Mixed Ligand Complexes of Transition Metals with Bipyridyl, Oxalic Acid & Malonic Acid as Primary Ligands & Benzimidazole-2-propionic Acid as a Secondary Ligand

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Stability constants of ternary complexes of the type MAL [where M = Cu(II), Ni(II), and Zn(II); A = 2,2'-bipyridyl (bipy), oxalic acid (Ox) and malonic acid (MA) and L = benzimidazole-2-propionic acid (BPA)] have been determined pH metrically in 50% (v/v) ethanol-water mixture at 30° and $I=0.1$ M (NaClO$_4$). The ternary chelate formation occurs in step equilibria where BPA coordinates as a secondary ligand. The stabilities of binary and ternary complexes are in conformity with Irving-William's natural order. With respect to the ligands the stability order is Ox > bipy > MA. Stability data indicate that the formation of ternary complexes is favoured over that of binary complexes.

Lane and Daly reported that benzimidazole-2-propionic acid (BPA) acted as bidentate ligand with transition metal ions forming a seven-membered chelate ring[1]. However BPA was shown to have a tendency to change to the lactam form in the presence of a metal ion. Hence a competition between chelation and lactam formation is expected. In this note we now report the formation constants of 1:1 and 1:2 binary and 1:1:1 ternary complexes of Cu(II), Ni(II) and Zn(II) with 2,2'-bipyridyl (bipy), oxalic (Ox) and malonic acid (MA) and benzimidazole-2-propionic acid (BPA) in 50% (v/v) ethanol-water mixture at 30° and ionic strength $(I)=0.1$ M (NaClO$_4$).

The ligand BPA (Ia) was synthesised by a known method[2] and its purity checked by elemental analyses
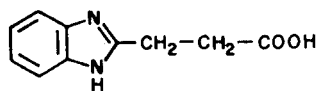
Ia

and spectral data. 2,2'-Bipyridyl (E Merck), Ox (BDH) and MA (Sigma) were of AR grade and used as such. Proton-ligand and metal-ligand formation constants of binary systems were determined using Irving-Rossotti pH titration technique[3], while the formation constants of ternary systems by the method of

Table 1—Formation Constants of Binary and Ternary Metal Chelates of Benzimidazole-2-propionic Acid

[$I=0.1$ M (NaClO$_4$); temp = 30°; medium = 50% (v/v) aq. ethanol]

Constant		Cu(II)	Ni(II)	Zn(II)
log K_{ML}^M		3.45	3.31	3.40
log $K_{ML_2}^{ML}$		2.98	2.78	2.81
log K_{MAL}^{MA2}	Ox:	5.58	4.91	4.41
	MA:	4.78	3.52	3.02
	Bipy:	5.47	4.02	3.12
Δlog K	Ox:	2.13	1.60	1.01
	MA:	1.33	0.21	−0.38
	Bipy:	2.02	0.71	−0.28
log $(K_{MAL}^{MA} - K_{ML_2}^{ML})$	Ox:	2.60	2.13	1.60
	MA:	1.80	0.24	0.21
	Bipy:	2.49	1.24	0.31

Ramamoorthy and Santappa[4,5]. pH meter readings (B) in 50% (v/v) ethanol-water were corrected by the method of Van Uitert and Haas[6]. The experimental procedures were similar to those described earlier[7–9].

Formation constants of M(II)-binary complexes of these ligands are presented in Table 1. The $pK(\overset{+}{N}H)$ and $pK(COOH)$ of BPA are found to be 4.36 and 5.77 respectively. Copper(II), Ni(II) and Zn(II) form both 1:1 and 1:2 complexes with BPA. The order of stabilities follow Irving-Williams's order. A large difference of about 4.0 log units is observed between proton-ligand formation constants suggesting that BPA has a lesser tendency to form chelates with the metal ions. Probably this may be due to the tendency of the ligand to change to the lactam form (Ib).
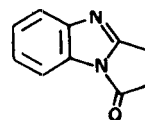
Ib

Formation of ternary complexes has been inferred from (i) a shift in pH of precipitation and (ii) a colour change or intensification of colour of the solution[4,5]. Further, the titration curves reveal that 1:1 M(II)-A complexes (A = bipy, Ox, MA) are formed in the lower pH range (below 4 pH) while the M(II)-BPA complexes are formed in the higher pH range (above 4 pH). The ternary M(II)-A-BPA complex curves coincide with 1:1 M(II)-A curve in the lower pH range and deviate at the pH where complexation of M(II)-BPA system occurs. This indicates the formation of ternary complexes in stepwise equilibria (Eqs 1 or 2) and the ligand BPA acts as a secondary ligand in the presence of bipy, Ox and MA.

$$M + A \rightleftharpoons MA \qquad \ldots(1)$$

$$MA + BPA \rightleftharpoons M - A - BPA \qquad \ldots(2)$$

The order of formation constants of the binary complexes with respect to the metal ions is Cu(II) > Zn(II) > Ni(II) while in ternary chelates the order is Cu(II) > Ni(II) > Zn(II). Though this is in accord with Irving-William's order of stabilities, yet the forces that govern the formation of binary complexes is not similar to those in ternary systems.

Further if the formation of ML_2 and MAL complexes (L = BPA) are assumed due to coordination of secondary ligand BPA to the primary complex ML and MA respectively in the stepwise formation, then the order $K_{MAL}^{MA} > K_{ML_2}^{ML}$ is expected on the basis of size (bulkiness) of the ligands. This is found to be so in the present study. However, the difference between log K_{MAL}^{MA} and log $K_{ML_2}^{ML}$ is relatively lower for the ternary systems of Zn(II) compared to Cu(II) and Ni(II). The additional stability of Cu(II) and Ni(II) chelates over those of Zn(II) may be attributed to the extensive π-interaction in the former ternary systems.

In the present study, the order of stabilities with respect to primary ligands, viz. Ox > bipy > MA, is in accord with the relative basicities of the ligands. However, the reversal in the stability sequence of MA and Ox systems may be due to the size of the chelate ring.

BPA is known to form a seven-membered chelate ring with bivalent metal ions[1]. The lower stabilities of M-bipy-BPA complex as compared to those of M-Ox-BPA complexes may be due to the hindrance caused by the bulkiness of the bipy ligand as compared to that by Ox. Further, the formation of ternary complexes is favoured over that of binary systems, as is evident from more or less positive Δ log K values for ternary systems.

Sigel et al.[10-12] have pointed out that nitrogen heterocyclics like imidazole and benzimidazole form ternary complexes of high stabilities and with high Δlog K values usually exceeding the statistically expected values. These authors attributed this to the metal$\rightarrow$L π-back bonding. In BPA a similar type of M $\rightarrow$Lπ-interactions may be expected because of structural similarities with imidazole or benzimidazole.

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