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Full Length Research Paper

Synthesis and Identification of Macrocycles and Complexes with (Cd^{2+})

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Abstract

The novel macrocycles ligands were synthesized by reacting of various amine compounds such as (ethylene diamine, methylene diamine, Glycine–amino acid, hydrazine) with di ketone compounds to produce five ligands ((DAP), (MAH), (PIP), (MCP), (MHD)) of macro cycles and their complexes with cadmium ion (II). The synthesized compounds were confirmed by (I.R, UV–Vis, (C.H.N)–analysis), molar conductance and melting points.

Keywords: Complex of cd, Big ligands, Ligand of imine.

INTRODUCTION

Macro cycles ligands have a long history of application in analytical and inorganic chemistry, the literature is flooded with reports of variety of biological activities of these compounds represented (anticancer, antibacterial anti–inflammatory, antiviral, anti malarial), other pharmacological synthesis of these compounds were prepared by condensation reaction with catalysis to give good yields from macro cyclic compounds (Hament and Ram, 2010; Nagham, 2013).

These compounds included Schiff bases–bi molecular at same time and some of them included Azo- group with Schiff base (Reda et al., 2013; Geindy et al., 2006; Sugam and Mangla, 2011; Muhammed et al., 2011; Maheshk et al., 2013; Sultan, 2012; Patel and Prajapati, 2012) [3-9] which give it ability to act as multi dentate ligands for transition metal ions, most of these compounds used are chelating ligands in coordination chemistry.

Experimental

Melting points were determined in open capillary tube and were uncorrected. The I.R-spectra were recorder in KBr–disc, Shimadzu (8300)., (C.H.N)–elemental analysis, Atomic absorption., UV–Vis –spectra photometer, molar conductance (DMSO –solvent).

Synthesis of ligand (DAP)

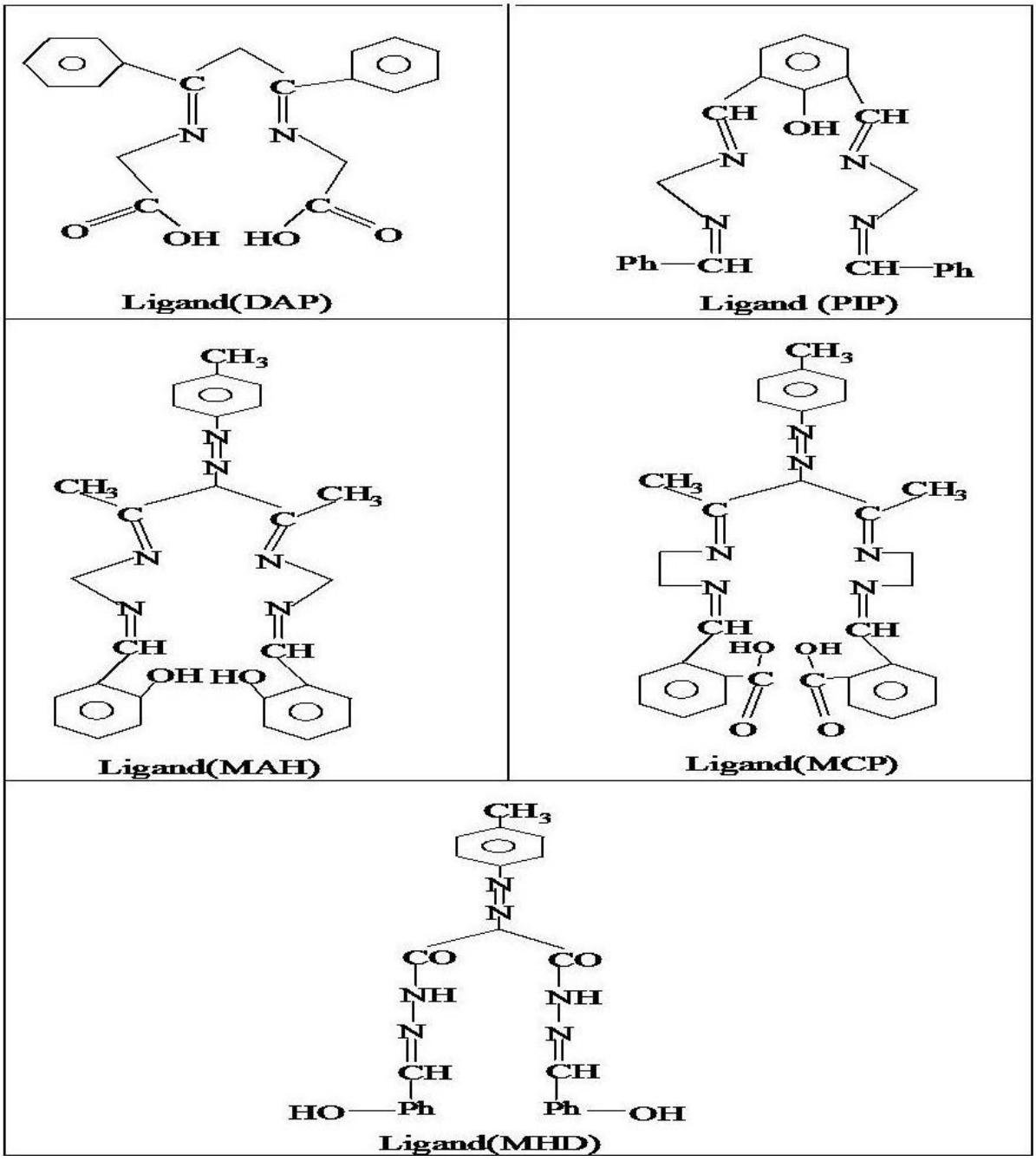
1,3 –(diphenyl) -1,3 –bis (acetic imine) propyl

They compound was synthesized according procedure (Nagham, 2013), 1,3–diphenyl–propane -1,3 –dione (0.01mole) and (0.02mole) from glycine were refluxed in presence of absolute ethanol with drops of glacial acetic acid for (3hrs), the precipitate was filtered and dried, then are crystallized with absolute ethanol to yield 87% of ligand (DAP).

Synthesis of ligand (PIP)

2,6 –bis (phenyl imine – methylene imine) phenol

2,6 –di formal phenol (0.01mole) was refluxed with (0.02mole) of methylene di amine in presence of absolute ethanol for (4hrs) with mechanical stir, the precipitate was filtered and re crystallized, which refluxed with (0.02mole) of benzaldeehyde to produce 84% of ligand (PIP).



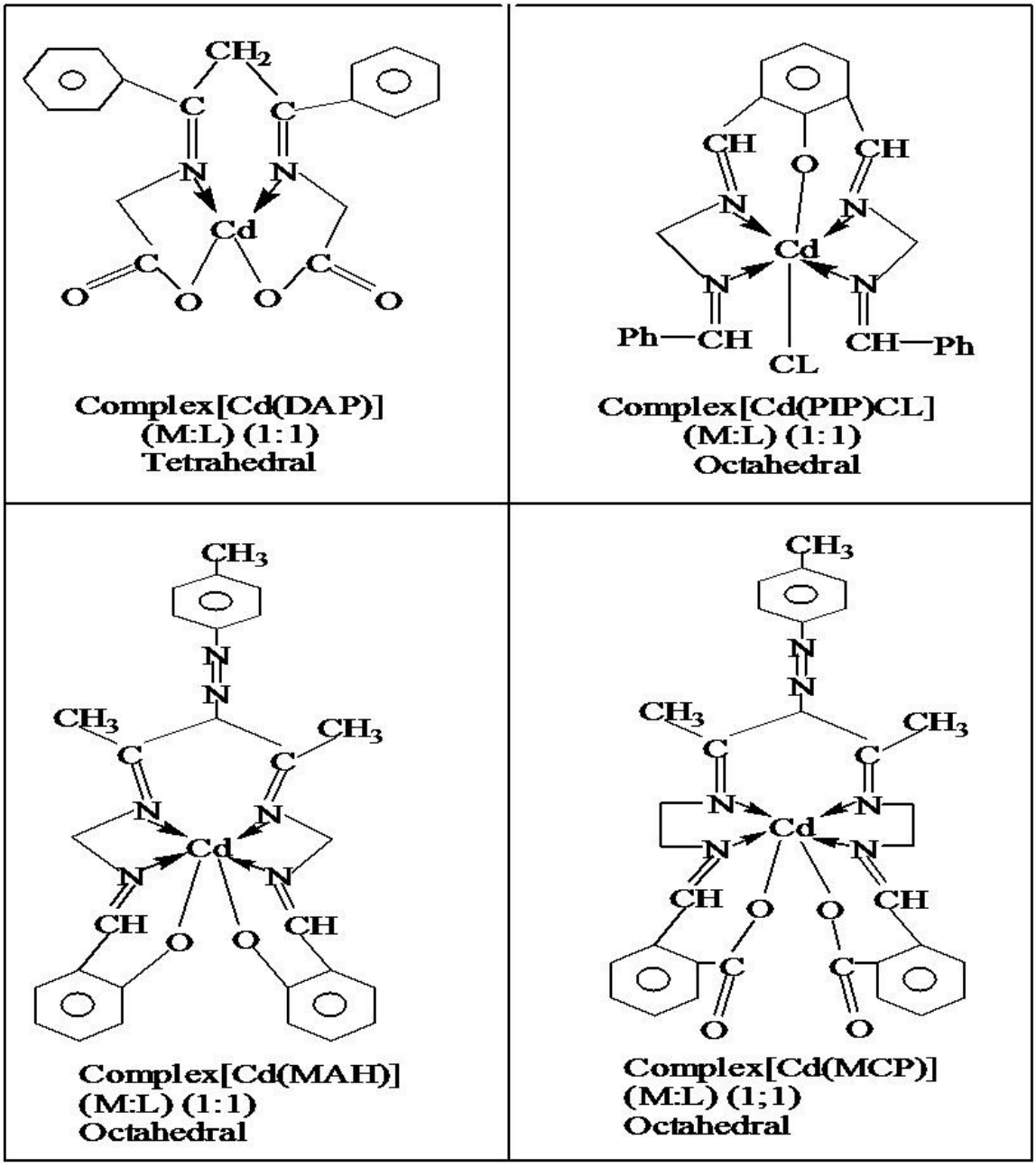
Scheme 1. Synthesis of ligands

Synthesis of ligand (MAH) and ligand (MCP)

3–(4-methyl benzene azo)-2,4- bis(2-hydroxyl benzyl imine methylene imine)-pentyl

3-(4-methyl benzene azo)-2,4–bis(2-carboxy benzene–ethylene di imine) pentyl

(0.01mole) of 4- methyl aniline was dissolved in (3ml) of hydro chloric acid and (0.6gm) of sodium nitrite in temperature (0-5)° C then ethanolic solution of acetyl acetone (0.01mole) added, after (48hrs), the precipitate was filtered and dried, which (0.01mole) refluxed with (0.02mole) of (methylene di amine or ethylene di amine) respectively . According to procedure 10. (Nagham, 2013; Nagham, 2013), the precipitate were filtered and dried, which (0.01mole) refluxed with (0.02mole) of (salicyldehyde , or 2- formal benzoic acid) respectively to yield (85%, 83%)from ligands (MAH) and (MCP) respectively.



Scheme 2. Figures of Complexes

Synthesis of ligand (MHD)

2-(4 –methyl benzyl azo) -1,3- bis (2- hydroxyl benzyl hydrazo imine) propane -1,3 –dione. 4- methyl aniline (0.01mole) was dissolved in (3ml) of hydrochloric acid and (0.7gm) of sodium nitrite at (0-5)° C, then ethanolic solution of diethyl malonate (0.01mole), after (48hrs), the precipitate was filtered and dried, which (0.01mole) refluxed with (0.02mole) of hydrazine to produce compound, which (0.01mole) refluxed with (0.02mole) of salicyldehyde for (4hrs) , the precipitate was filtered, are crystallized from ethanol to produce 86% of ligand (MHD).

Synthesis of complexes with (cd^{2+})

According to procedure (Nagham, 2013), the hot ethanolic solution of ligand [(DAP) ,or (MAH) or (PIP) or (MCP)] respectively was added to solution of cadmium chloride ($CdCl_2$) in mole ratio (metal:ligand) (1:1) respectively after stirring (1hrs), precipitates formed, dried and recrystallized to yield (80%, 83%, 81%, 84%)

Table 1. Physical properties and elemental analysis

Ligands and Complexes	M.P (C)^0	λ_{max}	$\Omega^{-1}.Cm^2.mole^{-1}$ Conductance	Calc./Found C%	H%	N%	Ni%
(DAP)	160	355	/	67.45	5.32	8.28	/
$C_{19}H_{18}N_2O_4$				67.39	5.27	8.17	/
(MAH)	190	390	/	69.70	6.22	17.42	/
$C_{28}H_{30}N_6O_2$				69.58	6.18	17.40	/
(PIP)	182	382	/	75.39	5.75	14.65	/
$C_{24}H_{22}N_4O$				75.27	5.68	14.59	/
(MCP)	198	398	/	67.84	6.00	14.84	/
$C_{32}H_{34}N_6O_4$				67.72	5.92	14.79	/
(MHD)	195	370	/	62.88	4.80	18.34	/
$C_{24}H_{22}N_6O_4$				62.73	4.71	18.27	/
[Cd(DAP)]	218	408	0.76	50.84	3.56	6.24	25.06
				50.71	3.48	6.18	25.00
[Cd(MAH)]	230	430	0.98	56.71	4.72	14.17	18.97
				56.60	4.65	14.08	18.90
[Cd(PIP)Cl]	>250	418	1.64	54.45	3.97	10.58	21.25
				54.36	3.88	10.44	21.16
[Cd(MCP)]	>250	445	1.23	56.77	4.73	12.41	16.61
				56.64	4.60	12.32	16.53

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

Ligands and Complexes	(CH=N) imine group	(-N=N-) azogroup	(-OH)	(M-N)	(M-O)
(DAP)	1652	/	3480	/	/
(PIP)	1643	/	3410	/	/
(MAH)	1645	1486	3425	/	/
(MCP)	1646	1490	3450	/	/
(MHD)	1630	1495	3415	/	/
[Cd(DAP)]	1640	/	/	495	582
[Cd(PIP)Cl]	1628	/	/	482	509
[Cd(MAH)]	1631	1436	/	470	557
[Cd(MCP)]	1634	1433	/	465	575

respectively from complexes of [(DAP), (MAH), (MCP), (PIP)] respectively. (Figure 1)

RESULTS AND DISCUSSION

All ligands and complexes were studied by many methods.

Study of optimal condition of complexes

The optimal conditions for formation of complexes with cadmium ion(II) were studied in this paper like calibration curves of optimal concentration of Cd^{2+}= ($0.65X10^{-4}$m), while concentration of ligands [$1X10^{-3}$M of ligand (DAP)., $0.5X10^{-3}$M of ligand (PIP)., $0.35X10^{-3}$M of ligand (MAH)., $0.40X10^{-3}$Mof ligand (MCP)]., while optimal (PH=8) was base medium to formation of complexes by job method and mole ratio method through series solutions were prepared having a constant concentration ($1X10^{-3}$M) of Cd salt ($CdCl_2$) and ligand, the (M:L) ratio was determined from relationship between the absorption of observed light and mole ratio (M:L) found to be (1:1) for all complexes. other studies of these complexes in table (1) and figs (1-5).

Other measurements

The elemental analysis shown in the Table (1) indicates that the Cd–complexes [(DAP), (PIP), (MAH),(MCP)] have stoichiometry (Metal:Ligand) (1:1) from results of mole ratio method.

The molar conductance values (0.76 -1.64) $ohm^{-1}.mol^{-1}.cm^2$ of ($1X10^{-3}$m) solution in DMSO indicate that the Cd–complexes are non–electrolytic in nature .I.R –spectra shown absorptionbands in ligands [(DAP), (PIP) ,(MAH) ,(MCP)] at (3410 -3480) cm^{-1} due to phenolic hydroxyl groups (Atmaram and Kiran, 2011) and hydroxyl groups of carboxylic group respectively in free ligands which disappeared in spectra of their complexes

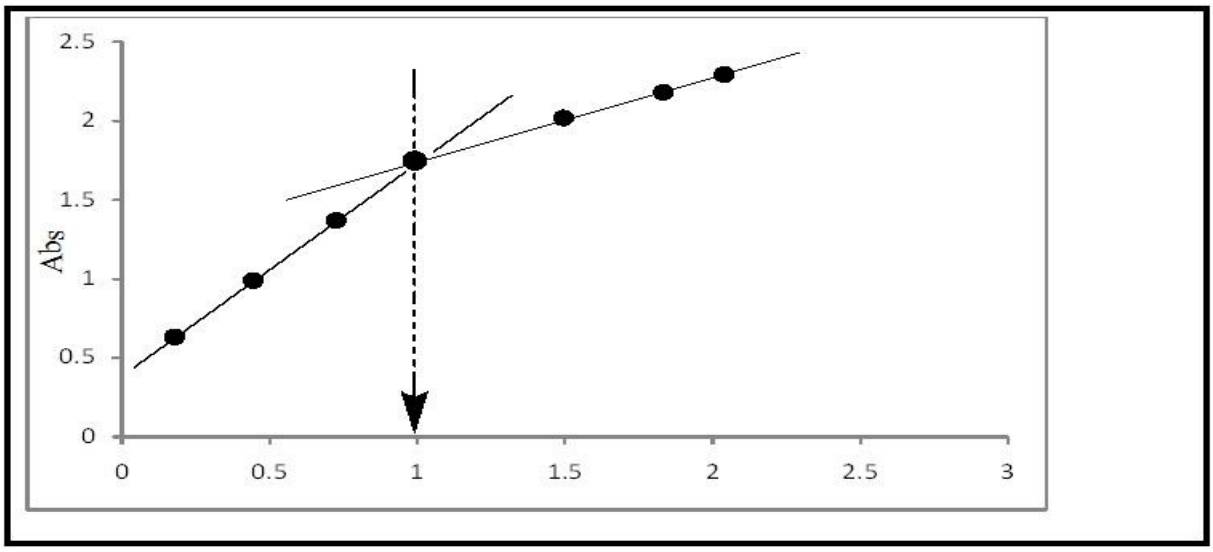


Figure 1. Mole ratio of Complex [Cd(MAH)]

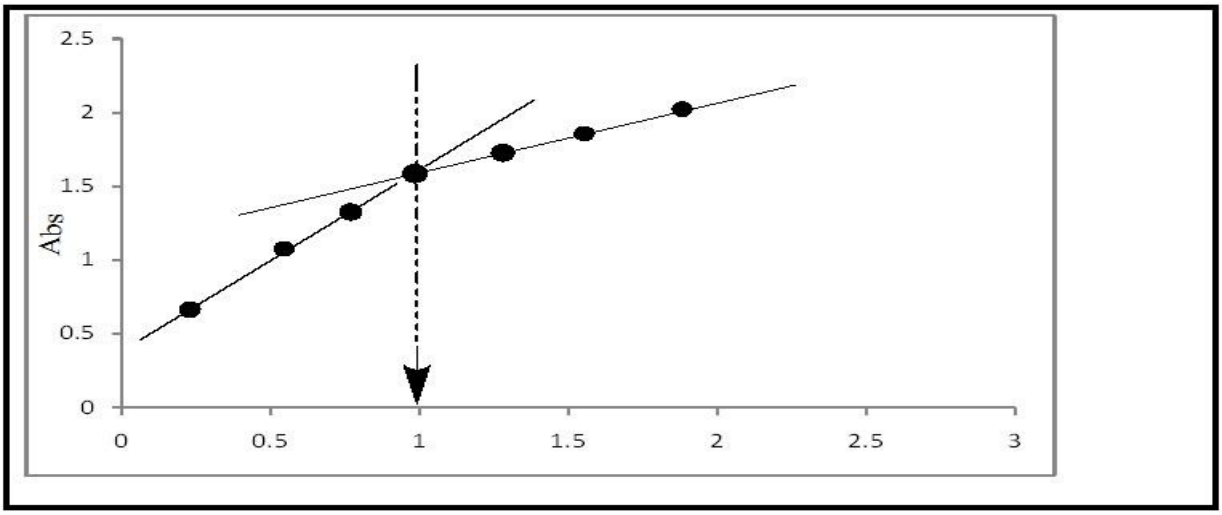


Figure 2. Mole ratio of Complex [Cd(MCP)]

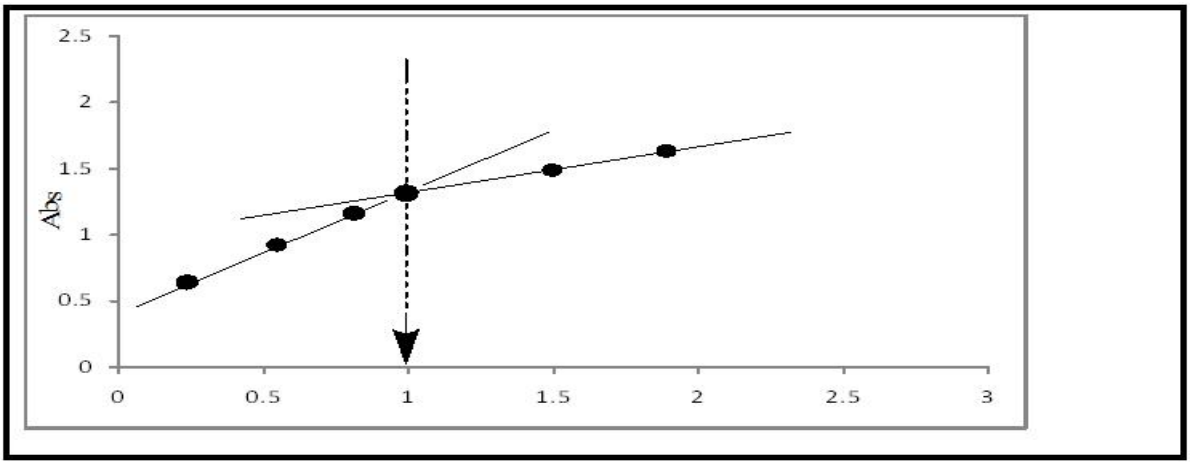


Figure 3. Mole ratio of Complex [Cd(DAP)]

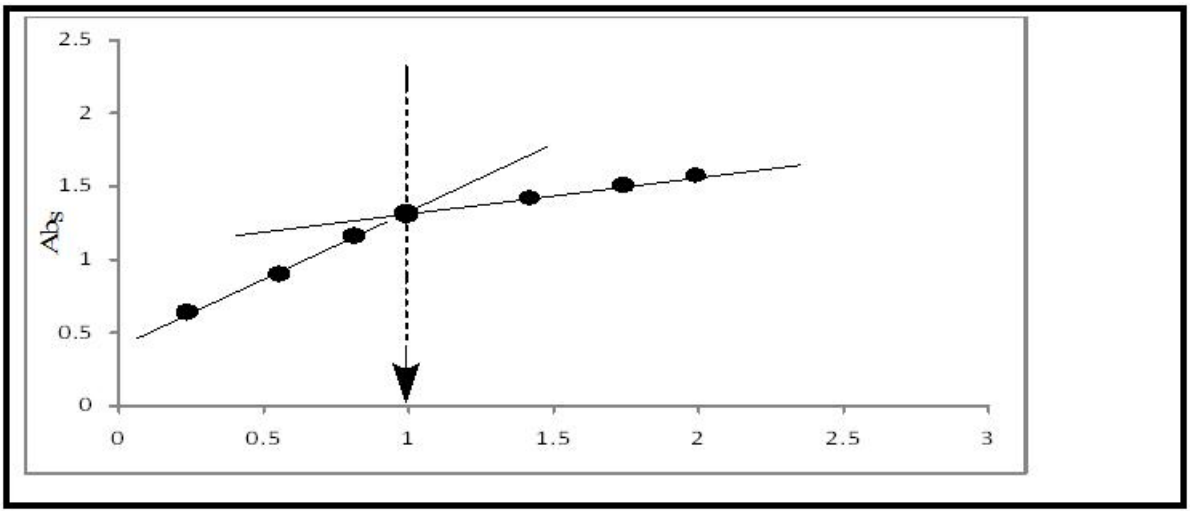


Figure 4. Mole ratio of Complex [Cd(PIP)CL]

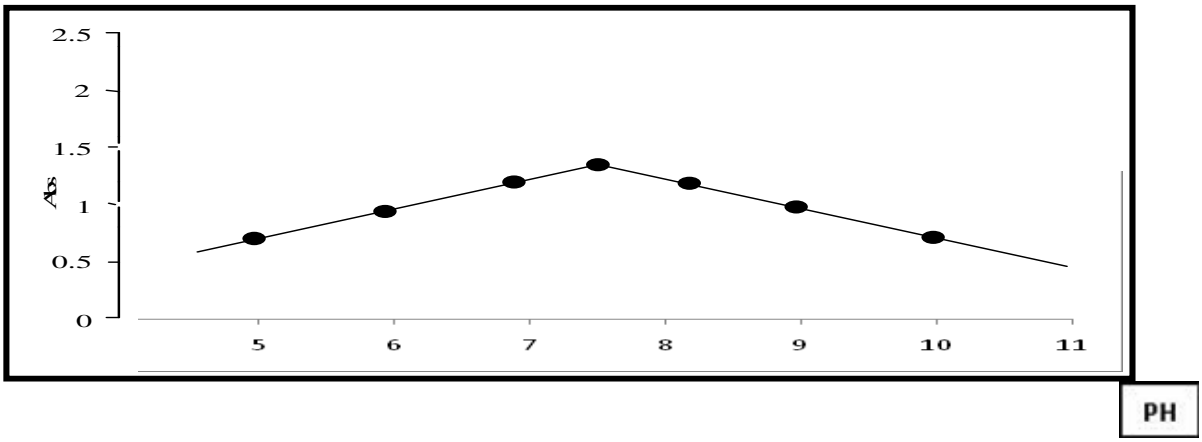
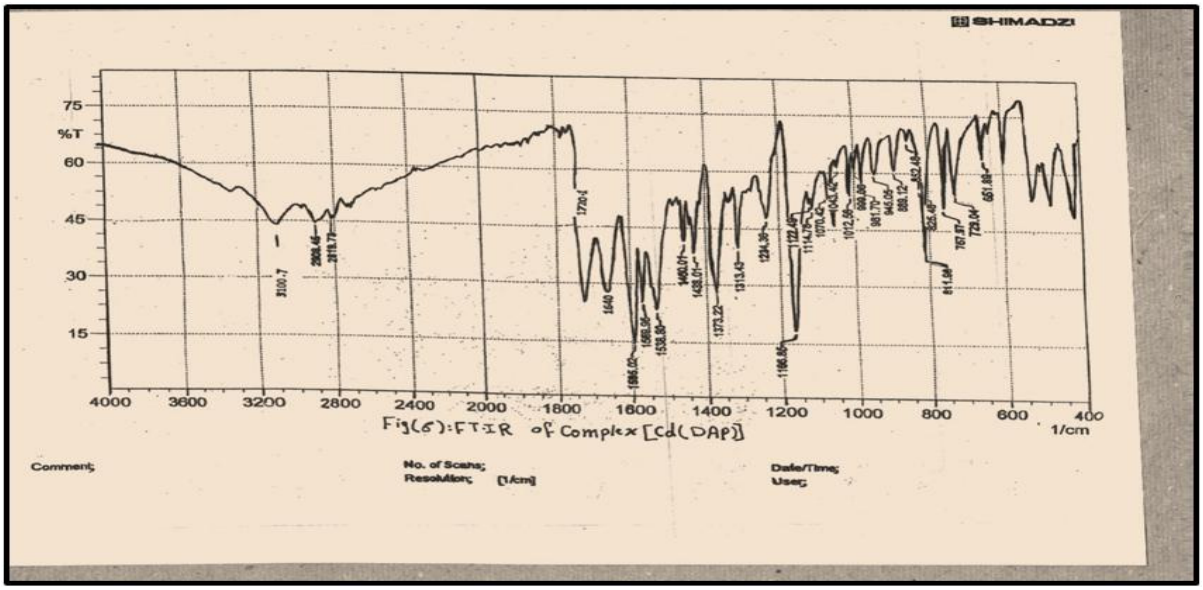
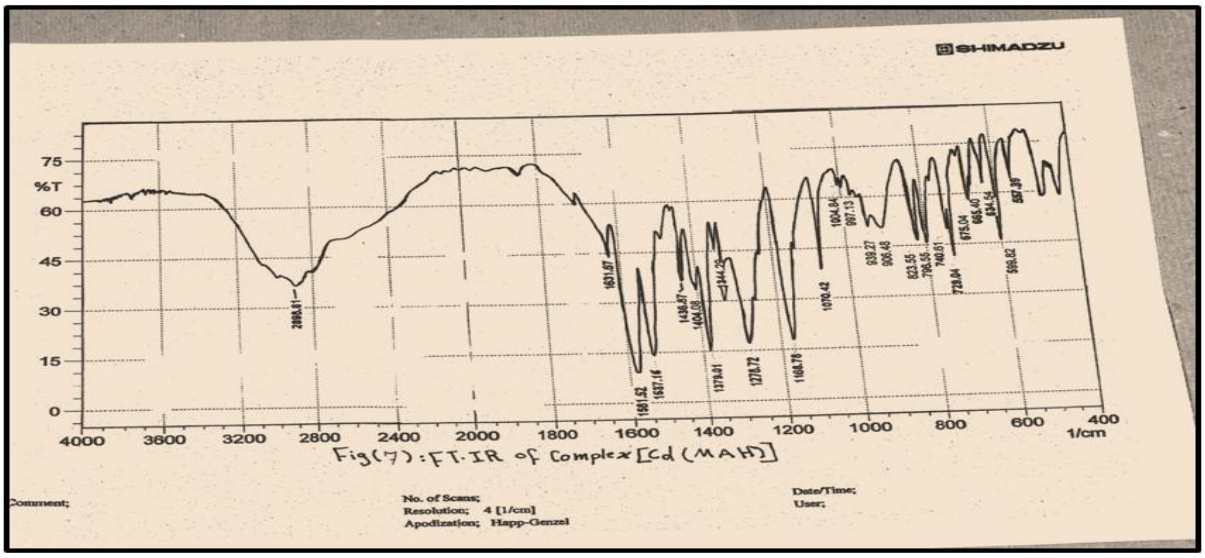


Figure 5. Variation of PH of Complexes

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Fig(7): FT-IR of Complex [Cd (MAH)]
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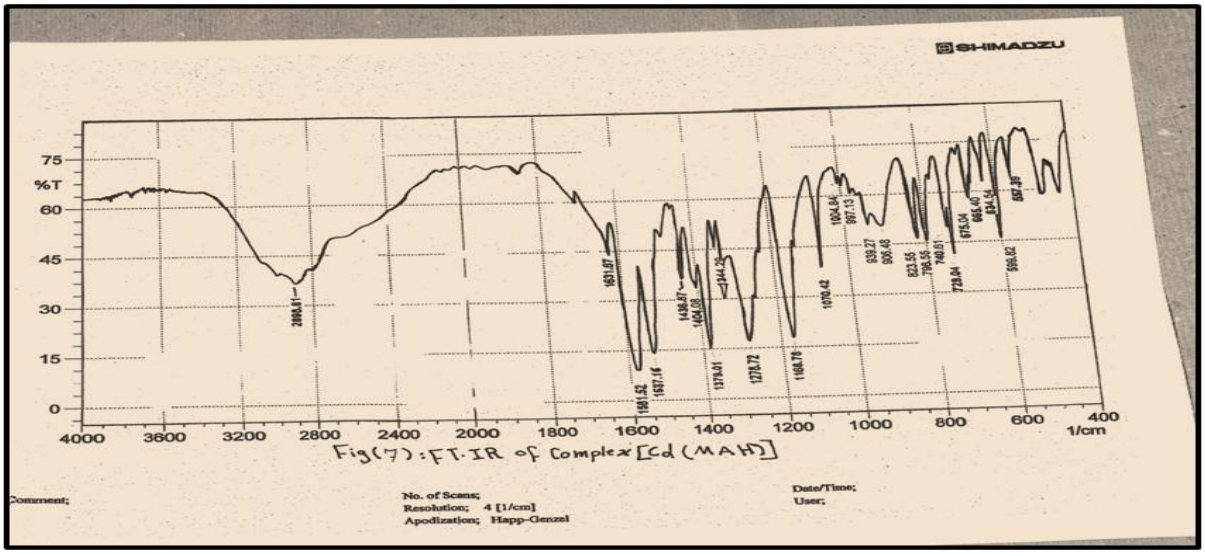
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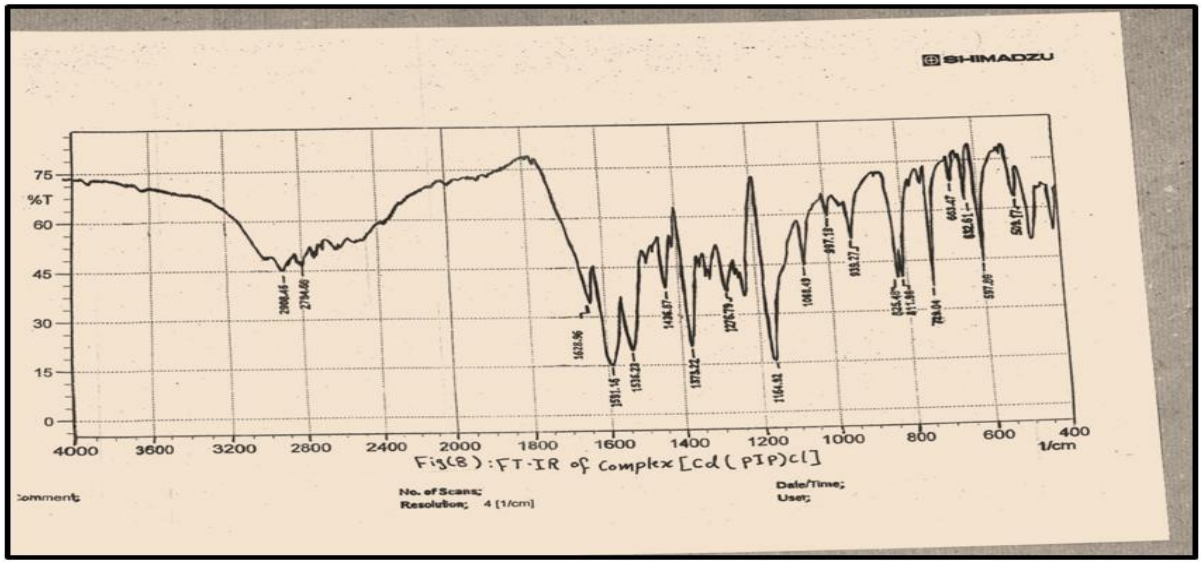
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Fig(8): FT-IR of Complex [Cd (PIP)Cl]
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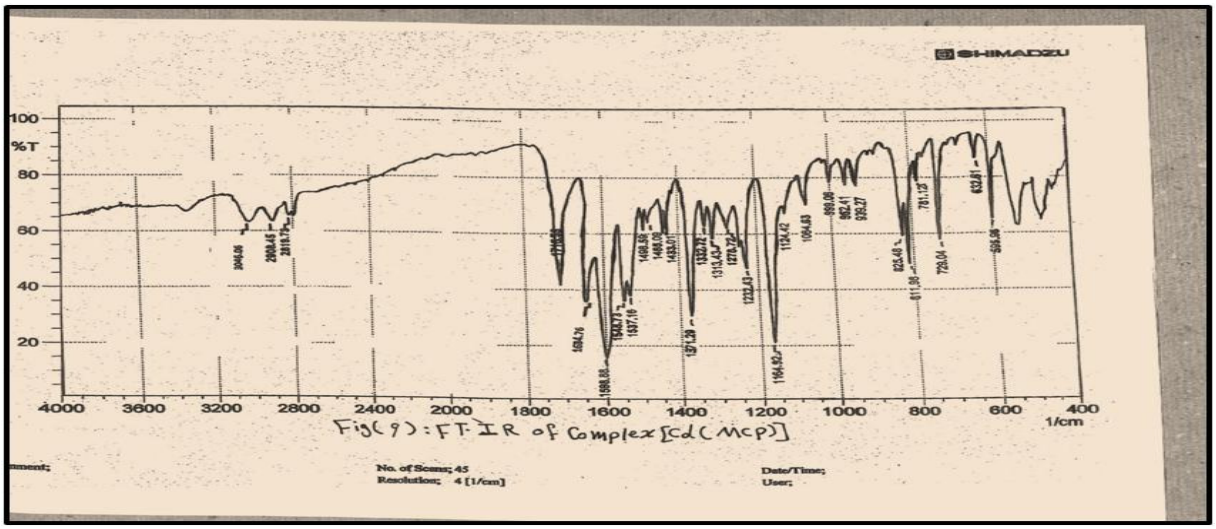

indicating the coordination through phenolic oxygen moiety and oxygen of carboxyl group at bond (M–O) are (509 -582) cm^{-1}. The I.R –spectra of (Schiff bases CH=N, Azo group-N=N-) (Shashikant et al., 2006; Pramili and Chandra, 2012; Giorgio and Paola, 2010; Wanale et al., 2012) respectively in ligands exhibit bands at (1643-1652 and 1486-1490)cm^{-1}respectively ,which have been shifted towards lower frequencies at (1628-1640 and 1433-1436) cm^{-1} respectively in complexes to coordination with (Cd^{2+}) –ion.

The coordination through nitrogen of imine group (CH=N) and Nitrogen of (-N=N-) azo group and oxygen of hydroxyl group of phenol or hydroxyl group of carboxyl in complexes. Table (2) and Figuress (6-9).

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