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SYNTHESIS OF LIGANDS FROM AMINO ACID AND STUDYING OF (SPECTRAL, COMPLEXATION, THERMAL, BIOLOGICAL) - APPLICATIONS

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ABSTRACT

The aim of this studying is preparation of three new inorganic ligands from amino acids with 2-formal thiazole in condensation reaction to formation anil compounds which has a wide applications in most of chemistry fields like as a reagents, ligands, polymers, monomers, liquid crystals, antimicrobial, anticancer, our new ligands with their complexes with cadmium ion studied through optimal conditions of complexes like (stoichiometric study, mole ratio, pH, concentration of metal, and ligands, molar conductance). All ligands with complexes were investigated by (UV-Vis spectra, FT.IR –spectra, H.NMR, melting points, Thermal Analysis, Biological activity).

KEYWORDS: Condition, Mole Ratio, Field

INTRODUCTION

Anil compounds derived from an amino acid and carbonyl compound are an special class of coordination ligands that coordinate to metal ions through nitrogen and have been studied extensively[1-3]. In anil derivatives, the (C=N) linkage is essential for biological activity, various derivatives from imine compounds have been reported to possess remarkable antimicrobial, antifungal, antitumor and ant malarial activities.

The biological activity, catalytic activity, analytical and organic applications [4-9] can be correlated to the structure of anil compounds and substituent group on it and the redox potential of the ion, the application of inorganic chemistry to medicine is a rapidly developing field, and novel therapeutic and diagnostic metal complexes are now having an impact on medicinal practice and in other fields [10-13]. The preparation of a new ligand was perhaps the most important step in the development of metal complexes which exhibit unique properties and novel reactivity. Since the electron donor and electron acceptor properties of the ligand, structural function groups and the position of the ligand in the coordination sphere together with the reactivity of coordination compounds may be the factor for different studies [14-16]. Various imine ligands containing more than one functional groups offer many practical advantages and unique structural environment for complication. The metal complexes of transition element with heterocyclic ligands, especially those containing nitrogen and sulphur have diverse applications in several fields including biology and ant herbicidal activities of anil ligands and its metal complexes are well known and get more attraction recently[17,25].

EXPERIMENTAL

Spectra of UV-Visible were measured on **(UV–Vis)–**spectrophotometer using 1cm quartz cells, **FT.IR**–spectra (4000-400 cm^{-1}) in KBr–disk were recorded on Shimadzu FT.IR 8400 Fourier, Transform infrared –spectrophotometer., **Molar conductance** (DMSO–solvent), **(H.NMR)-Spectra,** spectral studying for determination of optimal conditions for complication**, Thermal** Analysis, **Biological Activity** and **melting points** were measured by SMP 30 start, UK.

Synthesis of Ligand (L_1)

According to procedure [15], (0.01mole) of 2-formal thiazole refluxed with (0.01mole) of alanine with drops of glacial acetic acid in presence of absolute ethanol for (2 hrs), the precipitation was filtered and re crystallized to yield (78 %) of Ligand (L_1).

Synthesis of Ligand (L_2)

According to procedure [15], (0.01mole) of 2-formal thiazole refluxed with (0.01mole) of tryptophan with drops of glacial acetic acid in presence of absolute ethanol for (3 hrs), the precipitation was filtered and dried, then re crystallized to yield (72 %) of Ligand (L_2).

Synthesis of Ligand (L_3)

According to procedure [15], A mixture of (0.01mole) 2-formal thiazole refluxed with (0.01mole) of tyrosine with drops of glacial acetic acid in presence of absolute ethanol for (3 hrs),the precipitation was filtered and dried, then re crystallized to yield (80 %) of Ligand (L_3).

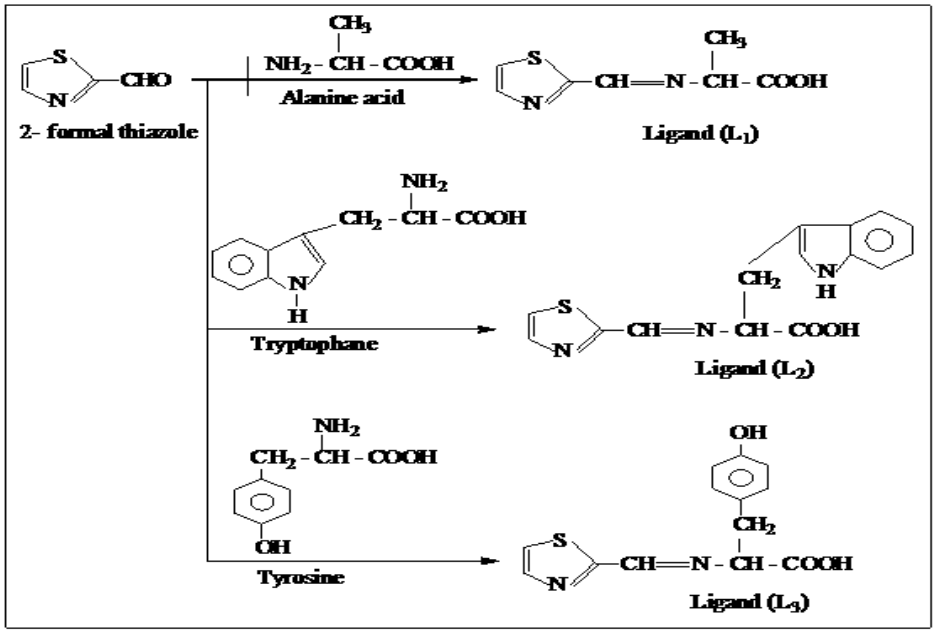

Figure: 1

Synthesis of Complexes

After determination the optimal conditions of each complex and, we prepared the complexes according to procedure[15],the complexes were synthesized through ethanolic solution of ligands [(L1),(L2),(L3)] respectively with ($CdCl_2$) salt respectively in mole ratio in (M:L) (1:2) with stirring for one hour, solid products formed, which was filtered and dried and re crystallized.

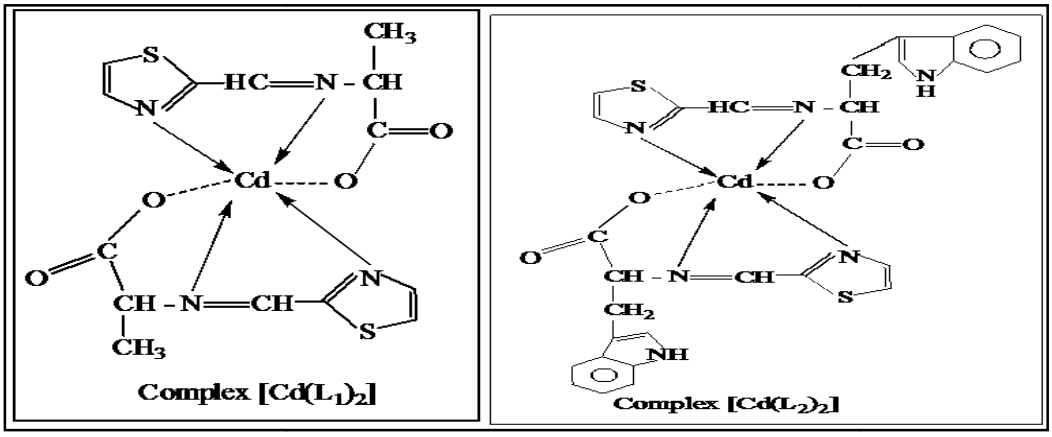

Figure: 2

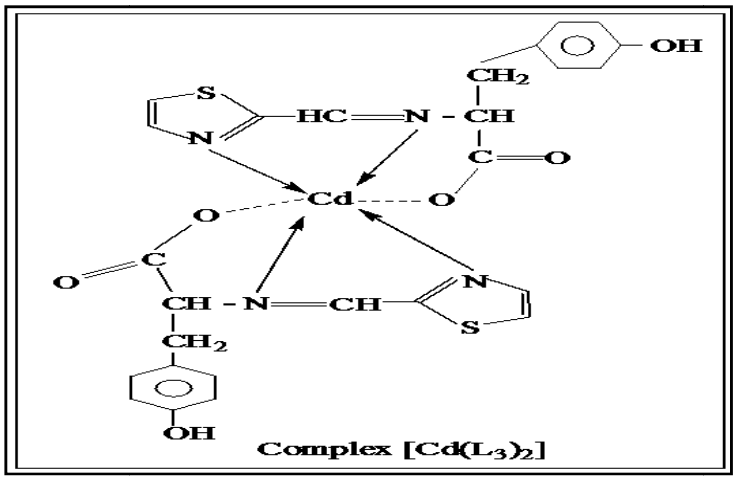

Figure: 3

RESULTS AND DISCUSSION

Studying of Optimal Condition of Complexation

The optimal conditions for preparation of complexes with Cd ion (II) were tested in this work from calibration curves, the optimal concentration of Ion (Cd^{2+}) ($0.8X10^{-4}$M) but ligands [($0.5X10^{-3}$M of(L_1)., $0.9X10^{-3}$M of(L_2)., $1X10^{-3}$M of (L_3)]., the maximum wave length shown in figures (1-3):

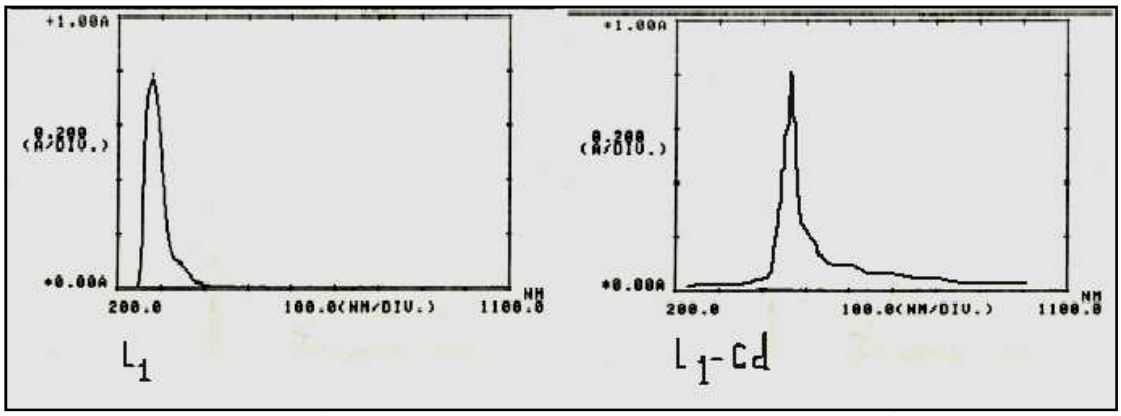

Figure 4: UV-Vis Spectrum of Ligand (L_1) and Complex

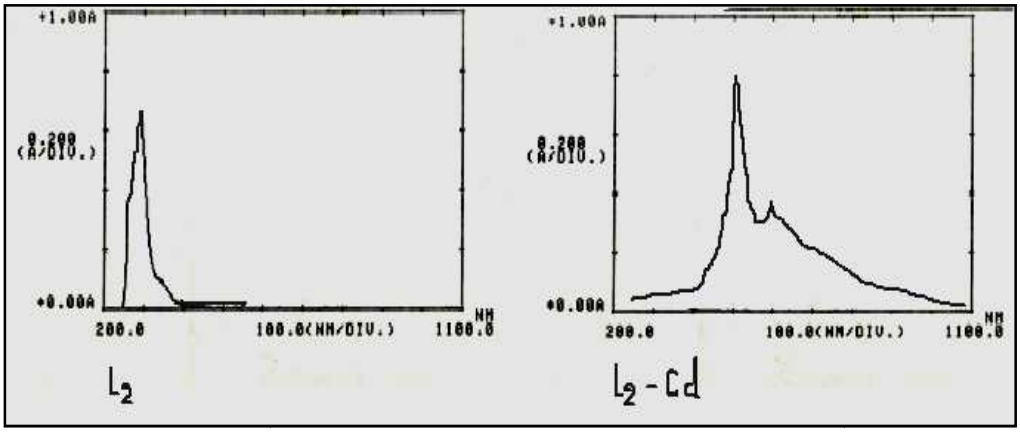

Figure 5: UV-Vis Spectrum of Ligand (L_2) and Complex

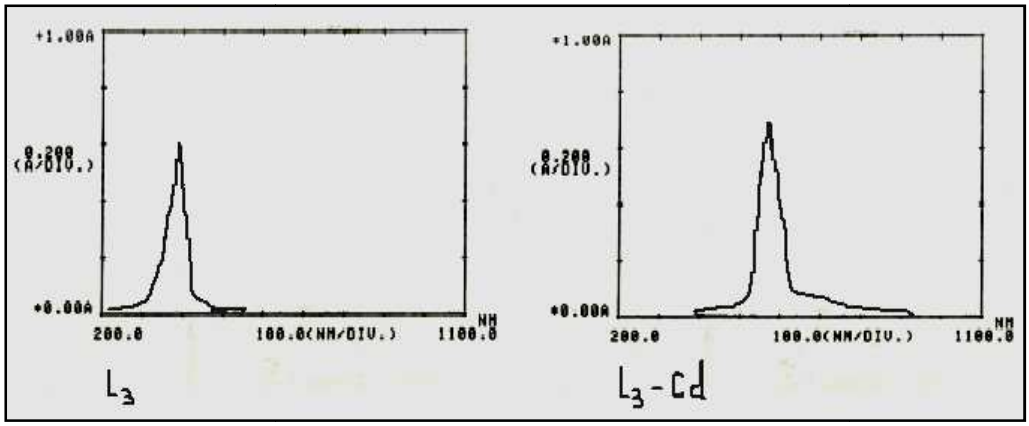

Figure 6: UV-Vis Spectrum of Ligand (L_3) and Complex

While optimal (PH=8.5) was base medium to formation of the three complexes., other studies represented by stoichiometric of complexes by Job method and mole ratio method through series of solutions were prepared having a constant concentration (10^{-3}M) of metal salt ($CdCl_2$) and ligands., the (M:L) ratio was determined from relationship between the absorption of observed light and mole ratio (M **:** L) found (1:2) for complexes of Cd with ligands. The studies of these complexes are appeared in Figures (4-6).The Table (1) indicates that the Cd –complexes [(L1), (L2),(L3)] have stoichiometry (M:L) (1:2) which appeared from results of mole ratio method and job method :

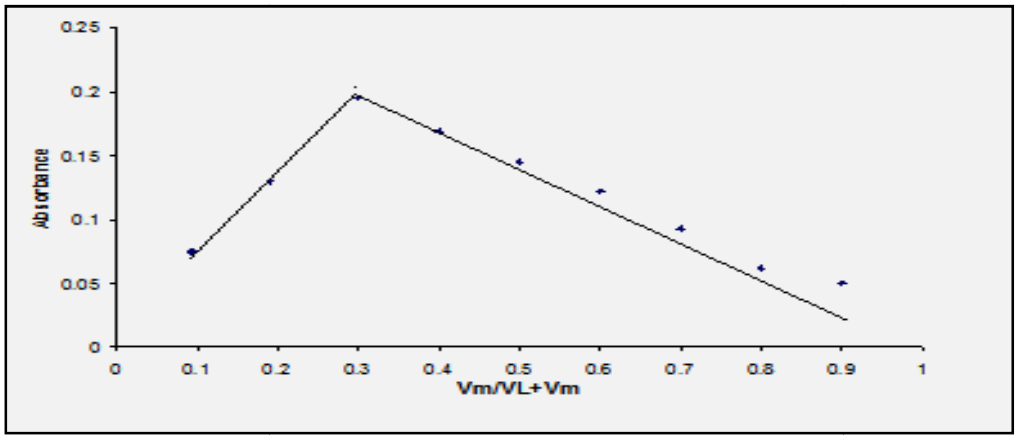

Figure 7: Job Method of Complexes

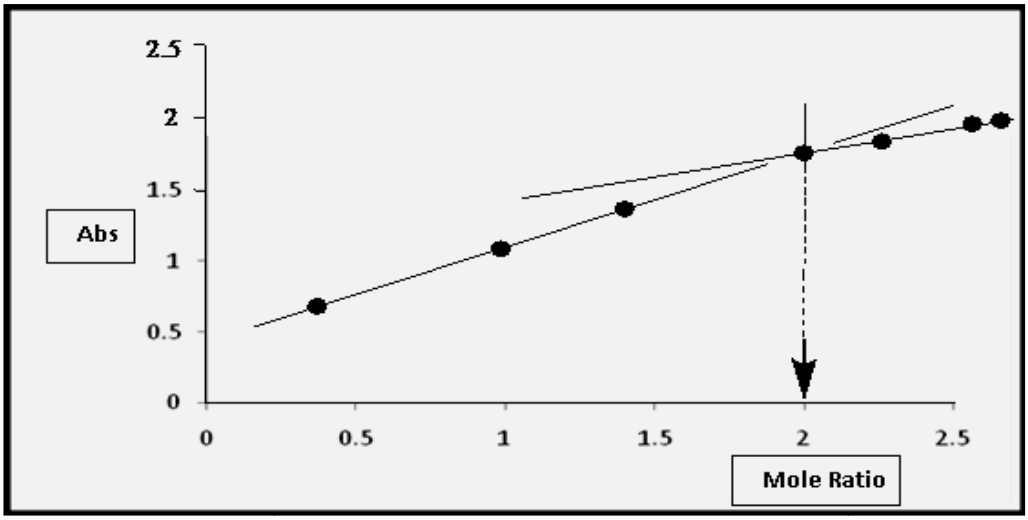

Figure 8: Mole ratio of Complexes

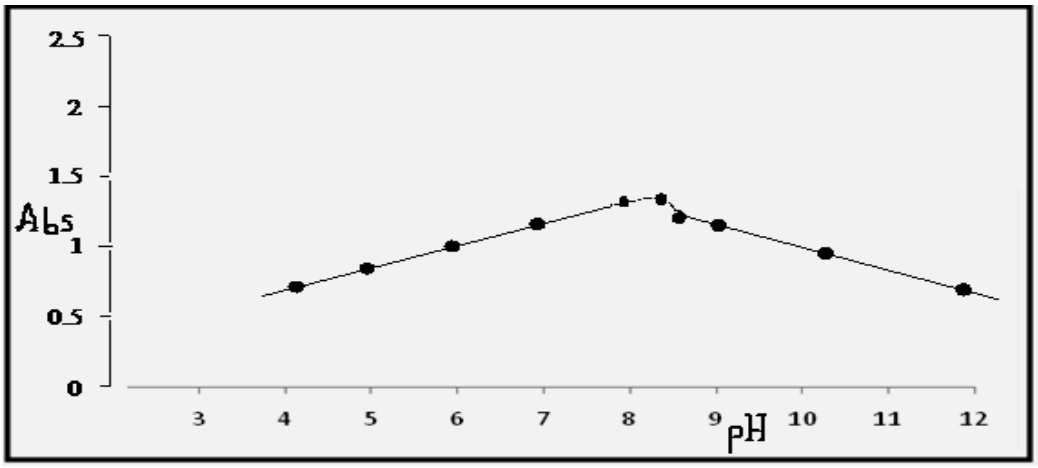

Figure 9: Variation of pH of Complexes

The Molar Conductance

The molar conductance data (1.12 -1.35 $ohm^{-1}.mol^{-1}.cm^2$) of (10^{-3}M) solution in DMSO – solvent indicate that the Cd – complexes are non –electrolytic in nature.

Table 1: Physical Properties of Ligands with Compounds

Ligands & Complexes	M.P $(C)^0$	$\Omega^{-1}.Cm^2.Mole^{-1}$ Conductance
Ligand (L_1)	172	/
Ligand (L_3)	198	/
Complex[Cd (L_1)]	218	1.27
Complex[Cd(L_2)]	234	1.35
Complex[Cd(L_3)]	242	1.12

I.R Spectra

The spectra exhibited frequencies in ligands [(L1), (L2),(L3)] at bands (3420 -3455) cm^{-1} due to phenolic hydroxyl groups and hydroxyl group of carboxylic acid respectively in free ligands which disappeared in spectra of their complexes indicating the coordination through phenolic oxygen moiety and oxygen of carboxyl group at bond (M–O) are

(509 -595) cm^{-1}. The I.R –spectra of Schiff bases in ligands exhibit a strong bands at (1630 -1640)cm^{-1} and azo group at (1490 -1498)cm^{-1},which have been shifted towards lower frequencies at (1622-1630) cm^{-1} of (CH=N) imine group[12,13] in complexes due to coordination with ((Cd)) ion.

The results appeared that the coordination through nitrogen of imine group (CH=N) and Nitrogen of (hetero cycle) which represented by (thiazole) ring and oxygen of hydroxyl group of carboxyl in complexes.

Table 2:FT.IR Data (Cm^{-1}) Of Ligands with Complexes.

Ligands & Complexes	(CH=N) Imine group	(CO-O) Carboxyl group	(OH) of carboxyl	(M-N)	(M-O)
Ligand (L_1)	1635	1720	3190	/	/
Ligand (L_2)	1642	1725	3200	/	/
Ligand (L_3)	1647	1722	3195	/	/
Complex [Cd (L_1)]	1610	1715	/	462	577
Complex [Cd(L_2)]	1619	1721	/	427	553
Complex [Cd(L_3)]	1620	1716	/	461	550

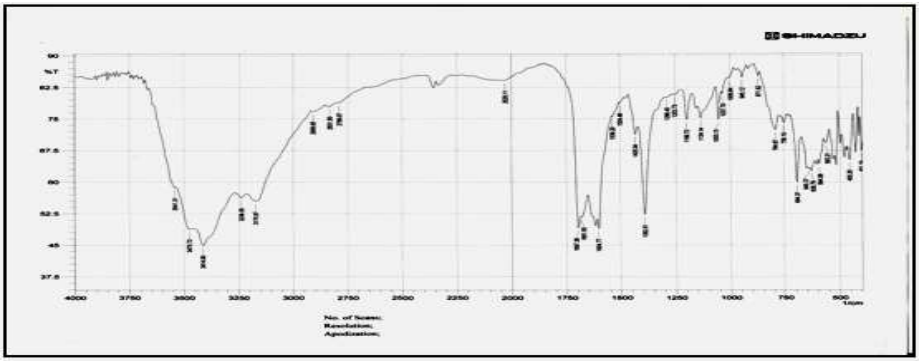

Figure 10: FT.IR of Ligand (L_1)

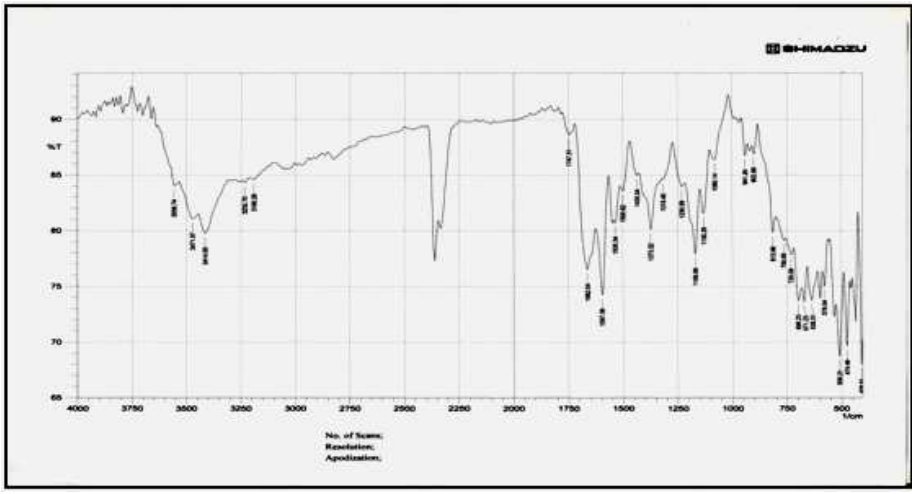

Figure 11: FT.IR of Complex [Cd (L_1)]

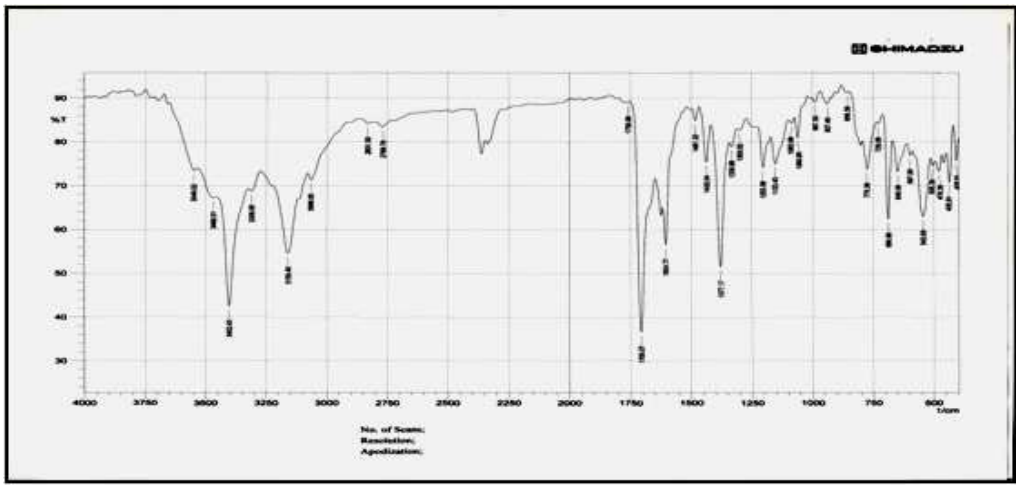

Figure 12: FT.IR of Ligand (L_2)

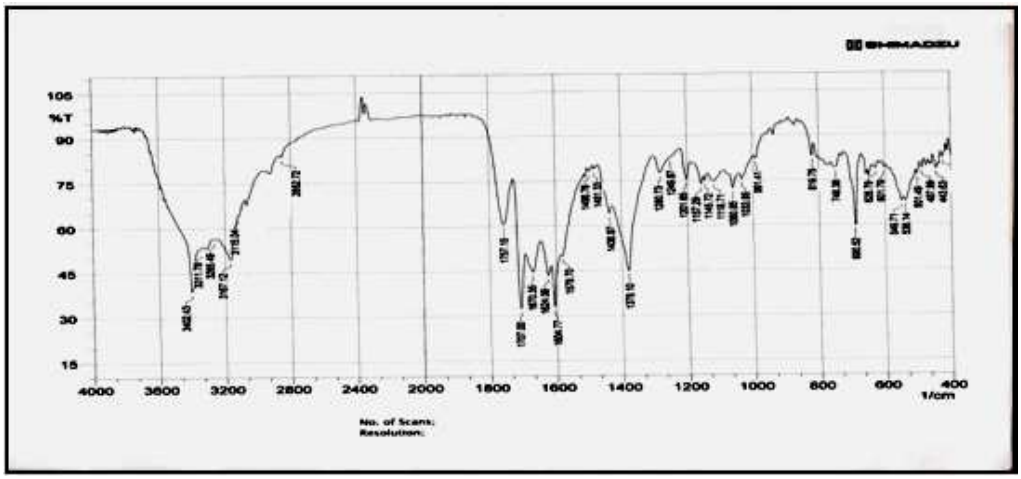

Figure 13: FT.IR of Complex [Cd (L_2)]

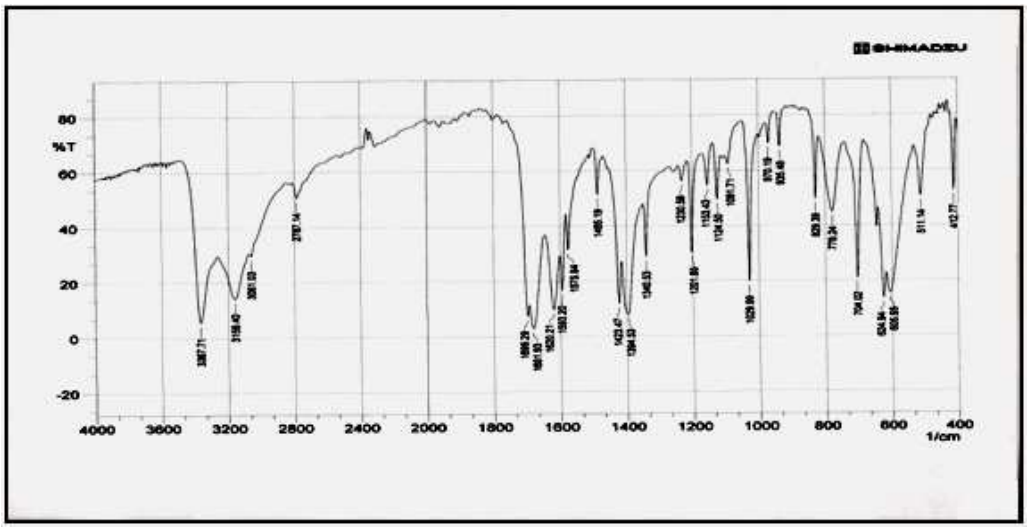

Figure 14: FT.IR of Ligand (L_3)

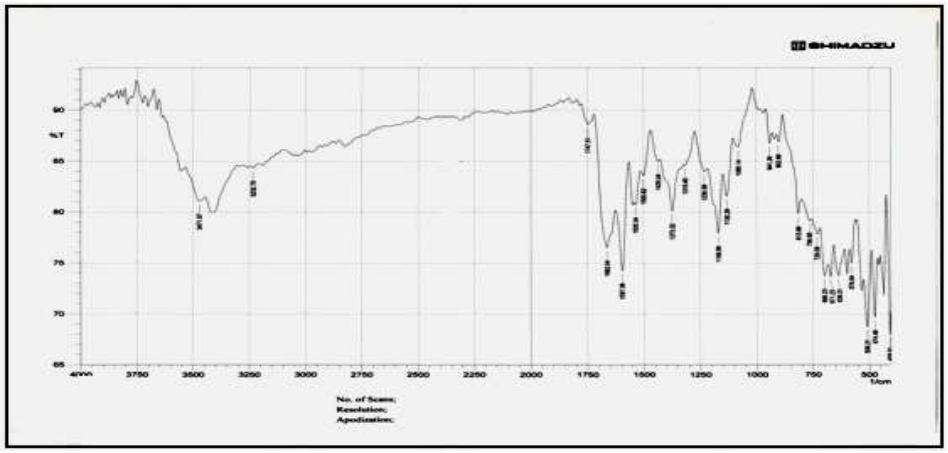

Figure 15: FT.IR of Complex [Cd (L_3)]

Studying of H.NMR- Spectra

Spectra of ligands showed peaks at **δ** (13.28, 12.98, 13.09) for hydroxyl group of carboxyl in free ligands., which disappeared in their complexes as a result of coordination with (Cd^{2+})., and other data are listed in table (3) and figures **(**13-16**)**.

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

Ligands & Complexes	(OH) Carboxyl	(CH=N) Anil group	Other groups ((only functional groups))
Ligand (L_1)	13.28	8.41	(Thiazole Ring) protons : (7.24– 7.84)., (CH_3, CH): 1.40, 1.58
Ligand (L_2)	12.98	8.11	(-Ph-): proton of phenyl ring : (6.99– 7.84)., (NH) : 8.00., (-CH_2-CH-):(1.40 – 1.58)
Ligand (L_3)	13.09	8.33	(-Ph-): proton of phenyl ring : (6.80– 7.77)., (OH) : 11.04., (-CH_2-CH-):(1.52 – 1.73)
Complex [Cd(L_1)]	/	8. 44	(Thiazole Ring) protons : (7.12– 7.61)., (CH_3, CH): 1.43, 1.59
Complex [Cd(L_2)]	/	8.16	(-Ph-): proton of phenyl ring : (6.91– 7.86)., (NH) : 8.06., (-CH_2-CH-):(1.46 – 1.59)
Complex [Cd(L_3)]	/	8.26	(-Ph-): proton of phenyl ring : (6.81– 7.74)., (OH) : 11.15., (-CH_2-CH-):(1.55 – 1.89)

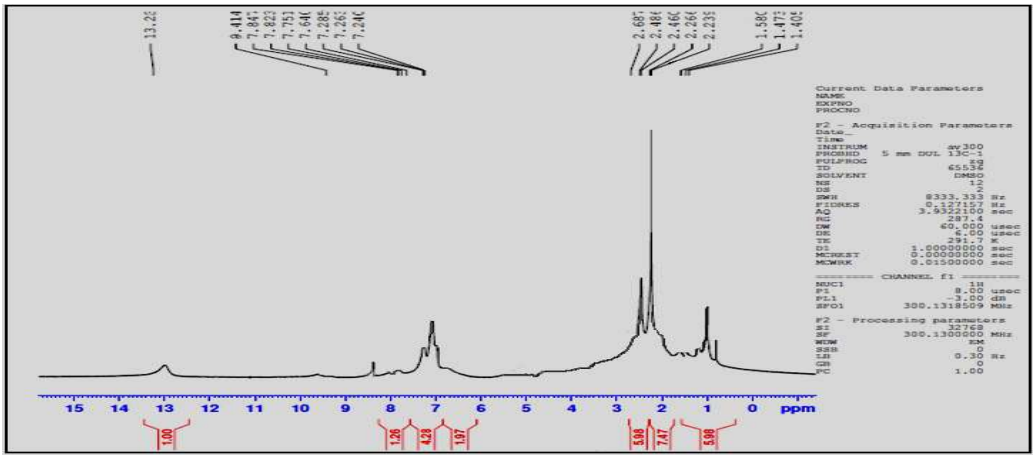

Figure 16: H.NMR of Ligand (L_1)

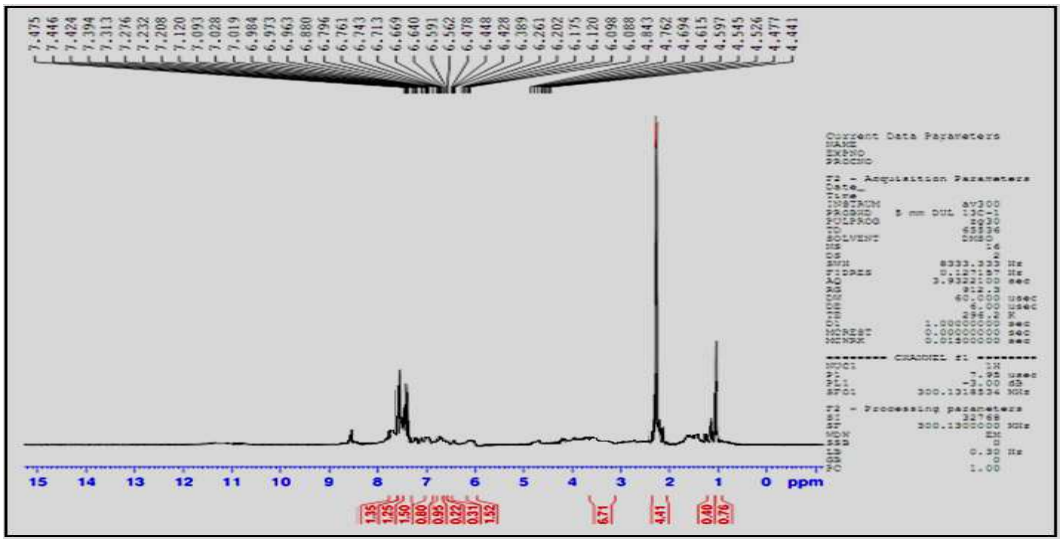

Figure 17: H.NMR of Complex [Cd (L_1)]

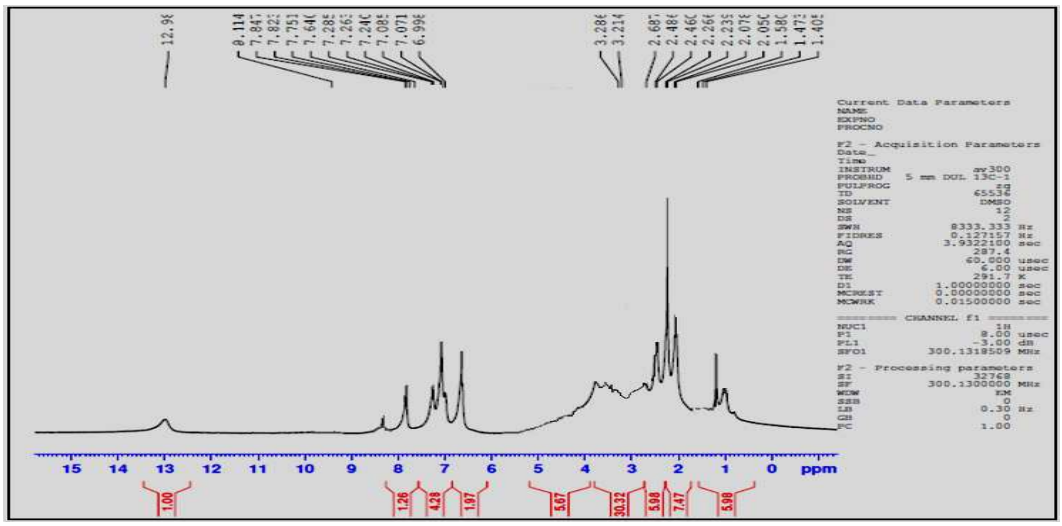

Figure 18: H.NMR of Ligand (L_2)

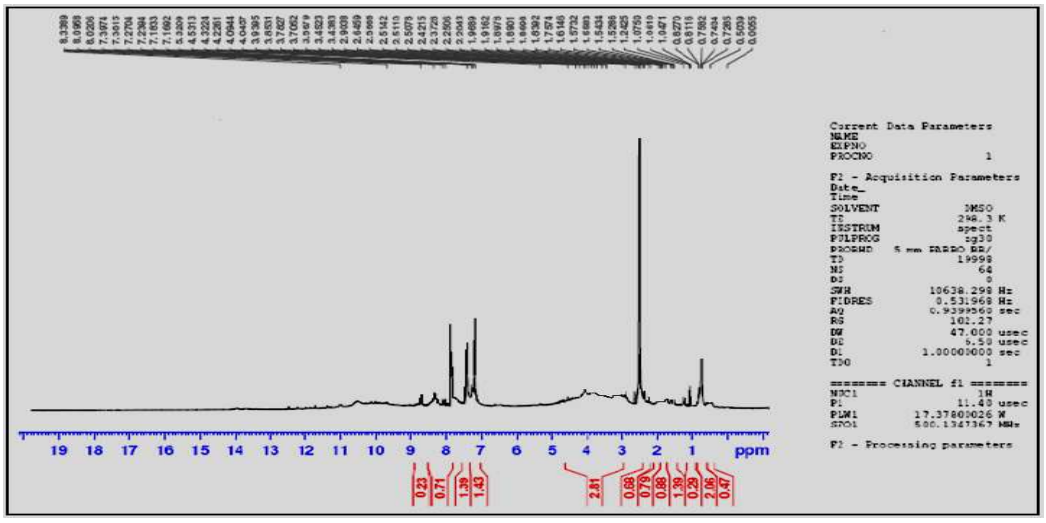

Figure 19: H.NMR of Complex [Cd (L_2)]

Thermal Studying of Complexes

DSC – measurements of all complexes tested for determination of complexes stability through high temperatures in thermal curves, figures (17- 19). From results of this thermal study, we noted high stability at high temperature for our complexes due to structures which involved sulfur atom with nitrogen atom in their structure.

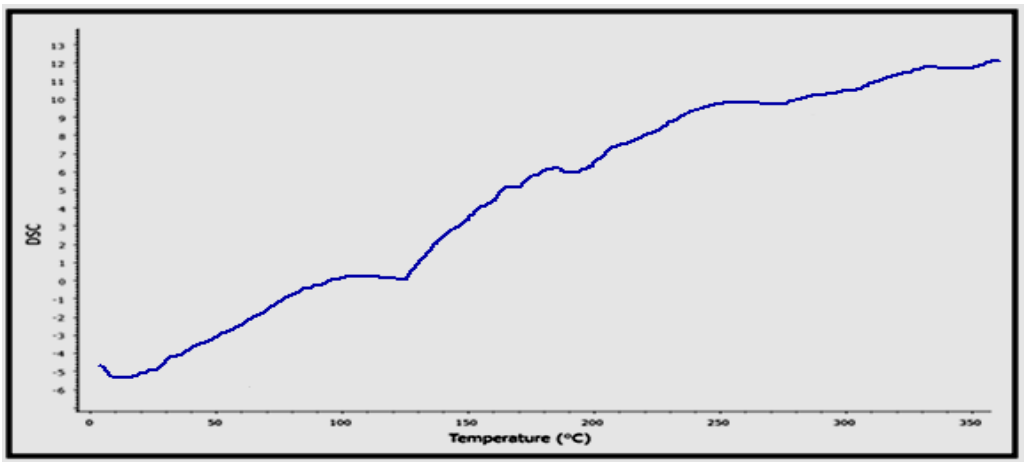

Figure 20: DSC of Complex [Cd (L_1)]

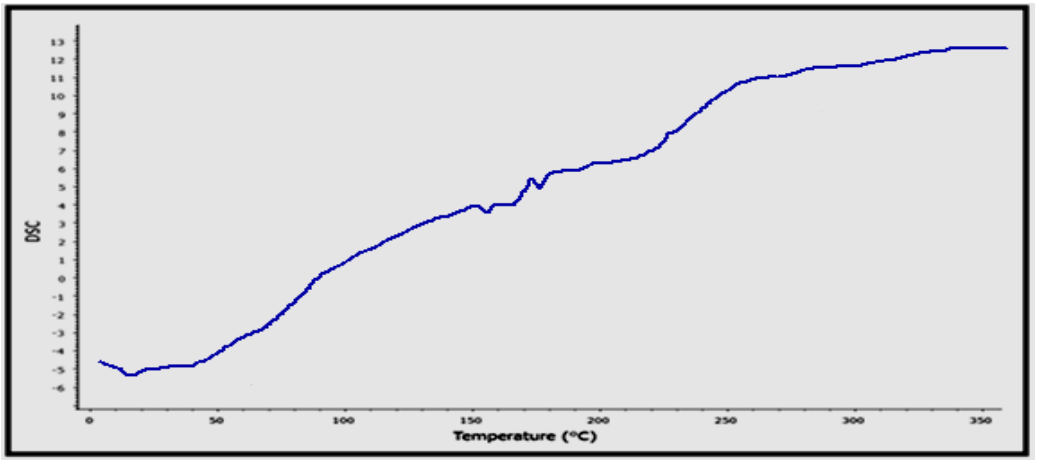

Figure 21: DSC of Complex [Cd (L_2)]

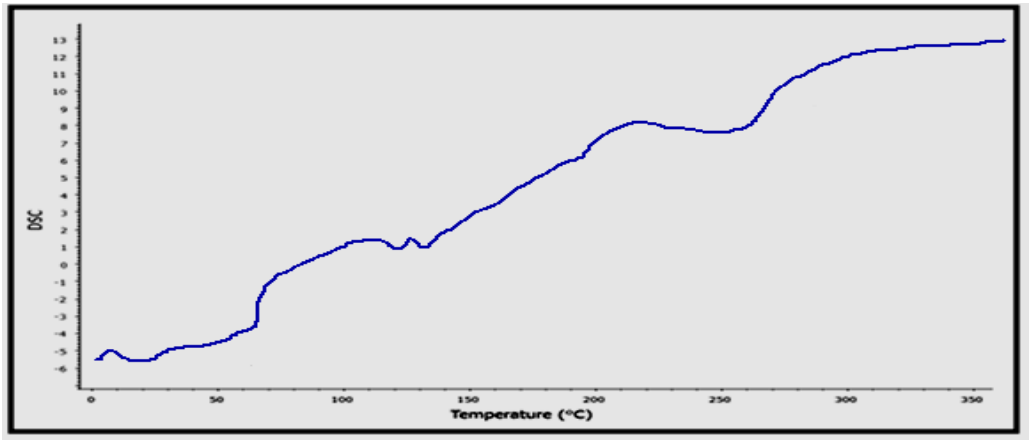

Figure 22: DSC of Complex [Cd (L_3)]

Biological Tests [14, 15]

In this work, we screened the effect of our complexes on two types of bacteria. The isolated bacterial were positive and negative for gram, which involved in this work on two classes of bacteria to measure the biological activity according to studies [19, 24] of certain compounds which bacteria positive for the dye gram (bacteria-**Staphylococcus aureu**) and negative gram (bacteria- **K. Pneuomona**), and Table (4) shows the diameter of inhibition zone for vehicles chemical measured in (mm) towards the species bacterial.

Table 4: Biological Activity (Inhibition Zone in (mm)) of Complexes in Concentration (0.005 M)

Complexes	(G +)Staphylococcus. Aureus	(G -)K. Pneuomona
Complex[Cd(L_1)]	10	6
Complex[Cd(L_2)]	12	8
Complex[Cd(L_3)]	10	8

The results showed the Biological Activity for complex with (L_2) is more than other complexes with (L_3, L_1) because the complex with (L_3) involved sulfur[14,15] as nitrogen atoms in its structure which supplied with high effectiveness on the two types of bacteria, and the following photos gave results:

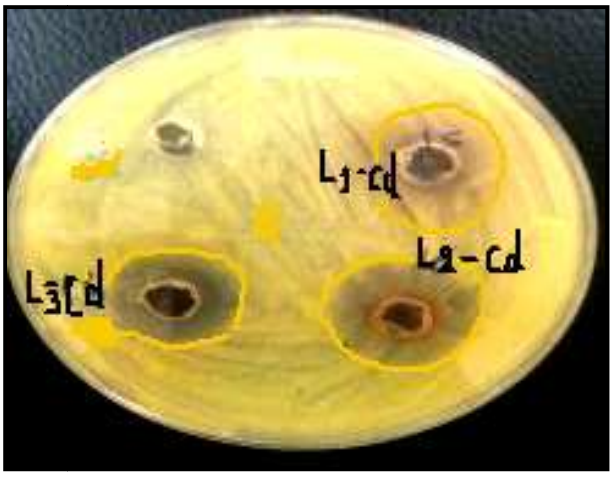

Figure 23: Inhibition of Complexes on Staphylococcus Aureu

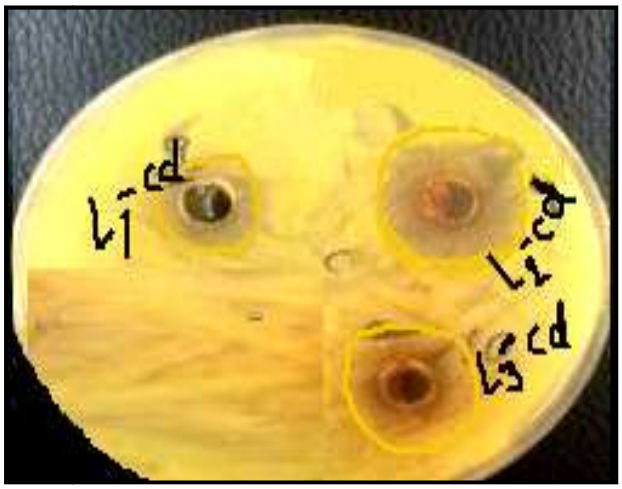

Figure 24: Inhibition of Complexes on K. Pneuomona

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