Mixed Ligand Complexes of Bivalent Metal ions in solution- with 2-Mercaptoethyl-benzimidazole and N-N, N-O or O-O- Donors

P. Seshi Reddy, Dev Das Manwal and A.V. Chandra Pal*

Department of Chemistry, Osmania University, HYDERABAD-500007.

2-Mercapto-benzimidazole is an industrially important compound. Solid complexes of this are widely used as catalysts in polymerization [1]. Metallic salts of 2-mercapto-benzimidazole are used for heat stabilization of polyamides [2]. It is suggested that 2-mercapto-benzimidazole coordinates with the metal ions through nitrogen and sulphur [3]. In continuation of our earlier studies on the co-ordinating tendencies of substituted benzimidazoles [4], the formation constants of ternary compelexes of type MAL [where M = Co^{2+}, Ni^{2+} & Zn^{2+}; L = 2-mercaptoethyl-benzimidazole (MEB) and A = glycine (GLY), ethylenediamine (EN), salicylic acid (SA)] have been determined pH-metrically in 50% v/v aq. ethanol at 30°C and I = 0.1 M ($NaClO_4$) and reported here.

EXPERIMENTAL

The ligand MEB was prepared by the reported method [5]. The other chemicals like $NaClO_4$, glycine, ethylenediamine and salicylic acid of AR grade were used as received.

An Elico digital pH-meter model LI-120 (accuracy of ± 0.01 pH unit) equipped with a glass and calomel combined electrode assembly was calibrated at different pH regions using the appropriate standard buffers viz. pH 4.00 & 9.20 (with necessary temperature corrections). The readings (B) from the pH meter in the 50% v/v aqueous ethanol medium were corrected by the method of Van Uitert & Haas [6]. The proton-ligand formation constants and metal-ligand formation constants were determined using Irving-Rossotti pH titration technique [7]. The formation constants of ternary system have been evaluated by method of Ramamurthy and Santappa [8]. Based on the trends in the titration curves and using suitable material balance equations [7,8], all calculations were performed on a CASIO-PB-110 Personal Computer.

RESULTS AND DISCUSSION

A perusal of the titration curves show

© ECSI, Bangalore

that the ternary titration curve coincide with binary curve of M(II)-MEB in the beginning and deviates from it at a later stage. This suggests stepwise complex formation. Equilibria involved in ternary complex formation can be represented by eq. (1) & (2), where MEB is the primary ligand (L) and ligand A [glycine, ethylenediamine and salicylic acid] act as secondary ligand.

$$M + L \rightleftharpoons ML \quad \ldots\ (1)$$
$$ML + A \rightleftharpoons MLA \quad \ldots\ (2)$$

Table 1

Formation Constants of Binary Complexes of 2-Mercaptoethyl-benzimidazole (MEB), Glycine (GLY), Ethylenediamine (EN) and Salicylic acid (SA)

T = 30°C; I = 0.1 M $NaClO_4$;
Medium 60 % aq. ethanol
(pK_{SH} of MEB = 10.16; pK_{NH} = 5.03;
log βH_2 = 15.19)

Parameter	Co^{2+}	Ni^{2+}	Zn^{2+}
log K_1 (MEB)	8.05	8.91	9.16
log K_2 (MEB)	6.74	8.14	9.05
log K (GLY)	5.74	6.31	5.74
log K (EN)	6.32	7.24	6.17
log K (SA)	7.26	7.51	7.61

The stability constant of binary complexes with glycine, ethylene diamine and salicylic acid with Co^{2+}, Ni^{2+} and Zn^{2+} are reported earlier. It is remeasured here (Table-1) as it is preferable to determine both binary and ternary constants under the same condition. The stability constants of the 1:1:1 ternary complexes M(II)-MEB-A were calculated by assuming that the 1:1 [M(II)-MEB] complex is completely formed before the co-ordination of the ligand A takes place. The values thus obtained are presented in Table 2.

Table 2

Formation Constants of Ternary Complexes of 2-Mercaptoethyl-benzimidazole

T = 30°C; I = 0.1 M $NaClO_4$;
Medium 60 % aq. ethanol

Parameter	Co^{2+}	Ni^{2+}	Zn^{2+}
MEB - GLY System			
log K^{ML}_{MLA}	4.76	5.41	5.01
Δlog K	-0.98	-0.90	-0.70
SUBS	0.39	0.44	0.41
% R.S.	-17.07	-14.26	-12.72
MEB -EN System			
log K^{ML}_{MLA}	5.72	6.88	5.86
Δlog K	-0.60	-0.36	-0.31
SUBS	0.35	0.42	0.36
% R.S.	-9.49	-4.97	-5.02
MEB -SA System			
log K^{ML}_{MLA}	6.31	6.72	7.06
Δlog K	-0.95	-0.79	-0.55
SUBS	0.36	0.39	0.41
% R.S.	-13.08	-10.52	- 7.22

The formation of ternary complexes is further supported by the non-superimposable nature of the theoretical composite curve over the experimental mixed ligand curves [9]. Three parameters - % relative stabilization - % R.S. (defined by eg. 3), stability per unit base strength - SUBS (defined by

$$\% RS = \frac{(\log K^{ML}_{MLA} - \log K^{M}_{MA}) \ 100}{\log K^{M}_{MA}} \quad \ldots.(3)$$

$$SUBS = \frac{\log K^{MA}_{MLA}}{\log \beta_n^{H(A)}} \quad \ldots.(4)$$

$$\log K = \log K^{ML}_{MLA} - \log K^{M}_{MA} \quad \ldots.(5)$$

eg.4) and Δlog K (defined by eg.5) are used as a measure of the relative ease of formation of mixed ligand complexes.

If the Δlog K values are positive or less negtive than the statistical values, the ternary complexes are more stable than the binary complexes. However, it should be noted here that negative values of Δlog K do not preclude the formation of ternary complexes in solution.

The perusal of data in Table 2 shows that binary (1:1) complexes are more stable than the ternary (1:1:1) complexes because negative Δlog K values have been obtained in all the systems. The stability sequence observed is: [M(II)-MEB-EN] > [M(II)-MEB-SA] > [M(II)-MEB-GLY]. This trend can be attributed to the basicities of the secondary ligands. The ligand, EN, has comparatively more basicity than SA or GLY. Therefore it has higher stability. The order of stabilities with respect to metal ion is found to be: Zn^{2+} > Ni^{2+} > Co^{2+} which is in conformity with the Irving - William natural order of stabilities.

REFERENCES

1. A. Takahashi and S. Kambara, *J. Polymer Sc.*, **3(4)** (1965) 279.
2. L.N. Lomakina and I.P. Alimarin, *Chem. Abstr.*, **66** (1967) 101, 220.
3. Yoshid and Toru, *Bull. Chem. Soc. Japn.*, **53(5)** (1980) 1449.
4. P. Seshi Reddy, K.L. Ompraksh, A.V. Chandra Pal and M.L.N. Reddy, *Indian J. Chem.*, **26A** (1987) 532.
5. J. Schoeneber and M.L. Pierre, *Acad. Sci. Paris Section C*, **278** (1974) 235.
6. L.G. Van Uitert and G. Haas, *J. Am. Chem. Soc.*, **75** (1953) 451.
7. H. Irving and H.S. Rossotti, *J. Chem. Soc.*, **(1953)** 3397; (1954) 2904.
8. S. Ramamoorthy and M. Santappa (a) *J Inorg. nucl. Chem.*, **32** (1970) 1623; (b) *Indian J. Chem.*, **9** (1971) 38.
9. G.H. Carey and A.E. Martell, *J. Am. Chem. Soc.*, **89** (1967) 2359.