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Study of transition metal complex with schiff's base derived from naphthaldehyde

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Abstract
The main objective in this paper is to report stability constant values of transition metals like Cu (II), Ni(II), co(II) and Zn(II) with schiff's base ligand. Schiff's base ligands were synthesized by the condensation reaction of β-Naphtaldehyde with 7-Hydroxy naphthalene 2-amine. The Stability constant values of metals for the given ligand were found to be in the order cu(II)>Ni(II), co(II)>Zn(II).

Keywords: Transition metal complex, schiff's base derived, naphthaldehyde

Introductions
A large number of polydentate Schiff's base compounds have been synthesized and their complexes have been structurally characterized and extensively investigated. But little is known for their stability in aqueous solution in which it is used. Hence, the title project have been under taken. Here in the stability constant of complexes of divalent transition metals i.e. Co(II), Ni(II), Cu(II) and Zn(II) with Schiff's base ligands have been determined.

Material and methods
Merck. All other chemicals used were AnalR grade and used without further purification. Elemental analysis of metal salts were done by volumetric and gravimetric methods. Double distilled and deionised water was used throughout the experiment. All titrations were done in aqueous-dioxane medium in the ratio 3:2 (v/v). Dioxane was purified by standard method.
Schiff's base ligands were synthesized by the condensation of β-Naphthaldehyde with 7-Hydroxy naphthalene –2– amine. 3.5g of aldehyde in solution was mixed with nearly 3.0 g amine. The mixture was boiled under reflux in the presence of glacial acetic acid for about 2 hours. The solution was concentrated and cooled to 0^0C. The product obtained was filtered, washed several times and re-crystallized from ethanol. The yield of product was nearly 2.6 g.

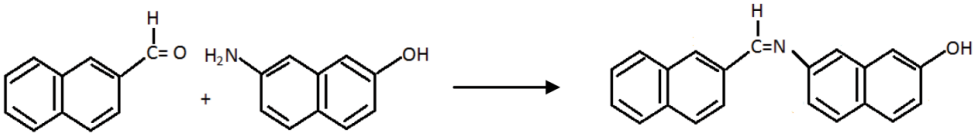


Table 1: Concentrations used in the experiment

Metal/ lons	V^o (mL)	Y	N^o	E^o	$T_L{}^o$	$T_M{}^o$
Co (II)	100	1	1.0 (M)	1.0×10^{-2} (M)	2.4×10^{-3} (M)	5.0×10^{-4} (M)
Ni(II)	100	1	1.0 (M)	1.0×10^{-2} (M)	2.4×10^{-3} (M)	5.0×10^{-4} (M)
Cu(II)	100	1	1.0 (M)	1.0×10^{-2} (M)	2.4×10^{-3} (M)	5.0×10^{-4} (M)
Zn(II)	100	1	1.0 (M)	1.0×10^{-2} (M)	2.4×10^{-3} (M)	5.0×10^{-4} (M)

Calvin – Bjerrum pH metric titration of acid, acid + ligand and acid + ligand + metal ions solutions were done at constant ionic strength of 0.1 M KNO_3 at 298 K temperature in an inert atmosphere of nitrogen.
The same process of titration was repeated for all the four Co, Ni, Cu and Zn metal ions. The change in colour and appearance of turbidity at particular pH value were recorded simultaneously. The change in pH of the solutions with each addition of alkali was recorded in Table no. 2.

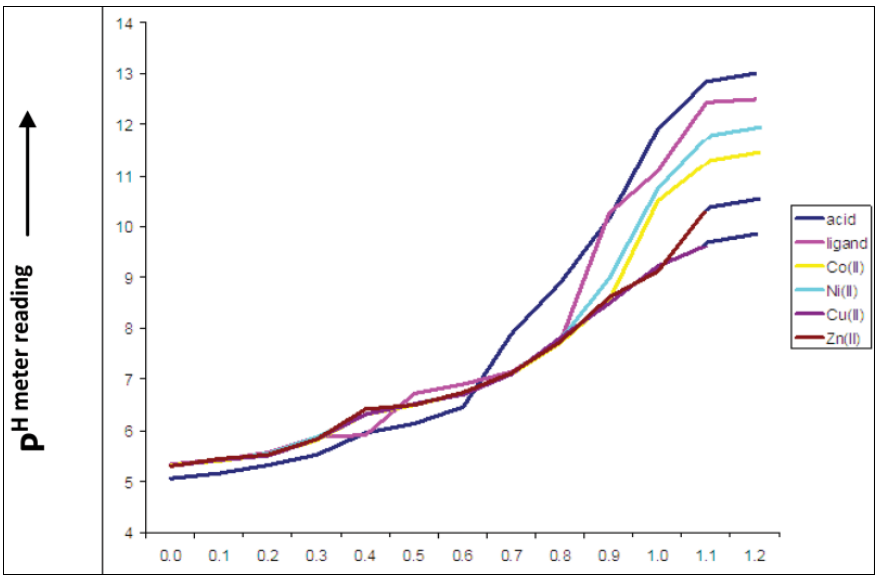
Table 2: Volume of alkali consumed in different titrations

Vol. of alkali added in mL	H^+	H^++L	H^+ +L + Co(II)	H^+ +L + Ni(II)	H^+ + L + Cu(II)	H^++ L + Zn(II)
0.0	5.05	5.35	5.32	5.3	5.3	5.3
0.1	5.43	5.43	5.4	5.42	5.42	5.44
0.2	5.33	5.57	5.52	5.55	5.5	5.52
0.3	5.53	5.87	5.8	5.86	5.82	5.82
0.4	5.95	5.91	6.32	6.32	6.32	6.42
0.5	6.13	6.73	6.5	6.52	6.52	6.5
0.6	6.45	6.9	6.72	6.72	6.7	6.74
0.7	7.9	7.15	7.1	7.12	7.1	7.12
0.8	8.9	7.75	7.72	7.79	7.82	7.74
0.9	10.15	10.27	8.55	8.98	8.5	8.62
1.0	11.9	11.1	10.5	10.75	9.22	9.12
1.1	12.85	12.43	11.25	11.75	9.62	10.3
1.2	13.15	12.57	11.70	12.10	10.20	10.56

Ligand - HNNCL(L_1)
Temp. 298 ±1K
μ° = 0.10 (M) KNO3
Water: dioxane medium (v/v) = 3:2

Discussion of the Results

A graph was plotted between pH meter reading [B] and volume of alkali added in each case, (Figure- 1) three titration curves obtained for each metal ions are acid titration curve (a), ligand titration curve (b) and complex titration curve (c) respectively.



Vol. of alkali in mL→
Temp. 298 ±1 Kμ°= 0.10(M) KNO3 Water: dioxane = 3:2(v/v)

Fig 1: Experimental curve with ligand HNNCI

The values of volumes (V_1, V_2, & V_3) corresponding to the same pH values were read from acid, ligand and complex titration curves (a), (b) and (c) respectively obtained from the experiment at temperature 298 K given in Figure - 1.

The $\bar{n}_A, \bar{n}$ & P^L are calculated using standard expressions

$\bar{n}_A = 1 + [(V_1-V_2) / (V^O + V_1)] (N^O + E^O) / T_L^O$

$\bar{n} = [(V_3 - V_2) / (V^O + V_1)][(N^O + E^O) / T] \times 1/ \bar{n}A$

$$P^L = \log\left[\sum_{j=0}^{j} \beta_j^0 H(1/anti\log B)(V^o + V_3)(T_L^o - \bar{n}T_M^o)V^o\right]$$

Proton ligand stability constant

The ligand titration curve is above the acid titration curve showing the basic nature of ligand and it is well separated from the acid titration curve at pH=6.3 at temp 298 K. The ligand curves run parallel to the acid titration curve indicating the smooth dissociation of the ligand. The values of $\bar{n}_A$ at various pH reading [B] was calculated from the acid and ligand titration curves and recorded in table 3.

Table 3: The values of $\bar{n}_A$ at various pH reading [B]

[B]	$V^2 - V^1$	log $\bar{n}_A$ An / (1 - $\bar{n}_A$)	
5.2	0.005	0.8878	
5.4	0.007	0.8840	
5.6	0.007	0.8832	
5.8	0.008	0.8812	
6.2	0.009	0.8742	
6.4	0.009	0.8724	
6.6	0.010	0.8682	
6.8	0.014	0.8610	
7.0	0.014	0.8442	
7.2	0.014	0.8362	
7.4	0.015	0.8360	1.2642
7.6	0.017	0.8282	1.2090
7.8	0.017	0.8196	1.0402
8.0	0.018	0.8121	1.0252
8.2	0.022	0.7986	0.8530
8.4	0.024	0.7964	0.7942
8.6	0.032	0.7882	0.7020
8.8	0.034	0.7834	0.6320
9.0	0.040	0.7602	0.4582
9.2	0.052	0.7120	0.3904
9.4	0.054	0.6794	0.3490
9.6	0.060	0.6555	0.2904
9.8	0.062	0.6274	0.2272
10.0	0.070	0.5996	0.4672
10.2	0.084	0.5674	0.4032
10.4	0.092	0.5322	0.3344
10.6	0.102	0.4883	0.2530
10.8	0.110	0.4782	0.0492
11.0	0.122	0.4672	0.0310
11.2	0.142	0.4394	-0.2050

Ligand – HNNCI
Temp.: 298 ± 1K
μ°= 0.10(M) KNO3

The formation curve obtained from the plot of $\bar{n}_A$ vs [B] extends from 0.43 to 0.88 (Figure 1) at temp 298 K.
The dissociation of ligand may be represented as
$HL \rightarrow H^+ + L^-$

The value of proton ligand stability constant was calculated by half integral method and it was further corroborated by linear plot method. (log $\bar{n}_A$ / (1 - $\bar{n}_A$) as [B].

Table 4: Values of protonation constant of ligand and stepwise stability constant of complexes of Co(II), Ni(II), Cu(II) and Zn(II) with ligand HNNCI calculation of n only symmetrical region of the curve was used

System Metal ions	Methods	log K_1	Ligand HNNCI log K_2
HNNCI(L_1)	A	10.96	
	b	-	
	c	10.96	
Co (II)	A	7.56	6.64
	b	7.58	6.66
	c	7.62	6.68
Ni (II)	A	7.52	6.66
	b	7.44	6.62
	c	7.46	6.68
Cu (II)	A	6.76	5.76
	b	6.64	5.04
	c	6.84	5.78
Zn (II)	A	6.62	5.76
	b	6.54	5.72
	c	6.68	5.86

Table 5: Stepwise and over all stability constant of complex compounds of various metals with ligand HNNCl at temperature 298K

System	Ligand–MNNCI(L_1)		
	log K_1	**Log K_2**	**Log**
HNCI (L_1)	10.98	–	10.98
Co(II)	6.76	5.70	12.46
NI(II)	7.48	6.68	14.10
Cu(II)	7.58	6.66	14.20
Zn(II)	6.60	5.78	12.34

Water–Dioxane medium (v/v) = 3:2
μ^o=0.10(M) KNO_3

The values of protonation constant and stepwise stability constant obtained by different computational methods at temperatures 298 K are summarized in table no. 4.

The different methods used are:
a. **Half:** Integral method.
b. **Mid:** Point calculation method.
c. Straight line plot method.

The order of stability constant of various metals for the given ligand

HNNCI are - Cu(II) > Ni(II) > Co (II) > Zn(II)

The values of stepwise stability constants and over all stability constants are as shown table no. 5 For the given ligand the stability constants of metals show the sequence

Cu(II) > Ni(II) > Co(II) > Zn(II)

This is natural order given by Irving – William. A theoretical justification of the order of stability constants follows from the consideration of the reciprocal of the ionic radii and 2nd ionization enthalpy of metal. Calvin – Bjerrum titration technique modified by Irving and Rossotti was used to determine the practical proton ligand and metal ligand stability constants at constant ionic strength maintained by using dilute KNO_3 solution. Irving and Rossotti pointed out that the formation constant of metal chelates can be obtained without converting the pH – meter reading [B] to stoichiometric hydrogen ion concentration and without knowing the stiochiometric concentration of neutral salts added to maintain ionic strength. This method is valid for both aqueous and non-aqueous medium.

Conclusion
The stability of the chelates is greatly affected by the electron density around the imino nitrogen (- C = N -). Higher the electron density around the nitrogen atom, stronger is the metal ligand bond.
The difference between the successive stepwise stability constant is large, which suggest that the formation of ML and ML_2 chelates take place.

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