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Coordination of (Oxazepine, Triazol ,Azitidine)–Ligands with (Cd^{2+}) and Studying of its Properties

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Abstract
The aim of this work , preparation of series ligands (five ligands) such as (Schiff base , oxazepine , triazol , azitidine) and optimal studying of conditions for its coordination with cadmium ion , other measurements were carried out in this studying. The five ligands and their coordination with cadmium ion were characterization by spectral studies such as{FT.IR–spectra **,** ^{1}H.NMR-spectra **,** UV.Vis –spectra} , and physical studies such as { molar conductance **.,** effect of polarity series solvents **.,**melting point } , and **.,** determination of optimal conditions of complexes . From results , the ligands behave as tridentate donor ligands forming chelates with (1:2) (Cd**:** ligand) stoichiometry .
Keywords : stok , point, tri .

1.Introduction

Most studies on metal Azo- complexes have been limited to those containing one azo or azomethine group per molecule of ligand or some time two groups in same ligand . An exception is the work reported on the spectroscopic properties of deprotonated Cd(II) complex of some Azo ligands containing two donator groups like (OH , Azo , or Azomethine) per molecule , the chemical attempts to design & synthesize analytical reagents as a ligands which will benefit in coordination with transition metals **(**Duvall et al 2002**,** Nishida et al 2009**)** . Azo ligands are very widely distributed in coordination chemistry and in many applications .Metal complexes of azo ligands have been studied extensively in recent years due to the sensitivity of these ligands **(** Saviklie et al 2005 **,** Nagham 2014 **,** Huda 2014 **)** towards most of metals (Nagham et al 2014) . It is well known from the literature that azo ligands containing heterocycles have biological activity as antibacterial , antifungal , antitumor , and other applications as an effective corrosion inhibitor , applications in synthesis of polymers & in other fields (Aded et al 2014 , Narjis et al 2011 , Adnan et al 2014) .

2.Experimental

Melting points were recorded on Gallenkamp melting point apparatus and were uncorrected . FT-IR spectra were recorded by using (FT-IR 8300 Shimadzu) in the range (400-4000) cm-1 as KBr discs . UV-Vis spectra for the compounds were measured in the region (200-900) nm for 10^{-3}M solution in DMSO by using VARIAN 100 conc uv-vis, **^{1}H.NMR**–spectra in DMSO–solvent were carried out in Kashan University , , and physical properties such as : **Molar conductance** in DMSO–solvent .

3. Preparation of Ligand 1

The ligand 1 was prepared according to papers (Nagham 2014 , Nagham et al 2014) .,2-amino thiazole (0.01mole) was dissolved in (3ml) of hydrochloric acid with solution of (0.64gm) sodium nitrite at temperature (0-5)C^{o} ,after that, ethanolic solution of p-formal phenol (0.01mole) was added ,after (48hrs) ,the precipitate was filtered and dried to give (88%) of azo ligand .

4. Preparation of Ligand 2

The ligand 2 was prepared according to papers (Nagham 2014 , Nagham et al 2014) ., (001 mole) of ligand 1 refluxed with P-nitro aniline for (3hrs) ,the precipitate was filtered and dried to give (80%) of azo – azomethine ligand .

5. Preparation of Ligand 3

The ligand 3 was prepared according to papers (0.01mole) from ligand2 refluxed with (0.01mole) of maleic anhydride in presence of dioxin (60ml) for (6 hrs)., the precipitate was filtered and dried , re crystallized to give (80 %) .

6. Preparation of Ligand 4

The ligand 4 was prepared according to procedure (Nagham 2014 , Nagham et al 2014) .,(0.01mole) from ligand3 was reacted with sodium azide (0.01mole) in presence of (60ml) of tetrahydrofuran with refluxing for (7hrs) ,the precipitate was filtered and dried , re crystallized from dioxan to give (78)% .

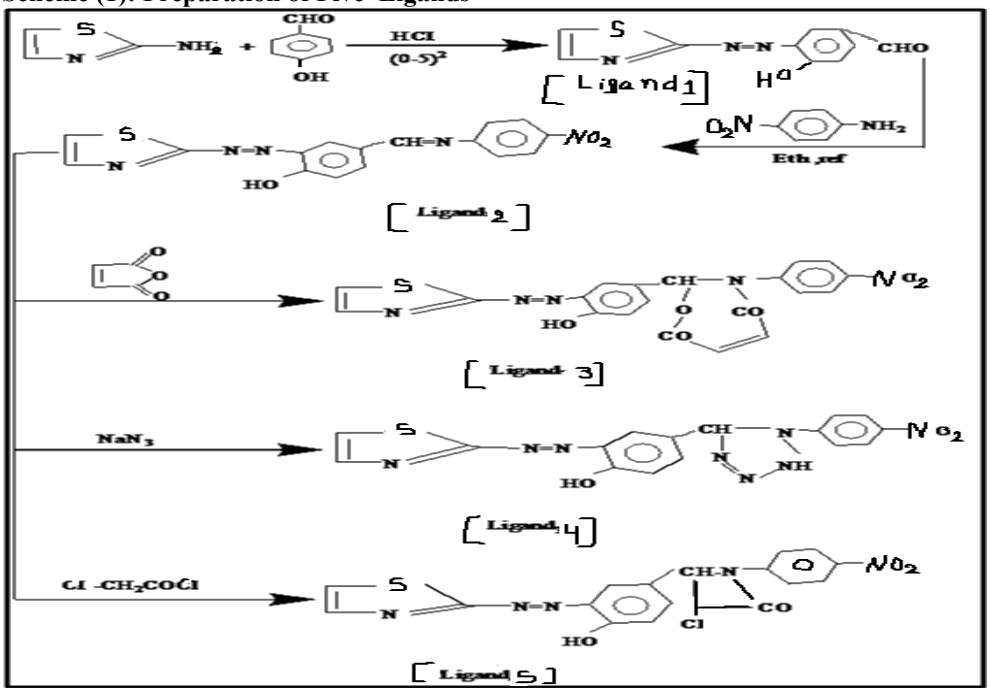
7. Preparation of Ligand 5

The ligand 5 was prepared according to procedure (Nagham 2014 , Nagham et al 2014) ., (0.01mole) from ligand4 reacted with (0.01mole) of chloro acetyl chloride in presence of (60ml) dioxan with tri ethyl amine at (5)C^{o} ,the mixture was stirred for (2hrs) ,after that ,the precipitate was filtered and dried to yield (76%).

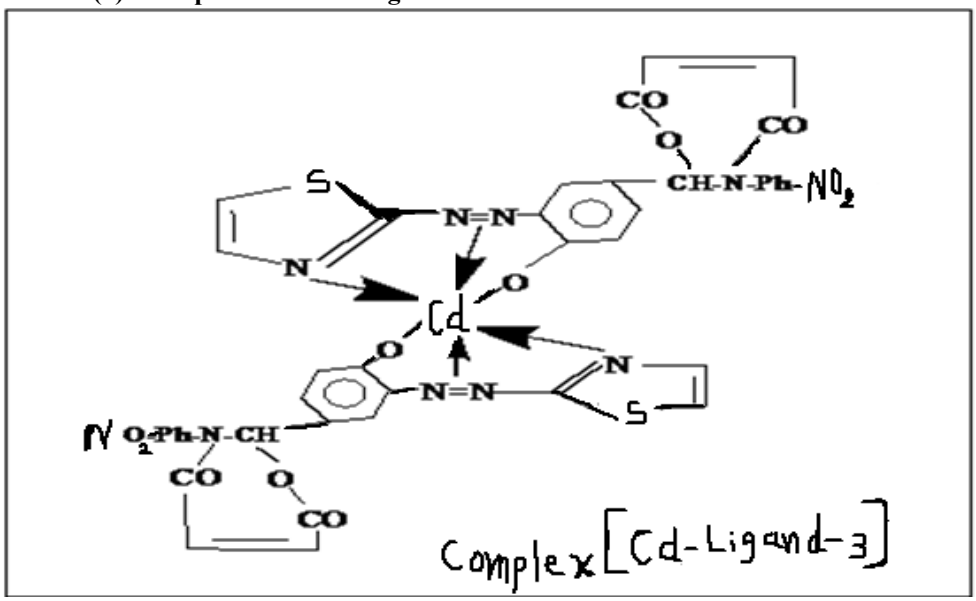
8. Complexation of Some Ligands with (Cd^{2+})

The complexation of Ligands were carried out according to procedure (Nagham 2014 , Nagham et al 2014) ., the hot solution of three ligands respectively were added to solution of cadmium salt ($CdCl_2$. $2H_2O$) in mole ratio (metal: ligand) (1:2) for all complexes ., after stirring (1hrs) ,the precipitates were precipitated ,dried and re crystallized to yield (84-80)% respectively of complexes .

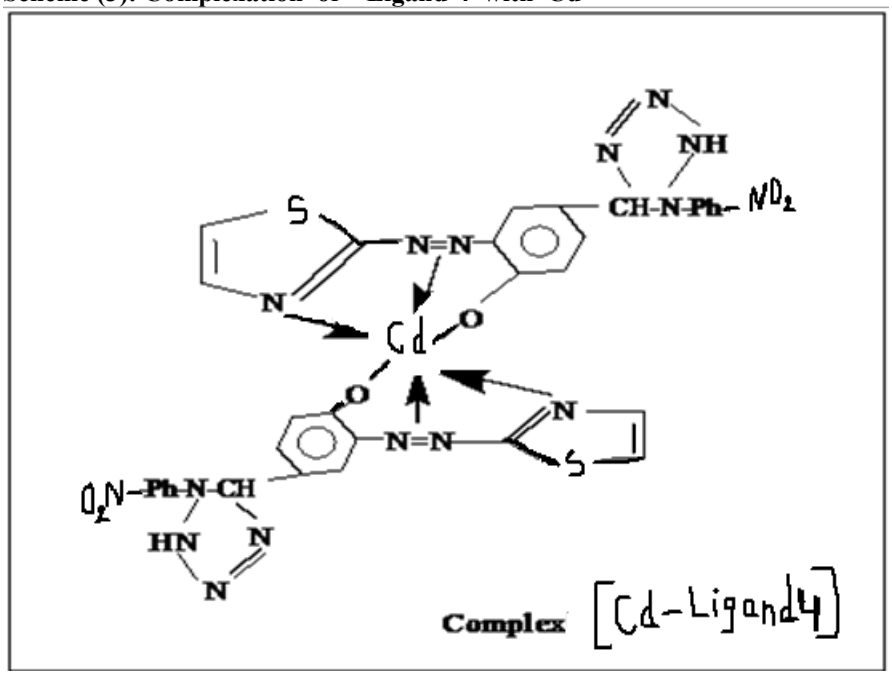
Scheme (1): Preparation of Five Ligands



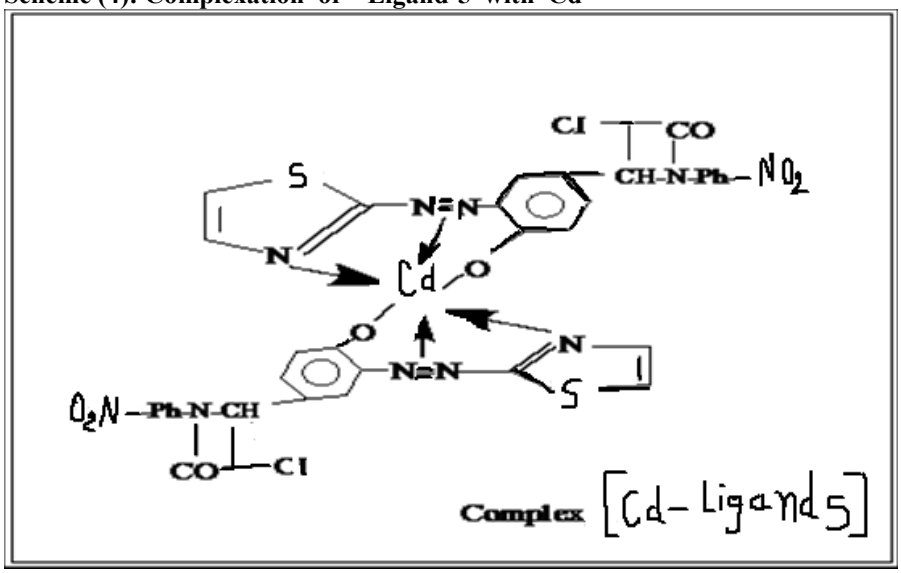
Scheme (2): Complexation of Ligand-3 with Cd^{2+}



Scheme (3): Complexation of Ligand-4 with Cd^{2+}



Scheme (4): Complexation of Ligand-5 with Cd^{2+}



8. Results and Discussion

Various ligands (oxazepine ,triazol ,azitidine)were prepared in this studying , and three complexes with (Cd^{2+}), Identification by many techniques and studying of optimal conditions of complexation :

8.1. Optimal Conditions of Complexation Method

Determination of optimal factors for complexation of ligands with metal ion like calibration curves of optimal concentration of (Cd^{2+} =0.80 x10^{-4}M), while concentration of ligands [0.20x10^{-3}M of **ligand3** , 0.40x10^{-3}M of **ligand4** .,0.40x10^{-3}M of **ligand5**] .,while the studying of optimal pH of complexes are [pH=8.5 for all ligands] ., the stochiometric of complexes in mole ratio method gave (M:L) ratio (1:2) for all complexes., and other chemical and physical studies of complexes in Table (1) and figures (1-5).

8.2. Some physical measurements

Some physical properties were measured such as melting point and chemical identification UV-Visible ,Table (1).All results ((mole ratio ,calibration curve , stoichiometry ,chemical spectra) indicate that the Cd- complexes with all ligands were stoichiometry

(metal **:** ligand) (1:2) .

8.3.The conductivity :

Table (1) showed all result of conductivity measurements which were (1.02 -1.96) $ohm^{-1}.mole^{-1}.cm^2$ of ($1x10^{-3}$M) solution in (DMSO) which indicates that the (Cd - complexes) are non-electrolytic in nature .

Table (1) : physical properties of Ligands with Complexes.

Ligands and Complexes	M.P (C^o)	λmax	Ω$ohm^{-1}.Cm^2.mole^{-1}$ conductance
Ligand1	162	364	/
Ligand2	180	376	/
Ligand3	198	384	/
Ligand4	204	396	/
Ligand5	194	398	/
[Cd(L3)$_2$]	234	432	1.35
[Cd(L4)$_2$]	244	430	1.02
[Cd(L5)$_2$]	238	446	1.96

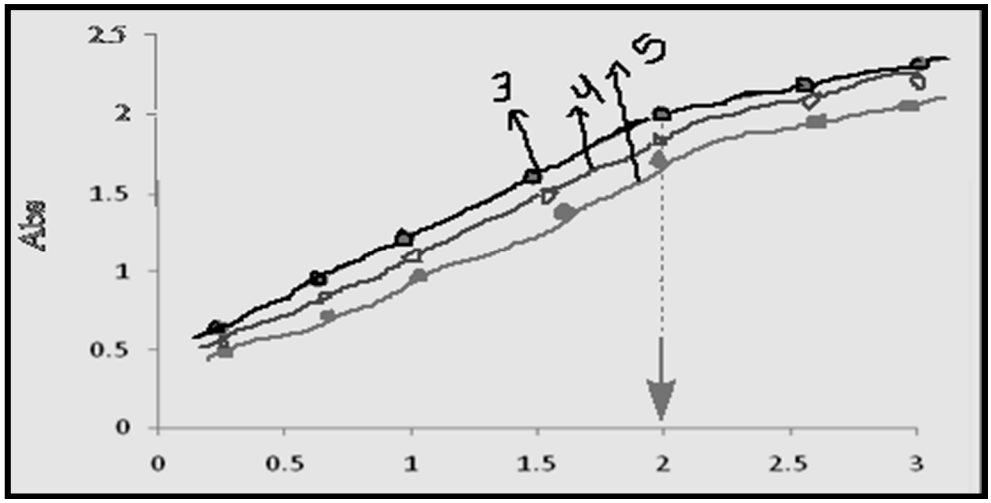
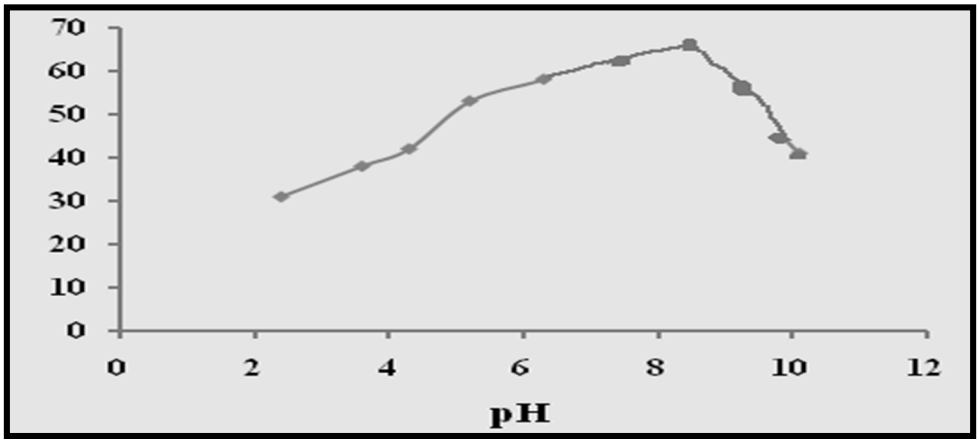


Fig (1) : Mole ratio of all Complexes [Cd(L)$_2$]



Fig(2): Optimal PH of Complexes

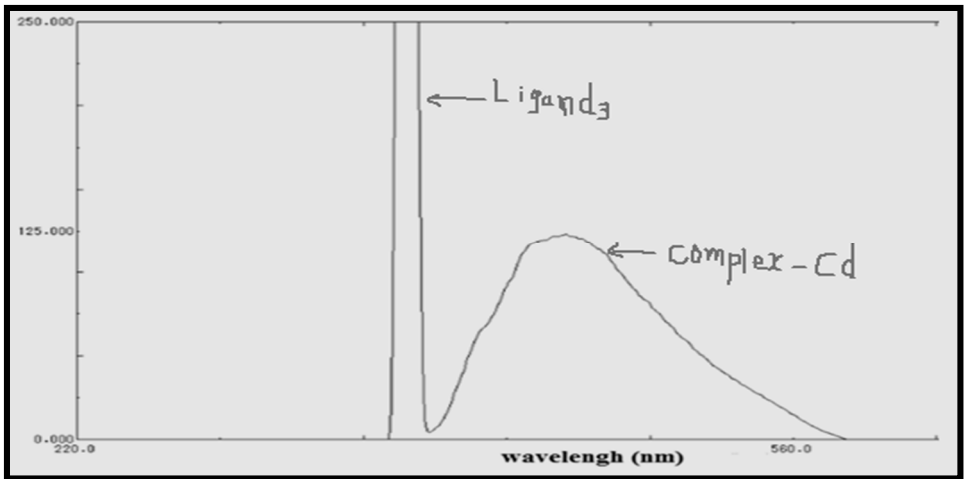


Fig (3): UV-Vis Spectrum of Ligand3 with complex

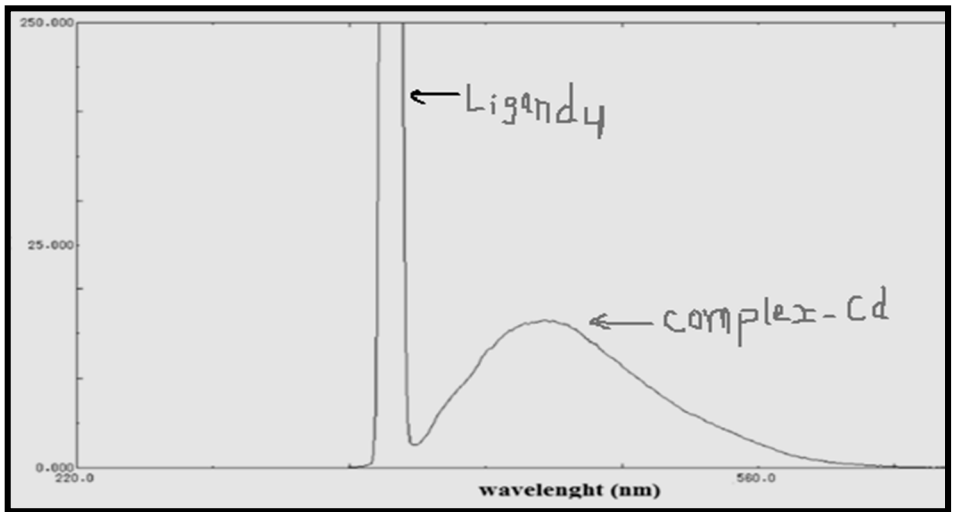


Fig (4): UV-Vis Spectrum of Ligand4 with complex

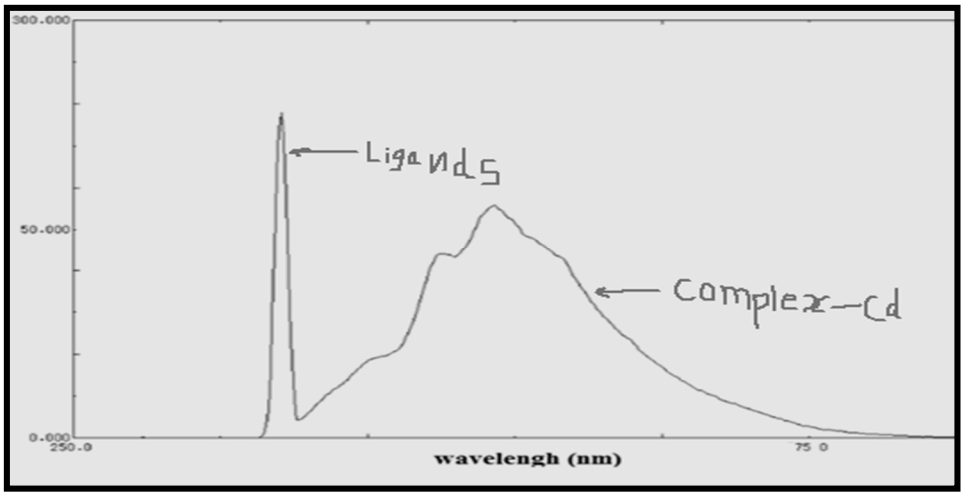


Fig (5): UV-Vis Spectrum of Ligand5 with complex

8.4.Studying of FT.IR- spectra :shown absorption bands in all ligands at (3455-3380)cm^{-1} due to hydroxyl group (OH) of phenol ring in free ligands which disappeared in spectra of their complexes and other bands appeared such as [(460-498) cm^{-1} and (510-586)cm^{-1}] due to [(M-N) and (M-O)] respectively in complexes as a result of coordination with lead ion (II) .,other bands at (1444-1492) cm^{-1} due to azo group (-N=N-) in all ligands which shifted towards lower frequency at (1413-1440) cm^{-1} respectively in their complexes .,other bands in table

(2) and figures (6-10).

Table (2) : FT.IR data (cm^{-1}) of ligands with complexes

Ligands & Complexes	(-N=N-) Azo	(OH)	(M-N)	(M-O)	Other groups
Ligand1	1464	3380	/	/	
Ligand2	1492	3455	/	/	(CH=N) :1628
Ligand3	1444	3450	/	/	(CO-O-)Lactone:1727, (CO-N-)lactam:1690 ,(=CH) alkene : 3090
Ligand4	1477	3400	/	/	(NH): 3254, (N=N-N):1276
Ligand5	1473	3472	/	/	(CO-N) :1687 ,(C-Cl) :782.
[Cd(L3)$_2$]	1413	/	498	510	(CO-O-)Lactone:1721, (CO-N-)lactam:1684, (=CH) alkene :3076
[Cd(L4)$_2$]	1440	/	460	541	(NH) :3216 ,(N=N-N): 1310
[Cd(L5)$_2$]	1432	/	452	586	(CO-N) :1686 ,(C-Cl) :766

Some figures of I.R - Spectra:

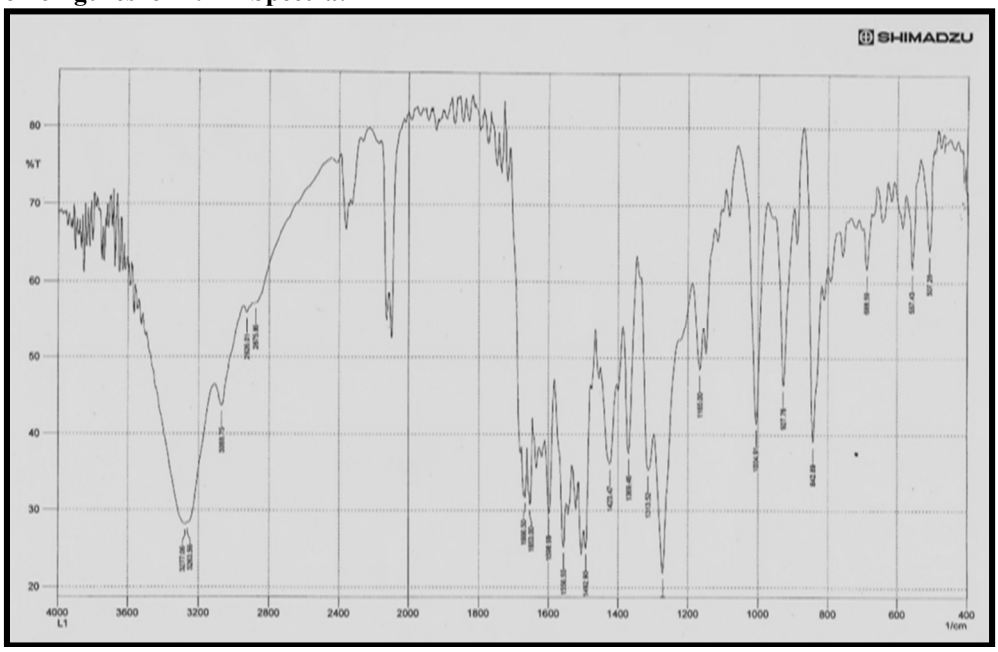


Fig (6): FT.IR of Ligand3

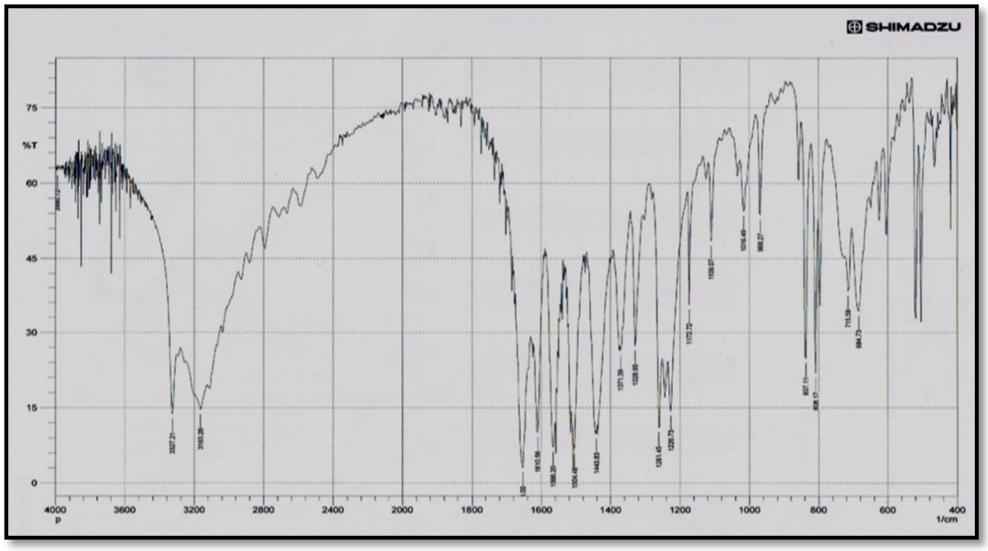


Fig (7): FT.IR of Ligand4

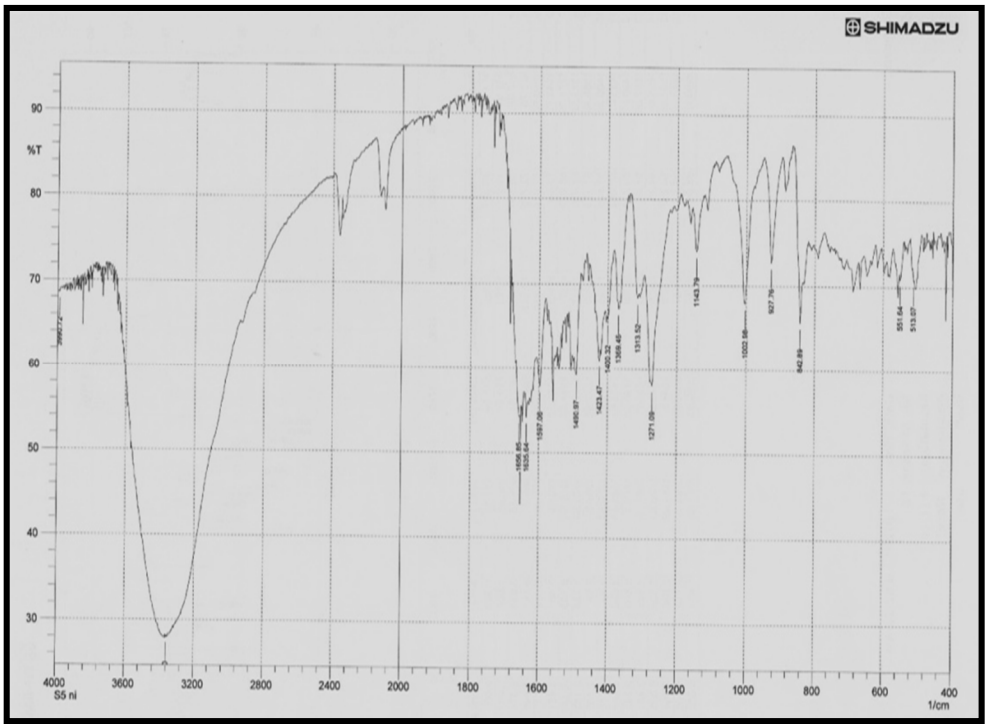


Fig (8): FT.IR of Ligand5

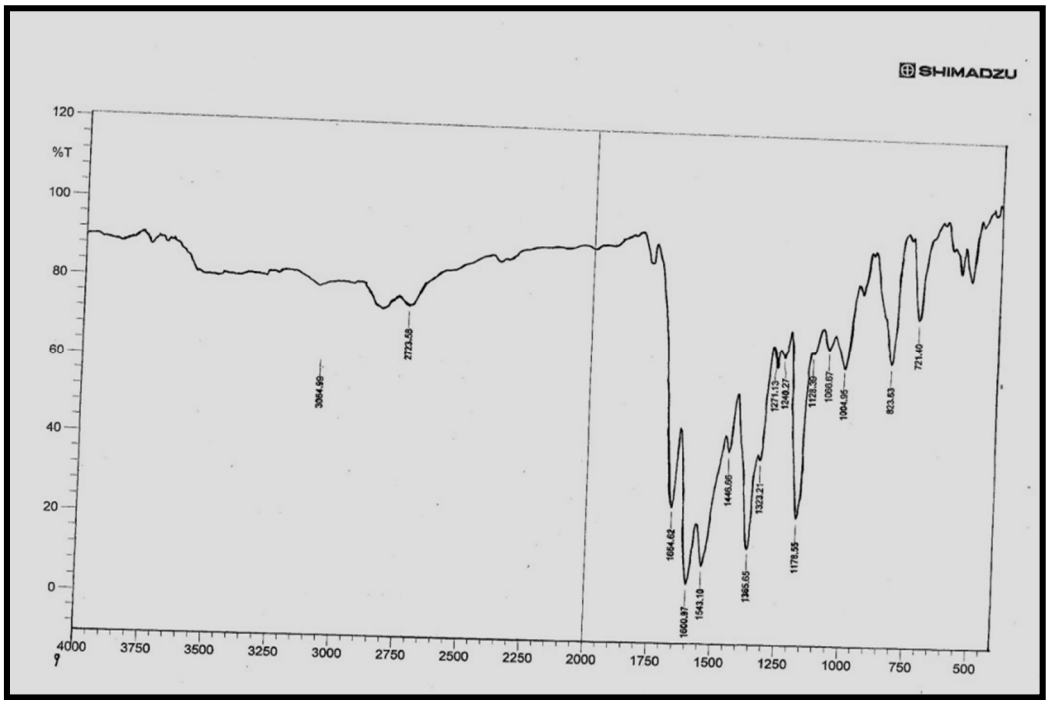


Fig (9): FT.IR of Complex of Ligand5- Cd

8.5.Studying of H.NMR- spectra :spectra of ligands showed signals at ***δ*** (11.40-11.91) for hydroxyl group (OH) in free ligands ., which disappeared in their complexes as a result of coordination with (Cd^{2+})., and other signals are shown in table (3) and some of figures **(**10 **,** 11**)** .

Table (3) : H.NMR data (δ ppm) of Ligands with Complexes .

Ligands & Complexes	(OH) phenol	Other groups ((only functional groups))
Ligand1	11.40	(-CHO-) proton of aldehyde : 12.53
Ligand2	11.31	8.63(CH=N) :proton of imine group.
Ligand3	11.91	3.54(O-CH-N) **.,** 4.00, 4.21(CO-CH=CH-CO)**.,**
Ligand4	11.66	3.08 (N-CH-N) ., 5.62 (NH) .
Ligand5	11.75	3.83 , 3.70 (N-CH-CH-Cl) .
[Cd(L3)$_2$]	/	3.00(O-CH-N) **.,** 3.96 , 3.98(CO-CH=CH-CO)
[Cd(L4)$_2$]	/	2.71 (N-CH-N) , 5.22 (NH) **.**
[Cd(L5)$_2$]	/	3.18 , 3.29 (N-CH-CH-Cl) **.,** **.**

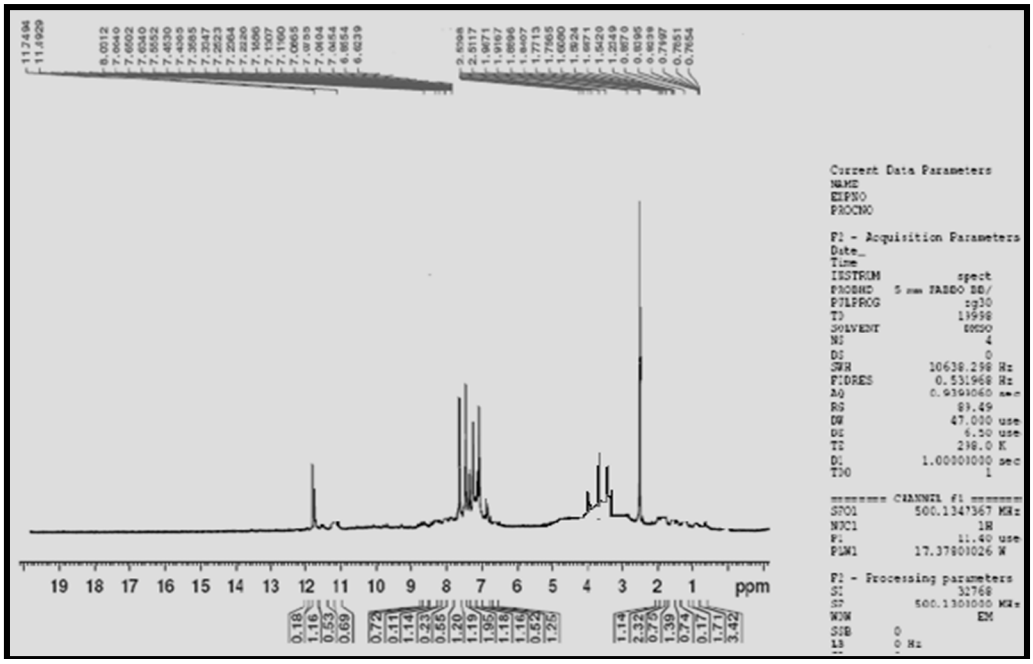


Fig (10): H.NMR of Ligand5

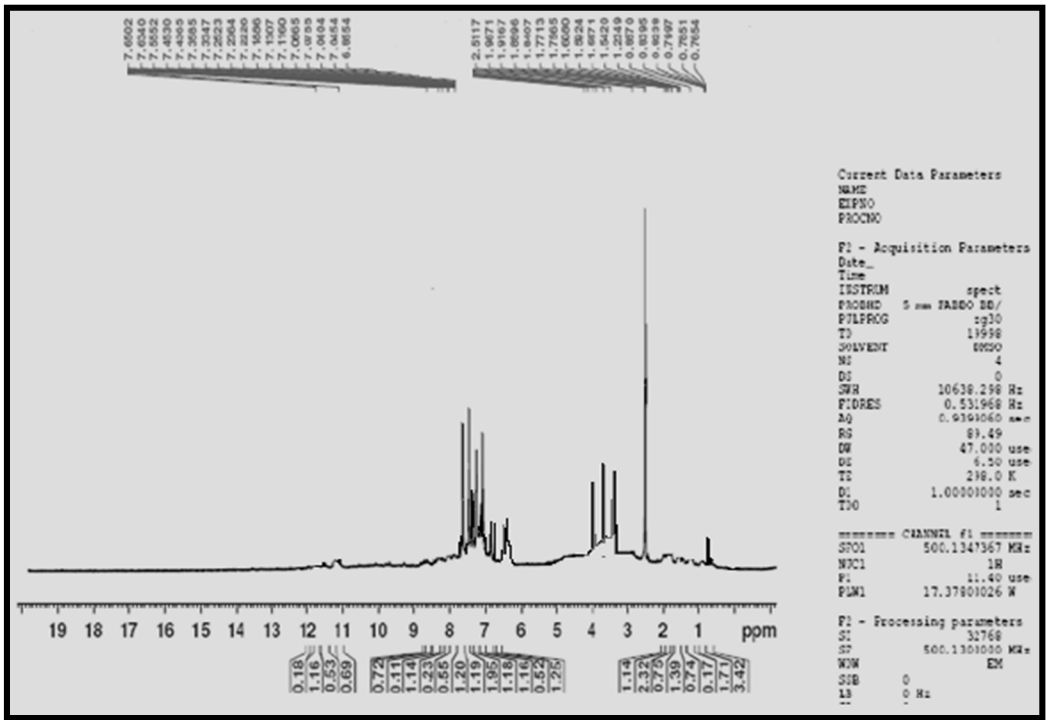


Fig (11): H.NMR of Complex [Cd (L5)$_2$]

8.6.Coordination of Ligands:

The results of studies showed that the ligands (**L3 ,L4 L5**) are tri dentate ,the coordination through nitrogen of azo group (-N=N-) and oxygen of hydroxyl group[4,8-11] with nitrogen atom of imidazole ring to give octahedral geometry (Six-coordination[4-11] complexes) in formula: (ML_2) .

8.7.Effect of different solvents in solubility of Ligands:

The solubility of all ligands was tested in series of solvents according to nature of solvents , the results are listed in table (4).

Table (4) : Solubility of ligands in Various Solvents.

Ligands	Solvents					
	Ethanol	Methanol	DMF	C_6H_6	1,4-Dioxan	THF
Ligand1	+	+	+	-	-	-
Ligand2	+	+	+	-	-	-
Ligand3	+	+	+	+	+	-
Ligand4	+	+	+	+	+	-
Ligand5	+	+	+	+	+	+

9. Conclusion

All studies in this work indicate that the ligands are tri dentate ,the coordination through nitrogen of azo group (-N=N-) and oxygen of hydroxyl group give octahedral complexes) in formula: (ML_2) .

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