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PRESSURE EFFECTS ON THE COMPLEXES OF COBALT(II) CHLORIDE AND COBALT(II) BROMIDE IN ACETONE SOLUTION

BY IZUMI ISHIHARA, KIMIHIKO HARA and JIRO OSUGI

The acetone solutions of cobalt(II) chloride and cobalt(II) bromide are blue under atmospheric pressure at room temperature and in both of them the main species is tetrahedrally coordinated $CoX_2(Ac)_2$, where Ac denotes an acetone molecule and X is Cl or Br. The visible absorption spectra of cobalt(II) chloride and cobalt(II) bromide in acetone solution measured under pressures up to 8,000 kg/cm^2 at room temperature showed that the following two kinds of equilibria coexist:

$$CoX_2(Ac)_2+4Ac \rightleftharpoons Co(Ac)_6^{2+}+2X^-, \qquad (I)$$
$$CoX_2(Ac)_2+X^- \rightleftharpoons CoX_3(Ac)^-+Ac. \qquad (II)$$

The value of ΔV_1, the volume change of equilibrium (I), is large with the negative sign and changes greatly with increasing pressure. $|\Delta V_2|$, the absolute value of the volume change of equilibrium (II), is small and scarcely depends on pressure. These experimental results indicate the nature of equilibrium (I) and eqilibrium (II): in equilibrium (I) the ionic species are formed and the coordination number increases by the shift to the right side, and in equilibrium (II) there is no change in the number of the charged species and in the coordination number on both sides.

In addition, ΔV_1 was estimated from the change of the intrinsic volume, the free volume and the effect of electrostriction.

Introduction

Cobalt(II) chloride and cobalt(II) bromide in solution form various complexes with various solvents and show the absorption spectra which depend largely on solvents. This phenomenon is caused by the difference in the coordination number and/or in the species of ligands.

Among the absorption spectra of crystalline cobalt(II) complexes, the weak absorption band around 20,000 cm^{-1} (=500 nm) for hexacoordinated species is pink and assigned to the $^4T_{1g}(F) \longrightarrow {}^4T_{1g}(P)$ transition, and the strong absorption band around 15,000 cm^{-1} (≒670 nm) for tetracoordinated species is blue and assigned to the $^4A_2(F) \longrightarrow {}^4T_1(P)$ transition[1]. As for in solution, cobalt(II) complexes have been studied on some cobalt(II) ions in water[2], tetra-*n*-butylammonium tetrahalocobaltate(II) complexes, methyltriphenylarsonium tetraiodocobaltate(II) complex and quinolinium tetrahalocobaltate(II) complexes[3], cobalt(II) chloride complexes in nitromethane and in dimethylformamide[4], and

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[1] C. J. Ballhausen, "Introduction to Ligand Field Theory", McGraw-Hill, New York (1962)

[2] C. J. Ballhausen and C. K. Jørgensen, *Acta Chem. Scand.*, **9**, 397 (1955)

[3] F. A. Cotton, D. M. L. Goodgame and M. Goodgame, *J. Am. Chem. Soc.*, **83**, 4690 (1961)

[4] S. Buffagni and T. M. Dunn, *J. Chem. Soc.*, **1961**, 5105

cobalt(II) ion in acetone with added lithium halides[5]. In every case, the similar assignments have been made.

The thermochromism of cobalt(II) chloride has been reported on various solvents (water, methanol, ethanol, 1-propanol, 2-propanol) in the range of $-80 \sim 95$°C[6]. The color of these solutions changes from blue to pink on cooling. The explanation of these phenomena was given qualitatively in terms of octahedral-tetrahedral configurational changes of solvated cobalt(II) complexes. Cobalt(II) chloride in acetone solution displays different behavior from that in alcoholic solution: the temperature effect of acetone solution is very small and it gives a different spectrum at about -80°C from that at room temperature. Thus, it was inferred that almost all cobalt(II) ions are tetrahedrally surrounded at room temperature[6,7] and the shift of the equilibrium to the new tetrahedral-like species plays an important role at -80°C[6]. Gill and Nyholm[8] studied the factors likely to favour the formation of tetrahalo complexes of bivalent transition metals. They noted that the color changes, usually from green to blue, with increasing temperature, and considered an equilibrium:

$$\mathrm{Co(H_2O)_6^{2+} + 4Cl^- \ (solv.) \rightleftharpoons CoCl_4^{2-} + 6H_2O},$$

which shifts to the right side due to the decrease in the solvation of the chloride ion. Scaife and Wood[9] studied the effect of temperature on the equilibrium for some cobalt(II) and nickel(II) halides in water and alcohols which give the intense blue color of the tetrahedral species on heating,

$$\mathrm{X^- + [MX_2 \cdot 4solv.]_{octahedral} \rightleftharpoons [MX_3 \cdot solv.]^-_{tetrahedral}},$$

where M denotes those metals and X is halogen.

The pressurechlomism of cobalt(II) complexes was known about the aqueous solution of cobalt (II) chloride[10]. The aqueous solutions of cobalt(II) chloride and cobalt(II) bromide with and without added salt were studied in the range of $25 \sim 500$°C and $1 \sim 6{,}000$ atm by Lüdemann and Franck[11]. Further, the pressure effects on the alcoholic solutions of cobalt(II) chloride and cobalt(II) bromide were reported[12]. In that paper it was supposed that the following equilibrium exists:

$$\mathrm{CoX_2(Alc)_2} + (n-2)\mathrm{Alc} \rightleftharpoons \mathrm{Co(Alc)}_n^{2+} + 2\mathrm{X}^-,$$

where X=Cl or Br, n=4 or 6 and Alc denotes the solvent alcoholic molecule. Virtually n was taken for 6. This equilibrium shifts to the right side with increasing pressure. And it was conclusively demonstrated that the pressure effect on the equilibrium constants depends on the molecular structure of the solvents.

The present paper is concerned with the pressure effects on the complexes of cobalt(II) chloride

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5) D. A. Fine, *J. Am. Chem. Soc.*, **84**, 1139 (1962)
6) W. C. Niewpoort, G. A. Wesselink and E. H. A. M. van der Wee, *Recueil*, **85**, 397 (1966)
7) L. I. Katzin and E. Gebert, *J. Am. Chem. Soc.*, **72**, 5464 (1950)
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10) F. G. Wick, *Proc. Am. Acad. Arts Sci.*, **58**, 555 (1923)
11) H.-D. Lüdemann and E. U. Franck, *Ber. Bunsenges. Phys. Chem.*, **71**, 455 (1967); **72**, 514 (1968)
12) Y. Kitamura, *This Journal*, **39**, 1 (1969)

and cobalt(II) bromide in acetone solution by measuring the visible absorption spectra.

Experimental

Materials

Anhydrous cobalt(II) chloride was prepared by drying the guaranteed reagent, $CoCl_2 \cdot 6H_2O$, (E. Merck) at about 150°C under reduced pressure for about 30 hours. The completion of the dehydration was confirmed by weighing the material.

Anhydrous cobalt(II) bromide was purified by the recrystallization of the commercial chemically-pure reagent, $CoBr_2 \cdot 6H_2O$, by using the spectroscopic grade acetone as the solvent and drying at 140 ~150°C under reduced pressure for about 30 hours. The completion of the dehydration and the desolvation was confirmed.

Acetone used as the solvent for the measurements of the absorption spectra was of spectroscopic grade.

Anhydrous lithium chloride was prepared by drying the commercial guaranteed reagent, LiCl, at about 120°C for about 5 hours.

Anhydrous lithium bromide was prepared by drying the ultra pure reagent, $LiBr \cdot (1 \sim 2)H_2O$, (E. Merck) at about 110°C under reduced pressure for about 30 hours.

Measurements of the absorption spectra

Three pairs of quartz cells with the path length of 1, 5 and 10 cm were used for the measurements at atmospheric pressure.

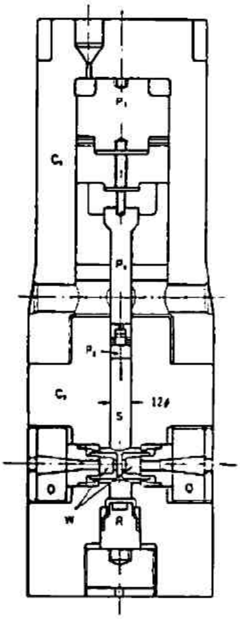

Fig. 1 Schematic diagram of high pressure vessel for optical measurement

P_1: Low pressure piston
P_2: High pressure piston
P_3: Piston rod
C_1: Low pressure cylinder
C_2: High pressure vessel
S : Sample solution
W: Sapphire window
O : Window plug
R : Closure

The pressure intensifier and the high pressure vessel for optical measurements were the same as the previously reported ones[12]. Fig. 1 shows the schematic diagram of the apparatus. A hand pump of screw type was used for increasing pressure, the pressure transmitting medium being silicon oil. The pressure was calibrated using the manganin pressure gauge as the secondary standard, which was inserted from the bottom plug of the optical vessel. The sapphire windows which had no absorption in the visible region were used in the optical vessel.

Spectra were measured on a Hitachi EPU-2A spectrophotometer. All measurements were carried out in the range of 22~25°C and up to 8,000 kg/cm^2. No obvious change of the spectrum with temperature was observed within this small range.

Results

Acetone solution of cobalt(II) chloride

The concentration of the solution used in the measurements at high pressure is 2.05×10^{-3} mole/*l*. At atmospheric pressure this solution obeys Beer's law. Namely, the molar extinction coefficient ε is independent of the dilution in the concentration to 10^{-4} mole/*l* within the experimental uncertainties. In acetone solution at atmospheric pressure and room temperature, cobalt(II) chloride exists mainly as $CoCl_2(Ac)_2$, where Ac denotes an acetone molecule[5,6]. This species has an absorption band in the range of about 500~750 nm and an absorption maxima at 673 nm ($\varepsilon_{max}=292$ *l*/mole · cm). The absorption spectra at various pressures are shown in Fig. 2. The intensity of the absorption band of this species decreases and a new band appears in the longer wavelength region by increasing pressure. This means the formation of a new species, whose intensity of the absorption band is not weak relative to that of $CoCl_2(Ac)_2$ in the range of about 580~700 nm.

In acetone solution, the complexes of cobalt(II) chloride exist as tetrahedrally coordinated species

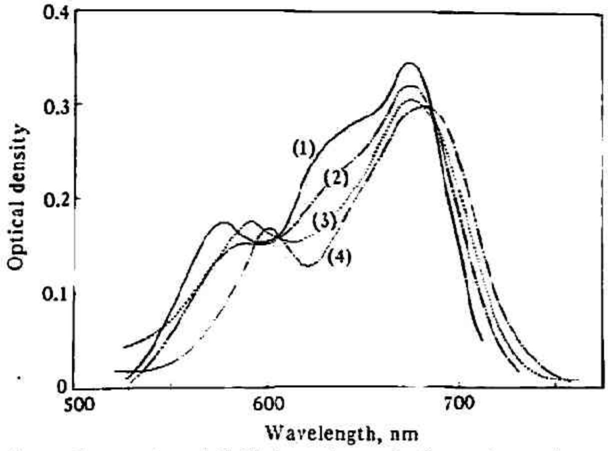

Fig. 2 Absorption spectra of $CoCl_2$ in acetone solution under various pressures
(Conc.: 2.05×10^{-3} mole/*l*. Path length: 7.0 mm)
(1) ———: 1 kg/cm^2 (2) ---—: 2000 kg/cm^2
(3) - - - -: 4000 kg/cm^2 (4) — · —: 8000 kg/cm^2

or octahedrally coordinated ones[6]. In the visible region the octahedrally coordinated species have a weak absorption band around 500nm[13]. This band is assigned to the parity-forbidden transition $^4T_{1g}(F) \longrightarrow {}^4T_{1g}(P)$, and so it is weak ($\varepsilon \approx 10$). Therefore, the newly formed species is a tetrahedrally coordinated one. Further, the equilibrium between $CoCl_2(Ac)_2$ and the octahedrally coordinated species whose amount is very small at atmospheric pressure and room temperature must be considered to give the quantitative explanation. Thus, the following two kinds of equilibria should be supposed; one is an equilibrium between a tetrahedrally coordinated species and an octahedrally coordinatecd one, and the other that between the two tetrahedrally coordinated ones. This is different from alcoholic solution in which only one kind of equilibrium exists[12].

To investigate the pressure effects on these two kinds of equilibria, the molar extinction coefficients of each species were determined. Those of $CoCl_2(Ac)_2$ were determined by assuming that all species have this form at atmospheric pressure and room temperature[5,6]. By the mole ratio method using lithium chloride and cobalt(II) chloride, the species produced at high pressure was identified as $CoCl_3(Ac)^-$ and the molar extinction coefficients at each wavelength were determined. Fig. 3 shows the molar extinction coefficients of $CoCl_2(Ac)_2$ and $CoCl_3(Ac)^-$ and Table 1 gives the maximum values of these together with each wavelength.

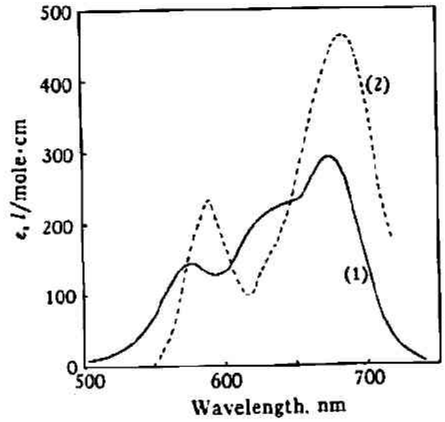

Fig. 3 Absorption spectra of $CoCl_2(Ac)_2$ and $CoCl_3(Ac)^-$

(1) ——: $CoCl_2(Ac)_2$

(2) - - - -: $CoCl_3(Ac)^-$

Table 1 ε and wavelength of $CoCl_2(Ac)_2$ and $CoCl_3(Ac)^-$ at absorption maxima

Species	Wavelength (nm)	ε (l/mole·cm)
$CoCl_2(Ac)_2$	578	145
	~630 (sh)	215
	673	292
$CoCl_3(Ac)^-$	590	232
	~630 (sh)	144
	684	462

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[13] B. F. Figgis, "Introduction to Ligand Fields", Interscience Publishers, New York (1966)

The previous investigations of cobalt(II) halide systems in organic solvents have indicated the possible presence of complexes having from one to four coordinated halides. It is most likely that the dihalo and trihalo complexes are tetrahedral with the remaining sites on the tetrahedron occupied by acetone molecules. The tetrahalo complex gives also a tetrahedral structure5). As the pentasolvated complex of the type $CoCl(Ac)_5^+$ has not been found, the octahedrally coordinated species is supposed to be $Co(Ac)_6^{2+}$. In addition, it is reported that the tetrahedrally coordinated species of $CoCl_4^{2-}$ whose intensity is stronger than those of $CoCl_2(Ac)_2$ and $CoCl_3(Ac)^-$ around 620~720 nm appears in the high chloride concentration range at atmospheric pressure and room temperature5). In the present experimental conditions, this was not observed by increasing pressure.

From these considerations, the two kinds of equilibria are depicted as follows:

$$CoCl_2(Ac)_2+4Ac \rightleftharpoons Co(Ac)_6^{2+}+2Cl^-, \qquad (1)$$

$$CoCl_2(Ac)_2+Cl^- \rightleftharpoons CoCl_3(Ac)^-+Ac. \qquad (2)$$

In equilibrium (1), as the charged species appear with the shift to the right side, this shift is caused by increasing pressure. As the result, the concentration of Cl^- increases, so the concentration of $CoCl_3(Ac)^-$ in equilibrium (2) increases. Assuming the equilibrium quotients are equal to the equilibrium constants, K_1 and K_2 of equilibria (1) and (2), the volume changes ΔV of the equilibria are estimated.

$$K_1=\frac{[Co(Ac)_6^{2+}][Cl^-]^2}{[CoCl_2(Ac)_2]}, \qquad (3)$$

$$K_2=\frac{[CoCl_3(Ac)^-]}{[CoCl_2(Ac)_2][Cl^-]}, \qquad (4)$$

where [ ] denotes the molar concentration. ΔV is given by the following equation:

$$\frac{\partial \ln K}{\partial P}=-\frac{\Delta V}{RT}+\Delta\nu\cdot\beta, \qquad (5)$$

where P is the pressure, R the gas constant and $\Delta\nu$ the change of the numbers of molecules on both sides of these equilibria. β denotes the compressibility of acetone, which is evaluated from the Tait equation; $\beta=C/(B+P)$ (B and C are constants, *i.e.* $B=755.7$ bar at 25.00°C, $C=931\times10^{-4}$ at 26.61°C14)).

First, the concentration of each species was determined. The molar extinction coefficients ε at each wavelength can be regarded as independent of pressure in the pressure range like this11).
$\varepsilon_i(CoCl_2(Ac)_2)$ denotes the molar extinction coefficient of $CoCl_2(Ac)_2$ and $\varepsilon_i(CoCl_3(Ac)^-)$ that of $CoCl_3(Ac)^-$ at wavelength i. OD_i denotes the optical density, l the path length. Thus, Eq. (8) holds at wavelength i. Similarly Eq. (9) holds at wavelength j. The pairs of i and j were chosen in the range of 600~700 nm where $Co(Ac)_6^{2+}$ has no absorption.

$$[CoCl_2(Ac)_2]+[CoCl_3(Ac)^-]+[Co(Ac)_6^{2+}]=C, \qquad (6)$$

$$2\cdot[CoCl_2(Ac)_2]+3\cdot[CoCl_3(Ac)^-]+[Cl^-]=2C, \qquad (7)$$

$$l\cdot[CoCl_2(Ac)_2]\cdot\varepsilon_i(CoCl_2(Ac)_2)+l\cdot[CoCl_3(Ac)^-]\cdot\varepsilon_i(CoCl_3(Ac)^-)=OD_i, \qquad (8)$$

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14) W. A. Adams and K. J. Laidler, *Canadian J. Chem.*, **45**, 123 (1967)

$$l\cdot[\mathrm{CoCl_2(Ac)_2}]\cdot\varepsilon_j(\mathrm{CoCl_2(Ac)_2})+l\cdot[\mathrm{CoCl_3(Ac)^-}]\cdot\varepsilon_j(\mathrm{CoCl_3(Ac)^-})=\mathrm{OD}_j, \qquad (9)$$

where C denotes the total concentration of cobalt. Ten pairs of i and j were chosen. The mean values were adopted as the concentration of each species at each pressure. Using those values, the equilibrium constants (3) and (4) of equilibria (1) and (2) were determined.

The relation between $\log K_1$ and pressure is expressed approximately by a quadratic equation:

$$\log K_1=a+bP+cP^2. \qquad (10)$$

Using the method of least squares, the constants a, b and c are found to be -7.87, 4.90×10^{-4} and -2.82×10^{-8}, respectively. The pressure dependence of K_1 is shown in Fig. 4. ΔV_1 obtained by Eq. (5) are listed in Table 2 together with the values of K_1.

The relation between $\log K_2$ and pressure is shown in Fig. 5. The pressure dependence of K_2 is

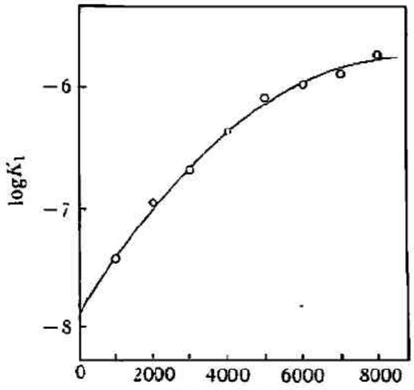

Fig. 4 Effect of pressure on the equilibrium constant K_1 of $CoCl_2$ in acetone solution

○ : Experimental points
——: Equation (10)

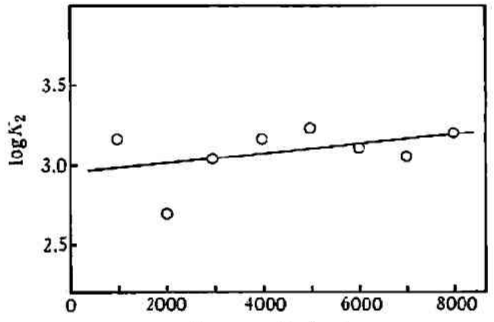

Fig. 5 Effect of pressure on the equilibrium constant K_2 of $CoCl_2$ in acetone solution

○ : Experimental points
——: Obtained by the method of least squares

Table 2 K_1 and ΔV_1 of $CoCl_2$ in acetone solution

P (kg/cm^2)	K_1 (mole^2/l^2)	ΔV_1 (cm^3/mole)
1		(−34)*
1000	3.7×10^{-8}	−28
2000	1.1×10^{-7}	−23
3000	2.1×10^{-7}	−20
4000	4.3×10^{-7}	−16
5000	8.3×10^{-7}	−13
6000	1.1×10^{-6}	−9
7000	1.3×10^{-6}	−6
8000	1.9×10^{-6}	−3

*: Extrapolated value

Table 3 K_2 and ΔV_2 of $CoCl_2$ in acetone solution

P (kg/cm^2)	K_2 (l/mole)	ΔV_2 (cm^3/mole)
1000	1.4×10^3	-2*
2000	5.0×10^2	
3000	1.1×10^3	
4000	1.4×10^3	
5000	1.7×10^3	
6000	1.3×10^3	
7000	1.1×10^3	
8000	1.6×10^3	

*: Obtained by the method of least squares

small and the relation between log K_2 and pressure is assumed to be expressed by a linear relationship. ΔV_2 was obtained by Eq. (5). Although the experimental points are somewhat dispersed as shown in Fig. 5, it seems probably reasonable to consider ΔV_2 is nearly zero and has almost no pressure dependence. The value is listed in Table 3 together with the values of K_2.

Acetone solution of cobalt(II) bromide

The concentration of solution used in the measurements at high pressure is 2.12×10^{-3} mole/l. This solution obeys Beer's law. Namely, in the concentration range of 2.12×10^{-3} mole/l to 2.15×10^{-4} mole/l, the molar extinction coefficient ε is independent of the concentration within the experimental uncertainties. At atmospheric pressure and room temperature, the main species of cobalt(II) bromide in acetone solution is $CoBr_2(Ac)_2$[5], which has an absorption band in the range of about 520∼750 nm and an absorption maximum at 673 nm($\varepsilon_{max}=400$ l/mole·cm). Fig. 6 shows the absorption spectra at various pressures. With increasing pressure, the absorption band of this species decreases and a new species emerges, which has a relatively strong absorption band compared with that of $CoBr_2(Ac)_2$ in the range of about 610∼650 nm and about 700 nm. By the similar consideration to cobalt(II) chloride, two kinds of equilibria are considered to coexist: one is an equilibrium between a

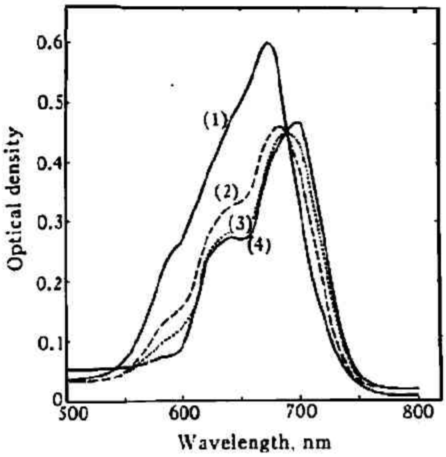

Fig. 6 Absorption spectra of $CoBr_2$ in acetone solution under various pressures
(Conc.: 2.12×10^{-3} mole/l, Path length: 7∼8 mm)

(1) ——: 1 kg/cm^2
(2) - - - -: 2000 kg/cm^2
(3) ·········: 4000 kg/cm^2
(4) ——: 8000 kg/cm^2

tetrahedrally coordinated species and an octahedrally coordinated one, and the other that between two kinds of tetrahedrally coordinated ones. The resulting species was identified as $CoBr_3(Ac)^-$ and the molar extinction coefficients were determined with lithium bromide and cobalt(II) bromide in the same way as $CoCl_3(Ac)^-$. The molar extinction coefficients of $CoBr_2(Ac)_2$ and $CoBr_3(Ac)^-$ are shown in Fig. 7 and the maximum values of these together with each wavelength are listed in Table 4. The octahedrally coordinated species is $Co(Ac)_6^{2+}$ as explained in the case of cobalt(II) chloride[5,6]. It was reported that tetrahedrally coordinated species of $CoBr_4^{2-}$ whose intensity of the absorption band is strong appears in the high bromide concentration range at atmospheric pressure and room temperature[5], but this species was not observed by increasing pressure.

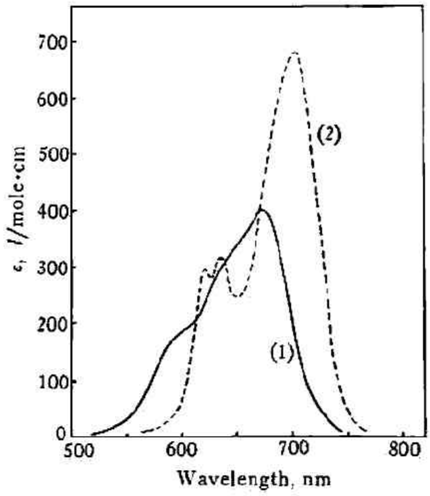

Fig. 7 Absorption spectra of $CoBr_2(Ac)_2$ and $CoBr_3(Ac)^-$

(1) ——: $CoBr_2(Ac)_2$
(2) - - - -: $CoBr_3(Ac)^-$

Table 4 ε and wavelength of $CoBr_2(Ac)_2$ and $CoBr_3(Ac)^-$ at absorption maxima

Species	Wavelength (nm)	ε (l/mole·cm)
$CoBr_2(Ac)_2$	~590 (sh)	167
	~640 (sh)	304
	673	400
$CoBr_3(Ac)^-$	620	293
	635	307
	703	678

From these considerations, the two kinds of equilibria are written as follows:

$$CoBr_2(Ac)_2 + 4Ac \rightleftharpoons Co(Ac)_6^{2+} + 2Br^-, \qquad (1)'$$

$$CoBr_2(Ac)_2 + Br^- \rightleftharpoons CoBr_3(Ac)^- + Ac. \qquad (2)'$$

The equilibrium constants K_1 and K_2 are

$$K_1 = \frac{[Co(Ac)_5^{2+}][Br^-]^2}{[CoBr_2(Ac)_2]}, \qquad (3)'$$

Table 5 K_1 and ΔV_1 of $CoBr_2$ in acetone solution

P (kg/cm²)	K_1(mole²/l²)	ΔV_1 (cm³/mole)
1		(−36)*
1000	5.3×10^{-8}	−28
2000	2.0×10^{-7}	−23
3000	4.2×10^{-7}	−18
4000	7.0×10^{-7}	−13
5000	8.3×10^{-7}	−8
6000	8.2×10^{-7}	−4
7000	1.3×10^{-6}	—
8000	1.2×10^{-6}	—

*: Extrapolated value

Table 6 K_2 and ΔV_2 of $CoBr_2$ in acetone solution

P (kg/cm²)	K_2 (l/mole)	ΔV_2 (cm³/mole)
1000	5.7×10^{2}	−4*
2000	7.7×10^{2}	
3000	9.1×10^{2}	
4000	1.1×10^{3}	
5000	1.3×10^{3}	
6000	1.5×10^{3}	
7000	1.6×10^{3}	
8000	1.8×10^{3}	

*: Obtained by the method of least squares

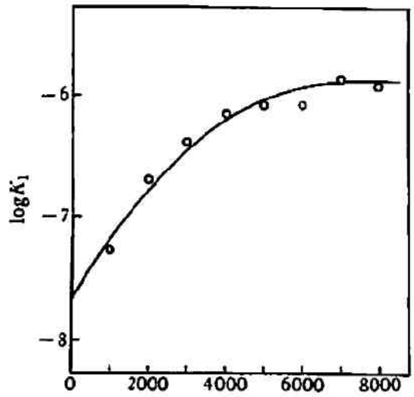

Fig. 8 Effect of pressure on the equilibrium constant K_1 of $CoBr_2$ in acetone solution

○ : Experimental points

——: Equation (10)

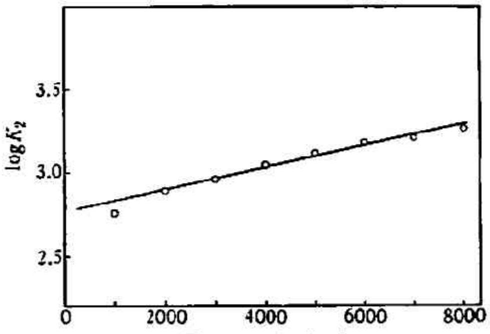

Fig. 9 Effect of pressure on the equilibrium constant K_2 of $CoBr_2$ in acetone solution

○ : Experimental points

——: Obtained by the method of least squares

$$K_2=\frac{[\mathrm{CoBr_3(Ac)^-}]}{[\mathrm{CoBr_2(Ac)_2}][\mathrm{Br^-}]}. \qquad (4)'$$

The relation between $\log K_1$ and pressure is expressed approximately by a quadratic equation:

$$\log K_1=-7.66+5.15\times10^{-4}P-3.81\times10^{-8}P^2,$$

which is shown in Fig. 8. ΔV_1 obtained by Eq. (5) is listed in Table 5 together with the values of K_1. The pressure dependence of K_2 is small and the relation between $\log K_2$ and pressure is expressed approximately by a simple equation using the method of least squares, which is shown in Fig. 9. ΔV_2 obtained by Eq. (5) is listed in Table 6 together with the values of K_2.

Consideration

The complexes of cobalt(II) chloride and cobalt(II) bromide in acetone solution have two kinds of equilibria at high pressure, that is,

$$\mathrm{CoX_2(Ac)_2}+4\mathrm{Ac}\rightleftharpoons\mathrm{Co(Ac)_6^{2+}}+2\mathrm{X^-}, \qquad (\mathrm{I})$$

$$\mathrm{CoX_2(Ac)_2}+\mathrm{X^-}\rightleftharpoons\mathrm{CoX_3(Ac)^-}+\mathrm{Ac}, \qquad (\mathrm{II})$$

where X is Cl or Br. These equilibria shift to the right side with increasing pressure. In equilibrium (I), ΔV_1 is large with the negative sign at lower pressure side and changes greatly with increasing pressure. On the other hand, $|\Delta V_2|$ is small and the pronounced pressure dependence is not observed. These experimental results are considered to indicate the nature of equilibria (I) and (II). When equilibrium (I) shifts to the right side, two kinds of ionic species are formed from neutral species, and especially one of them is an ionic species with +2 charge. So the solvation will considerably increase, which has negative contribution to ΔV_1 and causes a large pressure dependence. Moreover, the coordination number increases with the shift to the right side of the equilibrium, so some amount of the free volume will be lost. This has also a negative contribution to ΔV_1 and brings about a pressure dependence on ΔV_1. On the other hand, equilibrium (II) lies between halogen ion and $\mathrm{CoX_3(Ac)^-}$ ion, both of which would seem to be poorly solvated in acetone[15]. Therefore, the change of solvation with the shift of the equilibrium is probably small and its contribution to ΔV_2 is considered to be small. And since the coordination number is equal on both sides of equilibrium (II), the change of free volume is probably small, which contributes slightly to ΔV_2. These qualitative considerations about ΔV_1 and ΔV_2 agree with the experimental results.

Now, the volume change of equilibrium (I) is estimated from the various contributions. The method of calculation is as follows:

$$\Delta V_1=\Delta V_i+\Delta V_e(\mathrm{Co(Ac)_6^{2+}})+2\Delta V_f(\mathrm{Ac}), \qquad (11)$$

where ΔV_i is the change of the intrinsic volume, ΔV_e is the volume change caused by electrostriction and ΔV_f is the change of the free volume. Since the halogen ion is poorly solvated in acetone solution[15],

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[15] A. J. Parker, *Quart. Rev.*, 16, 163 (1962); *Adv. Org. Chem.*, 5, 1 (1965)

the value of $\Delta V_s(X^-)$ is assumed to be negligible.

ΔV_1 is roughly estimated by the following equation considering van der Waals' radius, the ionic radius and the bond length:

$$\Delta V_1 = \sum_{j=1}^{3} \pi \cdot r_j^2 \cdot \Delta l_{(j)}, \tag{12}$$

where r_j is the ionic radius or van der Waals' radius of each atom bound to cobalt(II) ion and $\Delta l_{(j)}$ is given by the following (i), (ii) and (iii).

(i) The change due to the elimination of $2X^-$ from $CoX_2(Ac)_2$; $\Delta l_{(1)}$

$\Delta l_{(1)}$=(The ionic radius of cobalt(II)[16])+(The ionic radius of halogen[16])
−(The bond length between cobalt and halogen[17])

$\Delta V_{(1)} = 2 \times \pi \times$(The ionic radius of halogen[16])$^2 \times \Delta l_{(1)}$

(ii) The change due to the difference between the cobalt-acetone bond length of $CoX_2(Ac)_2$ and that of $Co(Ac)_6^{2+}$; $\Delta l_{(2)}$

$\Delta l_{(2)}$=(The bond length between cobalt and oxygen of acetone in octahedral species[17])
−(That in tetrahedral species[17])

$\Delta V_{(2)} = 2 \times \pi \times$(van der Waals' radius of oxygen[18])$^2 \times \Delta l_{(2)}$

(iii) The change due to the coordination of four acetone molecules; $\Delta l_{(3)}$

$\Delta l_{(3)}$=(The bond length between cobalt and oxygen of acetone in octahedral species[17])
−{(The ionic radius of cobalt(II)[16])+(van der Waals' radius of oxygen[18])}

$\Delta V_{(3)} = 4 \times \pi \times$(van der Waals' radius of oxygen[18])$^2 \times \Delta l_{(3)}$

From the above (i), (ii) and (iii), Eq. (12) becomes as follows:

$$\Delta V_1 = \Delta V_{(1)} + \Delta V_{(2)} + \Delta V_{(3)}$$
$$= \begin{cases} 3.1\,(\mathrm{cm^3/mole}) \cdots\cdots \text{cobalt(II) chloride} \\ 3.6\,(\mathrm{cm^3/mole}) \cdots\cdots \text{cobalt(II) bromide} \end{cases} \tag{13}$$

$\Delta V_s(Co(Ac)_6^{2+})$ was estimated by Born's equation:

$$\Delta V_s = -\frac{Nq^2}{2rD^2} \cdot \frac{\partial D}{\partial P}, \tag{14}$$

where N is Avogadro's number, P is the pressure, D is the dielectric constant of solvent, r is the ionic radius and q is the charge of the ionic species. The r-value of $Co(Ac)_6^{2+}$ was estimated by the distance from oxygen to the end of van der Waals' sphere of methyl radical in acetone, which was estimated from reference[18] and the bond length between cobalt and oxygen[17]. Eq. (14) becomes[19]

$$\Delta V_s = -\frac{Nq^2}{2r} \cdot \frac{0.4343A}{B+P} (\mathrm{cm^3/mole}), \tag{15}$$

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[16] F. G. Smith, "Physical Geochemistry", p. 23, Addison-Wesley Publishing Company, INC. (1963)

[17] D. L. Werz and R. F. Kruh, *J. Chem. Phys.*, 50, 4313 (1969); *Inorg. Chem.*, 9, 595 (1970)

[18] L. Pauling, "The Nature of the Chemical Bond", 3rd ed., Cornell Univ. Press, Ithaca, New York (1960)

where A and B are independent of pressure, and B is a function of temperature. $A\cdot D=0.2577$[19] and $D=20.70$ at 25°C and 1 atm[20], from these A-value was determined. $B=755.7$ bar at 25°C[14] was used.

Next, $\Delta V_f(\mathrm{Ac})$, the change of the free volume caused by the coordination of acetone, will be explained. Acetone freezes at the pressure higher than 8,000 atm at 20°C and its compression at 8,000 atm is about 25%[21]. Thus, the following assumption was made: the volume of the ligand acetone molecule is compressed to be 0.75 times as large as that at atmospheric pressure and the free volume accompanying with the compression will be lost. In equilibrium (I), the free volume of the four acetone molecules decreases and that of $2X^-$ increases. Now, if the decrease of the free volume of an acetone and the increase of that of a halogen ion are supposed to be equal, the totally lost free volume corresponds to the decrease of the volume due to the compression of two acetone molecules by the coordination.

Table 7 Observed and calculated values of ΔV_1 for $CoCl_2$ and $CoBr_2$ in acetone solution

P (kg/cm²)	ΔV_1 (obs.) (cm³/mole)		ΔV_1 (calc.) (cm³/mole)
	$CoCl_2$	$CoBr_2$	$CoCl_2$, $CoBr_2$
1	(−34)*	(−36)*	−63
1000	−28	−28	−35
2000	−23	−23	−24
3000	−20	−18	−17
4000	−16	−13	−12
5000	−13	−8	−8
6000	−9	−4	−5
7000	−6	—	−3
8000	−3	—	−1

*: Extrapolated value

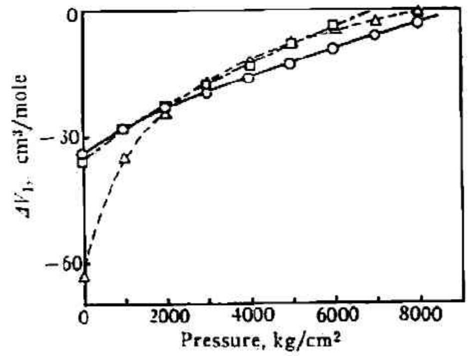

Fig. 10 Effect of pressure on ΔV_1 of $CoCl_2$ and $CoBr_2$ in acetone solution

——○——: ΔV_1 (obs.) of $CoCl_2$
- · -□- · -: ΔV_1 (obs.) of $CoBr_2$
- - -△- - -: ΔV_1 (calc.) of $CoCl_2$ and $CoBr_2$ obtained by Eq. (11)

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[19] B. B. Owen and S. R. Brinkley, *Phys. Rev.*, 64, 32 (1943)

[20] A. A. Mayott and E. A. Smith, "Table of Dielectric Constants of Pure Liquids", NBC Circular, 514, Aug. 10 (1951)

[21] P. W. Bridgman, "The Physics of High Pressure", G. Bell and Sons, LTD., London (1958)

Therefore

$$2\Delta V_r(\mathrm{Ac}) = 2\times(0.75V_0 - V_P), \tag{16}$$

where V_0 is the molar volume at atmospheric pressure and V_P is that at pressure P.

Substituting Eqs. (13), (15) and (16) in Eq. (11), the calculated ΔV_1 is obtained. As the difference of ΔV_i between cobalt(II) chloride and cobalt(II) bromide is very small as shown in Eq. (13), ΔV_1(calc.) is assumed to have the same value in both cases by neglecting the small difference and is contained in Table 7 together with the experimental values and shown in Fig. 10, in which the value of ΔV_i for cobalt(II) bromide was used. Among the various contributions to ΔV_1 (calc.), the contribution of ΔV_i is small and independent of pressure, and the other two terms have large contributions to ΔV_1 and to the pressure dependence. Namely, $\Delta V_s(\mathrm{Co(Ac)_6^{2+}})$ is negative and increases steeply at the lower pressure side and very gently at the higher pressure side. ΔV_r is also negative and increases more linearly than $\Delta V_s(\mathrm{Co(Ac)_6^{2+}})$ with increasing pressure. ΔV_1 (obs.) is smaller in the case of cobalt(II) chloride than in the case of cobalt(II) bromide in the moderate and higher pressure region. It is possible to think that this experimental fact reflects the difference between the electrostriction due to $\mathrm{Cl^-}$ and that due to $\mathrm{Br^-}$, but the experimental uncertainties being considered, it is rather difficult to state definitely on this point. ΔV_1 (obs.) decreases with increasing pressure in both cases. At this point ΔV_1 (calc.) agrees qualitatively with ΔV_1 (obs.). In the lower pressure region there are large differences between calculated and experimental values. About these discrepancies detailed discussion will be difficult, because the values of K_1 at atmospheric pressure are extrapolated values which depend greatly on the functions used to approximate the pressure dependence.

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