

## Publication

## Acid-Base and Metal-Ion-Coordinating Properties of Benzimidazole and Derivatives (= 1, 3-Dideazapurines) in Aqueous Solution : Interrelation between Complex Stability and Ligand Basicity

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The stability constants of the 1:1 complexes formed between  $\text{Mg}^{2+}$ - $\text{Ca}^{2+}$ ,  $\text{Sr}^{2+}$ ,  $\text{Ba}^{2+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$ , or  $\text{Cd}^{2+}$  (=  $\text{Mn}^{2+}$ ) and benzimidazole-type ligands sterically unhindered at the N3 position (= L), namely, benzimidazole, 1-methylbenzimidazole, 5(6)-chlorobenzimidazole, 6-chloro-5-fluorobenzimidazole, 5(6)-nitrobenzimidazole, 5,6-dichloro-1(beta-D-ribofuranosyl)benzimidazole, and 5,6-dinitrobenzimidazole (DNBI), were determined by UV/VIS spectrophotometry for DNBI and for all the other ligands by potentiometric pH titration in aqueous solutions (25 degrees C.  $I = 0.5 \text{ M}$ ,  $\text{NaNO}_3$ ). The acidity constants for the monoprotinated ligands  $\text{HL}^+$  were also measured. For the  $\text{HL}^+$  species which are symmetric with respect to the H(N1) and H(N3) sites, the corresponding micro acidity constants are also given. Plots of  $\log K\text{-ML}(\text{M})$ , versus  $\text{pK}(\text{HL})(\text{H})$ , (taking into account the micro acidity constants where appropriate) give straight lines. The equations for these least-squares lines allow calculation of the expected stability constant for a complex of any benzimidazole-type ligand, provided its  $\text{pK}(\text{HL})(\text{H})$  value (in the PK, range 2-6) is known. For the stabilities of  $\text{Fe}^{2+}$  complexes with benzimidazole-type ligands an estimation procedure is described. The effect of steric inhibition resulting from annelation (the fusion of a benzene ring to C4 and C5 of imidazole), is quantified and compared to that of a methyl group in the ortho position to the N atom binding the metal ion. The effect of annelation is considerable for the complexes of the divalent 3d metal ions (-0.3 to -0.7 log units) but practically nonexistent for those of the alkaline earth ions, which indicates outer-sphere complex formation for the latter. This interpretation agrees with the observation that the stability of the  $\text{ML}^{2+}$  complexes of  $\text{Ca}^{2+}$ ,  $\text{Sr}^{2+}$ , and  $\text{Ba}^{2+}$  is practically independent of the basicity of the benzimidazole derivative. The regression lines obtained for the complexes of the benzimidazole-type ligands now permit the determination of the extent of the steric inhibition of the (C6) $\text{NH}_2$  group on metal-ion binding at N7 of the adenine residue.

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