

## SYNTHESIS & CHARACTERIZATION OF SERIES LIGANDS AND THEIR COMPLEXES WITH (Ni<sup>2+</sup>)

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### ABSTRACT

This paper involved synthesized of five ligands from coupling reaction of azo compounds with diketone compound or with imine compounds to produce (azo-imine) compounds or (azo-azo) compounds and (imine-imine) compounds which named [(MPA), (HPA), (BHI), (MHI), (TIB)]. These compounds are used as ligands with (Ni<sup>2+</sup>) to formation of complexes and study of optimal conditions of complexes such as (stoichiometric study, mole ratio, Job method, PH, concentration of metal, and ligands, molar conductance). All ligands with complexes were characterized by (UV-Vis spectra, FT-IR-spectra, (C.H.N)-analysis, melting points).

**Keywords:** complex of Ni, coupling, azo

### INTRODUCTION

The chemistry of azo compounds is the most important in the discovery of new (reagents, ligands, drugs, other applications) it have been widely used as reagents for the spectra of photometric and extraction and determination of trace amount of metals in samples and as an organic reagents<sup>(1-5)</sup> in analytical chemistry. Schiff bases (imine) consider important roles in coordination chemistry as they easily form stable complexes with transition metal ions, these ligands included imine group with azo group at same ligand which have important applications<sup>(6-9)</sup> as antimicrobial, anticonvulsant, antihelmintic, anti-diabetic, other applications in industry, pharmacology, analytical chemistry. The presence of two important groups (azo and imine)<sup>(10)</sup> in same ligands act (bidentate, tridentate or multidentate) in some of these ligands via coordination through (-N=N-) and (N=CH) with other groups on same ligands such as (OH, COOH, .....).

These Pharmaceutical and analytical applications have made their synthesis considerably important in the field of synthetic chemistry.

#### Experimental

Absorption spectra were measured on (UV-Vis)-spectrophotometer using 1cm quartz cells, FT-IR-spectra (4000-400 cm<sup>-1</sup>) in KBr-disk were recorded on Shimadzu FT-IR 8400 Fourier Transform infrared-spectrophotometer (Japan), elemental analysis were carried out on Euro EA 3000 single elemental analyzer, Atomic content were measured on Shimadzu AA-6300 Atomic absorption spectra of photometer, melting points were measured by SMP 30 start, UK.

#### Synthesis of ligand (TIB)

##### 1-(2-thiazolazo)-2-(benzoic imine)-5-methyl benzene.

(0.01mole) of 2-amino thiazole dissolved in (3ml) of hydrochloric acid at (0-5) °C, (0.5gm) of sodium nitrite solution added to give diazonium salt, then ethanolic solution of 4-methyl aniline (0.01mole) added to mixture, after (48hrs), the precipitate was filtered and recrystallized to produce azo compound, which (0.01mole) refluxed with (0.01mole) of 2-formal benzoic acid in presence of absolute ethanol for (4hrs), the precipitate was filtered and recrystallized to yield 84% of ligand (TIB).

#### Synthesis of (MHI)

##### 2-(4-methoxy hydroxyl benzene azo)-2-(2-propanone)-2-(benzoic)-ethyl imine.

4-methyl-2-amino phenol (0.01mole) dissolved in (3ml) of hydrochloric acid at (0-5)°C, (0.6gm) of sodium nitrite solution added to give diazonium salt, then (6ml) of acetyl acetone added to

mixture to produce azo compound, the precipitate was filtered and recrystallized to produce azo compound, which (0.01mole) refluxed with (0.01mole) of o-amino benzoic acid in presence of absolute ethanol with drops of glacial acetic acid for (5hrs) to produce 83% of ligand (MHI).

#### Synthesis of (BHI)

##### 2-(3-benzoic)-1-(hydroxyl phenyl) phenylene di imine :

According to procedure<sup>(10)</sup>, (0.01mole) of phenylene diamine refluxed with (0.01mole) of salicylaldehyde in presence of absolute ethanol for (3hrs), the precipitate was filtered and recrystallized to yield 82% of imine compound, which refluxed with (0.01mole) of 2-formal benzoic acid for (4hrs) to produce 86% of ligand (BHI).

#### Synthesis of (MPA)

##### 2-(4-methyl phenol azo)-1-(phenyl imine) benzene.

According to procedure<sup>(10,11)</sup>, phenylenediamine (0.01mole) dissolved in (3ml) of hydrochloric acid at (0-5)°C, (0.6gm) of sodium nitrite solution added to give diazonium salt, then ethanolic solution of 4-methyl-2-amino phenol (0.01mole) added to mixture, the precipitate was filtered and recrystallized to produce azo compound, which refluxed with (0.01mole) of benzaldehyde in presence of absolute ethanol to yield 88% of ligand (MPA).

#### Synthesis of (HPA)

##### 1,2-bis(4-methyl hydroxyl phenyl azo)benzene.

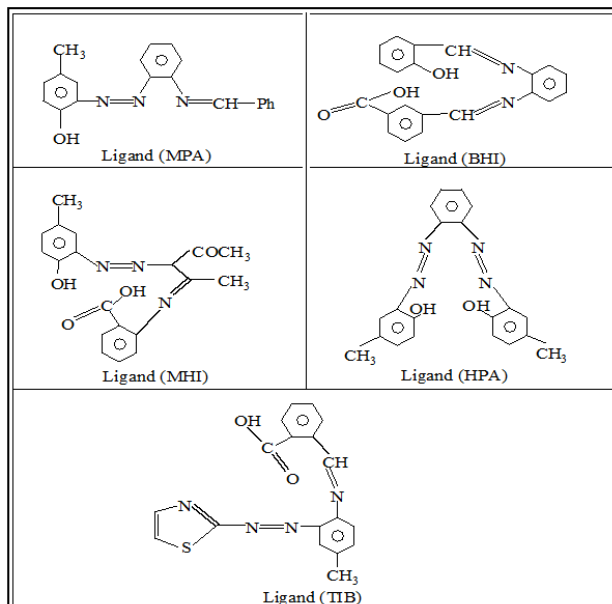
phenylene diamine (0.01mole) dissolved in (3ml) of hydrochloric acid at (0-5)°C, sodium nitrite solution (0.6gm) added to give diazonium salt, then ethanolic solution of 4-methyl phenol (0.02mole) added to mixture, the precipitate was filtered and recrystallized to yield 89% of ligand (HPA).

#### Study of optimal condition of complexes

The optimal conditions for formation of complexes with Nickel ion (II) were studied in this study from calibration curves, the optimal concentration of Ion Ni<sup>2+</sup> (0.7X10<sup>-4</sup>M) but ligands [1X10<sup>-3</sup>M of (MPA), 0.7X10<sup>-3</sup>M of (MHI), 0.65X10<sup>-3</sup>M of (HPA), 0.8X10<sup>-4</sup>M of (MHI)], while optimal (PH=8) was base medium to formation of complexes, other studies such as stoichiometric of complex by Job method and mole ratio method through series of solutions were prepared having a constant concentration (10<sup>-3</sup>M) of metal salt (NiCl<sub>2</sub>) and ligand, the (M:L) ration was determined from relationship between the absorption of observed light and mole

ratio (M:L) found to be (1:1) for complexes of Ni with ligands [(MHI), (HPA), (BHI)] but (1:2) for complex of Ni with ligand (MPA). Other studies of these complexes are shown in Table (1) and Figures (1-5) **Synthesis of complexes**

At optimal conditions of every complex and according to procedure<sup>(15)</sup>, the complexes were prepared by mix solution of ligands [(HPA), (MHI), (BHI)] respectively with NiCl<sub>2</sub> salt respectively in mole ratio (M:L) (1:1) except with (MPA) in (M:L) (1:2) with stirring for one hour, solid products formed, which was filtered and dried.



### Results and Discussion

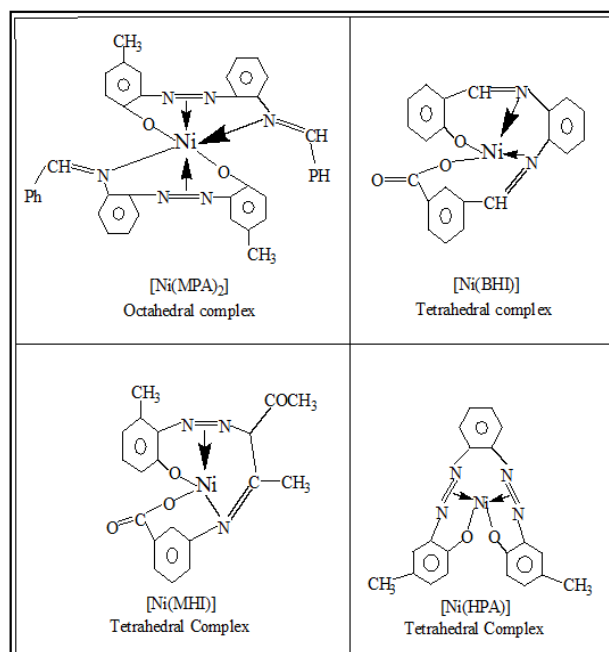
The elemental analysis shown in the Table (1) indicates that the Ni-complexes [(BHI), (MHI), (HPA)] have stoichiometry (M:L) (1:1) from results of mole ratio method while the Ni-complex (MPA) has mole ratio (M:L) (1:2).

The molar conductance values (0.76 -1.73 ohm<sup>-1</sup>.mol<sup>-1</sup>.cm<sup>2</sup>) of (10<sup>-3</sup>M) solution in DMSO indicate that the Ni-complexes are non-electrolytic in nature.

I.R-spectra exhibited frequencies in ligands [(MPA), (BHI), (MHI), (HPA)] at bands (3420 -3455) cm<sup>-1</sup> 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<sup>-1</sup>. The I.R-spectra of Schiff bases in ligands exhibit a strong bands at (1630 -1640) cm<sup>-1</sup> and azo group at (1490 -1498) cm<sup>-1</sup>, which have been shifted towards lower frequencies at (1622 -1630) cm<sup>-1</sup> of (CH=N) imine group<sup>(12,13)</sup> and at (1436 -1438) cm<sup>-1</sup> of (-N=N-) azo group<sup>(14,15)</sup> in complexes due to coordination with ((Ni)) 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.

### Figures of Complexes



**Table 1: physical properties & Elemental Analysis of Compounds**

Ligands & Complexes	M.P (C) <sup>o</sup>	$\lambda_{max}$	$\Omega^{-1} \cdot \text{cm}^2 \cdot \text{mole}^{-1}$	Conductance	Calc./Found			
					C%	H%	N%	Ni%
(MPA)	164	358	/	/	76.19	5.39	13.33	/
C <sub>20</sub> H <sub>17</sub> N <sub>3</sub> O					76.08	5.24	13.22	/
(BHI)	155	372	/	/	73.25	4.65	8.13	/
C <sub>21</sub> H <sub>16</sub> N <sub>2</sub> O <sub>3</sub>					73.10	4.50	8.05	/
(MHI)	176	386	/	/	84.58	5.38	11.89	/
C <sub>19</sub> H <sub>19</sub> N <sub>3</sub> O <sub>4</sub>					84.42	5.25	11.72	/
(HPA)	142	365	/	/	69.36	5.20	16.18	/
C <sub>20</sub> H <sub>18</sub> N <sub>4</sub> O <sub>2</sub>					69.21	5.09	16.08	/
(TIB)	184	395	/	/	61.71	4	16	/
C <sub>18</sub> H <sub>14</sub> N <sub>4</sub> O <sub>2</sub> S					61.62	3.92	15.89	/
[Ni(MPA) <sub>2</sub> ]	>250	415	0.95		69.89	4.65	12.23	8.54
					69.79	4.57	12.11	8.47
[Ni(BHI)]	242	430	1.15		62.88	3.49	6.98	14.64
					62.81	3.43	6.87	14.56
[Ni(MHI)]	235	450	1.73		55.65	4.14	10.25	14.32
					55.58	4.08	10.17	14.26
[Ni(HPA)]	215	435	0.76		59.59	3.97	13.90	14.57
					59.48	3.89	13.83	14.50

**Table 2: FT-IR data (cm<sup>-1</sup>) of ligands with complexes.**

Ligands & Complexes	(CH=N)	(-N=N-)	(OH)	(M-N)	(M-O)
	imine group	azo group			
(MAP)	1640	1490	3420	/	/
(BHI)	1635	/	3455	/	/
(MHI)	1637	1498	3430	/	/

(HPA)	/	1495	3450	/	/
(TIB)	1630	1498	3460	/	/
[Ni(MPA) <sub>2</sub> ]	1630	1436	/	478	549
[Ni(BHI)]	1629	/	/	478	509
[Ni(MHI)]	1622	1438	/	476	595
[Ni(HPA)]	/	1436	/	478	511

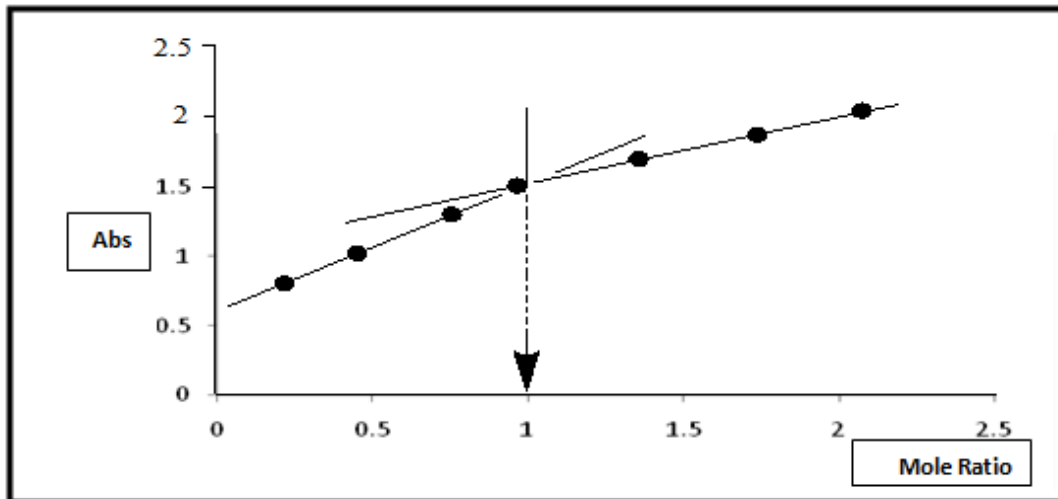
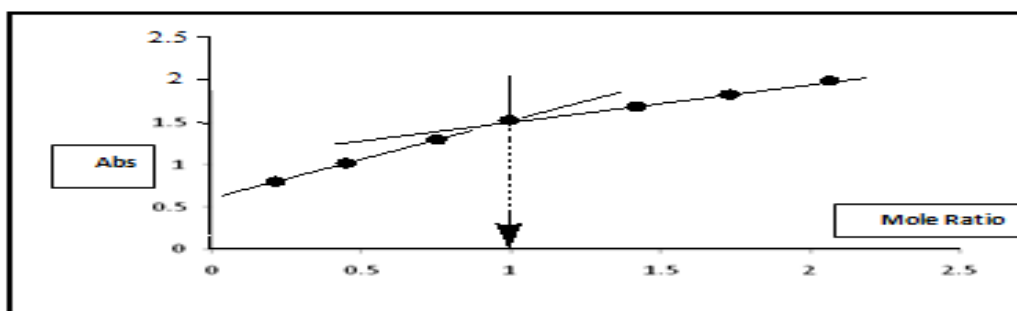


Fig (1) Mole ratio of complex [Ni(HPA)]



Fig(2): Mole ratio of complex [Ni(MHI)]

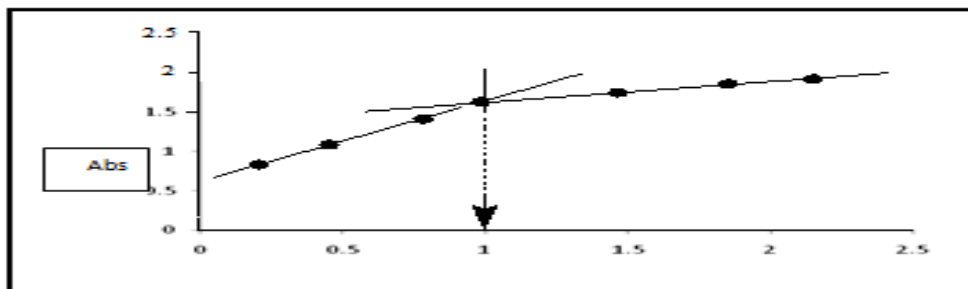


Fig (3): Mole ratio of complex [Ni(BHI)]

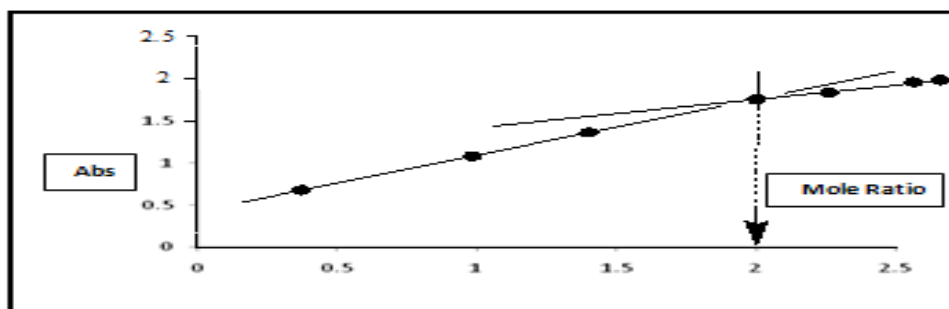
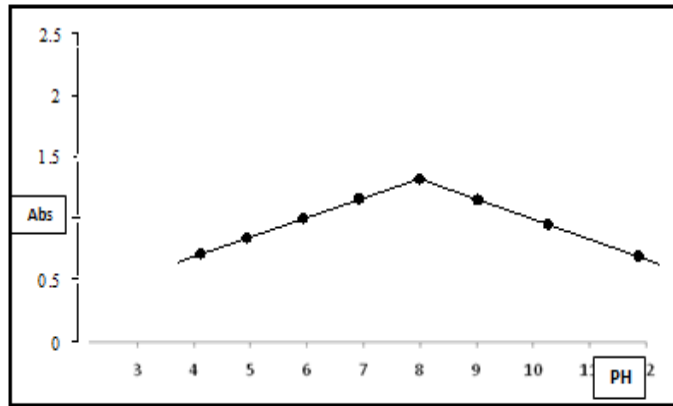
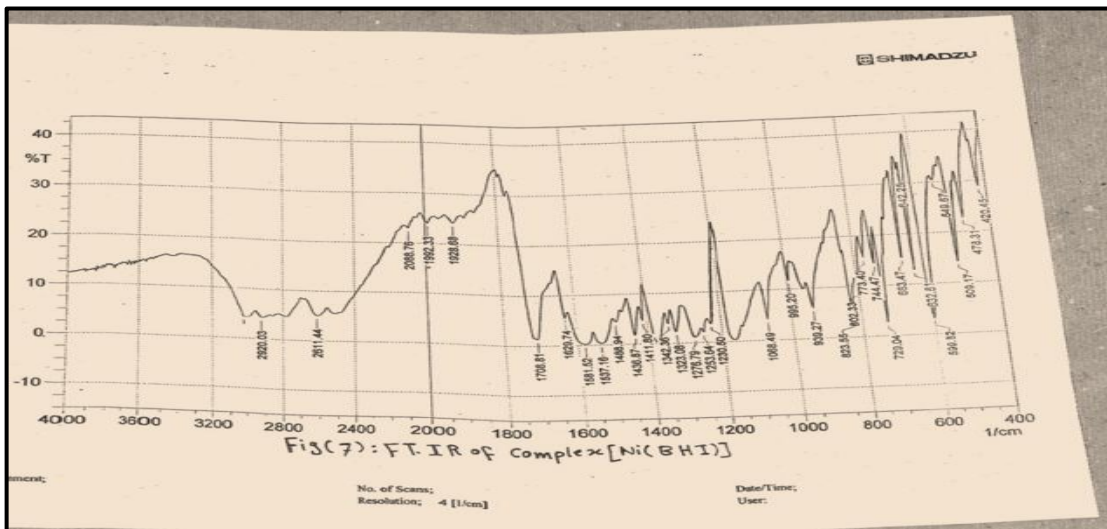
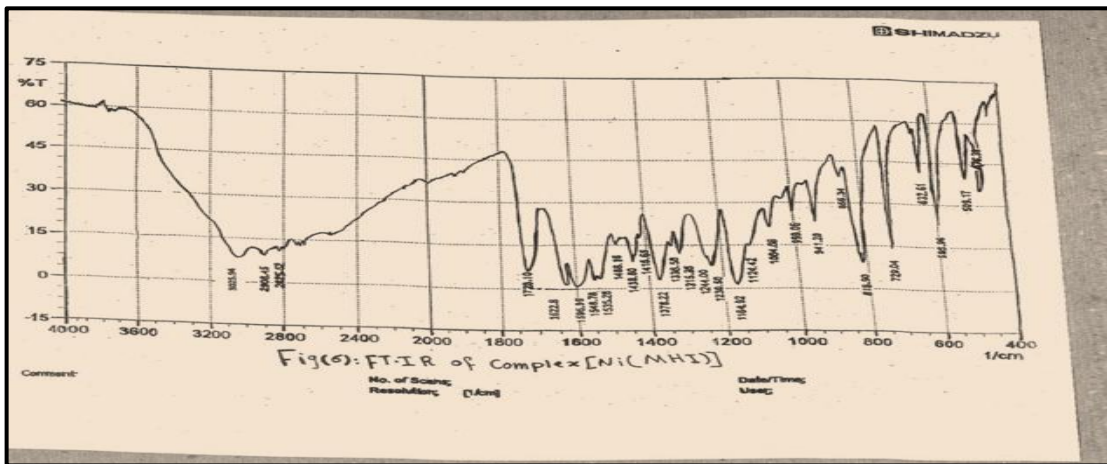
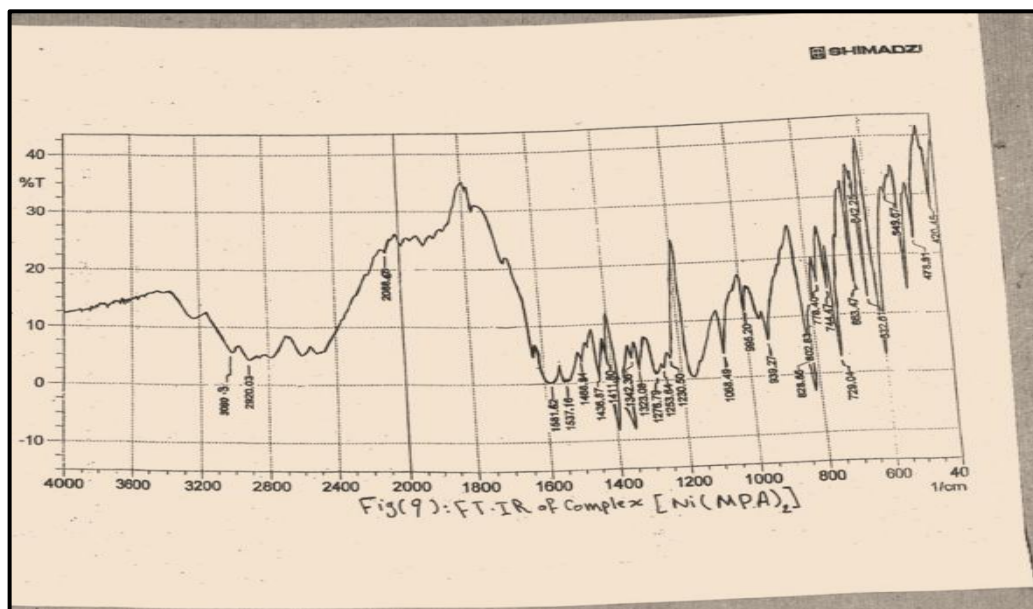
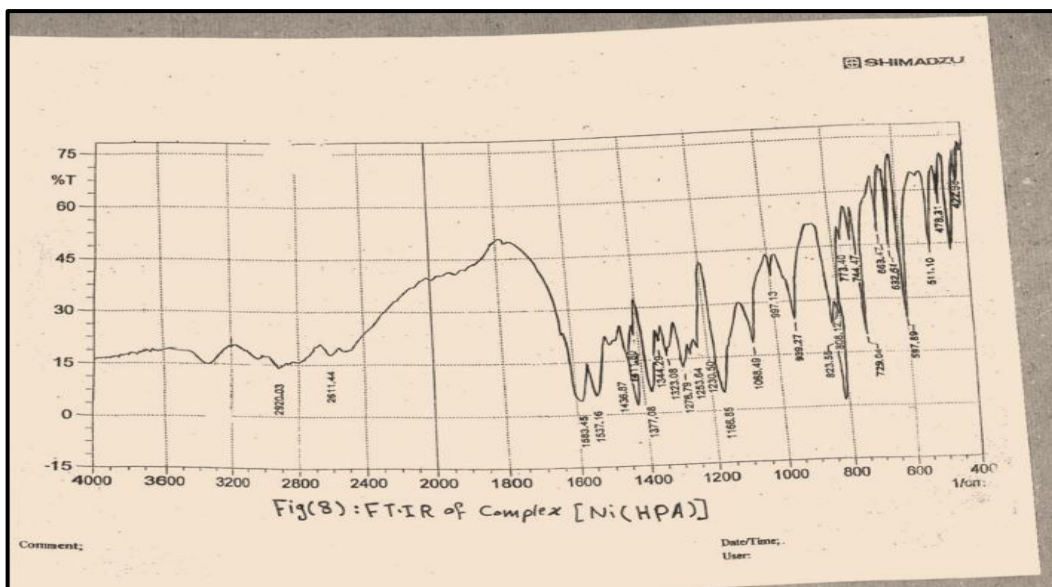


Fig (4): Mole ratio of complex [Ni(MPA)<sub>2</sub>]



Fig(5): Variation of PH of Complexes





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