

Mixed ligand formation constants of complexes of 2-[[{(1H-benzimidazol-2-ylmethyl)imino}methyl]phenol with some bivalent metal ions

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The formation of mixed ligand complexes of the type $M(II)-A-L$ where $A = 1,10$ -phenanthroline (phen), 2,2'-bipyridyl (bipy) or α -phenylenediamine (OPDA) and $L = 2-[[{(1H-benzimidazol-2-ylmethyl)imino}methyl]phenol$ (BMIMP) have been investigated by pH -metric technique at $30^\circ C$ in 60% (v/v) aqueous-methanol at $I = 0.1 M (NaClO_4)$. The ligand $[L]^-$ coordinates as a secondary ligand in presence of ligand $[A]$ in stepwise equilibria. The order of stabilities of ternary chelates with respect to the ligands is $bipy > phen > OPDA$ and that with respect to metal ions is $[Cu(II)] > [Ni(II)] > [Co(II)] > [Zn(II)] > [Cd(II)]$ in conformity with the Irving-Williams's natural order.

In continuation of our earlier studies^{1,2} on the coordinating tendencies of schiff bases with metal ions, we report herein the formation constants of ternary chelates of $Cu(II)$, $Ni(II)$, $Co(II)$, $Zn(II)$, $Cd(II)$ with 2,2'-bipyridyl (bipy), 1,10-phenanthroline (phen), α -phenylenediamine (OPDA) and 2-[[{(1H-benzimidazol-2-ylmethyl)imino}methyl]phenol (BMIMP) in 60% (v/v) aqueous methanol medium at $I = 0.1 M (NaClO_4)$ at $30^\circ C$.

Experimental

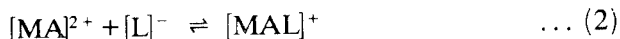
The proton-ligand and metal-ligand formation constants for binary system were determined using Irving-Rossotti pH titration technique³, and formation constants of ternary chelates of $M(II)-A-L$ systems ($L = BMIMP$; $A = bipy, phen, OPDA$) were evaluated by the method of Santappa and Ramamoorthy⁴. The general experimental procedures are similar to those reported earlier^{1,2}. The pH meter readings (B) in the aqueous methanol medium were corrected by the method of Van Uitert and Haas⁵.

Results and discussion

From the proton-ligand formation curves ($0.2 < \bar{n}_H < 1.8$) of BMIMP, the proton-ligand sta-

bility constants, $\log K_{OH}$ and $\log K_{NH(py)}^+$ were evaluated and the values were found to be 9.67 and 3.80 respectively. From the metal-ligand formation curves, the $\bar{n}$ values ($0.1 < \bar{n} < 1.8$) obtained for $M(II)-L$ systems indicate the formation of both 1:1 and 1:2 complexes².

In the ternary systems studied, the ternary $M(II)-A-L$ titration curves coincided with 1:1 $M(II)-A$ binary curves in the pH region < 3.5 where the 1:1 $M(II)-A$ complexes were formed. This indicates the formation of only $M(II)-A$ complexes and the non-coordination of $[L]^-$ with these metal ions in that pH region. The divergence of mixed ligand $M(II)-A-L$ curves from the binary $M(II)-A$ curves beyond pH 3.5 suggests the coordination of $[L]^-$ as a secondary ligand in presence of $[A]$. Hence, the formation of $M(II)-A-L$ ternary complexes could be considered in stepwise equilibria (Eqs 1 and 2).



(where $A = bipy, OPDA$ or $phen$; $L = BMIMP$)

The formation of ternary complexes is further supported by non-superimposable nature of the theoretical composite curve with respect to the experimental mixed ligand curve⁶.

From a knowledge of proton-ligand and metal-ligand formation constants, the distribution of the total metal among the various metal-ligand species as a function of pH has been calculated by computer program BEST due to Martell and Motekaitis⁷. As a representative case the species distribution diagram for $Cu(II)$ -bipy-BMIMP system is shown in Fig. 1. This diagram also reveals the formation of ternary complex in a stepwise manner.

A perusal of the data in Table 1 indicates that the stabilities of $M(II)$ -bipy- L ternary systems are higher than those of $M(II)$ -phen- L and $M(II)$ -OPDA- L systems. The higher stabilities of $M(II)$ -bipy- L and $M(II)$ -phen- L systems compared with those of $M(II)$ -OPDA- L systems may be due to the ability of phen and bipy to form π bonds as observed by Griesser and Sigel⁸ and Bhattacharya and coworkers⁹. The higher stabilities of $M(II)$ -bipy- L than those of $M(II)$ -phen- L may be due to the flexible nature of bipy molecule. The order of

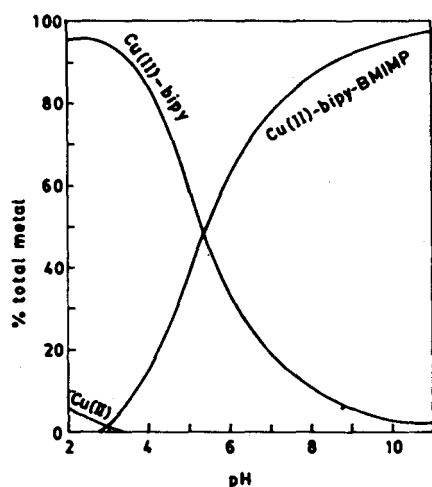


Fig. 1 – Distribution diagram of Cu(II)-bipy-BMIMP system.

Table 1 – Formation constants* of binary and ternary metal chelates of BMIMP in 60% (v/v) aq. methanol
[I = 0.1 M (NaClO₄); Temp. = 30°C]

Metal	$\log K_{ML}^M$	$\log K_{ML_2}^M$	$\log \beta_2$	$\log K_{MAL}^{MA}$		
				bipy	phen	OPDA
Cu(II)	9.27	7.64	16.91	8.59	8.46	8.29
Ni(II)	8.96	7.40	16.36	8.36	8.25	8.04
Co(II)	8.55	7.05	15.60	8.19	8.14	7.97
Zn(II)	8.10	6.88	14.98	7.72	7.52	7.39
Cd(II)	7.80	6.52	14.32	7.39	7.18	7.03

* Standard deviations are within ± 0.03 log units.

stabilities of ternary complexes with respect to metal ions [Cu(II) > Ni(II) > Co(II) > Zn(II) > Cd(II)] is in agreement with the Irving-William's order.

The stability constants of ternary chelates are lower than those of the binary ($\log K_{ML}^M$) ones probably due to the availability of lesser number of coordinating sites for [L]⁻ on [M(II)-A] than on the free [M(II)-(aq)] ions¹⁰.

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