Formation of Mixed-ligand Complexes of Cadmium(II) Halide with Tri-n-octylphosphine Oxide and Pyridine or Substituted Pyridines in 1,2-Dichloroethane

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The formation of mixed-ligand complexes of cadmium(II) chloride and bromide with tri-n-octylphosphine oxide (topo) and pyridine or substituted pyridines (R-py) [R-py = pyridine (py), 4-methyl- (4Me-py), 3-methyl- (3Me-py), 2-methyl-(2Me-py), 2-ethyl (2Et-py), 4-acetyl-(4MeCO-py), or 4-cyano-pyridine (4CN-py)] in 1,2-dichloroethane has been investigated. The formation constants given by equations (i) and (ii) were determined by means of solvent extraction

$$[CdX_2(topo)_2] + R\text{-}py \overset{K_1}{\rightleftharpoons} [CdX_2(topo)(R\text{-}py)] + topo \qquad (i)$$

$$[CdX_2(topo)(R\text{-}py)] + R\text{-}py \overset{K_2}{\rightleftharpoons} [CdX_2(R\text{-}py)_2] + topo \qquad (ii)$$

at 25.0 ± 0.1 °C. These constants linearly increase with increasing pK_a of the conjugate acid of the pyridine base except for the 2-methyl- and the 2-ethyl-pyridine complexes. The steric hindrance of the 2-substituents is not important in the monopyridine complexes of cadmium(II) chloride. The results for the topo systems are discussed by the comparison with those for the tetrahalogeno systems.

The formation of mixed-ligand complexes of some bivalent transition metals (M = Co^{II},[1,2] Zn^{II},[3] Cd^{II},[4] and Cu^{II} [5]) with halogenide ions (X = Cl^- [1,3–5] or Br^- [2]) and pyridine or substituted pyridines (pyridine base, R-py) has been investigated previously in aprotic non-polar solvents, 1,2-dihalogenoethanes. The formation equilibria of the tetrahedral mixed-ligand complexes are as in equations (1) and (2) where NBu_4X refers to

$$[NBu_4]_2[MX_4] + R\text{-}py \overset{K_1'}{\rightleftharpoons} [NBu_4][MX_3(R\text{-}py)] + NBu_4X \qquad (1)$$

$$[NBu_4][MX_3(R\text{-}py)] + R\text{-}py \overset{K_2'}{\rightleftharpoons} [MX_2(R\text{-}py)_2] + NBu_4X \qquad (2)$$

the tetra-n-butylammonium halide (chloride or bromide). The linear free-energy relationships (l.f.e.r.s) between the basicity of the pyridine bases (pK_a) and the stability of the complexes revealed that the bond between the metal ion and the nitrogen atom of the pyridine base is principally a σ bond, the contribution of π-back bonding being less important.

As the charge of the complex changes from minus two ($[MX_4{}^{2-}]$) to zero ($[MX_2(R\text{-}py)_2]$) with the substitution of halogenide ion by pyridine base, the contribution of electrostatic effects to equilibria (1) and (2) is considered to be quite large.[3] It was reported that the destabilization of the tetrahalogeno complex $[MX_4]^{2-}$ owing to the electrostatic and the steric repulsions between the halogenide ions causes a quite large difference between the equilibrium constants (K_1'/K_2' = 10^2—10^4).[5] Thus, it is interesting to examine the reactions of non-charged complexes with pyridine bases to elucidate the electrostatic effect on the complex formation.

Tri-n-octylphosphine oxide (topo) has been widely used for the extraction of metal ions as a neutral synergistic[6] reagent. In the present study the reactions of neutral topo complexes of cadmium(II) chloride and bromide with pyridine bases in 1,2-dichloroethane were investigated by means of solvent extraction at 25.0 ± 0.1 °C. The effect of the basicity and the steric effect of the pyridine bases on the formation of mixed-ligand complexes are discussed. The results for the chloride and bromide complexes are compared with those of tetrachloro complex systems.

Experimental

Reagents.—1,2-Dichloroethane and pyridine bases [R-py = pyridine (py), 4-methyl- (4Me-py), 3-methyl- (3Me-py), 2-methyl- (2Me-py), 2-ethyl- (2Et-py), 4-acetyl- (4MeCO-py), or 4-cyano-pyridine (4CN-py)] were purified by the methods described elsewhere.[1] The stock solutions of cadmium(II) chloride and bromide were prepared by dissolving G.R. grade cadmium(II) halides (Nakarai Chemicals) in 0.1 mol dm^{-3} sodium chloride or bromide (NaX) aqueous solution, respectively. The cadmium(II) concentration in the stock solution was determined by ethylenediaminetetra-acetate (edta) titration. G.R. grade topo (Tokyo Kasei) was dried under vacuum before use.

Procedure.—The extraction experiments were performed at 25.0 ± 0.1 °C by similar methods to those described elsewhere.[3,4] In order to avoid formation of hydroxo complexes of cadmium(II), the pH of an aqueous phase equilibrated with an organic phase was adjusted to *ca.* 5 by the addition of an appropriate amount of hydrochloric or hydrobromic acid to the aqueous phase before shaking. The concentration of free pyridine base in the organic phase was calculated from the pH of the aqueous phase by using the protonation constant and the distribution coefficient of the pyridine base.[3] The concentration of free topo in the organic phase can be approximated by the total concentration since the distribution of topo into the aqueous phase is negligible.

Results

Extraction of topo *Complex.*—The fact that the distribution ratio of cadmium(II) ($D \equiv c_{Cd,org}/c_{Cd}$) was not altered by

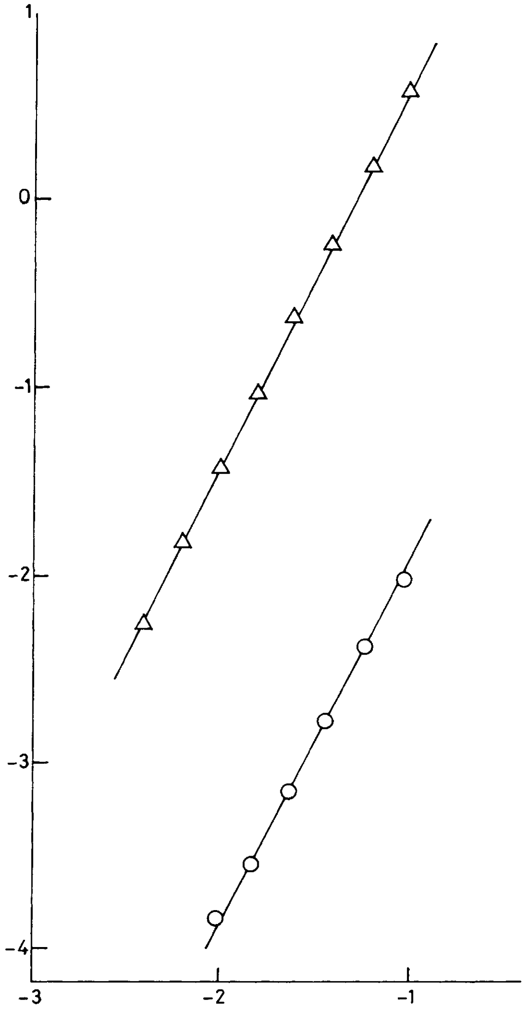

Figure 1. Plots of log D as a function of log $[\text{topo}]_{\text{org}}$ for the chloride (○) and the bromide (△) complexes at $c_{\text{Cd}} = 1.00 \times 10^{-4}$ mol dm^{-3} and $c_X = 0.1$ mol dm^{-3}

variation of the total cadmium(II) concentration indicates the formation of monomeric species in the organic phase. Thus, the extraction constant of cadmium(II) from NaX aqueous solution into 1,2-dichloroethane containing topo is given by equation (3), where 'org' denotes the species present in the organic phase.

$$K_{\text{ex},0} = \frac{[\text{CdX}_2(\text{topo})_n]_{\text{org}}}{[\text{Cd}^{2+}][\text{X}^-]^2[\text{topo}]_{\text{org}}^{\,n}} \qquad (3)$$

The total concentration of cadmium(II) in the aqueous phase, c_{Cd}, is given by $c_{\text{Cd}} = [\text{Cd}^{2+}]\alpha_{\text{Cd(X)}}$, where $\alpha_{\text{Cd(X)}}$ is the side reaction coefficient of cadmium(II) for the halogenide complexes. Thus, by using the conditional extraction constant defined by $K'_{\text{ex},0} = K_{\text{ex},0}\alpha_{\text{Cd(X)}}^{-1}$, the distribution ratio of cadmium(II) is given by equation (4).

$$\log D = \log K'_{\text{ex},0} + 2 \log [\text{X}^-] + n \log [\text{topo}]_{\text{org}} \qquad (4)$$

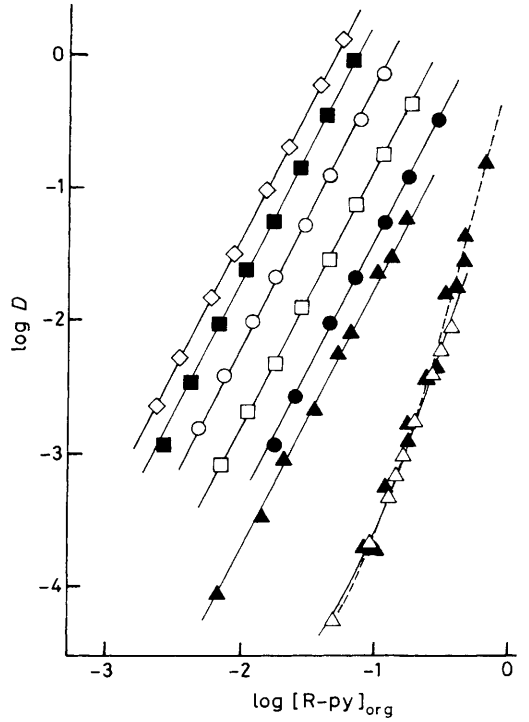

Figure 2. Plots of log D as a function of log $[\text{R-py}]_{\text{org}}$. Solid and broken lines were calculated for the bromide and the chloride complexes, respectively. $c_{\text{Cd}} = 1.00 \times 10^{-4}$ mol dm^{-3} and $c_X = 0.1$ mol dm^{-3}. R-py = py (○), 4Me-py (◇), 3Me-py (■), 2Me-py (□), 2Et-py (●), 4MeCO-py (▲), and 4CN-py (△)

Plots of log D as a function of log $[\text{topo}]_{\text{org}}$ at constant halogenide ion concentrations are shown in Figure 1. These plots are straight lines with slopes of two. Consequently, the extracted species were monomeric bis(topo) complexes, $[\text{CdCl}_2(\text{topo})_2]$ and $[\text{CdBr}_2(\text{topo})_2]$. The conditional extraction constants at 0.1 mol dm^{-3} NaX were log $K'_{\text{ex},0} = 2.04$ and 4.59 ± 0.03 for the chloride and bromide complex, respectively.

Extraction of Pyridine Complexes.—The extraction of cadmium(II) chloride from 0.1 mol dm^{-3} NaCl solution with pyridine base has been previously studied,[4] bis(pyridine) complexes $[\text{CdCl}_2(\text{R-py})_2]$ being reported [equation (5)]. The

$$\text{Cd}^{2+} + 2\,\text{Cl}^- + 2\,\text{R-py}_{\text{org}} \xrightleftharpoons{K_{\text{ex},2}} [\text{CdCl}_2(\text{R-py})_2]_{\text{org}} \qquad (5)$$

conditional extraction constants, $K'_{\text{ex},2} = K_{\text{ex},2}\alpha_{\text{Cd(Cl)}}^{-1}$, at 0.1 mol dm^{-3} NaCl are listed in Table 1.

By the same way as described in the literature,[4] the extraction of the pyridine complex of cadmium(II) bromide in a pyridine base solution of 1,2-dichloroethane was investigated. As shown in Figure 2, the plots of log D as a function of log$[\text{R-py}]_{\text{org}}$ are straight lines with slopes of two, except for the 4CN-py complex. Thus, the extraction of bis(pyridine) complexes $[\text{CdBr}_2(\text{R-py})_2]$ was confirmed. The conditional extraction constants at 0.1 mol dm^{-3} NaBr are listed in Table 1.

For the 4CN-py system, the slope of the plot exceeds two at higher concentrations of 4CN-py and approaches to four (Figure 2). This finding is explained by the formation of a six-co-ordinate tetrakis(pyridine) complex $[\text{CdBr}_2(\text{4CN-py})_4]$,[1,2] as in equation (6). As the five-co-ordinate complex is scarcely formed

$$[\text{CdBr}_2(\text{4CN-py})_2]_{\text{org}} + 2\ \text{4CN-py}_{\text{org}} \xrightleftharpoons{K_c} [\text{CdBr}_2(\text{4CN-py})_4]_{\text{org}} \qquad (6)$$

in solution,[7] the formation of the intermediate complex $[\text{CdBr}_2(\text{4CN-py})_3]$ can be ruled out.

By using the equilibrium constant, K_c, the distribution ratio of cadmium(II) is given by $D = K'_{\text{ex},2}(1 + K_c[\text{4CN-py}]_{\text{org}}^{\,2})$.

Table 1. Logarithmic formation constants of cadmium(II) complexes, log K_1 and log K_2,[a,b] in the organic phase and logarithmic conditional extraction constants of bis(pyridine) complexes, log $K'_{ex,2}$[b,c]

		log K_1		log K_2		log $K'_{ex,2}$	
R-py	pK_a[d]	Cl	Br	Cl	Br	Cl[e]	Br
4Me-py	6.03	0.61	0.60	−0.23	−0.57	2.42	4.62
2Me-py	5.96	0.49	0.02	−1.54	−1.46	0.99	3.15
2Et-py	5.76	0.36	−0.20	−2.07	−1.79	0.33	2.78
3Me-py	5.68	0.55	0.40	−0.51	−0.70	2.08	4.29
py	5.20	0.19	0.10	−0.59	−0.89	1.64	3.80
4MeCO-py	3.51	−0.60	−0.53	−1.1[f]	−1.80	0.3[f]	2.26
4CN-py	1.88		−1.43		−2.8[f]		0.4[f]

[a] Equilibrium constants in the organic phase: K_1 = [CdX$_2$(topo)(R-py)][topo]/[CdX$_2$(topo)$_2$][R-py] and K_2 = [CdX$_2$(R-py)$_2$][topo]/[CdX$_2$(topo)(R-py)][R-py]. [b] Estimated uncertainty: ±0.03. [c] $K_{ex,2}$ = [CdX$_2$(R-py)$_2$]$_{org}$/[Cd^{2+}][X$^-$]^2[R-py]$_{org}$^{2} where 'org' denotes the species exists in the organic phase; $K'_{ex,2} = K_{ex,2}\alpha_{Cd(X)}^{-1}$. [d] Ref. 3 and D. D. Perrin, 'Dissociation Constants of Organic Bases in Aqueous Solution, Supplement,' Butterworths, London, 1972. [e] Ref. 4. [f] Estimated uncertainty: ±0.3. Log $K'_{ex,0}$ = 2.04 and 4.59 ± 0.03 for the chloride and bromide complexes, respectively.

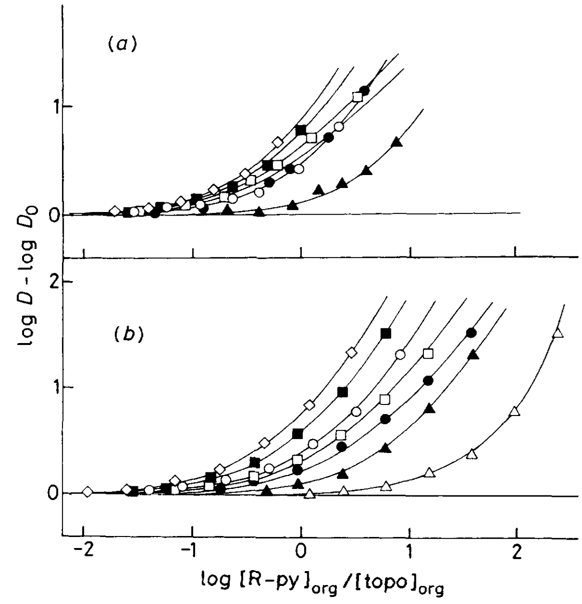

Figure 3. Plots of log D − log D_0 as a function of log [R-py]$_{org}$/[topo]$_{org}$ for the chloride complexes (*a*) and for the bromide complexes (*b*). Solid lines were calculated by using the values of log K_1 and log K_2. c_{Cd} = 1.00 × 10^{-4} mol dm^{-3}, $c_{topo,org}$ = 1.00 × 10^{-2} mol dm^{-3}. See Figure 2 for the definitions of symbols

Least-squares curve-fitting of a plot of log D as a function of log[4CN-py]$_{org}$ gave the formation constant of the tetrakis(pyridine) complex, K_c, and the extraction constant of the bis(pyridine) complex, $K'_{ex,2}$. In the same way, the extraction of the 4MeCO-py complex of cadmium(II) chloride was re-examined. The conditional extraction constants of the bis(pyridine) complexes are listed in Table 1, and the values of K_c were determined as log K_c = 1.2 and 1.0 ± 0.3 for [CdBr$_2$(4CN-py)$_4$] and [CdCl$_2$(4MeCO-py)$_4$], respectively. The calculated plots for the 4CN-py complex (——) and for the 4MeCO-py complex (– – – –) in Figure 2 reproduce well the experimental results.

Formation of Mixed-ligand Complexes.—The addition of pyridine base to the extraction systems for the bis(topo) complex causes an increase in the distribution ratio of cadmium(II) (Figure 3). This can be interpreted by the formation of a monopyridine complex [CdX$_2$(topo)(R-py)] [equation (7)], and a bis(pyridine) complex [CdX$_2$(R-py)$_2$] [equation (8)]. Consequently, the distribution ratio of cadmium(II) is given by equation (9) by using the successive

$$[\mathrm{CdX_2(topo)_2}]_{org} + \text{R-py}_{org} \xrightleftharpoons{K_1} [\mathrm{CdX_2(topo)(R\text{-}py)}]_{org} + \mathrm{topo}_{org} \quad (7)$$

$$[\mathrm{CdX_2(topo)(R\text{-}py)}]_{org} + \text{R-py}_{org} \xrightleftharpoons{K_2} [\mathrm{CdX_2(R\text{-}py)_2}]_{org} + \mathrm{topo}_{org} \quad (8)$$

$$\log D - \log D_0 = \log(1 + K_1Q + K_1K_2Q^2) \quad (9)$$

formation constants K_1 and K_2, where Q is the ratio of the ligand concentrations in the organic phase defined as [R-py]$_{org}$/[topo]$_{org}$ and D_0 denotes the distribution ratio of cadmium(II) in the absence of pyridine base. The overall formation constant of the bis(pyridine) complex, β_2, is obtained from the conditional extraction constants, as log β_2 = log $K'_{ex,2}$ − log $K'_{ex,0}$.

The successive formation constants, K_1 and K_2, were evaluated by a least-squares curve-fitting of the plot of log D − log D_0 as a function of log Q, satisfying the correlation $\beta_2 = K_1K_2$. The values of log K_1 and log K_2 thus obtained are listed in Table 1. The extraction curves calculated by using these constants are shown as solid lines in Figure 3.

Discussion

The topo complexes of cadmium(II) halides in the organic phase were determined to be monomeric, [CdX$_2$(topo)$_2$]. Consequently, the structure of the complex is estimated to be four-co-ordinate tetrahedral like the tetrachloro and the bis(pyridine) complexes. An X-ray structural study of the triphenylphosphine oxide complex of zinc(II) chloride indicates a four-co-ordinated monomeric structure.[8] The solution spectra of alkylphosphine oxide complexes of cobalt(II) also suggest a tetrahedral configuration.[9,10]

The extraction constant of the bis(topo) complex, $K'_{ex,0}$, of the bromide is much larger than that of the chloride. It can be assumed that the extraction of the cadmium(II) ion from the aqueous phase into the organic phase consists of four hypothetical steps; (i) formation of the dihalogeno complex, (ii) change from an octahedral to a tetrahedral configuration, (iii) phase transfer from the aqueous to the organic phase, and (iv) formation of the bis(topo) complex. Reactions (i) and (ii) occur in aqueous phase and (iv) in the organic phase.

The formation constants of the dibromo complexes are actually larger than those of the dichloro complex in the

Table 2. Logarithmic formation constants of the mixed-ligand complex $[CdX_2L(R\text{-py})]$, log K_{mix} *

L	$[CdCl_2L(R\text{-py})]$	$[CdBr_2L(R\text{-py})]$
topo	0.89	1.09
Halogenide ion	2.59	

* Mean values for the py, 4Me-py, and 3Me-py complexes.

Table 3. Slopes of the plots of log K_1 and log K_2 as a function of the pK_a of the conjugate acid of the pyridine base

	log K_1		log K_2	
System	Cl	Br	Cl	Br
topo	0.50	0.47	0.42[a]	0.50
Tetrahalogeno[b]	0.30		0.55[a]	

[a] Calculated from the values for the py, 4Me-py, and 3Me-py complexes. [b] Ref. 4.

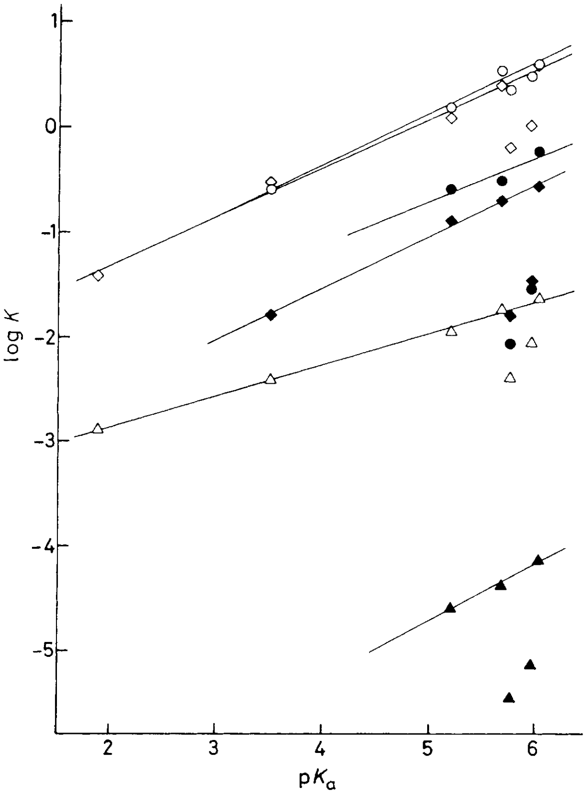

Figure 4. Plots of log K as a function of pK_a of the conjugate acid of the pyridine base for the $CdCl_2$–topo (○,●), $CdBr_2$–topo (◇,◆), and for the tetrachloro system (△,▲). Open symbols refer to log K_1 and filled ones to log K_2. The values of log K_2 for $[CdCl_2(4MeCO\text{-py})_2]$ and $[CdBr_2(4CN\text{-py})_2]$ were omitted from the plot since their uncertainties are large

aqueous phase.[7] However, this effect is not significant in the difference of the extraction constants since the difference between the logarithmic formation constants is 0.7 at most.[11] As can be seen from Table 1, the formation constants of the pyridine base complexes formed from topo complexes are not very different for the chloride and the bromide complexes; particularly the values of K_1 are scarcely different. This fact may indicate that the formation constants of $[CdX_2(topo)_2]$ in the organic phase [reaction (iv)] are eventually the same for the chloride and bromide. As the difference in size between the chloride and bromide ions is small compared with the volume of the complex $[CdX_2(topo)_2]$ the contribution of the phase-transfer step [reaction (iii)] to the difference in the extraction constants may not be important.

Consequently, the large difference between the extraction constants of bis(topo) complexes may be attributed to the configurational change from octahedral to tetrahedral. It is generally accepted that the bromo complex prefers the tetrahedral configuration rather the octahedral, compared with the chloro complex.[7] This is supported by the fact that the 4MeCO-py complex in the bromide system does not form the six-co-ordinate complex even at very high concentrations of 4MeCO-py where the chloro complex is predominantly in the six-co-ordinate structure.

The ratio of the successive formation constants, K_1/K_2, corresponds to the formation constant of the mixed-ligand monopyridine complex, K_{mix}, defined by equation (10), where L

$$[MX_2L_2] + [MX_2(R\text{-py})_2] \overset{K_{mix}}{\rightleftharpoons} 2\,[MX_2L(R\text{-py})] \quad (10)$$

denotes topo (in topo systems) or chloride ion (in the tetrachloro system). The mean values of K_{mix} for the 4Me-py, 3Me-py, and py complexes are summarized in Table 2. The values of the topo systems are much smaller than those of the tetrachloro system and are close to that statistically predicted, log K_{mix} = 0.6.[12] The large value for the tetrachloro systems has been interpreted in terms of the instability of the $[MCl_4]^{2-}$ complex caused by the electrostatic and steric repulsions between the chloride ions in the complex ion.[5] In the case of the bis(topo) complex, the co-ordinated ligand, topo, is electrically neutral and the co-ordinated oxygen atom is relatively small compared with chloride ion. Consequently, the effect of the destabilization of the $[MX_2(topo)_2]$ complex on K_{mix} is much less important. The relatively large values of log K_{mix} compared with those statistically predicted for the topo systems may be interpreted by the steric hindrance between the pyridine rings in the bis(pyridine) complex. The fact that the value of K_{mix} for the bromide complex is larger than that for the chloride is reasonably explained by the increased size of the bromide ion.

In Figure 4, the successive formation constants of pyridine complexes of cadmium(II) for the topo systems and for the tetrachloro system[4] are plotted as a function of the pK_a of the conjugate acid of the pyridine base. For all the systems these constants increase with increasing pK_a and show linear correlations except for the 2-substituted pyridine complexes. Similar correlations have been observed for the tetrahalogeno complexes of some other bivalent transition metals[1–5] and indicate that the nature of the bonding between the metal ion and nitrogen atom of the pyridine base is principally one of σ bonding and the contribution of π-back donation from the metal to the nitrogen is less important even for a relatively soft metal ion such as cadmium(II).[13]

The slopes of the plots of log K_1 and log K_2 as a function of pK_a are listed in Table 3. As the values of K_2 for the 4MeCO-py complex of the topo chloride and tetrachloro systems have a large error, the slopes of K_2 for the chloride systems were calculated from the values for the 4Me-py, 3Me-py, and py complexes. For the topo systems the slopes of the plots of log K_2 are almost the same as those of log K_1, in contrast to the slopes for the tetrachloro system. This difference in slopes may reflect the effect of the pyridine base co-ordinated in the monopyridine complex on the strength of the metal–leaving ligand bond. Since the metal–pyridine bonds are σ bonds both in the tetrachloro and the topo systems, these different phenomena may be due to the nature of the bond between the cadmium ion and the

Table 4. Differences in log K between the observed and the calculated values, $\Delta\log K$,[a] for the 2Me-py and the 2Et-py complexes

		$\Delta\log K_1$		$\Delta\log K_2$	
System		Cl	Br	Cl	Br
topo	2Me-py	0.12	0.52	1.23	0.89
	2Et-py	0.15	0.64	1.68	1.13
Tetrahalogeno	2Me-py	0.38[b]		0.96[b]	
	2Et-py	0.66[b]		1.17[b]	

[a] $\Delta\log K = \log K_{\text{calc.(l.f.e.r.)}} - \log K_{\text{obs}}$. [b] Ref. 4.

leaving ligand. The metal–oxygen bond may be principally a σ bond since the oxygen atom is 'harder' than the nitrogen atom in the topo complex.[14] Thus, these ligand substitution reactions in the topo system may be regarded as a simple σ bonding–σ bonding exchange reactions. Detailed discussions will be reported elsewhere.

The decrease in the values of K_1 and K_2 of the 2-methyl- and the 2-ethyl-pyridine (2R-py) complexes indicates the steric hindrance caused by the 2 substituent.[5] Values of $\Delta\log K$, the lowering of log K from the value interpolated by using the l.f.e.r., are listed in Table 4. It is seen that the steric hindrance of the 2-ethyl group does not differ greatly from that of the 2-methyl group for the topo systems as well as for the tetrachloro system.

The values of $\Delta\log K_1$ for the chloride complexes in the topo system are quite small compared with other 2R-py complex systems. This small steric hindrance may be caused by the peculiar combination of suitable ion sizes. In the monopyridine complex, cadmium(II) is co-ordinated by one nitrogen atom of the pyridine molecule, one oxygen atom of topo, and two chloride or bromide ions. The co-ordination of the relatively small oxygen atom (topo) to the relatively large cadmium(II) ion makes it possible to reduce the steric hindrance of the 2 substituent. In the bromo complexes, the bulkiness of the bromide ion may disturb this peculiar effect, even the co-ordination of topo. In the trichloro complexes this reduction of steric hindrance does not occur because of the bulkiness of the three chloride ions.

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Received 17*th August* 1988; *Paper* 8/03335H