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Pressure and Temperature Effects on Octahedral-Tetrahedral Equilibria in Pyridine Solutions of Some Cobalt(II) Halides

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The visible absorption spectra of CoX_2 (X=Cl, Br) in pyridine solutions have been measured in the ranges 1 bar—3 kbar at room temperature, and ≈4—≈70 °C at 1 atm. The equilibrium, $[CoX_2(py)_2]$(tetrahedral)+ $2py \rightleftharpoons [CoX_2(py)_4]$(octahedral), is found to be followed over these pressure and temperature ranges. High pressure favors the octahedral species, with the volume changes, −41 cm^3/mol for the chloride and ≈−30 cm^3/mol for the bromide at 1 atm. The pressure dependence of the volume change is less for the bromide than for the chloride. High temperature, however, favors the tetrahedral species, with the heats of reaction, 57.3 and 60.7 kJ/mol for the chloride and the bromide, respectively. Some discussions on both the effects are also presented.

Although the effects of pressure on the ionic equilibria between tetrahedral and octahedral species of cobalt(II) in solutions have been studied quantitatively using spectrophotometric method,[1–4] there exist large discrepancies between their ΔV values, the volume changes accompanying the shift of the equilibria to the octahedral species side with increasing pressure. For example, for $CoCl_2$ in an ethanol solution, Kitamura[1] obtained ΔV to be −154 cm^3/mol but Roariguez and Offen[2] −45 cm^3/mol under atmospheric pressure at 25 °C, and for $CoBr_2$ in an acetone solution, Ishihara *et al.*[3] estimated ΔV to be −36 cm^3/mol but later Ishihara[4] obtained −109 cm^3/mol as a more accurate value. These discrepancies appear to arise from the following reason: More than two kinds of complexes exist in each solution, so that the separation of the spectra seems to be difficult.

In some pyridine solutions, the very simple equilibrium is known to exist only as follows:[5–7]

$$\underset{\text{(tetrahedral)}}{[CoX_2(py)_2]} + 2py \rightleftharpoons \underset{\text{(octahedral)}}{[CoX_2(py)_4]}, \tag{1}$$

where X=Cl, Br, or I. On the basis of the method of continuous variations, Katzin and Gebert[5] have shown that the main coordinated species is $[CoCl_2(py)_4]$, but some $[CoCl_2(py)_2]$ is also present in the pyridine solutions of $CoCl_2$. Katzin[6] measured the temperature variation of the absorbance of these solutions in the range 32—66 °C; the validity of Eq. 1 has been confirmed over this temperature range. By means of optical spectroscopy and electrical conductivity, King *et al.*[7] have established that the only equilibrium of Eq. 1 occurs in the solutions of compounds of the type $[CoX_2(py)_2]$ where X is Cl, Br, or I.

As a part of the study on the pressure and temperature effects on tetrahedral-octahedral configuration equilibria and on the structures of some complexes in solutions of cobalt(II) halides, the authors describe the pressure and temperature variations of the absorption spectra of $CoCl_2$ and $CoBr_2$ in pyridine solutions. The spectrophotometric method should be useful for these investigations because the visible spectra of both the species are separate and well-defined.

Experimental

The commercial chemical pure reagent (C. P. grade) $CoCl_2$ was dried under reduced pressure at about 105 °C for 12 h. $CoBr_2 \cdot 6H_2O$ (C. P. grade) was also dried to constant weight. After dried with anhydrous $CaSO_4$, the commercial guaranteed reagent grade pyridine was distilled.

A clamp-type optical cell[8] was used to measure the absorption spectra under high pressures. Silicone O-rings and aluminum gaskets were fitted at the connection parts of the cell to prevent corrosion by the pyridine solutions as well as pressure leaks. The spectra were determined on a Hitachi 340 spectrophotometer at room temperature.

For the measurements with temperature change, however, a Shimadzu model MPS-50L spectrophotometer was used. The maintenance of a constant temperature for an optical cell was effected by circulating water from a thermostat by means of a pump. The temperature was measured with a calibrated chromel-alumel thermocouple inserted in the sample solutions, being kept constant within 1.0 °C. A silicone-rubber lid was fitted to the sample cell to keep constant concentration of the solutions.

Results and Discussion

Pressure Effect. Figure 1 shows the absorption spectra of $CoCl_2$ in pyridine at high pressures. The spectrum at one atmosphere has three peaks at 500, 524, and 608 nm and three shoulders at about 571, 637, and 664 nm in agreement with the results of Katzin.[6] It can be seen that the two higher-energy peaks belong to a strong absorption band (O), the 608-nm peak and the shoulders do to another weak band (T); the O-band is assigned to the ${}^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$ transition of Co^{II} in the octahedral species $[CoCl_2(py)_4]$, and the T-band to the ${}^4A_2(F) \rightarrow {}^4T_1(P)$ transition of that in the tetrahedral one $[CoCl_2(py)_2]$.[3,5–7]

Although an isosbestic point appears at about 539 nm but is not well-defined, the equilibrium of Eq. 1 is found to be followed over this pressure range. The equilibrium shifts to the $[CoCl_2(py)_4]$ species side with increasing pressure, because the intensity of the O-band increases and that of the T-band decreases with increasing pressure. The O-band position scarcely changes but the 608-nm peak and the 637-nm shoulder shift slightly towards higher frequencies with pressure, which is probably due to a larger degree of distortion or compression in the species $[CoCl_2(py)_2]$ than in the other species $[CoCl_2(py)_4]$.

Figure 2 shows the absorption spectra of $CoBr_2$ in pyridine at high pressures. The spectrum at one atmosphere shows two peaks at 522 and 539 nm, and a shoulder at about 492 nm, which belong to an O′-

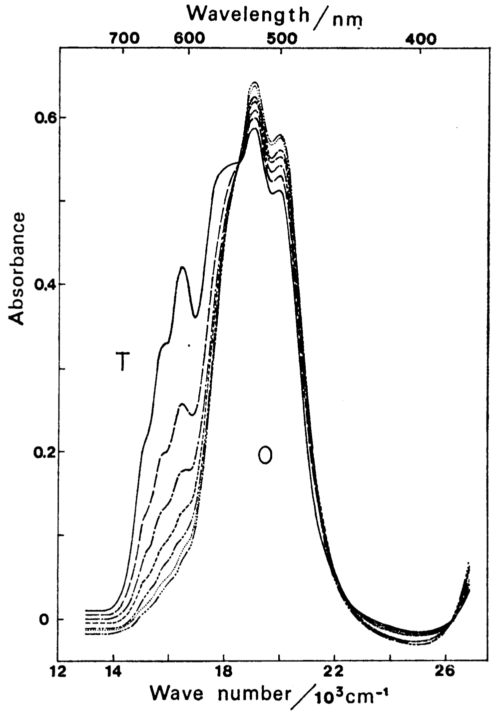

Fig. 1. Absorption spectra of $CoCl_2$ in pyridine at high pressures (25 °C), uncorrected for compression of solution.
Concn: 2.043×10^{-2} mol dm^{-3} (25 °C), optical path lenth: 1.6 cm.
——: 1 bar, — — —: 0.5 kbar, —·—: 1.0 kbar, ----: 1.5 kbar, ———: 2.0 kbar, ······: 2.6 kbar, —···—: 3.0 kbar.

band. A peak at 643 nm, and shoulders at about 593, 629, and 711 nm are part of a T′-band. An isosbestic point is observed at about 564 nm. Since the spectra, as a whole, show similar pressure dependence to those of the chloride (Figs. 1 and 2), the equilibrium of Eq. 1 occurs also in the case of the bromide and shifts to the $[CoBr_2(py)_4]$ species side with increasing pressure. The 522-nm peak and the 492-nm shoulder increase in intensity more rapidly than the 539-nm peak, and consequently the O′-band changes its shape and shifts slightly to higher frequencies with increasing pressure, which the O-band scarcely shows (Fig. 1). $[CoBr_2(py)_4]$ may therefore be more distorted or compressed than $[CoCl_2(py)_4]$ probably for steric reasons.

Although for the compounds of the type $[CoX_2(py)_2]$, both the bonds of Co–X and Co–py were observed to be stronger in the chloride than in the bromide by spectroscopic[9–11] and calorimetric[12] methods, it is difficult to observe these differences in Figs. 1 and 2.

Now, we will estimate the volume change accompanying the shift of the equilibrium of Eq. 1 to the octahedral species side. In general, for an equilibrium existing in a diluted solution, the volume change (ΔV) is given by[13]

$$\Delta V = -RT\left(\frac{\partial \ln K}{\partial P}\right)_T + \Delta\nu\cdot\kappa\cdot RT, \tag{2}$$

where K is the equilibrium constant expressed in terms of the molar concentration of each species, R is the gas constant, $\Delta\nu$ is the change in the number of the species due to the reaction, and κ is the isothermal compressibility of solvent.

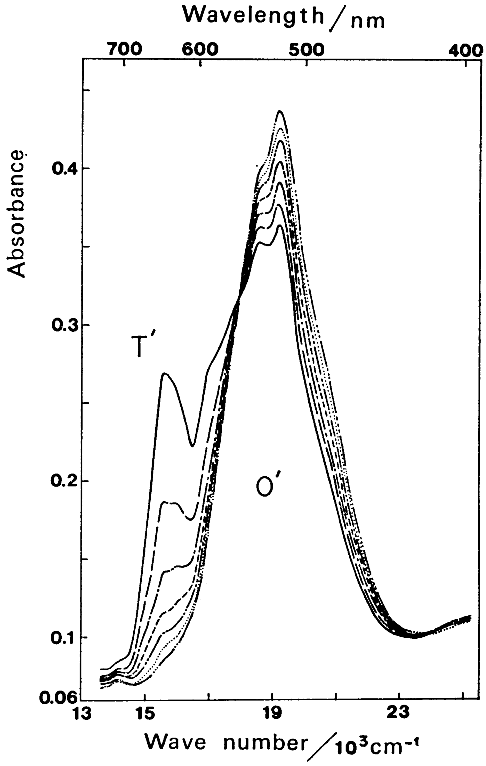

Fig. 2. Absorption spectra of $CoBr_2$ in pyridine at high pressures (20 °C), uncorrected for compression of solution.
Concn: 1.022×10^{-2} mol dm^{-3} (25 °C), optical path length: 1.6 cm.
——: 1 bar, — — —: 0.5 kbar, ———: 1.0 kbar, ----: 1.5 kbar, ———: 2.0 kbar, ······: 2.5 kbar, —···—: 3.0 kbar.

Assuming that activity coefficient of each species equals to unity, the equilibrium constant for Eq. 1 is given by

$$K = \frac{c_{[CoX_2(py)_4]}}{c_{[CoX_2(py)_2]} \times c_{py}^2}. \tag{3}$$

From Eqs. 2 and 3, we can obtain the volume change accompanying the shift of equilibrium of Eq. 1 to the octahedral species side, ΔV, as follows:

$$\Delta V = -RT\frac{d}{dP}\ln\left(\frac{c_{[CoX_2(py)_4]}}{c_{[CoX_2(py)_2]}}\right). \tag{4}$$

Although we can not estimate the value, $\ln (c_{[CoX_2(py)_4]}/c_{[CoX_2(py)_2]})$, at a given pressure, we can obtain the pressure dependence of this value using the integrated intensities of the octahedral and the tetrahedral band, assuming that the absorbance observed under high pressures follows the Beer-Lambert law (it did at atmospheric pressure), and that the molar absorption coefficient (ε) and the optical path length do not change in this pressure range.

Figure 3 shows the plots of the logarithm of the ratio of both the integrated intensities for the chloride and the absorbances of the peaks for the bromide *vs.*

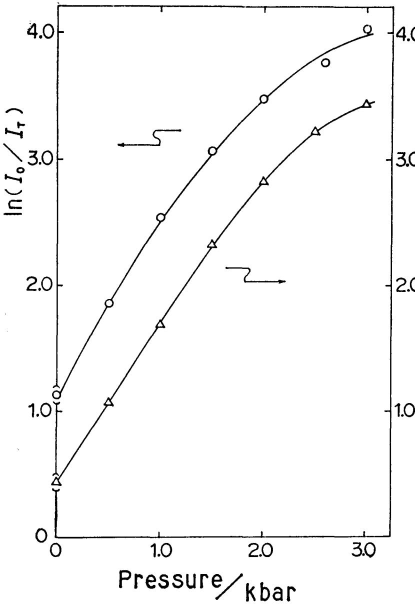

Fig. 3. Logarithm of the integrated-intensity ratio of the O-band to the T-band (I_O/I_T) for $CoCl_2$ and the ratio of the absorbance at 522 nm to that at 643 nm (A_{522}/A_{643}) for $CoBr_2$ *vs.* pressure.
O,△: Experimental, ——: calculated fitting curves.

Table 1. ΔV for $CoCl_2$ and $CoBr_2$ in pyridine solution

$\frac{P}{\text{kbar}}$	$\frac{-\Delta V}{\text{cm}^3\ \text{mol}^{-1}}$	
	$CoCl_2$	$CoBr_2$
0.001	41	29
0.5	35	31
1.0	29	31
1.5	24	28
2.0	18	23
2.5	13	16
3.0	7	6

pressure. For the bromide, instead of the integrated intensities, the absorbances of the peaks at 522- and 643-nm are used, because of the rather changes of the O′-band shape with pressure as described above. These plots are fitted to the following equations by the least-squares method:

$$\ln\frac{I_O}{I_T} = 1.10 + 1.64P - 0.227P^2, \text{ for the chloride,}$$

$$\ln\frac{A_{522}}{A_{643}} = 0.446 + 1.17P + 0.143P^2 - 0.0665P^3, \quad \text{for the bromide.} \qquad (5)$$

From Eqs. 4 and 5, the ΔV values are estimated and listed in Table 1. For the bromide, the absolute values of ΔV evaluated using the integrated intensities of the O′- and the T′-band are ≈5% larger than those in Table 1.

We can regard the ΔV value as the difference in the intrinsic volume between $[CoX_2(py)_4]$ and $[CoX_2(py)_2]$ solvated with two pyridine molecules. These intrinsic volumes, however, cannot be estimated at this stage without the knowledge of the details of the structure of both complexes. The absolute value of ΔV at atmospheric pressure is smaller for the bromide (≈30 cm³/mol) than for the chloride (41 cm³/mol). This may be explained as follows; since the ionic radius of Br^- is larger than that of Cl^-, the volume difference between $[CoX_2(py)_4]$ and $[CoX_2(py)_2]$ is probably smaller for the bromide than for the chloride. Comparison with the chloride, the ΔV for the bromide changes almost linearly with pressure up to ≈1.5 kbar (Fig. 3 and Table 1).

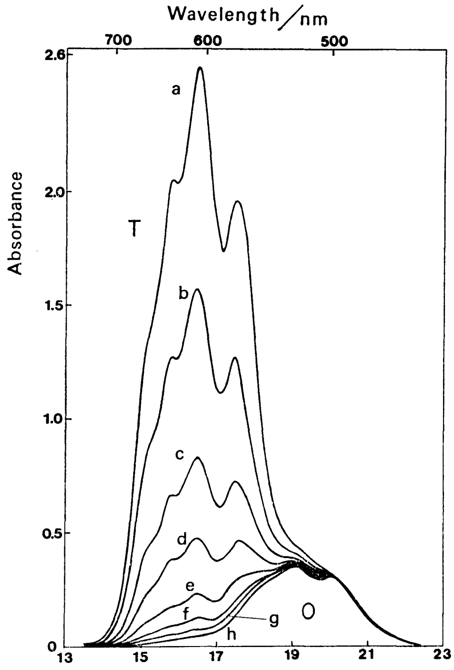

Fig. 4. Absorption spectra of $CoCl_2$ in pyridine at various temperatures (1 atm), uncorrected for thermal expansion of solution.
Concn: 2.043×10^{-2} mol dm⁻³ (25 °C), optical path length: 0.98 cm. a: 67.6 °C, b: 57.7 °C, c: 47.2 °C, d: 38.4 °C, e: 27.4 °C, f: 19.1 °C, g: 11.4 °C, h: 4.0 °C.

Temperature Effect. Figure 4 shows the absorption spectra of $CoCl_2$ in pyridine at various temperatures. The intensity of the T-band increases steeply with increasing temperature; in particular, the 571- and 637-nm shoulders become well-resolved peaks. The O-band spectra, however, is insensitive against temperature change and covered by the T-band at high temperatures. This may be caused by the fact that $\varepsilon_{[CoCl_2(py)_2]}$ is much greater than $\varepsilon_{[CoCl_2(py)_4]}$.[14]

For $CoBr_2$, the corresponding spectra are shown in Fig. 5. The changes of these spectra quite resemble those of the chloride, except that in this case the 593-nm shoulder becomes a well-resolved peak.

Although no isosbestic point is found in each figure, for both the systems the equilibrium of Eq. 1 presumably occurs and shifts to the tetrahedral-species side with increasing temperature. The equilibrium constant K' is given by

$$K' = \frac{c_{[CoX_2(py)_2]}\times c_{py}^2}{c_{[CoX_2(py)_4]}}. \qquad (6)$$

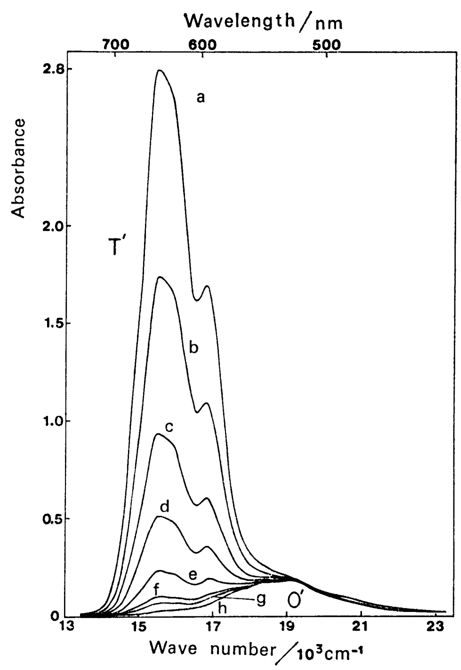

Fig. 5. Absorption spectra of $CoBr_2$ in pyridine at various temperatures (1 atm), uncorrected for thermal expansion of solution.
Concn: 1.022×10^{-2} mol dm^{-3} (25 °C), optical path length: 0.98 cm. a: 71.1 °C, b: 60.3 °C, c: 49.7 °C, d: 39.4 °C, e: 30.2 °C, f: 21.1 °C, g: 10.7 °C, h: 4.8 °C.

Because the concentrations of pyridine and $[CoX_2(py)_4]$ scarcely change, they can be assumed to be constant.[14] Therefore the change of K' can be followed by the intensity changes of the T′-band.

In Fig. 6, the logarithm of the corrected absorbance (A') of the 664-nm shoulder for the chloride and the 643-nm peak for the bromide is plotted against the reciprocal of absolute temperature. In order to correct the concentration, we used the approximate thermal expansion coefficient of pyridine (0.001[16]) over the temperature ranges. In order to express the intensity of the T-band, A' of the 664-nm shoulder is chosen, because there is little contribution of the intensity of the O-band at this wavelength. For the T′-band of the bromide, however, A' of the 643-nm peak subtracted out A'^{278}_{643} due to the O′-band is used. Linearities of the plots are obtained for both the halides. From each slope, the heat of reaction ΔH is estimated to be 57.3 for the chloride and 60.7 kJ/mol for the bromide. Since the similar ΔH values are obtained using the other peaks and shoulders for both cases, the equilibrium of Eq. 1 certainly occurs in each temperature range, and shifts to the $[CoX_2(py)_2]$ species side as temperature increases.

The ΔH value for the chloride is compatible with 56.1 kJ/mol obtained by Katzin.[6] Using the K' of 0.16 at 20 °C[15] and the ΔH of 57.3 kJ/mol, we can estimate ΔG to be ≈ 4.6 kJ/mol and $\Delta S \approx 0.18$ kJ/(K mol), these values being comparable with the previous results.[6,7]

ΔH is a measure of the Co–py bond strength in $[CoX_2(py)_4]$. Clark and Williams[9] studied the far-infrared spectra of $[CoX_2(py)_4]$ complexes (X=Cl, Br, or I) by means of mull and assigned the strong band at about 215 cm^{-1} to the asymmetric Co–py vibration, because of the little dependence of its frequency on the type of halogen ion. King *et al.*[7] obtained ΔH for $[CoX_2(py)_4]$ (X=Cl, Br, or I) in chloroform solutions by calorimetric measurements. They were in the order of increase $Cl^- < Br^- < I^-$ and 63.6, 65.3, 69.5 kJ/mol, respectively. Though we lack ΔH for the iodide,** the order in halogen ion shown by King *et al.* is consistent with our result. The result seems to support their following explanation of this halogen ion order: Because I^- is most polarisable, charge is readily transferred to the metal along the σ-bond. This induces two opposite effects; one is to lower the effective electron affinity of Co^{II} towards pyridines, the Co–py bond strength being in the sequence $Cl^- > Br^- > I^-$, and the other is to enhance the release of non-bonding d-electrons of Co^{II} to antibonding pyridine π-orbitals (dative π-bonding); when the latter is superior to the former, the Co–py bond strengthens in the order $Cl^- < Br^- < I^-$.

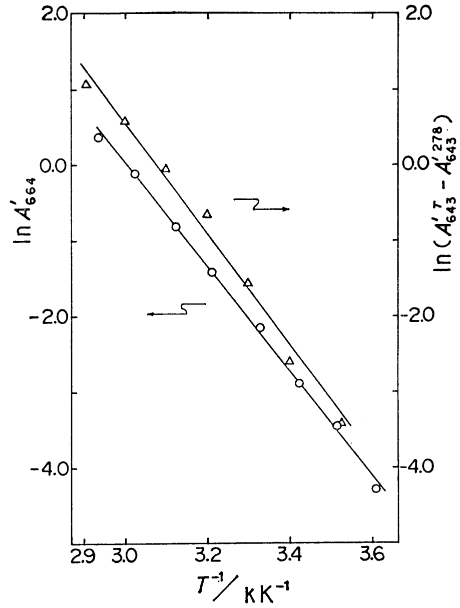

Fig. 6. Logarithm of the corrected absorbance for $CoCl_2$ (○) and for $CoBr_2$ (△) *vs.* reciprocal of absolute temperature.
A'^{278}_{643}, for example, denotes the absorbance at 643 nm and at 278 K corrected by approximate thermal expansion coefficient of pyridine. Solid lines are least-square fits to the data.

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**The experiment is in progress.

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14) From $K'=0.16$ at 20 °C[15] and Fig. 4, we can roughly estimate $c_{[\mathrm{CoCl_2(py)_2}]}/c_{[\mathrm{CoCl_2(py)_4}]} \approx 950$ (≈ 20 °C), ≈ 60 (≈ 70 °C), and $\varepsilon_{[\mathrm{CoCl_2(py)_2}]}/\varepsilon_{[\mathrm{CoCl_2(py)_4}]} \approx 490$.

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