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A Potentiometric Study on Mixed Ligand Cadmium(II) Complexes with 2-Pyridinecarboxylic Acid and 2-Aminoalkanoic Acids

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Formation constants of cadmium(II) complexes with 2-pyridinecarboxylic acid (Hpic) were determined in aqueous solutions containing 3 mol dm^{-3} $LiClO_4$ as a constant ionic medium at 25 °C by potentiometric titrations. On the basis of the formation constants of the complexes thus determined and those of the 2-aminoalkanoate complexes previously obtained, formation constants of mixed ligand cadmium(II) complexes CdL(pic) were determined, where L^- denotes a 2-aminoalkanoate ion such as glycinate (gly^-), α-alaninate (ala^-), 2-aminobutanoate (but^-), 2-aminopentanoate (pen^-), or 2-aminohexanoate (hex^-) ion. The formation constants $\log \beta_{111} = \log \{[CdL(pic)]/([Cd^{2+}][L^-][pic^-])\}$ of the 1:1:1 mixed ligand cadmium(II) complexes are: Cd(gly)(pic), 8.88; Cd(ala)(pic), 8.47; Cd(but)(pic), 8.42; Cd(pen)(pic), 8.73; and Cd(hex)(pic), 8.76. The equilibrium constant of the reaction between $Cd(gly)^+$ and pic^- was larger than that between $Cd(pic)^+$ and gly^-, and much larger than the equilibrium constants between CdL^+ and L'^- previously studied, where L^- and L'^- are 2-aminoalkanoate anions.

Formation equilibria of mixed ligand cadmium(II) complexes with various aliphatic 2-aminoalkanoic acids were studied in the previous work.[1)] In the present investigation we examined the formation of mixed ligand cadmium(II) complexes containing aliphatic amino acids and 2-pyridinecarboxylic acid (Hpic) which can form five-membered chelate rings with the central cadmium(II) ion. 2-Quinolinecarboxylic acid (Hquin) was also used as another aromatic amino acid-like ligand, but the formation constant of neither $Cd(quin)_2$ nor CdL(quin) complex ($L^- =$ 2-aminoalkanoate ion) could be determined because of the formation of precipitates in solutions at an early stage of titrations.

Experimental

Reagents. 2-Pyridinecarboxylic acid was obtained from Wako Pure Chemicals Ind., Osaka, and used without further purification. Other reagents such as cadmium(II) perchlorate, lithium perchlorate, and lithium hydroxide were prepared and purified by the methods described in the previous paper.[1)] Glycine (Hgly), α-alanine (Hala), 2-aminobutanoic acid (Hbut), 2-aminopentanoic acid (Hpen), and 2-aminohexanoic acid (Hhex) were used after analysis and purification by the previous method.[1)]

Method of Measurements. Glass electrode, a pH meter and cells used were the same as those employed in the previous study.[1)] Lithium perchlorate was used as an inert ionic medium (3 mol dm^{-3}).

The ratio of the total concentration of 2-pyridinecarboxylic acid (Hpic) to that of cadmium(II) ions (C^{t}_{pic}/C^{t}_{Cd}) was kept 5. When the mixed ligand systems were examined, the composition of the solution containing 2-pyridinecarboxylic acid, a 2-aminoalkanoic acid (HL), and cadmium(II) ion was kept 2.5:2.5:1, independent of the total concentrations of the species.

The method of emf measurements was essentially the same as that employed in the preceding work.[1)] All the measurements were carried out at 25.00 °C±0.02 °C in a liquid paraffin bath under a nitrogen atmosphere.

Results and Discussion

The formation constants of the 1:1 and 1:2 complexes of cadmium(II) ion with 2-pyridinecarboxylic acid are given in Table 1, together with the acid dissociation constants (pK_1 and pK_2) of the ligand. The values were compared with those determined in other media.[2—4)]

The formation constants of cadmium(II) complexes with 2-quinolinecarboxylic acid were determined under the same experimental conditions, but the formation constant (K_{12}) of the 1:2 complex was not determinable, because white precipitates were formed in solutions at an early stage of titrations. The acid dissociation constants of 2-quinolinecarboxylic acid were determined to be $pK_1 = 2.17$ and $pK_2 = 5.58$. The value

TABLE 1. FORMATION CONSTANTS OF CADMIUM(II) COMPLEX WITH 2-PYRIDINECARBOXYLIC ACID AT 25 °C

Ligand	Medium (mol dm^{-3})	pK_1	pK_2	$\log K_{11}$	$\log K_{12}$	$\log \beta_2$	Ref.
2-Pyridinecarboxylic acid	3.0 $LiClO_4$	1.99	5.93	4.47	3.70	8.17	Present work[a)]
	0.1 $NaNO_3$	1.60	5.54	4.36	3.18	7.54	2
	0	1.03	5.33	4.79	3.46	8.25	3
	0.5 $NaNO_3$	0.87	5.18	4.18	3.43	7.61	4

a) Standard deviations are ±0.02.

of $\log K_{11}$ for the 1 : 1 complex of cadmium(II) ion with 2-quinolinecarboxylic acid was 4.88, which was much larger than the literature value (4.12) at zero ionic concentration.[5)]

Formation constants of mixed ligand cadmium(II) complexes with 2-pyridinecarboxylic acid were determined by the same procedure as described in the previous paper.[1)] Typical titration curves are shown in Fig. 1, which were obtained in the Cd(II)–α-alanine–2-pyridinecarboxylic acid system. The solid lines in Fig. 1 were drawn by using calculated values of the degree of neutralization of the total ligands X (X_{calcd}) by the following equation:

$$X_{\mathrm{calcd}} = \frac{C_{\mathrm{L}}^{\mathrm{t}} + K_{\mathrm{i}}[\mathrm{H}^+]^{-1} - [\mathrm{H}^+] - \sum_p\sum_q\sum_r\sum_s q\beta_{pqrs}[\mathrm{Cd}^{2+}]^p[\mathrm{H}^+]^q[\mathrm{L}^-]^r[\mathrm{L}'^-]^s}{C_{\mathrm{L}}^{\mathrm{t}}}, \tag{1}$$

where K_{i} represents the autoprotolysis constant of water in the 3 mol dm^{-3} $\mathrm{LiClO_4}$ aqueous solution at 25 °C ($10^{-13.87}$ mol^2 dm^{-6} [6)]). Since the only 1:1:1 type of mixed ligand complexes without protons has been found under the present experimental conditions (*i.e.*, $p=1$, $q=0$, and $r=s=1$), the formation constant of the mixed ligand complex will be denoted as β_{111}. The results obtained are summarized in Table 2 with values of F_{m}, F'_{m}, and b, which are indices of deviation of the formation constant of the mixed ligand complex from the statistical values defined by the following equations:

$$\left.\begin{aligned} &\mathrm{CdL_2} + \mathrm{CdL'_2} = 2\mathrm{CdLL'} \\ &2\log\beta_{111} = \log\beta_{120} + \log\beta_{102} + \log F_{\mathrm{m}} \end{aligned}\right\}, \tag{2}$$

$$\left.\begin{aligned} &\mathrm{CdL^+} + \mathrm{CdL'^+} = \mathrm{CdLL'} + \mathrm{Cd^{2+}} \\ &\log\beta_{111} = \log\beta_{110} + \log\beta_{101} + \log F'_{\mathrm{m}} \end{aligned}\right\}, \tag{3}$$

$$\left.\begin{aligned} &\log F_{\mathrm{m}} = 2\log F'_{\mathrm{m}} + b \\ &b = \log\{(K_{110}\cdot K_{101})/(K_{120}\cdot K_{102})\} \end{aligned}\right\}. \tag{4}$$

It is well known that mixed ligand complexes which contain a ligand having a pyridine ring as one component are strongly stabilized.[7)] The present results show the trend with the indication of large $\log F_{\mathrm{m}}$ values compared with the statistical value of 0.6 and positive values of $\log F'_{\mathrm{m}}$. The b values obtained in the present systems were much larger than those reported in the previous systems containing only 2-aminoalkanoate anions as ligands.[1)]

The largest formation constant was obtained for the Cd(gly)(pic) complex. The degree of stabilization of mixed ligand 1:1:1 complex by coordination of the second ligand to the 1:1 complex can be indicated by the K_{12}^{m} value which is defined by the following equation:

$$\log K_{12}^{\mathrm{m}} = \log\beta_{111} - \log K_{11}. \tag{5}$$

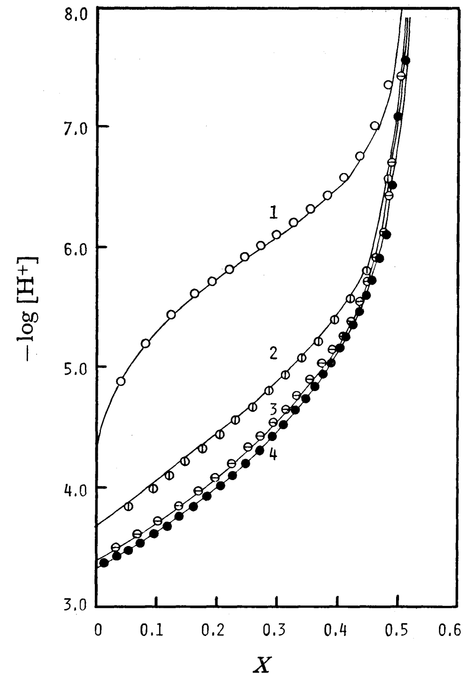

Fig. 1. Typical titration curves of cadmium(II)–α-alanine–2-pyridinecarboxylic acid mixed solutions. Curve 1 (○), C_{Cd}(mmol dm^{-3})$=0$, C_{ala}(mmol dm^{-3})$=$ 10.11, C_{pic}(mmol dm^{-3})$=10.31$; 2 (⦶), 2.156, 5.409, 5.420; 3 (⊖), 6.565, 16.36, 16.39; 4 (●), 11.01, 27.44, 27.49. Solid lines represent calculated titration curves by using values listed in Tables 1 and 3 and Eq. 1.

TABLE 2. FORMATION CONSTANTS OF MIXED LIGAND COMPLEXES OF CADMIUM(II) ION AND F_{m}, F'_{m}, AND b VALUES IN 3 mol dm^{-3} $\mathrm{LiClO_4}$ AT 25 °C

Complex[a)]	$\log\beta_{111}$[b)]	$\log F_{\mathrm{m}}$	$\log F'_{\mathrm{m}}$	b
Cd(gly)(pic)	8.88	2.10	0.40	1.30
Cd(ala)(pic)	8.47	1.84	0.31	1.22
Cd(but)(pic)	8.42	1.79	0.31	1.17
Cd(pen)(pic)	8.73	2.28	0.54	1.20
Cd(hex)(pic)	8.76	2.32	0.55	1.22

a) gly = Glycinate, ala = α-alaninate, but = 2-aminobutanoate, pen = 2-aminopentanoate, hex = 2-aminohexanoate, pic = 2-pyridinecarboxylate ions (α-picolinate ion). b) Standard deviations are ±0.02.

The log K_{12}^{m} values thus calculated are summarized in Table 3, together with those obtained for the mixed ligand cadmium(II) complexes with only 2-aminoalkanoate ions found in the previous work.[1)] It is obvious that the coordination of a 2-pyridinecarboxylate anion to a 2-aminoalkanoatocadmium(II) complex remarkably stabilizes the 1 : 1 : 1 mixed ligand complex, because of a large coordination ability of the pyridine ring by electron-withdrawing from the central metal ion. However, it should be noted that the formation constant K_{12}^{m} between the 2-pyridinecarboxylatocadmium(II) complex and a 2-aminoalkanoate ion (*i.e.*, $\mathrm{Cd(pic)^+ + L^- = CdL(pic)}$) was larger than that of the reaction between 2-aminoalkanoatocadmium(II) complex ($\mathrm{CdL^+}$) and another 2-aminoalkanoate ion $\mathrm{L'^-}$ ($\mathrm{L^- \neq L'^-}$) (see Table 3). The result indicates that the pyridine ring in the coordination sphere of the complex enhances the interaction between the central cadmium(II) ion and the entering 2-aminoalkanoate ion. It must be noted that the 2-pyridinecarboxylate anion coordinated to the central cadmium(II) ion does not significantly stabilize the interaction between the 2-pyridinecarboxyl-

TABLE 3. THE SECOND STEPWISE FORMATION CONSTANTS ($\log K_{12}^{m}$) OF THE CdLL′ COMPLEXES IN 3 mol dm^{-3} LiClO$_4$ AT 25 °C[a)]

CdL	L′					
	2-Pyridine carboxylate	Glycinate	Alaninate	2-Amino-butanoate	2-Amino-pentanoate	2-Amino-hexanoate
Cd(pic)$^+$	$\underline{\mathit{3.70}}$	4.41	4.00	3.95	4.26	4.29
Cd(gly)$^+$	4.87	$\underline{\mathit{3.48}}$$^{\mathrm{b)}}$	3.46$^{\mathrm{b)}}$	3.33$^{\mathrm{b)}}$	3.40$^{\mathrm{b)}}$	3.42$^{\mathrm{b)}}$
Cd(ala)$^+$	4.78	3.78$^{\mathrm{b)}}$	$\underline{\mathit{3.24}}$	3.44	3.46	3.55
Cd(but)$^+$	4.78	3.70$^{\mathrm{b)}}$	3.49	$\underline{\mathit{3.24}}$	3.41	3.56
Cd(pen)$^+$	5.01	3.69$^{\mathrm{b)}}$	3.43	3.33	$\underline{\mathit{3.29}}$	3.59
Cd(hex)$^+$	5.02	3.69$^{\mathrm{b)}}$	3.50	3.46	3.57	$\underline{\mathit{3.29}}$

a) Values underlined are $\log K_{12}$ of the bis(2-pyridinecarboxylato)- and bis(2-aminoalkanoato)cadmium(II) complexes. b) Values obtained from Ref. 1.

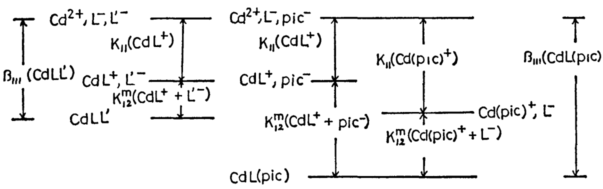

Fig. 2. A diagram showing relationships among the values of β_{111}, K_{11}, and K_{12}^{m}. Note that the magnitude of the K_{12}^{m} values are in the order (CdL$^+$+pic$^-$)>(Cd(pic)$^+$+L$^-$)>(CdL$^+$+L′$^-$).

atocadmium(II) complex and the second 2-pyridinecarboxylate ion (*i.e.*, Cd(pic)$^+$+pic$^-$=Cd(pic)$_2$).

The values of K_{12}^{m} of the reaction, CdL$^+$+pic$^-$=CdL(pic), are larger than K_{12}^{m} value of the reaction, Cd(pic)$^+$+L$^-$=CdL(pic) (Fig. 2), the fact, no doubt, indicating a large affinity of pic$^-$ compared with L$^-$ to a cadmium(II) ion. The K_{12}^{m} values of the reaction, Cd(pic)$^+$+L$^-$=CdL(pic), are larger than those of the reaction, CdL′$^+$+L$^-$=CdLL′. The result is explainable in terms of a large electron-withdrawing effect of the pyridine ring within pic$^-$ which leads to a decrease in the electron density at the cadmium atom of the Cd(pic)$^+$ complex. The lowered electron density at the cadmium atom of the Cd(pic)$^+$ complex allows to transfer electron pairs from an entering second 2-aminoalkanoate ion. Therefore, a stronger electron donation from the second ligand of the 2-aminoalkanoate ion to the Cd(pic)$^+$ complex in comparison with the reaction between CdL$^+$ and L′$^-$ can be done to form a strong σ-bonding between them. Thus, the K_{12}^{m} value of the CdL(pic) complex becomes larger than that of the CdLL′ complex.

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