Complexes of 1,5-, 1,6-, and 4,6-Benzo[*h*]naphthyridines with Zinc(II) and Their Stability Constants Determined by the Potentiometric Method

N. ZELICHOWICZ and A. GAUDYN

Institute of Chemistry, Pedagogical University, PL-42-201 Częstochowa

Received 4 April 1991

Using the potentiometric method the stability constants of complexes of 1,5-, 1,6-, and 4,6-benzo[*h*]naphthyridines with Zn(II) were determined.

Previously we described the stability constants of complexes of 1,5-, 1,6-, and 4,6-benzo[*h*]naphthyridines with some transition metal ions [1—4]. The present paper is a continuation of our research concerning the complexing properties of these azaaromatics.

EXPERIMENTAL

The stability constants of complexes of 1,5-, 1,6-, and 4,6-benzo[*h*]naphthyridines (bn) were determined by the potentiometric method, described in our former papers [1—4] at the constant ionic strength of 0.5 mol dm^{-3} and at 298 K.

Pure commercial products 1,5-bn (m.p. = 98 °C), 1,6-bn (m.p. = 95 °C), and 4,6-bn (m.p. = 118 °C) were used for experiments after recrystallization from cyclohexane [4].

Samples of an aqueous solution of 50 cm^3 each contained:

1,5-bn, 1,6-bn or 4,6-bn (c = 2.8 x 10^{-4} mol dm^{-3}), HNO_3 (c = 0.001 mol dm^{-3}), and KNO_3 added to adjust the ionic strength to I = 0.5 mol dm^{-3} (sample *A*);

1,5-bn, 1,6-bn or 4,6-bn (c = 2.8 x 10^{-4} mol dm^{-3}), $Zn(NO_3)_2$ (c = 0.001 mol dm^{-3}), HNO_3 (c = 0.001 mol dm^{-3}), and KNO_3 added to adjust the ionic strength to I = 0.5 mol dm^{-3} (sample *B*).

The sample *A* of protonated ligand was titrated by the standard 0.02 M-NaOH solution; at the determination of stability constants of complexes of 1,5-bn, 1,6-bn or 4,6-bn formed in the presence of $Zn(NO_3)_2$ (*B*) the same procedure was applied.

The measurements of pH were made by means of a digital pH-meter OP-211 (Radelkis, Budapest), equipped with a combined glass/calomel electrode, the pH accuracy being ± 0.01. In all cases the average of five experiments was taken.

RESULTS AND DISCUSSION

The stability constants of complexes of 1,5-, 1,6-, and 4,6-bn with Zn(II) were determined by titration of the sample *B* with standard NaOH solution. In the pH range 5—9 a strong shift between two titration curves was observed.

The concentration of the bound ligand was determined directly from the plot, using the Calvin—Melchior method [5]. Plots of titration of protonated 1,5-, 1,6-, and 4,6-benzo[*h*]naphthyridines in the absence and in the presence of the Zn(II) ions are shown in Fig. 1.

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

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

and the concentration of the free ligand is given by the equation

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

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

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

where a° is the titration fraction of the protonated 1,5-, 1,6- or 4,6-bn by NaOH at the given pH values, a the titration fraction (total amount of titrant to total amount of substance in solution) at the same pH value, in the presence of the Zn(II) cation, c_{HL} (mol dm^{-3}) is the concentration of the protonated ligand, K_1, K_2 are the protonation constants calculated by the method described in Ref. [2], c_m is the total metal ion concentration in the solution.

Construction of curves of complex formation, *i.e.* plots of the relation of the average number of ligand molecules against log {[L]} allowed the calculation of the stability constants by the *Bjerrum* method

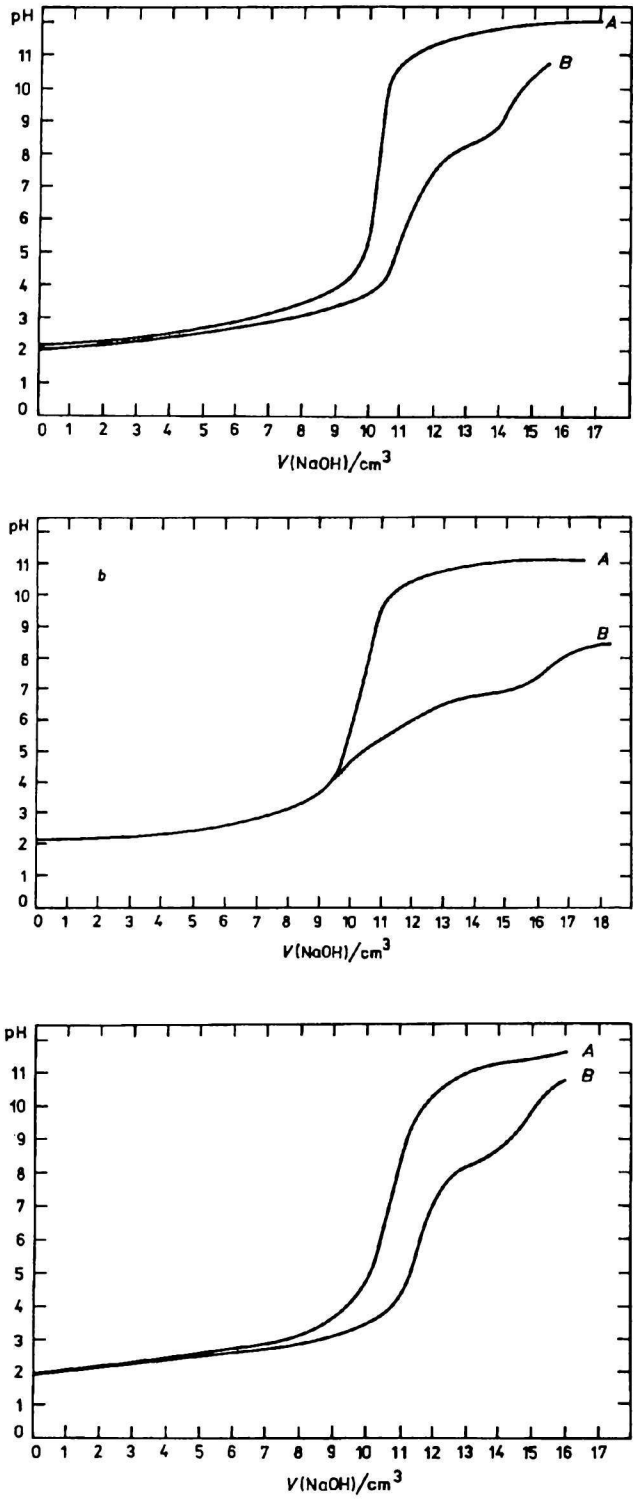

Fig. 1. Titration curves of 1,5-benzo[*h*]naphthyridine (*a*), 1,6-benzo[*h*]naphthyridine (*b*), and 4,6-benzo[*h*]-naphthyridine (*c*) with NaOH in the absence (*A*) and in the presence (*B*) of $Zn(NO_3)_2$.

[7]. In Fig. 2 the formation curves of complexes of 1,5-bn, 1,6-bn, and 4,6-bn with Zn(II) are presented. The results are summarized in Table 1, for comparative purposes the analogous values for 1,10-phenanthroline are given in [6, 8]. For complexes of 1,5-, 1,6-, and 4,6-benzo[*h*]naphthyridines with Zn(II) only two stability constants could be obtained.

Table 1. Stability Constants of Complexes of 1,5-, 1,6-, and 4,6-Benzo[*h*]naphthyridines with Zn(II); T = 298 K, I = 0.5 mol dm^{-3}

Ligand	Protonation constants			Stability constants	
	log K_1	log K_2	log K_3	log β_2	log β_3
1,5-bn	8.9	7.1	4.4	16.1	20.5
1,6-bn	8.8	6.9	–	15.7	–
4,6-bn	10.0	6.9	5.5	16.9	22.4
1,10-phen [8]	5.7	6.7	5.2	12.4	17.6

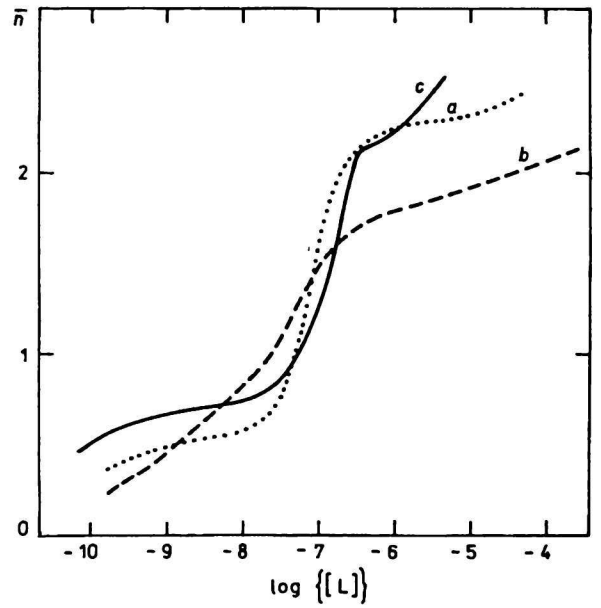

Fig. 2. Formation curves of complexes of 1,5-bn (*a*), 1,6-bn (*b*), and 4,6-bn (*c*) with Zn(II).

The stability constant values of the studied complexes are very similar, higher than in the case of 1,10-phenanthroline; the considered complexes are more stable than those of phen.

REFERENCES

1. Zelichowicz, N., Śliwa, W., and Gaudyn, A., *Z. Chem. 36,* 110 (1986).
2. Zelichowicz, N., Śliwa, W., and Gaudyn, A., *Chem. Papers 42,* 507 (1988).
3. Zelichowicz, N., Śliwa, W., and Gaudyn, A., *Transition Met. Chem.* (Weinheim, Germany) *12,* 423 (1987).
4. Zelichowicz, N. and Gaudyn, A., *Chem. Papers 45,* 735 (1991).
5. Calvin, M. and Melchior, N. C., *J. Am. Chem. Soc. 70,* 3270 (1948).
6. Irving, H. and Mellor, D., *J. Chem. Soc. 1962,* 5222.
7. Bjerrum, J., *Dan. Mat. Phys. Med. 4,* 21 (1974).
8. Anderegg, G., *Helv. Chim. Acta 46,* 2397 (1963).