Formation Constants of Metal Complexes of Substituted Benzimidazoles with Different Bivalent Metal Ions

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The formation constants of the complexes of 4 (or 7)-methylbenzimidazole, 2-(2'-hydroxyphenyl)benzimidazole, 2-(2'-hydroxy-5'-bromophenyl)benzimidazoles, 2-(2'-hydroxy-3-methoxy)benzimidazole, 2-(1'-hydroxyethyl)benzimidazole with Mn(II), Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) have been determined pH metrically at different ionic strengths, temperatures and in solutions of varying dielectric constants. The results show that the metal ion reacts with the neutral ligand in the first stage and with anionic ligand in the second stage.
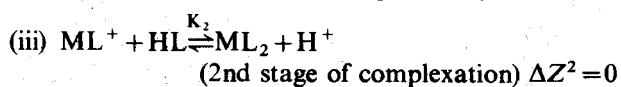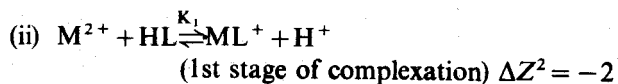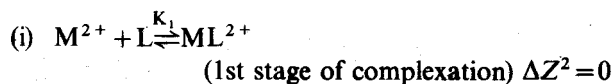
In continuation of our earlier work[1,2], we report herein the stability constants of complexes of 4(or 7)-methylbenzimidazole (MBz), 2-(2'-hydroxyphenyl)benzimidazole (OHPBz), 2-(2'-hydroxy-5'-bromophenyl)benzimidazole (HBPBz), 2-(2'-hydroxy-3'-methoxy)benzimidazole (HMBz) and 2-(1'-hydroxyethyl)benzimidazole (HEBz) with Mn(II), Co(II), Ni(II), Cu(II), Zn(II), and Cd(II). The effects of varying ionic strength (0.02 to 0.26 M KNO$_3$), dielectric constant and temperature on the stability constants of the metal complexes have been studied.

The TLC-pure ligands MBz, OHPBz and HMBz were prepared in the laboratory. All other chemicals used were of AR grade. Metal nitrates were dissolved in CO$_2$-free distilled water and the solutions standardized by titrating against standard EDTA
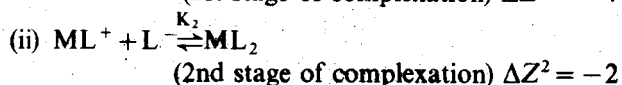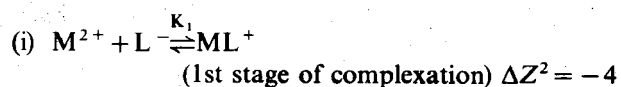
solution using suitable indicators[3]. An ELICO digital pH-meter model LI-120 having glass-calomel electrode assembly (accuracy $\pm 0.01 pH$ unit) was used to determine the pH. The volume and the pH corrections in solutions of various aquo-organic mixtures were applied as suggested by Rao and Mathur[4] and Van Uitert and Hass[5] respectively. The experimental method and procedure for computation of the formation constants were the same as those given in our earlier publication[1]. The formation constants were determined in 60% (v/v) aq. methanol at $\mu = 0.1 M$ (KNO$_3$) and 35°C.

The ligands MBz (L) and OHPBz (HL) react with the metal ion, M^{2+} in one of the following ways:

(a) Direct interaction of the metal with the ligand

(i) $\quad M^{2+} + L \overset{K_1}{\rightleftharpoons} ML^{2+}$

$\quad$ (1st stage of complexation) $\Delta Z^2 = 0$

(ii) $\quad M^{2+} + HL \overset{K_1}{\rightleftharpoons} ML^+ + H^+$

$\quad$ (1st stage of complexation) $\Delta Z^2 = -2$

(iii) $\quad ML^+ + HL \overset{K_2}{\rightleftharpoons} ML_2 + H^+$

$\quad$ (2nd stage of complexation) $\Delta Z^2 = 0$

(b) Ionization of the ligand followed by complexation

(i) $\quad M^{2+} + L^- \overset{K_1}{\rightleftharpoons} ML^+$

$\quad$ (1st stage of complexation) $\Delta Z^2 = -4$

(ii) $\quad ML^+ + L^- \overset{K_2}{\rightleftharpoons} ML_2$

$\quad$ (2nd stage of complexation) $\Delta Z^2 = -2$

The stability constants of the metal complexes of MBz(L) with Co(II), Ni(II) & Cu(II) at different ionic strengths (0.02 to 0.26 M KNO$_3$) and of OHPBz (HL) with Cu(II) and Ni(II) in the ionic strength range of

Table 1—Metal-Ligand Stability Constants of Complexes of MBz and OHPBz with Co(II), Ni(II) and Cu(II) at Different Ionic Strengths

Metal ion		Ionic strengths (μ)							
		0.04	0.1	0.18	0.26	0.02	0.05	0.07	0.1
			MBz				*OHPBz*		
Co(II)	log K_1	3.02	3.11	3.20	3.27	—	—	—	—
Ni(II)	log K_1	3.06	3.16	3.31	3.41	4.36	4.24	4.19	4.13
	log K_2	—	—	—	—	3.49	3.38	3.31	3.25
						7.85	7.62	7.50	7.38
Cu(II)	log K_1	3.10	3.21	3.34	3.4	9.23	9.12	9.06	9.00
	log K_2	—	—	—	—	6.86	6.74	6.66	6.60
	log β_2	—	—	—	—	16.09	15.86	15.72	15.60

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0.02 to 0.1 $M(KNO_3)$ in 60% (v/v) methanol-water at 35°C were also determined (Table 1). The ΔZ^2 values calculated from the Brønsted equation are found to be zero for MBz complexes indicating that complexation occurs by the mechanism (a-i). The small change observed in $\log K$ values (Table 1) of the metal complexes of MBz with Co(II), Ni(II) and Cu(II) with increase in ionic strength is attributed to the salting-out effect. In the case of the metal complexes of OHPBz (HL) with Cu(II) and Ni(II) the $\log K_1$ values are found to decrease with increase in ionic strength (Table 1). A plot of $\log K_1$ against $\sqrt{\mu}/1 + \sqrt{\mu}$ is linear, from which ΔZ^2 values have been calculated as -2.02 and -1.92 for Cu(II) and Ni(II) respectively. These values indicate that complexation in this case occurs by the mechanism (a-ii).

In the case of second stage of complexation of OHPBz with Cu(II) and Ni(II), the $\log K_2$ values again decrease with increase in ionic strength. The ΔZ^2 values calculated (-2.04 and -1.90) are close to the theoretical value (-2.0) suggesting that the complexation takes place via the mechanism (b-ii).

The stability constants of the Cu(II) complexes of MBz, DMBz and OHMBz have also been determined in solutions of different dielectric constants at 35°C and $\mu=0.1 M(KNO_3)$. The dielectric constant of the medium is varied by varying the percentage of organic component, methanol and acetone in aquo-organic mixtures. The plots of $\log \beta_2$ versus $1/D$ of the medium are linear with positive slopes indicating that the complexation is favoured in solutions of low dielectric constants.

The stability constants of Co(II), Ni(II) & Cu(II) complexes with DMBz and Cu(II) with OHPBz have also been determined in isodielectric mixtures ($D = 48.6$) at four different temperatures in the range of 15 to 45°C and $\mu=0.1 M(KNO_3)$. The thermodynamic

Table 2—Thermodynamic Parameters for Complexation of DMBz with Co(II), Ni(II) and Cu(II) and of OHPBz and HMBz with Cu(II)

{Solvent dielectric constant $=48.6$; $\mu=0.1 M(KNO_3)$; temp. $=35°C$}

Metal ion	$-\Delta G^*$ (kJ mol^{-1})	$-\Delta H^*$ (kJ mol^{-1})	$-\Delta S\dagger$ (JK^{-1}mol^{-1})
DMBz			
Cu(II)	18.41	34.31	52.3
Ni(II)	18.41	32.64	46.02
Co(II)	18.83	22.18	10.46
OHPBz			
Cu(II) 1st stage	53.14	186.19	430.95
2nd stage	38.91	100.42	200.83
HMBz			
Cu(II) 1st stage	64.43	192.46	414.22
2nd stage	56.07	90.79	112.97

* Uncertainty: ± 2.0 kJ mol^{-1}.
† Uncertainty: ± 8.0 JK^{-1}mol^{-1}.

Table 3—Stability Constants of Complexes of 2-Substituted Benzimidazoles with Different Bivalent Metal Ions

{Solvent $=60\%$ (v/v) aq. methanol; $\mu=0.1 M(KNO_3)$; temp. 35°C}

Stability† constant	Mn(II)	Co(II)	Ni(II)	Cu(II)	Zn(II)	Cd(II)
DMBz						
$\log K_1$	3.00	3.11	3.16	3.21	3.42	3.20
OHPBz						
$\log K_1$	4.20	5.70	4.13	9.00	6.20	5.00
$\log K_2$	3.10	4.90	3.25	6.60	5.50	4.50
$\log \beta_2$	7.30	10.60	7.38	15.60	11.70	9.50
HMBz						
$\log K_1$	5.00	5.38	7.33	10.90	6.40	5.50
$\log K_2$	3.30	4.65	6.23	9.48	5.93	4.40
$\log \beta_2$	8.30	10.03	13.56	20.38	12.33	9.90
HEBz						
$\log K_1$	5.20	6.67	7.15	9.16	7.78	5.80
$\log K_2$	4.70	6.57	6.80	7.93	7.55	4.80
$\log \beta_2$	9.90	13.95	13.95	17.09	15.33	10.60
HBPBz						
$\log K_1$	3.95	5.77	5.95	—	6.60	4.80
*NBz**						
$\log K_1$	3.02	3.1	3.28	3.39	3.23	3.10
*MNBz**						
$\log K_1$	3.18	3.25	3.40	3.57	3.36	3.27
*PNBz**						
	3.11	3.18	3.34	3.46	3.29	3.18

* literature values   † uncertainty ± 0.02 units

parameters ΔG, ΔH and ΔS have been calculated using Harned-Robinson equation at 35°C (Table 2). The negative ΔS values in all the metal complexes show loss of entropy during the formation of complexes which are more polar than the reactants and hence strongly solvated and the overall reaction for complexation can be written as:

$$M^{2+} + HL + L^- \rightleftharpoons ML_2 + H^+$$

The formation constants of the metal complexes of DMBz, OHPBz, HMBz, HEBz, HBPBz, with Mn(II), Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) in 60% (v/v) methanol-water mixture at 35°C and μ $= 0.1\,M\,(KNO_3)$ were determined and compared with those of NBz, MNBz and PNBz. The data in Table 3 show that the stability constants of the metal complexes with any one of the ligands follow the order: Mn(II) < Co(II) < Ni(II) < Cu(II) < Zn(II) > Cd(II), and are in agreement with the Irving — Williams order.

The plots of $\log K$ versus pK_a of the ligands for different metal ions are linear with slopes greater than unity indicating that the effect of substitution on the metal-ligand stability constant is more compared to the effect on the ionization constant. The plot of $\log \beta_2$ of OHPBz with the aforesaid metal ions against the $\log \beta_2$ of HMPBz with the same metal ions is linear with unit slope and an intercept equal to the difference in ionization constants of the two ligands.

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Announcement

A national symposium on *Recent trends in instrumental methods of analysis*, sponsored by the CSIR, DST and INSA, New Delhi, will be held at the Department of Chemistry, University of Roorkee, Roorkee during 23-25 February 1985. Further details can be had from the convener, Prof. S.N. Tandon, Department of Chemistry, University of Roorkee, Roorkee 247 667.