Formation of Mixed-ligand Complexes of Zinc(II) with Chloride and Substituted Pyridines in 1,2-Dichloroethane as Solvent

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The formation of mixed-ligand complexes of zinc(II) chloride with pyridine (py) and substituted pyridines R-py [R-py = 4-methyl- (4Me-py), 3-methyl- (3Me-py), 2-methyl- (2Me-py), 2-ethyl- (2Et-py), 4-acetyl- (4MeCO-py), and 4-cyano-pyridine (4CN-py)] in 1,2-dichloroethane has been investigated at 25.0 °C by means of solvent extraction. The extraction equilibrium of zinc(II) between the NaCl aqueous phase and the NBu^t_4Cl–1,2-dichloroethane phase is given by equation (i), where the

$$Zn^{2+} + 2\,Cl^- + 2\,NBu^t_4Cl\ (org) \overset{K_{ex,o}}{\rightleftharpoons} (NBu^t_4)_2ZnCl_4\ (org) \qquad (i)$$

thermodyanamic extraction constant $\log K_{ex,o} = 5.61 \pm 0.03$ and 'org' denotes the species in the organic phase. The addition of substituted pyridines in this extraction system gives rise to the equilibria (ii) and (iii).

$$(NBu^t_4)_2ZnCl_4\ (org) + R\text{-}py\ (org) \overset{K_1}{\rightleftharpoons} (NBu^t_4)ZnCl_3(R\text{-}py)\ (org) + NBu^t_4Cl\ (org) \qquad (ii)$$

$$(NBu^t_4)ZnCl_3(R\text{-}py)\ (org) + R\text{-}py\ (org) \overset{K_2}{\rightleftharpoons} ZnCl_2(R\text{-}py)_2\ (org) + NBu^t_4Cl\ (org) \qquad (iii)$$

The successive formation constants, K_1 and K_2, were determined as $\log K_1 = 0.45, 0.25, -0.07, -0.47, 0.07, 0.13$, and -0.48 ± 0.03, and $\log K_2 = -1.09, -1.34, -3.21, -3.33, -1.70, -3.56$, and -4.86 ± 0.03 for the 4Me-py, 3Me-py, 2Me-py, 2Et-py, py, 4MeCO-py, and 4CN-py complexes, respectively. Except for the 2Me-py and 2Et-py complexes, the values of $\log K_1$ and $\log K_2$ show linear correlations with the pK_a of the conjugate acid of the substituted pyridines.

The role of π back-donation from zinc to nitrogen in the mixed-ligand complexes of zinc(II) chloride with substituted pyridines, $ZnCl_2(R\text{-}py)_2$ [R-py = 4-methyl- (4Me-py), 3-methyl- (3Me-py), 2-methyl- (2Me-py), 2-ethyl- (2Et-py), 4-acetyl- (4MeCO-py), and 4-cyano-pyridine (4CN-py)], has been discussed. Wong and Brewer have emphasized the role of π bonding in the Zn–N bond from the results of i.r. spectra [1,2] and heat of formation.[3] That is, when R is more electron donating than hydrogen, the Zn–N bond is strengthened by an increase in σ bond strength. Alternatively if R is more electron attracting than hydrogen, the σ bond is weakened by the decrease in electron density on the nitrogen atom of the pyridine base, but the π bonding becomes important. Thus, the Zn–N bond is also strengthened by the electron-attracting substituent.

On the other hand, Steffen and Palenik [4] have studied the crystal structures of a series of $ZnCl_2(R\text{-}py)_2$ complexes and have suggested that the linear correlation between Zn–N bond length and the ligand pK_a, which is an indication of the σ bond nature of the pyridine base, indicates the minimal contribution of π bonding to the Zn–N bond.

In a previous paper we investigated the formation of the mixed-ligand complexes of cobalt(II), $CoX_2(R\text{-}py)_2$ [X = Cl^- (ref. 5) or Br^- (ref. 6)], spectrophotometrically and reported a linear correlation between the logarithmic formation constants of the mixed-ligand complexes and the pK_a of the conjugate acids of the substituted pyridines. In the present paper the formation of the complexes of zinc(II), $ZnCl_3(R\text{-}py)^-$ and $ZnCl_2(R\text{-}py)_2$, is investigated by means of solvent extraction, and the results are compared with those for the cobalt(II) complexes.

Experimental

Reagents.—1,2-Dichloroethane was pre-equilibrated with a sodium chloride aqueous solution. Tetrabutylammonium chloride and the substituted pyridines (R-py) were prepared by methods similar to those described in a previous paper.[5] Zinc chloride was prepared by dissolving pure metal (99.999%) in concentrated hydrochloric acid.

Procedure.—The distribution of pyridine bases at various pH was studied by means of u.v. spectrophotometry at 25.0 ± 0.2 °C (Shimadzu double-beam spectrophotometer UV-200). The pH of the aqueous phase equilibrated with the organic phase was measured by a Corning digital pH meter M 130.

A quantity of the aqueous phase (20 cm^3) containing sodium chloride and zinc(II) was contacted with 20 cm^3 of the 1,2-dichloroethane phase containing tetrabutylammonium chloride and/or substituted pyridine in a 50 cm^3 stoppered centrifuge tube at 25.0 ± 0.2 °C. In order to minimize the formation of hydroxo-complexes of zinc(II) and the effect of protonation of the pyridine bases, the pH of the aqueous phase equilibrated with the organic phase was adjusted to *ca*. 7. Shaking for 30 min was found sufficient for complete equilibrium. After separation of the phases, the concentration of zinc(II) in the aqueous phase was determined by means of atomic absorption spectrophotometry (a.a.s.) (Shimadzu atomic absorption spectrophotometer AA 640-01). After the back-extraction with 0.01 mol dm^{-3} HNO_3, the concentration of zinc(II) in the organic phase was determined by a.a.s.

The ionic strength of the aqueous phase was not kept constant. That is, addition of electrolytes to adjust the ionic strength causes a change in the concentration of NBu^t_4Cl in the organic phase by the exchange of the chloride ion with the anions added in the aqueous phase. Thus, the thermodynamic extraction constants were evaluated by taking into consideration the activity coefficients of the ionic species in the aqueous phase. The activity coefficients of the uncharged species were considered as unity.

Table. Distribution coefficient of R-py, K_d, successive formation constants of $(\mathrm{NBu^t_4})\mathrm{ZnCl_3(R\text{-}py)}$, K_1, and $\mathrm{ZnCl_2(R\text{-}py)_2}$, K_2, and extraction constants of $(\mathrm{NBu^t_4})_2\mathrm{ZnCl_4}$, $K_{ex,0}$, and $\mathrm{ZnCl_2(R\text{-}py)_2}$, $K_{ex,2}$ [a]

R-py	pK_a obs.	pK_a lit.[b]	log K_d	log $K_{ex,2}$ [c]	log K_1	log K_2
4Me-py	6.03	6.03	1.23	4.97	0.45 [d]	−1.09
3Me-py	5.72	5.68	1.28	4.52	0.25 [d]	−1.34
2Me-py	6.02	5.96	1.20	2.33	−0.07	−3.21 (−3.22 [d])
2Et-py	5.76		1.74	1.81	−0.47	−3.33 [d]
py	5.28	5.20	0.78	3.98	0.07 [d]	−1.70
4MeCO-py		3.51	1.07	2.15	0.13	−3.56 (−3.59 [d])
4CN-py		1.88	1.16	0.27	−0.48	−4.86 [d]

[a] Estimated uncertainty ±0.03. [b] pK_a values evaluated by other methods; see ref. 7. [c] log $K_{ex,0}$ = 5.61. [d] Calculated by using $K_{ex,2}$; see text.

Results

Extraction of Substituted Pyridines.—The semi-thermodynamic acid dissociation constant of the conjugate acid of the substituted pyridines (R-py) is given by equation (1),

$$K_a = \frac{a_{H^+}[\mathrm{R\text{-}py}]}{[\mathrm{HR\text{-}py^+}]} \qquad (1)$$

where square brackets denote the equilibrium concentration. The distribution ratio of R-py, $D_{R\text{-}py}$, is given by equation (2),

$$D_{R\text{-}py} = \frac{C_{R\text{-}py(org)}}{C_{R\text{-}py}} = \frac{[\mathrm{R\text{-}py}]_{org}}{[\mathrm{R\text{-}py}](1 + K_a^{-1}a_{H^+})} \qquad (2)$$

where C denotes the total concentrations in each phase and 'org' refers to the species in the organic phase.

Substitution of the distribution coefficient of R-py, K_d (= $[\mathrm{R\text{-}py}]_{org}/[\mathrm{R\text{-}py}]$), into equation (2) leads to equation (3).

$$\log D_{R\text{-}py} = \log K_d - \log(1 + K_a^{-1}a_{H^+}) \qquad (3)$$

By curve fitting of the plot of the experimental results (log $D_{R\text{-}py}$ *vs.* pH) with the normalized curve [$-\log(1 + x)$ *vs.* log x], we obtained the pK_a and log K_d of the substituted pyridines. The values thus obtained are listed in the Table, where the pK_a is the thermodynamic constant corrected for the activity coefficients and is in good agreement with the confirmed value.[7]

Extraction of Tetrachloro-complex.—Zinc(II) was extracted from 1.0 mol dm^{-3} NaCl aqueous solution into 1,2-dichloroethane containing various concentrations of tetrabutylammonium chloride. The logarithmic distribution ratio of zinc(II), log D_0 ($D_0 = C_{Zn(org)}/C_{Zn}$), is plotted as a function of log $[\mathrm{NBu^t_4Cl}]_{org}$ in Figure 1. The dissociation of the ion pair and the distribution into the aqueous phase of $\mathrm{NBu^t_4Cl}$ are negligible under these experimental conditions.[8] As the formation of dimeric $\mathrm{NBu^t_4Cl}$ is anticipated at higher concentrations of $\mathrm{NBu^t_4Cl}$ (log $[\mathrm{NBu^t_4Cl}] > -2$), such high concentrations were not used[8]. Thus, as the concentration of $\mathrm{Zn^{II}}$ is much smaller than that of $\mathrm{NBu^t_4Cl}$, the equilibrium concentration of $\mathrm{NBu^t_4Cl}$ in the organic phase is approximated by the total concentration of the $\mathrm{NBu^t_4Cl}$ added.

By assuming the extraction of the monomeric chloro-complex, the extraction equilibrium is given by equation (4). The thermodynamic extraction constant of the chloro-complex, $K_{ex,0}$, is defined by equation (5) where F is the activity coefficient term, $F = f_{Zn}f_{Cl}^2$.

$$\mathrm{Zn^{2+}} + 2\,\mathrm{Cl^-} + n\,\mathrm{NBu^t_4Cl\,(org)} \xrightleftharpoons{K_{ex,0}} (\mathrm{NBu^t_4})_n\mathrm{ZnCl_{2+n}\,(org)} \qquad (4)$$

$$K_{ex,0} = \frac{[(\mathrm{NBu^t_4})_n\mathrm{ZnCl_{2+n}}]_{org}}{[\mathrm{Zn^{2+}}][\mathrm{Cl^-}]^2[\mathrm{NBu^t_4Cl}]_{org}^{\,n}F} \qquad (5)$$

The distribution ratio of zinc(II) is given by equation (6), where α_{Zn} is the side-reaction coefficient of the zinc(II) ion for the hydroxo- and chloro-complexes in the aqueous phase.

$$D_0 = \frac{[(\mathrm{NBu^t_4})_n\mathrm{ZnCl_{2+n}}]_{org}}{[\mathrm{Zn^{2+}}]\alpha_{Zn}} \qquad (6)$$

Substitution of equation (6) into equation (5) leads to equation (7). As shown in Figure 1, the

$$\log D_0 = \log K_{ex,0} + 2\log[\mathrm{Cl^-}] + \log F\alpha_{Zn}^{-1} + n\log[\mathrm{NBu^t_4Cl}]_{org} \qquad (7)$$

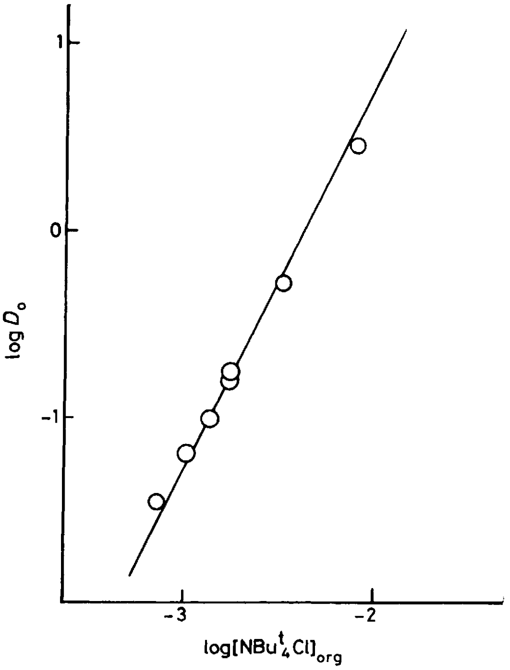

Figure 1. Plot of log D_0 as a function of log $[\mathrm{NBu^t_4Cl}]_{org}$ where C_{NaCl} = 1.0 mol dm^{-3} and $C_{Zn} + C_{Zn(org)}$ = 9.81 × 10^{-4} mol dm^{-3}

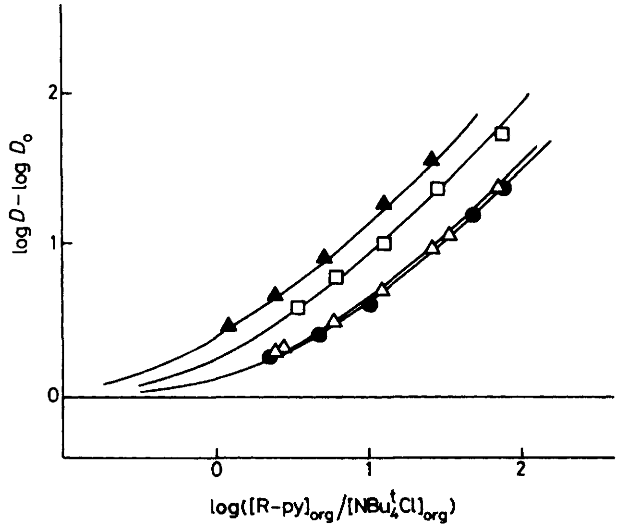

Figure 2. Plot of $\log D - \log D_0$ as a function of $\log([R\text{-py}]_{org}/[NBu^t_4Cl]_{org})$ where $C_{NBu^t_4} = 2 \times 10^{-3}$ mol dm^{-3} for 2Me-py, 2Et-py, and 4CN-py (4.4×10^{-3} mol dm^{-3} for 4MeCO-py); $C_{NaCl} = 1.0$ mol dm^{-3}; and $C_{Zn} + C_{Zn(org)} = 9.81$ mol dm^{-3}. For definition of symbols see legend of Figure 3

plot of $\log D_0$ as a function of $\log [NBu^t_4Cl]_{org}$ falls on a straight line with a slope of 2 (solid line). This fact indicates the extraction of the tetrachloro-complex, $(NBu^t_4)_nZnCl_{2+n}$ ($n = 2$). From the intercept of the plot $\log K_{ex,0}$ is obtained as 5.61 ± 0.03 where, as will be shown below, the coefficient term is $\log F\alpha_{Zn}^{-1} = -1.08$ ($C_{NaCl} = 1.0$ mol dm^{-3}). The distribution ratio does not change upon change in the zinc(II) concentration. Thus, the extraction of monomeric species was confirmed.

Formation of Monopyridine Complexes.—The addition of the pyridine bases to the extraction system of the tetrachloro-complex causes an increase in the distribution ratio of zinc(II). Thus, the formation of mixed-ligand complexes containing the pyridine base is anticipated. If the formation of a monopyridine complex is given as equation (8), the formation constant of the monopyridine complex is then given by equation (9) and the distribution ratio of zinc(II) by equation (10).

$$(NBu^t_4)_2ZnCl_4\ (org) + R\text{-py}\ (org) \xrightleftharpoons{K_1} (NBu^t_4)ZnCl_3(R\text{-py})\ (org) + NBu^t_4Cl\ (org) \quad (8)$$

$$K_1 = \frac{[(NBu^t_4)ZnCl_3(R\text{-py})]_{org}[NBu^t_4Cl]_{org}}{[(NBu^t_4)_2ZnCl_4]_{org}[R\text{-py}]_{org}} \quad (9)$$

$$D = \frac{[(NBu^t_4)_2ZnCl_4]_{org} + [(NBu^t_4)ZnCl_3(R\text{-py})]_{org}}{[Zn^{2+}]\,\alpha_{Zn}} = \frac{[(NBu^t_4)_2ZnCl_4]_{org}(1 + K_1[R\text{-py}]_{org}/[NBu^t_4Cl]_{org})}{[Zn^{2+}]\,\alpha_{Zn}} \quad (10)$$

Substitution of equation (6) into equation (10) leads to equation (11). The plot of $\log D - \log D_0$ as a function of

$$\log D - \log D_0 = \log\{1 + K_1[R\text{-py}]_{org}/[NBu^t_4Cl]_{org}\} \quad (11)$$

$\log([R\text{-py}]_{org}/[NBu^t_4Cl]_{org})$ is shown in Figure 2. By means of curve-fitting with the normalized curve, $\log(1 + x)$ *vs.* $\log x$ (solid lines in Figure 2), the values of K_1 for the 2Me-, 2Et-4MeCO-, and 4CN-py complexes are obtained (Table). As will be shown below, the formation constant of the bis-pyridine complexes is so small compared with K_1 that the formation of the higher pyridine complex is negligible under these conditions.

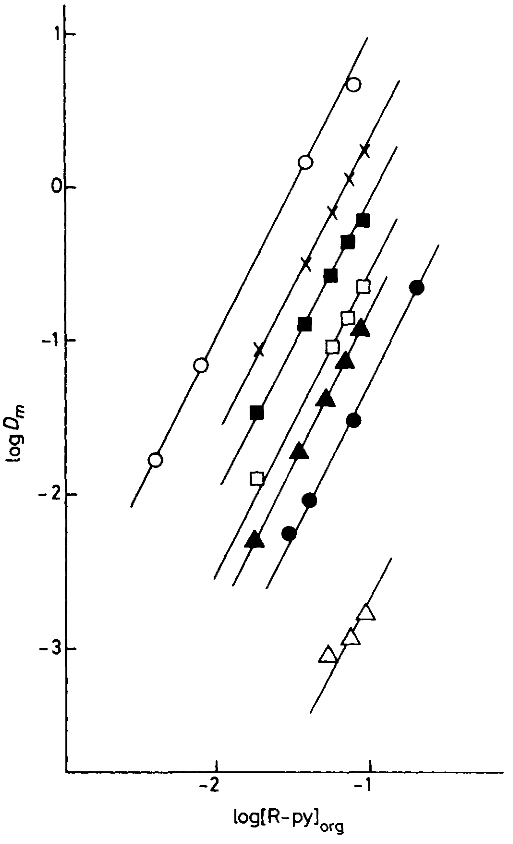

Figure 3. Plot of $\log D_m$ as a function of $\log [R\text{-py}]_{org}$ where $C_{NaCl} = 0.1$ mol dm^{-3} for 4Me-py and 3Me-py; 1.0 mol dm^{-3} for 2Me-py, 2Et-py, 4MeCO-py, and 4CN-py; and $C_{Zn} + C_{Zn(org)} = 9.81 \times 10^{-4}$ mol dm^{-3}. R-py = 4Me-py (×), 3Me-py (■), 2Me-py (□), 2Et-py (●), py (○), 4MeCO-py (▲), and 4CN-py (△)

Extraction of Bis-pyridine Complexes.—Zinc(II) was extracted from a sodium chloride aqueous phase into 1,2-dichloroethane with the substituted pyridines. By the assumption of the extraction of the monomeric species, the extraction equilibrium is given by equation (12). The thermodynamic extraction constant of the mixed-ligand complex, $ZnCl_2(R\text{-py})_m$, is defined by equation (13) and the distribution ratio of zinc(II) by equation (14). Substitution of equation (13) into equation (14) leads to equation (15). The plot of $\log D_m$ as a function of $\log [R\text{-py}]_{org}$ ($[Cl^-]$ = constant) is shown in Figure 3.

$$Zn^{2+} + 2Cl^- + mR\text{-py}\ (org) \xrightleftharpoons{K_{ex,m}} ZnCl_2(R\text{-py})_m\ (org) \quad (12)$$

$$K_{ex,m} = \frac{[ZnCl_2(R\text{-py})_m]_{org}}{[Zn^{2+}][Cl^-]^2[R\text{-py}]_{org}{}^m F} \quad (13)$$

$$D_m = \frac{[ZnCl_2(R\text{-py})_m]_{org}}{[Zn^{2+}]\,\alpha_{Zn}} \quad (14)$$

$$\log D_m = \log K_{ex,m} + 2\log[Cl^-] + \log F\alpha_{Zn}^{-1} + m \log [R\text{-py}]_{org} \quad (15)$$

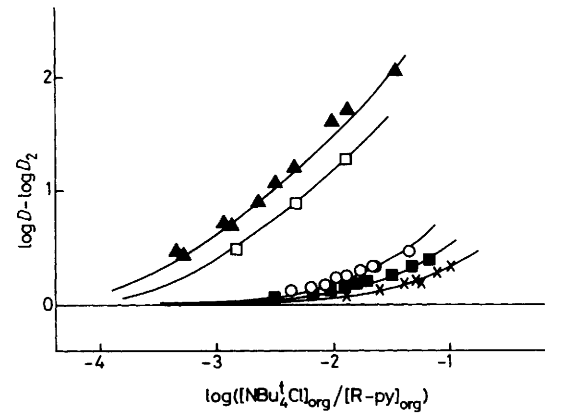

Figure 4. Plot of log D − log D_2 as a function of log ([$\mathrm{NBu^t{}_4Cl}$]$_{org}$/[R-py]$_{org}$) where $C_{R-py} + C_{R-py(org)} = 0.1$ mol dm^{-3} for 2Me-py, py, and 4MeCO-py; 6×10^{-2} mol dm^{-3} for 3Me-py; and 4×10^{-2} mol dm^{-3} for 4Me-py; $C_{NaCl} = 0.1$ mol dm^{-3} for 4Me-py, 3Me-py, and py; 1.0 mol dm^{-3} for 2Me-py and 4CN-py; and $C_{Zn} + C_{Zn(org)} = 9.81 \times 10^{-4}$ mol dm^{-3}. For definition of symbols see legend of Figure 3

The plot falls on a straight line with a slope of 2 (solid lines in Figure 3), *i.e.* the number of R-py co-ordinated to zinc(II) is obtained as $m = 2$. The extraction constant of the bis-pyridine complex, $K_{ex,2}$, obtained from the intercept of the plot is listed in the Table where, as will be shown below, the coefficient term at $C_{NaCl} = 0.1$ mol dm^{-3} is log $F\alpha_{Zn}^{-1} = -0.61$. The extraction constant does not change with changes in the zinc(II) concentration, and this indicates the formation of the monomeric complex.

Formation of Bis-pyridine Complexes.—The formation constant of bis-pyridine complexes [equation (16)], K_2, was determined by the addition of $\mathrm{NBu^t{}_4Cl}$ in the extraction system of the bis-pyridine complexes. When the concentration of $\mathrm{NBu^t{}_4Cl}$ is much smaller than that of R-py, the formation of $\mathrm{(NBu^t{}_4)_2ZnCl_4}$ is negligible. Thus, the distribution ratio of zinc(II) is given by equation (17). Substitution of equation (14) into equation (17) leads to equation (18). The plot of log D − log D_2 as a function of log ([$\mathrm{NBu^t{}_4Cl}$]$_{org}$/[R-py]$_{org}$) is shown in Figure 4. The equilibrium constant, K_2, evaluated by the curve fitting with the normalized curve [log (x + 1) *vs.* log x] is listed in the Table.

$$\mathrm{(NBu^t{}_4)ZnCl_3(R\text{-}py)\ (org) + R\text{-}py\ (org)} \xrightleftharpoons{K_2} \mathrm{ZnCl_2(R\text{-}py)_2\ (org) + NBu^t{}_4Cl\ (org)} \quad (16)$$

$$D = \frac{[\mathrm{ZnCl_2(R\text{-}py)_2}]_{org} + [\mathrm{(NBu^t{}_4)ZnCl_3(R\text{-}py)}]_{org}}{[\mathrm{Zn^{2+}}]\,\alpha_{Zn}} = \frac{[\mathrm{ZnCl_2(R\text{-}py)_2}]_{org}(1 + K_2^{-1}[\mathrm{NBu^t{}_4Cl}]_{org}/[\mathrm{R\text{-}py}]_{org})}{[\mathrm{Zn^{2+}}]\,\alpha_{Zn}} \quad (17)$$

$$\log D - \log D_2 = \log (1 + K_2^{-1}[\mathrm{NBu^t{}_4Cl}]_{org}/[\mathrm{R\text{-}py}]_{org}) \quad (18)$$

Activity Coefficient.—The mean activity coefficient of sodium chloride[9] was used as the activity coefficient of the chloride ion, f_{Cl}. The activity coefficient of zinc(II) ion, f_{Zn}, at low ionic strength ($I = 0.1$ mol dm^{-3}) was calculated by the Davies equation.[10] Thus, the activity coefficient term at I = 0.1 mol dm^{-3} was obtained as log $F = -0.61$. The formation of pyridine and hydroxo-complexes in the aqueous phase is negligible at pH *ca.* 7.[11] The formation of the chloro-complexes is also negligible at low NaCl concentration.[11] Thus, the side-reaction coefficient of zinc(II) at $C_{NaCl} = 0.1$ mol dm^{-3} can be approximated as $\alpha_{Zn} = 1$.

At higher NaCl concentration ($C_{NaCl} = 1.0$ mol dm^{-3}) reliable values of the activity coefficients and side-reaction coefficients are difficult to obtain. These values were evaluated by the comparison of the distribution ratio of the bis-pyridine complex at high NaCl concentration with that at low NaCl concentration. Thus, the coefficient term at 1.0 mol dm^{-3} NaCl solution was obtained as log $F\alpha_{Zn}^{-1} = -1.08$.

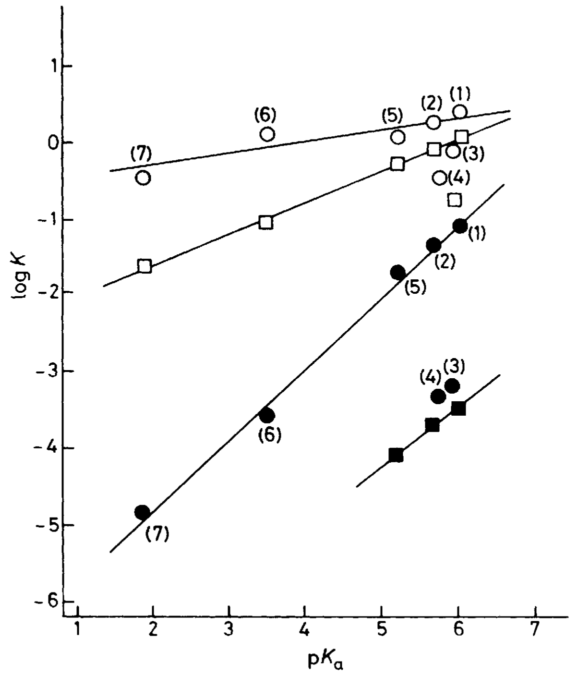

Figure 5. Plot of log K_1 (○) and log K_2 (●) of zinc(II) complexes and log K_1 (□) and log K_2 (■) of cobalt complexes as a function of pK_a. R-py = 4Me-py (1), 3Me-py (2), 2Me-py (3), 2Et-py (4), py (5), 4MeCO-py (6), and 4CN-py (7)

Discussion

The complexes formed in the organic phase have a tetrahedral configuration, and the anionic species, $\mathrm{ZnCl_3(R\text{-}py)^-}$ and $\mathrm{ZnCl_4^{2-}}$, form uncharged ion- pairs with the cation, $\mathrm{NBu^t{}_4^+}$, as $\mathrm{[NBu^t{}_4]^+[ZnCl_3(R\text{-}py)]^-}$ and $\mathrm{[NBu^t{}_4]^+{}_2[ZnCl_4]^{2-}}$.[12,13] Although the octahedral complexes of dihalogenocobalt(II) are comparably easy to form,[5,6,14,15] that of zinc(II), $\mathrm{ZnCl_2(R\text{-}py)_4}$, is scarcely formed.[16] As can be seen from Figure 3, it is not formed under the conditions of this study.

The formation constants of mixed-ligand complexes in the organic phase, K_1 and K_2, are correlated with the extraction constants, $K_{ex,0}$ and $K_{ex,2}$, as $K_1K_2 = K_{ex,2}/K_{ex,0}$. Thus, K_1 of the 4Me-py, 3Me-py, 2Me-py, 4MeCO-py, and py complexes and K_2 of the 2Me-py, 2Et-py, 4MeCO-py, and 4CN-py complexes were evaluated by this correlation and are listed in the Table (denoted by footnote *d*). As shown in the Table, the formation constants of the 2Me-py and 4MeCO-py complexes are obtained by both methods. The fact that these values are in agreement with each other corroborates the validity of equations (8) and (16).

Log K_1 and log K_2 are plotted in Figure 5 as a function of pK_a

of the conjugate acid of R-py along with the results of cobalt(II) complexes,[5] where the constants K_1 and K_2 of the cobalt(II) complexes are defined in a previous paper as $K_4 = K_1^{-1}$ and $K_3 = K_2^{-1}$. The plots of zinc(II) complexes show linear correlations as well as those of cobalt(II) complexes; that is, the Zn–N bond strength increases with an increase in electron density on the nitrogen atom. This fact may be interpreted by the minimal contribution of π bonding in the Zn–N bond and is consistent with the results of Steffen and Palenik.[4] Lack of participation of the $3d^{10}$ state in π bonding has been suggested.[17,18] Thus, π bonding is much weaker than σ bonding in zinc(II) complexes.

The slopes of the plots of log K_1 and log K_2 of the zinc(II) complexes are almost the same as those of the cobalt(II) complexes. In particular the plots of the 4Me-py, 3Me-py, and py complexes are almost parallel between the zinc(II) and cobalt(II) complexes. This fact may indicate the minimal contribution of π bonding in the cobalt(II)–pyridine bond. That is, if the π bond were significant in the Co–N bond, the increase in the σ bond strength upon the increase in electron density on the nitrogen atom will be partially compensated for by a decrease in π bond strength; thus, the slope of the plot of the cobalt(II) complexes should be smaller than that of the zinc(II) complexes.

As the MCl_4^{2-} ion releases a chloride ion and receives R-py in the case of equilibrium (8) (K_1), the electron density on the zinc atom of the host complex ion does not change with change in the R-py. On the other hand, in the case of equilibrium (16) (K_2), the chloride ion is released from the complex ion co-ordinating R-py, $ZnCl_3(R\text{-py})^-$. Thus, the electron density on the zinc co-ordinating an R-py having a higher electron density on the nitrogen atom (larger pK_a) is higher than that co-ordinated to one of smaller pK_a. An increase in electron density on zinc causes a decrease in the bond strength with the second entering R-py; that is, the effect of the increase in the basicity of R-py on the formation constant of the bis-pyridine complexes will be partially compensated. Thus, from the viewpoint of Zn–(R-py) bond strength, the slope of the plot of K_2 should be smaller than that of K_1.

As can be seen from Figure 5, the results are contrary to the above argument; that is, the slope of the plot of K_2 is larger than that of K_1 for complexes of both cobalt(II) and zinc(II). This information may indicate that the Zn–Cl bond strength is weakened by the co-ordination of R-py having the higher basicity and the effect of the change in the electron density on the zinc atom on the metal–chloride ion bond is more significant than that on the metal–(R-py) bond. Thus, the substitution reaction of the complex ion, MCl_4^{2-}, is less sensitive to the change in the basicity of R-py than is that of $MCl_3(R\text{-py})^-$.

The fact that the bond length of Zn–Cl in the $ZnCl_2(R\text{-py})_2$ complexes is shorter than that in the $ZnCl_4^{2-}$ complex ion has been interpreted as indicating that the increase in electron density on the zinc atom by the co-ordination of R-py is removed *via* $d\pi$–$d\pi$ bonds to the chlorine atoms, thus increasing the Zn–Cl bond strength.[19] However, the effect of the steric repulsion between chloride ions is not taken into consideration in the above argument; that is, the lone-pair repulsion between chlorine atoms is expected to be larger than that of bond-pair repulsion between the pyridines.[20] As is reported by Steffen and Palenik,[4] the change in the Zn–Cl bond length in the $ZnCl_2(R\text{-py})_2$ complexes with change in the basicity of R-py is quite small. Thus, the Zn–Cl bond length is less sensitive to the Zn–(R-py) bond strength.

The values of K_1 and K_2 of the 2Me-py and 2Et-py complexes are much smaller than those of the complexes of the other pyridine bases having comparable pK_a values. Thus, the substituent at the 2-position of pyridine gives rise to a considerable steric effect. It is reasonable that the magnitude of the steric effect of the bis-pyridine complexes is much larger than that of the mono-pyridine complexes.

The magnitude of the steric effect of the 2Et-py complexes does not differ much from that of the 2Me-py complexes for both the mono-pyridine and bis-pyridine complexes. The molecular structure of $CoCl_2(2MeO\text{-py})_2$ has been determined.[21] The methyl group of the methoxy group is oriented outward from the central metal ion in the complex. The complex, $ZnCl_2(2Et\text{-py})_2$, is considered to have the same structure as $CoCl_2(2MeO\text{-py})_2$. This molecular model of $ZnCl_2(2Et\text{-py})_2$ indicates that the methyl group in the 2-Et substituent has little steric effect in the tetrahedral complexes; thus, the steric effect of the 2-Et group is in the same order of magnitude as that of the 2-Me group.

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