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NOTE

Potentiometric determination of formation constants of metal ion complexes with 4-hydrazinobenzofuro[3,2-*d*]pyrimidine Schiff base

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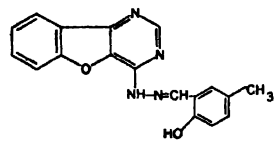
Solution equilibrium studies on the complex formation of bivalent Mg, Co, Ni, Zn, Cd, Hg and Cu with the Schiff base derived from condensation of 4-hydrazinobenzofuro[3,2-*d*]pyrimidine with 5-methylsalicylaldehyde by pH-titration technique at 30 ± 1° at a constant ionic strength, 0.1 *M* ($NaClO_4$) in 70 : 30% (v/v) alcohol-water medium, indicate the order : Cu > Co > Ni > Zn > Hg > Cd > Mg of stability constants of the complexes.

In view of the biological importance of the benzofuran derivatives[1], it was thought worthwhile to study the solution stabilities of complexes of biologically important metal ions[2] with the Schiff base (**1**) derived from condensation of 4-hydrazinobenzofuro[3,2-*d*]pyrimidine with 5-methylsalicylaldehyde (HL). The stability constants of metal complexes with bivalent Cu, Ni, Co, Zn, Cd, Hg and Mg have been determined pH-metrically in 70 : 30% (v/v) alcohol-water medium at 30 ± 1° and at constant ionic strength of 0.1 *M* ($NaClO_4$) following Calvin-Bjerrum pH-technique as adopted by Irving-Rossotti[3].



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Results and Discussion

The ligand contains only one dissociable proton due to phenolic OH group. The protonation of the HC=N- (imino nitrogen) does not takes place in the pH range under study. Metal-ligand complex formation occurred at pH lower than that of at metal ion hydrolysis[4]. Mg^{II}, Hg^{II}, Zn^{II} and Cu^{II} for 1 : 1 complexes, whereas Ni^{II}, Cd^{II} and Co^{II} form both 1 : 1 and 1 : 2 complexes. The values of the stability constants of the metal-ligand systems studied follow in the usual order[5] : $Cu^{II} > Co^{II} > Ni^{II} > Zn^{II} > Hg^{II} > Cd^{II} > Mg^{II}$.

Table 1. Proton-ligand and metal-ligand stability constants of metal complexes

Temp. = 30 ± 1°, solvent : 70 : 30% (v/v) ethanol : water mixture, I = 0.1 *M* $NaClO_4$

pK^{H}_{HL} = 9.79

	Mg^{II}	Co^{II}	Ni^{II}	Cu^{II}	Zn^{II}	Cd^{II}	Hg^{II}
log K_1	4.17	8.14	7.05	9.79	6.98	5.70	6.38
log K_2	–	7.89	6.27	–	–	5.40	–

Experimental

All chemicals used were of A.R. grade.

Schiff base : The Schiff base ligand (HL) was synthesized by refluxing equimolar quantity (2.5 mol) of 4-hydazinobenzofuro[3,2-*d*]pyrimidine[6] and 5-methylsalicylaldehyde in absolute alcohol and the reaction mixture was refluxed on a water-bath for ~4 h. On partial evaporation of the solvent the light yellowish colored solid that separated out was washed with alcohol and crystallized from alcohol, yield 85%, m. p. 284°, ν_{max} 1640 (C=N) and 3175 cm^{-1} (NH).

An Elico LI-122 pH meter equipped with combined glass electrode type CL-51 was used.

To account for the difference in acidity, basicity, dielectric constants and ionic activities in non-aqueous solutions compared to the pure solutions, the pH meter readings were corrected as per literature[7]. All titrations were carried out in double-walled glass cell in an inert atmosphere of nitrogen at 30 ± 1°. There was no hydrolysis of ligand under the experimental conditions as indicated by no change in pH of the solution with time. The following solutions : (a) 0.01 *M* $HClO_4$, (b) (a) + 0.02 *M* ligand (HL) and (c) (b) + 0.01 *M* metal ion solution, each of initial volume 50 ml in 70 : 30% (v/v) ethanol-water mixture, were pH-metrically titrated with 0.105 *M* NaOH in the same solvent mixture at 30 ± 1° maintaining a constant ionic strength, I = 0.1 *M* ($NaClO_4$).

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