

THERMAL DECOMPOSITION OF SOLID COMPLEXES OF CADMIUM CHLORIDE WITH SUBSTITUTED PYRIDINES

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ABSTRACT

Thermal decomposition of a series of complexes of type $\text{CdCl}_2(\text{R-py})_n$ (where py = pyridine (py), R = 4-methyl (4Me), 3-methyl (3Me), 2-methyl (2Me), 2-ethyl (2Et), and 4-cyano (4CN); $n = 4, 2$ or 1) has been studied by means of TG-DTA measurements. The decomposition took place through several steps, and all steps proceeded as a two-dimensional phase boundary reaction. The activation energy and the rate constant at various temperatures for each step have been determined on the basis of thermogravimetry. The thermal stability was mainly dependent on the σ -donating power of ligand (R-py) which is associated with its basicity. In addition to this, thermal stability was considerably affected by the crystal packing structure and the sterical character of the complex.

INTRODUCTION

There have been many studies on the thermal stability of the metal complexes [1]. The complex formation of the cadmium(II) halogenides with pyridine bases have been studied in aprotic solvents as 1,2-dichloroethane [2]. The stability of these complexes shows good linear correlation with the $\text{p}K_a$ of conjugate acid of the pyridine base which is the measure of σ -bond character. This indicates that the contribution of π -back donation from metal to nitrogen atom in the metal–pyridine bond is not important even in complexes of a relatively soft ion such as cadmium(II).

It is expected that the thermal stability of the metal–ligand bond of solid complexes would vary depending on the values of $\text{p}K_a$ of the conjugate acid of the substituted pyridines. In this work, the complexes of cadmium chloride with pyridine and several substituted pyridines were prepared, and the thermal decomposition of the solid complexes was studied by means of thermogravimetric analysis (TG) and differential thermal analysis (DTA). The effect of the ligand basicity (Table 1) [2], steric hindrance and the

TABLE 1

The pK_a values of ligands [2]

Ligand ^a	py	4Me-py	3Me-py	2Me-py	2Et-py	4CN-py
pK_a	5.20	6.03	5.68	5.96	5.76	1.88

^a py, 4Me-py, 3Me-py, 2Me-py, 2Et-py and 4CN-py denote pyridine, 4-methylpyridine, 3-methylpyridine, 2-methylpyridine, 2-ethylpyridine and 4-cyanopyridine, respectively.

crystal packing of the complex on the thermal stability of the solid cadmium complexes are discussed briefly.

EXPERIMENTAL

Reagents

The guaranteed grade reagents of pyridine (py), 4-methylpyridine (4Me-py), 3-methylpyridine (3Me-py), 2-methylpyridine (2Me-py), 2-ethylpyridine (2Et-py) and 4-cyanopyridine (4CN-py) were purified by distillation or recrystallization.

Complexes $CdCl_2(R-py)_n$, were generally prepared by the following method. The pyridine or substituted pyridine was added to ethanolic solution of cadmium chloride, and the mixture was refluxed or allowed to stand with stirring for 2–10 days. The white complex was filtered with suction and then dried under ambient conditions or reduced pressure. The complexes $CdCl_2(R-py)_n$ ($n = 2, 1$ or $2/3$) were also prepared by the thermal decomposition of the complexes having a higher ratio of ligand R-py to cadmium metal.

The amounts of cadmium and chloride ions of these complexes were determined by means of titration with EDTA and $AgNO_3$, respectively. The amounts of pyridine bases were determined by thermogravimetry. The complexes prepared from ethanolic solution are listed in Table 2 together with the complexes obtained by the thermal decomposition method.

The complexes 2Me-py and 2Et-py form only uni-pyridine-base complexes, $CdCl_2(R-py)$. This phenomenon seems to be ascribable to the steric hindrance of 2-methyl and 2-ethyl groups.

Measurements

About 10 mg of specimen were weighed into an aluminium crucible: α -alumina was used as reference material. TG-DTA curves were simultaneously recorded on a Rigaku Thermoflex TG-DTA M 8075 apparatus at a heating rate of $10^\circ C \text{ min}^{-1}$, in a flowing dry nitrogen atmosphere (flow rate $50 \text{ cm}^3 \text{ min}^{-1}$).

TABLE 2

Complexes, $\text{CdCl}_2(\text{R-py})_n$, prepared from ethanolic solution and from thermal decomposition

(R-py)	From ethanolic solution			From thermal decomposition		
	<i>n</i>			<i>n</i>		
	4	2	1	2	1	2/3
4Me-py	✓	✓	✓	✓	✓	✓
3Me-py	✓	✓	✓	✓	✓	✓
py	—	✓	✓	—	✓	—
2Me-py	—	—	✓	—	—	—
2Et-py	—	—	✓	—	—	—
4CN-py	—	✓	✓	—	—	—

The powder X-ray diffraction pattern was obtained by a Rigaku-Denki Geigerflex diffractometer using $\text{Cu } K\alpha$ radiation.

RESULTS AND DISCUSSION

$\text{CdCl}_2(4\text{Me-py})_n$ ($n = 4, 2$ or 1) complexes

Figure 1 shows the TG and DTA curves for the thermal decomposition of $\text{CdCl}_2(4\text{Me-py})_4$. The decomposition started at 43°C . At around 100°C

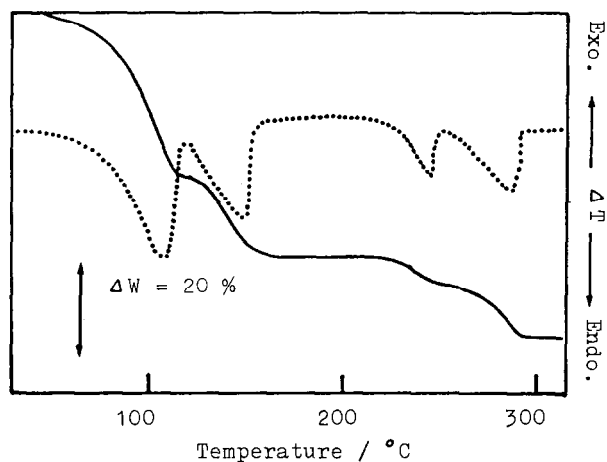


Fig. 1. TG (solid line) and DTA (broken line) for the thermal decomposition of $\text{CdCl}_2(4\text{Me-py})_4$.

there is a plateau corresponding to the composition, $\text{CdCl}_2(4\text{Me-py})_2$, and at around 150°C there is a well-defined plateau corresponding to $\text{CdCl}_2(4\text{Me-py})$. The $\text{CdCl}_2(4\text{Me-py})$ started to decompose at 215°C , and at 242°C there is a plateau corresponding to $\text{CdCl}_2(4\text{Me-py})_{2/3}$. This intermediate finally transformed to CdCl_2 . Corresponding to the above processes four endothermic peaks (T_p) were observed at 106, 145, 242, and 286°C in the DTA curve (Table 3); the compositions of the above inter-

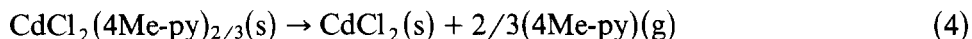
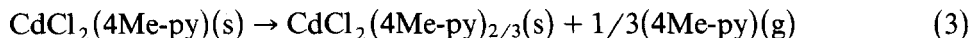
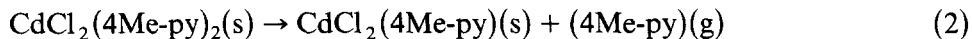
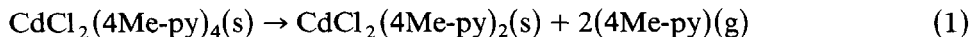
TABLE 3

Thermoanalytical and kinetic data for each step of the thermal decomposition of solid complexes of cadmium chloride with pyridine and substituted pyridines

Step of Decomp.	Ligand	Temper- ature ($^\circ\text{C}$)	T_p ($^\circ\text{C}$) ^b	E (kJ mol^{-1})	A (min^{-1}) ^c	k (min^{-1}) ^d
(1)	4Me-py	43–114	106	84.5	4.00×10^{11}	k_{80} 0.127
	3Me-py	24– 85	77	81.3	7.96×10^{11}	0.751
(2)	py	94–163	161	117.6	1.77×10^{14}	k_{130} 0.102
	4Me-py	99–163	155	119.3	2.54×10^{14}	0.0889
	3Me-py	95–154	146	128.4	6.78×10^{15}	0.156
	4Me-py ^e	114–152	145	143.0	6.30×10^{17}	0.187
	3Me-py ^e	85–149	141	110.7	5.88×10^{13}	0.267
(3)	4Me-py	215–269	260	152.6	5.68×10^{15}	k_{190} 0.0349
	3Me-py	187–216	200	143.6	4.37×10^{15}	0.279
	py ^e	163–236	233	137.0	1.03×10^{14}	0.0365
	4Me-py ^e	152–247	242	147.9	3.46×10^{15}	0.0723
	3Me-py ^e	149–201	191	135.0	6.42×10^{14}	0.382
(4)	py ^e	236–285	270	146.3	3.65×10^{13}	k_{270} 0.311
	4Me-py ^e	247–292	286	184.3	1.52×10^{17}	0.286
	3Me-py ^e	206–280	276	141.1	2.40×10^{13}	0.647
(5) + (2')	4CN-py	144–302	263 276	92.5	3.79×10^8	k_{200} 0.0232
(5)	4CN-py	184–285	274	135.4	4.88×10^{12}	k_{210} 0.0112
(5')	2Me-py	152–253	240	124.7	2.76×10^{12}	0.0909
	2Et-py	149–225	215	123.2	9.87×10^{12}	0.0472

^a See text. ^b Peak temperature of the DTA curve. ^c Pre-exponential factor. ^d k_{80} , k_{130} , k_{190} , k_{200} , k_{210} and k_{270} denote the rate constants at 80, 130, 190, 200, 210 and 270°C , respectively. ^e Data determined for the specimens prepared by means of thermal decomposition.

mediate and final products were confirmed by chemical analysis. From these results, the following scheme is proposed for the decomposition of $\text{CdCl}_2(4\text{Me-py})_4$



This process of the thermal decomposition of the cadmium complex is very similar to that of the cobalt(II) complex [3].

Figure 2(1) shows the TG-DTA curves for the thermal decomposition of $\text{CdCl}_2(4\text{Me-py})_2$. There are three steps corresponding to steps (2), (3) and (4) of the decomposition of $\text{CdCl}_2(4\text{Me-py})_4$. Figure 2(5) shows the TG-DTA curves for the thermal decomposition of $\text{CdCl}_2(4\text{Me-py})$. The two endothermic peaks corresponding to steps (3) and (4) were observed at 260 and 286°C in the DTA curve, although these two steps were not isolated separately in the TG curve. The peak temperatures of the DTA curves T_p for a series of the complexes are summarized in Table 3.

The crystal structures of the pyridine base adduct complexes of metal halogenides have been extensively studied and various types of structure have been reported for these complexes. The tetrakis-pyridine base complexes of divalent metal halogenides, $\text{MX}_2(\text{R-py})_4$, have a monomeric *trans*-octahedral structure [4,5]. A series of bis-pyridine complexes of zinc(II) chloride, $\text{ZnCl}_2(\text{R-py})_2$, has a monomeric tetrahedral structure [6], whereas the bis-pyridine complexes of cadmium(II) chloride have a chain polymer structure of octahedral cadmium(II) bridged by two chloride ions [7]. Recently, it has been determined that the complexes $\text{CdCl}_2(3\text{Me-py})_2$ and $\text{CdCl}_2(4\text{Me-py})_2$ also have the octahedral chain polymer structure [8], although the packing of these chains is considerably different from that of the pyridine complex.

It has been suggested that the $\text{MCl}_2(\text{R-py})$ and $\text{MCl}_2(\text{R-py})_{2/3}$ complexes (where M is Co and Ni) form double and triple chains by eliminating the pyridine base from the single chain of $\text{MX}_2(\text{R-py})_2$ [9]. Therefore, the decomposition steps, (1), (2), (3) and (4) of $\text{CdCl}_2(4\text{Me-py})_2$ seems to correspond to the structural change from the octahedral monomer to octahedral polymer of single, double and triple chains, respectively.

$\text{CdCl}_2(3\text{Me-py})_n$ ($n = 4, 2$ or 1) complexes

The decomposition of $\text{CdCl}_2(3\text{Me-py})_n$ took place through the same steps as $\text{CdCl}_2(4\text{Me-py})_n$, i.e. the complex $\text{CdCl}_2(3\text{Me-py})_4$ decomposed successively by a loss of two, one, one third and two thirds molecules of 3Me-py to give ultimately anhydrous cadmium chloride (Fig. 2(2) and (6)).

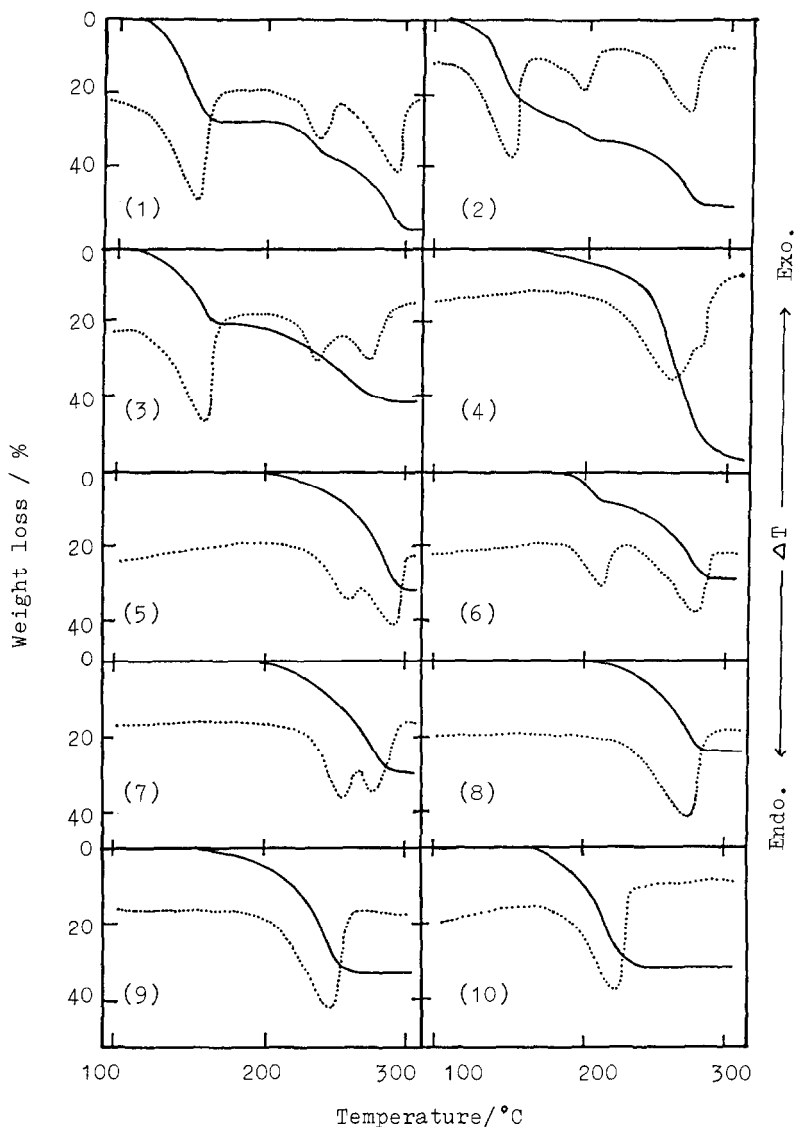


Fig. 2. TG (solid line) and DTA (broken line) for the thermal decomposition of $\text{CdCl}_2(\text{R-py})_n$. (1) $\text{CdCl}_2(4\text{Me-py})_2$, (2) $\text{CdCl}_2(3\text{Me-py})_2$, (3) CdCl_2py_2 , (4) $\text{CdCl}_2(4\text{CN-py})_2$, (5) $\text{CdCl}_2(4\text{Me-py})$, (6) $\text{CdCl}_2(3\text{Me-py})$, (7) CdCl_2py , (8) $\text{CdCl}_2(4\text{CN-py})$, (9) $\text{CdCl}_2(2\text{Me-py})$, and (10) $\text{CdCl}_2(2\text{ET-py})$.

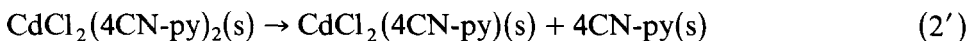
That the crystal structure of $\text{CdCl}_2(3\text{Me-py})_2$ is essentially the same as that of $\text{CdCl}_2(4\text{Me-py})_2$ indicates that the bond nature and the structures of the 3Me-py complexes are very similar to those of the 4Me-py complexes. Thus, it is understandable that the scheme of thermal decomposition of the complex $\text{CdCl}_2(3\text{Me-py})_4$ is the same as that of $\text{CdCl}_2(4\text{Me-py})_4$.

CdCl₂py_n (n = 2 or 1) complexes

The decomposition of CdCl₂py₂ proceeded through steps (2), (3) and (4) (Fig. 2(3)). In the DTA curve of CdCl₂py₂, two endothermic peaks corresponding to steps (3) and (4) were recognized at 233 and 270°C, although these two steps could not be resolved clearly in the TG curve as shown in Fig. 2(3).

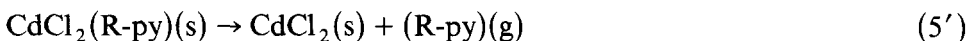
CdCl₂(4CN-py)_n (n = 2 or 1) complexes

From the TG analysis of CdCl₂(4CN-py)₂, the decomposition seems to take place as a one-step reaction, but the endothermic peak accompanying a shoulder at 276°C was observed at 263°C (Fig. 2(4)). The complex, CdCl₂(4CN-py) obtained from ethanolic solution decomposed directly to CdCl₂ as shown in eqn. (5) (Fig. 2(8)), and the endothermic peak was recognized at 274°C. From this, the shoulder observed at 276°C on the decomposition of the bis-4CN-py complex was confirmed as corresponding to step (5) below. These results suggest two successive steps as follows



CdCl₂(2Me-py) and CdCl₂(2Et-py) complexes

The smoothness of the TG-DTA curves of these complexes (Fig. 2(9) and (10)) shows that the decomposition proceeds as a one-step reaction



Kinetic analysis

The kinetics of the thermal decomposition of these complexes was studied on the basis of the TG curves by use of the integral method [10]. The integral kinetic equation for the thermal decomposition of solid under isothermal condition can be expressed by

$$G(\alpha) = \int_0^t k \, dt \quad (6)$$

where α is the decomposed fraction after time t , $G(\alpha)$ is a function depending on the decomposition mechanism as shown in Table 4 [11] and k is the rate constant. According to the Arrhenius equation, the rate constant is a function of absolute temperature T as $k = A \exp(-E/RT)$, where A , E and R are the pre-exponential factor, activation energy and gas constant,

respectively. When a linear heating rate $b = dT/dt$ is substituted in eqn. (6), we obtain

$$G(\alpha) = \int_0^t k \, dt = (A/b) \int_{T_0}^T \exp(-E/RT) \, dT \quad (7)$$

where T_0 is the value of T at $t = 0$. Since the rate of decomposition is very slow at low temperature, the next approximation can be employed [12]

$$\int_{T_0}^T \exp(-E/RT) \, dT \cong \int_0^T \exp(-E/RT) \, dT \quad (8)$$

The right-hand side of eqn. (8) is expressed by Doyle's p function [13]

$$\int_0^T \exp(-E/RT) \, dT = (E/R) p(E/RT) \quad (9)$$

If $20 < E/RT < 60$, $p(E/RT)$ can be approximated as

$$\ln[p(E/RT)] \cong -2.315 - 0.4567(E/RT) \quad (10)$$

Therefore, the logarithmic form of eqn. (7) becomes

$$\log G(\alpha) = \log(AE/bR) - 2.315 - 0.4567(E/RT) \quad (11)$$

The mechanism of decomposition was judged by the linearity of the plots of $\log G(\alpha)$ against $1/T$ in accordance with eqn. (11), and the activation energy E and pre-exponential factor A were determined from the linear plots. Figure 3 shows typical plots for the decomposition step (1) of $\text{CdCl}_2(4\text{Me-py})_4$. The plot of $R_2(\alpha)$ vs. t shows the best linearity over nearly the whole range of the step; hence the step was found to proceed as a two-dimensional phase boundary reaction [11,13]

$$G(\alpha) = R_2(\alpha) = 2[1 - (1 - \alpha)^{1/2}] \quad (12)$$

The results of kinetic analyses show that all other steps of the decomposition of the complexes treated in this study also had a characteristic of the two-dimensional phase boundary reaction ($R_2(\alpha)$). The values of E and A determined are shown in Table 3, together with the thermoanalytical data.

TABLE 4

Commonly used mathematical expressions of $G(\alpha)$ for solid reactions

$G(\alpha)$	Symbol	Rate-controlling process
$\alpha^2/2$	D_1	One-dimensional diffusion
$(1 - \alpha) \ln(1 - \alpha) + \alpha$	D_2	Two-dimensional diffusion
$(3/2)[1 - (1 - \alpha)^{1/3}]^2$	D_3	Three-dimensional diffusion
$2[1 - (1 - \alpha)^{1/2}]$	R_2	Two-dimensional phase boundary reaction
$3[1 - (1 - \alpha)^{1/3}]$	R_3	Three-dimensional phase boundary reaction
$-\ln(1 - \alpha)$	F_1	First-order reaction
$2[-\ln(1 - \alpha)]^{1/2}$	A_2	Random-nucleation reaction (1)
$3[-\ln(1 - \alpha)]^{1/3}$	A_3	Random-nucleation reaction (2)

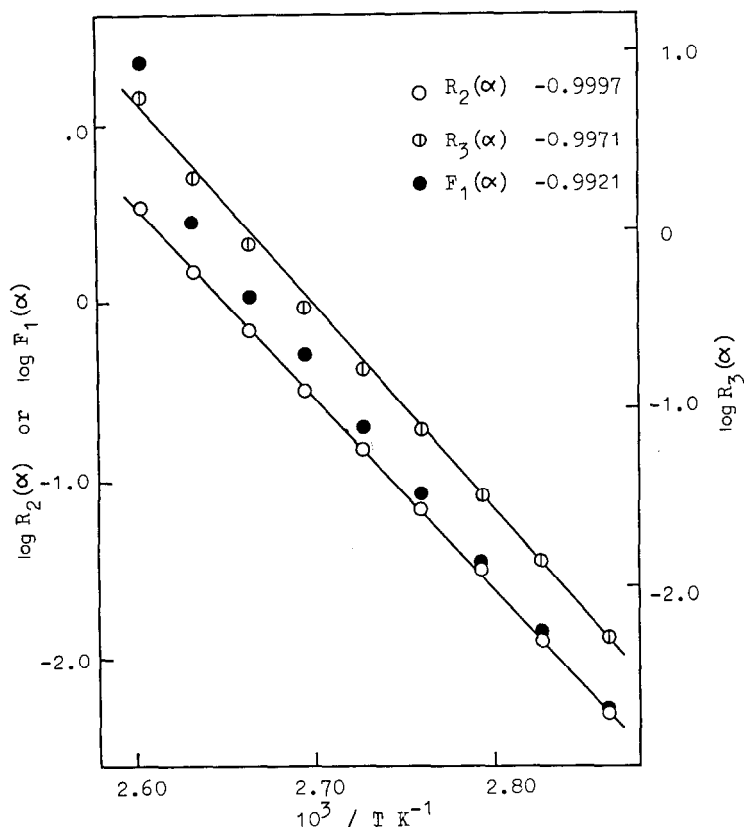


Fig. 3. Typical $\log G(\alpha)$ vs. $1/T$ plots for step (1) of the thermal decomposition of $\text{CdCl}_2(4\text{Me-py})_4$ in the α range 0.1–0.9. Correlation coefficients are given in the figure.

The value of E is expected to increase with increase in the basicity of the pyridine bases. So it is a reliable measure to compare the thermal stability of complexes. Moreover, in the present decomposition, the values of A tend to increase with increasing values of E . This finding indicates the presence of some kinetic compensation effect in the decomposition. Therefore, the rate constant at a given temperature also may be a reasonable measure to compare the stability of these complexes. In addition, it has been known that in the phase boundary reaction the diffusion of the product takes place rapidly and the rate of overall reaction is exclusively dependent on the chemical process occurring at the reactant–product interface [11,13]. Consequently, the value of k also reflects the strength of the metal–ligand bond.

The thermal stability of solid complexes is generally expected to vary depending on the basicity of the ligand and the properties of the structure such as crystal packing.

Because the X-ray diffraction profile of $\text{CdCl}_2(4\text{Me-py})_n$ ($n = 4, 1$ or $2/3$) resembles that of $\text{CdCl}_2(3\text{Me-py})_n$, both the respective complexes seem

to have a similar structure. Consequently, the structural effect on the relative stability between 4Me-py and 3Me-py complexes must be minimal, and their thermal stability may be predominantly dependent on the basicity of the ligands. In each decomposition step, the 4Me-py complexes decomposed at higher temperatures than 3Me-py complexes, and the values of E for the former were higher than those of the latter, except for step (2). These results suggest that the 4Me-py complexes are more stable than the 3Me-py complexes, which is reasonably expected on the basis of the basicity of the pyridine bases. The rate constant of the 3Me-py complex for step (2) is larger than that of the 4Me-py complex, although the value of E of the former is slightly higher than that of the latter.

By taking into account the ligand basicity (4Me-py > 3Me-py > py), the thermal stability of the 4Me-py, 3Me-py and py complexes is expected to decrease in this order. However, the thermal stability of the py complex was mostly intermediate between those of the 4Me-py and 3Me-py complexes, and this could not be explained clearly from the ligand basicity alone. Since the crystal structures of $\text{CdCl}_2(\text{R-py})_n$ ($n = 1$ and $2/3$) have not been elucidated, no clear explanation can be given at present. Comparison of the crystal structure of the CdCl_2py_2 complex with those of the $\text{CdCl}_2(4\text{Me-py})_2$ and $\text{CdCl}_2(3\text{Me-py})_2$ complexes indicates that the packing of the CdCl_2py_2 complex may be more unfavourable than those of the $\text{CdCl}_2(4\text{Me-py})_2$ and $\text{CdCl}_2(3\text{Me-py})_2$ complexes to form a double chain polymer by eliminating the pyridine bases in step (2) [7,8].

Because the decomposition scheme of the group of 2Me-py, 2Et-py and 4CN-py complexes differs from that of 4Me-py, 3Me-py and py complexes, the thermal stability of the groups of complexes cannot be compared directly.

In the decomposition step (5') 2Et-py and 2Me-py complexes decomposed at relatively low temperatures, and their peak temperatures of DTA curves (T_p) appeared at the temperature region corresponding to those of step (3) of the other complexes. This suggests that both of these complexes decompose through steps (3) and (4). Because of the steric hindrance of 2-substituent of pyridine, however, the intermediate, $\text{CdCl}_2(\text{R-py})_{2/3}$ is so sterically unstable that it probably decomposes to CdCl_2 immediately.

Although the difference in the pK_a values of 2Me-py and 2Et-py is small, the values of E and the rate constants of step (5') show that the 2Me-py complex is more stable than the 2Et-py complex. This finding seems to be in accordance with the expectation based on the difference of steric effect [2] of methyl and ethyl groups, i.e. the steric hindrance caused by a bulky ethyl group may be stronger than that by a methyl group.

It is also reasonable that the 4CN-py complex is more stable than the 2Me-py and 2Et-py complexes because of the absence of such steric effect.

The complexes prepared from ethanolic solution, $\text{CdCl}_2(\text{R-py})_n$ (R-py = 4Me-py and 3Me-py; $n = 2$ or 1) have a similar X-ray diffraction profile to

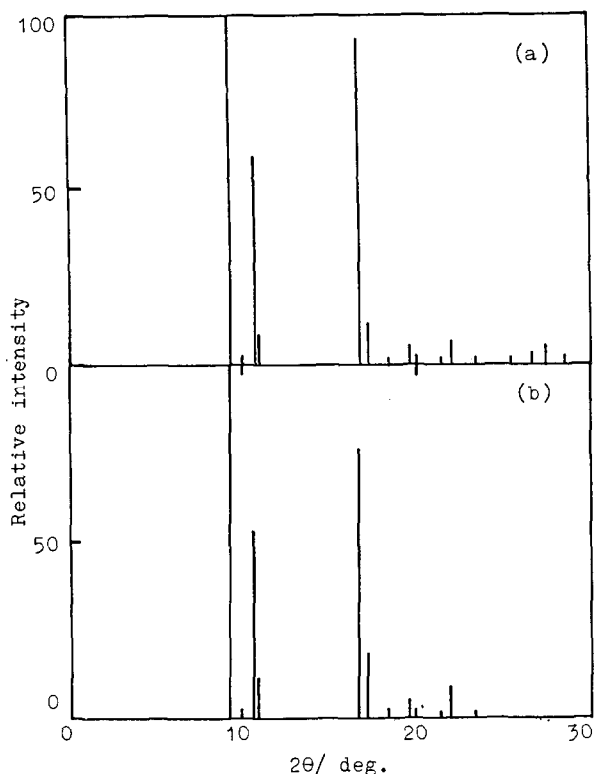


Fig. 4. Powder X-ray diffraction profiles of $\text{CdCl}_2(4\text{Me-py})_2$: (a) prepared from ethanolic solution, and (b) obtained from the thermal decomposition of $\text{CdCl}_2(4\text{Me-py})_4$.

those obtained by means of the thermal decomposition method (Fig. 4). Each of the decomposition steps (2), (3) and (4) for the former however takes place at a higher temperature than for the latter. In addition, the rate constant obtained for the former at a given temperature is smaller than that of the latter. This suggests that the former is more thermally stable than the latter: the stability seems to be concerned with the crystal form of the complexes. From microscopic observation, the complexes obtained from thermal decomposition have porous structures formed by the evolution of the ligands in the preceding decomposition steps. It is reasonable to expect that the porous structures would facilitate the evolution of the ligands in the following decomposition steps.

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