WORLD JOURNAL OF PHARMACEUTICAL RESEARCH
SJIF Impact Factor 7.523
Volume 6, Issue 7, 239-253. Research Article ISSN 2277–7105

SPECTROPHOTOMETRIC STUDIES OF SOME TRANSITION ELEMENTS AS COMPLEXES WITH NEW AZODYE 2-(SULFAPYRIDINE AZO)-4,5-DIPHENYL IMIDAZOLE

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Article Received on
30 April 2017,
Revised on 20 May 2017,
Accepted on 10 June 2017
DOI: 10.20959/wjpr20177-8790

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ABSTRACT

The yellow (λ_{max} 440nm.) azodye ligand 2-(Sulfapyridine azo)-4,5-Diphenyl Imidazole (L) forms a stable red (λ_{max} 480nm.), orange (λ_{max} 480nm.) and red-violet (μ_{max} 500nm.) color complexes with divalent cations cobalt, nickel and copper respectively, with stoichiometry of all 1:2 (M:L). The complexes were characterized by FT-IR, M.P., visible, molar conductivity and atomic absorption spectroscopic. The suitable pH values for forming complexes are 11, 9 and 12 respectively. With molar absorptivity coefficients 4.2, 3.5 and 3.0 10^4 $l.mole^{-1}.cm^{-1}$ respectively. And obeyness of Beer's law up to 8.1 ppm of Co, 8.1 ppm of Ni and 7.6 ppm of Cu. The optimum conditions of the formation of complexes were investigated and their stability formation constants were determined by using of corresponding solutions method. The chemical formula of their complexes were suggested.

KEYWORDS: Sulfapyridine, Azodyes, Corresponding solutions method, Formation constant, Stoichiometery, Complexes and Spectral studies, Molar conductivity

INTRODUCTION

Most of azodyes are weak acids or weak bases of very important class of chemical compounds containing a heterocyclic moieties which have attracted the attention of many researchers in recent years. They have high soluble in common solvents and highly colored (from yellow to blue, due to conjugated π system). Several studies have been published on the synthesis and spectral properties of azo dyes.[1-6] This reflects their widely important applications in different field. Most of azodyes have acid – base properties with presence of a fixed isobestic points (which represent the number of equilibriums in such azodye), for this reason they are used as acid – base indicators.[7,8] Thiazolylazo dyes and their applications in analytical chemistry were reviewed.[9] A series of orange and red 1:1 copper-azo dye complexes, derived from 1- (3'-N-benzenesulphonamido)phenyl-3-methyl-5-pyrazolone, have been synthesized ;some of azodyes can be used as metallochromic indicator , antipyretic reagents and inhibitors corrosion.[10] For complexes of Ni(II) with azodyes, the two azodyes 4,4'-(diazene-1,2-diyl)bis(N - carbamimidoyl benzene sulfonamide) and 4,4'- (diazene-1,2-diyl)bis(N-(pyrimidin-2-yl)benzene sulfonamide) were used at λ_{max} of 500 ($\varepsilon_{max} = 1.83x10^4$ $l.mole^{-1}.cm^{-1}$) and 510 nm. ($\varepsilon_{max} = 2.48x10^4$ $l.mole^{-1}.cm^{-1}$) respectively.[11] Complexes of organomercury azodyes with Cupper (II) were prepared from 4-acetaminophenol and mercerized aniline derivatives ; include 2-(2-mercury chloride-4-X- phenyl azo)-4-acetamido phenol (X= sulfonic acid, acetyl, carboxyl , nitro and sulphamide).[12]

Some new azo compounds were prepared by coupling the diazonium salts of amines and 2,7-dihydroxynaphthalene and 1,6-dihydroxynaphthalene. Complexes of cobalt(II), nickel(II), copper(II) with a heterocyclic azo derivatives heve been synthesized and characterized. Analytical data revealed that all the complexes exhibited 1:2 metal–ligand ratio.[13]

Azo dyes compounds which containing 4,5–diphenyl imidazole group which were (6–NO_2BTADI), (6–MBTADI) and (6–MeBTADI) have been synthesized ; the complexes of these reagents have been prepared with the metal ions Co (II), Ni(II) and Cu(II) and were spectrally studied after fixing the optimum conditions.[14] Coupling of diazotized sulfamethizole with 2-ethyl-4-methyl phenol and the complex of cobalt (II) with the azo dye ligand have been synthesized.[15] Some azodye ligands derived from the coupling of sulfaguanidine diazonium salt with 2,4-dihydroxy-benzaldehyde , sulfadiazine diazonium salt with salicylaldehyde and 2,4-dihydroxy-benzaldehyde ,they used for complexation with Co (II) , Ni(II) and Cu(II) ions.[16] The present work includes complex formation of new azodye 2-(Sulfapyridine azo)-4,5-Diphenyl Imidazole with Co (II), Ni(II) and Cu(II) ions. The optimum conditions and characterization were studied.

EXPERMINTAL

Double distilled water, solvents (for spectral use) and all chemicals of highest purity were used.

Apparatus and materials

Visible absorption spectra were recorded by using PD-303 UV.,V. spectrophotometer, FT-IR-8400S spectrophotometer (Shimadzw) College of science Basrah university, pH-meter (H.Jurgons Co. Beremen, L. Puls Munchen 15), Bunchi B190K for melting point measurement, accurate balance E-Mette Weender (Land Strasse) 94-108,The molar conductivity (**Λ)** measurements were measured by (Germany condi 315), The complexes were recorded by using and element analysis (C.H.N.), they were carried out by perkin elemer 2400-11 element analysis and AAs measurements by U.K., Pg instruments AA500 .

Solutions

- 1×10^{-3} M of 2-(Sulfapyridine azo)-4,5-Diphenyl Imidazole (L)
- 1×10^{-3} M of the nitrate salts of Co(II),Ni(II) and Cu(II), and standardized by recommended methods[17]
- pH (1.4 -12) (Universal, Hexamine and acetate buffer solutions)[18]
- 1×10^{-2} M stock solutions of nitrate salts of Li^+، Na^+، K^+ ، Mg^{2+} ،Mn^{2+},Ag^+ , Ba^{2+} ،Pb^{2+} ، Ca^{2+} ، Cr^{3+} ، Zr^{4+} ، Ti^+ ، Fe^{3+} , VO^{2+} ,Zn^{2+}, Sr^{2+} , La^{3+} , $EDTA.Na_2.2H_2O$ and Cl^- ,SO_4^{2-}, PO^{3-} .

Procedure

For complex formation, the absorbance of series solutions of 0.001M of azodye and studied ions were measured at wavelength range of 350 – 650 nm. and at the optimum conditions, interference, determination of formation constants and Beer's law and at λ_{max} also, by using the azodye were carried out as blank.

RESULTS AND DISSCUSION

The azodye (L of m.p. 163-165 C) (Fig. 1) was prepared and described by FT- IR, NMR., CHN and Visible spectroscopic. The acid-base properties and ionization and protonation constants were studied at different pH values (2-12), then the solvents effect of different polarities was studied at previous work.[19]

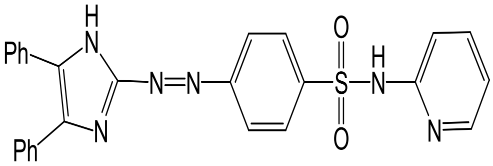


Fig.(1): 2-(Sulfapyridine azo)-4,5-Diphenyl Imidazole (L)($C_{26}H_{20}N_6O_2S$)

The studied ions complexes

The yellow color of azodye (L, λ_{max} 440 nm.) forms a stable red (λ_{max} 480nm.), orange (λ_{max} 480nm.), red-violet (λ_{max} 500nm.), color complexes with divalent cations cobalt, nickel and copper respectively. The complexes were characterized by measuring of melting point which be increased due to the combination of metal ion with azodye liganad (Table 1). The complex characterized by C.H.N. technique (Table 1), which shows good agreement between calculated and found values.

Table 1: C.H.N., %M and molar conductivity of the ligand complexes.

Formula	**Λ ohm^{-1} cm^{2}mol^{-1}**	**M.P.**	**% C**		**% H**		**% N**		**% M**	
			Cal.	**Fou.**	**Cal.**	**Fou.**	**Cal.**	**Fou.**	**Cal.**	**Fou.**
$Co(L)_2(NO_3)_2$	23	>300	54.59	53.25	3.50	3.88	17.15	17.40	5.16	5.22
$[Ni(L)_2](NO_3)_2$	49	227	54.61	53.87	3.50	3.72	17.15	16.99	5.14	5.95
$[Cu(L)_2](NO_3)_2$	89	183	54.38	54.71	3.49	3.40	17.08	16.89	5.54	5.63

IR – studies

The complexes were also characterized by IR spectra (Fig. 2),it was found a clear difference between azodye spectrum and their complexes. It was found there are differences between the spectra of free ligand azodye L and their complexes (L-Co ,L-Ni ,L-Cu, L-Cd and L-Hg) spectra . in all spectra there are bands at 3423 cm^{-1} due to stretching vibration for N - H and O-H bonds, that means this bond don't sharing with metal ions .In case of stretching vibration of C=N cm^{-1} showed lower shifts in absorption , the means the possibility of coordination between azodye and metal ion . In case of stretching vibration for N=N (azo group) bond in all complexed metal ions there are clear lower shift in frequency of azo in the range of (10 – 15 cm^{-1}), due to forming coordination bonds between metal ion and azodye.

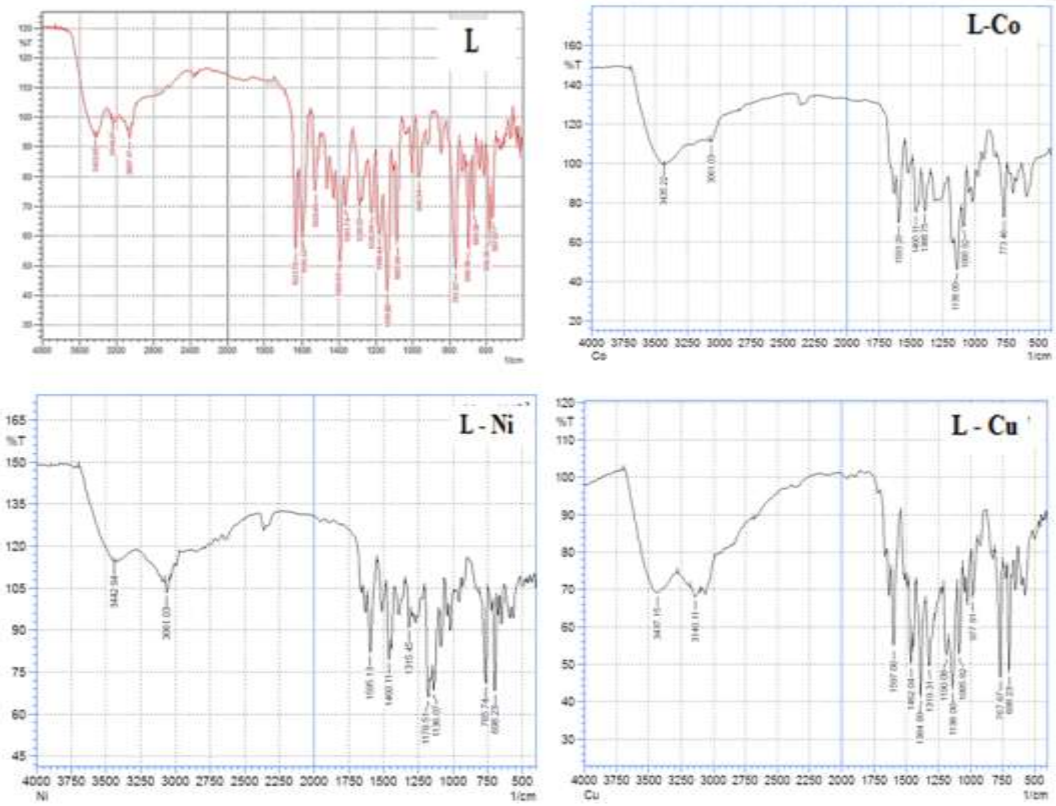


Fig. (2): IR spectrum of azodye L and its complex M-L.

Optimum conditions for forming complexes

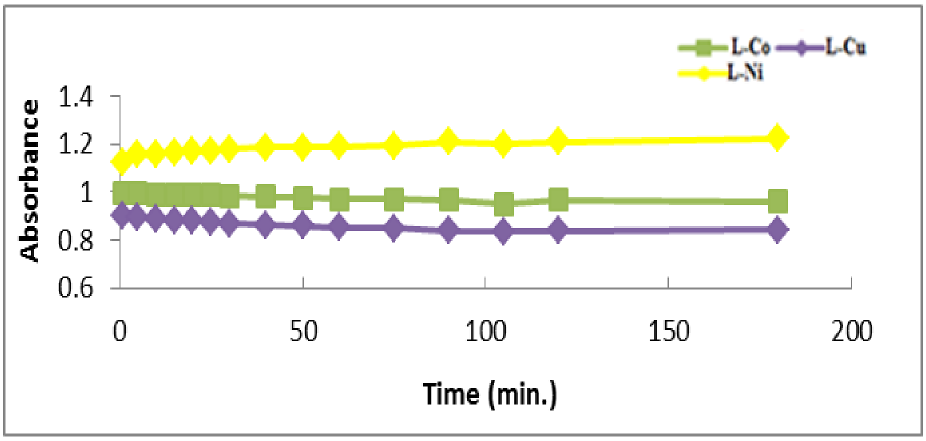
The important Optimum conditions for forming M-L complexes include.

Effect of time

The stability of complexes with time at λ_{max} was listed in Table.2, from the data obtained it was found that the Absorbance reached of highest value and be constant for a long times (over the night 1440 sec.) as shown in (Fig.3). Generally no change in absorbance with time so the complex will be stable.

Table (2): Time effect on the absorbance of M-L complexes.

Time mn.		**1**	**5**	**10**	**20**	**40**	**60**	**90**	**180**	**1440**
A	**Co-L $\lambda_{max\ 480}$**	0.996	0.993	0.991	0.987	0.980	0.970	0.965	0.965	0.950
	Ni-L $\lambda_{max\ 480}$	1.120	1.154	1.158	1.167	1.186	1.191	1.210	1.224	1.200
	Cu-L $\lambda_{max\ 490}$	0.903	0.896	0.890	0.879	0.862	0.835	0.839	0.842	0.835



Fig(3): Time effect on the absorbance of M-L complexes.

pH effect

In the visible region (350 – 650 nm.) the absorbance of a complexes were measured by using universal and acetate buffer solutions of pH range (1.4-12) by using a buffer solution as blank. From Fig.4 ,it was found that the pH of 11 the best value for giving highest absorbance at $\lambda_{max\ 480}$ for Co-L complex , pH 9 at $\lambda_{max\ 480}$ for Ni-L and pH 12 at $\lambda_{max\ 490}$ for Cu-L .

Kinds of best buffer solution

Two kinds of buffer solutions were used, for knowing the best one which gives highest absorbance. It was found that the universal buffer solution is the best and gives highest absorbance as shown in Fig. 5.

Sequence of edition

This study shows three probabilities sequences of additions (Table 3)

Table (3): The different sequence of editions for forming complex.

No.	**Sequence of edition**	**Absorbance at λ_{max}**		
		Co-L	**Ni-L**	**Cu-L**
1	L + M + pH	0.999	1.077	0.981
2	L + pH + M	0.916	1.058	0.821
3	M + pH + L	0.920	1.188	0.93

[M] = [L] = $4x10^{-5}$ M

So, it was found the sequence L + Co + pH_{11} , L + Cu + pH_{12} and Ni + pH_9 + L is the best sequence for Co, Cu and Ni respectively.

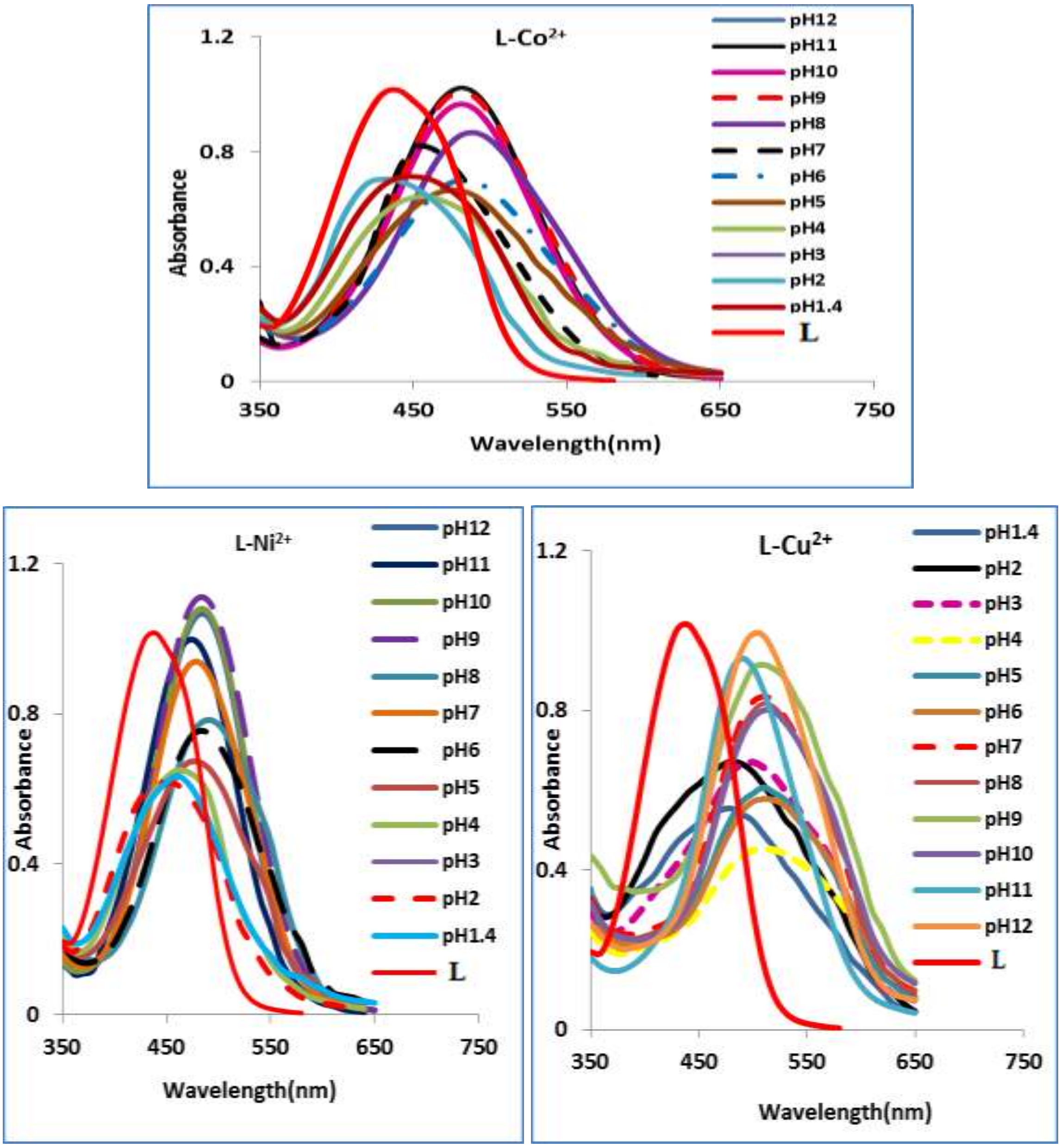
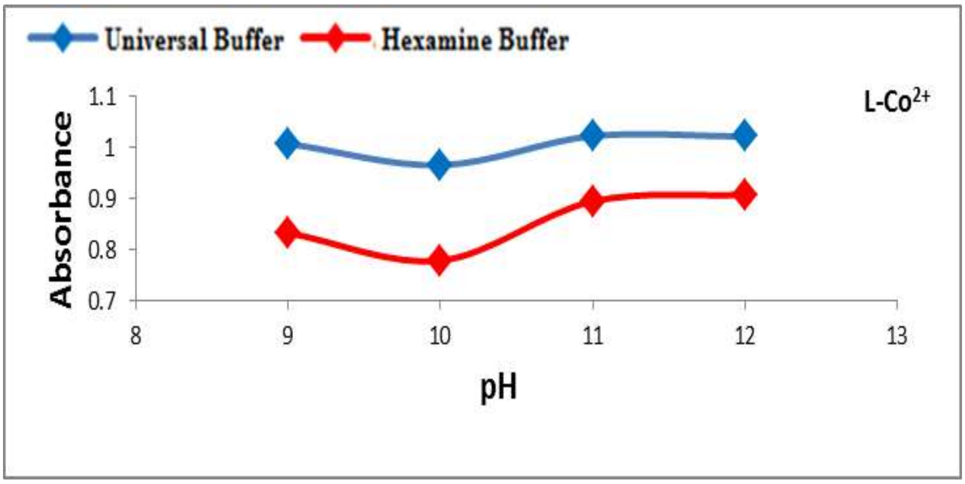


Fig.(4): Spectra of M-L complexes ([M]=[L]= 4 x 10^{-5} M)



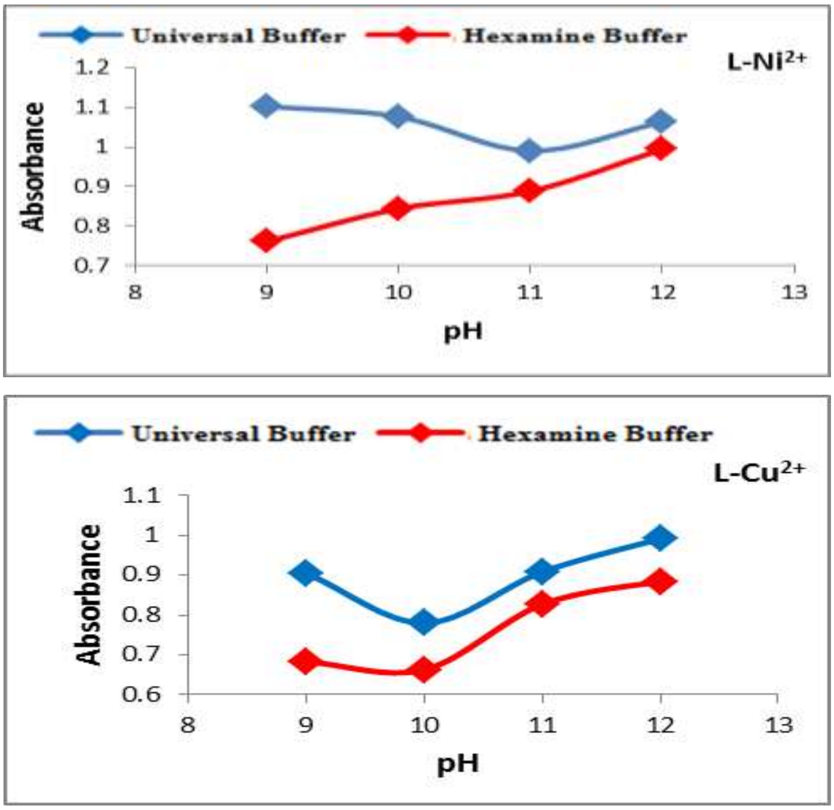


Fig.(5): Kinds of buffer solutions at different pH values.

Study stoichiometry of M-L complexes and mole ratio method

By using of the mole ratio method for knowing chemical composition (Stoichiometery) of a complex , A serious of solutions prepared by keeping concentration of metal constant (2 x10^{-5} M) with varying concentration of azodye (0.4 – 6 x10^{-5} M). Then the absorbances were measured at λ_{max} with azodye as blank solution . From Fig.6, it was shown that the ratio M : L is 1 : 2.

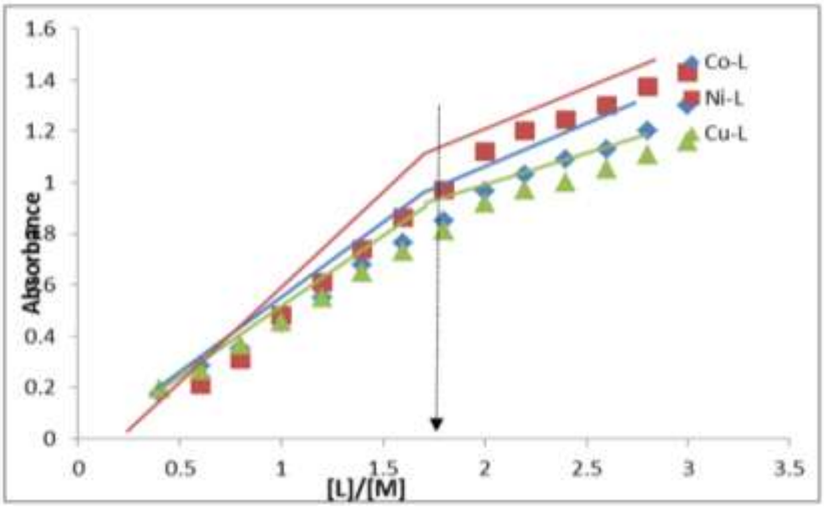


Fig. (6) : The mole ratio method for M-L complexes.

Molar Conductometry

In order to get more identifications on prepared complexes with respect of ionic character of complexes , it was necessary to measure the molar conductivity of complexes solutions using DMF as solvent . The results show molar conductivity of 23, 49 and 89 $cm^2.mole^{-1}.ohm^{-1}$ for Co-L ,Ni-L and Cu-L complexes respectively .The low value of molar conductivity of Co-L complex means that the complex not having ionic character, while the two other complexes havening ionic character.

By the aid of, I.R. spectra, the stoichiometry studies and molar conductivity, the chemical structures of complexes were suggested (Fig. 7).

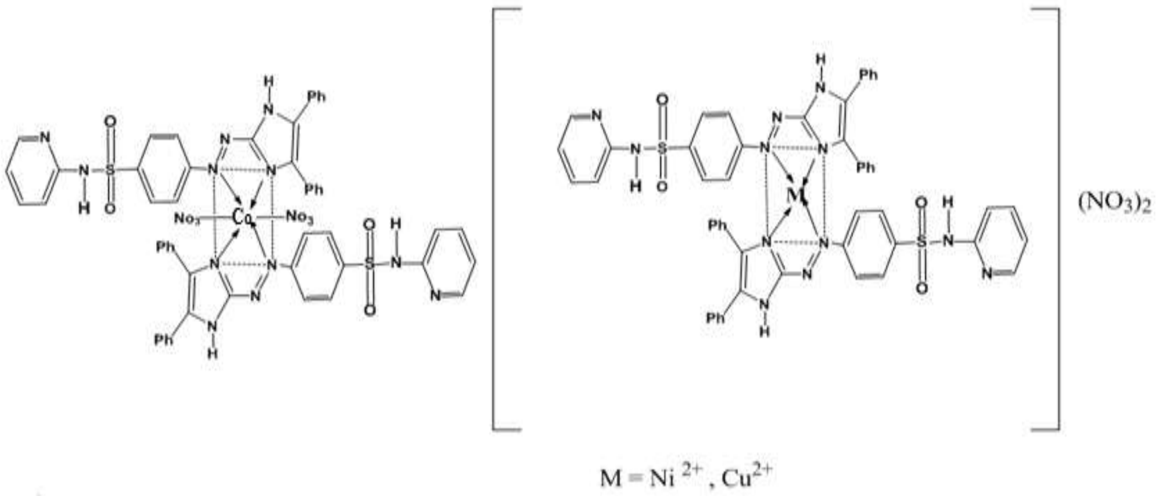


Fig.(7): The Suggested chemical structures of M-L complexes

Sensitivity and Beer’s law.

A serious solutions mixture of variable concentrations of metal ions with excess constant concentration, the absorbances were measured at λ_{max}. Beer’s law was obeyed to the complexes under investigation for the spectrophotometric determination of metal , with linear calibration curves passing through the origin were obtained (Fig. 8). Better results were obtained by applying the optimum blank composition technique[20] i.e using the amount of the unreacted azodye as the blank from knowledge of the stoichiometry of complexes. Table (4) shows the high sensitivity, which is represented by the values of specific absorptivity (a), the molar absorpitivity coeff. (ε) and sensitivity index (S) for complexes M-L with high precision that represented by the values of standard deviation (S.D.), and high linearity of Beer‘s law which represent by the correlation coeff. (r) which is nearly to unity.

Table (4): Data obtained from Beer's law for M-L complexes

Complex	λ max nm	DL µg.ml^{-1}	S.D	S×10^{-3} µg.cm^{-2}	r	a ml.g-1.cm^{-1}	ε L.mol^{-1}.cm^{-1} × 10^{4}	Beer's law up to
Co-L	480	0.2730	0.0134	1.4	0.994	0.7141	4.2	8.1
Ni-L	480	0.1640	0.0221	1.7	0.983	0.5863	3.5	8.1
Cu-L	500	0.0700	0.0091	2.21	0.993	0.4710	3.0	7.6

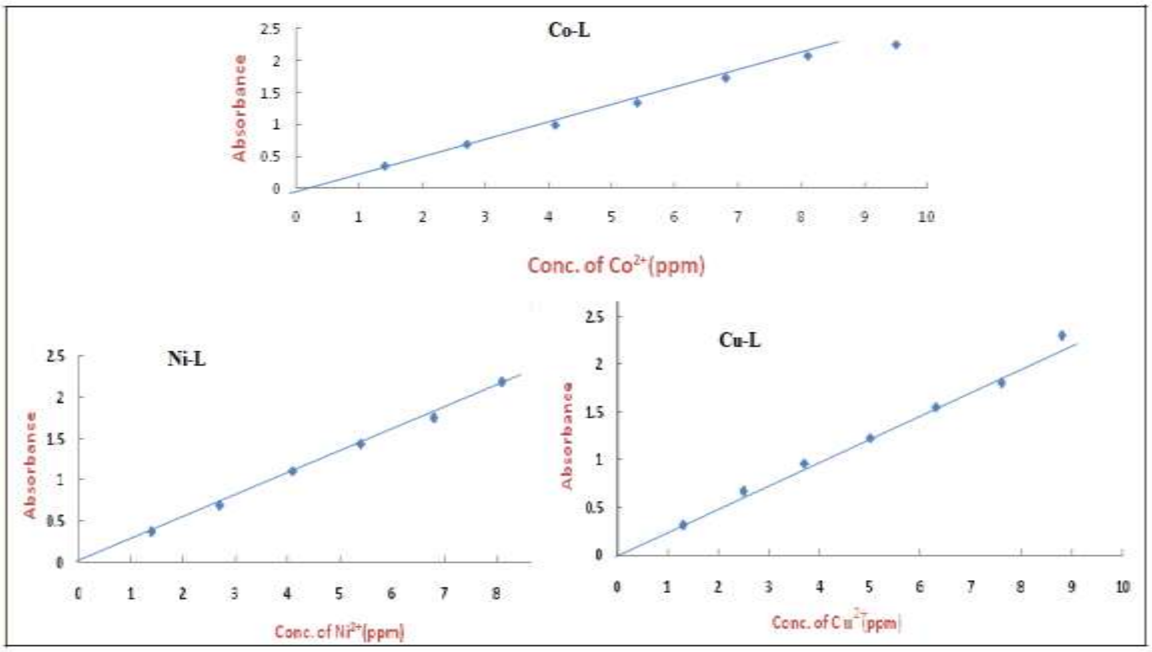


Fig.(8): Beer's law for M-L complexes

Interferences of foreign ions

It is important to study the effects of foreign ions on the absorbance of M-L complexes .So that happened by using (1 fold , 5 folds & 10 folds) of foreign ions concentrations . The Absorbance will be compared with that in absent of foreign ions. (The formed complexes Cd-L and Hg-L will give absorbance of 1.105 and 0.838 respectively in absent of foreign ions).

For interferences with Cd-L , it was found that the ions (Li^{+}، Na^{+}، K^{+} ، Mg^{2} ،VO^{2+} ، Mn^{2+} , ، Ni^{2+}، Hg^{2+}، Sr^{2+}، Cd^{2+}، Ba^{2+} ،Pb^{2+} ، Ca^{2+} ، Cr^{3+} ، Fe^{3+} ، La^{3+} ،Zr^{4+} ، Cl^{-} ،SO$_4^{2-}$ ،PO$_4^{3-}$) don't interfering, but the ions (Ag^{+}،Co^{2+} ،Zn^{2+}and EDTA.Na$_2$.2H$_2$O) will do (Table 5).

For interferences with Hg-L , it was found that the ions (Li^{+}، Na^{+}، K^{+} ، Mg^{2+} ،VO^{2+} ، Mn^{2+} ، Ni^{2+}، Sr^{2+}،Cu^{2+}، Hg^{2+}،Ba^{2++} ،Pb^{2} ، Ca^{2+} ، Cr^{3+} ،Fe^{3++} ، La^{3+} ،Zr^{4}، Cl^{-} $^{-}$،SO$_4^{2}$ ،PO$_4^{3-}$) don't interfering but the ions (Ag^{+}، Cu^{2+}، Cd^{2+}، Zn^{2+}and EDTA.Na.2H$_2$O) will do (Table 5).

For interferences with Cu-L , it was found that the ions (Li^+، Na^+، K^+ ، Mg^2 ،VO^{2+} ، Mn^{2+} ، Hg^{2+} ،Sr^{2+}، Ba^{2+} ،Pb^{2+} ، Ca^{2+} ، Cr^{3+} ، Fe^{3+} ، La^{3+} ،Zr^{4+} ، Cl^- ،SO_4^{2-} ،PO^{3-}) don't interfering but the ions (Co^{2+} ،Ni^{2+} ،$Zn^{2+}$and Cd^{2+}) will do (Table 5).

Table (5): Interferences of foreign ions the absorbance of ([Co] =[Ni]=[Cu] = [L] = 4 x 10^{-5} M The complexes Co-L , Ni-L and Cu-L will give absorbance of 0.968 , 0.972 and 0.983 respectively in absent of foreign ions

ion	**Absorbance of Co-L**			**Absorbance of Ni-L**			**Absorbance of Cu-L**		
	1-fold	**5-fold**	**10-fold**	**1-fold**	**5-fold**	**10-fold**	**1-fold**	**5-fold**	**10-fold**
Li^+	0.958	0.943	0.975	0.968	0.965	0.975	0.987	0.992	0.987
Na^+	0.963	0.965	0.975	0.963	0.975	0.975	0.976	0.979	0.971
K^+	0.941	0.952	0.978	0.971	0.968	0.978	0.992	0.988	0.983
Ag^+	0.889	0.876	0.898	0.898	0.875	0.902	0.926	0.934	0.947
Mg^{2+}	0.949	0.953	0.938	0.967	0.963	0.968	0.975	0.970	0.976
VO^{2+}	0.951	0.958	0.975	0.968	0.976	0.981	0.979	0.973	0.982
Mn^{2+}	0.912	0.902	0.914	0.960	0.965	0.985	0.992	0.995	0.987
Ni^{2+}	0.967	0.973	0.969	0.972	0.984	0.979	0.922	0.914	0.909
Cu^{2+}	0.891	0.884	0.821	0.901	0.896	0.888	0.901	0.886	0.897
Zn^{2+}	0.860	0.875	0.855	0.905	0.879	0.893	0.972	0.982	0.987
Sr^{2+}	0.958	0.962	0.966	0.968	0.963	0.969	0.918	0.903	0.899
Cd^{2+}	0.999	0.954	0.983	0.893	0.899	0.923	0.978	0.988	0.990
Hg^{2+}	0.923	0.913	0.901	0.963	0.973	0.977	0.911	0.900	0.905
Ba^{2+}	0.958	0.969	0.971	0.958	0.967	0.976	0.958	0.967	0.976
Pb^{2+}	0.949	0.974	0.957	0.949	0.974	0.957	0.949	0.974	0.957
Ca^{2+}	0.981	0.972	0.975	0.985	0.976	0.971	0.985	0.976	0.971
Cr^{3+}	0.941	0.943	0.975	0.961	0.953	0.972	0.961	0.953	0.972
Fe^{3+}	0.961	0.965	0.975	0.971	0.976	0.979	0.971	0.976	0.979
La^{3+}	0.941	0.952	0.978	0.962	0.968	0.978	0.962	0.968	0.978
Zr^{4+}	0.942	0.959	0.945	0.972	0.969	0.969	0.972	0.969	0.969
Cl^-	0.970	0.955	0.978	0.975	0.965	0.980	0.979	0.985	0.976
SO_4^{2-}	0.984	0.943	0.942	0.966	.975	0.979	0.986	0.965	0.975
PO_4^{3-}	0.954	0.943	0.942	0969	0.978	0.979	0.963	0.975	0.975

Determination of stability constant of M-L.

By the aid of the corresponding solutions method[21] the stability constants of M-L complexes were calculated using Half-value method.[22] This method requires two series of solutions of total metal ion concentration C1M (concentrated series) and C2M (diluted series) (where C1M > C2M) and varying azodye ligand concentrations C1L and C2L. The absorbencies were measured at λ_{max} (Table 6). The corresponding solutions are those which have the same absorbance at different ligand concentrations. Then the diluted series was multiplied by the factor (C1M / C2M). From the absorbance - CL plot (Fig.9). Many pairs of C1L and C2L, consequently, ñ (Complex formation function) and [L] (free ligand concentration) can be determined (Table 6).

ñ = (C1L – C2L) / (C1M – C2M) and [L] = (C1M x C2L – C2M x C1L) / (C1M – C2M)

By using the half value method log K (stability constant) was obtained from a plot of ñ against pL (Table 7), at ñ = 0.5 and 1.5 the log K_1 and log K_2 were determined (Fig. 10).

Table (6): The absorbance of dil. serious and concn. seriouses

Concn. series x 10^{-5} M(C1L)	Concn. series (C1M=$8x10^{-5}$M) Absorbance at λ_{max} Co-L	Ni-L	Cu-L	Dil. series x 10^{-5} M (C2L)	Dil. series (C2M=$4x10^{-5}$M) Absorbance at λ_{max} Co-L	Ni-L	Cu-L
1.6	0.318	0.418	0.336	0.8	0.436	0.37	0.362
2.4	0.616	0.616	0.537	1.2	0.618	0.576	0.512
3.2	0.864	0.864	0.729	1.6	0.9	0.75	0.672
4	1.09	1.09	0.97	2	1.25	1.016	1.022
4.8	1.3	1.3	1.263	2.4	1.49	1.266	1.232
5.6	1.455	1.56	1.364	2.8	1.79	1.596	1.5
6.4	1.918	1.918	1.75	3.2	1.83	1.688	1.578

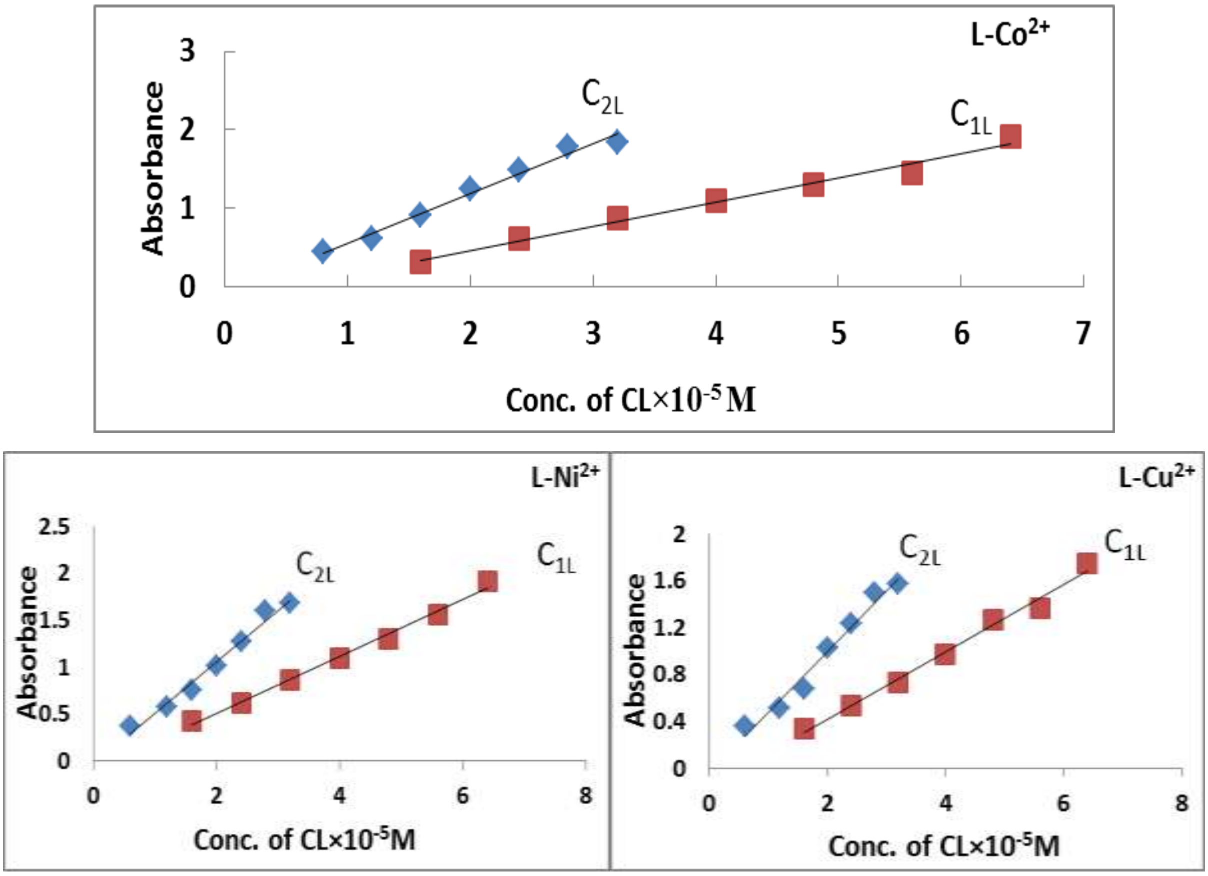


Fig.(9): The absorbance – Cl curve or the M-L complexes.

Table (7): Pairs of same absorbance C_{1L} and C_{2L} and getting ñ & pL values

A	**Co-L**					**Ni-L**					**Cu-L**				
	$C_{1L} \times 10^{-5}$	**$C_{2L} \times 10^{-5}$**	**ñ**	**$[L] \times 10^{-5}$**	**pL**	**$C_{1L} \times 10^{-5}$**	**$C_{2L} \times 10^{-5}$**	**ñ**	**$[L] \times 10^{-5}$**	**pL**	**$C_{1L} \times 10^{-5}$**	**$C_{2L} \times 10^{-5}$**	**ñ**	**$[L] \times 10^{-5}$**	**pL**
0.4	1.8	0.8	0.25	- 0.2	5.7						1.8	1	0.2	0.2	5.7
0.5	2.2	1	0.3	-0.2	5.7						2.2	1.2	0.25	0.2	5.7
0.6	2.65	1.2	0.36	-0.25	5.6	2.4	1.25	0.29	0.1	6	2.3	1.3	0.25	0.3	5.52
0.7	3.08	1.38	0.43	0.32	5.5	2.7	1.42	0.41	0.14	5.85					
0.8	3.4	1.54	0.47	0.32	5.5	3.02	1.6	0.41	0.18	5.74	2.9	1.61	0.32	0.32	5.49
0.9	3.54	1.6	0.49	0.34	5.47	3.44	1.82	0.43	0.2	5.7	3.4	1.9	0.38	0.4	5.4
1	4.1	1.86	0.56	-0.38	5.42	3.7	2	0.47	0.3	5.52	3.76	2.1	0.42	0.44	5.36
1.1						4.08	2.2	0.58	0.32	5.49	4	2.24	0.44	0.48	5.32
1.2	4.6	2.1	0.63	-0.4	5.4	4.44	2.4	0.58	0.36	5.42	4.5	2.5	0.5	0.5	5.3
1.3	4.96	2.28	0.67	-0.4	5.4	5	2.68	0.6	0.36	5.42	4.7	2.6	0.53	0.5	5.3
1.4	5.24	2.4	0.71	-0.44	5.36	5.18	2.78	0.65	0.38	5.42	5.08	2.8	0.57	0.52	5.28
1.5						5.56	2.98	0.66	0.4	5.4	5.46	3	0.62	0.54	5.27
1.6	5.7	2.6	0.78	-0.5	5.3	5.78	3.14	0.68	0.5	5.3	5.82	3.2	0.66	0.58	5.24
1.7	6	2.72	0.82	-0.56	5.25	6.8	3.8	0.75	0.8	5.09	6.4	3.55	0.71	0.7	5.15
1.8	6.32	2.88	0.86	-0.56	5.25	7.58	4.2	0.56	0.82	5.08	7	3.95	0.76	0.9	5.05
1.9						8.2	4.6	0.9	1	5	8	4.5	0.88	1	5
2						9.89	5.5	1.1	1.11	4.95					
2.1	7.2	3.2	1	-0.8	5.09	10.42	5.8	1.61	1.18	4.93	8.19	4.65	0.89	1.11	4.95
2.3						11.19	6.22	1.42	1.25	4.9	9.2	5.2	1	1.2	4.92
2.4	8.42	3.3	1.28	-1.82	4.74										
2.5						11.46	6.37	1.73	1.28	4.89	11.16	6.2	1.24	1.24	4.91
2.7	9.4	3.5	1.47	-2.4	4.6	12.2	6.75	1.36	1.3	4.87	12.2	6.8	1.35	1.4	4.85
2.9						12.83	7.1	1.43	1.37	4.86	13.9	7.8	1.53	1.7	4.77
3.1	10.6	3.8	1.7	-3.0	4.52	13.1	7.25	1.46	1.4	4.85					

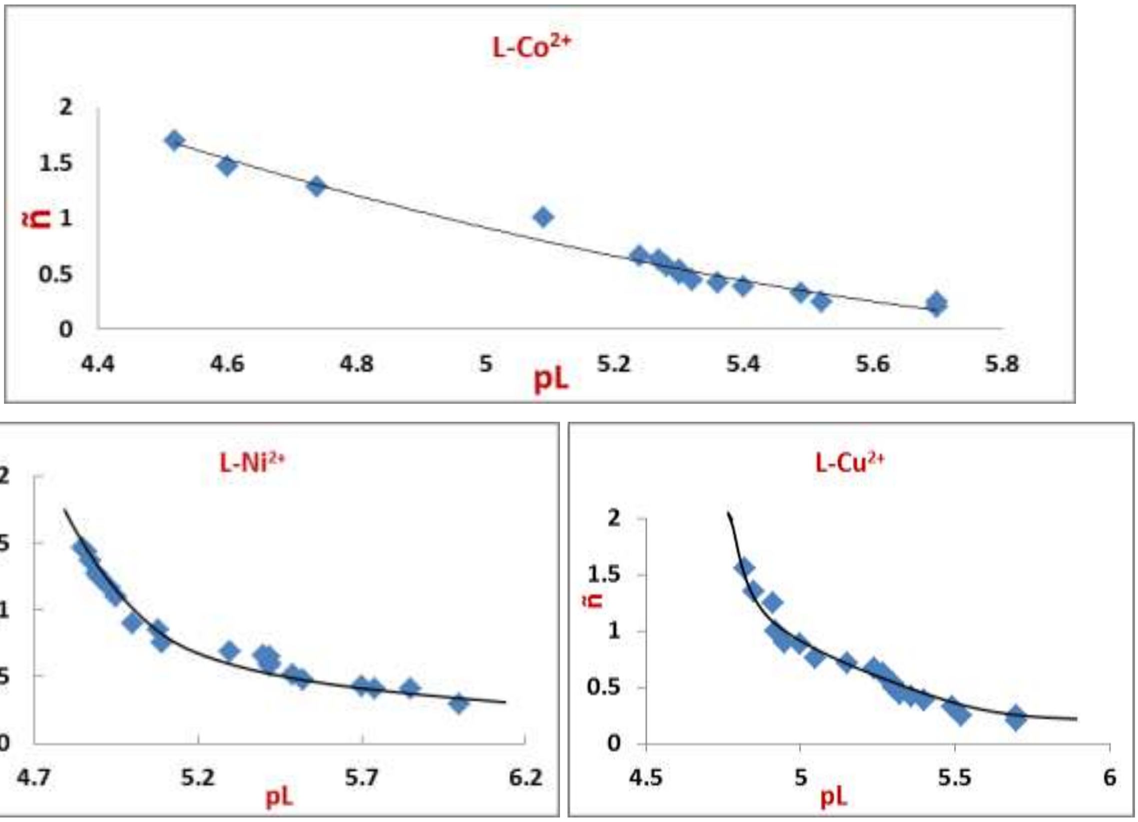


Fig.(10) :Half-height method (ñ - pL curves)

Table (8) lists the values of Logβ_1 and Logβ_2 for complexes Co-L , Ni-L and Cu-L . From the table it was found that the most stable complex is Ni-L ,then Cu-L and the last is Co-L

Table(8): Logβ_1 and Logβ_2 for complexes.

Log β	**Co-L**	**Ni-L**	**Cu-L**
Logβ_1	5.47	5.49	5.52
Logβ_2	10.07	10.34	10.29

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