Pressure and Temperature Effects on Octahedral–Tetrahedral Equilibria in 4-Methylpyridine and 2-Methylpyridine Solutions of Some Cobalt(II) Halides

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The visible absorption spectra of CoX_2 (X=Cl, Br) in solutions of both 4-methylpyridine (4-Me-py) and 2-methylpyridine (2-Me-py) have been measured in the pressure range of 1 bar —3 kbar at room temperature, and in the temperature range of ≈ 6—$\approx 75\,°C$ at 1 bar. In the 4-Me-py solution system, the configuration equilibrium, $[CoX_2(4\text{-Me-py})_2]$ (tetrahedral) $+2(4\text{-Me-py}) \rightleftarrows [CoX_2(4\text{-Me-py})_4]$ (octahedral), was found to exist over the experimental pressure range. Increasing the pressure shifted the equilibrium toward the octahedral species side with volume changes of $-26\ cm^3\,mol^{-1}$ for the chloro complex and $-25\ cm^3\,mol^{-1}$ for the bromo complex at 1 bar. The above equilibrium held fairly well over the whole experimental temperature range for the chloro complex, but in the restricted temperature range for the bromo complex. Increasing the temperature tended to increase the formation of the tetrahedral species, the heats of reaction, being $53.3\ kJ\,mol^{-1}$ and $62.6\ kJ\,mol^{-1}$ for the chloro and bromo complexes, respectively. On the other hand, in the 2-Me-py solution system, increasing the pressure or temperature could hardly confirm the existence of the octahedral-tetrahedral configuration equilibrium. A charge-transfer band between the solvent molecule 2-Me-py and the free ion X^- decreased in intensity with increasing temperature. The above results in the 4-Me-py and 2-Me-py systems were compared with those of the pyridine (py) and 3-methylpyridine (3-Me-py) systems mentioned in the literature.

As a typical configuration equilibrium between the tetrahedral and octahedral complexes of Co(II), the following reaction is known in some nonaqueous solvents

$$[CoX_2(R\text{-py})_2] + 2(R\text{-py}) \xrightleftharpoons{K} [CoX_2(R\text{-py})_4],\quad (1)$$

<div style="text-align:center">(tetrahedral)   (octahedral)</div>

where K is the equilibrium constant, X=Cl, Br, or I, and R-py=py or methylpyridines.

By means of spectrophotometric measurements of the $CoCl_2$–py system, Katzin[1] could study the temperature effect on the equilibrium and determined the value of ΔH. Using a series of R-py, Nelson et al.[2,3] have obtained thermodynamic data related to the equilibrium by means of spectroscopic, electrical, and calorimetric measurements. They interpreted the data in terms of the dative π-bonding from Co(II) to the pyridine base, which depends first on the kind of X^- and R-py and, secondly, on the hydrogen bond between the ligand and the solvent molecule. However, Libus et al.[4] have pointed out the importance of the hydrogen bond. Sawada et al.[5,6] have spectrophotometrically investigated the equilibrium of Eq. 1 for 1,2-dihaloethane solutions and found a linear correlation between the strength of the Co(II)–N bond and pK_b of R-py. On the other hand, the kinetic parameters related to the equilibrium have been determined by using nitrogen-14 NMR[7] and the temperature-jump method.[8,9]

All of the above reports, except for Katzin's,[1] have dealt with the equilibrium of Eq. 1 at atmospheric pressure and near room temperature. On the other hand, the effects of pressure and temperature on the equilibrium of Eq. 1 in the systems of R-py=py and 3-Me-py have been reported in previous papers.[10–12] There have been many studies[13] of high-pressure

effects on inorganic reactions which involve ionic species. In these reactions, the contribution of electrostriction to the reaction volume or the activation volume is significant. However, the reaction of Eq. 1 involves no ionic species; therefore, the effect of electrostriction seems to be negligible.

Both the py[10,11] and 3-Me-py[12] systems under high pressures favored the octahedral species; however, at high temperatures the tetrahedral species was favored. Thus, from the variation of K with pressure and temperature, the values of ΔV and ΔH could be estimated. In the 3-Me-py system,[12] the 400-nm band which becomes stronger with increasing temperature was assigned to a charge-transfer transition between the solvent molecule (3-Me-py) and X^- arising from a dissociation of the tetrahedral species $[CoX_2(3\text{-Me-py})_2]$.

In the present paper, the pressure and temperature effects on the equilibrium of Eq. 1 (X=Cl, Br, R-py=4-Me-py, 2-Me-py) are described. The results are discussed in comparison with those of the py[10,11] and 3-Me-py[12] systems.

Experimental

$CoCl_2$ and $CoBr_2 \cdot 6H_2O$ were used after drying and 4-Me-py and 2-Me-py were used after drying and distillation. Sample solutions of CoX_2 in 4-Me-py or in 2-Me-py were prepared just before spectroscopic measurements.

High-pressure spectra were recorded at room temperature on a Shimadzu UV-365 spectrophotometer equipped with a clamp-type cell[14] (optical path length: 1.6 cm). High-temperature spectra were recorded at atmospheric pressure on a Shimadzu MPS-2000 instrument equipped with a pair of thermostated quartz cells (optical path length: 0.98 cm).

The experimental details were described in a previous paper.[10]

Results and Discussion

Spectra at Atmospheric Pressure and Room Temperature. The positions of the visible absorption spectra of CoX_2 in 4-Me-py and 2-Me-py solutions at atmospheric pressure and room temperature are listed in Table 1 together with those of the py[10,11] and 3-Me-py[12] systems. In the 4-Me-py system, the spectra are composed of both the O- and T-bands. This feature is similar to that in the py[10,11] or 3-Me-py[12] system. The O-band is due to the $^4T_{1g}(F){\rightarrow}^4T_{1g}(P)$ electronic transition of the octahedral complex and the T-band is due to the $^4A_2(F){\rightarrow}^4T_1(P)$ transition of the tetrahedral complex. On the other hand, in the spectra of the 2-Me-py system, a strong T-band is observed, but an O-band is hardly found. Similar results have been mentioned in the earlier reports[2,5,6,15-17] which described how the $[CoX_2(2\text{-Me-py})_4]$ complex seems to be little formed owing to a steric hindrance by the methyl group in 2-Me-py.

It can be seen in Table 1 that for octahedral or tetrahedral halo complexes having different ligands of amine bases, the energy of the strongest peak decreases in the order: py$\geqslant$4-Me-py$>$3-Me-py$>$2-Me-py. The position of the strongest peak could be a rough measure for the strength of the ligand field, though the position of the center of a band should be an exact measure of that. Therefore, the above order of R-py also reveals roughly a decreasing order of the ligand-field strength. This dependence of the ligand-field strength on R-py may result from a steric effect. This result is in contrast with earlier results.[5,6,16-18] The positions of the T-band have been reported to remain almost unchanged regardless of ligand R-py, namely, $[CoX_2(4\text{-Me-py})_2]$ or $[CoX_2(2\text{-Me-py})_2]$ in chloroform[16] and $[CoX_2(py)_2]$ or $[CoX_2(2\text{-Me-py})_2]$ in py or 2-Me-py

solution.[17] Sawada et al.[5,6] have also found that the peak positions of $[CoX_2(R\text{-py})_2]$ in 1,2-dihaloethane solutions do not depend on the kind of ligand R-py. As for octahedral complexes, Goodgame and Hayward[18] have shown that for solid complexes the O-band of $[CoBr_2(4\text{-Me-py})_4]$ lies at longer wavelength than that of $[CoBr_2(3\text{-Me-py})_4]$.

For both the chloro and bromo complexes, the intensity ratio of the O-band to the T-band at atmospheric pressure and room temperature decreases in the order: py$>$4-Me-py$>$3-Me-py$\gg$2-Me-py. This order is the same as that of the decreasing strength of the ligand field and that of the decreasing equilibrium constant K of Eq. 1.[2,3,5,6]

Pressure Effect. Figure 1 shows the pressure dependence of the spectra of $CoCl_2$ in 4-Me-py. For both chloro and bromo (not shown) complexes, the intensities of the T-band decrease, but those of the O-band increase with increasing pressure. Therefore, it can be concluded that the equilibrium of Eq. 1 shifts toward the octahedral species $[CoX_2(4\text{-Me-py})_4]$ with increasing pressure. A similar feature has been also found in the py[10] or 3-Me-py[12] system.

The absorption spectra of $CoCl_2$ in 2-Me-py at various pressures are shown in Fig. 2. Two bands were found in addition to the T-band: a weak band at about 510 nm, and a weak, broad band ranging from $\approx$360 to $\approx$410 nm (see also Fig. 5). These two bands are discussed below in the section concerning the tempera-

Table 1. Positions of the Visible Absorption Spectra

Complex	Position[a] (in nm)	Reference
	O-band	
$[CoCl_2(py)_4]$	524, 500	10
$[CoCl_2(4\text{-Me-py})_4]$	525, 503, 557[sh], 571[sh]	This work
$[CoCl_2(3\text{-Me-py})_4]$	530, 503, 560[sh]	12
$[CoBr_2(py)_4]$	522, 539, 492[sh]	10
$[CoBr_2(4\text{-Me-py})_4]$	520, 543, 570[sh], 505, 483	This work
$[CoBr_2(3\text{-Me-py})_4]$	526, 543, 570[sh], 490[sh]	12
	T-band	
$[CoCl_2(py)_2]$	608, 637[sh], 571, 664[sh]	10
$[CoCl_2(4\text{-Me-py})_2]$	610, 636, 575, 664[sh]	This work
$[CoCl_2(3\text{-Me-py})_2]$	613, 640, 578, 665[sh]	12
$[CoCl_2(2\text{-Me-py})_2]$	615, 634, 581, 662[sh]	This work
$[CoBr_2(py)_2]$	643, 629[sh], 593, 711[sh]	10
$[CoBr_2(4\text{-Me-py})_2]$	646, 628[sh], 595, 671[sh]	This work
$[CoBr_2(3\text{-Me-py})_2]$	648, 626[sh], 597, 675[sh]	12
$[CoBr_2(2\text{-Me-py})_2]$	650, 630[sh], 597	This work

sh: shoulder.
a) In each complex, the peaks and shoulders are aligned in the order of decreasing intensity on going from left to right.
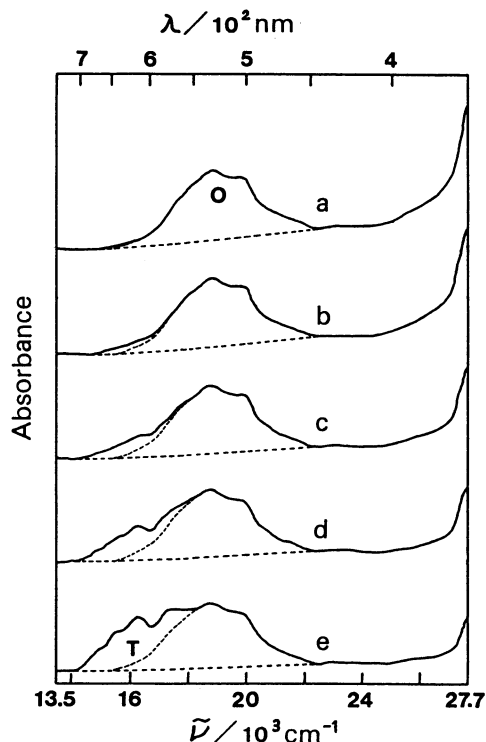
Fig. 1. Absorption spectra of $CoCl_2$ in 4-Me-py at high pressures (28.2 °C), uncorrected for compression of solution. Each broken line shows the separation of the bands. Concn: 8.16×10^{-4} mol dm^{-3}. a: 3.0 kbar, b: 2.1 kbar, c: 1.0 kbar, d: 0.5 kbar, e: 1 bar.
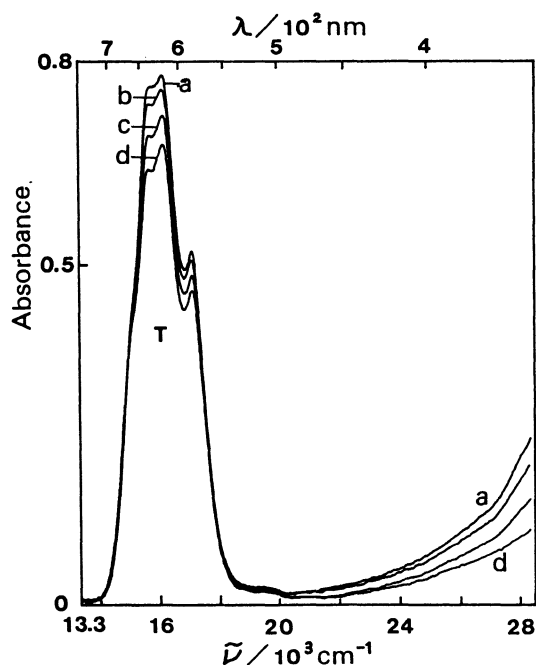
Fig. 2. Absorption spectra of CoCl₂ in 2-Me-py at high pressures (27.7°C), uncorrected for compression of solution. Concn: 7.70×10^{-4} mol dm⁻³. a: 3.0 kbar, b: 2.0 kbar, c: 1.1 kbar, d: 1 bar.
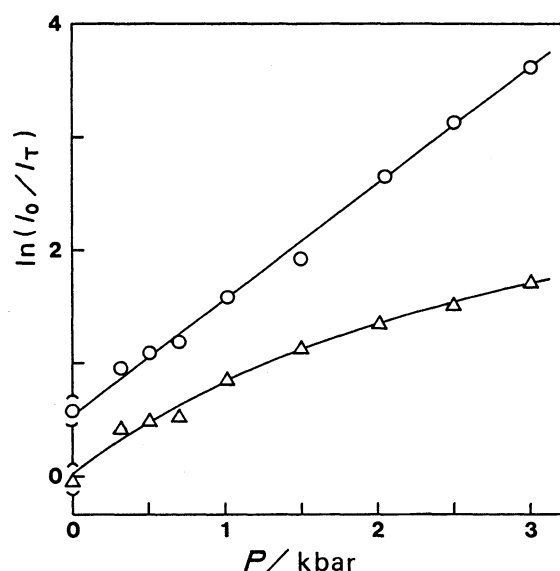

Fig. 3. Logarithm of the integrated-intensity ratio of the O-band to the T-band (I_O/I_T) vs. pressure in the 4-Me-py solution system. O: CoCl₂, △: CoBr₂, ——: calculated fitting lines.

Table 2. ΔV for the Reaction of $[CoX_2(R\text{-}py)_2]+2(R\text{-}py)$ $\rightleftarrows [CoX_2(R\text{-}py)_4]$ at Various Pressures

P	$-\Delta V$						
kbar	cm³ mol⁻¹						
	4-Me-py[a]		3-Me-py[b]			py	
	Cl	Br	Cl	Br	Cl[c]	Br[c]	I[d]
0.001	26	25	18	19	41	29	6
0.5	26	20	21	19	35	31	6
1.0	26	16	24	19	29	31	6
1.5	26	13	27	19	24	28	6
2.0	26	10	29		18	23	6
2.5	26	9	32		13	16	6
3.0	26	8	34		7	6	6

a) This work. b) Ref. 12. c) Ref. 10. d) Ref. 11.

ture effect. Contrary to the 4-Me-py system, the T-band in the 2-Me-py system apparently becomes stronger with increasing pressure. This tendency has also been observed in the high-pressure spectra of the tetrahedral complex $[CoCl_4]^{2-}$ in CH_3NO_2.[19] Even if the spectra are corrected for a compression of the solution, the T-band intensity changes little with pressure. Therefore, in the 2-Me-py system, the equilibrium of Eq. 1, if it exists, may be scarcely affected by the pressure.

Consider the equilibrium of Eq. 1 in the 4-Me-py system described above. When the pressure increases, the equilibrium shifts toward the octahedral complex side with a volume change (ΔV) of the system. ΔV is calculated by the equation[10]

$$\Delta V = - RT \frac{d}{dP} \ln (I_o/I_T),$$ (2)

where R is the gas constant and I_o and I_T are the integrated intensities of the O- and T-bands, respectively.

As described in Ref. 10, Eq. 2 is derived by assuming that the molar absorption coefficients of both the $[CoX_2(4\text{-}Me\text{-}py)_4]$ and $[CoX_2(4\text{-}Me\text{-}py)_2]$ complexes hardly depend on the pressure at relatively low pressures.[20] The activity coefficient of solvent 4-Me-py is also assumed to be independent of pressure; this seems to be reasonable at relatively low pressures.

The plots of $\ln(I_o/I_T)$ vs. pressure in Fig. 3 were fitted to the following equations by a least-squares method:

$\ln(I_o/I_T) = 0.565 + 1.017P$, for the chloro complex, and

$\ln(I_o/I_T) = 0.0254 + 0.995P - 0.209P^2 + 0.0211P^3$,

for the bromo complex.   (3)

From Eqs. 2 and 3, the values of ΔV were estimated to be all negative; these are listed in Table 2 together with those of the py[10,11] and 3-Me-py[12] systems.

From Eq. 1, ΔV equals $V_{oct}-(V_{tet}+2V_{sol})$, where V_{oct}, V_{tet}, and V_{sol} are the intrinsic molar volumes of the octahedral species, the tetrahedral species, and the solvent, respectively. The values of V_{oct} and V_{tet} are not available, but the molar volumes of some related complexes in solutions have been reported. Libus et al. have estimated the molar volumes of $[ZnCl_2(py)_2]$ and $[NiCl_2(py)_4]$ in py solutions to be 198.7 ± 1.3 cm³ mol⁻¹[21] and 333 ± 10 cm³ mol⁻¹,[22] respectively. Narbutt and Siekierski[23] have obtained the molar volume of $[Co(NCS)_2(4\text{-}Me\text{-}py)_4]$ in benzene solutions as 428 ± 15 cm³ mol⁻¹. The molar volumes of py and methylpyridines can be estimated from their densities to be of the order of 80 and 100 cm³ mol⁻¹, respectively. On the basis of the above values, the magnitude of $|\Delta V|$ at 1 bar (Table 2) seems reasonable.

The values of $|\Delta V|$ at 1 bar were found to decrease

according to the ligand sequence py>4-Me-py>3-Me-py. This sequence shows that V_{oct} relative to the sum of V_{tet} and $2V_{sol}$ becomes large in the order, py<4-Me-py<3-Me-py, owing to the steric hindrance of R-py ligands in each octahedral complex.

The differences in $|\Delta V|$ at 1 bar between the chloro and bromo complexes are large in the py system, but are small in the 4-Me-py and 3-Me-py systems. This fact suggests that the contribution of X to both V_{oct} and V_{tet} is smaller in the methylpyridine systems than in the py system.

It can be seen in Table 2 that for both the chloro and bromo complexes the ratios of the values of $|\Delta V|$ at high pressures to those at 1 bar increase in the order, py<4-Me-py<3-Me-py. It is impossible to discuss further this pressure dependence of $|\Delta V|$, since the activities and compressibilities of solvents R-py were not obtained at high pressures.

Temperature Effect. The absorption spectra of $CoCl_2$ in 4-Me-py at various temperatures are shown in Fig. 4. The intensity of the T-band increases steeply with increasing temperature. Although the change in the O-band with temperature could be obscured due to the intense T-band, the equilibrium of Eq. 1 probably shifts toward the tetrahedral species $[CoCl_2(4\text{-Me-py})_2]$ with increasing temperature, contrary to the pressure effect described above. A similar result was obtained

Fig. 5. Absorption spectra of $CoBr_2$ in 2-Me-py at various temperatures, uncorrected for thermal expansion of solution. Concn: 2.18×10^{-3} mol dm^{-3}. a: 5.5 °C, b: 26.3 °C, c: 44.5 °C, d: 75.3 °C.

for the bromo complex (not shown). Such a tendency is similar to that of the py[10] or 3-Me-py[12] system.

Figure 5 shows the absorption spectra of $CoBr_2$ in 2-Me-py at various temperatures. Contrary to the 4-Me-py system, the intensity of the T-band apparently decreases slightly with increasing temperature. Therefore, the equilibrium of Eq. 1 in the 2-Me-py system may be hardly shifted with increasing temperature.

In the 4-Me-py system, the heat of reaction for $[CoX_2(4\text{-Me-py})_4] \rightleftarrows [CoX_2(4\text{-Me-py})_2]+2(4\text{-Me-py})$, ΔH, can be obtained by the method described in Ref. 10: The variation of the equilibrium constant for the reaction of $[CoX_2(4\text{-Me-py})_4] \rightleftarrows [CoX_2(4\text{-Me-py})_2]+2(4\text{-Me-py})$ with temperature can be approximately followed by the change of the T-band intensity. As the intensity of the T-band, the absorbance of the 664-nm shoulder for the chloro complex and that of the 646-nm peak for the bromo complex are used. In Fig. 6, the logarithm of the corrected absorbance A' is plotted against the reciprocal absolute temperature. In order to obtain A', the observed absorbance is corrected by use of the thermal expansion coefficient for solvent 4-Me-py (1.038×10^{-3} K^{-1}[24]). The plots in Fig. 6 can be fitted to straight lines, indicating that each value of ΔH is constant over each temperature range. The slopes of the lines give ΔH as follows: 53.3 kJ mol^{-1} for the chloro complex over the range of 5.8—74.8 °C and 62.6 kJ mol^{-1} for the bromo complex over the range of

Fig. 4. Absorption spectra of $CoCl_2$ in 4-Me-py at various temperatures, uncorrected for thermal expansion of solution. Concn: 7.39×10^{-4} mol dm^{-3}. a: 74.8 °C, b: 64.4 °C, c: 54.6 °C, d: 44.8 °C, e: 35.2 °C, f: 25.0 °C, g: 14.9 °C, h: 5.8 °C.
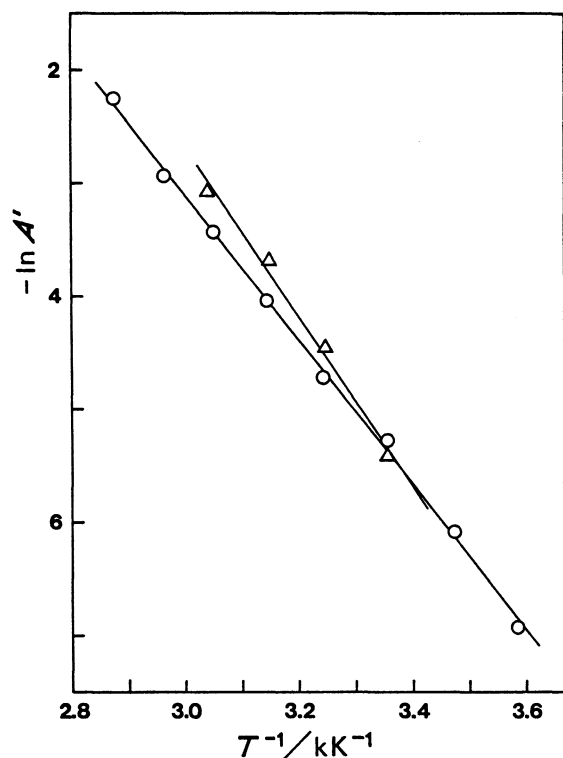
Fig. 6. Logarithm of the corrected absorbance A' vs. reciprocal absolute temperature in the 4-Me-py solution system. O: CoCl₂, △: CoBr₂, ——: calculated fitting lines.

Table 3. ΔH for the Reaction of $[CoX_2(R\text{-py})_4] \rightleftarrows$ $[CoX_2(R\text{-py})_2]+2(R\text{-py})$

R-py (ligand)	Solvent	ΔH kJ mol⁻¹			Reference
		Cl	Br	I	
py	py	57.3	60.7	65.3	10, 11
	CHCl₃	63.6	65.3	69.5	2
4-Me-py	4-Me-py	53.3	62.6		This work
	CHCl₃	65.7			3
3-Me-py	3-Me-py	56.7	58.6		12
	CHCl₃	56.1			3

25.0—55.8 °C These values are listed in Table 3 together with the values for the py and 3-Me-py complexes in each R-py solution[10-12] and in CHCl₃ solutions.[2,3]

As described above, the values of ΔH are determined by the same method as that described in the literature,[1,8,9,25] by assuming that the concentration of the octahedral complex is constant in the experimental temperature range.[10] This assumption seems reasonable when the concentration of the octahedral complex is much larger than that of the tetrahedral complex. In order to examine the validity of this assumption, in the CoCl₂-4-Me-py system (Fig. 4), for example, the decrease in the concentration of [CoCl₂(4-Me-py)₄] with increasing temperature was attempted to be taken into account by subtracting the concentra-

tion of [CoCl₂(4-Me-py)₂] from the total concentration of Co(II). The concentration of [CoCl₂(4-Me-py)₂] was determined by using the molar absorption coefficient at 615 nm of 663 dm³ mol⁻¹ cm⁻¹ for [CoCl₂(4-Me-py)₂] in CHCl₃-4-Me-py mixtures,[16] since the value in the 4-Me-py solution could not be obtained. Using the spectral data in Fig. 4, the above procedure gives a ΔH which is larger by 2.5 kJ mol⁻¹ than 53.3 kJ mol⁻¹ in Table 3.

In spectroscopic studies of solution equilibrium, few studies have taken into account the temperature dependence of the activity of the solvent. Exceptionally, in an aqueous solution system, Swaddle and Fabes[26] regarded the relative density $\rho_r(=\rho_{T,P}/\rho_{298 K, 1 bar})$ as an activity of the solvent water at high temperatures and high pressures on the basis of the solvent effect on the oscillator strength of the absorption band. In addition to the above consideration concerning the concentration of [CoCl₂(4-Me-py)₄], taking the activity of solvent 4-Me-py into account with the method by Swaddle and Fabes,[26] the value of ΔH is 53.8 kJ mol⁻¹. This is only by 0.5 kJ mol⁻¹ larger than 53.3 kJ mol⁻¹ in Table 3.

Since the above procedures give similar effects concerning the values of ΔH in the other CoX₂-R-py systems, the values of ΔH in Table 3 seem to be reasonable.

It seems to be difficult at present to determine the values of the absorption coefficients of the octahedral and tetrahedral complexes in solutions of py, 3-Me-py, and 4-Me-py and the values of the activities of solvents at high temperatures. However, the method for determining ΔH used in the present and previous[10-12] reports seems to be reasonable.

As Table 3 shows, ΔH of the 4-Me-py system is larger for ligand Br⁻ than for ligand Cl⁻, which is similar to the py,[10,11] 3-Me-py,[12] and CHCl₃[2,3] solution systems. This trend seems to be explained in terms of the dative π-bonding from Co(II) to the pyridine base proposed by King et al.:[2] Charge is readily transferred from ligand X⁻ to Co(II) in the order Cl⁻ < Br⁻ < I⁻. This enhances the release of non-bonding d-electrons of Co(II) to antibonding pyridine base π-orbitals, thereby strengthening the Co(II)-N bond in the order Cl⁻ < Br⁻ < I⁻.

The heats of dissociation of the solid complexes [CoX₂(R-py)₄] in the reaction, [CoX₂(R-py)₄](solid) $\rightleftarrows$ [CoX₂(R-py)₂](solid)+2(R-py)(gas), have been reported to increase in the order I⁻ < Br⁻ < Cl⁻ for the 4-Me-py[3,27] and 3-Me-py[3] complexes. The fact that this order for the heats of dissociation is opposed to the order for ΔH seems to be important in a further discussion of the X⁻ dependence of the dative π-bonding in solutions.

In the CoBr₂-R-py systems ΔH decreases in the order of ligand R-py: 4-Me-py > py > 3-Me-py (Table 3). This order agrees with that of the CoCl₂-CHCl₃ systems.[2,3] Cabral et al.[3] have pointed out that 3-Me-py

is the weakest π-acceptor since the charge densities on the 2-, 4-, and 6-positions, on which charges from Co(II) are concentrated, increase through a 3-methyl substituent. Therefore, the smallest ΔH for the 3-Me-py complex is mainly due to the dative π-bonding from Co(II) to ligand 3-Me-py. However, the largest ΔH for the 4-Me-py complexes may not be interpreted only in terms of the dative π-bonding, since 4-Me-py is a weaker π-acceptor than py; nevertheless, ΔH is larger for the 4-Me-py complexes than for the py ones. In the $CoCl_2$-R-py systems, the dependence of ΔH on ligand R-py is not the same as that of the $CoBr_2$-R-py systems. Especially, ΔH in the $CoCl_2$-4-Me-py system seems to be comparatively small (Table 3).

Lastly, temperature effects for the 2-Me-py solution system are discussed. As stated above, the intensity of the T-band for $CoBr_2$ in 2-Me-py apparently decreases with increasing temperature (Fig. 5). A similar result has been observed for $CoCl_2$ (not shown). Even if the intensity was corrected for the thermal expansion coefficient (1.123×10^{-3} K^{-1}[24]), it decreases with increasing temperature (not shown). The temperature effect on broadening the T-band is found to be small; thus, the oscillator strength of the T-band may decrease slightly with increasing temperature. This fact is interesting from the view point of the temperature dependence of the oscillator strength of the T-band.

Assuming that only the tetrahedral complex $[CoX_2(2\text{-Me-py})_2]$ exists in the CoX_2-2-Me-py solutions at room temperature and atmospheric pressure, the molar absorption coefficient is estimated to be $\varepsilon_{615}=537$ $dm^3\,mol^{-1}\,cm^{-1}$ for the chloro complex and $\varepsilon_{650}=800$ $dm^3\,mol^{-1}\,cm^{-1}$ for the bromo complex. In the literature, the values of ε_{615} (693[16] and 610 dm^3 $mol^{-1}\,cm^{-1}$[17]) and those of ε_{650} (853[16] and 832 $dm^3\,mol^{-1}$ cm^{-1}[17]) have been reported; these values seem to be too large compared with those of this work. It is interesting that the inconsistency among the values of ε is large not for the bromo complex but for the chloro one. There are two possible explanations for this inconsistency. One is that no subtraction of the base lines for the T-bands was taken into account by Graddon and Watton[16] and by Libus et al.;[17] the other is that a partial dissociation of $[CoX_2(2\text{-Me-py})_2]$ probably occurs in the 2-Me-py solutions. This possible dissociation may be supported by the existence of both a weak band centered at about 510 nm and a weak, broad band ranging from $\approx$360 to $\approx$410 nm (Fig. 5).

The 510-nm band may be due to an ionic octahedral species of the type $[CoX_x(2\text{-Me-py})_{6-x}]^{2-x}$[2,3] ($x$=0 or 1). According to a previous paper,[12] the band ranging from $\approx$360 to $\approx$410 nm may be assigned to a charge-transfer band arising in a contact pair of solvent molecule 2-Me-py with free ion X^-. $[CoX_x(2\text{-Me-py})_{6-x}]^{2-x}$ and free X^- may result from a dissociation of the tetrahedral complex $[CoX_2(2\text{-Me-py})_2]$.

As Fig. 5 shows, the intensity of the CT band in the 2-Me-py system decreases with increasing temperature, which is contrary to that of the 3-Me-py system.[12] An explanation may be that in the 2-Me-py system the concentration of the free X^- ion decreases with increasing temperature, probably because of the formation of such an ionic tetrahedral species as $[CoX_3(2\text{-Me-py})]^-$ by a reaction between X^- and $[CoX_2(2\text{-Me-py})_2]$ at high temperatures.

The intensity of the CT band in the 2-Me-py system is less than that of the 3-Me-py system[12] at room temperature and the CT band is hardly observed in the py[10] and 4-Me-py systems. From these results, it is concluded that free ion X^- can be easily formed in solvents in the order 4-Me-py, py$\ll$2-Me-py$<$3-Me-py.

Referring to the literature[28,29] showing structures of the ion pairs as
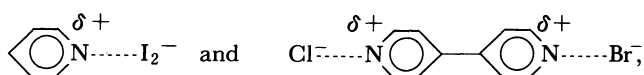
the structure of the CT complex in the present study may be:
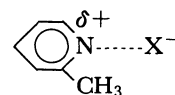
where X^- is a donor and nitrogen is an acceptor.

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24) The thermal expansion coefficient of 4-Me-py, 1.038×10^{-3} K^{-1}, is evaluated from the slope of the least-square fitting straight line for the plots of the reciprocals of densities of 4-Me-py vs. temperatures. Those densities are given in "Beilsteins Handbuch der Organishen Chemie," ed. by Deutschen Chemischen Gesellschaft, Springer-Verlag, Berlin (1935), Hauptwerk Band XX, p. 240 and *ibid.*, ed. by Beilstein-Institut für Literatur der Organischen Chemie, Springer-Verlag, Berlin (1978), Ergänzungswerk III/IV, Band XX, p. 2734. By the same manner, the thermal expansion coefficients of the other amine bases are estimated as follows: 1.084×10^{-3} K^{-1} for py, 0.875×10^{-3} K^{-1} for 3-Me-py, and 1.123×10^{-3} K^{-1} for 2-Me-py. In Refs. 10 and 12, the values of ΔH for the py and 3-Me-py systems (X=Cl, Br) have been obtained by using the approximate thermal expansion coefficient 1×10^{-3} K^{-1}. The values of ΔH estimated by using the above new coefficients are found to agree with those in the previous reports[10,12] within the experimental error.

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