

## TERNARY CHELATES WITH 2,2'-DIPYRIDYL AND 1,10-PHENANTHROLINE\*

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Ternary chelates  $ZnA_2B$  and  $ZnAB_2$ , formed during extraction of a zinc salt with acetylacetone (HA) and 2,2'-dipyridyl or 1,10-phenanthroline (B), have been studied. The  $ZnA_2B$  chelate has the character of an adduct with a higher stability and extractability than  $ZnA_2$ . The cationic chelate is extracted into chloroform as an ion-associate,  $(ZnAB_2^+, ClO_4^-)$ . This chelate passes into the aqueous phase in extraction systems involving benzene. The stability constants of the ternary chelates were determined by graphical analysis of the dependence of the zinc distribution ratio on the equilibrium concentration of B in the aqueous phase with the concentration of  $A^-$  constant.

In the previous papers, ternary complexes formed as adducts of an inert central particle with an organic base<sup>1,2</sup> and a ternary complex formed by ligand substitution in a binary complex<sup>3</sup> were studied. The aim of the present paper is description of systems involving the formation of ternary zinc chelates with bidentate nitrogen-containing ligands, 2,2'-dipyridyl and 1,10-phenanthroline (B), and acetylacetone (HA); the  $ZnA_2B$  adduct is formed and the  $ZnAB_2^+$  chelate appears at higher concentrations of B, due to substitution.

Woodward and Freiser<sup>4</sup> studied an extraction system of ternary zinc chelates of this type (HA 8-hydroxyquinoline, B 1,10-phenanthroline and 4,7-dimethyl-1,10-phenanthroline) and found that the composition of the chelates extracted into chloroform depended on the perchlorate concentration. At a millimole concentration,  $ZnA_2B$  and  $(ZnAB_2^+, Cl_4^-)$  chelates are formed; at perchlorate concentrations higher than decimolar, the extraction of the ion-associate predominates and at concentrations higher than 3·3M the  $(ZnB_3^{3+}, 2 ClO_4^-)$  species is extracted.

In agreement with the results of the mentioned paper<sup>4</sup>, the  $ZnAB_2^+$  ternary chelates studied here are extracted into chloroform as ion-associates. The system of the ternary chelates with 2,2'-dipyridyl was also studied in the benzene–water extraction system, in which the ligand is sufficiently soluble. We found that the distribution ratio of the zinc salt decreased in the B concentration region corresponding to the formation of the  $ZnAB_2^+$  chelate, since the chelate is transferred into the aqueous phase. The previously unpublished stability constants of the cationic chelates and adducts (including the adduct with 4,4'-dipyridyl) were determined using the Dyrssen<sup>5</sup> and Valentová<sup>1</sup> graphical methods.

\* Part IV in the series Stability of Mixed Complexes of Zinc Determined by the Extraction Method; Part III: This Journal 40, 2025 (1975).

## EXPERIMENTAL

## Chemicals and Procedure

Acetylacetone (Lachema, Brno) was distilled; the other chemicals (Lachema, Brno) were of *p.a.* purity. The organic and aqueous phases were prepared employing the procedure described in paper<sup>1</sup>. Dipyridyl and phenanthroline were dissolved in the organic phase, together with acetylacetone. The aqueous phase contained  $5 \cdot 10^{-5} \text{M} \cdot 6.5 \text{ZnSO}_4$  with activity of about  $15 \cdot 10^3$  impulses per ml. The overall electrolyte concentration was  $0.1 \text{M} \cdot (\text{NaOH} + \text{NaClO}_4)$ , except for curves 3 and 4 in Fig. 1. The distribution constants of 1,10-phenanthroline, 2,2'-dipyridyl and 4,4'-dipyridyl in the benzene-water system were determined titrimetrically<sup>1</sup>. During the determination of the base distribution constants, the aqueous phase always contained  $0.1 \text{M} \cdot \text{NaClO}_4$ .

## RESULTS

*Selection of Experimental Conditions*

The presence of cationic complexes  $\text{ZnA}^+$  in the aqueous phase can be prevented if the pH interval is selected so that, during extraction with acetylacetone (HA), the zinc salt distribution ratio,  $D$ , equals the zinc acetylacetonate distribution constant ( $K_D(20)$ ). This pH range is 7.4 to 8.4 for extraction into benzene<sup>1</sup> and 8.0 to 9.0 for extraction into chloroform (Fig. 1, curve 2). As the dissociation constants of the proto-

TABLE I

The Stability Constants,  $K_{ij}$ , and the Distribution Constants,  $K_D(ij)$ , of Ternary Zinc Chelates,  $\text{ZnA}_i\text{B}_j$ , with Acetylacetone (HA) and Dipyridyl or Phenanthroline (B) at ca 20°C in  $0.1 \text{M} \cdot \text{NaClO}_4$

B	pK <sub>a</sub>	Org. phase	log K <sub>D</sub> (B)	log K <sub>D</sub> (21)K <sub>21</sub>	log K <sub>D</sub> (12)	log K <sub>12</sub>
2,2'-Dipy	4.44 <sup>a</sup>	C <sub>6</sub> H <sub>6</sub>	1.25	4.99 <sup>d</sup>	—	3.84
		CHCl <sub>3</sub>	3.90 <sup>b</sup>	—	2.25	3.84
4,4'-Dipy	4.82 <sup>a</sup>	C <sub>6</sub> H <sub>6</sub>	0.43	2.82	—	—
1,10-Phen	4.86 <sup>a</sup>	C <sub>6</sub> H <sub>6</sub>	0.40	4.21	—	—
		CHCl <sub>3</sub>	3.05 ± 0.15 <sup>c</sup>	8.35 ± 0.30 <sup>e</sup>	3.30	11.67 ± 0.15 <sup>h</sup>
1,10-Phen HA = Oxin <sup>4</sup>		CHCl <sub>3</sub>	3.05 ± 0.15 <sup>c</sup>	9.0 ± 0.2 <sup>c,f</sup>	5.4 ± 0.6 <sup>c,g</sup>	—

<sup>a</sup> For the dissociation constant of the base protonated form at 20°C (25°C with 1,10-Phen) see ref.<sup>2,3</sup>; <sup>b</sup> According to equation (4); <sup>c</sup> see ref.<sup>4</sup>, temperature, 25°C, variable perchlorate concentration; <sup>d</sup> log K<sub>D</sub>(21) ≈ 1.65 (assessed); <sup>e</sup> log K<sub>D</sub>(21) = 2.70 ± 0.15; <sup>f</sup> log K<sub>D</sub>(21) = 4.0 ± 0.2; <sup>g</sup> log K<sub>D</sub>(12) k<sub>A</sub>; <sup>h</sup> log K<sub>12</sub>k<sub>A</sub>, for k<sub>A</sub> see equation (3); Dipy = dipyridyl, Phen = phenanthroline.

nized forms of bases B (Table I) are lower than these pH values, it can be assumed that the dependence of the logarithm of distribution ratio  $D$  on the pH in synergistic systems will exhibit a constant section in the same pH region as the curve for this dependence in the initial system (this is verified for 2,2'-dipyridyl in Fig. 1, curve 1).

Cationic complexes,  $ZnB_2^+$ , can be neglected when  $\log D \geq \log K_D(20)$ , i.e.  $\log Y \equiv \log [D/K_D(20)] \geq 0$ ; this condition is fulfilled for low concentrations of B, as can be seen in Figs 2 and 3.

If ion-pairs ( $ZnAB_2^+$ ,  $ClO_4^-$ ) are extracted, the distribution ratio for the zinc salt in the synergistic system depends on the perchlorate ion concentration (this is verified for extraction with 1,10-phenanthroline in Fig. 1, curve 3). 0.1M- $NaClO_4$  was selected for study of the dependence of the distribution ratio on the concentrations of ligands  $[A^-]$  and  $[B]$ . If ion-pairs are not extracted, the distribution ratio is independent of the perchlorate concentration (curve 4 in Fig. 1 for 2,2'-dipyridyl).

All dependences on the concentration of ligand B were measured up to the B solubility value in the extraction system. The extraction system of the ternary chelates with dipyridyl in chloroform (Fig. 3, curves 4 and 5) was not investigated at low concentrations.

### The Determination of the Stability Constants

The increase in the distribution ratio of the zinc salt,  $D$ , at low concentrations of base B depends solely on this concentration and is independent of the concentration  $[A^-]$ ; this corresponds to the formation of the  $ZnA_2B$  adduct. At higher concentra-

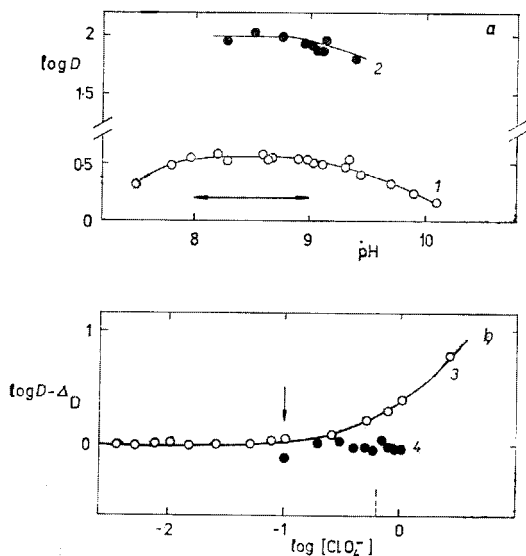


FIG. 1

Dependence of the Zinc Salt Distribution Ratio on the pH (a) and the Perchlorate Concentration (b)

a) The 0.1M-acetylacetone +  $xM$ -2,2'-dipyridyl system in a chloroform-aqueous solution of 0.1M-( $NaOH + NaClO_4$ );  $x$  (mol/l): 1 0; 2 0.05. b) The system of an organic phase- $NaClO_4$  aqueous solution with variable ionic strength: 3 0.1M-acetylacetone +  $2.5 \cdot 10^{-5}M$ -1,10-phenanthroline in chloroform, pH 8.4 to 8.7;  $\Delta_D = 0.95$ ; 4 0.2M-acetylacetone + 0.01M-2,2'-dipyridyl in benzene, pH  $\approx 7.6$ ,  $\Delta_D = -0.25$ . The pH range and the perchlorate concentrations selected for further experiments are indicated by arrows.

tions of B. ligand  $A^-$  is replaced with formation of the  $ZnAB_2^+$  chelate and the distribution ratio is a function of  $[B]$  and  $[A^-]$  (Figs 2 and 3).

If chloroform constitutes the organic phase, the  $ZnAB_2^+$  chelate is extracted as an ion-associate ( $ZnAB_2^+$ ,  $ClO_4^-$ ). The distribution ratio decreases with increasing concentration  $[A^-]$  and increases with increasing  $[ClO_4^-]$  (Fig. 1, curve 3 and Fig. 2). For  $[Zn] \rightarrow 0$  the relationship for the distribution ratio can be formulated as follows:

$$D_c = ([ZnA_2]_c + [ZnA_2B]_c + [ZnAB_2^+, ClO_4^-]_c) / ([ZnA_2] + [ZnA_2B] + [(ZnAB_2^+, ClO_4^-)]) = (K_D(20)_c + K_D(21)_c K_{21}[B] + K_D(12)_c K_{12} k_A [B]^2) \cdot [A^-]^{-1} [ClO_4^-] / (1 + K_{21}[B] + K_{12} k_A [B]^2 [A^-]^{-1} [ClO_4^-]), \quad (1)$$

where  $K_D(ij)_c$  is the distribution constant of the  $ZnA_iB_j$  chelate,

$$K_{ij} = \beta_{ij} / \beta_{20}, \beta_{ij} = [ZnA_iB_j] / [Zn^{2+}] [A^-]^i [B]^j, \quad (2)$$

$$k_A = [(ZnAB_2^+, ClO_4^-)] / [ZnAB_2^+] [ClO_4^-], \quad (3)$$

$$[B] = c_B / (K_D(B)_c + 1) \text{ (if no protonation occurs),}$$

$$[A^-] = c_{HA} (K_{HA} / [H^+]) [K_D(HA)_c + 1 + (K_{HA} / [H^+])]^{-1},$$

$$[ClO_4^-] = c_{ClO_4}.$$

The square brackets denote the equilibrium concentrations in the aqueous phase, those with subscripts  $c$  or  $b$  denote the concentrations in the chloroform or benzene phases, respectively.  $c_L$  is the total concentration of substance L in the extraction system and  $K_D(L)$  its distribution constant.

Distribution constants  $K_D(B)_b$  were determined titrimetrically and are given in Table I. The  $K_D(\text{Dipy})_c$  value for 2,2'-dipyridyl exceeded  $10^3$  and was thus difficult to measure; it was therefore calculated from an empirical equation, defined analogously to that of Smith<sup>6</sup>:

$$[K_D(\text{Dipy})/K_D(\text{Phen})]_c = [K_D(\text{Dipy})/K_D(\text{Phen})]_b. \quad (4)$$

It can be assumed that a formally identical equation also holds for  $K_D(ij)/K_D(20)$  and consequently subscripts  $c$  or  $b$  can be omitted in these ratios. This assumption is verified in Fig. 3, where the theoretical curve, calculated under these assumptions, is drawn through the experimental points.

The following values were used for acetylacetone:  $pK_{HA} = 8.82$  (according to ref.<sup>7</sup>),  $\log K_D(HA)_b = 0.77$  (according to ref.<sup>8</sup>) and  $\log K_D(HA)_c \approx -0.10$ , taken from the data in the book<sup>9</sup> (0.1M-NaClO<sub>4</sub>, 25°C).

The replacement of the concentration variable by  $\log c_B$  does not affect the shape of the  $\log D$  dependence on  $\log [B]$ , since this variable is merely shifted by  $\log (K_D(B) + 1)$  to lower values with respect to  $\log c_B$ .

In the extraction system containing benzene, the  $ZnAB_2^+$  chelate passes into the aqueous phase. The distribution ratio then increases with increasing concentration  $[A^-]$  and decreases with increasing  $[B]$  (Fig. 3) and can be expressed by the relationship

$$D_b = ([ZnA_2B]_b + [ZnA_2]_b) / ([ZnA_2] + [ZnA_2B] + [ZnAB_2^+]),$$

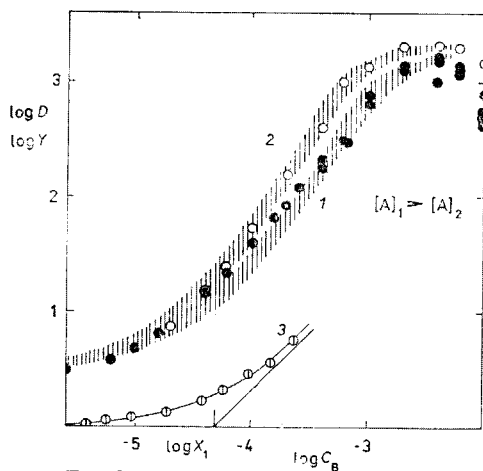


FIG. 2

Dependence of the Zinc Salt Distribution Ratio,  $D$ , on the Concentration of 1,10-Phenanthroline ( $c_B$ ) at a Constant Concentration of the Acetylacetonate Anion,  $[A^-]$

Aqueous phase, 0.1M- $NaClO_4$ , organic phase, 0.1M-acetylacetonate in chloroform;  $\log [A^-]$  (pH-range): 1 — 1.53 (8.50 to 8.58); 2 — 1.97 (7.95 to 7.98). The theoretical dependences of  $\log D$  on  $\log c_B$ , following from the values given in Table I according to equation (1) and taking into account the probable errors in the constants used, are indicated by shading. 3 organic phase, benzene (0.1M-acetylacetonate);  $\log Y \equiv \log D/K_D(20)$ , pH = 7.6 to 8.4.  $\log X_1 = -\log K_D(21) K_{21} K_D(20)^{-1} + \log (K_D(B) + 1)$ .

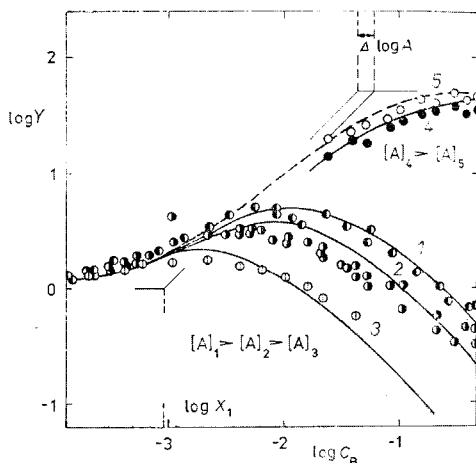


FIG. 3

Dependence of the Zinc Distribution Ratio,  $Y = D/K_D(20)$ , on the Concentration of 2,2'-Dipyridyl ( $c_B$ ) at a Constant Concentration of the Acetylacetonate Anion,  $[A^-]$

0.1M-Acetylacetonate in the organic phase — aqueous solution of 0.1M- $NaClO_4$ . Organic phase, benzene;  $\log [A^-]$  (pH-range): 1 — 2.40 (8.15 to 8.40); 2 — 2.80 (7.95); 3 — 3.60 (7.10). The curves were calculated from equation (5) using the values given in Table I. For  $\log X_1$  see Fig. 2. Organic phase, chloroform: 4 — 1.53 (8.60); 5 — 1.67 (8.30). Curve 5 (dashed) was calculated from equation (1), where  $\log k_A = 1.6$  (according to ref.<sup>10</sup>) and  $\log K_D(12)/K_D(20) = 1.70$ , the other values were taken from Table I for extraction into benzene.  $\Delta \log A = \log [A^-]_4 - \log [A^-]_5 = 0.14$ .

so that

$$Y_b \equiv D_b/K_D(20)_b = (1 + K_D(21) K_D(20)^{-1} K_{21}[B]) / (1 + K_{21}[B] + K_{12}[B]^2 [A^-]^{-1}). \quad (5)$$

For low concentrations  $[B]$ , the product of the stability constant of the adduct,  $ZnA_2B$ , and its distribution constant (*i.e.* the two-phase stability constant) can be determined by the two-parameter method<sup>5</sup>. It holds in this region of  $[B]$  that

$$\log D_{c,b} \approx \log K_D(20)_{c,b} (1 + K_D(21) K_D(20)^{-1} K_{21}[B]) \equiv \log Q_y (1 + Q_x[B]). \quad (6)$$

In this method, a theoretical curve of the  $\log(1 + [B])$  vs  $\log[B]$  dependence is constructed through the experimental points and constants  $Q_x$  and  $Q_y$  are determined from the relative shift of the theoretical and experimental curves.

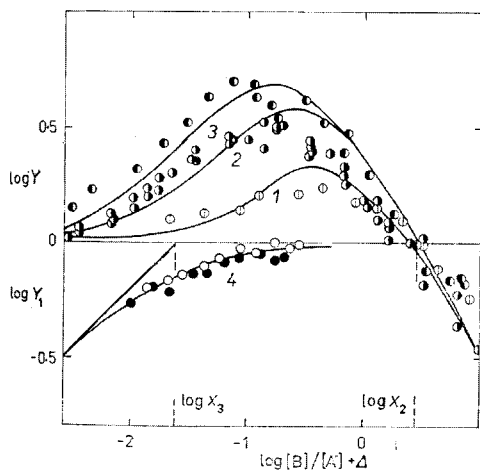


FIG. 4

Dependence of the Distribution Ratio,  $Y \equiv D/K_D(20)$ , on the Ligand Concentration Ratio,  $[B]/[A^-]$ , for Extraction with 2,2'-Dipyridyl

The curves are denoted in the same way as in Fig. 3. Organic phase, benzene, curves 1, 2, 3,  $\Delta = 0$ ; organic phase, chloroform,  $\log Y_1 \equiv \log D/K_D(12)$ ,  $\Delta \equiv -\log \cdot [ClO_4^-] + \log K_D(21)/K_D(20) = 2 \cdot \log X_2 - \log X_3 = \log k_A$ , see equations (7) and (8).

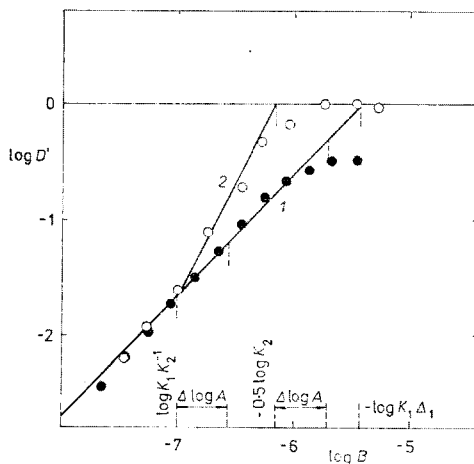


FIG. 5

Dependence of the Normalized Distribution Ratio,  $D'$ , (equation (9)) on the Equilibrium Concentration of Phenanthroline in the Aqueous Phase,  $[B]$

The experimental values were taken from Fig. 2; the curves are denoted in the same way as in Fig. 2. The determination of the stability constants by the graphical method<sup>1</sup> is shown in the graph,  $\Delta \log A = \log [A^-]_1 - \log [A^-]_2 = 0.44$ .

This method can be applied to the system containing 2,2'-dipyridyl during extraction into chloroform at high concentrations,  $[B]$  (Fig. 3, curves 4 and 5). The  $ZnAB_2^+$  associate with perchlorate is then assumed to be present in the organic phase and  $ZnA_2B$  in the aqueous phase, so that it holds that

$$Y_{1c} \equiv D_c/K_D(12)_c \approx (K_{12}k_A/K_{21}) ([B]/[A^-]) [ClO_4^-]$$

and for  $Y_{1c} = 1$

$$([B]/[A^-])_{1c} [ClO_4^-] = K_{21}/K_{12}k_A \quad (7)$$

is obtained. In the extraction system with benzene it follows from relationship (5) for  $Y_b = 1$  (assuming that  $K_D(21)_b - K_D(20)_b \approx K_D(21)_b$ ) that

$$([B]/[A^-])_{1b} K_D(20)/K_D(21) = K_{21}/K_{12} \quad (8)$$

The ratio of equations (8) and (7) is evaluated graphically in Fig. 4 and yields the value of  $\log k_A \approx 2.0 (\pm 0.30)$ , which is comparable with the results given in ref.<sup>10</sup>,  $\log k'_A = 1.35$  to  $1.6$  for the association constant of  $(Zn^{2+}, ClO_4^-)$  in an aqueous medium ( $20^\circ C$ , variable ionic strength). The more precise value,  $\log k_A = 1.6$ , taken from this paper, was employed for the calculation of curve 5 in Fig. 3 and constants  $k_2^2$  in Fig. 6 (see below).

From relationship (8) the value of the product,  $(K_D(21) K_{21} K_D(20)^{-1}) K_{12}^{-1}$ , can be determined, where the value of the term in parentheses was determined graphically from relationship (6). Thus all the necessary constants except for  $K_D(21)$  are now available for the calculation of the curve of the theoretical  $Y_b$  vs  $[B]$  dependence from equation (5). The value of  $K_D(21)$  was assessed; the agreement of the theoretical curves with the experimental points can be evaluated in Fig. 3.

The two-phase stability constants for both ternary chelates,  $ZnA_2B$  and  $(ZnAB_2^+, ClO_4^-)$ , can also be obtained by the two parameter method from the  $\log D_c$  vs  $\log [ClO_4^-]$  dependence given in Fig. 1b (curve 3). Assuming that both chelates are present in the organic phase and  $ZnA_2$  is present in the aqueous phase, the relationship

$$D_c = K_D(21)_c K_{21} [B] (1 + K_D(12) K_D(21)^{-1} K_{12} k_A K_{21}^{-1} [A]^{-1} [B] [ClO_4^-])$$

is valid. The following constant values are obtained (the values obtained by graphical analysis<sup>1</sup> in Fig. 4 are given in parentheses):  $\log K_D(21)_c K_{21} = 8.60 (8.04)$ ;  $\log K_D(12) \cdot K_D(21)^{-1} K_{12} k_A K_{21}^{-1} = 6.32 (6.93)$ .

The stability constant values are summarized in Table I. For the sake of comparison, the  $K_D(21)_b K_{21}$  value for the adduct of zinc acetylacetonate with a single molecule of 4,4'-dipyridyl, obtained by the two-parameter method from the  $\log Y_b$  vs

$\log c_B$  dependence, is also given in this table. (Twelve points were measured in the range,  $\log c_B = -4.5$  to  $-2$ ,  $\log Y_b = 0$  to  $1$ ; the shape of the curve is analogous to that of curve 3 in Fig. 2).

The sigmoid shape of curves 1 and 2 for the  $\log D_c$  vs  $\log c_B$  dependence in Fig. 2 makes it possible to employ the graphical method described in ref.<sup>1</sup> for evaluation of the stability constants. For  $c_B \rightarrow 0$ ,  $\log D_c \approx \log K_D(20)_c$ , for  $c_B \rightarrow \infty$ ,  $\log D_c \approx$

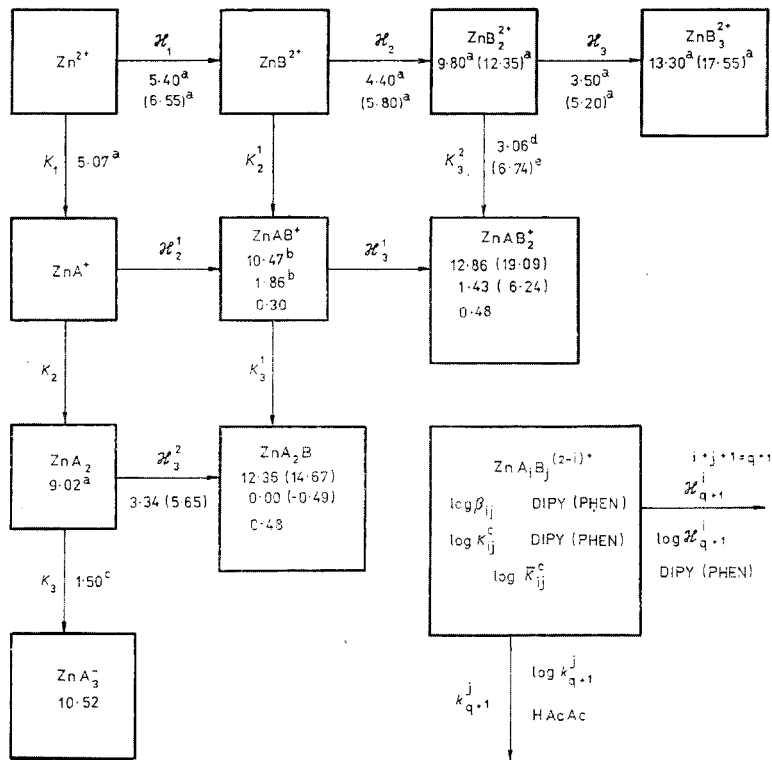


FIG. 6

The Graphical Representation of the Formation of Complexes of Divalent Zinc with Acetylacetone (HA) and 2,2'-Dipyridyl (1,10-Phenanthroline) (B)

$k_{q+1}^j$  and  $k_{q+1}^i$  are the equilibrium constants for bonding of a single ligand  $A^-$  or  $B$ , respectively, to the  $ZnA_iB_j^{(2-i)+}$  complex,  $\beta_{ij}$  is the overall stability constant (equation (2)),  $K_{ij}^k$  is the coproportionation constant (equation (14)) and  $\bar{K}_{ij}^k$  is its statistical value (equation (13)).

<sup>a</sup> See ref.<sup>7</sup>; <sup>b</sup> according to equation (16); <sup>c</sup> see ref.<sup>25</sup>; <sup>d</sup>  $\log K_{12} + \log \beta_{20} - \log \beta_{02}$ ;  $\log K_{12}$  taken from Table I; <sup>e</sup>  $\log K_{12}k_A - \log k_A + \log \beta_{20} - \log \beta_{02}$ ;  $\log K_{12}k_A$  taken from Table I,  $\log k_A = 1.6$  according to ref.<sup>10</sup>.



$\approx \log K_D(12)_c$ . The slight decrease is neglected. The normalized distribution ratio,  $D'$ , depends on  $[B]$  according to relationship (9) following from equation (1):

$$D' \equiv (D - K_D(20))/K_D(12) = (1 + K_1 A_1 [B] + K_2 [B]^2)/(1 + K_1 [B] + K_2 [B]^2), \quad (9)$$

where  $K_j = K_{ij} k_A^{(2-i)} [A^-]^{-(2-i)} [ClO_4^-]^{(2-i)}$ ,  $i = 1$  and  $2$  and  $A_1 \equiv (K_D(21) - K_D(20))/K_D(12)$ . If complexes with one and two molecules of  $B$  are formed successively, the slope of the  $\log D'$  dependence on  $\log [B]$  equals unity for low values of  $[B]$ , as follows from the relationship

$$(d \log D')/(d \log [B]) \approx 1 - K_1 [B]/(1 + K_1 [B]). \quad (10)$$

When only the second complex is formed, the slope for small  $[B]$  equals two, since the relationship

$$(d \log D')/(d \log [B]) \approx 2(1 - K_2 [B]^2/(1 + K_2 [B]^2)) \quad (11)$$

holds. The abscissa of the point at which the slope value changes is obtained by comparing the right-hand sides of equations (10) and (11). The break occurs at  $[B] = K_1/K_2$  and appears only with those systems for which  $K_1/K_2$  lies at low concentrations,  $[B]$ , so that the approximate relationships, (10) and (11), are valid (Fig. 5). For unit slope (dependence 2 in Fig. 5) the values  $-\log K_1 A_1$  and  $-0.5 \log K_2$  are obtained as abscissae for coordinates  $\log D' = 0$  and  $-0.3$ , respectively. Further, the relationship

$$\log K_1 A_1 = K_2/K_1 \quad (12)$$

is valid. For dependences with a slope equal to two (curve 1 in Fig. 5), the  $-0.5 \log K_2$  value is found as the abscissa of coordinate  $\log D' = 0$ . This analysis thus provides  $\log K_1 A_1$  and two values of  $\log K_2$ , the difference of which equals the difference between the logarithms of concentrations  $[A^-]$ . Constant  $K_1$  is determined by substituting the average  $\log K_2$  value into expression (12). The average of the constants obtained from curve 3 in Fig. 1b and from Fig. 5 is given in Table I.

The determined values of the stability constants of the ternary chelates are also given in Fig. 6 as part of the graph characterizing the successive formation of binary and ternary zinc complexes with the studied ligands. This scheme was first proposed by Kanemura and Watters<sup>11</sup> (for a Zn(II)-oxalate-ethylenediamine system) and described in terms of graph theory by Yatsimirskii<sup>12</sup>. Equilibrium constants  $k_{i+j+1}^i$  characterize the bonding of ligand A to the  $ZnA_i B_j$  complex and  $\alpha_{i+j+1}^i$  the bonding of ligand B to the same complex. The overall stability constant of the ternary chelate involves the factor<sup>11,12</sup>

$$\bar{K}_{ij}^k = \binom{i+j}{i}, \quad (13)$$

expressing the number of paths along which the  $ZnA_iB_j$  complex is formed from the zinc(II) cation. The coproportionation constant,  $K_{ij}^k$ , *i.e.* the equilibrium constant for the formation of this ternary complex from binary complexes with the same coordination number,  $i + j = q$ , given by the relationship<sup>12,13</sup>

$$K_{ij}^k = [ZnA_iB_j]/[ZnA_q]^{i/q} [ZnB_q]^{j/q} = \beta_{ij}/\beta_{0q}^{i/q}\beta_{q0}^{j/q}, \quad (14)$$

equals this factor in "statistical" cases, when the ligands do not interact in the coordination sphere.

Systems of ternary complexes  $ZnAB^+$  with 2,2'-dipyridyl (B) and various ligands HA ( $A^-$  = thioethercarboxylate or the anion of sulphoxide and sulphone derivatives<sup>14</sup>, the anion of polyhydroxy compounds<sup>15</sup>, the anion of salicylic or thiosalicylic acid or amino acids<sup>16</sup>, of hydroxy or mercapto acids<sup>17</sup>) were found in the literature. Here it holds that

$$k_2^1 \approx k_1, \text{ i.e. } \beta_{11} \approx 2k_1\alpha_1. \quad (15)$$

The expression

$$K_{11}^k = 2(k_1\alpha_1/k_2\alpha_2)^{1/2} \quad (16)$$

is obtained from the equivalency of paths in the graph on the Fig. 6. This constant has a higher value than  $\bar{K}_{11}^k = 2$ , since  $k_1 > k_2$  and  $\alpha_1 > \alpha_2$ ; the  $ZnAB^+$  complex is stabilized. The value of the coproportionation constant, assessed according to equation (16) and based on the assumption that relationship (15) is also valid for the complex with acetylacetonone, is given in Fig. 6.

If the  $K_{21}$  values determined from the extraction data in 0.1M-NaClO<sub>4</sub> are to be compared with the  $K_{21}$  values obtained by other methods in non-aqueous media, the relationship

$$K_{21}^{org} = K_{21}K_D(21)/(K_D(20)K_D(B)) \quad (17)$$

is used. The comparison is given in Table II.

## DISCUSSION

The following aspects of the systems of mixed chelates (with the charges omitted) will be discussed: *a*) The relationship among the stabilities of ternary chelates  $ZnA_iB_{q-i}$  and binary chelates  $ZnA_q$ ,  $ZnB_q$ . *b*) The relationship among the stabilities of ternary chelates  $ZnA_2B$  with various ligands A. *c*) The effect of the structure of B on the stability constant of  $ZnA_2B$ .

a) A system of ternary complexes of the metal, in which the ligands do not interact in the coordination sphere, is the reference system for evaluating the successive stability constants  $k_{i+j+1}^j$  and  $\kappa_{i+j+1}^i$  or the coproportionation constants  $K_{ij}^k$  (relationship (14)) (ref.<sup>13</sup>). The coproportionation constant assumes the statistical value in this system (equation (13)). The successive stability constants are then dependent solely on the ligand type and the overall number of ligands in the coordination sphere of the initial complex (e.g.  $k_3^2 \approx k_3$ ,  $\kappa_3^2 \approx \kappa_3$ ), so that this system is described by four constants, e.g.  $k_1$ ,  $k_2$ ,  $k_3$  and parameter  $p = k_1/\kappa_1 = k_2/\kappa_2 = k_3/\kappa_3$  (ref.<sup>12</sup>). It can be seen from Fig. 6 that this parameter is not constant in the studied systems. In the system with 2,2'-dipyridyl, the relationship,  $\kappa_3^2 \approx \kappa_3$ ,  $k_3 < k_3^2 < k_2$ , holds among the successive stability constants. In the system with 1,10-phenanthroline it holds that  $\kappa_3^2 \approx \kappa_2$ ,  $k_3^2 > k_1$  and the  $\text{ZnAB}_2^+$  chelate has a high value of  $K_{12}^k$ . Woodward and Freiser<sup>4</sup> assumed the relationships,  $\kappa_3^2 \approx \kappa_2$  and  $k_3^2 \approx k_2$  in the system of zinc(II) chelates with 8-hydroxyquinoline and 1,10-phenanthroline.

TABLE II

The Equilibrium Constants,  $K_{21}^{\text{org}}$ , for the Reaction,  $\text{ZnA}_2 + \text{B} \rightleftharpoons \text{ZnA}_2\text{B}$ , Determined by Calorimetric Titration<sup>21,24</sup> and by the Extraction Method

HTTA thenoyltrifluoroacetone, HTBzTA thiobenzoyltrifluoroacetone, HAcAc acetylacetone.

B	HA	$\log K_{21}^{\text{org}}$	°C	Medium	Ref.
2,2'-Dipy	HTTA	$1.95 \pm 0.01$	25	$\text{CHCl}_3$	21
	HTBzTA	$>6.00$	30	$\text{C}_6\text{H}_6$	24
	HAcAc	4.39	20	$\text{C}_6\text{H}_6/0.1\text{M-NaClO}_4$	this paper
4,4'-Dipy	HTTA	$1.71 \pm 0.01$	25	$\text{CHCl}_3$	21
	HAcAc	2.99	20	$\text{C}_6\text{H}_6/0.1\text{M-NaClO}_4$	this paper
1,10-Phen	HTTA	$2.50 \pm 0.28$	25	$\text{CHCl}_3$	21
	HAcAc	4.46	20	$\text{C}_6\text{H}_6/0.1\text{M-NaClO}_4$	this paper
	HAcAc	4.44	20	$\text{CHCl}_3/0.1\text{M-NaClO}_4$	this paper

According to Marcus, Eliezer and Zangen<sup>18</sup>, the coproportionation constant values,  $\log K_{21}^k$  and  $\log K_{12}^k$ , can be analogously correlated with the differences in the logarithms of the stability constants of the binary complexes, i.e. with the difference values,  $(2/3) \log \beta_{30} - (1/3) \log \beta_{03}$  for the  $\text{ZnA}_2\text{B}$  complexes and  $(1/3) \log \beta_{30} - (2/3) \log \beta_{03}$  for the  $\text{ZnAB}_2$  complexes. In the present paper, this order is valid only for  $\text{ZnAB}_2$  with dipyrindyl and phenanthroline, but not for the  $\text{ZnA}_2\text{B}$  complexes.

b) The stability constants of the  $\text{ZnA}_2\text{B}$  complexes with various ligands HA and the same ligand B can be compared according to the Pearson criterion<sup>19</sup> (the same local

symmetry and the same oxidation state of the central atom in the complexes), which ensures the same acceptor properties of the metal in various complexes. This comparison is justified when ligand B is a pyridine base or an aromatic amine, since the type of bonding through the nitrogen atom to zinc then primarily determines the stability of the complex formed<sup>1,3</sup> and the other bonds of the central atom do not interact with this bond (see the  $\text{Zn}-\text{C}_5\text{H}_5\text{N}$  model used in the analysis of the spectra of tetrahedral complexes<sup>20</sup>). For the studied ligands, B, it is possible to compare the effect of the medium on the magnitude of  $K_{21}^{\text{org}}$  in Table II, assuming that the simplified model of zinc complexes is valid, *i.e.* that the  $\text{Zn}-\text{A}$  bonds do not affect the  $\text{Zn}-\text{B}$  bonds. The lower values of these constants found by calorimetric titration in chloroform<sup>21</sup> can probably be explained by the formation of solvates with chloroform, which is hydrogen-bonded to the diketone carbonyl group<sup>22</sup>.

c) The values of the logarithms of the stability constants,  $\log K_{21}$ , for complexes  $\text{ZnA}_2\text{Dipy}$  and  $\text{ZnA}_2\text{Phen}$  (where Dipy = 2,2'-dipyridyl and Phen = 1,10-phenanthroline) reflect the effect of benzene ring fusion similar to the  $\log K_{22}$  values for complexes  $\text{ZnA}_2\text{Py}_2$  and  $\text{ZnA}_2\text{Quin}_2$  (ref.<sup>1</sup>) (Py = pyridine, Quin = quinoline, HA = acetylacetonate). For these four complexes, constant differences  $\Delta \log K_{21}$  and  $\Delta \log K_{22}$  were found for replacement of pyridine by quinoline or dipyridyl by phenanthroline (about 2.3). Analogously, comparable differences in the  $\log K_{22}$  and  $\log K_{21}$  values can be found when a monodentate ligand is replaced by a bidentate (with the pairs, Py-Dipy and Quin-Phen, this value is *c.* -1.45). It follows from comparison of the  $K_{21}^{\text{org}}$  constant for the adduct of  $\text{ZnA}_2$  with 4,4'-dipyridyl ( $\log K_{21}^{\text{org}} = 2.99$  in Table II) with this constant for 4-methylpyridine (2.99 according to ref.<sup>1</sup>) that here the bond strength is primarily affected by substitution in position 4 on the pyridine ring.

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#### LIST OF SYMBOLS

- $b, c$  subscripts on variables and constants characterizing extraction systems of benzene (b) or chloroform-water (c)
- $c_B, c_{\text{HA}}$  overall concentrations of substances B or HA, respectively, in the extraction system
- $D$  zinc salt distribution ratio
- $D' = (D - K_D(20))/K_D(12)$ , normalized distribution ratio
- $k_A = [(\text{ZnAB}_2^+, \text{ClO}_4^-)]/[\text{ZnAB}_2^+][\text{ClO}_4^-]$ , association constant of  $(\text{ZnAB}_2^+, \text{ClO}_4^-)$
- $k'_A = [(\text{Zn}^{2+}, \text{ClO}_4^-)]/[\text{Zn}^{2+}][\text{ClO}_4^-]$ , association constant of  $(\text{Zn}^{2+}, \text{ClO}_4^-)$
- $k_i = [\text{ZnA}_i]/[\text{ZnA}_{i-1}]$ , successive stability constant of  $\text{ZnA}_i$
- $k_{i+j+1}^j = [\text{ZnA}_{i+1}\text{B}_j]/[\text{ZnA}_i\text{B}_j]$ , equilibrium constant for bonding of ligand A to  $\text{ZnA}_i\text{B}_j$
- $K_{ij} = \beta_{ij}/\beta_{20}$ , the increase in the stability of chelate  $\text{ZnA}_i\text{B}_j$  with respect to  $\text{ZnA}_2$
- $K_j = K_{ij}k_A^{(2-i)}[\text{A}^-]^{-(2-i)}[\text{ClO}_4^-]^{(2-i)}$ ,  $i = 2$  and  $1$ ,  $i + j = 3$ ; relationship (9)
- $K_{ij}^k = \beta_{ij}/\beta_{0q}^{i/q}\beta_{q0}^j/q_0$ , equilibrium constant for the formation of ternary complex  $\text{ZnA}_i\text{B}_j$  from binary complexes  $\text{ZnA}_q$  and  $\text{ZnB}_q$ ,  $i + j = q$

- $\bar{K}_{ij}^k = \binom{i+j}{i}$ , the  $K_{ij}^k$  value in the statistical case, when ligands A and B do not interact in the coordination sphere
- $K_{21}^{\text{org}} = K_{21} K_D(21)/(K_D(20) K_D(B))$ , equilibrium constant for the reaction,  $\text{ZnA}_2 + \text{B} \rightleftharpoons \text{ZnA}_2\text{B}$ , in the organic phase
- $K_D(\text{HA}), K_D(\text{B})$  distribution constants of substances HA or B, respectively
- $K_D(ij)$  distribution constant of complex  $\text{ZnA}_i\text{B}_j$
- $K_{\text{HA}}$  dissociation constant of [HA]
- $K_a$  dissociation constant of  $[\text{BH}^+]$
- $p = k_i/\alpha_i, i = 1, 2, 3$ ; parameter in the system of ternary complexes, where the two types of ligands do not interact in the coordination sphere
- $Q_x, Q_y$  intercepts on the axes in the application of the Dyrssen method (equation (6))
- $Y = D/K_D(20)$
- $Y_{1c} = D_c/K_D(12)_c$ ; in equation (7)
- $\beta_{ij} = [\text{ZnA}_i\text{B}_j]/[\text{Zn}^{2+}] [\text{A}^-]^i [\text{B}]^j$ , the overall stability constant of  $\text{ZnA}_i\text{B}_j$
- $\Delta_1 = (K_D(21) - K_D(20))/K_D(12)$ , normalized distribution constant for  $\text{ZnA}_2\text{B}$ , equation (9)
- $\alpha_i = [\text{ZnB}_i]/[\text{ZnB}_{i-1}]$ , successive stability constant of  $\text{ZnB}_i$
- $\alpha_{i+j+1} = [\text{ZnA}_i\text{B}_{j+1}]/[\text{ZnA}_i\text{B}_j]$ , equilibrium constant for bonding of ligand B to  $\text{ZnA}_i\text{B}_j$
- $[ ]_a, [ ]_b, [ ]_c$  equilibrium concentrations in the aqueous, benzene and chloroform phases, respectively

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