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

Kiyoshi Sawada,* Toshio Mitsuyose, and Toshio Suzuki
Laboratory of Analytical Chemistry, Faculty of Science, Niigata University, Niigata, Japan 950-21

The formation of mixed-ligand complexes of cadmium(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, given by equations (i) and (ii), has been investigated at 25.0 °C by means of solvent extraction. The successive

$$(NBu_4)_2CdCl_4 + R\text{-}py \overset{K_1}{\rightleftharpoons} (NBu_4)CdCl_3(R\text{-}py) + NBu_4Cl \qquad (i)$$

$$(NBu_4)CdCl_3(R\text{-}py) + R\text{-}py \overset{K_2}{\rightleftharpoons} CdCl_2(R\text{-}py)_2 + NBu_4Cl \qquad (ii)$$

formation constants, K_1 and K_2, were determined as $\log K_1 = -0.56, -0.24, -0.34, -0.66, -1.00, -1.02$, and -1.50 ± 0.03, and $\log K_2 = -3.20, -2.74, -2.98, -3.75, -4.07, -3.89 \pm 0.05$, and < -4.5 for the py, 4Me-py, 3Me-py, 2Me-py, 2Et-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 bond nature of the tetrahedral complexes of the type $MX_2(R\text{-}py)_2$ ($M = Co^{II}$,[1-5] Ni^{II},[6] or Zn^{II};[7-10] X = halide ion; R-py = substituted pyridine) has been discussed. Drago and Wayland,[1,3] La Mar,[2] and Horrocks and co-workers[6] have investigated the spin delocalization from metal to pyridine base in the cobalt(II) and nickel(II) complexes and the effect of halide ion on it by means of proton n.m.r. Steffen and Palenik[9] have determined the crystal structures of a series of $ZnCl_2(R\text{-}py)_2$ complexes and reported a linear correlation between the Zn–N bond length and the basicity of R-py. These results suggest the minimal contribution of π bonding to the metal–nitrogen bond. On the other hand, Wong and Brewer[7,8] have suggested that when the basicity of the substituted pyridine is low (low electron density on nitrogen atom), the role of the π bonding on the M–N bond becomes important in the complexes.

In previous papers, we investigated the formation of the mixed-ligand complexes, $MX_2(R\text{-}py)_2$ and $MX_3(R\text{-}py)^-$, of Co^{II} [X = Cl (ref. 4) or Br (ref. 5)] and Zn^{II} [X = Cl (ref. 10)] in 1,2-dihalogenoethane solvents. The results indicated a minimal contribution of π bonding to the metal–pyridine bond in these complexes. In the present paper the formation of mixed-ligand complexes of cadmium(II), which is a relatively large and soft ion compared with the cobalt(II) and zinc(II) ions, is investigated by means of solvent extraction.

Experimental

Reagents.—1,2-Dichloroethane, tetrabutylammonium chloride, 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)] were prepared by methods similar to those described in previous papers.[4,10] Cadmium chloride was prepared by dissolving pure metal (99.99%) in concentrated hydrochloric acid.

Procedure.—A quantity of 0.1 mol dm^{-3} sodium chloride aqueous solution (20 cm^3) containing cadmium chloride was shaken with 20 cm^3 of 1,2-dichloroethane containing tetrabutylammonium chloride and/or substituted pyridine in a 50-cm^3 stoppered centrifuge tube at 25.0 ± 0.2 °C for 30 min. In order to minimize the formation of hydroxo-complexes of cadmium(II) and the effect of the protonation of the pyridine base, the pH of the aqueous phase equilibrated with the organic phase was adjusted to *ca*. 7 by addition of an appropriate amount of NaOH to the aqueous phase before shaking. After centrifugation, the concentration of cadmium(II) in each phase was determined by the methods similar to those described in the previous paper (atomic absorption spectrophotometry).[10]

Results

Extraction of Tetrachloro-complex.—The extraction equilibrium of cadmium(II) from 0.1 mol dm^{-3} NaCl aqueous solution into 1,2-dichloroethane containing tetrabutylammonium chloride is given by equation (1), where 'org' denotes the species in the organic phase and $K_{ex,0}$ is the thermodynamic extraction constant. The conditional extraction

$$Cd^{2+} + 2Cl^- + nNBu_4Cl(org) \overset{K_{ex,0}}{\rightleftharpoons} (NBu_4)_nCdCl_{2+n}(org) \qquad (1)$$

constant of the chloro-complex, $K'_{ex,0}$, is defined by equation (2), where α_{Cd} is the side-reaction coefficient of the cadmium(II)

$$K'_{ex,0} = \frac{[(NBu_4)_nCdCl_{2+n}]_{org}}{[Cd^{2+}]\alpha_{Cd}[Cl^-]^2[NBu_4Cl]_{org}^{\,n}} \qquad (2)$$

ion for the hydroxo- and chloro-complexes in the aqueous phase. As the chloride concentration and the pH are kept constant, the values of α_{Cd} and the activity coefficient of ions in the aqueous phase are constant. The distribution ratio of cadmium(II), D_0, is given by equation (3), where C denotes the total concentration of cadmium(II) in each phase.

$$D_0 = \frac{C_{Cd(org)}}{C_{Cd}} = \frac{[(NBu_4)_nCdCl_{2+n}]_{org}}{[Cd^{2+}]\alpha_{Cd}} \qquad (3)$$

Substitution of equation (2) into equation (3) leads to equation (4). The plot of $\log D_0$ as a function of $\log [NBu_4Cl]_{org}$

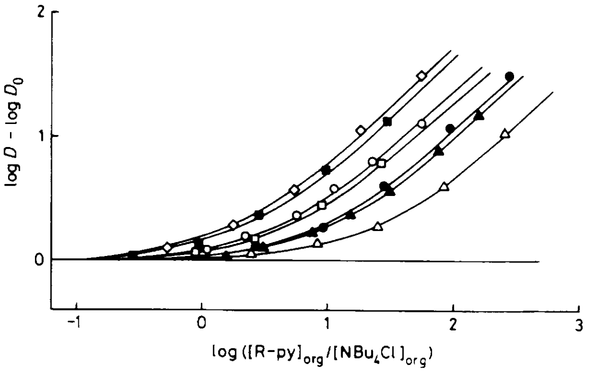

Figure 1. Plot of log D − log D_0 as a function of log ($[\text{R-py}]_{org}/[NBu_4Cl]_{org}$) where $C_{NBu_4Cl(org)} = 10^{-3}$ mol dm^{-3}, $C_{NaCl} = 0.1$ mol dm^{-3}, and $C_{Cd} + C_{Cd(org)} = 10^{-4}$ mol dm^{-3}. R-py = 4Me-py (◇), 3Me-py (■), 2Me-py (□), 2Et-py (●), py (○), 4MeCO-py (▲), and 4CN-py (△)

$$\log D_0 = \log K'_{ex,0} + 2 \log [Cl^-] + n \log [NBu_4Cl]_{org} \qquad (4)$$

is a straight line with a slope of 2. This fact indicates the formation of a tetrachloro-complex, $(NBu_4)_2CdCl_4$, in the organic phase. From the intercept of the plot, the conditional extraction constant of $(NBu_4)_2CdCl_4$ was obtained as log $K'_{ex,0} = 5.40 \pm 0.03$. The distribution ratio does not change upon change in the cadmium 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 cadmium(II). By assuming the formation of a monopyridine complex [equation (5)], the distribution ratio, D, is given by equation (7) by using the formation constant of the monopyridine complex, K_1 [equation (6)]. Substitution of equation (3) into equation (7) leads to equation (8). The plot of log

$$(NBu_4)_2CdCl_4(org) + \text{R-py}(org) \overset{K_1}{\rightleftharpoons} (NBu_4)CdCl_3(\text{R-py})(org) + NBu_4Cl(org) \qquad (5)$$

$$K_1 = \frac{[(NBu_4)CdCl_3(\text{R-py})]_{org}[NBu_4Cl]_{org}}{[(NBu_4)_2CdCl_4]_{org}[\text{R-py}]_{org}} \qquad (6)$$

$$D = \frac{[(NBu_4)_2CdCl_4]_{org} + [(NBu_4)CdCl_3(\text{R-py})]_{org}}{[Cd^{2+}]\alpha_{Cd}}$$

$$= \frac{[(NBu_4)_2CdCl_4]_{org}(1 + K_1[\text{R-py}]_{org}/[NBu_4Cl]_{org})}{[Cd^{2+}]\alpha_{Cd}} \qquad (7)$$

$$\log D - \log D_0 = \log \{1 + K_1[\text{R-py}]_{org}/[NBu_4Cl]_{org}\} \qquad (8)$$

D − log D_0 as a function of log ($[\text{R-py}]_{org}/[NBu_4Cl]_{org}$) is shown in Figure 1, where the concentration of pyridine base in the organic phase, $[\text{R-py}]_{org}$, was calculated by using the distribution ratio of R-py determined in the previous paper.[10] The values of log K_1 obtained by curve-fitting with the normalized curve, log (1 + x) *vs.* log x (solid lines in Figure 1) are listed in the Table. As can be seen from equation (8), the value of K_1 is obtained independent of the side reaction and activity coefficients of ions in the aqueous phase. The calculated curves are in good agreement with the experimental results. As will be shown below, the formation constant of the bis-pyridine complex is so small compared with K_1 that the formation of the higher pyridine complexes is negligible under these conditions.

Table. Successive formation constants of $(NBu_4)CdCl_3(\text{R-py})$, K_1, and $CdCl_2(\text{R-py})_2$, K_2, and extraction constants of $(NBu_4)_2CdCl_4$, $K'_{ex,0}$, and $CdCl_2(\text{R-py})_2$, $K'_{ex,2}$ [a]

R-py	pK_a [b]	log $K'_{ex,2}$ [c]	log K_1	log K_2
4Me-py	6.03	2.42	−0.24	−2.74
3Me-py	5.68	2.08	−0.34	−2.98
2Me-py	5.96	0.99	−0.66	−3.75
2Et-py	5.76	0.33	−1.00	−4.07
py	5.20	1.64	−0.56	−3.20
4MeCO-py	3.51	0.49	−1.02	−3.89
4CN-py	1.88	< −0.6	−1.50	< −4.5

[a] Estimated uncertainty ±0.03 for log $K'_{ex,2}$ and log K_1 and ±0.05 for log K_2. [b] Ref. 10 and D. D. Perrin, 'Dissociation Constants of Organic Bases in Aqueous Solution, Supplement,' Butterworths, London, 1972. [c] log $K'_{ex,0} = 5.40 \pm 0.03$.

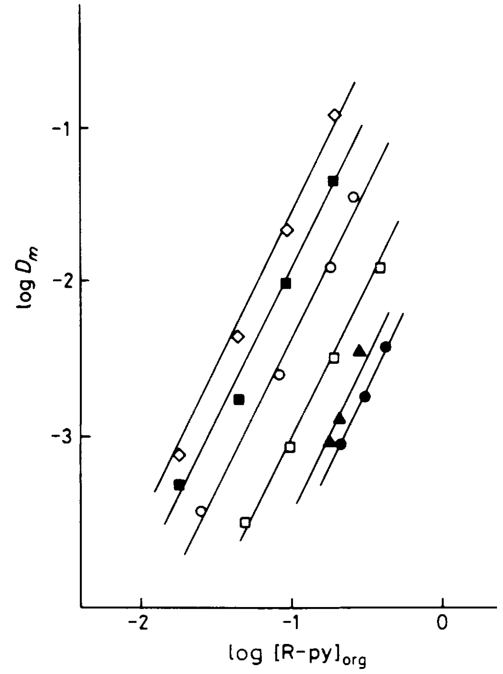

Figure 2. Plot of log D_m as a function of log $[\text{R-py}]_{org}$ where $C_{NaCl} = 0.1$ mol dm^{-3} and $C_{Cd} + C_{Cd(org)} = 10^{-4}$ mol dm^{-3}. For definition of symbols see legend of Figure 1

Formation of Bis-pyridine Complexes.—The extraction equilibrium of cadmium(II) from a sodium chloride aqueous solution into 1,2-dichloroethane containing the substituted pyridine is given by equation (9). The conditional extraction

$$Cd^{2+} + 2Cl^- + m\text{R-py}(org) \overset{K_{ex,m}}{\rightleftharpoons} CdCl_2(\text{R-py})_m(org) \qquad (9)$$

constant of the mixed-ligand complex, $CdCl_2(\text{R-py})_m$, is defined by equation (10), and the distribution ratio of

$$K'_{ex,m} = \frac{[CdCl_2(\text{R-py})_m]_{org}}{[Cd^{2+}]\alpha_{Cd}[Cl^-]^2[\text{R-py}]_{org}{}^m} \qquad (10)$$

cadmium(II), D_m, by equation (11). Substitution of equation (10) into equation (11) leads to equation (12). The plot of

$$D_m = \frac{[\mathrm{CdCl_2(R\text{-}py)}_m]_{\mathrm{org}}}{[\mathrm{Cd}^{2+}]\alpha_{\mathrm{Cd}}} \qquad (11)$$

$$\log D_m = \log K'_{\mathrm{ex},m} + 2 \log [\mathrm{Cl}^-] + m \log [\mathrm{R\text{-}py}]_{\mathrm{org}} \qquad (12)$$

$\log D_m$ as a function of $\log [\mathrm{R\text{-}py}]_{\mathrm{org}}$ is shown in Figure 2. The plot falls on a straight line with a slope of 2 (solid lines in Figure 2). Thus, the number of m is obtained as 2, *i.e.*, the extracted species is determined as $\mathrm{CdCl_2(R\text{-}py)_2}$. The values of $K'_{\mathrm{ex},2}$ obtained from the intercept of the plot are listed in the Table. The extraction constant of the 4CN-py complex is too small to obtain a reliable value.

The successive formation constant of the bis-pyridine complex in the organic phase, K_2 [equation (13)], is correlated with the formation constant, K_1, and the extraction constants, $K'_{\mathrm{ex},0}$ and $K'_{\mathrm{ex},2}$ as $K_1K_2 = K'_{\mathrm{ex},2}/K'_{\mathrm{ex},0}$. The formation

$$\mathrm{(NBu_4)CdCl_3(R\text{-}py)(org)} + \mathrm{R\text{-}py(org)} \xrightleftharpoons{K_2} \mathrm{CdCl_2(R\text{-}py)_2(org)} + \mathrm{NBu_4Cl(org)} \qquad (13)$$

constants of the bis-pyridine complexes, K_2, thus obtained are listed in the Table.

Discussion

The complexes formed in the organic phase have a tetrahedral configuration, and the anionic species form uncharged ion pairs with the cation, $\mathrm{NBu_4^+}$, as $[\mathrm{NBu_4}]^+[\mathrm{CdCl_3(R\text{-}py)}]^-$ and $[\mathrm{NBu_4}]^+{}_2[\mathrm{CdCl_4}]^{2-}$.[4,10,11] As can be seen from Figure 2, the octahedral complexes of dichlorocadmium(II), $\mathrm{CdCl_2(R\text{-}py)_4}$, are scarcely formed, even at relatively high R-py concentration. The plots of $\log K_1$ and $\log K_2$ as a function of the pK_a of the conjugate acid of R-py are shown in Figure 3 along with the results of the zinc(II) (ref. 10) and cobalt(II) (ref. 4) complexes. The plots of $\log K_1$ and $\log K_2$ of the cadmium(II) complexes show linear correlations with the pK_a as well as those of the zinc(II) and cobalt(II) complexes. The positive slope of the plots indicates that the cadmium–nitrogen bond strength increases with increase in electron density on the nitrogen atom. Thus, the contribution of π bonding in the metal–pyridine bond is minimal even in complexes of a relatively soft ion such as cadmium(II).[12]

The slope of the plot of $\log K_1$ of the cadmium complexes is almost the same as those of the cobalt(II) and zinc(II) complexes. However, the slope of $\log K_2$ of the cadmium(II) complexes is relatively small compared with those of the other metal complexes and almost the same as those of $\log K_1$. The fact that the slopes of $\log K_2$ of the cobalt(II) and zinc(II) complexes are larger than those of $\log K_1$ suggests that the co-ordination of the substituted pyridine, having a higher electron density on the nitrogen atom, causes the decrease in the bond strength of M–Cl (ref. 10). On the other hand, the fact that the slope of $\log K_2$ of the cadmium complex is almost the same as that of $\log K_1$ suggests that the Cd–Cl bond strength is less sensitive to the electron density on the nitrogen atom of R-py. This may be interpreted by the relatively large ion size and softness [12] of the cadmium(II) ion.

The 2Me-py and 2Et-py complexes of cadmium(II) have smaller K_1 and K_2 values compared with the other complexes of pyridine bases having a comparable pK_a. Thus, the substituent at the 2-position of pyridine gives rise to a steric effect even in the complexes of comparably large ion such as cadmium(II). But as can be seen from Figure 3, the effect is less significant than that in the cobalt(II) and zinc(II) complexes.

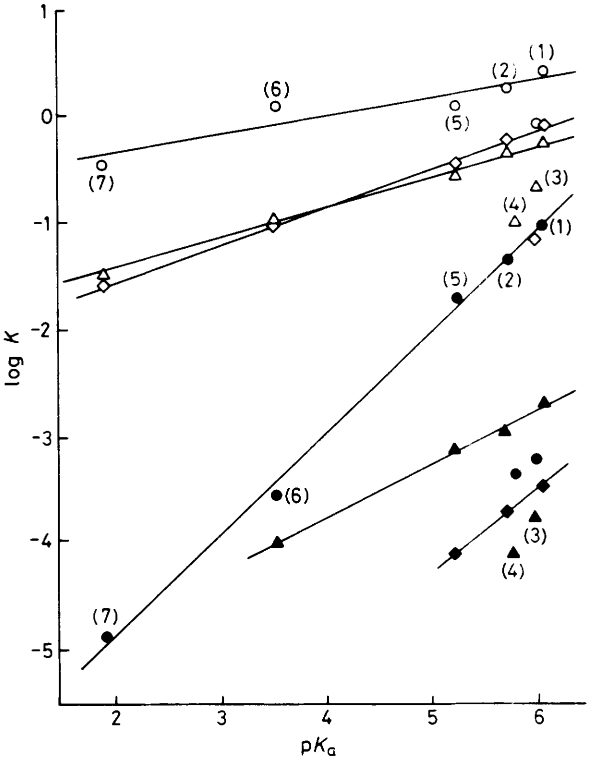

Figure 3. Plot of $\log K_1$ (open symbols) and $\log K_2$ (filled symbols) of cadmium(II) (△, ▲), zinc(II) (○, ●), and cobalt(II) (◇, ◆) complexes as a function of the pK_a of the conjugate acid of the substituted pyridine. R-py = 4Me-py (1), 3Me-py (2), 2Me-py (3), 2Et-py (4), py (5), 4MeCO-py (6), and 4CN-py (7)

Acknowledgements

We are grateful to the Ministry of Education, Science, and Culture (Japan) for financial support.

References

1 B. B. Wayland and R. S. Drago, *J. Am. Chem. Soc.*, 1966, **88**, 4597.
2 G. N. La Mar, *Inorg. Chem.*, 1967, **6**, 1936.
3 R. S. Drago and B. B. Wayland, *Inorg. Chem.*, 1968, **7**, 628.
4 K. Sawada and T. Suzuki, *J. Inorg. Nucl. Chem.*, 1981, **43**, 2031.
5 K. Sawada, K. Miura, and T. Suzuki, *Bull. Chem. Soc. Jpn.*, 1982, **55**, 780.
6 R. H. Holm, G. W. Everett, jun., and W. D. Horrocks, jun., *J. Am. Chem. Soc.*, 1966, **88**, 1071.
7 P. T. T. Wong, *Inorg. Chem.*, 1975, **14**, 2271.
8 P. T. T. Wong and D. G. Brewer, *Can. J. Chem.*, 1969, **47**, 4589.
9 W. L. Steffen and G. J. Palenik, *Inorg. Chem.*, 1977, **16**, 1119.
10 K. Sawada, T. Sakaguchi, and T. Suzuki, *J. Chem. Soc., Dalton Trans.*, 1983, 447.
11 I. M. Walker and R. S. Drago, *J. Am. Chem. Soc.*, 1968, **90**, 6951.
12 S. Yamada and M. Tanaka, *J. Inorg. Nucl. Chem.*, 1975, **37**, 587.

Received 11*th July* 1983; *Paper* 3/1186