

STABILITY CONSTANTS OF MIXED LIGAND COMPLEXES OF TRANSITION METAL(II) IONS WITH 1-[(1E)-N-(2,4 DICHLOROPHENYL) ETHANIMIDOYL] NAPHTHALEN-2-OL AND 2-{(E)-[(4-BROMO-3- METHOXYPHENYL)IMINO]METHYL}PHENOL

A. K. Mapari*

*Department of Chemistry, Ramnarain Ruia College, Matunga (E),
 Mumbai-400019, Maharashtra, India.

*E-mail: akmapari@gmail.com

ABSTRACT

Binary and ternary complexes of the type M-Y and M-X-Y [M = Co(II), Ni(II), Cu(II) and Zn(II); X = 2-{(E)-[(4-bromo-3-methoxyphenyl)imino]methyl}phenol as primary ligand and Y = 1-[(1E)-N-(2,4-dichlorophenyl)ethanimidoyl]naphthalen-2-ol as secondary ligand have been examined pH-metrically at $27 \pm 0.5^\circ\text{C}$ and at constant ionic strength, $\mu = 0.1 \text{ M}$ (KCl) in 75 : 25 (v/v) 1,4-dioxane-water medium. The stability constants for Binary (M-Y) and ternary (M-X-Y) systems were calculated.

Keywords: Binary complexes, Ternary complexes, mixed ligand, Stability constant.

© RASĀYAN. All rights reserved

INTRODUCTION

Schiff bases play important roles in coordination chemistry as they easily form stable complexes with most transition metal ions^{1, 2}. Many attempts have been made to evaluate different factors affecting the stability of the metal chelates along with their stability constants³⁻⁵. In the present study the stability constants of the mixed ligand complexes of Co(II), Ni(II), Cu(II) and Zn(II) with 2-{(E)-[(4-bromo-3-methoxyphenyl)imino]methyl}phenol (X) as primary ligand (Figure-1) and 1-[(1E)-N-(2,4-dichlorophenyl)ethanimidoyl]naphthalen-2-ol (Y) as secondary ligand (Figure-2) in 75: 25 (v/v) 1,4-dioxane-water medium at $27 \pm 0.5^\circ\text{C}$ have been reported by employing pH-metric titration technique⁶⁻⁸. Under identical conditions the stability constants of binary metal complexes of 1-[(1E)-N-(2,4-dichlorophenyl)ethanimidoyl]naphthalen-2-ol (Y) have also been investigated.

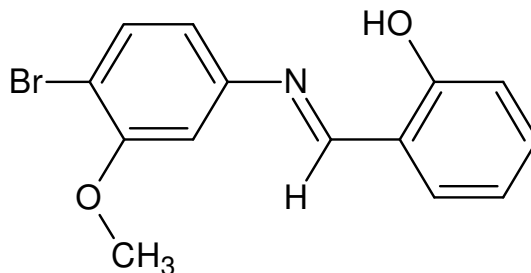


Fig.-1: Primary ligand: 2-{(E)-[(4-bromo-3-methoxyphenyl)imino]methyl}phenol

EXPERIMENTAL

The pH-meter model no. EQ-614 supplied by Equiptronics, a precision research pH-meter with wide range of glass electrode and calomel reference electrode was used for pH measurements. The pH-meter

was standardized with potassium hydrogen phthalate and phosphate buffers before performing the titrations. The ligands (L^1H and L^2H) were prepared by the condensation of the corresponding aldehyde / ketone and amine in 1:1 molar ratio by refluxing in ethanol.^{9,10}

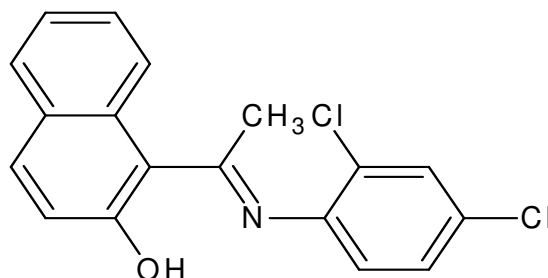


Fig.-2: Secondary ligand: 1-[(1E)-N-(2,4-dichlorophenyl)ethanimidoyl]naphthalen-2-ol

The solutions of ligands were prepared in 1,4-dioxane. All the metal ion solutions were prepared in double distilled water and standardized by using conventional procedures¹¹. A solution of KOH (0.2 M) was prepared in double distilled water and standardized with standard solution of succinic acid. The titrations were carried out in an inert atmosphere of nitrogen. All the measurements were carried out at temperature $27 \pm 0.5^\circ\text{C}$. The method of Bjerrum and Calvin as modified by Irving and Rossotti was used to determine \bar{n}_A (average number of protons associated with secondary ligand); \bar{n} (average number of secondary ligand molecules attached per metal ion); \bar{n}_{mix} (average number of secondary ligand molecules attached per $(M.X)^-$ ion); pL (free ligand exponent for binary (M-Y) system) and pL_{mix} (free ligand exponent for ternary (M-X-Y) system) values^{6,7}. All the solvents and chemicals used were of A R grade. For the determination of proton-ligand stability constant of secondary ligand (Y) and metal-ligand stability constants of binary (M-Y) and ternary (M-X-Y) complexes, the following sets of solutions were prepared keeping the total volume $V_o = 40$ mL. All titrations were carried out at the ionic strength of 0.1 M using KCl as an electrolyte in 75:25 (v/v) 1,4-dioxane-water medium against standard carbonate free KOH (0.2 M) solution.

- 4.0 mL HCl (0.16 M) + 3.36 mL KCl (1.0 M) + 2.64 mL distilled water + 30.0 mL 1,4-dioxane.
- 4.0 mL HCl (0.16 M) + 3.36 mL KCl (1.0 M) + 2.64 mL distilled water + 4.0 mL secondary ligand (0.04 M) + 26.0 mL 1,4-dioxane.
- 4.0 mL HCl (0.16 M) + 3.24 mL KCl (1.0 M) + requisite volume of metal(II) chloride solution to give 0.001 M metal(II) chloride concentration in the final solution + requisite amount of distilled water + 4.0 mL secondary ligand (0.04 M) + 26.0 mL 1,4-dioxane.
- 4.0 mL HCl (0.16 M) + 3.36 mL KCl (1.0 M) + 2.64 mL distilled water + 4.0 mL secondary ligand (0.01 M) + 26.0 mL 1,4-dioxane.
- 4.0 mL HCl (0.16 M) + 3.24 mL KCl (1.0 M) + requisite volume of metal(II) chloride solution to give 0.001 M metal(II) chloride concentration in the final solution + requisite amount of distilled water + 4.0 mL primary ligand (0.01 M) + 4.0 mL secondary ligand (0.01 M) + 22.0 mL 1,4-dioxane.

The ratio of metal (M): secondary ligand (Y) was maintained at 1:4 in the binary system. In the ternary system the ratio of metal (M): primary ligand (X): secondary ligand (Y) was maintained at 1:1:1. The pH-meter readings were plotted against the volume of alkali (KOH) used for each titrations.

RESULTS AND DISCUSSION

Proton-ligand stability constants of secondary ligand (Y)

From the titration curves of solutions (i) and (ii), \bar{n}_A values at various pH were calculated. The proton ligand formation curve was obtained by plotting the values of \bar{n}_A vs. pH-meter readings. From the graph

the values of $\log K_1^H$ and $\log K_2^H$ were evaluated by half integral method (A). The values of $\log K_1^H$ and $\log K_2^H$ were also evaluated using graphical method (B) by plotting the graph of $\log [\bar{n}_A / (1-\bar{n}_A)]$ against pH and $\log [(2-\bar{n}_A) / (\bar{n}_A-1)]$ against pH, respectively. The values obtained by method A and B are in agreement with each other, the average values of $\log K_1^H$ and $\log K_2^H$ has been found to be 8.62 and 2.18 respectively.

Metal-ligand stability constants of the Binary (M-Y) complexes

The metal ligand stability constants of binary complexes were evaluated assuming the polynuclear complexes and hydrolyzed products were not formed. The metal-ligand binary binding proposed structure is shown in Figure-3. An examination of titration curves indicate that complex formation takes place in the solution on the following grounds: (I) The metal titration curve of solution (iii) shows displacement with respect ligand (Y) titration curve of solution (ii) along the volume axis. This indicates the affinity of the ligand to metal ions which release proton and produce volume difference. (II) The color change of ligand appeared in the presence of metal ion shows the formation of new species due to coordination. (III) The hydrolysis of the metal ion was suppressed due to the complex formation and precipitation did not appear during the titrations.

From the titration curves of solutions (ii) and (iii), \bar{n} and pL values were calculated. The formation curves were obtained by plotting the values of \bar{n} vs. pL. From the graph the values of $\log K_{MY_1}^M$ and $\log K_{MY_2}^{MY}$ were evaluated by half integral method (A) and in the similar way the values of $\log K_{MY_1}^M$ and $\log K_{MY_2}^{MY}$ were evaluated using graphical method (B) by plotting the graph of $\log [\bar{n} / (1-\bar{n})]$ against pL and $\log [(2-\bar{n}) / (\bar{n}-1)]$ against pL respectively. The values obtained by method A and B are in agreement with each other, the average values of $\log K_{MY_1}^M$ and $\log K_{MY_2}^{MY}$, along with metal-ligand stability constants the $\log \beta$ values of the binary complexes are given in Table 1.

The variations of \bar{n} was found to be between 0.0-2.0 for the binary (M-Y) complexes of Co(II), Ni(II), Cu(II) and Zn(II) metal ions, which indicate that the composition of the complexes were 1:2 in solution. The $\log K_{MY_1}^M$ values for the binary complexes of the metal ions are in the following order: Cu(II) > Ni(II) > Co(II) > Zn(II).

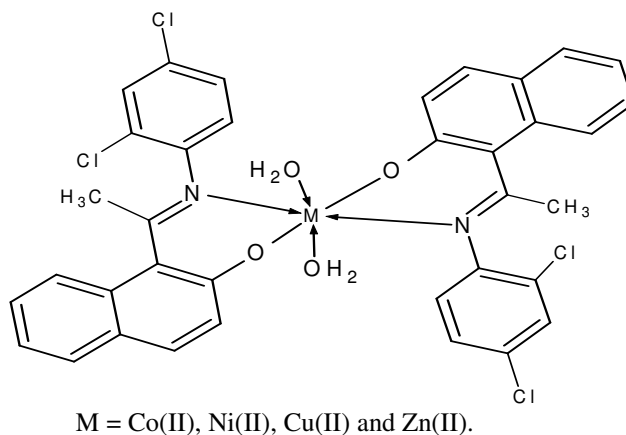


Fig.-3: The metal-ligand binary binding proposed structure.

Metal-ligand stability constants of the ternary (M-X-Y) complexes

The metal-ligand stability constants of ternary complexes were evaluated assuming that the formation of polynuclear complexes and hydrolyzed products were not formed. The metal-ligand ternary binding proposed structure is shown in Figure-4. In this ternary (M-X-Y) complexes it is observed that the metal forms the complex first with the primary ligand (X) at lower pH and then metal-primary ligand (M-X)

curves comes in to contact with the secondary ligand (Y) to form the mixed ligand complex at higher pH. Secondary ligand does not come into contact with metal ions at lower pH. In other words mixed ligand complex formation takes place when M-X complex formation is complete. The horizontal distance between mixed ligand metal curves and secondary ligand curve correspond to the amount of secondary ligand which gets bound with M-X complex (binary). The titration curves of ternary complex coincide with binary curve up to pH = 4.8 – 5.3, after this above pH = 5.0, the ternary curves deviate, the secondary ligand introduce itself and combines with M-X complex to form ternary complex (M-X-Y).

From the titration curves of solutions (iv) and (v), \tilde{n}_{mix} and pL_{mix} values were calculated. The values of $\log K_{MXY}^{MX}$ have been evaluated from the formation curves (\tilde{n}_{mix} vs. pL_{mix}). At $\tilde{n}_{\text{mix}} = 0.5$, in the formation curve, $pL_{\text{mix}} = \log K_{MXY}^{MX}$ (method A). The values of $\log K_{MXY}^{MX}$ were also evaluated by the graphical method (B), by plotting the graph of $\log [\tilde{n}_{\text{mix}} / (1 - \tilde{n}_{\text{mix}})]$ against pL_{mix} . The values of \tilde{n}_{mix} vary from 0.0-1.0, thus confirm the formation of 1:1:1 mixed ligand complexes. The values obtained by method A and B are in agreement with each other, the average values of $\log K_{MXY}^{MX}$ are included in Table-1.

The values of $\log K_{MXY}^{MX}$ are slightly lower than $\log K_{MY_1}^M$ and higher than $\log K_{MY_2}^{MY}$, which is due to the fact that the tendency of the secondary ligand (Y) to get bound with aquated metal ion $[M(\text{aq})]^{2+}$ is more than to combine with the metal ion already bound with primary ligand (X).¹²

The relative stability of the ternary complexes compared with corresponding binary complexes can be qualitatively expressed in many different ways. We have expressed the relative stabilities in terms of $\Delta \log K_T$ ($\Delta \log K_T = \log K_{MXY}^{MX} - \log K_{MY_1}^M$). The $\Delta \log K_T$ values for all the metal(II) ions in the present study (Table 1) is negative. This indicates that ternary 1:1:1 (M-X-Y) complexes are less stable than binary 1:1 (M-Y) complexes.^{13,14}

In the ternary system studied, the order of stability constants of mixed ligand complexes with respect to the metal ions was found to be Cu(II) > Ni(II) > Co(II) > Zn(II); which is same as in the corresponding binary (M-Y) systems. This is in accordance with the Irving-Williams series of stability constant.^{15,16}

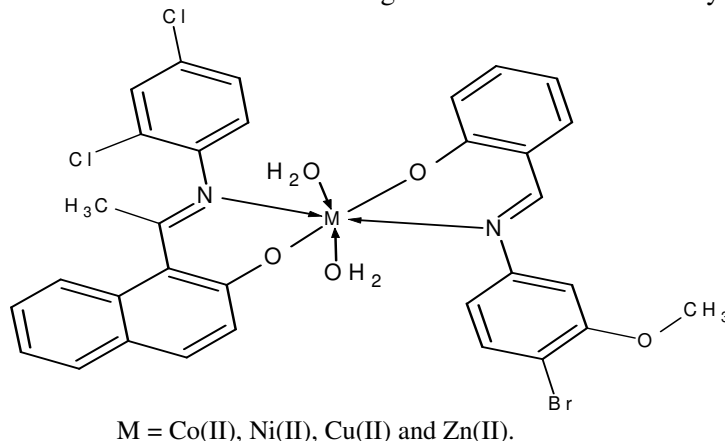


Fig.-4: The metal-ligand ternary binding proposed structure.

CONCLUSION

The value of $\log K_{MXY}^{MX}$ are slightly lower than $\log K_{MY_1}^M$ and higher than $\log K_{MY_2}^{MY}$, which is due to the fact that the tendency of the secondary ligand (Y) to get bound with aquated metal ion $[M(\text{aq})]^{2+}$ is more than to combine with the metal ion already bound with primary ligand (X). The relative stability ($\Delta \log K_T$) values of the ternary complexes with corresponding binary complexes for all the metal(II) ions in the present study is negative indicating that ternary 1:1:1 (M-X-Y) complexes are less stable than binary 1:1 (M-Y) complexes. In the ternary system studied, the order of stability constants of mixed ligand

complexes with respect to the metal ions was found to be Cu(II) > Ni(II) > Co(II) > Zn(II); which is same as in the corresponding binary (M-Y) systems.

Table-1: Metal-ligand stability constants of binary (M-Y), ternary (M-X-Y) systems and $\Delta \log K_T$ values in 75: 25 (v/v) 1,4-dioxane-water medium at $27 \pm 0.5^\circ\text{C}$ and $\mu = 0.1 \text{ M}$ (KCl).

System	Metal-ligand stability constants / $\Delta \log K_T$	Metal(II) ions (M)			
		Co(II)	Ni(II)	Cu(II)	Zn(II)
Binary (M-Y)	$\log K_{MY_1}^M$	5.42	5.89	7.68	4.43
	$\log K_{MY_2}^{MY}$	3.82	3.92	5.73	3.42
	$\log \beta$	9.24	9.81	13.41	7.85
Ternary (M-X-Y)	$\log K_{MXY}^{MX}$	5.26	5.47	7.30	4.12
(M-Y) and (M-X-Y)	$\Delta \log K_T$	-0.26	-0.42	-0.38	-0.31

REFERENCES

1. C. Spinu, M. Pleniceanu and C. Tigae, *Turkish J. Chemistry*, **32**, 487(2008).
2. B. Clarke, N. Clarke, D. Cunningham, T. Higgins, P. McArdle, M.N. Cholchu and M. O’Gara, *J. Organometallic Chem.*, **55**, 559(1998).
3. C.N. Mukherjee and T. Ghosh, *J. Indian Chem. Soc.*, **74**, 8(1977).
4. K. Kiramany, Y. Prashanthi, N.J.P. Subhashini and Shivraj, *J. Indian Chem. Soc.*, **2(1)**, 375(2010).
5. B.C. Khade, P.M. Deore, and B.R. Arbad, *Int. J. Chemtech Res.*, **2(2)**, 1036(2010).
6. H.M. Irving and H.S. Rossotti, *J. Chem. Soc.*, **74**, 3397(1953).
7. H.M. Irving and H.S. Rossotti, *J. Chem. Soc.*, **76**, 2904(1954).
8. A.K. Mapari, *Int. J. Chemtech Res.*, **6(2)**, 1511(2014).
9. S.S. Rout, J. Panda, P.K. Sahu and M. Banerjee, *Rasayan J. Chem.*, **4(1)**, 136(2011).
10. S.B. Ade, M.N. Deshpande and J.H. Deshmukh, *Rasayan J. Chem.*, **5(1)**, 10(2012).
11. A.I. Vogel, *Text Book of Quantitative Practical Inorganic Chemistry*, ELBS, (1984).
12. A.K. Patel and J.D. Joshi, *J. Indian Chem. Soc.*, **74**, 222(1997).
13. S. Satyanarayana and K.V. Reddy, *Indian J. Chem.*, **28(A)**, 169(1989).
14. M.A. Neelakantan and M.S. Nair, *Iranian J. Chem. and Chem. Eng.*, **23 (1)**, 97(2004).
15. H. Irving and R.J.P. William, *J. Chem. Soc.*, **11**, 3192(1953)
16. H. Irving and R.J.P. William., *Nature*. **162**, 746(1948).

[RJC-1652/2017]