1,6- and 4,6-benzo[*h*]naphthyridines and stability constants of their complexes with manganese(II) and iron(II)

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Using potentiometric method the stability constants of complexes of isomeric 1,6- and 4,6-benzo[*h*]naphthyridines with manganese(II) and iron(II) were determined.

In continuation of our research concerning complexing ability [1—4], reactivity [5, 6], and biological activity [7] of benzo[*h*]naphthyridines (bn) and having in view the growing attention paid to complexes of pyridines with metal ions [8, 9] we describe in the present paper the determination of stability constants of 1,6- and 4,6-bn complexes with manganese(II) and iron(II).
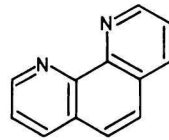
The considered azaaromatics are isomeric with 1,10-phenanthroline (phen) [10], however of lower symmetry.
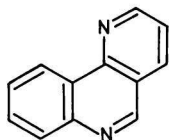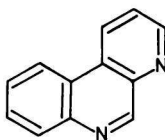
1,6 – bn   4,6 – bn   phen

Experimental

The reagents used for preparation of solutions 0.02 M-NaOH, 0.01 M-$(NH_4)_2SO_4$ $FeSO_4$ $6H_2O$, and 0.01 M-$MnSO_4$ were of the anal. grade purity. 0.0138 M-1,6- and 0.0138 M-4,6-benzo[*h*]naphthyridine were used; samples were recrystallized from cyclohexane.

The stability constants of complexes of 1,6- and 4,6-bn with manganese(II) and iron(II) were determined by potentiometric method.

The titrations of samples of protonated forms of 1,6- and 4,6-bn in aqueous solution were carried out with standard 0.02 M-NaOH, one in the absence and the second in the presence of the metal ion Mn(II) or Fe(II). The measurements were performed using an OP-211 digital pH-meter (Radelkis, Budapest) (pH accuracy to ± 0.01 units) at 25 °C with calomel and glass electrodes. Titrations were made at the constant ionic strength of 0.5 mol dm^{-3}, in all cases taking the average of five measurements.

Both Mn(II) and Fe(II) complexes were formed in the pH range 5—9; in this pH region strong shifts in the titration curves have been observed.

In the case of Mn(II) complexes $\log \beta_2$ and $\log \beta_3$ values were not determined having in view the possible formation of hydroxo complexes at higher pH.

The concentration of the bound ligand was found directly from the titration curves using the Calvin—Melchior method [11] and stability constants were determined by the Bjerrum method [12].

Results and discussion

The concentration of the bound ligand is defined by the following expression

$$[L_{bound}] = (a - a^\circ)c_{HL} \tag{1}$$

The concentration of the free ligand is given by the relation

$$[L_{free}] = \frac{c_{HL} - (a - a^\circ)c_{HL}}{\alpha_{L(H)}} \tag{2}$$

Thus, the average number of ligands $\bar{n}$ is given by

$$\bar{n} = \frac{(a - a^\circ)c_{HL}}{c_m} \tag{3}$$

where a° is the titration fraction of the protonated ligand HL at the given pH value, a the titration fraction at the same pH value, in the presence of the metal ion, c_m total metal ion concentration in the solution sample, and $\alpha_{L(H)}$ coefficient of side reactions.

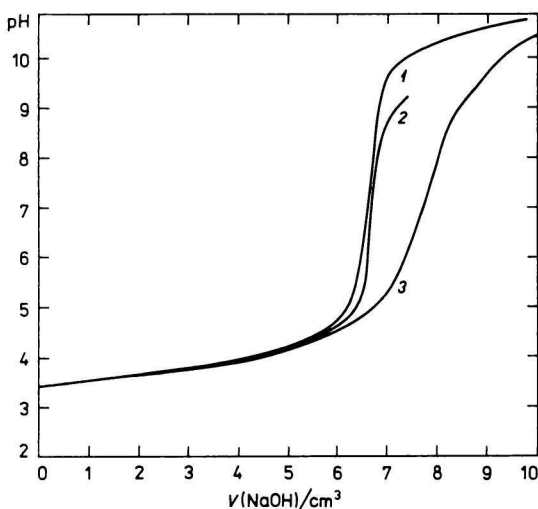$$\alpha_{L(H)} = 1 + [H^+]K_1 + [H^+]^2 K_1 K_2 \tag{4}$$

Fig. 1. Titration curves of 1,6-benzo[h]naphthyridine with 0.02 M-NaOH in the absence (1) and in the presence of 0.01 M-MnSO$_4$ (2) and 0.01 M-(NH$_4$)$_2$Fe(SO$_4$)$_2$ (3).

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The K_1 and K_2 values were calculated from the relation

$$\log K_i = \log \frac{(1 - a + n - 1)c_{H_nL} - [H^+] + [OH^-]}{(a - n + 1)c_{H_nL} + [H^+] - [OH^-]} + pH \qquad (5)$$

where K_i is the ith protonation constant, a degree of neutralization, n the basicity of the base, c_{H_nL} concentration of the protonated bn [10].

Plots of titration curves of protonated 1,6- and 4,6-bn, in the absence and in the presence of the metal ion are shown in Figs. 1 and 2.
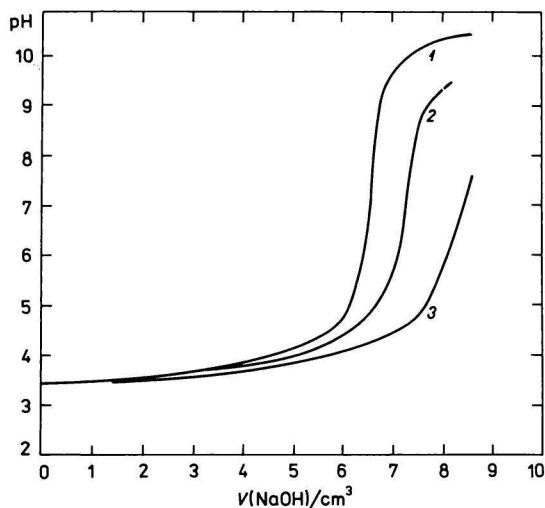

Fig. 2. Titration curves of 4,6-ben-zo[h]naphthyridine with 0.02 M--NaOH in the absence (1) and in the presence of 0.01 M-MnSO₄ (2) and 0.01 M-(NH₄)₂Fe(SO₄)₂ (3).

Plots of $\bar{n}$ vs. $\log[L_{free}]$ (Figs. 3 and 4) allowed calculation of the stability constants by the Bjerrum method [12].

The values of stability constants found by presented method are summarized in Table 1 and for comparative purposes, the analogous values for phen are given [13, 14].

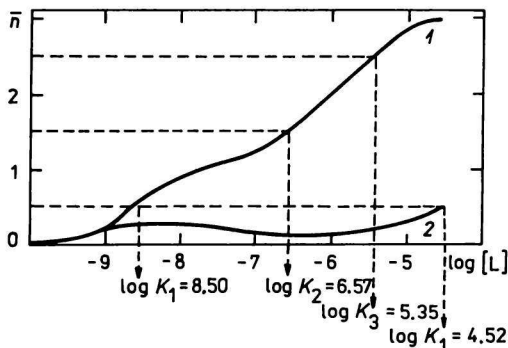It was observed that the $\log \beta_1$ values for Fe(II) complexes increase in the

Fig. 3. Formation curves of complexes of 1,6-benzo[h]naphthyridine with Fe(II) (1) and Mn(II) (2).

Table 1
Stability constants of 1,6- and 4,6-benzo[*h*]naphthyridines with Mn(II) and Fe(II)

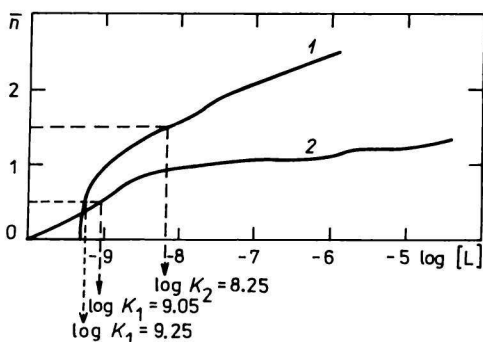| Ligand	Protonation constants		Metal ion	Stability constants	
	$\log K_1$	$\log K_2$		$\log \beta_2$ ($\log K_1 + \log K_2$)	$\log \beta_3$ ($\log K_1 + \log K_2 + \log K_3$)
1,6-bn	10.80	3.86	Mn(II)	—	—
			Fe(II)	15.07	20.42
4,6-bn	10.60	3.04	Mn(II)	—	—
			Fe(II)	17.50	—
phen[a]	4.95	—	Mn(II)	7.61	10.31
			Fe(II)	11.10	21.30

a) Ref. [13, 14].

Fig. 4. Formation curves of complexes of 4,6-benzo[*h*]naphthyridine with Fe(II) (*1*) and Mn(II) (*2*)

order: phen, 1,6- and 4,6-bn (5.90, 8.50, 9.25, respectively), the same regularity is found in the case of Mn(II) (4.13, 4.52, 9.05, respectively) and the $\log \beta_3$ values are the highest in the case of the phen complexes with Fe(II) and Mn(II).

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