model 1650PC. The ^{1}HNMR spectrometer (solvent DMSO-d^{6}) were recorded on Bruker DMX-500 Spectrophotometer-300 MHz spectrometer with TMS, AL-Bayt University, Jordan.

The ^{13}CNMR spectrometer (solvent DMSO-d^{6}) were recorded on Bruker DMX-500 Spectrophotometer-300 MHz spectrometer, AL-Bayt University, Jordan. Mass spectrometer agilent technologies 5975 at 70C and MSD energy, Tarbiat Modarres University, Iran. 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 (pH±0.001). The metal contents of the complexes were measured by using atomic absorption techique by shimadzu AA-160. Magnetic susceptibilities were measured by using Faraday method blanc magnetic technique.

2-Preparation of the ligand (4-SuBAI)

The hetero cyclic azo ligand was prepared according to the general method [13] by dissolving (4.03gm, 0.01 mol) of sulfanilamide 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 (0-5) °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 pH=6). The precipitate was filtered off, washed with distilled water and re-crystallized ice from hot ethanol and dried in oven at 60 °C for 24 hour. The yield was 75% of dark orange crystals the procedure was seen in scheme1.



Scheme(1) :-Preparation of the ligand (4-SuBAI)

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) metal salts as a 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(4-SuBAI) with the metal ions mentioned above different color crystals depending on the nature of metal ion. The complexes were 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 .

Table(1): Analytical data and physical properties of the ligand (4-SuBAI) and it`s complexes.

No.	Compound	Optimal pH	Color	m.P °C	Yield %	Metal analysis %		%Element analysis Calc. (Found)%			
						Calculat.	Found	C	H	N	S
1	L=(4-SuBAI)	6	Dark orange	258-260	75	—	—	62.53 (63.65)	4.21 (4.58)	17.36 (16.57	7.94 (7.36)
2	$[CuL_2Cl_2]\ .H_2O$	8	Magenta	150-152	79	6.57	6.48	—	—	—	—
3	$[Co\ L_2\ Cl_2]\ .H_2O$	7.5	Dark brown	121-123	71	6.17	5.99	—	—	—	—
4	$[Ni\ L_2Cl_2]\ .H_2O$	6.5	Brown orange	199-201	70.8	6.15	6.22	—	—	—	—
5	$[Zn\ L_2\ Cl_2]\ .H_2O$	7	Orange	187-189	63.5	6.75	6.43	—	—	—	—
6	$[Cd\ L_2\ Cl_2]\ .H_2O$	7	Bright reed	203-205	77	11.07	10.92	—	—	—	—
7	$[Hg\ L_2\ Cl_2]\ .xH_2O$	6.5	Bright reed	212-214	79	—	—	—	—	—	—

3.1- Mass, ^{1}HNMR and ^{13}CNMR spectrum of new ligand (4-SuBAI) :

The mass spectrum of (4-SuBAI) a number group of peaks, figure-1- and scheme 2 ,while ^{1}HNMR and ^{13}CNMR spectrum, figures 2 and 3, showed the following data [7.35-7.50(dd,2H aromatic proton), 7.55-7.75(dd,2H aromatic proton), 8.0-8.2(m,10H aromatic proton), 7.4-7.70(m,NH_2, NH)] and [123-129(aromatic carbons), 146(C-NH ring, C=N ring)] respectively.

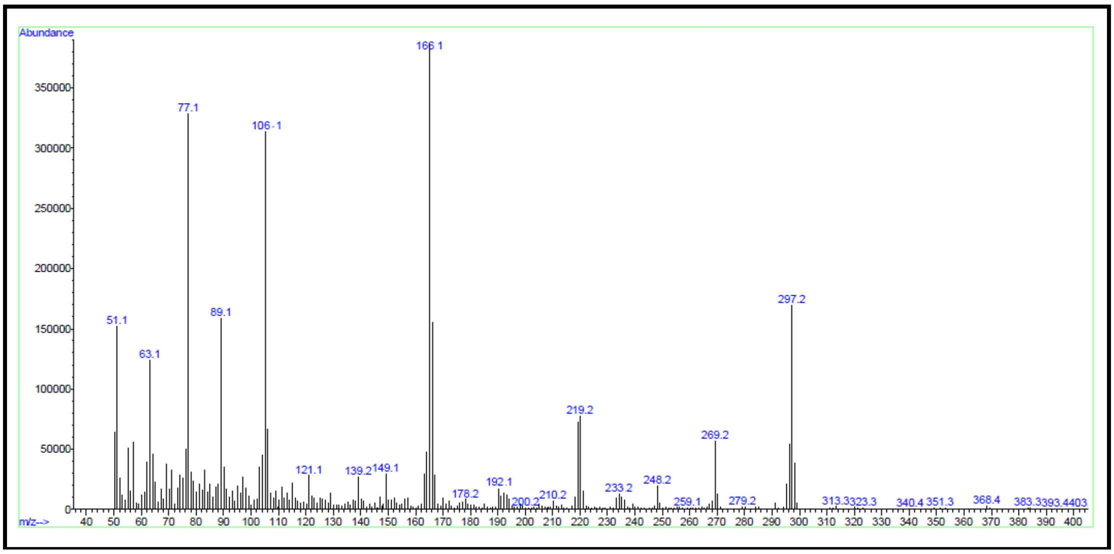
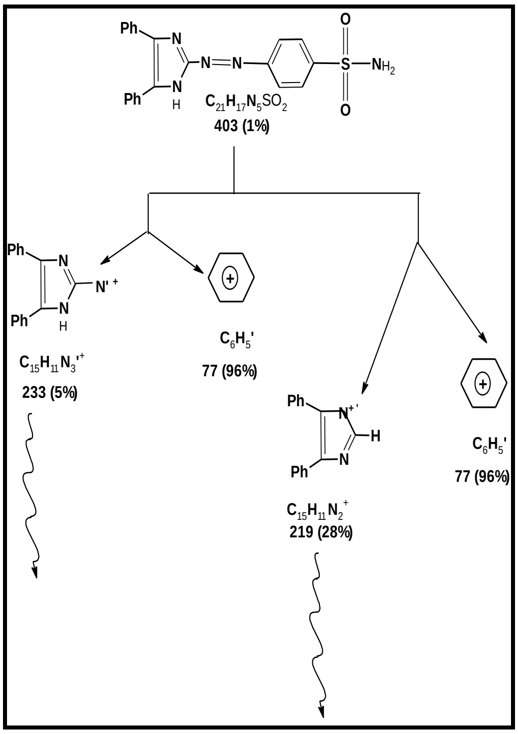


Fig. (1): Mass spectrum of new ligand (4-SuBAI).



Scheme(2): Fragmentation pattern of ligand(4-SuBAI).

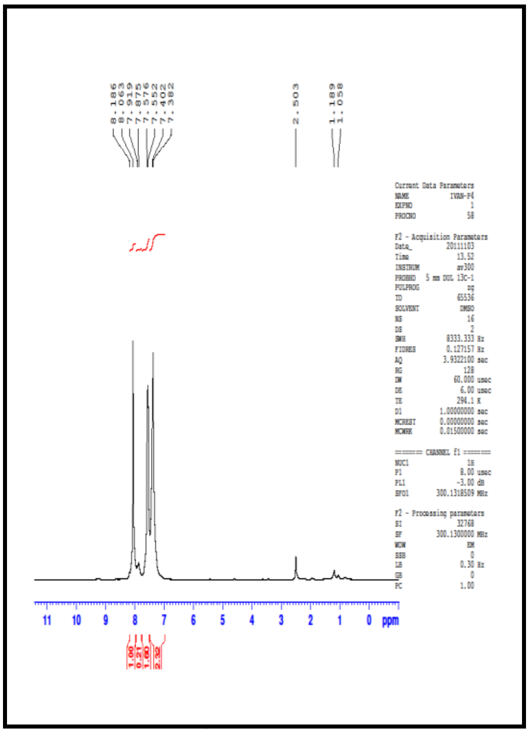


Fig.(2): The ^{1}HNMR spectrum of ligand (4-SuBAI).

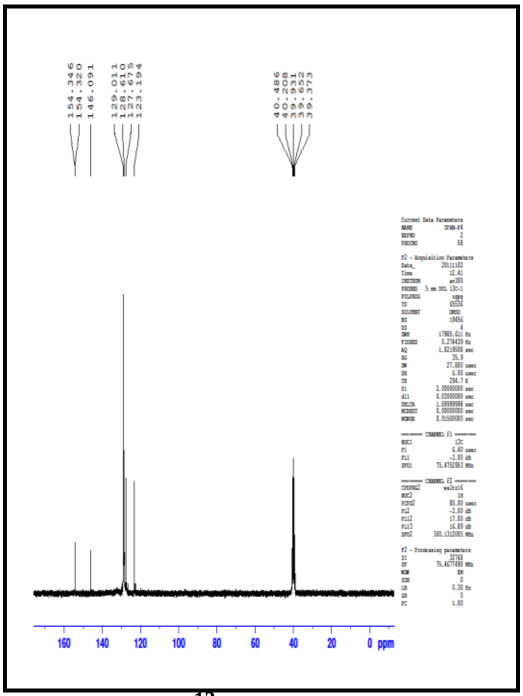


Fig.(3): The ^{13}CNMR of ligand (4-SuBAI).

3.2- Effect of pH and concentration:

The molar concentration of the solution of the prepared compounds 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 at 2.5x10^{-5} M, while the optimum pH values in buffer solution are shown in figures 4, have been studied in buffer solution.

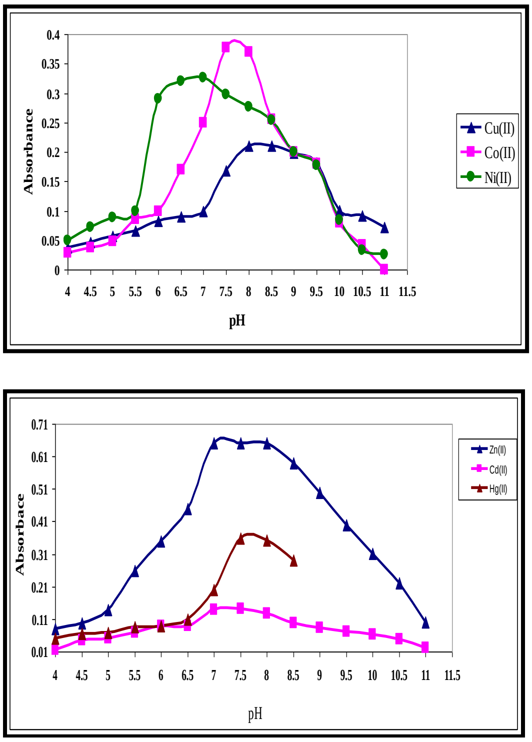


Fig.(4): Effect of pH on absorbance at (λ_{max}) for (4-SuBAI) complexes at optimum concentration.

3.3--Metal:ligand ratios

Composition of chelate complexes were investigated by mole ratio method at fixed concentration of metal ion ($2.5x10^{-5}$ M) 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.

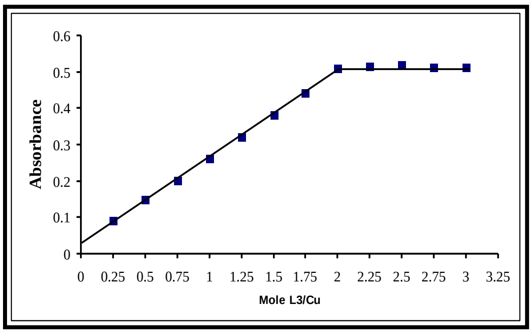


Fig.(5): Mole ratio plot for ligand Cu complex solution.

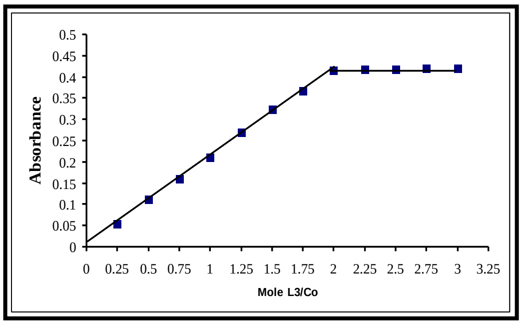


Fig.(6): Mole ratio plot for ligand Co complex solution.

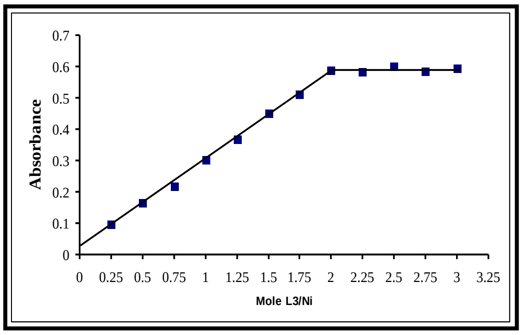


Fig.(7): Mole ratio plot for ligand Ni complex solution.

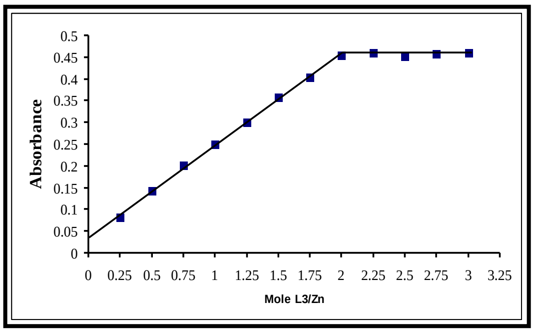


Fig.(8): Mole ratio plot for ligand Zn complex solution.

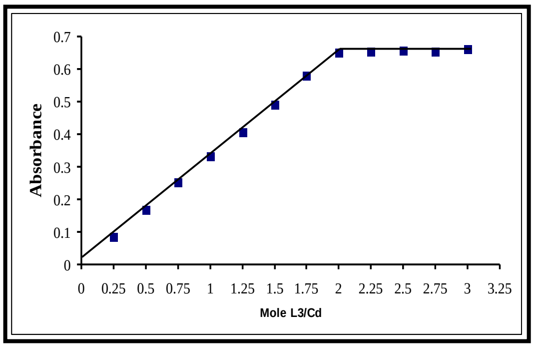


Fig. (9): Mole ratio plot for ligand Cd complex solution.

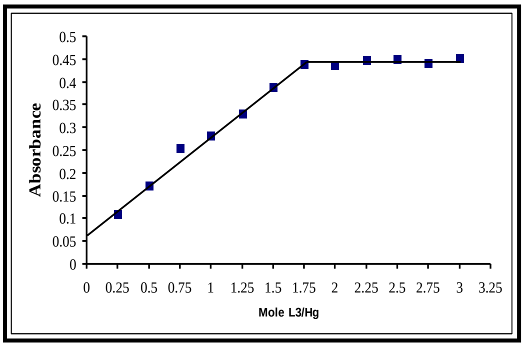


Fig.(10): Mole ratio plot for ligand Hg complex solution.

3.4-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[14], $\beta=(1-\alpha/4\alpha^3c^2)$ for 1:2 metal complexes and $\beta=(1-\alpha/\alpha^2c)$ for 1:1 metal chelate and $\alpha=Am-As/Am$ where As and Am are the absorbance of the partially and fully formed complex respectively at optimium concentration. The calculated β and log β values for the prepared complexes are given in table2.

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 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.[15]

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

Metal Ions	M: L ratio	(λ_{max}) nm	Optimum pH	(€)x10^4 L.mol^{-1} .cm^{-1}	β L^2.mol^{-2}	Molar conductivity s.mol^{-1}.cm^2
Cu(II)	1:2	513	8	3.0920	1.988×10^{15}	1.06
Co(II)	1:2	476	7.5	3.4600	1.089×10^{15}	13.40
Ni(II)	1:2	469	6.5	3.5160	1.2947×10^{15}	0.95
Zn(II)	1:2	460	7	2.5680	1.1177×10^{14}	13
Cd(II)	1:2	460	7	4.3000	8.616×10^{13}	3.23
Hg(II)	1:2	444	6.5	3.4080	2.689×10^{13}	3.69

3.6-FT-IR spectra

Infrared spectra data (KBr disk) of ligand (4-SuBAI) 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 C=N group of imidazole, and the azo bridge absorption regions.

1. The FT-IR spectrum of the ligand 4-SuBAI show bands in the range (3247) cm^{-1} corresponding to ν(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 2970) cm^{-1}which were assigned to the aromatic and aliphatic (C-H) stretching vibrations, respectively.
3. Band were observed within the range (1600) cm^{-1}, this band was attributed to ν(C=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 [(1396), (1423) and (1458)] cm^{-1}, 1180 cm^{-1} and [(800) and (840)]cm^{-1}. The first three group band positions were assigned to the ν($N=N$) while the second group represents the vibrations of ν($C-N=N-C$) + ν($N=N$), and the third group band positions represents ν($C-N=N-C$) + ν(C=N) . On complexation , a small shift were observed for the ν($N=N$) stretching vibrations, while shifting or splitting was recommended for the bands represents the ν($C-N=N-C$) + ν($N=N$).
5. Significant changes were also observed for the thrid bands ν($C-N=N-C$) + ν(C=N) , indicating the engagement of those groups in the coordination with the metal ions.
6. A group of bands located at (1095) cm^{-1} and [(723),(723)and (763)] 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. The FT-IR showed bands at [(1217-1218) and (1338)] cm^{-1} attributed to sulfonamide group. These bands non effected on complexation.
8. New band assigned to ν(M-N) in the range (483-486) cm^{-1} appeared on complexation, which proved the coordination of metal ions with ligands through nitrogen atom.

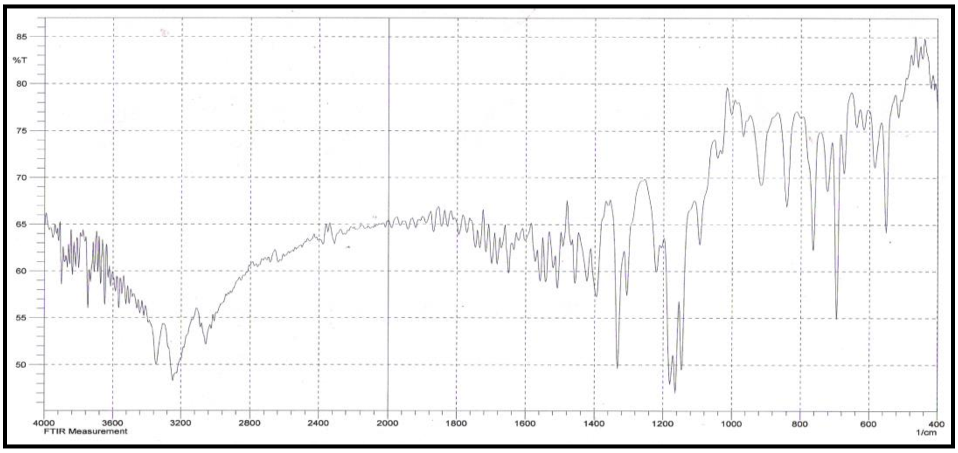


Fig.(11): IR- spectrum of ligand (4-SuBAI) .

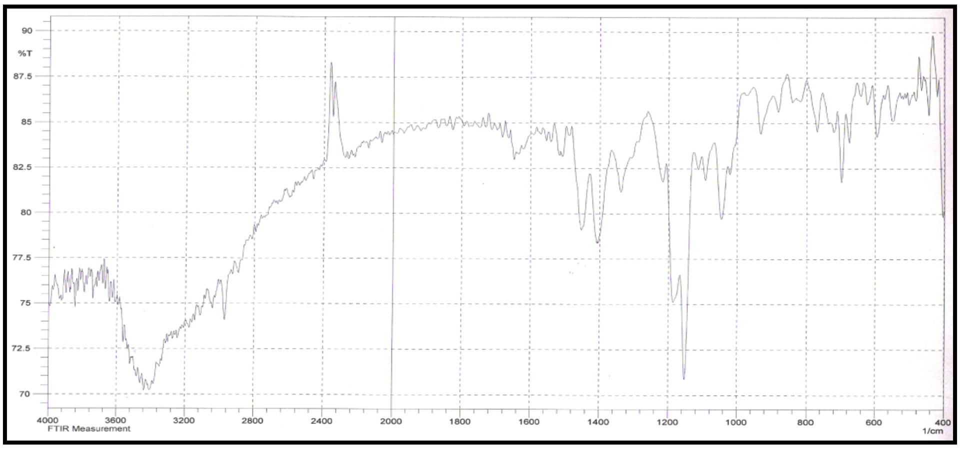


Fig.(12): IR- spectrum of [Cu $(4\text{-SuBAI})_2$ Cl_2] .

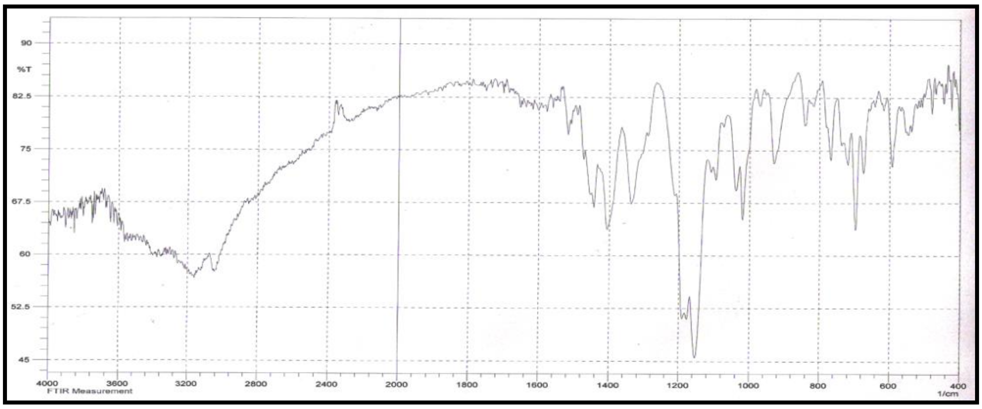


Fig.(13): IR- spectrum of [Co (4-SuBAI)$_2$ Cl$_2$] .

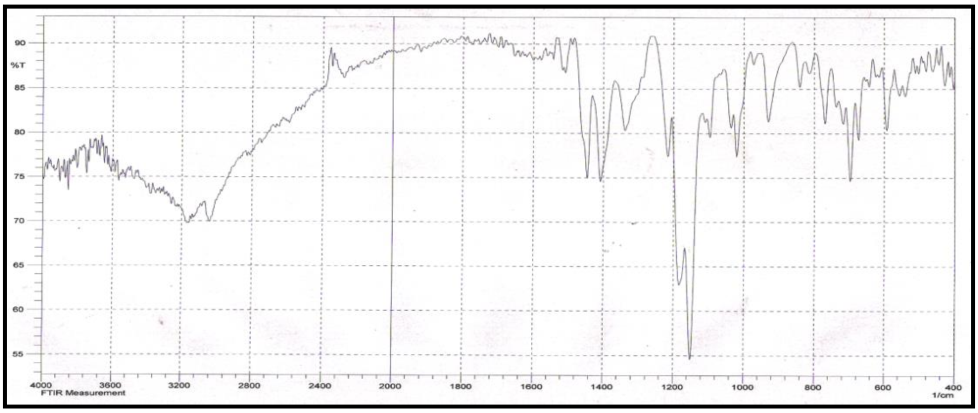


Fig.(14): IR- spectrum of [Ni (4-SuBAI)$_2$ Cl$_2$] .

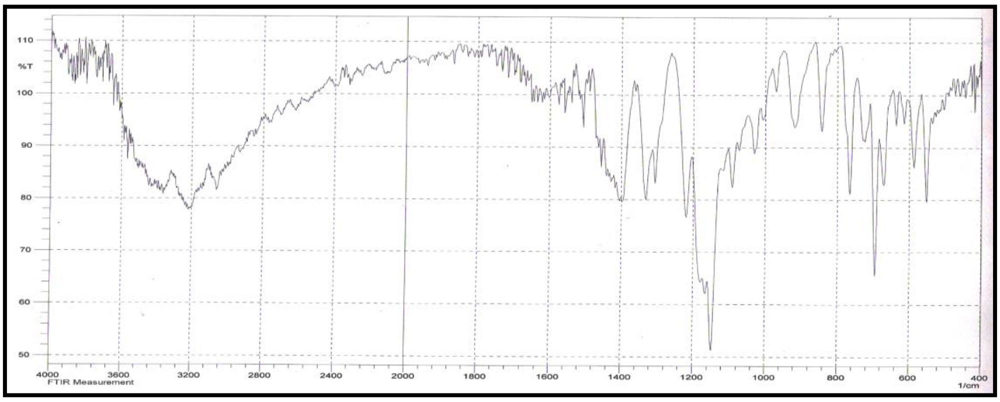


Fig.(15): IR- spectrum of [Zn (4-SuBAI)$_2$ Cl$_2$] .

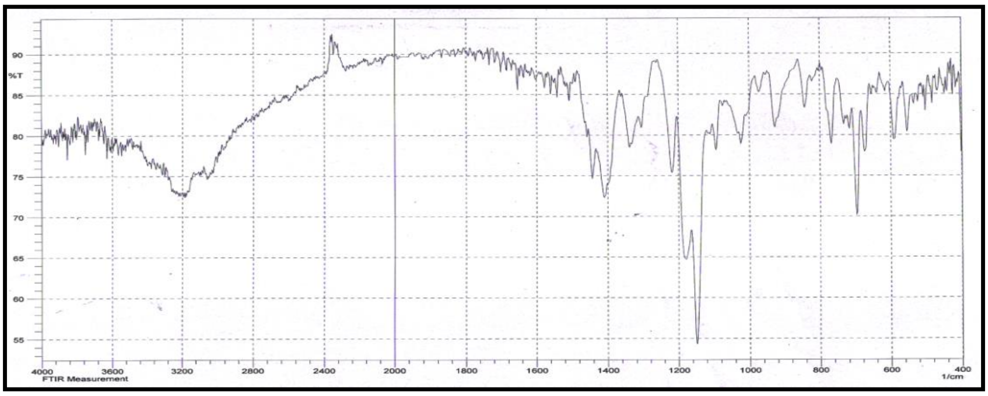


Fig.(16): IR- spectrum of [Cd (4-SuBAI)$_2$ Cl$_2$] .

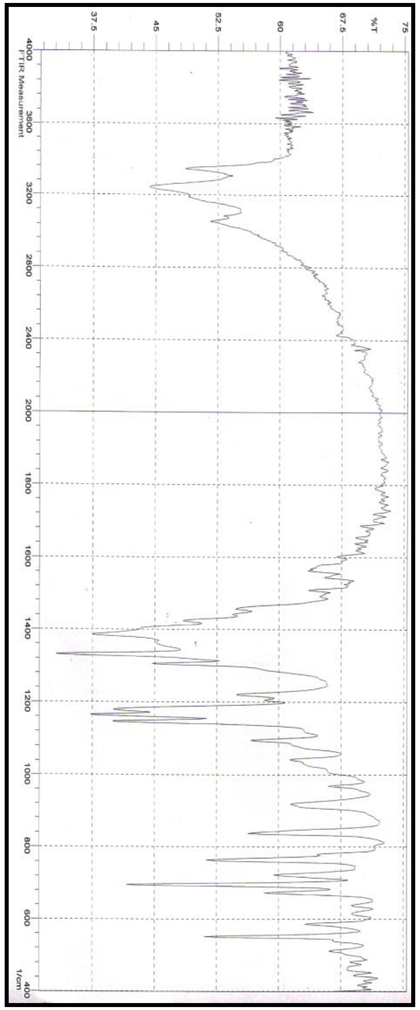


Fig.(17): IR- spectrum of [Hg (4-SuBAI)$_2$ Cl$_2$] .

Table(3): Characteristic IR absorption bands of the ligand (4-SuBAI) and its complexes in cm^{-1} units (KBr disk) .

No.	Compound	υ(O?H)	υ(NH)	υ(C-H) alph.	υ(C-H) arom.	υ(N=N)	υ(C=N)	ν C-N=N-C + ν C=N	ν C-N=N-C + ν N=N	υ (M? N)	ν Benz. R. Deff.	ν Imi. R. Deff.	ν H$_2$N-SO$_2$
1	L=(4-SuBAI)	3247	3346	2970	3056	1396 1423 1458	1600	800 840	1180	—	1095	723 723 763	1217 1338
2	[Cu L$_2$Cl$_2$] .nH$_2$O	3436	—	2972	3054	1406 1452	1598	811 845	1186	486	1093 1114	725 735 769	1217 1338
3	[Co L$_2$ Cl$_2$] . nH$_2$O	3282	—	2970	3050	1406 1444 1452	1588	813 840	1190	483	1050 1108	719 733 781	1217 1338
4	[Ni L$_2$Cl$_2$] . nH$_2$O	3168	—	2970	3055	1407 1446	1592	813 840	1182	485	1095 1138	7:71 735 769	1218 1338
5	[Zn L$_2$ Cl$_2$]. nH$_2$O	3197	3442	2966	3060	1398 1438 1458	1596	815 842	1178	486	1050 1091	729 729 765	1217 1338
6	[Cd L$_2$ Cl$_2$]. nH$_2$O	3164	3313	2970	3055	1400 1409 1442	1589	817 842	1178	483	1042 1093	720 730 767	1218 1338
7	[Hg L$_2$ Cl$_2$]. nH$_2$O	3242	3344	2968	3055	1400 1423 1448	1568	800 837	1164 1178	485	1045 1095	725 740 780	1217 1338

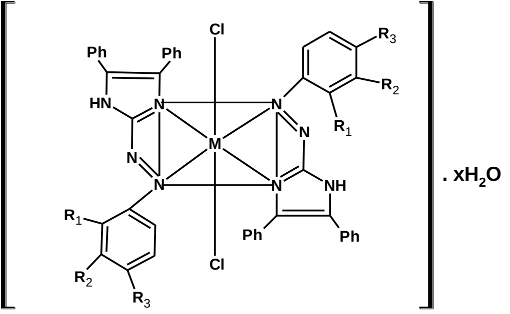
3.7-Electronic spectra and magnetic properties

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, 289 nm and 432nm. The first one can be attributed to a $\pi\rightarrow\pi^*$transition with in hetrocyclic imidazole ring[16] while the second UV band observed at a longer wavelength can be ascribed to the excitation of the π-electrons of the phenyl system.[17] . The third peak may be attributed to the n→ π* 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 ($>C=N-$) and ($>C=O$) in addition to intermolecular charge-transfer taken place from benzene ring to the hetro imidazole ring through the azo group($-N=N-$).[18,19] This band showed at a red shift on coordination with a metal ions.[2,20]

The magnetic susceptibility measurements show that:

1. The magnetic values of Cu(II) complexes were (1.75)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. .
2. The Co(II) complexes give magnetic values (4.62) 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 eg^2) which indicated spin-oribt 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 (2.89)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 by proposed in this figure :



	R_1	R_2	R_3
L=	H	H	$H_2N\text{-}SO_2$

M(II) = Cu, Co, Ni, Zn, Cd, Hg

x= 1 for Co and Ni complexes

and 2 for Cu, Zn and Cd complexes

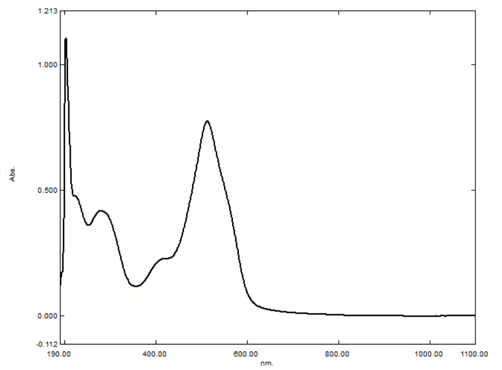


Fig.(18): UV-Vis spectra of[Cu (4-SuBAI)$_2$ Cl$_2$].

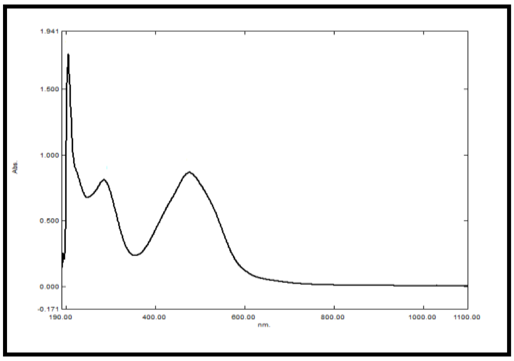


Fig.(19): UV-Vis spectra of [Co (4-SuBAI)$_2$ Cl$_2$].

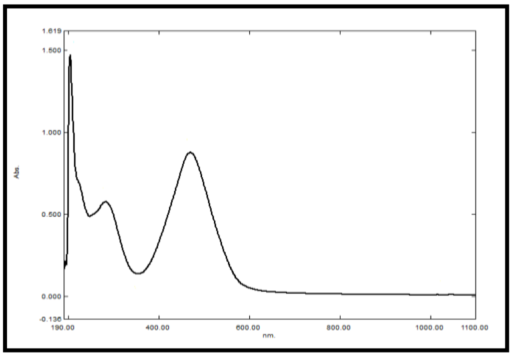


Fig.(20): UV-Vis spectra of [Ni (4-SuBAI)$_2$ Cl$_2$].

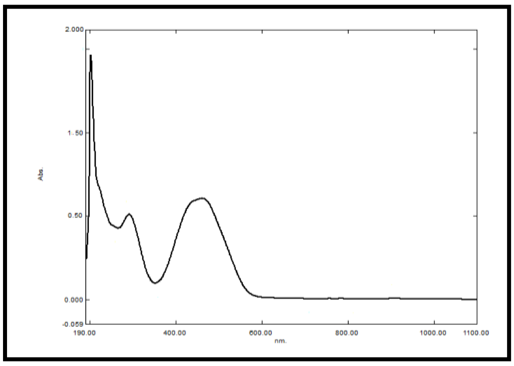


Fig.(21): UV-Vis spectra of [Zn (4-SuBAI)$_2$ Cl$_2$].

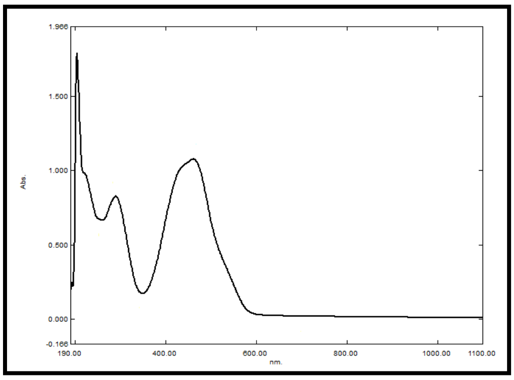


Fig.(22): UV-Vis spectra of [Cd (4-SuBAI)$_2$ Cl$_2$].

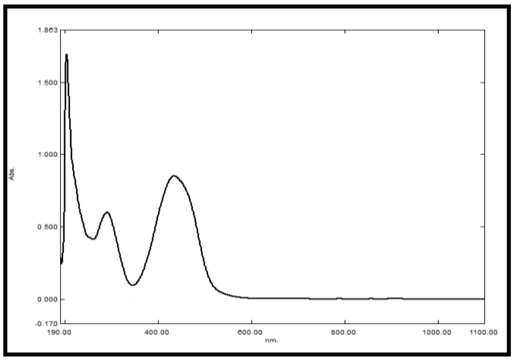


Fig.(23): UV-Vis spectra of [Hg (4-SuBAI)$_2$ Cl$_2$].

Conclusions:

In this present study we report the preparation characterization and spectroscopy study of new azo ligand derived from imidazole and its complexes with Cu(II), Cu(II),Ni(II), Zn(II), Cd(II) and Hg(II) metal ions. The isolated complexes were characterized by available techniques. The aryl azo imidazole ligand (4-SuBAI) behaves as a bidentate chelating agent and coordinating through the N_3 atom of imidazole and another nitrogen atom of azo group which is the farthest of imidazole ring to form five-memberd metalo ring. The coordination of all metal ions with ligand (4-SuBAI) are to give hexa coordinated show octahedral stereochemistry.

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تحضير وتشخيص بعض المعقدات لليكاند الازو غير متجانس الحلقة2-[(4ُ- سلفوامايد فنيل)ازو4,5-ثنائي فنيل اميدازول

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الخلاصة:

تحضير وتشخيص معقدات ايونات النحاس (II) ،الكوبلت (II) ،النيكل(II) ،الخارصين(II) ،الكادميوم(II) والزئبق(II) مع ليكاند الازو غير متجانس الحلقه **2**-[(4'-سلفوامايد فنيل)ازو4,5-ثنائي فنيل اميدازول] (4-SuBAI) تمت دراستها باستخدام تحليل العناصر، المطيافية تحت الحمراء و الضوئية، الحساسية المغناطيسية بالاضافة الى التوصيلية المولارية. اوضحت النتائج التحليلية بان الفلز:الليكاند لكل المعقدات هي 2:1 .

الصيغة العامة للمعقدات هي: $[ML_2X_2]$]. nH_2O ; L= 2-[(4'-سلفوامايد فنيل)ازو4,5-ثنائي فنيل اميدازول] و X= Cl والشكل الفراغي لجميع المعقدات هو ثماني السطوح .

الكلمات المفتاحية: مواصفات، معقدات الفلزات، حلقية غير متجانسة ، ازو، ليكاند.