

# Complexes of 1,6-benzo[*h*]naphthyridine with copper(II) and cadmium(II) and their stability constants

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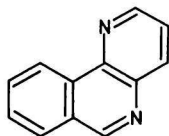
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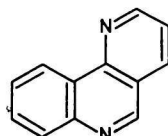
Stability constants of complexes of 1,6-benzo[*h*]naphthyridine with copper(II) and cadmium(II) were determined by potentiometric method and compared with those of 1,10-phenanthroline.

Константы устойчивости комплексов 1,6-бензо[*h*]нафтиридина с Cu(II) и Cd(II) определены потенциометрическим методом и сравнены с константами устойчивости аналогичных комплексов 1,10-фенантролина.

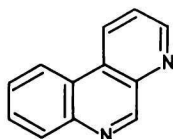
The present paper is a continuation of our research concerning 1,5-, 1,6-, and 4,6-benzo[*h*]naphthyridines (bn). Benzo[*h*]naphthyridines and their derivatives reveal biological activities, *e.g.* antibacterial and antifungal [1, 2], therefore it is of interest to investigate their complexation properties.



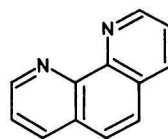
1,5-bn



1,6-bn



4,6-bn



phen

Previously we described the stability constants of complexes of 1,5-, 1,6-, and 4,6-bn with iron(II), cobalt(II), and nickel(II) [3, 4], and complexes of 1,5- and 4,6-bn with copper(II) and cadmium(II) [3]. The present paper deals with complexes of 1,6-bn with copper(II) and cadmium(II).

For comparative purposes the data of 1,6-bn complexes with iron(II) [2] as well as those of analogous complexes of 1,10-phenanthroline (phen) [5, 6], an efficient complexing agent, isomeric with bn, are given.

### Experimental

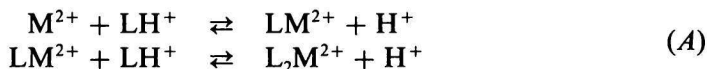
The stability constants have been determined potentiometrically, the measurements being taken as in our previous work, at 25°C and at the constant ionic strength of 0.1 mol dm<sup>-3</sup>.

The applied reagents were of anal. grade quality, 1,6-bn has been recrystallized from cyclohexane, m.p. = 95°C [1].

For the titration of 0.1 M solution of 1,6-bn in solution of H<sub>2</sub>SO<sub>4</sub>\* with 0.02 M-NaOH the Radelkis OP-211 digital pH-meter with the calomel and glass electrodes was used, the pH accuracy being ±0.01; in all cases the average of five experiments was taken.

The measurements were accomplished by two titrations, the first one of the protonated bn, and the second, under the same conditions, in the presence of the corresponding metal ion.

When the complex is formed, the reaction (A) occurs, and hence the shift of the titration curve takes place.



where L is the ligand and M<sup>2+</sup> the metal ion.

If at the pH range of 5—9 a strong shift of the titration curve is observed, which was the case in our experiments, the concentration of the bound ligand can be found directly from the plot, using the Calvin—Melchior method [7].

The concentration of the bound ligand is equal to

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

where *a*, *a*<sup>°</sup> are the titration fractions.

$$\text{titration fraction} = \frac{\text{total amount of a titrant in solution}}{\text{total amount of substance in solution}}$$

The concentration of the free ligand is given by eqn (2)

$$[L_{\text{free}}] = \frac{c_{\text{HL}} - [L_{\text{bound}}]}{1 + [H^+]K_1 + [H^+]^2K_1K_2} \quad (2)$$

\* H<sub>2</sub>SO<sub>4</sub> was used in the amount sufficient to protonation of 1,6-bn, its excess being back titrated with 0.02 M-NaOH; this was taken into account in calculations.

Thus

$$[L_{\text{free}}] = \frac{c_{\text{HL}} - (a - a^{\circ})c_{\text{HL}}}{1 + [\text{H}^+]K_1 + [\text{H}^+]^2K_1K_2} \quad (3)$$

where  $a$  is the titration fraction of the protonated ligand at the given pH value and  $a^{\circ}$  the titration fraction at the same pH in the presence of the metal ion.  $c_{\text{HL}}/(\text{mol dm}^{-3})$  is the concentration of the protonated ligand and  $K_1, K_2/(\text{dm}^3 \text{mol}^{-1})$  are protonation constants.

Thus, the average ligand number  $\bar{n}$  is

$$\bar{n} = \frac{(a - a^{\circ})c_{\text{HL}}}{c_{\text{m}}} \quad (4)$$

where  $c_{\text{m}}$  is the total metal ion concentration in the solution.

## Results

Construction of curves of complex formation, *i.e.* plots of the relation  $\bar{n}$  against  $\log \{[L]\}$  allowed to calculate the stability constants by the *Bjerrum* method [8].

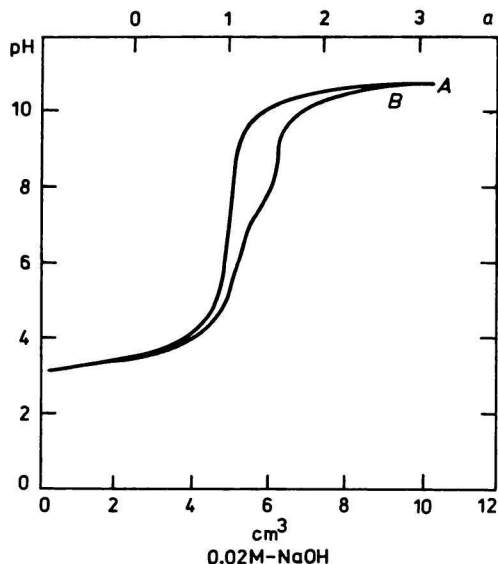


Fig. 1. Titration curves of 1,6-benzo[*h*]naphthyridine with 0.02 M-NaOH in the absence (*A*) and in the presence (*B*) of 0.001 M-Cu(NO<sub>3</sub>)<sub>2</sub>.

Fig. 1 shows the titration curve of the protonated 1,6-bn with the 0.02 M-NaOH (A) and the same curve in the presence of 0.001 M solution of Cu(II) ions (B). Fig. 2 shows the same curves in the presence of 0.001 M solution of Cd(II) ions.

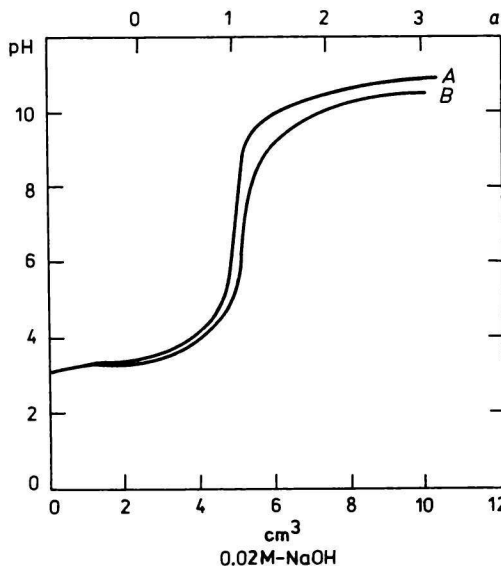


Fig. 2. Titration curves of 1,6-benzo[h]naphthyridine with 0.02 M-NaOH in the absence (A) and in the presence (B) of 0.001 M-Cd(NO<sub>3</sub>)<sub>2</sub>.

In Fig. 3 the formation curves of both complexes are presented; from this diagram their stability constants could be determined by the Bjerrum method. The 1,6-bn complexes with Cu(II) and Cd(II) are formed at the pH range of 5–9 (Figs. 1 and 2); in the case of Cu(II) complex the shift of the titration curve is stronger than with the Cd(II) complex.

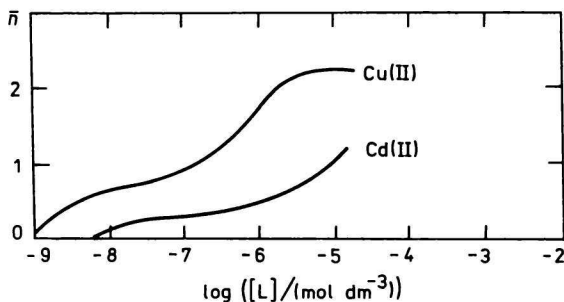


Fig. 3. Formation curves of complexes of 1,6-benzo[h]naphthyridine with Cu(II) and Cd(II).

Table 1

Stability constants of 1,6-benzo[h]naphthyridine complexes with Cu(II) and Cd(II) in aqueous solution at 25°C, at ionic strength of 0.1 mol dm<sup>-3</sup>

Ligand	log $K_1$	log $K_2$	Metal ion	Stability constants		
				log $\beta_1$	log $\beta_2$	log $\beta_3$
bn	10.80	3.86	Cu(II)	7.97	14.02	—
			Cd(II)	5.80	—	—
			Fe(II)	8.50	15.07	20.42
phen	4.95	—	Cu(II)	9.25	16.0	21.35
			Cd(II)	5.78	10.82	14.92
			Fe(II)	5.90	11.20	21.30

The found protonation constants of 1,6-bn and the stability constants of its complexes with copper(II) and cadmium(II) are summarized in Table 1; for comparative purposes the analogous data of 1,6-bn with iron(II) [3] as well as the corresponding values of phen [5, 6] are given.

Among complexes of 1,6-bn, the strongest is that with iron(II) and the weakest with cadmium(II), as it could be expected. Table 1 shows that the 1,6-bn complex with Cu(II) is weaker than that of phen.

For the 1,6-bn complex with Cd(II) only log  $\beta_1$  value could be found, while in the case of such complex of phen three stability constants have been determined, therefore the bn complex with Cd(II) is less stable than the analogous phen complex.

## References

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