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## Research Article



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## Equilibrium studies on Bi-valent transition metal chelates with 1-phenyl – 3 – (2' – mercaptophenyl) – N – (3 – hydroxyl – 1'', 2'', 4'' triazolyl) propene – 1 – imine (PMHTPI)

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### Abstract

Metal complexes have attracted the attention of the chemist to study the structure, antifungal antibacterial and physiological activity of the ligand and their complexes. Metal ligand stability constant of above system are to be determined by Calvin Bjerrum pH metric titration technique as adopted by Irving-Rossotti.

**Keywords:** pH metric titration, chelates, proton ligand, stability constant.

### Introduction

Metal complexes have attracted the attention of the chemist to the study the structure, antifungal, antibacterial and physio-logical activity of the ligand and their complexes. Literature survey reveals that determination of stability constant and related thermodynamical parameters is not much studies. For this purpose, we have selected most common transition metals of first transition series. These are Co, Ni, Cu, Zn and Cd. The ligands is biologically active 1-phenyl – 3 – (2' – mercaptophenyl) – N – (3 – hydroxy – 1'', 2'', 4'' triazolyl ) propene – 1 – imine (PMHTPI).

We have determined stepwise and overall stability constant stepwise and overall stability constant of

bivalent transition metals with pre selected ligands by B. Jerrum method of pH metric titration techniques adopted by Irving and Rossotti. Practical proton ligand stability constant were calculate from formation curve. Average number of hydrogen ion attached to a ligand ( $\bar{n}_A$ ) and average number of ligand bound to a metal ( $\bar{n}$ ) are also calculated. The values of proton ligand stability constant were Calculated by half – integral method and these values were further corroborated by linear plot method.

$P^L$  calculation was done by using standard expression. These values were further corroborated from the straight line plot of  $\log(\bar{n}/1-\bar{n})$  vs  $P^L$  and  $(2-\bar{n})/(\bar{n}-1)$  vs  $P^L$ .

## Experimental

### Preparation of standard solution

Preparation and standardization of sodium hydroxide solution (1.0 M), potassium nitrate solution (1.0M), nitric acid solution (1.0M), EDTA solution (0.01M), metal nitrate solution of copper (0.01M), Nickel (0.01), cobalt (0.01M), zinc (0.01M) and cadmium (0.01M) by literature method.

### Preparation of indicator

- 1) Xylenol orange indicator: 0.5 g xylenol orange was dissolved in 100 mL of distilled water.
- 2) Fast sulphon Black: 0.5 g of the solid in 100 mL of double distilled water.
- 3) Murexide indicator: 0.1g of murexide was mixed with 10 g of  $\text{KNO}_3$

### Preparation of Buffer solution

Ammonia – ammonium chloride buffer: 35.0 g of  $\text{NH}_4\text{Cl}$  was dissolved in exactly 284 mL of AR grade liquid  $\text{NH}_3$  and diluted to 500 mL with double distilled water. The Ammonia – ammonium chloride buffer has  $\text{pH} = 10.0$ .

### Preparation of ligand :

One mole of chalcone in 30 ml of ethanol was taken in round bottom flask and 3 – hydroxy 4 – amino – 1,2,4 triazole was added the reaction mixture was refluxed for 6-7 hours solvent was evaporated on water bath and separated solid was collected. The product was washed with absolute alcohol and crystallized from rectified spirit to obtain yellow coloured crystals.

Yield = 2.12 g

MP =  $172.8^{\circ}\text{C}$

(Anal found: C, 64.50%, H, 4.63%, N, 16.09% and 1s, 14.78%)

$\text{pH}$  metric titration were done in dioxane water (v/v 50:50) medium at constant ionic strength 0.10 (M)  $\text{KNO}_3$  at 308K.

### Titration procedure

The following sets of mixtures were prepared for titrations.

1. 1.0 mL  $\text{HNO}_3$  + 15 mL  $\text{KNO}_3$  + 34 ml water + 50 ml dioxane.
2. 1 ml  $\text{HNO}_3$  + 15 ml  $\text{KNO}_3$  + 5 ml ligand solution + 34 ml water + 45 ml dioxane.
3. 1 ml  $\text{HNO}_3$  + 15 ml  $\text{KNO}_3$  + 1 ml metal ion solution + 5ml ligand solution + 33 ml water + 45 ml dioxane.

Total volume  $V^0$  in each set was 100.0 ml and dioxane water ratio was 50:50 (v/v). The titration were carried out in a small neck beaker called cell. The cell stirrer, microburette and electrode of the pH meter in water thermostat at 308 K temperature within  $\pm 1$ .

#### 1) Titration of the acid mixture no. 1:-

Mixture no. 1 is taken in the titration cell when it attain a constant temperature, it was titrated against standard alkali solution (1.0M). The change in pH of the solution with each addition was occurred Table No. – 2.

#### 2) Titration of the mixture No. 2 containing acid and ligand.:-

Mixture No. 2 is taken in a clear titrating beaker and when it attained the same constant temperature it was titrated against alkali solution (1.0 M). The change in pH of the solution recorded (Table. 2)

#### 3) Titration of the mixture No. 3 containing acid, ligand and metal ion:-

Mixture No.3 was taken in a titrating beaker and when it attain the same constant temperature, it was titrated as above. The change in pH recorded (Table. 2).

The metal ion selected for our study were Co(II), Ni(II), Cu(II), Zn(II) and Cd(II). During the titration the change in colour and appearance of turbidity at particular pH value were recorded simultaneously.

A graph between P<sup>H</sup> meter reading [B] and volume of alkali added was plotted in each case.

The three titration curve so obtained for each metal ions are referred as :

- Acid titration curve
- Ligand titration curve
- Complex titration curve respectively.

The concentration used in experiment are given in table. 1.

The values of volume V<sub>1</sub>, V<sub>2</sub>& V<sub>3</sub> , corresponding to the same pH values were read from a) , b) & c) respectively from the experimental curve (Graph - I).

**Table 1: Concentrations used in the experiment**

Metal / Ions	V <sup>o</sup> (mL)	Y	N <sup>o</sup>	E <sup>o</sup>	T <sub>L</sub> <sup>o</sup>	T <sub>M</sub> <sup>o</sup>
Co (II)	100	1	1.0 (M)	1.0 x 10 <sup>-2</sup> (M)	2.4 x 10 <sup>-3</sup> (M)	5.0 x 10 <sup>-4</sup> (M)
Ni(II)	100	1	1.0 (M)	1.0 x 10 <sup>-2</sup> (M)	2.4 x 10 <sup>-3</sup> (M)	5.0 x 10 <sup>-4</sup> (M)
Cu(II)	100	1	1.0 (M)	1.0 x 10 <sup>-2</sup> (M)	2.4 x 10 <sup>-3</sup> (M)	5.0 x 10 <sup>-4</sup> (M)
Zn(II)	100	1	1.0 (M)	1.0 x 10 <sup>-2</sup> (M)	2.4 x 10 <sup>-3</sup> (M)	5.0 x 10 <sup>-4</sup> (M)
Cd(II)	100	1	1.0 (M)	1.0 x 10 <sup>-2</sup> (M)	2.4 x 10 <sup>-3</sup> (M)	5.0 x 10 <sup>-4</sup> (M)

**Table 2: Volume of alkali consumed in different titrations**

Ligand PMHTPI (L<sub>1</sub>)

Temperature: 308 ± 1K

~<sup>o</sup> = 0.10 (M) KNO<sub>3</sub>

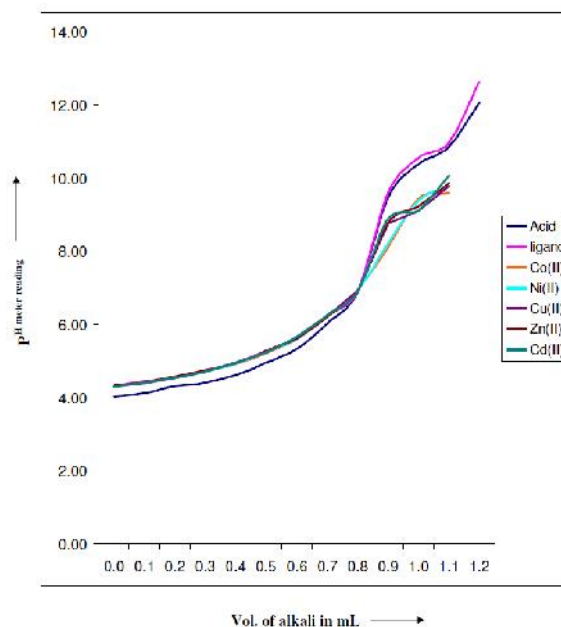
Water – dioxane medium (v/v) = 50: 50

Vol. of alkali added in mL	pH – meter reading [B]						
	H <sup>+</sup>	H <sup>+</sup> + L	H <sup>+</sup> + L + Co(II)	H <sup>+</sup> + L + Ni(II)	H <sup>+</sup> + L + Cu(II)	H <sup>+</sup> + L + Zn(II)	H <sup>+</sup> + L + Cd(II)
0.0	4.04	4.32	4.30	4.32	4.32	4.34	4.30
0.1	4.14	4.46	4.44	4.42	4.40	4.44	4.42
0.2	4.32	4.54	4.54	4.56	4.54	4.58	4.54
0.3	4.42	4.74	4.76	4.74	4.72	4.76	4.72
0.4	4.62	4.96	4.92	4.92	4.96	4.94	4.96
0.5	4.96	5.28	5.23	5.26	5.24	5.28	5.24
0.6	5.34	5.62	5.62	5.60	5.62	5.64	5.68
0.7	6.04	6.24	6.22	6.26	6.25	6.22	6.26
0.8	6.90	6.92	6.96	6.94	6.92	6.94	6.92
0.9	9.50	9.62	8.14	8.22	8.78	8.80	8.90
1.0	10.40	10.56	9.46	9.40	9.12	9.24	9.14
1.1	10.86	10.98	9.60	9.78	9.80	9.86	10.08
1.2	12.08	12.65					

**Graph – I**  
**Experimental curve with ligand PMHTPI (L<sub>1</sub>)**  
**Temp. 308 ± 1 K**

$\sim^0 = 0.10$  (M) KNO<sub>3</sub>

Water: dioxane = 1:1(v/v)



**Practical proton ligand stability constant.**

The value of  $\bar{n}_A$  at various pH reading [B] were calculated from the acid and ligand titration curves and recorded in table no. 3.

**Table – 3**

Ligand : PMHTPI

Temp: 308 ± 1K

[B]	V <sub>2</sub> – V <sub>1</sub>	$\bar{n}_A$	$\log \bar{n}_A / (1 - \bar{n}_A)$
5.2	0.005	0.888	
5.4	0.005	0.884	
5.6	0.006	0.8842	
5.8	0.006	0.8812	
6.0	0.007	0.8802	
6.2	0.007	0.876	
6.4	0.008	0.8732	
6.6	0.008	0.868	
6.8	0.020	0.8612	
7.0	0.012	0.8522	
7.2	0.014	0.8442	1.3260
7.4	0.014	0.8412	1.2950
7.6	0.016	0.8282	1.2092

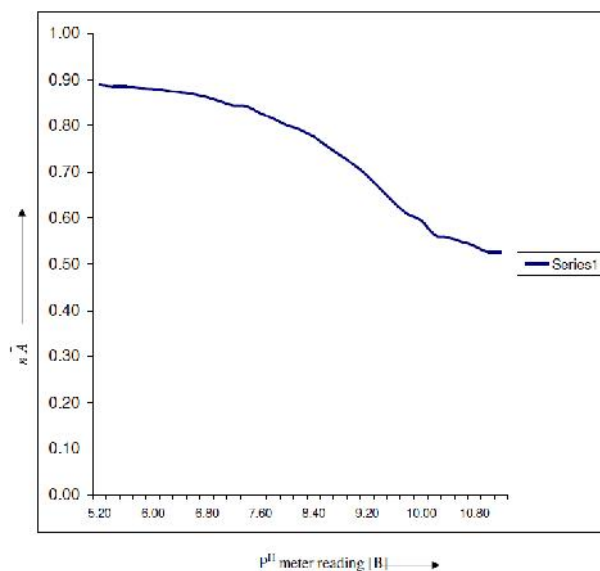
7.8	0.020	0.8156	1.0470
8.0	0.022	0.8012	0.8730
8.2	0.026	0.7922	0.8162
8.4	0.030	0.7762	0.7486
8.6	0.032	0.7554	0.6730
8.8	0.040	0.7354	0.6066
9.0	0.042	0.7152	0.5462
9.2	0.052	0.6922	0.4802
9.4	0.056	0.6642	0.4096
9.6	0.062	0.6356	0.3442
9.8	0.070	0.6074	0.2840
10.0	0.080	0.5952	0.2184
10.2	0.096	0.5632	0.1412
10.4	0.106	0.5584	0.2752
10.6	0.110	0.5492	0.2040
10.8	0.116	0.5396	0.0442
11.0	0.126	0.5274	-0.0494
11.2	0.140	0.527	-0.2262

**Graph No. – II**  
**Formation curve of ligand PMHTPI (L<sub>1</sub>)**

**Plot of  $n\bar{A}$  Vs [B]**

**Temp. 308 ± 1 K**

$\sim^0 = 0.10$  (M) KNO<sub>3</sub>



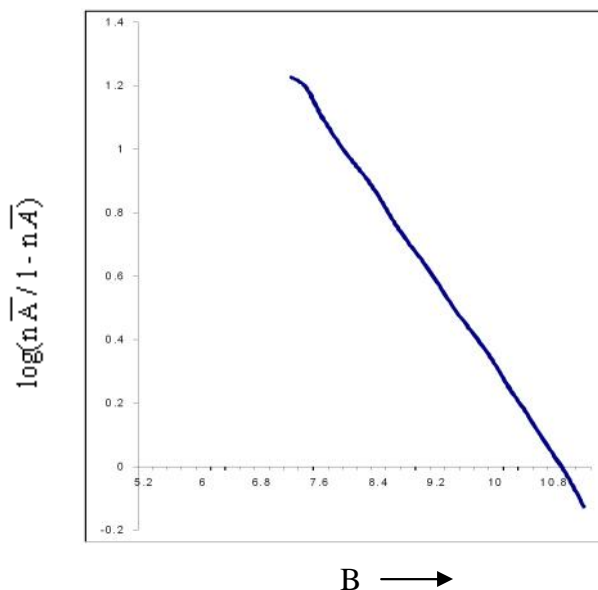
The values of proton ligand stability constant were calculated by Half integral method and the values were further corroborated by linear plot method (Graph III).

**Graph. III**

**Linear plot of  $\log(\bar{n}_A / 1 - \bar{n}_A)$  Vs [B]**

$\mu^0 = 0.10$  (M)  $\text{KNO}_3$

**Temp.  $308 \pm 1$  K**



**Co(II) + PMHTPI system**

Metal ligand titration curve crossed over ligand titration curve at pH 5.26. The values of  $\bar{n}$  extend between 0.20 to 1.82 (Graph IV, Table 4) indicating the formation of ML and  $\text{ML}_2$  type

complexes. The values of  $\log K_1$  and  $K_2$  were calculated by half integral method. It was further corroborated from the linear plot of  $\log \bar{n} / 1 - \bar{n}$  vs  $P^L$  and  $\log 2 - \bar{n} / \bar{n} - 1$  vs PL (Graph V(a), V(b) and Table. 5.

**TABLE – 4**

Co (II) + PMHTPI

Temperature: 308 K

<b>B</b>	<b><math>V_3 - V_2</math></b>	<b><math>\bar{n}</math></b>	<b><math>P^L</math></b>
5.2	0.008	0.2018	9.0646
5.4	0.010	0.3036	8.8736
5.6	0.014	0.3274	8.6854
5.8	0.022	0.4014	8.5026
6.0	0.028	0.6056	8.3220
6.2	0.040	0.7448	8.1366
6.4	0.052	1.10346	7.9568
6.6	0.064	1.3408	7.7800
6.8	0.076	1.5726	7.6076
7.0	0.082	1.6758	7.4334
7.2	0.090	1.8170	7.2666

Figure no. – IV

Formation curve of Co(II)

Plot of  $\bar{n}$  Vs  $P^L$

Metal: Co(II)

Ligand : PMHTPI

Temp.  $308 \pm 1$  K

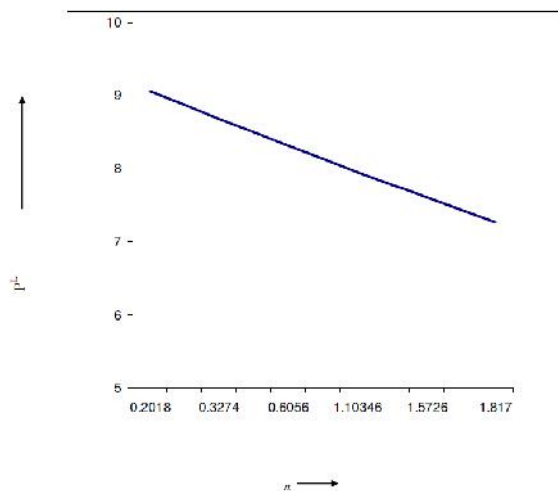


Table – 5

Co (II) + PMHTPI

Temperature 308 K

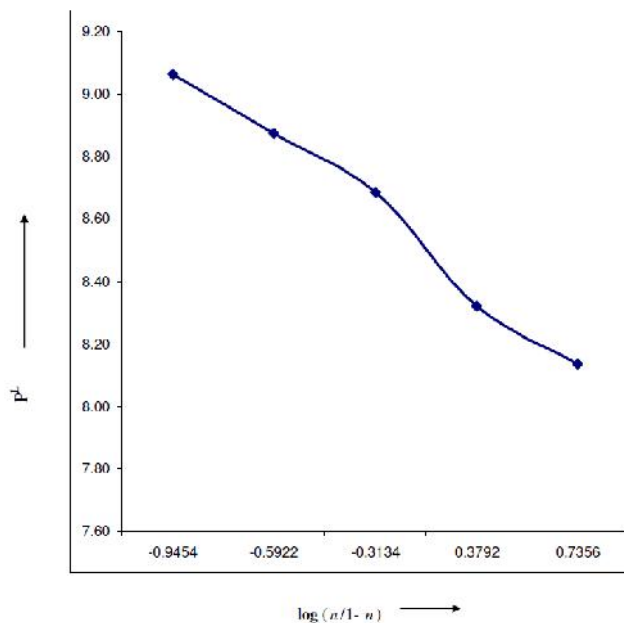
$\log \frac{\bar{n}}{1-\bar{n}}$	$P^L$	$\log \frac{2-\bar{n}}{\bar{n}-1}$	$P^L$
-0.9454	9.0646	0.5994	7.7800
-0.5922	8.8734	0.0578	7.6076
-0.3134	8.6850	-0.4190	7.4332
0.3792	8.3224		
0.7356	8.1362		

Graph No. – V (a)

Linear Plot of  $\log (\bar{n}/1-\bar{n})$  Vs  $P^L$

Metal ion: Co(II)  
Ligand : PMHTPI

Temp.  $308 \pm 1$  K

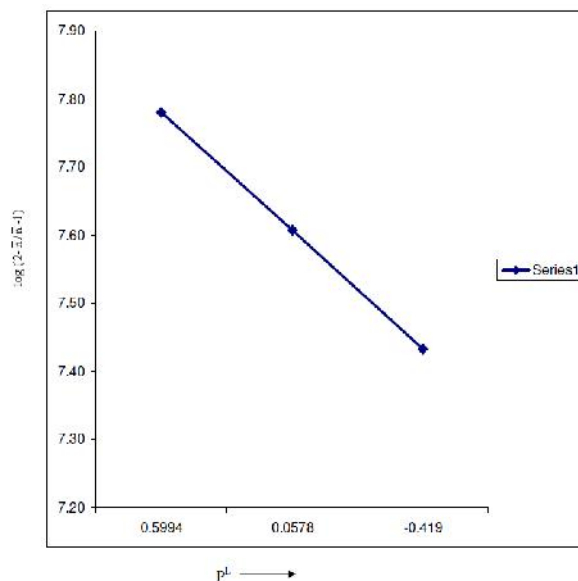


Graph No. – V(b)

Linear plot of  $\log (2-\bar{n}/\bar{n}-1)$  Vs  $P^L$   
Metal : Cobalt (II)

Ligand : PMHTPI

Temp:  $308 \pm 1$  K





**Ni(II) + PMHTPI system**

The complex titration curve on the system crossed the ligand mixture curve at pH =4.90. The curve increased regularly upto pH =7.48 indicating constant rate of release of proton and then complex titration curve diverges indication quick but incomplete discussion of ligand. No turbidity appear, hence hydrolysis does not take place. The calculation of  $\bar{n}$  was done by using titration

curve. The value of  $\bar{n}$  extended between 0.10 to 1.95 indicating the formation of complexes ML and ML<sub>2</sub> type (Graph VI, Table 6)

The formation curve ( $\bar{n}$  vs P<sup>L</sup>) gave the value log K<sub>1</sub>, and log K<sub>2</sub> by half integral method. These value were further corroborated from the linear plot of log  $\bar{n}/1 - \bar{n}$  vs PL and log 2 -  $\bar{n}/\bar{n} - 1$  vs PL (Graph VII a, VII b and Table 7).

**Table – 6**

Ni (II) + PMHTPI

Temp : 308 ± 1K

B	V <sub>3</sub> – V <sub>2</sub>	$\bar{n}$	P <sup>L</sup>
5.0	0.006	0.1016	7.8648
5.2	0.012	0.2656	7.6796
5.4	0.020	0.4294	7.4946
5.6	0.032	0.6156	7.3132
5.8	0.038	0.8034	7.1322
6.0	0.046	0.9932	6.9520
6.2	0.054	1.2096	6.7766
6.4	0.066	1.4306	6.6024
6.6	0.082	1.6972	6.4364
6.8	0.090	1.9598	6.2722

**Graph No. – VI**  
**Formation curve of Ni(II)**  
**Plot of  $\bar{n}$  vs P<sup>L</sup>**

**Metal : Ni(II)**  
**Ligand: PMHTPI**

**Temp 308 ± 1K**

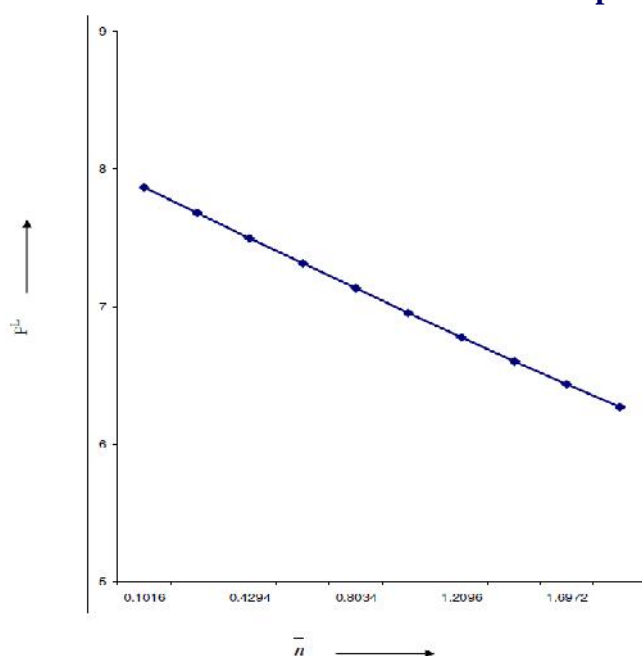


Table – 7

Ni (II) + PMHTPI  
 $\sim^0 = 0.10(M) KNO_3$

Temp:  $308 \pm 1K$   
 Water : Dioxane = 1:1(v/v)

$\log(\bar{n} / 1 - \bar{n})$	$P^L$	$\log(2 - \bar{n} / \bar{n} - 1)$	$P^L$
-0.9456	8.8646	0.5756	7.7766
-0.4418	8.6798	0.1214	7.6025
-0.1236	8.4948	-0.3620	7.4363
0.2048	8.3134		
0.6116	8.1326		

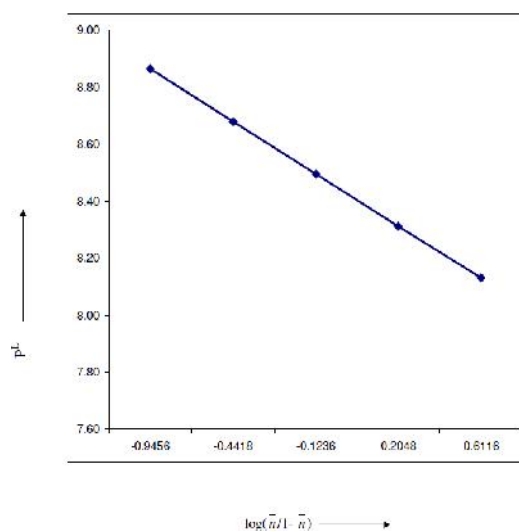
Graph No. - VII (a)

Linear plot of  $\log(\bar{n} / 1 - \bar{n})$  Vs  $P^L$

Metal: Ni(II)

Ligand : PMHTPI

Temp.  $308 \pm 1 K$

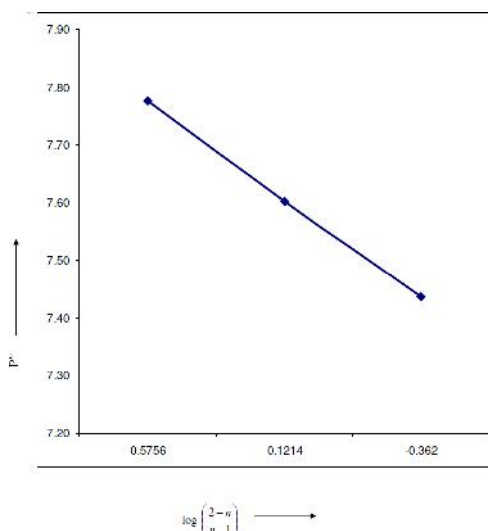


Graph No. – VII (b)

Linear plot of  $\log(2-\bar{n} / \bar{n} - 1)$  Vs  $P^L$

Metal: Ni(II)  
Ligand : PMHTPI

Temp.  $308 \pm 1$  K



**Cu(II) + PMHTPI system**

The complex titration curve crossed the acid titration curve and well separated from ligand titration curve at pH = 5.92. The curve increased regularly and run parallel to ligand titration curve upto pH =9.2. During the titration equilibrium is attained very quickly, no turbidity appears, hence hydrolysis does not take place. The value of  $\bar{n}$  extended from 0.16 to 1.86 indication the

formation of ML and  $ML_2$  type complexes(Graph VIII Table -8)

The formation curve for the system was very symmetrical, it gave the values of  $\log K_1$  and  $\log K_2$  by half integral method. These values were further verified from mid-point slope method and linear plot of  $\log(\bar{n} / 1 - \bar{n})$  vs  $P^L$  and  $\log(2-\bar{n} / \bar{n} - 1)$  vs  $P^L$  (Graph IX a, IX b and Table 9).

Table – 8

Cu(II) + PMHTPI

Temp :  $308 \pm 1$  K

$[B]$	$V_3 - V_2$	$\bar{n}$	$P^L$
6.2	0.012	0.1640	7.2700
6.4	0.016	0.2472	7.0782
6.6	0.014	0.3722	6.8892
6.8	0.020	0.5006	6.7018
7.0	0.026	0.6314	6.5146
7.2	0.036	0.7846	6.3302
7.4	0.040	0.9372	6.1460
7.6	0.052	1.1220	5.9662
7.8	0.060	1.3116	5.7880
8.0	0.070	1.5724	5.6206
8.2	0.082	1.8632	5.4584

Graph No. – VIII

Formation curve of Cu(II)

Plot of  $\bar{n}$  Vs  $P^L$

Metal: Cu(II)

Ligand : PMHTPI

Temp.  $308 \pm 1$  K

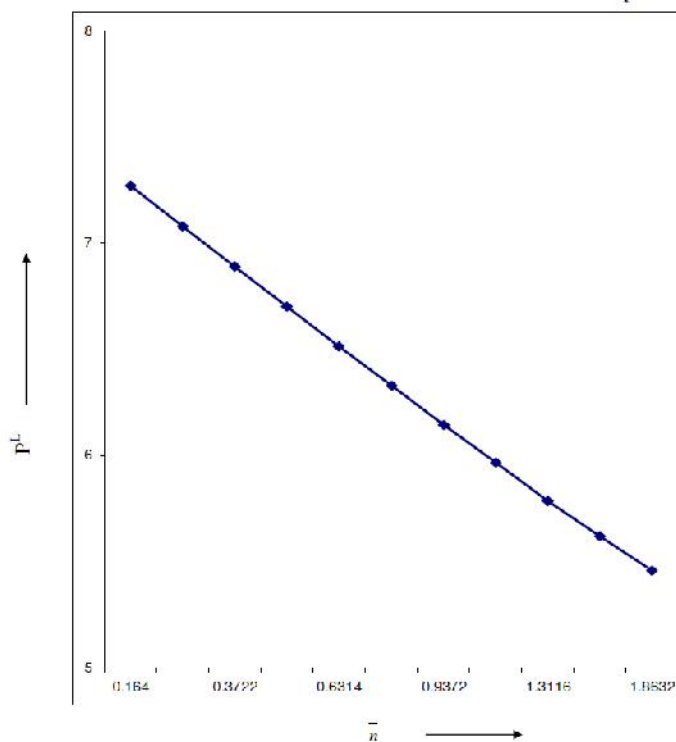


Table – 9

Cu (II) + PMHTPI

Temp:  $308 \pm 1$  K

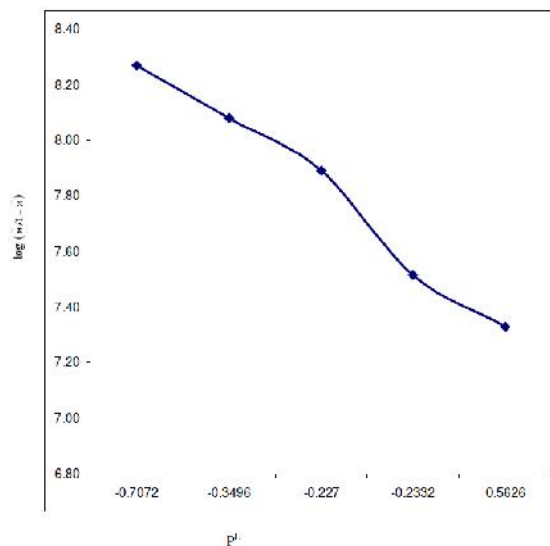
$\log (\bar{n} / 1 - \bar{n})$	$P^L$	$\log (2 - \bar{n} / \bar{n} - 1)$	$P^L$
-0.7072	8.2704	0.8566	6.9666
-0.3496	8.0786	0.3444	6.7888
-0.2270	7.8896	-0.1274	6.6206
-0.2332	7.5144	-0.7996	6.4590
0.5626	7.3306		

Graph No. - IX (a)

Linear plot of  $\log (\bar{n}/1-\bar{n})$  Vs  $P^L$

Metal: Cu(II)  
Ligand :PMHTPI

Temp :  $308 \pm 1K$

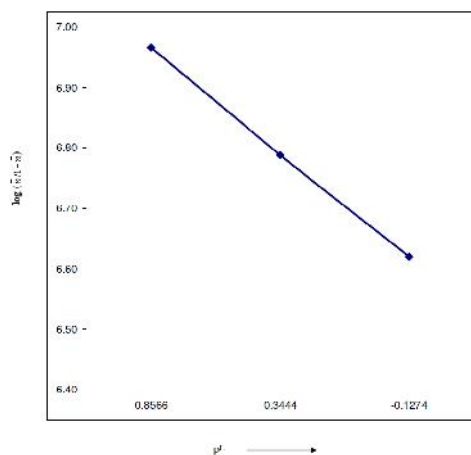


Graph No. - IX (b)

Linear plot of  $\log (2 - \bar{n}/\bar{n} - 1)$  Vs  $P^L$

Metal: Cu(II)  
Ligand :PMHTPI

Temp :  $308 \pm 1K$



### Zn (II) + PMHTPI System

Metal ligand titration curve is well separated from ligand titration curve at  $P^H = 5.92$  and complex titration curve diverges at higher  $P^H$ , indication the incomplete dissociation of ligand. The values of  $\bar{n}$  extended from 0.40 to 1.86 (Graph X, Table -10). The values of  $\log K_1$  and  $\log K_2$  were

calculated by half integral method. It was further verified by mid-point calculation method. The values of  $\log K_1$  and  $\log K_2$  were further corroborated from the linear plot of  $\log \bar{n}/1 - \bar{n}$  vs  $P^L$  and  $\log 2 - \bar{n}/\bar{n} - 1$  vs  $P^L$  (Graph IX a, IX b and Table - 11).

Table – 10

Zn (II) + PMHTPI

Temp: 308 ± 1K

$B$	$V_3 - V_2$	$\bar{n}$	$P^L$
6.0	0.006	0.406	7.4590
6.2	0.008	0.1020	7.2698
6.4	0.010	0.1854	7.0782
6.6	0.014	0.3718	6.8896
6.8	0.020	0.5006	6.7014
7.0	0.026	0.6310	6.5146
7.2	0.034	0.7846	6.3302
7.4	0.040	0.9372	6.1460
7.6	0.052	1.1220	5.9666
7.8	0.064	1.3116	5.7880
8.0	0.076	1.5724	5.6206
8.2	0.088	1.8636	5.4584

Formation curve of Zn(II)

Plot of  $\bar{n}$  Vs  $P^L$

Metal: Zn(II)

Ligand : PMHTPI

Temp. 308 ± 1 K

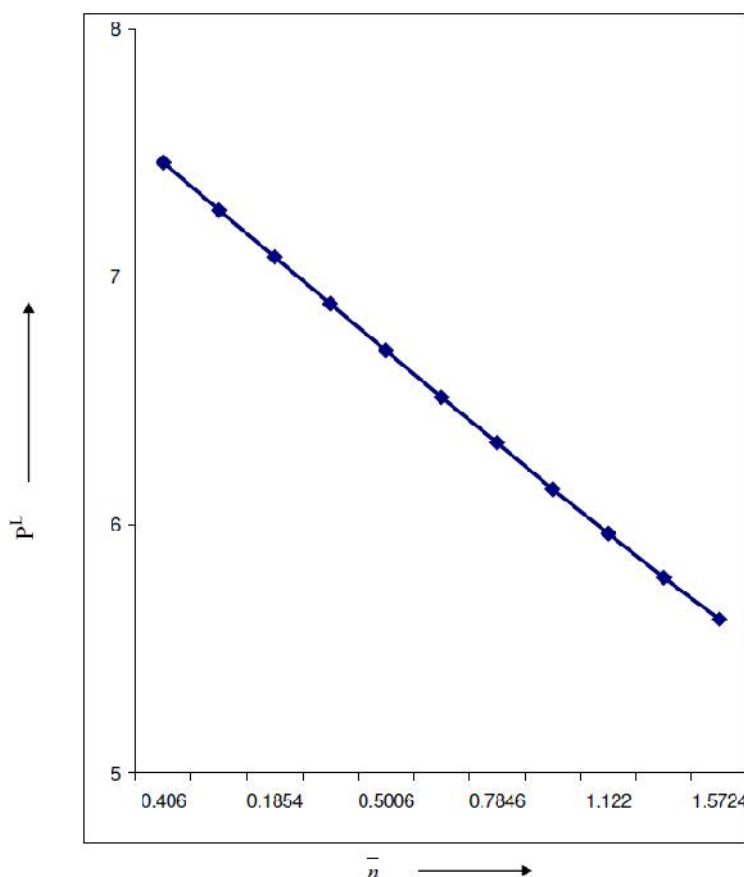


Table – 11

Zn (II) + PMHTPI

Temp: 308 ± 1 K

$\log (\bar{n}/1-\bar{n})$	$P^L$	$\log (2-\bar{n}) / (\bar{n} - 1)$	$P^L$
-0.7070	8.2700	0.8566	6.9666
-0.3494	8.0786	0.3440	6.7888
-0.2268	7.8896	-0.1274	6.6206
-0.2330	7.5146	-0.7996	6.4586
0.5624	7.3302		

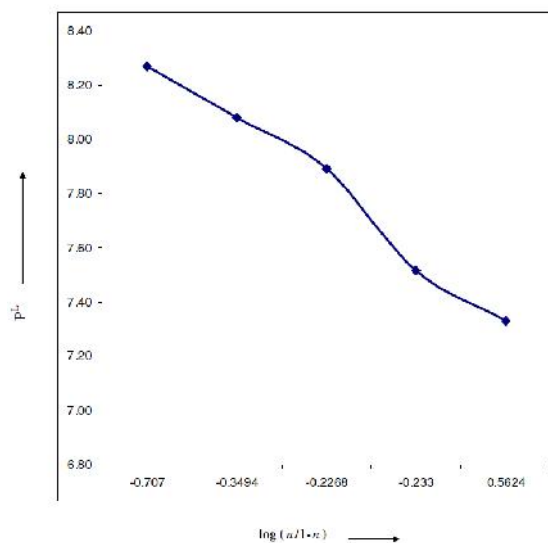
Figure no. - XI (a)

Linear Plot of  $P^L$  Vs  $\log (\bar{n}/1-\bar{n})$

Metal: Zn(II)

Ligand : PMHTPI

Temp. 308 ± 1 K



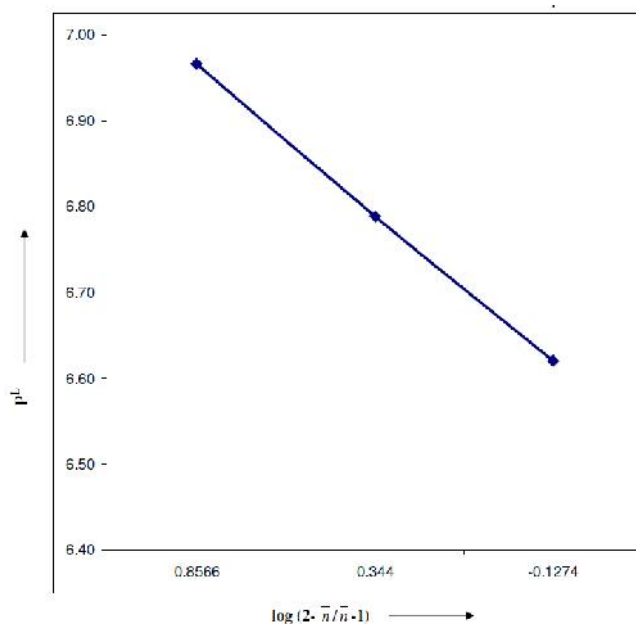
Graph No. – XI (b)

Linear Plot of  $\log (2 - \bar{n}/\bar{n} - 1)$  Vs  $P^L$

Metal: Zn(II)

Ligand : PMHTPI

Temp.  $308 \pm 1$  K



**Cd(II) + PMHTPI system:-**

The complex titration curve are well separated from ligand titration curve at  $P^H = 6.46$ . No turbidity is observed and hydrolysis does not take place. The values of  $\bar{n}$  extended from 0.04 to 1.72 indicating the formation of ML and  $ML_2$  type complexes (Graph- XII, Table – 12).

Formation curves were nearly symmetrical the values of  $\log K_1$  and  $\log K_2$  were calculated from the formation curve by half integral method and corroborated from mid-point slope method and linear plot of  $\log \bar{n}/1 - \bar{n}$  vs  $P^L$  and  $\log 2 - \bar{n}/\bar{n} - 1$  vs  $P^L$  (Graph XII a, XII b and Table – 13).

Table – 12

Metal: Cd(II)

Ligand: PMHTPI

Temperature :  $308 \pm 1$  K

$B$	$V_3 - V_2$	$\bar{n}$	$P^L$
6.0	0.006	0.0414	8.0590
6.2	0.008	0.1240	7.8664
6.4	0.010	0.2296	7.6764
6.6	0.014	0.3784	7.4902
6.8	0.026	0.5726	7.3086
7.0	0.036	0.7668	7.1280
7.2	0.044	0.9710	6.9496
7.4	0.058	1.2024	6.7756
7.6	0.066	1.4354	6.6036
7.8	0.076	1.7280	6.4407



Graph No. – XII

Formation curve of Cd(II)

Plot of  $\bar{n}$  Vs  $P^L$

Metal: Cd(II)

Ligand : PMHTPI

Temp.  $308 \pm 1$  K

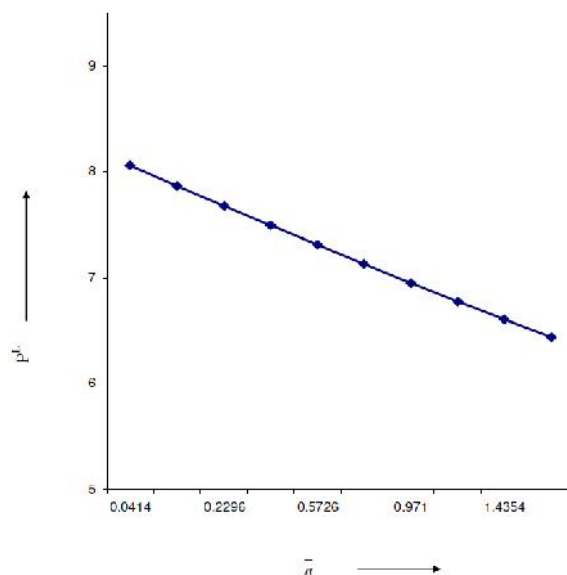


Table – 13

Cd (II) + PMHTPI

Temperature  $308 \pm 1$  K

$\log(\bar{n}/1-\bar{n})$	$P^L$	$\log(2-\bar{n}/\bar{n}-1)$	$P^L$
-0.8476	7.8668	0.5956	6.7757
-0.5262	7.6766	0.1120	6.6032
-0.2152	7.4902	-0.4286	6.4406
0.1276	7.3086		
0.5778	7.2180		

Graph No. – XIII (a)

Linear Plot of  $\log(\bar{n}/1-\bar{n})$  Vs  $P^L$

Metal: Cd(II)  
Ligand : PMHTPI

Temp.  $308 \pm 1$  K

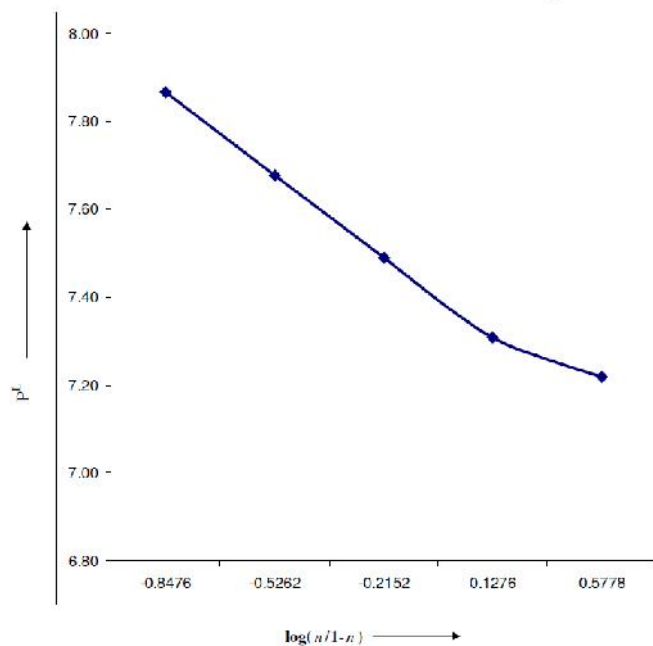
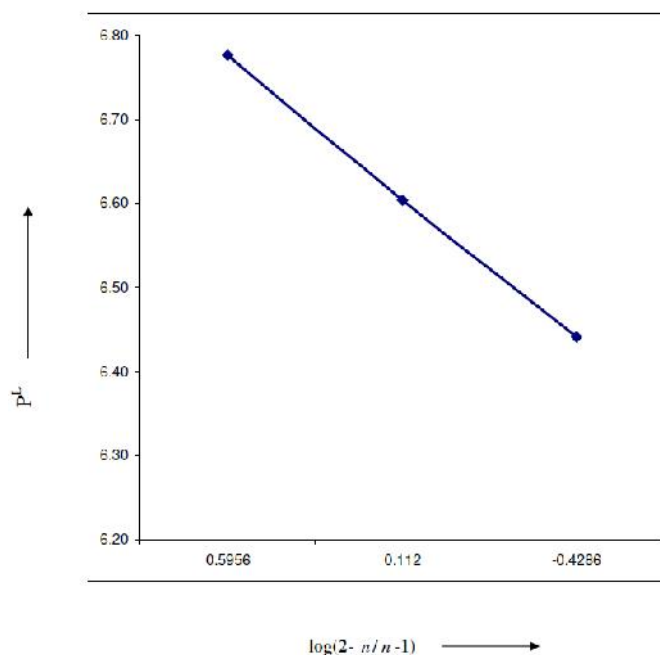


Figure no.– XIII (b)

Linear Plot of  $\log(2-\bar{n}/\bar{n}-1)$  Vs  $P^L$

Metal: Cd(II)  
Ligand : PMHTPI

Temp.  $308 \pm 1$  K



## Results and Discussion

The values of stepwise stability constant obtained by different computational methods were recorded in Table No. – 14. The different methods are –

- Half – integral method
- Mid – point calculation method
- Straight line plot method.

The most representative value of stability constant were tabulated in Table No. – 15.

**Table – 14**

**Values of protonation constant of ligand and stepwise stability constant of complexes of Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) with ligand PMHTPI at temperature 308K**

System		Temp. 308 K	
		$\log K_1$	$\log K_2$
PMHTPI	a		10.84
	b		-
	c		10.84
Co (II)	a	7.48	6.56
	b	7.46	6.50
	c	7.50	6.54
Ni (II)	a	7.40	6.50
	b	7.36	6.56
	c	7.38	6.58
Cu (II)	a	6.70	5.66
	b	6.60	5.60
	c	6.76	5.62
Zn (II)	a	6.50	5.66
	b	6.56	5.72
	c	6.46	5.70
Cd (II)	a	6.32	5.56
	b	6.36	5.30
	c	6.36	5.58

Table – 15

Stepwise and over all stability constant at temperature 308 K respectively of complex compounds of various metals.

Ligand – PMHTPI WATER – DIOXANE MEDIUM (V/V) = 50:50  $\sim^0 = 0.10(M) KNO_3$

System	Temp. 308 K		
	$\log K_1$	$\log K_2$	$\log S$
H – PMHTPI	10.86	-	10.84
Co ( II)- PMHTPI	7.44	6.56	14.10
Ni (II) – PMHTPI	7.38	6.56	13.90
Cu (II) – PMHTPI	6.68	5.68	12.36
Zn (II) – PMHTPI	6.50	5.70	12.24
Cd (II) – PMHTPI	6.36	5.56	11.84

The standard thermodynamic expression was used to obtain the free energy change ( $\Delta G$ ) of complexation reaction. The free energy change is

given  $\Delta G = 2.303 RT \log_{10}K$ . The most representative values of free energy change were tabulated in Table. 16.

Table – 16

Values of stepwise free energy changes. Enthalpy changes and entropy changes in the formation of complexes of different metals with the ligand PMHTPI

Ligand – PMHTPI

Water – dioxane medium (V/V) = 50:50

$\sim^0 = 0.10(M) KNO_3$

System	Temp 308 ± 1K	
	$\Delta G_1$ in k. cal	$\Delta G_2$ in k. cal
Co (II)	-9.26	-7.80
Ni (II)	-10.20	9.06
Cu (II)	-10.36	-9.08
Zn (II)	-9.06	-7.86
Cd (II)	-8.76	-7.70

The practical proton – ligand and metal ligand constant were determined by Calvin – Bjerrum titration technique using nitric acid and constant ionic strength was maintained with potassium nitrate. The method is valid in both water and water-dioxane medium. The nitrate ion was very slight complexing tendency and the competition

between nitrate ion and the ligands under study is of minor importance.

For a given ligand the stability constants of metal show the sequence  $Cu > Ni > Co > Zn > Cd$  with PMHTPI.

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