Thermal Stability of Pyridine Base Complexes of Cadmium Chloride

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The heat of decomposition of a series of crystalline pyridine base (Rpy) complexes of cadmium chloride was determined by means of differential scanning calorimetry, where the complexes were bis(pyridine base) complexes, $CdCl_2{\cdot}2Rpy$ (Rpy = pyridine and 4-methyl-, 3-methyl-, 4-acetyl- and 4-cyanopyridine) and mono(pyridine base) complexes, $CdCl_2{\cdot}Rpy$ (Rpy = 2-methyl- and 2-ethylpyridine). The heats of dissolution of the pyridine base complexes, cadmium chloride $CdCl_2$, and pyridine bases in a non-polar aprotic solvent, 1,2-dichloroethane, containing tetrabutylammonium chloride were determined by a calorimetry. The stability of the crystalline complexes is discussed in connection with the heat of dissolution and reaction of the complexes in solution. The stability of the complexes is explained by various interactions, such as the basicity and steric hindrance of the pyridine bases and the intermolecular interaction between the complexes.

Pyridine base (Rpy) complexes of metal halides comprise one of the most simple systems to study the effect of the basicity and structure of the ligand on complex formation. The crystal structures of the pyridine complex[1,2] and 3- and 4-methylpyridine complexes[2] of cadmium chloride, $CdCl_2{\cdot}2Rpy$, have been determined by single-crystal X-ray diffraction. The cadmium atom in the complex is octahedrally coordinated with four chloride ions in the equatorial plane, and two nitrogen atoms of the pyridine base are in axial positions, and is bridged by two chloride ions to form a polymeric linear chain. This structure is quite common in a type of $MX_2{\cdot}2L$ (X, halide ion; L, monodentate ligand) complexes.[3] We studied the mechanism of thermal decomposition of crystalline pyridine base complexes of cadmium chloride by means of thermogravimetry (TG) and differential thermal analysis (DTA),[4] and reported that the decomposition of the complexes proceeds by a stepwise loss of the pyridine base in the same manner as the complexes of cobalt(II)[5] and other transition metals.[6]

When those complexes are dissolved in water, they are decomposed into the component molecules and ions because of the high hydration energy of the metal ion. On the other hand, they form a stable complex in non-solvating solvents, such as 1,2-dichloroethane (1,2-DCE). We have studied the thermodynamics of complex formation of metal halide with a pyridine base in solution. The bis(pyridine base) complexes of cadmium halide, $CdCl_2(Rpy)_2$, generally have a tetrahedral configuration in a non-coordinating solvent. The stability of the complex, i.e., the cadmium-pyridine bond strength, increases due to an increase in the basicity of the pyridine base (pK_a of conjugate acid of Rpy)[7,8] in the same manner as that of the other divalent transition metal complexes.[9] This fact indicates that the metal-pyridine bond is predominantly σ-bonding, and that the contribution of π-bond is minimal in the complexes.

The stability and kinetics of the decomposition of the crystalline complexes do not show a direct correlation with the basicity of Rpy.[4,5] The intermolecular interaction is important in the crystalline complexes in addition to an intramolecular interaction, i.e., the coordination of a pyridine base to a metal ion. Thus, in order to understand the interactions in a crystalline complex it is important to discuss the stability by comparing with the results of solution thermodynamics, which give information about the intramolecular interaction. There has been no investigation combined the decomposition reaction of crystals with the solution thermodynamics.

In the present study, the decomposition of the pyridine base complexes of cadmium chloride was studied by thermogravimetry (TG) and differential scanning calorimetry (DSC). The heat of dissolution of the complexes and component compounds were also measured by calorimetry. The stability of the complexes was discussed by taking into consideration the thermodynamics of the dissolution and complex formation in solution.

Experimental

Reagents. Bis(pyridine base) and mono(pyridine base) complexes of cadmium chloride were prepared by a method described elsewhere.[4] G. R. grade cadmium chloride (Nakarai Chemicals) was dried at 110 °C in vacuo. After washing twice with distilled water, 1,2-dichloroethane was dehydrated with molecular sieve 3A (Wako) and distilled. Tetrabutylammonium chloride (T·Cl) was of analytical grade (Tokyo Kasei).

Measurements. TG and DTA curves of the complexes were measured by a Rigaku Thermoflex TG–DTA M 807 (heating rate: 10 $°C\ min^{-1}$) under the conditions of flowing dry nitrogen (flow rate: 50 $cm^3\ min^{-1}$). The heat of decomposition of crystalline complexes was obtained from differential scanning calorimetric (DSC) curves recorded on a Shinku Rikou 1500 M5/L. About 10 mg of a specimen was placed in an aluminum crucible and α-alumina was used as a reference material for both measurements, TG–DTA and DSC. The experiment was triplicated. The heat of

DSC was calibrated with the heat of melting of indium. The heat of dissolution of the pyridine base complexes, cadmium chloride and pyridine bases into 0.1 mol dm^{-3} tetrabutylammonium chloride 1,2-dichloroethane solution was measured at 25.0 °C by a twin-type conduction microcalorimeter (Oyodenki CM 204 S 2), which was calibrated by an electrical heater. A glass ampule containing about 100 mg of a sample was broken in 40 cm^3 of a 0.1 mol dm^{-3} T·Cl 1,2-DCE solution, and the temperature difference was recorded. The experiment was duplicated. The heats of DSC and dissolution were obtained from the peak area.

Results and Discussion

Heat of Decomposition. The TG and DSC curves of the thermal decomposition of bis(pyridine base) complexes, $CdCl_2py_2$ and $CdCl_2(4ac\text{-}py)_2$, are shown in Fig. 1 as examples, where py and 4ac-py refer to pyridine and 4-acetylpyridine, respectively. As can be seen from the TG and DSC curves of the pyridine complex (Fig. 1, solid lines), the thermal decomposition of bis(pyridine base) complexes, $CdCl_2{\cdot}2py$, is generally given by the following three steps[4] in a similar manner as the decomposition of cobalt(II) complexes:[5]

$$CdCl_2{\cdot}2Rpy(c) \rightarrow CdCl_2{\cdot}Rpy(c) + Rpy(g), \qquad (1)$$

$$CdCl_2{\cdot}Rpy(c) \rightarrow CdCl_2{\cdot}2/3Rpy(c) + 1/3Rpy(g), \qquad (2)$$

$$CdCl_2{\cdot}2/3Rpy(c) \rightarrow CdCl_2(c) + 2/3Rpy(g), \qquad (3)$$

where (c) and (g) refer to the crystal and gas phases, respectively. The weight losses form $CdCl_2{\cdot}2py$ to $CdCl_2{\cdot}py$ [step (1); 22.8%] and form $CdCl_2{\cdot}2py$ to $CdCl_2$ [steps (1) to (3); 45.9%], obtained by TG measurements, agree with those of the calculated values (23.2 and 46.4%). The weight loss obtained from the TG curve shows good agreement with calculated value for any complexes. The heat of decomposition (ΔH_{dec}) of each step was determined by analyzing the DSC curve. The complexes of 3-methylpyridine (3Me-py) and 4-methylpyridine (4Me-py) show the same decomposition steps as the py complex. In the case of the 4-acetylpyridine (4ac-py) complex (Fig. 1, dotted line), the sum of ΔH_{dec} of the steps (1) and (2) were obtained because the decomposition point of step (1) shifted to a high temperature, and this step merged with step (2). The results of the heat of decomposition for each step obtained by the DSC are listed in Table 1. The sum of the heat of steps (1), (2) and (3) is depicted as ΔH_{dec}(tot) in Table 1, which corresponds to the following overall decomposition reaction:

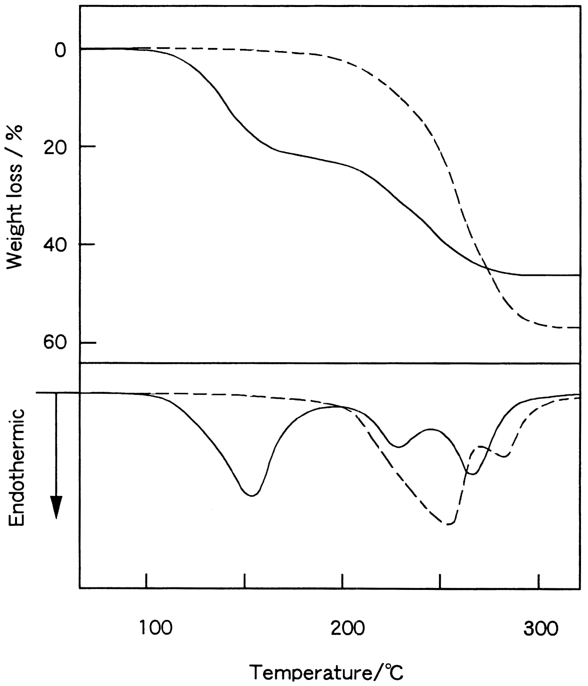


Fig. 1. TG and DSC curves of thermal decomposition of pyridine complex $CdCl_2{\cdot}2py$(solid lines) and 4-acetylpyridine complex $CdCl_2{\cdot}2(4ac\text{-}py)$ (broken lines).

$$CdCl_2{\cdot}2Rpy(c) \rightarrow CdCl_2(c) + 2Rpy(g). \qquad (4)$$

Pyridine bases having a substituent at the 2-position, 2-methylpyridine (2Me-py) and 2-ethylpyridine (2Et-py), do not form bis(pyridine base) complexes but only mono(pyridine base)

Table 1. Heat of Decomposition of Pyridine Base Complexes of Cadmium Chloride[a)]

Rpy	4Me-py	3Me-py	py	4ac-py	4CN-py	2Me-py	2Et-py
pK_a	6.03	5.68	5.20	3.51	1.88	5.96	5.76
ΔG_R[b)]	2.2	0.2	−2.3	−9.7	−17.5	−6.0	−9.7
Step (1)	74.0	75.1	73.2	134.8[c)]	79.0		
Step (2)	24.8	30.1	27.0		79.7[d)]	74.2[d)]	70.2[d)]
Step (3)	63.8	53.4	54.7	52.1			
Steps (2)+(3)	88.6	83.5	81.7		79.7	74.2	70.2
ΔH_{dec}(tot)[e)]	162.6	158.6	154.9	186.9	158.7		

a) kJ mol^{-1}. Estimated error is ±2 kJ mol^{-1}. b) Free energy change of reaction of $CdCl_2{\cdot}(Rpy)_2$ with T·Cl in solution at 25.0 °C. See text. c) Sum of Steps (1) and (2). d) Sum of Steps (2) and (3). e) Sum of Steps (1), (2) and (3).

complexes in a crystal, although the tetrahedral complex $CdCl_2{\cdot}(Rpy)_2$ is formed in solution, as described later. Thus, the heat of decomposition of the monopyridine complexes was measured. Because steps (2) and (3) of these complexes overlap with each other, the total heat of decomposition of $CdCl_2{\cdot}Rpy$ to $CdCl_2$ (Eq. 5) was obtained (Table 1):

$$CdCl_2{\cdot}Rpy(c) \rightarrow CdCl_2(c) + Rpy(g). \tag{5}$$

Heat of Dissolution. In order to study the stability of the pyridine base complexes of cadmium chloride in solution, the heats of dissolution of $CdCl_2{\cdot}2Rpy$, $CdCl_2$ and Rpy were measured. 1,2-Dichloroethane (1,2-DCE) was chosen as the solvent, because it has been most commonly used to study complex formation in a non-solvating solvent. Because of the low solubility of bis(pyridine base) complexes and cadmium chloride in a pure solvent, the heat of dissolution into tetrabutylammonium chloride (T•Cl) 1,2-DCE solution was measured. Under the present experimental conditions, the predominant species of the cadmium ion in the solution is a tetrachloro complex.[7] The dissolution reaction of the crystalline complex, $CdCl_2{\cdot}2Rpy$, into a 1,2-DCE solution of T•Cl is given by:

$$CdCl_2{\cdot}2Rpy(c) + 2T{\cdot}Cl(s) \rightarrow T_2CdCl_4(s) + 2Rpy(s). \tag{6}$$

This reaction consists of following two steps:

$$CdCl_2{\cdot}2Rpy(c) \rightarrow CdCl_2(Rpy)_2(s) : \Delta H_{dis}(comp), \tag{7}$$

$$CdCl_2(Rpy)_2(s) + 2T{\cdot}Cl(s) \rightarrow T_2CdCl_4(s) + 2Rpy(s) : \Delta H_R(comp). \tag{8}$$

Thus, the heat of dissolution of $CdCl_2{\cdot}2Rpy$ is given by $\Delta H_{dis}(comp) + \Delta H_R(comp)$ [A], where the complexes $CdCl_2{\cdot}(Rpy)_2$ and T_2CdCl_4 are tetrahedral monomer in a 1,2-DCE solution (Scheme 1). In the same manner, the dissolution reaction of crystalline $CdCl_2$ is

$$CdCl_2(c) + 2T{\cdot}Cl(s) \rightarrow T_2CdCl_4(s), \tag{9}$$

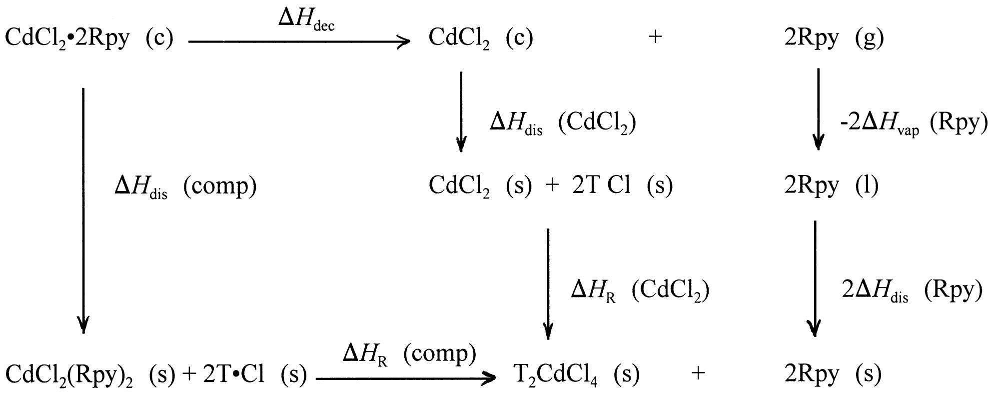
which consists of following two steps:

$$CdCl_2(c) \rightarrow CdCl_2(s) : \Delta H_{dis}(CdCl_2), \tag{10}$$

$$CdCl_2(s) + 2T{\cdot}Cl(s) \rightarrow T_2CdCl_4(s) : \Delta H_R(CdCl_2). \tag{11}$$

The heat of dissolution of $CdCl_2$ is given by $\Delta H_{dis}(CdCl_2) + \Delta H_R(CdCl_2)$ [B]. The heat of dissolution of gaseous Rpy into 1,2-DCE solution is given by the heats of vaporization (ΔH_{vap}) and dissolution (ΔH_{dis}) of liquid Rpy as $2[\Delta H_{dis}(Rpy) - \Delta H_{vap}(Rpy)]$ per two moles [C]. The experimentally obtained values of each reaction ([A], [B] and [C]) are listed in Table 2, where the values of $\Delta H_{vap}(Rpy)$ are cited from the literature.[10]

The heat of thermal decomposition of crystalline $CdCl_2{\cdot}2Rpy$ to $CdCl_2$ is also given by the heat of the cycle through the solution reactions, as shown in Scheme 1. Accordingly, the heat of decomposition, ΔHdec(calc), is evaluated by



(c), Crystal; (s), Solution; (l), Liquid; (g), Gas

Scheme 1.

Table 2. Heats of Dissolution and Reaction of Bis(pyridine base) Complexes, Cadmium Chloride, and Pyridine Bases[a)]

R_{py}	4Me-py	3Me-py	py	4ac-py	4CN-py
$\Delta H_{dis}(comp) + \Delta H_R(comp)$	30.3	17.4	18.8	25.9	18.3
$\Delta H_{dis}(Rpy)$	−0.86	−0.78	−0.10	−0.49	0.70
$\Delta H_{vap}(Rpy)^{b)}$	39.2	39.1	35.1	51.8	42.9
$\Delta H_{dis}(CdCl_2) + \Delta H_R(CdCl_2)$ −54.2					
$\Delta H_{dec}(calc)^{c)}$	164.6	151.4	143.4	184.7	156.9

a) kJ mol^{-1}. Estimated error is ±0.5 kJ mol^{-1} except for $\Delta H_{dis}(Rpy)$ (±0.1 kJ mol^{-1}). b) Ref. 10.
c) $\Delta H_{dec}(calcd) = [\Delta H_{dis}(comp) + \Delta H_R(comp)] - [\Delta H_{dis}(CdCl_2) + \Delta H_R(CdCl_2)] - 2[\Delta H_{dis}(Rpy) - \Delta H_{vap}(Rpy)]$.

$$\Delta H_{\mathrm{dec}}(\mathrm{calc}) = \underbrace{[\Delta H_{\mathrm{dis}}(\mathrm{comp}) + \Delta H_{\mathrm{R}}(\mathrm{comp})]}_{[\mathrm{A}]} - \underbrace{[\Delta H_{\mathrm{dis}}(\mathrm{CdCl_2}) + \Delta H_{\mathrm{R}}(\mathrm{CdCl_2})]}_{[\mathrm{B}]} - 2\underbrace{[\Delta H_{\mathrm{dis}}(\mathrm{Rpy}) - \Delta H_{\mathrm{vap}}(\mathrm{Rpy})]}_{[\mathrm{C}]}. \tag{12}$$

The values of the total heat of decomposition of $CdCl_2$•2Rpy to $CdCl_2$, calculated by Eq. 12, ΔH_{dec}(calc), are listed in Table 2. The value of heat of decomposition of the complex obtained by calorimetric measurements, ΔH_{dec}(calc), almost agrees with that obtained by DSC measurements, ΔH_{dec}(tot) (Table 1), although the discrepancies between them are somewhat larger than those estimated from the experimental errors. This discrepancy might be caused by the temperature difference between the two methods, i.e., the temperature of the final product, $CdCl_2$, of TG (decomposition point) is much higher than 25 °C and ΔH_{dec}(tot) must change by temperature.

Stability of Pyridine Base Complexes of Cadmium Chloride. The crystal structures of bis(pyridine base) complexes of cadmium chloride, $CdCl_2$•2Rpy, were determined for py,[1,2] 3Me-py and 4Me-py complexes.[2] The crystal structures of these complexes are substantially the same among them. That is, the cadmium atom is octahedrally coordinated with four chloride ions in a di-μ-chloro polymeric linear chain and two nitrogen atoms of pyridine in a trans configuration. There is no particular interaction, such as hydrogen bond, between the chains, and the crystal is stabilized by a van der Waals interaction between the pyridine bases of the neighboring chains. It was confirmed by an X-ray powder diffraction that the structure of the final product, $CdCl_2$, of the thermal decomposition of the complexes is the same irrespective of the kind of pyridine bases. Thus, the heat of decomposition of the complex, ΔH_{dec}(tot), indicates the relative stability of crystalline complexes, $CdCl_2$•2Rpy. The fundamental structure of the $CdCl_2$ crystal is similar to that of $CdCl_2$•2Rpy. That is, $CdCl_2$ consists of a linear polymeric chain of cadmium atoms bridged by two chloride ions in the same manner as that of $CdCl_2$•2Rpy complexes, while the axial positions of the cadmium atom are coordinated by chloride ions of the neighboring chains.[3]

The values of pK_a of the conjugate acids of pyridine bases and the free energy change for the formation of T_2CdCl_4 from $CdCl_2(Rpy)_2$ in 1,2-DCE [ΔG_{R}(comp) for equilibrium 8][7a] are listed in Table 1. The value of ΔG_{R}(comp) shows a good linear correlation with pK_a, except for the sterically hindered complexes (2Me- and 2Et-py), i.e., the stability of the complex decreases due to a decrease in the basicity of the pyridine base (pK_a) in solution.

The value of ΔH_{dec}(tot) of 4Me-py, 3Me-py and pyridine complexes decreases in the order of 4Me-py $>$ 3Me-py $>$ py, which agrees with the order of the basicity of pyridine base (Table 1). These results indicate that the difference in the stability between those complexes is predominantly explained by that of coordination ability of the pyridine bases in the same manner as in solution. On the other hand, ΔH_{dec}(tot) of 4ac-py complex shows a quite large value, and that of 4CN-py complex is relatively large in spite of the very low basicity of 4CN-py. These data suggest that some extra interaction exists in these complexes in the crystalline state. As can be seen from Table 2, the values of heat of vaporization of 4ac-py and 4CN-py are larger than those of py or 3Me- and 4Me-py. This fact indicates the existence of an intermolecular interaction between the liquid molecules of the former pyridine bases, which may be caused by the polarity of the substituents. Thus, the relatively high stability of crystalline 4ac- and 4CN-py complexes suggests that a similar intermolecular interaction operates between the neighboring pyridine bases of polymeric linear chains. The fact that the heat of dissolution of Rpy, ΔH_{dis}(Rpy), does not differ very much among the pyridine bases indicates that the intermolecular interaction between the pyridine base (4ac-py or 4CN-py) and the solvent operates in the solution in the same manner as in the liquid Rpy.

As shown in Table 1, the value of ΔG_{R} of bis(pyridine base) complexes of the 2Me- and 2Et-py in solution is smaller than that of the py complex, although the basicity of those pyridine bases is higher than that of py. This result is interpreted by a lowering of the stability caused by a steric hindrance of the 2-substituent of pyridine. The extent of the steric hindrance, however, is not very large in solution, i.e., the monomeric tetrahedral complexes. That is, the enthalpy change of the reaction (8) of $CdCl_2(2Me\text{-}py)_2$ in solution is not very small (ΔH_{R} = 1 kJ mol^{-1}) compared with that of $CdCl_2(py)_2$ (ΔH_{R} = 6 kJ mol^{-1})[8] and the steric hindrance was not observed for the mono(pyridine base) complex of 2Me-py.[7] On the other hand, the formation of bis(pyridine base) complexes of 2Me- and 2Et-py is prevented in a crystal because of the very high steric hindrance for the octahedral coordination. The values of the heat of decomposition of mono(pyridine base) complexes (Eq. 5) of the 2Me- and 2Et-py, ΔH_{dec} of steps (2) + (3), are smaller than that of the 4CN-py complex. These results indicate that the crystalline complexes of 2-substituted pyridine bases, which may have an octahedral configuration,[3] is sterically hindered, even in the mono(pyridine base) complex.

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