Synthesis, Spectroscopic and Biological Studies of Some Metal Complexes with 2,2-Diamino–N–Phenyl Hydrazo Benzene

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Abstract

The ligand of 2,2`–diamino–N–phenyl hydrazo benzene (L) has been prepared from the reaction of ortho amino hydrazo benzene with ortho amino phenyl thiol in mole ratio1:1and characterized by elemental analysis (C, H, N), IR, UV-Vis. The complexes of bivalent (Co, Ni, Cu, Zn, Pd, Cd, Hg and Pb)ions and trivalent (Cr)ion have been prepared and characterized too. The structural diagnosis were established by IR, UV-Visible spectrum, Conductivities, atomic absorption and magnetic susceptibility. The complexes showed octahedral geometry around the metal ion with the (N,N,N) ligand coordinated in tridentate mode except pd complex showed trigonal bibyramidal. α, k_f, ϵ_{max} for the complexes were estimated too. β for Co – complex was calculated. The study of biological activity of the ligand (L) and its complexes showed various activity toward Streptococcus pyogenes, Staphylococcus aureus, E. coli, Pseudomonas aeruginosa and Candida albicans.

Keywords: synthesis, hydrazo benzene, complexes.

Introduction

The chemistry of hydrazides, hydrazones derived from hydrazine have been intensively investigated in recent years. The reasons are manifold; first is the coordinating ability of these compounds to chelate metal ions particularly transition and lanthanide ions(1- 3). The synthesis and characterization of many metal ions complexes that contain arange of ancillary ligands such as macrocyclic ligands incorporating benzimidazol(4), leucine–o–acetic acid(5), oxadiazole derivatives(6), Triazol derivatives(7, 8), dioxadiazole and ditriazole(9), ortho amino phenyl thiol derivatives(10, 11), bis oxadiazole derivatives(12). A considerable number of a bove compounds have been reported to demonstrate antibacterial and antifungal activities(13-18). In this paper we report the synthesis, characterization and biological activities of 2, 2` - diamino– N – phenyl hydrazo benzene and its complexes with (Cr, Co, Ni, Cu, Zn, Pd, Cd, Hg and Pb).

Experimental

a- Chemicals:

All reagents used were analar or chemically pure grade by British Drug Houses (BDH), Merk and Fluka.

-The chemical materials: ortho amino phenyl thiol (C_6H_7NS), ortho amino hydrazo benzene ($C_{12}H_{13}N_3$), Cobalt chloride hexahydrate ($CoCl_2.6H_2O$), Nickel chloride hexa hydrate ($NiCl_2.6H_2O$), Paladium chloride ($Pd\ Cl_2$), Cadimum chloride dihydrate ($Cd\ Cl_2.2\ H_2O$), Mercury chloride($Hg\ Cl_2$),Copper Sulphate pentahydrate($Cu\ SO_4.5H_2O$), Zinc sulphate heptahydrate ($Zn\ SO_4.\ 7\ H_2O$), Lead nitrate ($Pb(NO_3)_2$), Chromium trichloride hexahydrate ($CrCl_3.6H_2O$)Ethanol 99% (CH_3CH_2OH), Dimethyl formamide 99.5% (DMF), Dimethyl sulphoxide 99.5% (DMSO), Tetra chloro carbon 99.5% (CCl_4), Chloroform 99% ($CHCl_3$), Toluene 99% ($C_7\ H_8$).

b- Instruments:

- -Elemetal analyses C, H, N, were determined by calibration type: Linear Regression Euro EA Elemental Analysis.
- -Melting points were determined by Gallen-Kamp apparatus.
- -IR spectra were recorded as KBr discs in the range (4000 – 400) cm^{-1} using Shimadzu-FTIR.
- -UV-Visible spectra were recorded by Shimadzu –UV–VIS –160A Ultra violet spectro photometer at 25 c^{o}, using 1 cm

quartz cell and examined at the range of (200–1100)nm at 10^{-3}M in DMSO.

-Atomic Absorption (A. A) technique using a shimadzu AA 680 G atomic absorption spectro photometer.

-Molar conductivity of the complexes were measured on pw 9526 digital conductivity in DMSO at 10^{-3} M

-Magnetic susceptibility were recorded by Magnetic susceptibility Blance, model, MsB – MK_1.

Preparation

Synthesis of 2,2`-diamino–N–phenyl hydrazo benzene (L)

Orthoaminophenyl thiol (0.125 gm, 0.001 mol)and ortho aminohydrazo benzene (0.29 gm, 0.001 mol) in ethanol (20 cm^3) was stirred under reflex for (6 hours). The precipitate was filtered and recrystallized from hot absolute ethanol, a fine yellow crystals were obtained m.p at 94 c^o yield 88% and soluble in most organic solvents.

Complexes

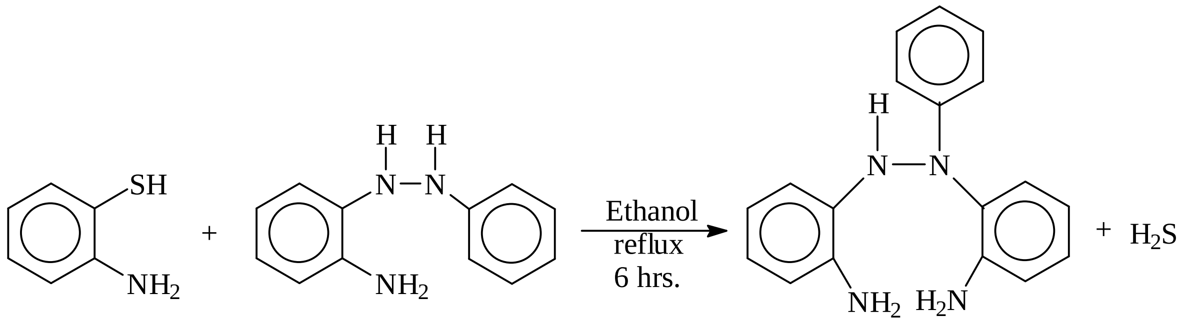
Synthesis of the metal complexes

An ethanolic solution of metal salts one mole was added to one mole of the ligand (L) [$CrCl_3.6\ H_2O$ (0.26 gm. 1.00 mmol), $CoCl_2.\ 6\ H_2O$(0.24gm. 1.00 mmol), $NiCl_2.6\ H_2O$ (0.24 gm. 1.00 mmol), $CuSO_4.\ 5H_2O$ (0.24gm. 1.00 mmo)l, $ZnSO_4.7\ H_2O$(0.28 gm. 1.00 mmol), $PdCl_2$(0.17 gm.1.00 mmol), $CdCl_2.\ 2\ H_2O$ (0.22 gm.1.00 mmol), $HgCl_2$ (0.27 gm. 1.00 mmol) and $Pb(NO_3)_2$ (0.33 gm. 1.00 mmol)] were added to (0.29gm.1.00 mmol) of the ligand (L). The mixture was stirred for 30 min. The product was filtered and washed with distilled water and dried under vacuum. Color, melting point, yield, metal analysis and solubility of the ligand and its complexes are given in (Table (1)).

Results and Discussion

Synthesis and characterization of the ligand 2,2`-diamino–N-phenyl hydrazo benzene (L)

The ligand was obtained by the reaction of one mole of orthoaminophenyl thiol and slightly excess one mole of ortho amino hydrazo benzene.



Elemental analysis (C, H, N) confirmed the purity of the ligand (L) with formula C18H18N4.

The infrared spectrum of the ligand (L) in the solid state doesnot contain the υ (S – H) which appears in the starting material orthoaminophenyl thiol at (2600 – 2500) cm^{-1} region. This indicates the displacement of SH in orthoaminophenyl thiol. Bands observed at 3379 cm^{-1}, 1581 cm^{-1} and 1303 cm^{-1} are diagnostic of the primary aromatic amine(19).Bands around 3301 cm^{-1} are due to υ(N–H)(20) group. (Fig. (1)).

The infrared spectra of all complexes showed, the multi bands in the range (3460 – 3209) cm^{-1} and split or broader band at (1604 – 1542) cm^{-1} and at (1335) cm^{-1} with the formation of a new absorption bands for the coordination bands (M – N) in the region (540 – 500) cm^{-1} suggesting the coordination through nitrogen atom(21-22). M – N stretching vibration have been assigned in Table (2). The bands characteristic of coordinated water and (M–O) are seen in complexe in the region (856 - 817) cm^{-1} and (570 – 547) cm^{-1}(23). The Cu, Zn complexes showed bands at 1020 cm^{1}, 960 cm^{-1}, 678 cm^{-1} and was assigned to coordinated sulphato group(24). The Pb complex spectrum exhibited bands at 925cm^{-1}, 680 cm^{-1} due to coordinate nitrato ion(25, 26). (Table (2)) describes characteristic stretching vibration frequencies (cm^{-1}) located in the FT–IR of the ligand and its complexes.

The UV – Visible spectra of the ligand (L) and complexes

The UV–Visible spectra of the ligand (L) in DMSO solution exhibited strong absorption bands at (266 nm, 37593 cm^{-1}) and (351 nm, 28490 cm^{-1}). This may attributed to the $\pi - \pi^*$ transition(27). (Fig.(2)).

The UV–Visible spectrum for Cr^{+3} complex showed one band in the region (575 nm, 17391 cm^{-1}) is due to ${}^4A_2g \longrightarrow {}^4T_2g$ (28).

The UV–Visible spectrum for Co^{+2} complex showed three bands in the region(800 nm, 12500 cm^{-1}) due to ${}^4T_1g \longrightarrow {}^2Eg$, (660 nm, 15151cm^{-1}) due to ${}^4T_1g \longrightarrow {}^4A_2g$ and (550 nm, 18181 cm^{-1}) due to ${}^4T_1g(F) \longrightarrow {}^4T_1g(p)$ (29,30). The ratio of 18181 cm^{-1} to 12500 is 1.54 which fits with Tanaba–Sugano d^7 curve (Fig.(3)) for E/B = 26 and $\Delta 0 / B^{`} = 17$. $\Delta 0 = 12500$ cm^{-1}

$B^{`}$ complex = 12500 / 17 = 735 cm^{-1}

B for free Co^{+2} = 971 cm^{-1}

B (nephelauxetic effect) = $B^{`}$ complex / B Co^{+2} = 735 / 971 = 0.756.

Which indicates of d – electron delocalization on the ligand hence a significant covalent character in the complex (31).

The UV-Visible spectrum for Ni^{+2} showed one band at (823 nm, 12150 cm^{-1}) which is due to ${}^3A_2g \longrightarrow {}^3T_1g$. The spectrum of the Cu^{+2} complex exhibited a band at (660 nm, 15151cm^{-1}) which is due to ${}^2Eg \longrightarrow {}^2T_2g$. The brown palladium complex exhibited astrong band at (400 nm, 25000 cm^{-1}) due to d – π^* transition(32). The UV-Visible spectra of Zn$^{+2,}$ Cd^{+2}, Hg^{+2} and Pb^{+2} complexes showed shifted bands compared with free ligand (L) are due to charge transfer (Table (3)).

The molar conductance of all complexes in DMSO were found to be low which suggested coordination of anion to the metal.

The µeff value of Cr,Co,Ni,Cu complexes are within the range (3.75,4.46,2.90,1.99) respectively expected for spin–free octahedral structures(33,34). Electronic spectra, Conductance in (DMSO), Magnetic moment (B.M) of the ligand and its complexes are given in Table (3)

Study of Cr$^{+3,}$ Ni^{+2} complexes formation in solution

The complexes of the ligand (L) with selected metal ions (Cr^{+3}, Ni^{+2}) were studied in solution using ethanol as solvent in order to determine (M:L) ratio in the prepared complexes, following molar ratio method(35). A series of solutions were prepared having a constant concentration (C) 10^{-3} M of the hydrated metal salts and the ligand (L).The results of complexes formation in solution are given in (Table (4)).

The stability constant (kf) was evaluated using the following equations:

$$Kf = 1 - \alpha / \alpha^2 c \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \text{(1)}$$

$$\alpha = Am - As / Am \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \text{(2)}$$

(α) is the degree of the dissociation, (c) is the concentration of the complex (10^{-3} M). (As) and (Am) are the absorbance value of the partially and fully formed complex respectively Table (5).

The absorbance of the solutions were measured at (λmax) of the maximum absorption. The molar absorptivity (Єmax) (eq.3) has been calculated using equation:

$$A = Єmax.\ b.\ c \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \text{(3)}$$

(A) is the average of three measurement of the absorption containing the same amount of metal ion and three fold excess of ligand, (b) is the depth of the quartz cell usually equal 1 cm.

The atomic absorption analysis was used to confirm our molar ratio calculation of [metal:ligand] (M:L) for Synthesis complex as well.The results showed a ratio M:L (1:1) for all complexes (Table (1)).

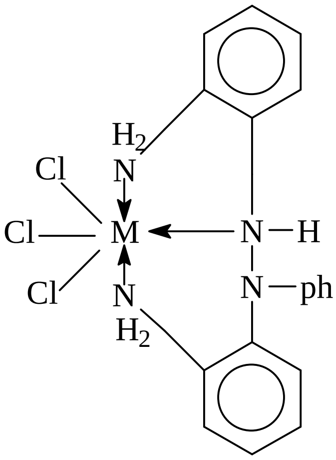
Study of biological activity

The biological activity of the prepared new ligand and its complexes were studied against selected types of microorganisms which include gram positive bacteria like Streptococcus pyogenes, Staphylococcus aureus and gram negative bacteria like E. coli, Pseudomonas aeruginosa and yeast like Candida albicans, in agar diffusion method, which include Cephalosporin, Amoxicillin and Nystatin as control. Agar diffusion method involves the exposure of the inhibition zone toward the diffusion of microorganisms on agar plate. The plates were incubated for (24) hrs at (37 C^o). The inhibition zone of bacterial growth around the disc was observed.

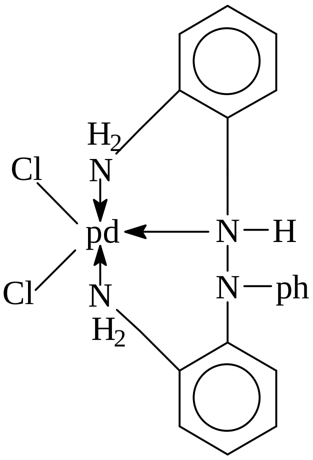
Conclusion

A series of complexes of Cr^{+3}, Co^{+2}, Ni^{+2}, Cu^{+2}, Zn^{+2}, Cd^{+2}, Hg^{+2}, Pb^{+2},with 2, 2`–diamino–N–phenyl hydrazo benzene(L)have been prepared and characterized.

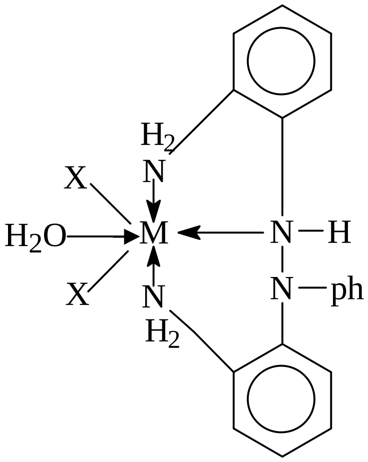
The tridentate ligand (L) (N,N,N) is binding metal ion forming octahedral structure except with Pd^{+2} is forming trigonal bipyramindal as follows.



M^{+3} = Cr



M^{+2} = pd



M^{+2}=Co, Ni, Cd, Hg
X=Cl^{-1}
M^{+2}=Cu, Zn
X_2=SO_4^{-2}
M^{+2}=pb
X=NO_3^{-1}

Biological effects of new ligand and its complexes indicated that the new ligand and its complexes exhibited antibacterial activity against both gram positive and gram negative bacteria specially zinc and mercury complexes, while the effects of new ligand and its complexes on candida albicans showed less than effects except zinc and mercury complex. generally the results of the prepared complexes exhibited antimicrobial activity toward bacteria more than yeast candida albicans.

Table (1)

Color, melting point, yield, metal analysis and solubility of the ligand and its complexes.

No.	***Compound***	***Color***	***m. p. c^o or (D)***	***Yield %***	***Metal analysis found (calculated)***				***Solubility***
					C %	***H %***	***N %***	***M %***	
1	(L) C18 H18 N4	Yellow	94 c^o	88	74.399 (74.482)	6.206 (6.206)	19.300 (19.310)	–	ETOH, CCl4,CH Cl3 C7H8,DMF,DMSO
2	L – Cr Cl_3	Green	220 c^o	82	48.159 (48.160)	4.012 (4.013)	12.484 (12.486)	11.56 (11.59)	DMF, DMSO
3	L – Co $Cl_2.H_2O$	Dark blue	180 c^o	75	49.316 (49.315)	4.569 (4.566)	12.786 (12.788)	13.35 (13.47)	DMF, DMSO
4	L – Ni $Cl_2.H_2O$	Light green	120 c^o	91	49.349 (49.348)	4.570 (4.569)	12.795 (12.794)	13.40 (13.41)	DMF, DMSO
5	L –Cu $SO_4.H_2O$	blue	180 c^o	87	46.202 (46.203)	4.277 (4.278)	11.979 (11.978)	13.59 (13.58)	DMF, DMSO
6	L –Zn $SO_4.H_2O$	yellow	220(D)	79	46.023 (46.025)	4.260 (4.261)	11.930 (11.932)	13.90 (13.91)	DMF, DMSO
7	L – Pd Cl_2	brown	224 (D)	86	46.200 (46.213)	3.849 (3.851)	11.985 (11.981)	22.79 (22.76)	DMF, DMSO
8	L – Cd $Cl_2.H_2O$	Light yellow	192 c^o	92	43.954 (43.956)	4.06 (4.07)	11.397 (11.396)	22.86 (22.87)	DMF, DMSO
9	L – Hg $Cl_2.H_2O$	violet	202 c^o	71	37.270 (37.273)	3.450 (3.451)	9.665 (9.663)	34.57 (34.59)	DMF, DMSO
10	L–Pb $(NO_3)_2.H_2O$	Light yellow	134 c^o	94	33.798 (33.797)	3.127 (3.129)	13.144 (13.143)	32.39 (32.40)	DMF, DMSO

***D** = Decomposition*

Table (2)
Characteristic stretching vibrational frequencies (cm^{-1}) located in the FT – IR of the ligand (L) and its complexes.

No.	**Compound**	**υ(N-H) cm^{-1}**	**υ(C-H) cm^{-1} Ar.**	**υ(N-N) cm^{-1}**	**υ(M-N) cm^{-1}**	**υ(M-X) cm^{-1}**	**υ(M-O) + υ(OH2)aq. cm^{-1}**	**υSO4-2 υNO3- cm^{-1}**
1	(L) C18 H18 N4	3379(asym) (m.s) 3301(sym) (s.s) 1612 (s.s), 1581(m.s.) 1303 (s.s), 1242 (s.s)	3186 (m.s) 3062 (m.s) 856 (di-sub) 758 (mon - sub)	1442 (s.s)	–	–	–	–
2	L – Cr Cl_3	3379,3301(asym)(sp)(m.br) 3209 (sym) (sh) 1612 (s.s),1590 (sh),1558(m.s) 1380 (sh), 1303 (s.s) 1242(s.s),1230(sh)	3120 (sh) 3030 (m.s)	1400 (sh) 1442(m.s)	547 (s.s)	462 (m. br)	–	–
3	L – Co $Cl_2.H_2O$	3417 (asym) (s. br) 3379 (sym) (s. br) 1618 (s.s), 1580 (m.s) 1300(sh), 1305(m.s),1245(m.s)	3120 (sh) 3040 (m.br)	1434(m.br)	520(m.br)	440 (m. br)	570 (m.br) 825 (m.br)	–
4	L – Ni $Cl_2.H_2O$	3284 (asym)(m.s), 3247,3211(sym)(m.s) 1610(sh), 1593 (m.s) 1315 (m.s), 1278 (m.s)	3124 (m.s) 3085 (w.s)	1430 (sh) 1442 (m.s)	510 (w.s)	416 (m.s)	547 (m.s) 825 (s.s)	–
5	L –Cu $SO_4.H_2O$	3386,3301(asym) (m.s) 3200(sym) (sh) 1620 (s.s), 1575 (sh) 1303 (s.s), 1242 (m.s)	3120 (sh) 3062 (sh)	1435 (sh) 1442 (m.s)	520 (m.br)	420 (m.br)	555 (m.br) 856 (m.s)	1020(sh) 960 (sh) 675(m.br)
6	L –Zn $SO_4.H_2O$	3379(asym)(m.br) 3247,3209 (sym) (m.br) 1589 (s.s), 1550 (m.s), 1380 (m.br) 1310 (m.s), 1280 (s.s) 1226 (s.s)	3124 (m.br) 3085 (sh)	1440 (m.s)	510 (m.br)	416 (m.s)	547 (s.s) 825 (s.s)	1018(s.s) 948(m.s) 678(m.s)
7	L – Pd Cl_2	3440-3332 (asym) (m.br) 3280 (sym) (m.br) 1604(s.s), 1560 (sh), 1388(m.br) 1303 (s.s), 1249 (s.s),1203 (sh) 1290 (sh)	3170 (m.br) 3055 (m. br)	1430 (sh) 1442 (m.s)	540 (m.br)	420 (m.br)	v	–
8	L – Cd $Cl_2.H_2O$	3448-3355 (asym) (m.br) 3286 (sym) (m.br) 1604 (s.s), 1550 (sh) 1325 (sh), 1303 (s.s) 1270 (sh),1250 (sh)	3147 (m.br) 3055(m.br)	1419(m.s)	500 (sh)	415 (m.s)	555 (m.br) 817(s.s)	–
9	L – Hg $Cl_2.H_2O$	3448-3325 (asym) (m.br) 3278 (sym) (m.br) 1604 (s.s), 1560 (sh) 1303 (s.s), 1250 (sh)	3147 (m.br) 3030 (m.br)	1400 (m.s)	500 (sh)	440 (s.s)	555 (s.s) 817 (s.s)	–
10	L–Pb $(NO_3)_2.H_2O$	3460,3380 (asym) (m.br) 3320 (sym) (sh) 1605 (s.s), 1570 (sh) 1380 (m.s), 1315 (s.s) 1240 (s.s), 1200 (m.s)	3180 (m.br) 3050 (m.s)	1450 (m.s)	535 (m.br)	440 (m.br)	560 (m.br) 820 (s.s)	925 (s.s) 680 (s.s)

Ar. = aromatic, Ali = aliphatic, asym = asymmetric, sym = symmetric, sh = shoulder
S = sharp, br = broad, m = meduim, s = strong, w = weak

Table (3)
Electronic spectra (DMSO), conductance in DMSO, Magnetic moment (B.M) of the ligand (L) and its complexes.

No.	**Compound**	**λ (nm) cm^{-1}**	**Assignment Bands**	**Λ s. cm^{-1} DMSO (10^{-3} M)**	**μeff (B.M)**
1	(L) C18 H18 N4	37593 (266) 28490 (351)	$\pi - \pi^*$	–	–
2	L – Cr Cl_3	17391 (575)	${}^4A_2g \longrightarrow {}^4T_2g$	20.72	3.75
3	L – Co $Cl_2.H_2O$	18181 (550) 15151 (660) 12500 (800)	${}^4T_1g_{(F)} \longrightarrow {}^2T_1g_{(P)}$ ${}^4T_1g \longrightarrow {}^4A_2g$ ${}^4T_1g \longrightarrow {}^4Eg$	12.35	4.46
4	L – Ni $Cl_2.H_2O$	12150 (823)	${}^3A_2g \longrightarrow {}^3T_1g$	10.59	2.90
5	L –Cu $SO_4.H_2O$	15151 (660)	${}^2Eg \longrightarrow {}^2T_2g$	11.53	1.99
6	L –Zn $SO_4.H_2O$	27777 (360)	Charge – Transfer	7.95	–
7	L – Pd Cl_2	25000 (400)	$d - \pi^*$	5.32	–
8	L – Cd $Cl_2.H_2O$	27777 (360)	Charge - Transfer	9.44	–
9	L – Hg $Cl_2.H_2O$	31746 (315)	Charge - Transfer	10.39	–
10	L–Pb $(NO_3)_2.H_2O$	28169 (355)	Charge - Transfer	11.34	–

B. M = Bohr Magneton
Vm = volume of metal in ml
VL = volume of ligand in ml

Table (4) Fig.(4) (a)

L – Cr Cl_3		
V M	***VL***	***Abs***
1 ml	0.25	0.15
1	0.50	0.31
1	0.75	0.46
1	1	0.60
1	1.25	0.59
1	1.50	0.61
1	1.75	0.62
1	2	0.59
1	2.25	0.58
1	2.50	0.62
1	2.75	0.63
1	3	0.59
1	3.25	0.58
1	3.50	0.61
1	3.75	0.61
1	4	0.60

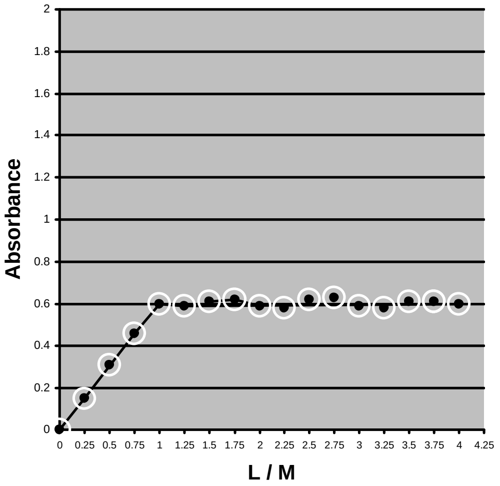


Fig. (4) (a) Continous variation slop forCr^{+3} ion l (368 nm).

Table (4) Fig. (4) (b)

L – Ni $Cl_2.H_2O$		
V M	***VL***	***Abs***
1 ml	0.25	0.28
1	0.50	0.59
1	0.75	0.91
1	1	1.20
1	1.25	1.19
1	1.50	1.21
1	1.75	1.22
1	2	1.19
1	2.25	1.18
1	2.50	1.21
1	2.75	1.19
1	3	1.22
1	3.25	1.21
1	3.50	1.21
1	3.75	1.19
1	4	1.22

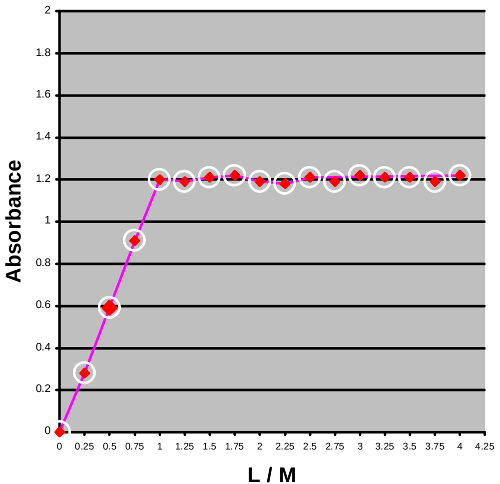


Fig. (4) (b) Continous variation slop for Ni^{+2} ion l (390 nm).

Table (5)

As, Am, Kf, Єmax and λmax of the Cr^{+3} and Ni^{+2} complexes.

No.	***Compound***	***As***	***Am***	***a***	***Formation constant (Kf)***	***molar absorpitivity Єmax L. $mol^{-1}.cm^{-1}$***	***l max (nm)***
1-	Cr – complex	0.60	0.63	0.047	4.314×10^5	3276	368
2-	Ni – complex	1.20	1.22	0.016	3.843×10^6	2925	390

Table (6)

Effect of ligand and its complexes on gram positive bacteria.

Compound	***Diameter of inhibition zone (mm)at concentration 1mg|ml***		***Diameter of inhibition zone (mm)at concentration 5mg|ml***	
	E. coli	***Pseudomonas aeruginosa***	***E. coli***	***Pseudomonas aeruginosa***
Cephalosporin	26.4	25.8	28.6	27.2
(L) C18 H18 N4	14.6	14	15.2	14.8
L – Cr Cl_3	12.4	11.8	12.8	12
L – Co $Cl_2.H_2O$	13.2	13	13.4	13.4
L – Ni $Cl_2.H_2O$	16.2	16	16.6	16
L –Cu $SO_4.H_2O$	15	15	15.4	15.2
L –Zn $SO_4.H_2O$	17.2	17	17.8	17
L – Pd Cl_2	12.8	12.6	13	13
L – Cd $Cl_2.H_2O$	14.4	13.6	14.8	13.8
L – Hg $Cl_2.H_2O$	17.6	16.6	18	17.2
L–Pb $(NO_3)_2.H_2O$	17.2	16	17.4	16

Table (7)

Effect of ligand and its complexes on gram negative bacteria.

Compound	***Diameter of inhibition zone (mm)at concentration 1mg|ml***		***Diameter of inhibition zone (mm)at concentration 5mg|ml***	
	Streptococcus pyogenes	***Staphylococcus aureus***	***Streptococcus pyogenes***	***Staphylococcus aureus***
Amoxicilin	27.4	27	29.2	28.6
(L) C18 H18 N4	14.8	14.6	15.2	14.8
L – Cr Cl_3	13.6	12.8	14	13
L – Co $Cl_2.H_2O$	12.6	12.4	13	12.6
L – Ni $Cl_2.H_2O$	17.2	17	17.4	17
L –Cu $SO_4.H_2O$	14.4	14	14.6	14
L –Zn $SO_4.H_2O$	16.6	16	17.2	16.4
L – Pd Cl_2	13.4	12.6	13.6	12.8
L – Cd $Cl_2.H_2O$	13.8	13.6	13.8	13.8
L – Hg $Cl_2.H_2O$	18.2	17.6	18.8	17.8
L–Pb $(NO_3)_2.H_2O$	18	17.4	18	17.6

Table (8)

Effect of ligand and its complexes on Candida albicans.

Compound	***Diameter of inhibition zone (mm)at concentration 1mg|ml***	***Diameter of inhibition zone (mm)at concentration 5mg|ml***
Nystatin	15.6	18.4
(L) C18 H18 N4	13.6	13.8
L – Cr Cl_3	10.2	10.8
L – Co $Cl_2.H_2O$	9.8	10.2
L – Ni $Cl_2.H_2O$	10.4	10.4
L –Cu $SO_4.H_2O$	12.4	12.4
L –Zn $SO_4.H_2O$	11.8	12
L – Pd Cl_2	10	10.4
L – Cd $Cl_2.H_2O$	10.2	10.2
L – Hg $Cl_2.H_2O$	14.8	15.6
L–Pb $(NO_3)_2.H_2O$	9.8	10

References

[1] H. H. Fox and J. T.Gibas, "pyridine carboylic acid Hydrazides and Benzoic Acid Hydrazides", J. organic chem. Easton, 17, 5, 1953, 1653 – 1660.

[2] S.Prasad and R. K.Agarwal, "synthesis physico–chemical and Biological properties of complexes of cobalt (II) Derived from Hydrazones of Isonicotinic Acid Hydrazide", J. Inorg. Chem, 1, 1, 2008, 17–26.

[3] S. Prasad and R. K.Agarwal, "Isonicotinic Acid Hydrazide and Hydrazone", J. of the Korean chem., soc, 53,1, 2009, 26 – 35.

[4] C.C.William, C. J.Lockhart, and F. H. Musa, "Preparation and complexation of polydentate and macrocyclic ligands incorporating benzimidazol.X-ray Crysdtal Structure of 6,7,9,10,12,13,16

octahydro 23H, 25H bis – (benzimidazol [1,2 –j:2,1` – 0]) [1,4,7,13,10,16 tetraoxdciazacyclo– octa – decine", J. Chem. Soc, Dalton Trans, 1, 47, 1986, 53-60.

[5] F. H. Musa, A. A.AL-Rawi and B. M.Serhan, "Synthesis biological activities studies of leucine–o–Acetic acid and its complexes", Iraq. J. chem., 1, 22, 1997, 197–207.

[6] F. H.Musa and I. A. Othman, "Synthesis of 5–phenyl – 1,3, 4 – oxadiazo – 2 – thioderivatives and their reactions with some transition metal salts", J–IBN – AL – Haitham for pure and appl, 9, 11,1998, 85 – 87.

[7] F. H. Musa, H. A. AL – Bayti, and I. A. Othman, "Synthesis, characterization of chrom(III),cobalt (II), Nickel(II), Copper(II) and Palladium (II) complexes with 4,5 – Diphenyl 1,2,4 – Trizole – 2yl thio Acetic acid (TRBAC) and 4,5 – Diphenyl – 3 – Benzyl thio 1,2,4 Triazol (TRBZ)", Iraq. J. chem., 28, 24,2002, 507 – 513.

[8] H. A. AL – Bayti, I. A.Othman and F. H. Musa, "Synthesis and studies of Bis – [3,4 – Diphenyl 1,2,4 – Triazol – 5yl – thio] methane and its complexes with Cr(III), Co(II), Cu(II), Pd(II) and Pt(II)", Iraq. J. chem., 28, 11, 2002, 501 – 505.

[9] F. H. Musa, "preparation and characterization of Dioxadiazol and Ditriazol complexes with Divalent; Co, Ni Cu, Zn and Hg", Iraq. J. chem., 24, 5, 1998, 239 – 245.

[10] S. H. Naji, H. A. Fathel, and F. H. Musa, "Synthesis, characterization of some metal salts with 1, 1` bis – (orthoaminophenylthio) – methane", J. Al–Mustansiriya. sci., 19, 12, 2008, 59 – 62.

[11] S. H. Naji, "Synthesis and spectral studies of the transition metals(Co(II), Ni(II), Cu(II), Cd(II), Hg(II), Pb(II) with aniline – 2–thio methylene chloride complexes", J. Al–Mustansiriya. sci,19,11, 2008, 53 – 56.

[12] H. A. Mohammed, F. H. Musa and A.I. Abdullah,"Synthesis and studies of 1`,2`- bis (5`` - 2`` thiol ethylsulphide – 1,3,4 – oxadiazole – 2yl) Ethane and its complexes with (M(II), Cu, Ni, Co, Hg", J. Rof. Sci, 20, 9,2002, 75 – 89.

[13] A. N. Gursoy and T. G. Otuk, "Synthesis of new hydrazides –hydrazones, thiosemicarbazides and thiazolidines as possible antimicrobials Eur", J. Med. Chem, 32, 11, 1997,753 – 759.

[14] N. K. Dodoff, M. O. Grancharov and N.M. Spassovska, "Platinum (II) complexes of 4– methoxy and 4– chlorobenzoic Acid Hydrazides synthesis, characterization and cytotoxic effect", J. Inorg.Biochem, 60, 5, 1995, 257 – 266.

[15] S. Tabakova and N. Dodoff, "Effect of Platinum (II) complexes of Benzoic and 3 – methoxy benzoic acid Hydrazides on saccharomyces cerevisae z", Naturforsch, 50, 6, 1995, 34 – 734.

[16] D. G. Rand, D. M. Sato, L. M. signera, A. F. Malvezz, C. Q. Leite, A.G. Amaral, E. I. Ferreira and L.D. Tavaves,"potential Tuberculostatic Agent. Topliss Application on Benzoic acid [(s – Nitrothiophen – 2 – yl) – Methylene] – hydrazide series",Bio.organic and Med. Chem, 10,12,2002,557 – 560.

[17] M. G. Mamolo, D. V. Falagiani, O. L. Zamper and E. W.Banfi, "Synthesis and antimicrobacterial activity of [5 – (pyridine – 2 yl) – 1,3,4 – thiadiazole – 2 – yl thio] acetic acid arylidene hydrazide derivatives", Farmaco, 56,17, 2001, 580 – 592.

[18] S. Rollas, N. N. Gulerman, and H.F.Erdenz, "Synthesis and antimicrobial activity of some new hydrozones of 4. flourobenzoic acid hydrazide and 3 – acetyl – 2, 5 – disubstituted – 1, 3, 4 – oxa diazolines", Farmaco, 57, 7,2002, 171 – 174.

[19] M. N. Keeton and A.B.Lever,"Four, Five, and Six coordinate metalcomplexes of di(2 pyridyl) disulphide and 1, 2 –di (2` – pyridyl) ethane", Inorg. Chem, 10,5, 1971, 49 – 52.

[20] N. J. AL – Obadi, K. K. Abid and Y. J. AL – Naimi, "Transition metal complexes of 2 –(thiosemicarbazino) – 5 –(o–hydroxyl phenyl) – 1,3,4 – oxadiazole", J. Tikrit.sci, 11, 24, 2006, 164, 167.

[21] B. G. Saha and S. K.Banerji, "Synthesis and characterization of complexes", J. Indian Chem., Soc, 1, 5, 1982, 928 – 932.

[22] S.C. Bahel, "Synthesis and structural studies of complexes of Zn(II),Ni(II),and Co(II) with 3 – Aryloxymethyl 4 – aryl – 5 mercapto–1, 2, 4 – triazoles", J. Indian, 1, 3, 1982,1127 – 1135.

[23] M. F.Iskender, L.El –Sayed, A. F. Hefny and S. E. Zayan, "structural studies of some metal ions", J. Inorg chem, 38, 1, 1976, 13 – 19.

[24] S. C. Behei, D. N. Nath and J. K.Srivasava, "Synthesis and structural studies of the complexes of Zn(II),Ni(II),Cu(II) and Co(II)with3–Aryloxmethyl – 4 – aryl – 5 mercapto – 1,2,4 – triazoles", J. Indian chem, 1, 5, 1982, 1127 – 1135.

[25] W.G:Greay.,"Coordination Chemistry reviews", Elsevier publishing company, Amsterdam,1970, 112 – 115.

[26] R. J. Clark and W. R. Errington, "Sulpher donor complexes", Inorg. chem, 5, 2,650–660.

[27] W. N. Kadeoka, "Crystal and Molecular structure of Dichloro bis (2 – pyridyl) disulphide cobalt (II)", Inorg Chem, 15, 12, 1976, 812 – 820.

[28] J. C: Foresman and C, A: Frisch., "Exploring chem, With Elecronic structure methods", Gaussian – Inc, Pittsuburgh, 1996,101.

[29] W. K.Rudolph, "Mixed chelates from thio picolinamides and β – diketones", Inorg Chem, 4, 11, 1965, 1047 – 1055.

[30] A. A. El – Asmy, "Structural studies on Cd(II), Co(II),Cu (II),Ni (II) and Zn(II) complexes of 1 – malonyl –bis(4-phenyl thio semicarbazide)", Transition Met. Chem, 4, 5, 1990, 12 – 20.

[31] D.L: Sutton., "Electronic spectra of Transition metal complexes",Mc Graw–Hill, London,1968, 138.

[32] M. R. Gajendragad and U.A.Agarwula, "synthesis and characterization of complexes", J. Inorg Nucl. chem., 37, 11, 1975, 29 – 35.

[33] B. N: Figgis and J.N: Lewis., "Modern coordination chemistry", eddited by Lewis and wilkins R.G. Interscience, New York, 1967, 403.

[34] S. N. Dubey and B. N.kaushik, "Triazoles copmplexing Agent", Indian J.Chem, 24, 8, 1985, 950-959.

[35] D. A: Skoog., "Fundamental of Analytical chemistry", Wiley Inter, New York, 1988, 2441.

الخلاصة

حضر الليكاند (L) 2 ، $2^{/}$ – ثنائي امينو – N – فنيل هيدرازو بنزين (L) من تفاعل اورثو امينو هيدرازو بنزين مع اورثو امينو فنيل ثايول وبنسبة 1:1 وشخص بواسطة التقنيات تحليل العناصر (N, H,C), الأشعة تحت الحمراء والاشعة فوق البنفسجية – المرئية كما حضرت وشخصت معقدات أملاح بعض ايونات العناصر الثنائية التكافؤ Hg,Cd, Pd, (Pb ,Zn, Cu,Ni, Co) والثلاثي التكافؤ (Cr) استخدمت تقنيات طيف الاشعة تحت الحمراء,الأشعة فوق البنفسجية– المرئية, التوصيلية الكهربائية, الامتصاصية الذرية والخواص المغناطيسية واستنتج من التحاليل ان المعقدات لها شكل ثماني السطوح حول ايون الفلز مع الليكاند (L) ثلاثي السن (N, N, N) ماعدا Pd معطيا الشكل ثنائي الهرم مثلثي.وقد تم حساب قيم kf,α ، Єmax للمعقدات وحساب β لمعقد الكوبلت.كما تم دراسة الفعالية البايولجية لليكاند ومعقداته وقد أظهرت النتائج امتلاكها فعالية متباينة اتجاه,

Staphylococcus, Pseudomonas aeruginosa, E. coli, Streptococcus pyogenes, aureus, Candida albicans.

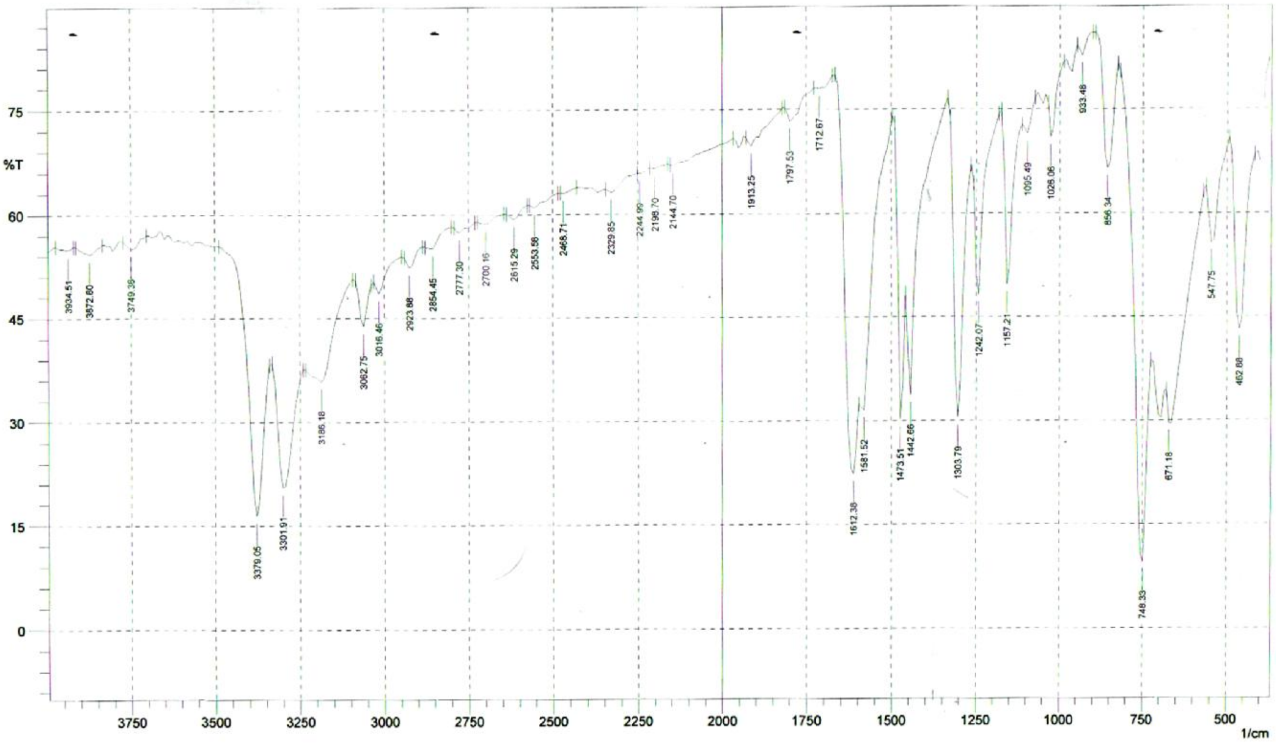


Fig.(1a) Infrared spectra of Ligand (L).

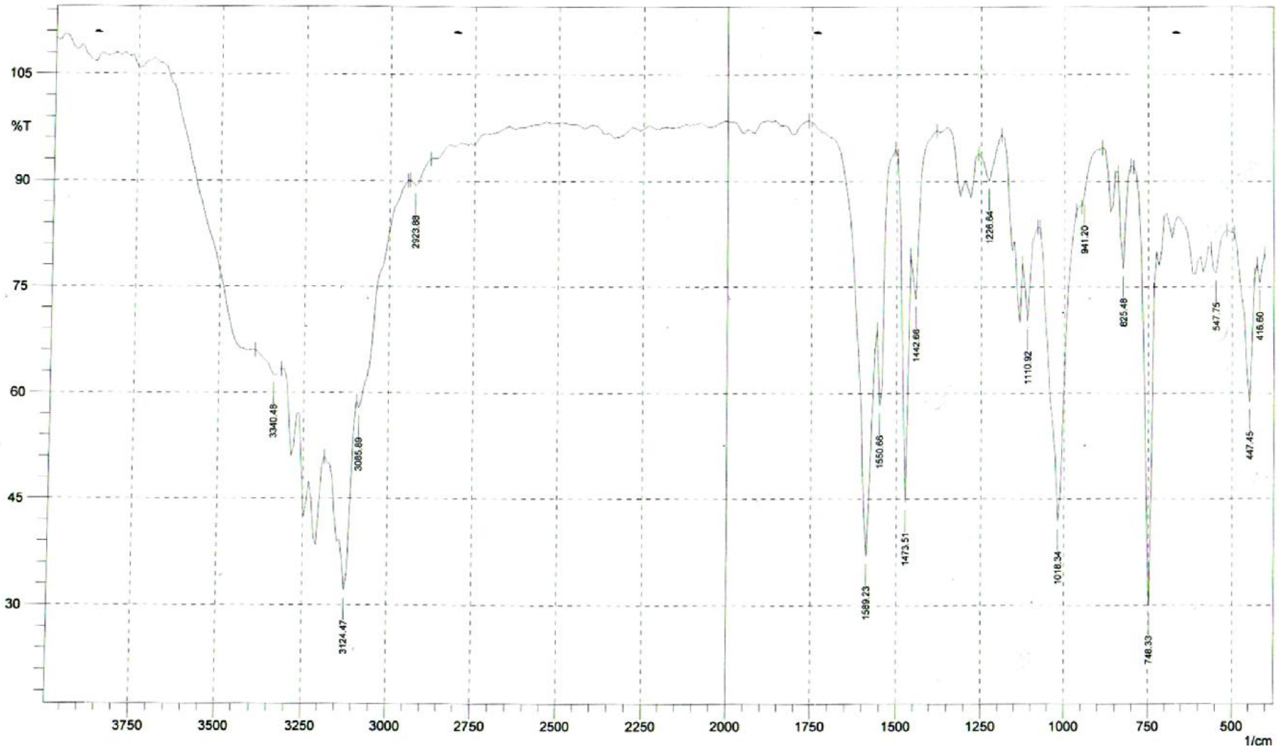


Fig.(1b) Infrared spectra of L.NiCl$_2$.H$_2$O.

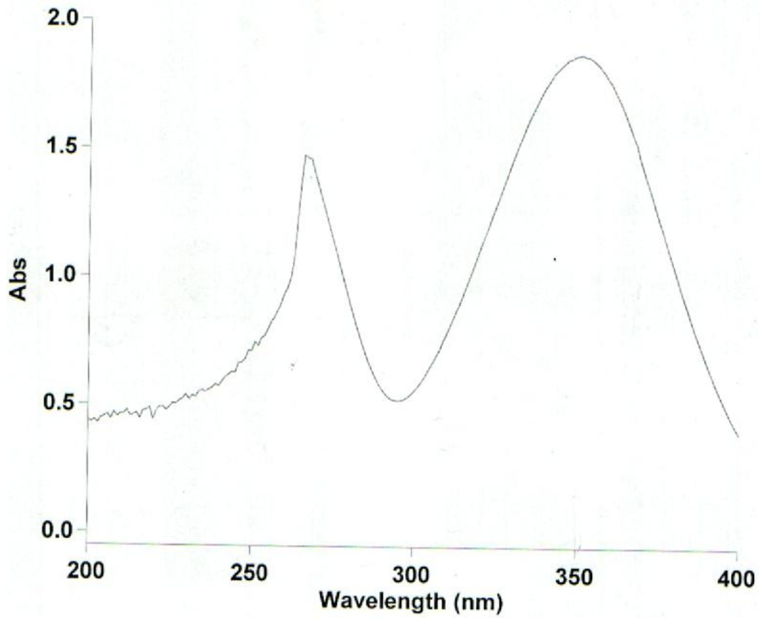


Fig.(2a) UV-visible spectra of Ligand (L).

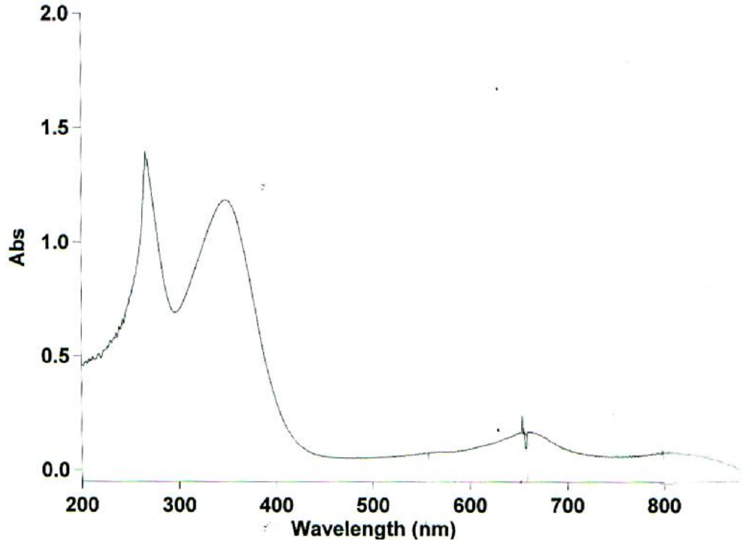


Fig.(2b) UV-Visible spectra of L.$CoCl_2.H_2O$.

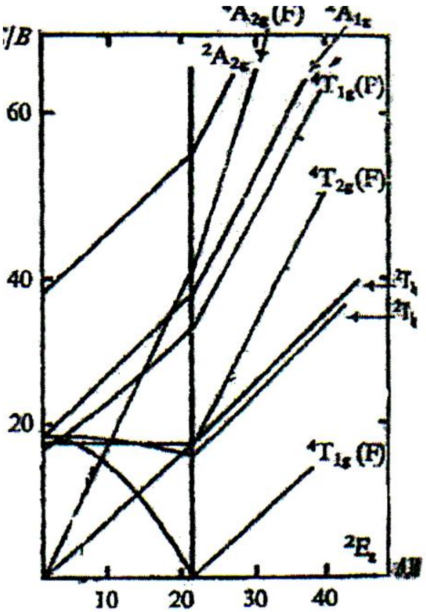


Fig.(3) Tanabe-Sugano diagram for the Co^{+2} ion in octahedral complexes.