Thermodynamic Study of Steric Effects on the Formation of Tetrahedral Pyridine-base Complexes of Cadmium(II) Halides

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The formation of tetrahedral complexes of cadmium(II) chloride or bromide with pyridine (py) or methyl-substituted pyridines (R-py) (R-py = 3-methyl-, 4-methyl-, 2-methyl-, 2,4-dimethyl-, 2,6-dimethyl- or 2,4,6-trimethyl-pyridine) and the steric effect of methyl substituents at pyridine on the formation of the complexes in 1,2-dichloroethane have been studied by means of liquid–liquid extraction at 25.0 °C. The formation of pyridine-base complexes from the tetrahedral trioctylphosphine oxide (topo) complex is given by equations (i) and (ii) where X refers to Cl^- or Br^-. The logarithmic formation

$$[CdX_2(topo)_2] + R\text{-}py \xrightleftharpoons{\beta_1} [CdX_2(topo)(R\text{-}py)] + topo \qquad (i)$$

$$[CdX_2(topo)_2] + 2R\text{-}py \xrightleftharpoons{\beta_2} [CdX_2(R\text{-}py)_2] + 2\ topo \qquad (ii)$$

constants, log β_1 and log β_2, of the complexes having no steric hindrance show a good linear free energy relationship with pK_a of the conjugate acid of the pyridine base. The formation constants of the 2- and 2,6-substituted pyridine complexes are lowered by the steric hindrance of the substituents. Thermodynamic parameters for the formation of bis(pyridine) complexes, $[CdX_2(R\text{-}py)_2]$, have been determined from the temperature dependence of the formation constants. For the bromo complexes, the formation of the pyridine complexes is enthalpy driven and the increase in the formation constant with increase in pK_a is due to the increase in enthalpy of the reaction, $-\Delta_r H°$. The decrease in the formation constants for the sterically-hindered complexes is caused predominantly by the decrease in entropy, *i.e.*, a decrease in a freedom of rotation of the co-ordinating pyridine. The formation of bis(pyridine) complexes of cadmium(II) chloride is entropy driven and the introduction of a steric effect causes a decrease in both of the enthalpy and entropy terms.

The formation of pyridine complexes of metal halides is one of the most simple equilibria in complex formation and is quite convenient for the study of the bond nature and steric effects of metal–ligand interactions.[1–10] The formation of tetrahedral pyridine complexes $[MX_3(R\text{-}py)]^-$ and $[MX_2(R\text{-}py)_2]$ from tetrahalogeno complexes $[MX_4]^{2-}$ (M = first-row transition metal, X = Cl^- or Br^-, R-py = substituted pyridine) has been studied in the non-polar aprotic solvent 1,2-dichloroethane.[1–4] The formation constant of the pyridine-base complex shows a good linear free energy relationship (l.f.e.r.) with the basicity of pyridine base pK_a and indicates a minimal contribution of π bonding to the M–N bond. This finding agrees with the prediction derived from the crystal structures of $[ZnCl_2(R\text{-}py)_2]$ (R = H, 4-Me, 4-PhCH=CH, 4-HO_2C or 4-CN).[11] For the reaction of the tetrahalogeno complexes $[MX_4]^{2-}$, the charge of the complex changes upon formation of the pyridine complex (from −2 to 0). The formation of $[CdX_2(R\text{-}py)_2]$ from the trioctylphosphine oxide (topo) complex $[CoX_2(topo)_2]$ has been studied by means of liquid–liquid extraction.[5] The formation constants of the mono- and bis-(pyridine) complexes $[CdX_2(topo)(R\text{-}py)]$ and $[CdX_2(R\text{-}py)_2]$ also show good l.f.e.r.s with pK_a of R-py. The stability of the 2-substituted pyridine complex is lowered by the steric hindrance of the 2-substituent.

In this paper, the formation of cadmium(II) halide complexes of methyl-substituted pyridines has been studied by means of liquid–liquid extraction and thermodynamic parameters determined by the temperature dependence of the equilibrium constants. Thermodynamic properties and an evaluation of steric effects on the formation of the pyridine-base complexes are also discussed.

Experimental

Reagents.—1,2-Dichloroethane and pyridine bases [R-py = pyridine (py), 3-methyl- (3Me-py), 4-methyl- (4Me-py), 2-methyl- (2Me-py), 2,4-dimethyl ($2,4Me_2$-py), 2,6-dimethyl- ($2,6Me_2$-py) or 2,4,6-trimethyl-pyridine ($2,4,6Me_3$-py)] were purified by distillation. The stock solutions of cadmium(II) chloride and bromide were prepared by dissolving the cadmium(II) halides in 0.1 mol dm^{-3} NaX (NaCl or NaBr) aqueous solution. 1,2-Dichloroethane solutions containing topo or R-py were prepared by methods described elsewhere.[5]

Procedure.—Distribution ratios of substituted pyridines from 0.1 mol dm^{-3} NaX aqueous solution to 1,2-dichloroethane were measured as a function of pH at various temperatures (15.0, 25.0, 35.0 and 45.0 °C). The distribution coefficients, K_d, and pK_a of the substituted pyridines at given temperatures were determined by the method described elsewhere.[2] Cadmium(II) halide was extracted from 0.1 mol dm^{-3} NaX aqueous solution to an equivalent volume of a 1,2-dichloroethane solution of topo and/or R-py (20 cm^3:20 cm^3). The pH of the aqueous solution was adjusted to *ca.* 6 in order to prevent the formation of hydroxo complexes of cadmium(II). The concentration of cadmium(II) in each phase was determined by atomic

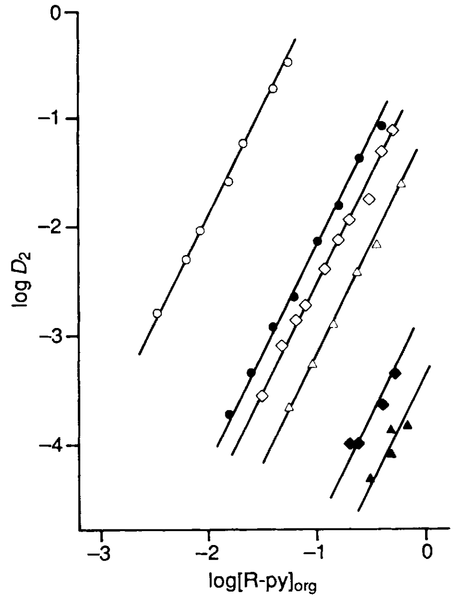

Fig. 1 Plots of log D_2 as a function of log $[\text{R-py}]_{org}$. $c_{Cd} = 10^{-4}$–10^{-3} mol dm^{-3} and $c_{NaX} = 0.1$ mol dm^{-3}. R-py = 2,4Me$_2$-py (●,○), 2,6Me$_2$-py (▲,△), 2,4,6Me$_3$-py (◆,◇). Filled symbols, chloride; open symbols, bromide

absorption spectrophotometry. The concentration of substituted pyridine in the organic phase was calculated from the pH of the aqueous solution, pK_a and K_d.[2]

Results

Formation Constants of Pyridine-base Complexes.—The extraction of cadmium(II) halides from 0.1 mol dm^{-3} NaX solution with pyridine bases has been previously studied,[3,5] the bis(pyridine) complexes $[\text{CdX}_2(\text{R-py})_2]$ [equation (1)] being reported for several R-py ligands. The extraction constant, $K_{ex,2}$ is given by equation (2) where subscript 'org' denotes

$$\text{Cd}^{2+} + 2\text{X}^- + 2\text{R-py} \xrightleftharpoons{K_{ex,2}} [\text{CdX}_2(\text{R-py})_2]_{org} \quad (1)$$

$$K_{ex,2} = \frac{[\text{CdX}_2(\text{R-py})_2]_{org}}{[\text{Cd}]^2[\text{X}]^2[\text{R-py}]_{org}^2} \quad (2)$$

the species in the organic phase. The distribution ratio of cadmium(II), $D_2 (= c_{Cd}/c_{Cd,org})$, where c_{Cd} and $c_{Cd,org}$ are the total concentrations of cadmium(II) in the aqueous and organic phases, respectively, is given by equation (3). The conditional extraction constant $K'_{ex,2}$ is defined as $K'_{ex,2} = K_{ex,2}\ \alpha_{Cd(X)}$,

$$\log D_2 = \log K'_{ex,2} + 2 \log [\text{R-py}]_{org} + 2 \log [\text{Cl}] \quad (3)$$

where $\alpha_{Cd(X)}$ is the side reaction coefficient of cadmium(II) ion for the halogeno complexes in aqueous solution. Plots of log D_2 for cadmium(II) extracted from 0.1 mol dm^{-3} NaX are shown in Fig. 1 as a function of log $[\text{R-py}]_{org}$. These plots are straight lines with slopes of two and indicate the extraction of the species $[\text{CdX}_2(\text{R-py})_2]$. The conditional extraction constants at 0.1 mol dm^{-3} NaX, $K'_{ex,2}$, were obtained from Fig. 1.

Table 1 Logarithmic formation constants of mono(pyridine) (log β_1) and bis(pyridine) complexes (log β_2) in 1,2-dichloroethane

		log β_1		log β_2	
R-py	pK_a	Cl	Br	Cl	Br
py *	5.2	0.19	0.10	−0.40	−0.79
3Me-py *	5.68	0.55	0.40	0.04	−0.30
4Me-py *	6.03	0.61	0.60	0.38	0.03
2Me-py *	5.96	0.49	0.02	−1.05	−1.44
2,4Me$_2$-py	6.75	0.92	0.50	−0.33	−0.43
2,6Me$_2$-py	6.64	−1.03	−1.16	−3.53	−3.72
2,4,6Me$_3$-py	7.25	−0.54	−0.77	−2.91	−3.10

* Ref. 5.

Table 2 Thermodynamic parameters for the extraction of the bis(topo) complexes *

System	log$K_{ex,0}$	$-\Delta_{trs}G^\circ_0$	$-\Delta_{trs}H^\circ_0$	$T\Delta_{trs}S^\circ_0$
Chloride	2.04	11.6	20	−8
Bromide	4.59	26.2	33	−7

* Units kJ mol^{-1}. Estimated error for $-\Delta_{trs}H^\circ_0$ and $T\Delta_{trs}S^\circ_0$, ±2 kJ mol^{-1}.

The extraction of cadmium halides into 1,2-dichloroethane solutions of topo has been studied and the extraction equilibria of the tetrahedral species $[\text{CdX}_2(\text{topo})_2]$ were reported[5] as in equation (4). The distribution ratio of cadmium, D_0, is given by equation (5). The conditional extraction constant of $[\text{CdX}_2(\text{topo})_2]$, $K'_{ex,0}$ $[= K_{ex,0}\ \alpha_{Cd(X)}]$, was determined as log $K'_{ex,0}$ = 2.04 for the chloro complex and 4.59 for the bromo complex.[5]

$$\text{Cd}^{2+} + 2\text{X}^- + 2\ \text{topo}_{org} \xrightleftharpoons{K_{ex,0}} [\text{CdX}_2(\text{topo})_2]_{org} \quad (4)$$

$$\log D_0 = \log K'_{ex} + 2 \log [\text{topo}]_{org} + 2 \log [\text{X}] \quad (5)$$

Under the experimental conditions that the concentrations of NaX in the aqueous solution are the same in the extraction of the topo and R-py complexes, $\alpha_{Cd(X)}$ is taken as the same for both systems. Thus the ratio of the conditional extraction constants $K_{ex,2}/K_{ex,0}$ is given by equation (6) where β_2 is the

$$K_{ex,2}/K_{ex,0} = \frac{[\text{CdX}_2(\text{R-py})_2]_{org}[\text{topo}]_{org}^2}{[\text{CdX}_2(\text{topo})_2]_{org}[\text{R-py}]_{org}^2} = \beta_2 \quad (6)$$

overall formation constant of the bis(pyridine) complex [equation (7)]. The formation constants β_2 obtained from the

$$[\text{CdX}_2(\text{topo})_2]_{org} + 2\text{R-py}_{org} \xrightleftharpoons{\beta_2} [\text{CdX}_2(\text{R-py})_2]_{org} + 2\ \text{topo}_{org} \quad (7)$$

ratio $K_{ex,2}/K_{ex,0}$ are listed in Table 1.

The addition of topo to the R-py extraction system causes an increase in the distribution ratio of cadmium(II), D (Fig. 2). The results shown in Fig. 2 cannot be explained by the formation of only the $[\text{CdX}_2(\text{topo})_2]$ complex but also requires the formation of the mono(pyridine) complex $[\text{CdX}_2(\text{topo})(\text{R-py})]$ [equation (8)].

$$[\text{CdX}_2(\text{topo})_2]_{org} + [\text{R-py}]_{org} \xrightleftharpoons{\beta_1} [\text{CdX}_2(\text{topo})(\text{R-py})]_{org} + [\text{topo}]_{org} \quad (8)$$

Thus the distribution ratio in the presence both of topo and R-py is given by equation (9), where D_2 is the distribution ratio in the absence of topo. The formation constants of the mono-

$$D = c_{Cd,org}/c_{Cd} = \frac{[\text{CdX}_2(\text{topo})_2]_{org} + [\text{CdX}_2(\text{topo})(\text{R-py})]_{org} + [\text{CdX}_2(\text{R-py})_2]_{org}}{[\text{Cd}]\alpha_{Cd(X)}} = D_2[\beta_2^{-1}([\text{topo}]_{org}/[\text{R-py}]_{org})^2 + \beta_1\beta_2^{-1}([\text{topo}]_{org}/[\text{R-py}]_{org}) + 1] \quad (9)$$

Table 3 Thermodynamic parameters for the formation of the bis(pyridine) complexes *

		$\log \beta_2$		$-\Delta_rG^\circ$		$-\Delta_rH^\circ$		$T\Delta_rS^\circ$	
R-py	pK_a	Cl	Br	Cl	Br	Cl	Br	Cl	Br
py	5.20	−4.00	−0.79	−2.3	−4.5	6	−9	−8	5
3Me-py	5.68	0.04	−0.31	0.2	−1.8	7	−5	−7	3
4Me-py	6.03	0.38	0.03	2.2	0.2	5	−5	−3	5
2Me-py	5.96	−1.05	−1.44	−6.0	−8.2	1	−7	−7	−1
2,6Me$_2$-py	6.64	−3.53	−3.72	−20.1	−21.2	−11	−1	−9	−20

* Units kJ mol^{-1}. Estimated error for $-\Delta_rH^\circ$ and $T\Delta_rS^\circ$, ±3 kJ mol^{-1} for Cl system and ±2 kJ mol^{-1} for Br system.

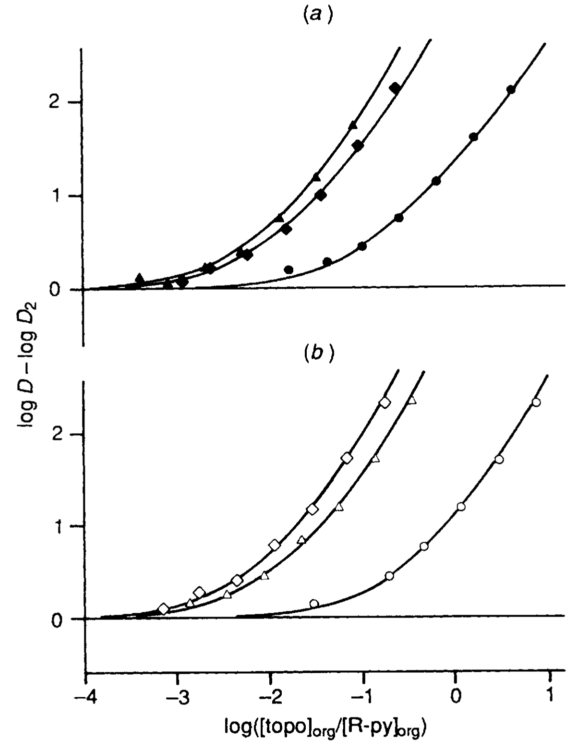

Fig. 2 Plots of $\log D - \log D_2$ as a function of $\log [\text{topo}]_{org}/[\text{R-py}]_{org}$ for the chloride complexes (*a*) and for the bromide complexes (*b*). Solid lines were calculated by using the values of $\log \beta_1$ and $\log \beta_2$. $c_{Cd} = 10^{-4}$–10^{-3} mol dm^{-3} and $c_{NaX} = 0.1$ mol dm^{-3}. $c_{R\text{-}py} = 3 \times 10^{-2}$–0.5 mol dm^{-3}. See Fig. 1 for the definition of symbols

(pyridine) complexes, β_1, were evaluated by a least-squares curve fitting of the plot of $\log D - \log D_2$ as a function of $\log [\text{topo}]_{org}/[\text{R-py}]_{org}$. The values of β_1 thus obtained are listed in Table 1. As shown in Fig. 2, solid lines, the extraction curves calculated by using the constants β_1 and β_2 listed in Table 1 reproduce the experimental data.

Thermodynamic Parameters.—The extraction constants of the bis(topo) complexes $K'_{ex,0}$ were determined at various temperatures under the same solution conditions. The enthalpy change of the extraction of [CdX$_2$(topo)$_2$] was evaluated from the slope of the plot of $\log K_{ex,0}$ *vs.* $1/T$ (Fig. 3). The standard enthalpies of transfer given by equation (4), $-\Delta_{trs}H^\circ_0$, are listed in Table 2 together with the other thermodynamic parameters for the extraction of the bis(topo) complexes, where $RT \ln K_{ex,0} = -\Delta_{trs}G^\circ_0 = -\Delta_{trs}H^\circ_0 + T\Delta_{trs}S^\circ_0$. The large difference in extraction constant $K_{ex,0}$ between the chloro and bromo complexes is caused by the difference in the enthalpy term, *i.e.*, the enthalpy of transfer of the bromo complex $-\Delta_{trs}H^\circ_0$ (=33 kJ mol^{-1}) is much larger than that of the chloro complex (20 kJ mol^{-1}). This result corroborates the conclusion deduced in the previous paper[5] that this difference is attributed to the configurational change of cadmium from octahedral to tetrahedral in the aqueous phase. That is, the enthalpy term of the bromo complex is advantageous to the formation of a tetrahedral complex, and the larger enthalpy change $-\Delta_rH^\circ$ of the bromo complex compared with the chloro complex makes it easier to form the tetrahedral bromo complex.[12–14]

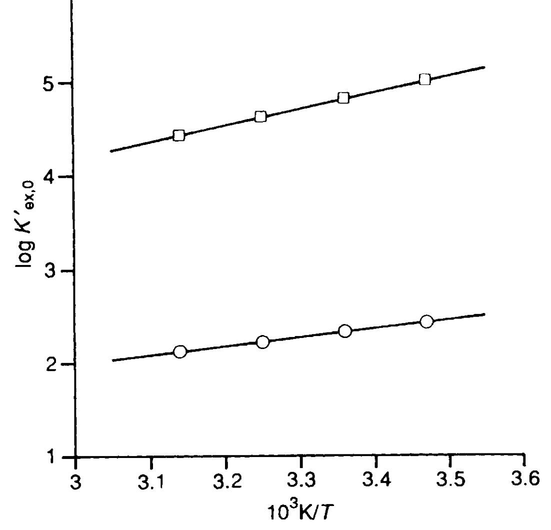

Fig. 3 Plots of $\log K'_{ex,0}$ as a function of $1/T$. $c_{Cd} = 10^{-4}$ mol dm^{-3} and $c_{NaX} = 0.1$ mol dm^{-3}. $c_{topo} = 0.1$ mol dm^{-3} for the chloride complex (○) and 5×10^{-3} mol dm^{-3} for bromide complex (□)

The temperature dependence of the extraction constants of the bis(pyridine) complexes $K_{ex,2}$ is shown in Fig. 4. The standard enthalpies of transfer of the [CdX$_2$(R-py)$_2$] complexes given by equation (1), $-\Delta_{trs}H^\circ_2$, were obtained from the slope of the plot of $\log K_{ex,2}$ *vs.* $1/T$. The free energy change for the formation of the bis(pyridine) complexes [CdX$_2$(R-py)$_2$] from [CdX$_2$(topo)$_2$] in the organic phase, *i.e.*, the standard free energy of the reaction given by equation (7), $-\Delta_rG^\circ$, is obtained from the relationship of equation (6) as $-\Delta_rG^\circ = -\Delta_{trs}G^\circ_0 + \Delta_{trs}G^\circ_0$. In the same manner, the standard enthalpy and the standard entropy of the reaction are given by $-\Delta_rH^\circ = -\Delta_{trs}H^\circ_2 + \Delta_{trs}H^\circ_0$ and $T\Delta_rS^\circ = T\Delta_{trs}S^\circ_2 - T\Delta_{trs}S^\circ_0$, respectively. Thermodynamic parameters of equation (7) thus obtained are listed in Table 3.

Discussion

Steric Hindrance.—The logarithmic overall formation constants of the mono(pyridine) complexes, β_1, and the bis(pyridine) complexes, β_2, are plotted as a function of pK_a of the conjugate acid of the pyridine base in Fig. 5. The logarithmic formation constants of R-py complexes having no substituent at the 2- or 2,6-position of pyridine show a good linear free energy relationship (l.f.e.r.) with the pK_a of the pyridine base (solid lines). The slopes of $\log \beta_1$ and $\log \beta_2$ are almost the same for both the chloro and bromo complexes.

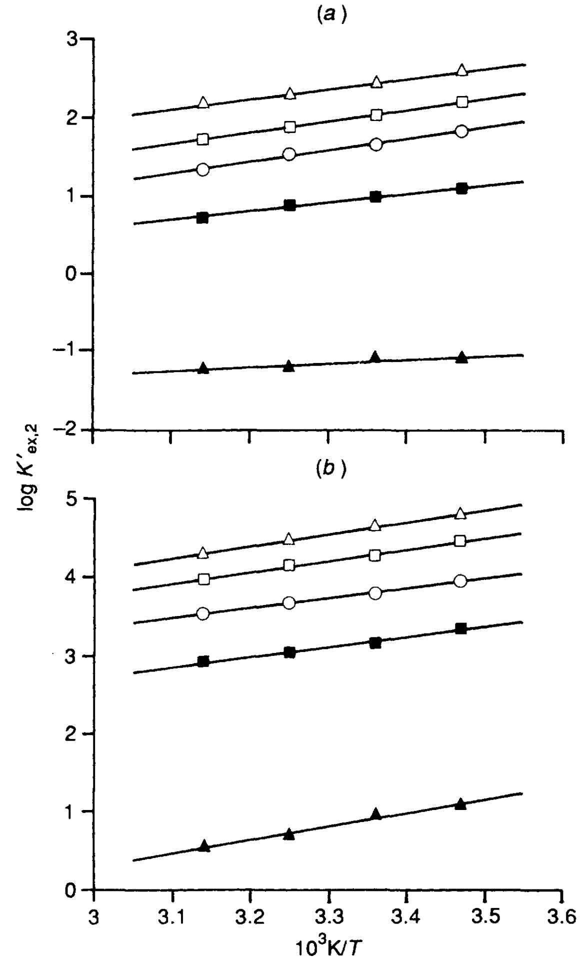

Fig. 4 Plots of log $K_{ex,2}$ as a function of $1/T$ for the chloride complexes (*a*) and for the bromide complexes (*b*). $c_{Cd} = 10^{-4}$ mol dm^{-3} and c_{NaX} = 0.1 mol dm^{-3}. $c_{R\text{-}py} = 10^{-3}$–0.4 mol dm^{-3}; R-py = py (○), 2Me-py (■), 3Me-py (□), 4Me-py (△), 2,6Me$_2$-py (▲)

Table 4 Difference in log β caused by steric effects*

R-py	Δlog β_1 Cl	Δlog β_1 Br	Δlog β_2 Cl	Δlog β_2 Br
2Me-py	0.08	0.54	1.36	1.40
2,4Me$_2$-py	0.05	0.53	1.38	1.17
2,6Me$_2$-py	1.95	2.13	4.48	4.36
2,4,6Me$_3$-py	1.77	2.10	4.44	4.33

* Δlog β = log $\beta_{calc(l.f.e.r.)}$ − log β_{obs}.

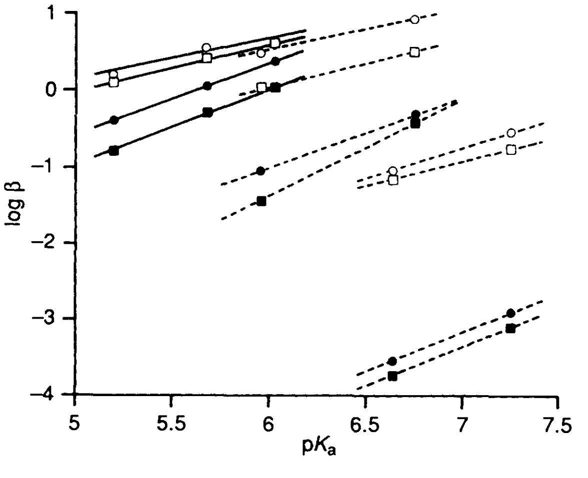

Fig. 5 Plots of log β as a function of pK_a of the conjugate acid of the pyridine base for the chloride complexes (○,●) and the bromide complexes (□,■). Open symbols, log β_1; filled symbols, log β_2. Solid lines, non-steric complexes; dotted lines, 2- or 2,6-substituted pyridine complexes

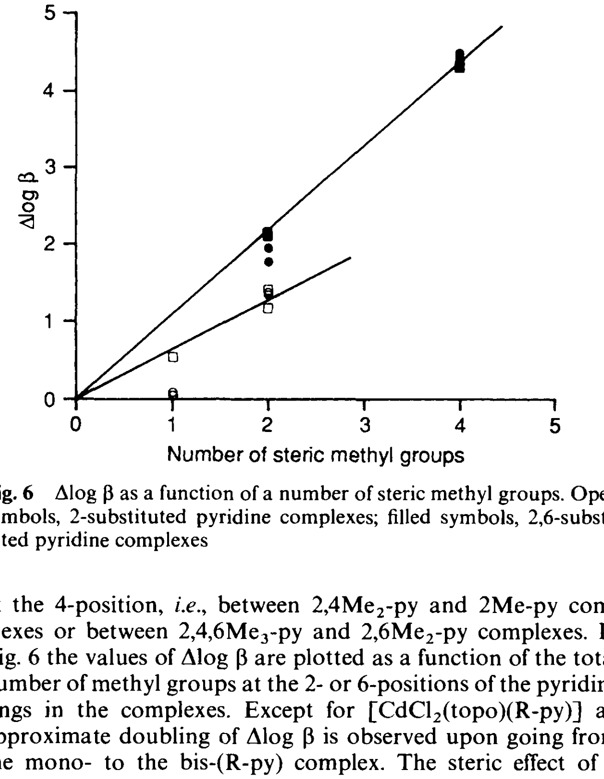

Fig. 6 Δlog β as a function of a number of steric methyl groups. Open symbols, 2-substituted pyridine complexes; filled symbols, 2,6-substituted pyridine complexes

The complexes of 2- or 2,6-substituted pyridine show a decrease in formation constant caused by the steric effect of these substituents. The formation constants of the 2,4Me$_2$-py and 2,4,6Me$_3$-py complexes are larger than those of the corresponding complexes of 2Me-py and 2,6Me$_2$-py having the same steric substituent(s) [*i.e.* at the 2 (and 6) positions], respectively. The slope of log β *vs.* pK_a between those complexes (dotted line) is almost the same as that of the complexes having no steric hindrance, that is, the effect of the basicity of the pyridine base, pK_a, on the formation constant is not altered by the steric hindrance.

Values of Δlog β and the lowering of log β of sterically hindered complexes from the values interpolated by using the l.f.e.r., are listed in Table 4. It is quite reasonable that the value of log β for the 4-substituted pyridine complex is almost the same as that of corresponding complex having no substituent at the 4-position, *i.e.*, between 2,4Me$_2$-py and 2Me-py complexes or between 2,4,6Me$_3$-py and 2,6Me$_2$-py complexes. In Fig. 6 the values of Δlog β are plotted as a function of the total number of methyl groups at the 2- or 6-positions of the pyridine rings in the complexes. Except for [CdCl$_2$(topo)(R-py)] an approximate doubling of Δlog β is observed upon going from the mono- to the bis-(R-py) complex. The steric effect of a 2-substituted pyridine complex is smaller than that of a 2,6-substituted pyridine complex even if the total number of steric methyl groups in the complex is the same, *i.e.*, the steric effect for [CdBr$_2$(2Me-py)$_2$] is smaller than that of [CdBr$_2$(topo)(2,6Me$_2$-py)]. This fact suggests that the bis(2-methylpyridine) derivatives in which the steric methyl groups are attached to different pyridines are less sterically demanding relative to a mono(2,6-dimethylpyridine) derivative. The steric hindrance of bis(pyridine) complexes scarcely differs between the chloro and bromo complexes. On the other hand, the values of Δlog β_1 for the chloro complex [CdCl$_2$(topo)(R-py)] are smaller than in other systems, in particular Δlog β_1 of [CdCl$_2$(topo)(2Me-py)] is quite small. This small steric effect may be caused by a peculiar combination of suitable sizes of the co-ordinating atoms, *i.e.* the co-ordination of the relatively small oxygen atom of topo and relatively small chloride ions to cadmium reduces the steric influence of the 2-Me substituent.

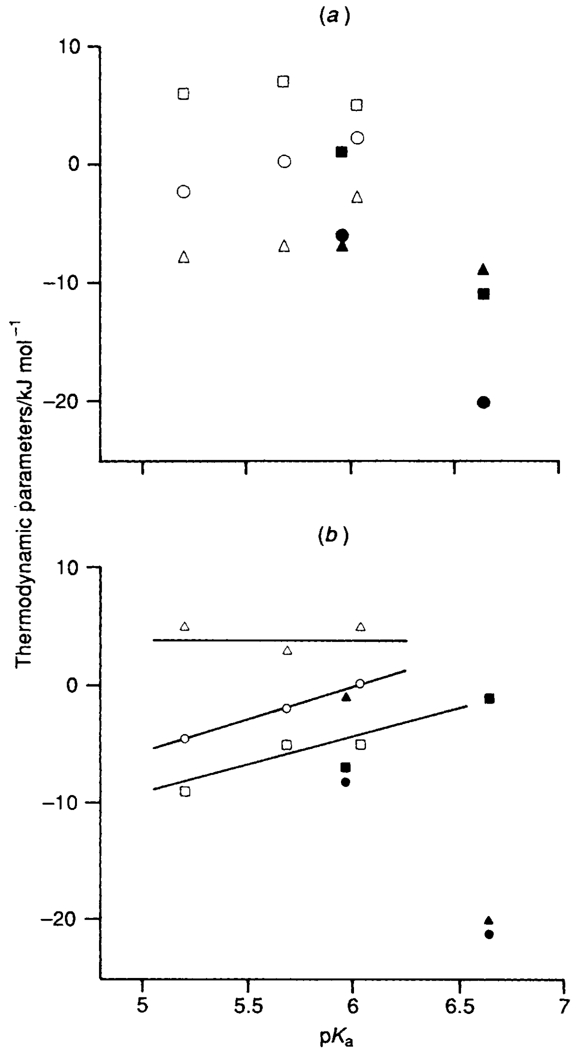

Fig. 7 Plots of thermodynamic parameters for the formation of bis(pyridine) complexes as a function of pK_a of the conjugate acid of the pyridine base for the chloride complexes (*a*) and the bromide complexes (*b*). $-\Delta_rG^\circ$ (○), $-\Delta_rH^\circ$ (□), $T\Delta_rS^\circ$ (△). Open symbols, non-steric complexes; filled symbols, 2- or 2,6-substituted pyridine complexes

Thermodynamic Parameters.—As can be seen from Table 3, the enthalpy and entropy of the formation of the bis(pyridine) complexes are quite different between the chloride and bromide systems in spite of the small difference in the free energy between them. That is, the formation of the chloro complexes having no steric hindrance is driven by enthalpy, whereas that of the bromo complexes is dominated by entropy. The thermodynamic parameters for the formation of the bis(pyridine) complexes [equation (7)] are plotted in Fig. 7 as a function of pK_a of the pyridine base. For the bromo complex system, $T\Delta_rS^\circ$ of the non-sterically hindered complexes scarcely changes with change in pK_a and the increase in $-\Delta_rG^\circ$ is caused by the increase in $-\Delta_rH^\circ$. This indicates that the increase in the stability of bis(pyridine) complexes with the basicity of the pyridine base is predominantly attributed to the strengthening of the ligand–metal bond, *i.e.* the M–N bond, by an increase in the electron density on the nitrogen atom.

The reaction enthalpy $-\Delta_rH^\circ$ for the [CdBr$_2$(2,6Me$_2$-py)$_2$] complex is larger than that of the other bromo complexes, *i.e.*, $-\Delta_rH^\circ$ increases according to the increase in the basicity. The decrease in the stability of the complex [CdBr$_2$(2,6Me$_2$-py)$_2$] is attributed to the lower value of the $T\Delta_rS^\circ$ term. These results suggest that the steric effect of the methyl groups of the 2,6-substituent does not cause a weakening of M–N bond and according to a molecular model, the nitrogen atom in [CdBr$_2$-(2,6Me$_2$-py)$_2$] can co-ordinate to the central cadmium ion directly. Thus, the decrease in the stability caused by the 'steric hindrance' is actually due to a decrease in the freedom of rotation, *i.e.* by the restriction of rotation of the pyridine molecule about the metal–nitrogen bond. King *et al.*[14] estimated the rotational entropy for this axis rotation as S_{rot} = 32 J K^{-1} mol^{-1}, *i.e.*, TS_{rot} = 9.6 kJ mol^{-1} at 25.0 °C for one molecule of pyridine. As can be seen from molecular models, the molecules of 2,6-Me$_2$py in [CdBr$_2$(2,6-Me$_2$py)$_2$] have almost no freedom of rotation. Thus, the decrease in entropy for the bis(2,6-dimethylpyridine) complexes compared with the non-sterically hindered complexes ($\Delta T\Delta_rS^\circ \approx$ 24 kJ mol^{-1}, Fig. 7), might be of reasonable magnitude. In the case of the 2-methylpyridine complex however, it is difficult to derive a clear conclusion because of a relatively small $\Delta\log\beta$.

Although for the chloride system contributions of $-\Delta_rH^\circ$ and $T\Delta_rS^\circ$ to the formation constants are not so clear compared with the bromide system, the steric effect in the complex [CdCl$_2$(2,6Me$_2$-py)$_2$] is caused by a decrease in both $-\Delta_rH^\circ$ and $T\Delta_rS^\circ$. Further information such as spectroscopic or crystallographic data will be required for a detailed discussion on the difference between the chloride and bromide systems.

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