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

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Synopsis. Temperature and pressure effects on the configuration equilibrium of cobalt(II) iodide in pyridine solution have been studied spectrophotometrically. High temperature favors the tetrahedral species but high pressure favors the octahedral species, the heat and volume changes being 65.3 kJ mol^{-1} and -6 cm^3 mol^{-1}, respectively. Comparisons among three kinds of halide are also made.

We have reported[1] the ΔH and the ΔV values determined in terms of the shift of the equilibrium $[CoX_2(py)_2]$ (tetrahedral)$+2py \rightleftharpoons [CoX_2(py)_4]$ (octahedral), where X is Cl or Br. This note deals with the case of X= I and discusses the relation among the chloride, the bromide and the iodide complexes.

The experimental details (except that the commercial chemical pure reagent $CoI_2 \cdot 4H_2O$ was used after dehydration in the present study) and the method of determining the values of ΔH and ΔV were the same as previously described.[1]

Results and Discussion

Figure 1 shows the absorption spectra of CoI_2 in pyridine at various temperatures. There found two bands, the one is the T-band due to the tetrahedral species $[CoI_2(py)_2]$ and the other the O-band due to the octahedral species $[CoI_2(py)_4]$. The T-band intensity increases steeply with increasing temperature; two peaks at 658, 685 nm and a shoulder near 626 nm are well-resolved at 74.6 °C. This trend suggests that the equilibrium mentioned above shifts to the tetrahedral-species side with increasing temperature, although the variation of the O-band spectrum with the temperature changes is not found to be clear because of the low molar absorption coefficient of $[CoI_2(py)_4]$.

A plot of the logarithm of A'_{685} *vs.* T^{-1} in Fig. 2 gives a straight line, from the slope of which the ΔH value of 65.3 kJ mol^{-1} is obtained, being comparable with the value of 69.4 kJ mol^{-1}.[2]

The ΔH values increase in the order $Cl^- < Br^- < I^-$, which is consistent with the result of King *et al.*[2] They proposed that this order is ascribed to the degree of contribution of the dative π-bonding to the Co–py bond and that this π-bonding is related to the polarizability of halide ion. By plotting the ΔH values *vs.* the electronic polarizability of halide ions in crystals[3] in Fig. 3, we can find the linear relation between them. Furthermore, we are concerned in the relation between the ΔH values and the electronegativity of halide ions.

Because CoI_2 is less soluble in pyridine (its solubility is the order of one-hundredth of those of the other halides), the intensities of the O- and T-band are weak at room temperature and 1 atm, so that the changes in the absorption spectra with the variation of pressure are not very clear (not shown). However, from the plot of the logarithm of the ratio of the integrated-intensities

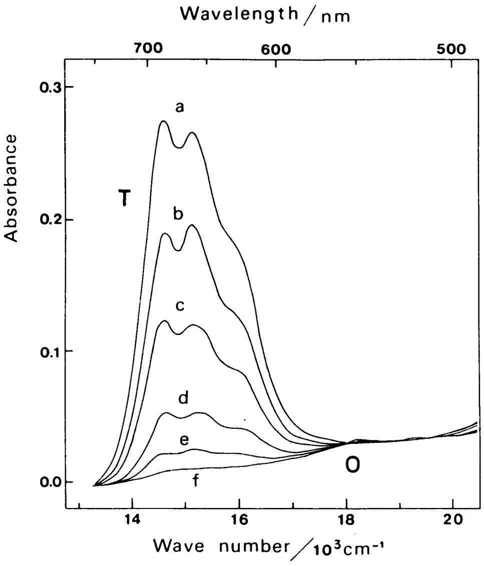

Fig. 1. Absorption spectra of CoI_2 in pyridine at various temperatures (1 atm), uncorrected for the thermal expansion of the solution. Concn: 5.320×10^{-4} mol dm^{-3} (25 °C), optical path length: 0.98 cm.
a: 74.6 °C, b: 62.6 °C, c: 55.0 °C, d: 43.2 °C, e: 34.6 °C, f: 24.4 °C.

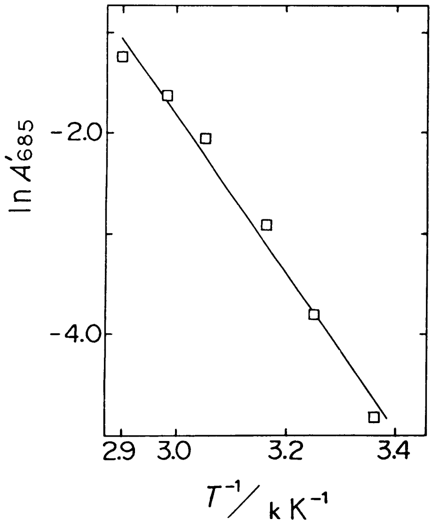

Fig. 2. Logarithm of the corrected absorbance for CoI_2 *vs.* reciprocal of the absolute temperature.
A'_{685} denotes the absorbance at 685 nm corrected by the approximate thermal expansion coefficient of pyridine as in Ref. 1. The line is the least-square fit to the data.

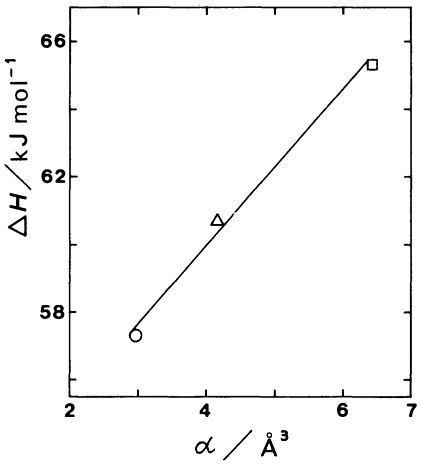

Fig. 3. ΔH *vs.* electronic polarizability of halide ions. ○: Cl$^-$, △: Br$^-$, □: I$^-$. ΔH values for the chloride and bromide are taken from Ref. 1.

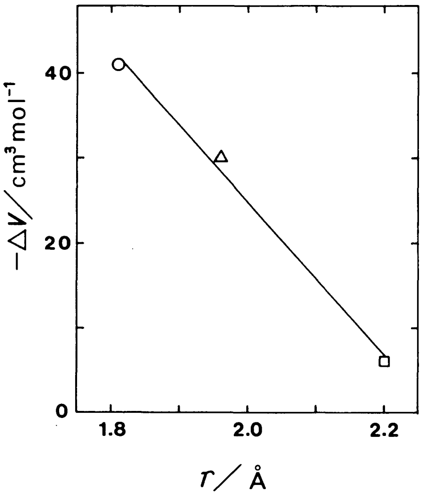

Fig. 4. ΔV at 1 atm *vs.* ionic radii of halide ions. ○: Cl$^-$, △: Br$^-$, □: I$^-$. ΔV values for the chloride and bromide are taken from Ref. 1.

of the O-band to those of the T-band against pressure, we obtain the ΔV value of -6 cm^3 mol^{-1} over the pressure range 1 bar to 3 kbar.

The values of ΔV at 1 atm show a linear variation with the ionic radii of the halide ions, as exhibited in Fig. 4. This implies that the larger the ionic radius, the smaller the volume difference between [$CoX_2(py)_4$] and [$CoX_2(py)_2$] solvated with two pyridine molecules.

Another effect of pressure on the relation between ΔV and pressure has been described previously.1) In the present study, the relation for the iodide is found to be the most linear.

References

1) K. Kojima, M. Saida, M. Donoue, and J. Matsuda, *Bull. Chem. Soc. Jpn.*, **56**, 684 (1983).

2) H. C. A. King, E. Körös, and S. M. Nelson, *J. Chem. Soc., A*, **1963**, 5449.

3) J. R. Tessman, A. H. Kahn, and W. Shockley, *Phys. Rev.*, **92**, 890 (1953).