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In Situ Observations of the Phase Transition among Cobalt(II) Dichloride Hydrates and Crystal Structures of the Tetra- and Hexahydrates

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Transformation among cobalt(II) dichloride hydrates in aqueous solutions was studied by the optical microscopic method. Although there are three hydrates ($CoCl_2\cdot 6H_2O$, $CoCl_2\cdot 4H_2O$, and $CoCl_2\cdot 2H_2O$) in the phase equilibrium diagram, the only solution mediated transformation between $CoCl_2\cdot 6H_2O$ and $CoCl_2\cdot 2H_2O$ could be observed under the present experimental conditions and it was confirmed that $CoCl_2\cdot 4H_2O$ hardly formed compared with the other two hydrates. In order to investigate the reason why $CoCl_2\cdot 4H_2O$ was hardly crystallized at the transformation from $CoCl_2\cdot 6H_2O$ through $CoCl_2\cdot 2H_2O$ and vice versa, the crystal structure of $CoCl_2\cdot 4H_2O$ was investigated by the X-ray diffraction method. The structure of $CoCl_2\cdot 6H_2O$ was reexamined because previously reported results had a relatively large R-factor. The crystal of $CoCl_2\cdot 4H_2O$ is monoclinic, space group $P2_1/a$ with $a=11.548(1)$ Å, $b=9.342(1)$ Å, $c=6.056(1)$ Å, $\beta=110.79(1)^\circ$, and $Z=4$. The complex has a slightly distorted octahedral geometry about Co^{2+} ion and two Cl^- ions are located at the cis-position. The crystal of $CoCl_2\cdot 6H_2O$ is monoclinic, space group $C2/m$ with $a=10.380(2)$ Å, $b=7.048(1)$ Å, $c=6.626(1)$ Å, $\beta=122.01(1)^\circ$, and $Z=2$. The geometry around the cobalt ion is also octahedral with four water molecules and two chloride ions at the equatorial and the axial positions, respectively. The remaining two water molecules are linked to the two Cl^- ions by hydrogen bonding. The difficulty of crystallization of $CoCl_2\cdot 4H_2O$ crystals in solutions was explained in terms of the relatively unstable cis-dichloro structure of the $[CoCl_2(H_2O)_4]$ moiety and its crystal structure stabillized by hydrogen bonding network between the cis-form moieties.

The problem how crystals form from solutions still remains unsolved, although attempts to elucidate this problem have been examined from various viewpoints. Transformation of a hydrate into other hydrates draws attention of industries to apply the phenomenon to heat storage processes.[1,2] Structures of hydrate crystals have been discussed in relation to the structure of hydrated ions in solution from the viewpoint of crystal growth. Recently, Yamaguchi et al.[3] studied the structure of calcium(II) dichloride hydrate melt by means of X-ray diffraction and suggested that the structural dissimilarity between $CaCl_2\cdot 6H_2O$ crystal and its melt should be responsible for the easy supercooling.

Transition metal dihalides form various hydration states in the solid state. Aqueous solutions of cobalt(II) chloride have well been studied from their characteristic visible absorption spectra to determine the structure of species in solution and it is well accepted that the hexahydrated octahedral cobalt(II) ion changes its structure to tetrahedral in a highly concentrated solution of chloride ions at high temperatures. From the structural analyses of $CoCl_2$ aqueous solutions by X-ray diffraction[4–8] and visible absorption spectra,[9,10] it has been found that the following species can be present: $[Co(H_2O)_6]^{2+}$ (octahedral), $[CoCl(H_2O)_5]^+$ (octahedral), $[CoCl_4]^{2-}$ (tetrahedral) as the major species and $[CoCl_2(H_2O)_4]$ (octahedral) and $[CoCl_3(H_2O)]^-$ (tetrahedral) as the minor ones.

Cobalt(II) dichloride forms three hydrates ($CoCl_2\cdot nH_2O$, $n=6$, 4, and 2) over the temperature range of 0 to 100 °C. Among them, the tetrahydrate can exist in relatively narrow range of the composition and temperature in aqueous solution compared with the other hydrates (Fig. 1). Indeed, Etard[11] could not find the formation of the tetrahydrate, but Benrath[12] observed the formation of $CoCl_2\cdot 4H_2O$ through a careful experiment by the use of the gravimetric method at the temperature range between 48 and 57 °C as shown in Fig. 1.

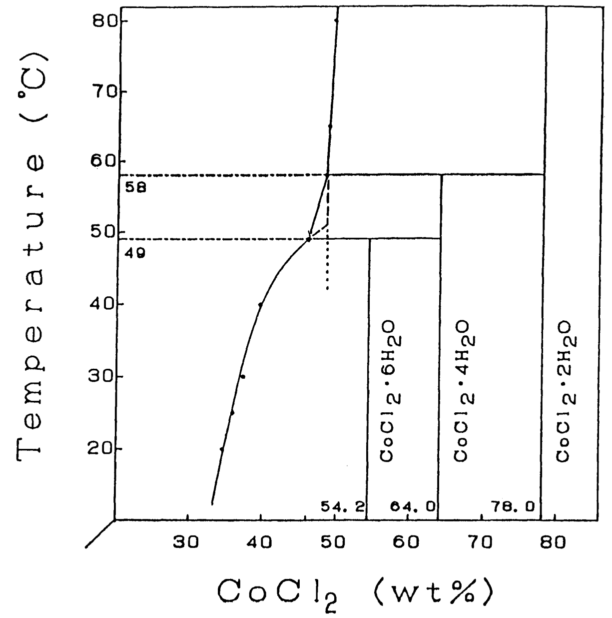


Fig. 1. $CoCl_2$-H_2O binary phase diagram. Solid lines are those determined by Benrath,[12] dashed lines by Etard.[11] A dotted line is drawn from the present experiment for the supercooled system containing $CoCl_2\cdot 2H_2O$.

The crystal structure determination of $CoCl_2\cdot2H_2O$ has been made by Vainshtein[13] and later by Morosin et al.[14] in more detail including the hydrogen atoms in its analysis with a final reliability factor of R=0.073. The crystal structure of $CoCl_2\cdot6H_2O$ was determined by several authors[15] and by Mizuno[16] without considering contributions of hydrogen atoms. However, no report has been given for the crystal structure of $CoCl_2\cdot4H_2O$.

In the present study we aimed at elucidating the mechanism of the transformation of the $CoCl_2\cdot nH_2O$ crystals from the structural viewpoint of complexes in solution and in crystal in each phase, and we examined observations of changes in the crystal form under a microscope. The X-ray structural determination of $CoCl_2\cdot4H_2O$ crystal was also carried out. Since a rather large R-factor was reported by Mizuno[16] at his crystal structural analysis of $CoCl_2\cdot6H_2O$, we redetermined its structure.

The difficulty of the formation of $CoCl_2\cdot4H_2O$ compared with $CoCl_2\cdot6H_2O$ and $CoCl_2\cdot2H_2O$ is discussed from the viewpoint of its molecular structure and hydrogen bonding network in the crystal.

Experimental

(A) Observations under Microscope. Cobalt dichloride hexahydrate of reagent grade was purchased from Junsei Chem. Co., Ltd. and used without further purification. Aqueous solutions of $CoCl_2$ were prepared by dissolving $CoCl_2\cdot6H_2O$ in water. Solutions with different concentrations were kept as thin layers of about 1.0 mm thickness between two pieces of round cover glass and sealed with an adhesive to observe crystals in dark colored solutions. The sealed chip was put in a glass cell thermostated within ±0.2 °C.

A $CoCl_2$ aqueous solution saturated at 68.0 °C was kept at 63.0 °C, and then $CoCl_2\cdot2H_2O$ crystals deposited from the solution. Then, the $CoCl_2\cdot2H_2O$ crystals and the mother liquid was cooled from 63.0 °C to 46.0 °C with the velocity of 1.5 °C min^{-1}.

When a solution saturated at 70.0 °C was kept at 45.0 °C, and thus, $CoCl_2\cdot6H_2O$ crystals were formed, and then the temperature of the liquid containing the $CoCl_2\cdot6H_2O$ crystals was elevated from 45.0 °C to 60.0 °C with the velocity of 1.5 °C min^{-1}.

In both experiments, the cells were set up on the stage of an optical microscope and the transformation of crystals in the solutions were observed. Several experiments were examined with different heating and cooling rates, but the crystal formation of $CoCl_2\cdot4H_2O$ was not observed in the present study.

In the experiments, $CoCl_2\cdot2H_2O$ crystals could be distinguished from $CoCl_2\cdot6H_2O$ crystals, since the latter has the prismatic well-developed (1 0 0) faces,[16] whereas the former has a characteristic needle or prismatic morphology[17] parallel to [0 0 1].

(B) Structure Determination by Means of X-Ray Diffraction. Preparation of Samples. $CoCl_2\cdot4H_2O$ crystals for the X-ray analysis were obtained at 53.0 °C, according to the phase diagram given in Fig. 1, from an aqueous solution of cobalt dichloride saturated at 60.0 °C. After several days, dark red crystals of $CoCl_2\cdot4H_2O$ were obtained in the form of an approximately cubo-octahedron. Dark pink $CoCl_2\cdot6H_2O$ crystals were obtained at 25.0 °C from a solution saturated at 30.0 °C.

X-Ray Structure Analysis. Crystals of $CoCl_2\cdot4H_2O$ and $CoCl_2\cdot6H_2O$ with approximate dimensions of $0.25\times0.3\times0.3$ mm and of $0.30\times0.40\times0.50$ mm, respectively, were used for collecting intensity data. Each crystal was coated with paraffin to avoid the conversion to other hydrate complexes during the measurement. Both unit cell dimensions and diffraction intensities were measured on a Rigaku AFC-5R automated, four-circle diffractometer with graphite-monochromatized Mo-$K\alpha$ radiation ($\bar{\lambda}$=0.71073 Å). The crystal data for $CoCl_2\cdot4H_2O$ and $CoCl_2\cdot6H_2O$ are given in Table 1 together with those for $CoCl_2\cdot2H_2O$. Intensities of 2073 and 825 reflections ($\pm h$, $+k$, $+l$) for $CoCl_2\cdot4H_2O$ and $CoCl_2\cdot6H_2O$, respectively, were measured within the range $2\theta<60°$ with the ω-2θ scan mode at a scanning rate of 4° min^{-1} in ω and with the scan width of $(1.0+0.5\tan\theta)°$. Reflections were monitored every 100 points by three standard reflections. There was no significant variation in the intensities during the data collection. The intensities were converted to F_o data in a usual manner. No absorption correction was applied. The standard deviations, $\sigma(F_o)$, were estimated by counting statistics. The determination of the crystal structures was carried out by using 1757 and 451 independent reflections for $CoCl_2\cdot4H_2O$ and $CoCl_2\cdot6H_2O$, respectively, with $|F_o|>3\sigma(|F_o|)$.

Structure Determination. Both structures of $CoCl_2\cdot4H_2O$ and $CoCl_2\cdot6H_2O$ were solved by the heavy atom method and refined by the full matrix least-squares method. A preliminary X-ray examination showed that the $CoCl_2\cdot$

Table 1. Crystal Data of Cobalt Dichloride Hydrates

	$CoCl_2\cdot6H_2O$	$CoCl_2\cdot4H_2O$	$CoCl_2\cdot2H_2O$[17]
Space group	$C2/m$	$P2_1/a$	$C2/m$
Molecular weight	237.93	201.89	165.87
a/Å	10.380(2)	11.598(1)	7.256
b/Å	7.048(1)	9.342(1)	8.575
c/Å	6.626(1)	6.056(1)	3.554
β/°	122.01(1)	110.79(1)	97.55
V/Å^3	441.0	613.4	219.2
D_x/g cm^{-3}	1.922	2.186	2.513
Z	2	4	2
μ(Mo $K\alpha$)/cm^{-1}	27.8	36.8	50.9

$6H_2O$ crystal is monoclinic and the unit cell contains two units of $[CoCl_2(H_2O)_4]$. The systematic absence of diffractions from hkl for $h+k=2n+1$, $h0l$ for $h=2n+1$, and $0k0$ for $k=2n+1$ indicated three possible space groups $C2/m$, Cm, or $C2$. Among them, $C2/m$ was tentatively assumed and the successive Fourier syntheses revealed an approximate structure. Finally, the full matrix least-squares refinement was carried out for the three possible space groups and the result showed that the space group $C2/m$ was the most probable one.

Several cycles of refinement including refinements for anisotropic thermal parameters were carried out. The weighting scheme used at the final stage was $w=\{[\sigma(|F_o|)]^2+(0.015|F_o|)^2\}^{-1}$. The positions of all H atoms were determined by the difference Fourier map method and the atomic parameters were refined isotropically. The final R and R_w values were 0.025 and 0.039, respectively, for $CoCl_2\cdot 4H_2O$, and 0.058 and 0.073, respectively, for $CoCl_2\cdot 6H_2O$. The final difference maps showed no significant features. Atomic scattering factors and anomalous dispersion terms were taken from "International Tables for X-Ray Crystallography," (1974).[18] All calculations were carried out on a HITAC M-680H computer at the Computer Center of the Institute for Molecular Science by using the UNICS III[19] program system. Final atomic parameters are listed in Tables 2 and 3 for $CoCl_2\cdot 4H_2O$ and $CoCl_2\cdot 6H_2O$, respectively.

Our results obtained for $CoCl_2\cdot 6H_2O$ were essentially the same as those by Mizuno[16] and Saffar.[20]

Table 2. Atomic Parameters for $CoCl_2\cdot 4H_2O$[a)]

	x	y	z	B_{eq} or $B/Å^2$
Co	7655.3(2)	1700.8(2)	7516.2(4)	1.3
Cl(1)	6197.2(4)	3644.8(5)	6512 (1)	1.8
Cl(2)	9324.7(4)	3060.6(5)	10278 (1)	2.0
O(1)	8391 (1)	2276 (2)	4909 (2)	1.9
O(2)	6971 (1)	1151 (1)	10227 (2)	1.9
O(3)	8674 (1)	−201 (2)	8301 (3)	2.5
O(4)	6321 (1)	417 (2)	5032 (3)	2.3
H(1A)	917 (3)	194 (3)	525 (6)	4.1
H(1B)	803 (3)	204 (3)	361 (6)	4.2
H(2A)	697 (3)	39 (3)	1033 (6)	4.2
H(2B)	626 (3)	135 (3)	1007 (6)	3.9
H(3A)	878 (3)	−49 (4)	725 (6)	4.7
H(3B)	933 (4)	−23 (5)	937 (9)	10.0
H(4A)	574 (3)	69 (3)	415 (5)	3.0
H(4B)	655 (4)	−18 (5)	464 (8)	8.6

a) Atomic coordinates ($\times 10^4$; for $H\times 10^3$), equivalent isotropic temperature factors for non-H atoms and isotropic temperature factors for H atoms. $B_{eq}=4/3(a\beta^2_{11}+2ab\cos\gamma\beta_{12}\cdots)$.

Table 3. Atomic Parameters for $CoCl_2\cdot 6H_2O$[b)]

	x	y	z	B_{eq} or $B/Å^2$
Co	0	0	0	1.1
Cl	2743 (2)	0	1690 (3)	1.7
O(1)	299 (4)	2028 (6)	2496 (6)	1.9
O(2)	2203 (7)	5000	3057 (10)	1.5
H(1A)	108 (9)	301 (16)	278 (12)	5.0
H(1B)	−73 (10)	295 (18)	205 (14)	6.9
H(2A)	290 (16)	500	415 (20)	4.9
H(2B)	210 (19)	500	146 (26)	7.1

b) Atomic coordinates ($\times 10^4$; for $H\times 10^3$), equivalent isotropic temperature factors for non-H atoms and isotropic temperature factors for H atoms. $B_{eq}=4/3(a\beta^2_{11}+2ab\cos\gamma\beta_{12}\cdots)$.

Results

(A) Observations under Microscope. In a pre-

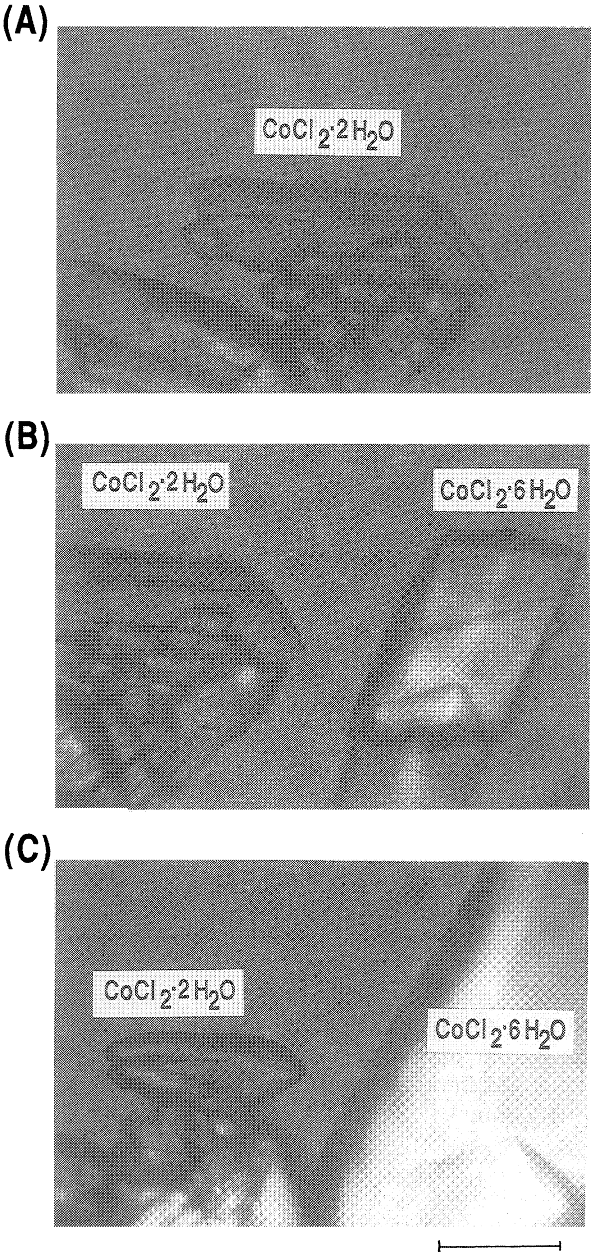


Fig. 2. The transformation of $CoCl_2\cdot 2H_2O$ into $CoCl_2\cdot 6H_2O$ without $CoCl_2\cdot 4H_2O$. In (A) (50.0 °C), $CoCl_2\cdot 2H_2O$ crystals grow even in the stable region of $CoCl_2\cdot 6H_2O$. $CoCl_2\cdot 6H_2O$ crystals are growing on the right hand side in pictures (B) and (C) (46.0 °C) and $CoCl_2\cdot 2H_2O$ crystals are dissolving on the left hand side in the pictures. The intervals between (A) and (B) and between (B) and (C) were about 2.7 minutes and about one minute, respectively.

liminary experiment, we observed that $CoCl_2\cdot 2H_2O$ prepared at 63.0 °C continuously grew up with decreasing temperature and the crystals were growing even at temperatures lower than 57.0 °C at which $CoCl_2\cdot 2H_2O$ crystal should transform to $CoCl_2\cdot 4H_2O$. The crystal growth was still continued at temperature lower than 49.0 °C at which $CoCl_2\cdot 4H_2O$ crystal should transform to $CoCl_2\cdot 6H_2O$ (Fig. 2 (A)). Then, $CoCl_2\cdot 6H_2O$ crystals formed in the solution in which $CoCl_2\cdot 2H_2O$ crystals still remained, and the $CoCl_2\cdot 6H_2O$ crystals started to grow with a further decrease in temperature. With the growth of $CoCl_2\cdot 6H_2O$ crystals, the $CoCl_2\cdot 2H_2O$ crystals stopped growing and then the crystals were gradually dissolved (Fig. 2 (B)—(C)). Finally, the reaction reached an equilibrium between $CoCl_2\cdot 6H_2O$ crystals and the solution.

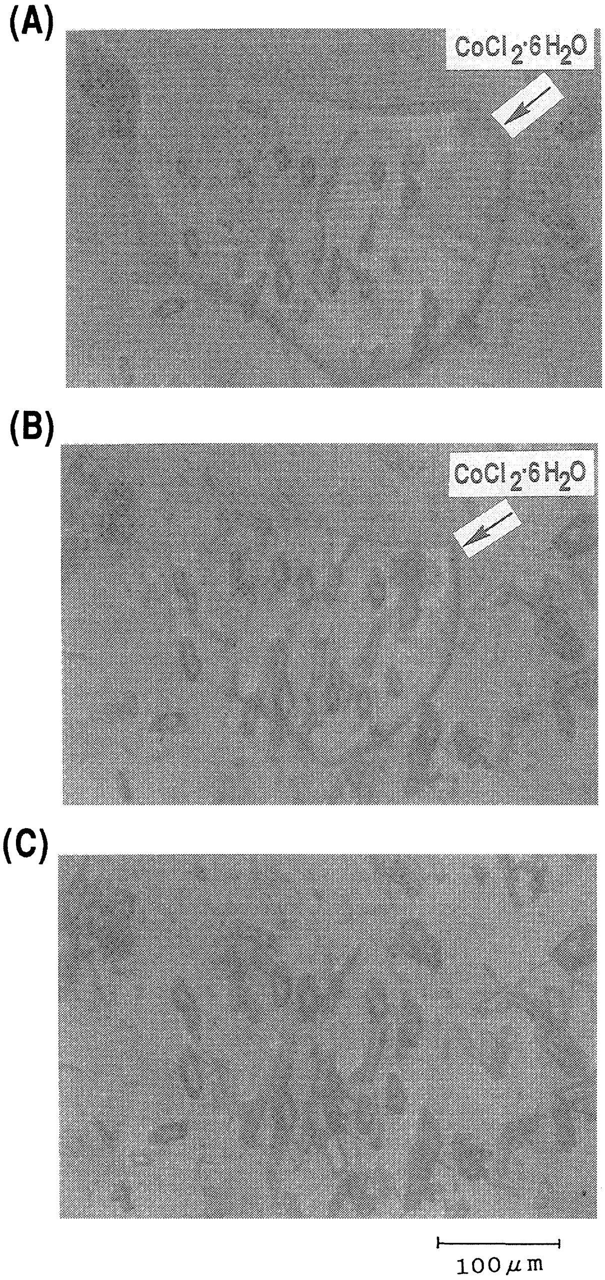


Fig. 3. The transformation of $CoCl_2\cdot 6H_2O$ into $CoCl_2\cdot 2H_2O$ without $CoCl_2\cdot 4H_2O$ at about 50 °C. In (A) and (B), $CoCl_2\cdot 6H_2O$ crystals located near the center of the photographs are quickly dissolving and a number of small $CoCl_2\cdot 2H_2O$ crystals are growing around $CoCl_2\cdot 6H_2O$ crystals. In (C), $CoCl_2\cdot 6H_2O$ crystals were completely dissolved. The interval between (A) and (B) or (B) and (C) was a few seconds.

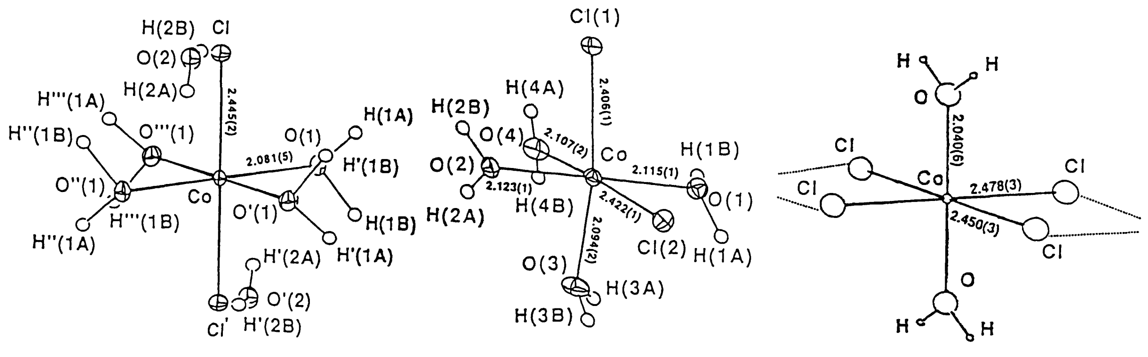
We examined the reverse process in which $CoCl_2\cdot 6H_2O$ crystals formed at 45.0 °C were dissolved with rising temperature. At about 50.0 °C $CoCl_2\cdot 2H_2O$ crystals were started to form and grew around $CoCl_2\cdot 6H_2O$ crystals, which quickly dissolved in the solution (Fig. 3 (A)—(C)). Some small $CoCl_2\cdot 2H_2O$ crystals once formed disappeared with increasing temperature and large crystals remained in the solution equilibrated with the crystals at 60.0 °C.

In these observations, formation of $CoCl_2\cdot 4H_2O$ crystals and the transformation of $CoCl_2\cdot 6H_2O$ or $CoCl_2\cdot 2H_2O$ to $CoCl_2\cdot 4H_2O$ could not be seen due probably to a relatively large velocity of temperature changes and the only solution-mediated transformation between $CoCl_2\cdot 6H_2O$ and $CoCl_2\cdot 2H_2O$ was observed. From the present in-situ observations it is confirmed that the formation of $CoCl_2\cdot 4H_2O$ crystals were especially difficult in the course of the successive crystal formation process from $CoCl_2\cdot 6H_2O$ through $CoCl_2\cdot 2H_2O$ and vice versa.

(B) Structure of $CoCl_2\cdot 4H_2O$. Molecular structure of $CoCl_2\cdot 4H_2O$ determined is shown in Fig. 4 (B) with the atomic numbering by ORTEP drawing.[21] The bond lengths and bond angles are listed in Table 4. The structure around the cobalt(II) ion in $CoCl_2\cdot 4H_2O$ is distorted octahedral with the cis-configuration with respect to the Cl^- ions. The cobalt(II) ion is displaced by 0.05 Å out of the plane defined by the three water oxygen atoms and one chloride ion towards the axial chloride ion. The molecular structure is similar to that of $MnCl_2\cdot 4H_2O$.[22] The axial Co-O bond length in this complex was 2.094(2) Å, which is compared with the median Co-O bond length (2.090 Å) from 121 compounds reported previously.[23] However, the lengths

Table 4. Bond Lengths/Å and Angles/° for $CoCl_2\cdot 4H_2O$

Co-Cl(1)	2.406(1)	Co-Cl(2)	2.422(1)
Co-O(1)	2.115(1)	Co-O(2)	2.123(1)
Co-O(3)	2.094(2)	Co-O(4)	2.107(2)
Cl(1)-Co-Cl(2)	95.54(2)	Cl(1)-Co-O(1)	93.05(4)
Cl(1)-Co-O(2)	87.55(4)	Cl(1)-Co-O(3)	170.83(5)
Cl(1)-Co-O(4)	88.74(2)	Cl(2)-Co-O(1)	86.88(4)
Cl(2)-Co-O(2)	91.10(4)	Cl(2)-Co-O(3)	92.22(5)
Cl(2)-Co-O(4)	174.83(5)	O(1)-Co-O(2)	177.94(6)
O(1)-Co-O(3)	92.22(6)	O(1)-Co-O(4)	90.01(6)
O(2)-Co-O(3)	87.44(6)	O(2)-Co-O(4)	91.97(6)
O(3)-Co-O(4)	83.76(6)		



(A) (B) (C)

Fig. 4. Schematic comparison of octahedral units. (A) hexa-, (B) tetra-, and (C) dihydrates of cobalt dichloride. (A) and (B) are ORTEP drawings with thermal ellipsoids scaled at 30% probability level.[21] In (C), each Cl^- ion is linked by two Co^{2+} ions.[14] H atoms are represented by small circles with 0.1 Å radius.

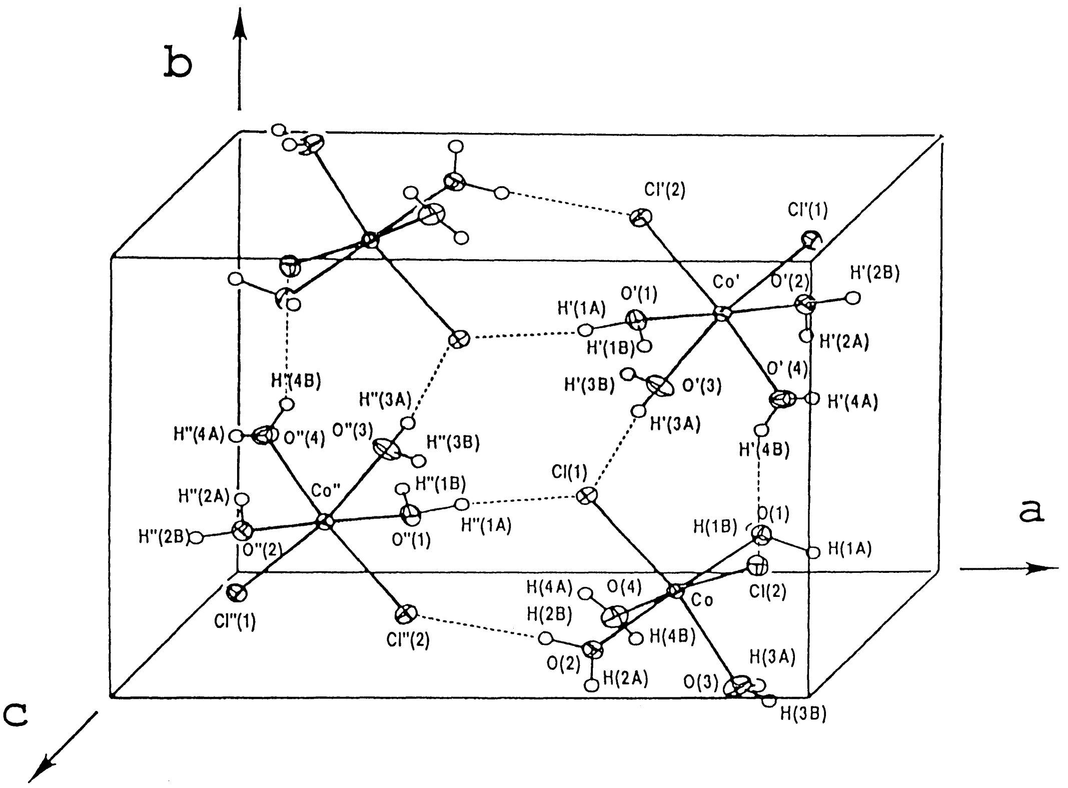


Fig. 5. An ORTEP drawing of the crystal structure for $CoCl_2 \cdot 4H_2O$ with thermal ellipsoids scaled at 30% probability level.[21] H atoms are represented by small circles with 0.1 Å radius.

of the three equatorial Co-O bonds (2.107(2), 2.115(1), and 2.123(1) Å) are significantly longer than that of the axial one.

On the other hand, the axial Co-Cl bond length (2.406 Å) is also significantly shorter than that of the equatorial Co-Cl bond length, 2.422(1) Å, and the median Co-Cl bond length (2.417 Å) estimated from 11 compounds reported in the literature.[23] The relatively short axial Co-Cl bond length suggests that the bond may have covalent nature (Co-Cl=2.31 Å=1.32 Å (Co)+0.99 Å (Cl))[24] rather than ionic (Co-Cl=2.56 Å =0.75 Å (Co^{2+} (high spin))+1.81 Å (Cl^-)).[25]

In the crystal distorted octahedral $[CoCl_2(H_2O)_4]$ units are connected with each other by hydrogen bonds (broken lines in Fig. 5);

Cl(1)···O′(3)=3.160(2) Å, Cl(1)···O″(1)=3.166(1) Å,
Cl″(2)···O(2)=3.168(2) Å, and Cl(2)···O′(4)=3.307(1) Å.

The lengths of the hydrogen bonds are in good agreement with those of the typical Cl···O hydrogen bonds.[26] In these hydrates, hydrogen bonds between water molecules and coordinated chloride ions may play an essential role in the formation of their crystal structures and contribute to make the cis-configuration.

Grindstaff et al.[27] suggested that the molecular structure of $CoCl_2\cdot 4H_2O$ was similar to that of the $[CoCl_2(H_2O)_4]$ molecular unit of $CoCl_2\cdot 6H_2O$ crystal because the reflectance spectra and magnetic moments for the hexa- and tetrahydrates are very similar. However, the molecular structure of $CoCl_2\cdot 4H_2O$ determined in this work is different from their expectation and has the cis-configuration.

(C) Structure of $CoCl_2\cdot 6H_2O$. Molecular structure of $CoCl_2\cdot 6H_2O$ is shown in Fig. 4(A) with atomic numbering. The bond lengths and bond angles are summarized in Table 5. The geometry about the cobalt(II) ion is the hexa-coordinated one with four water molecules at the equatorial positions of a square plane with a crystallographically complete planar fashion and two chloride ions at the trans position. The remaining two water molecules are linked to the two chloride ions with hydrogen bonds (Cl···O=2.176(2) Å). The equatorial Co-O bond length, 2.081(5) Å, is comparable to the median Co-O bond length given in the literature (2.090 Å)[23] and also to the axial Co-O bond length in $CoCl_2\cdot 4H_2O$. The axial Co-Cl bond length, 2.445(2) Å, is significantly longer than the axial and equatorial Co-Cl bond lengths in $CoCl_2\cdot 4H_2O$.

The unit cell of the crystal structure of $CoCl_2\cdot 6H_2O$ contains two discrete octahedral groups of $[CoCl_2(H_2O)_4]$ and four water molecules as shown in Fig. 6. The cobalt ion is located at the center of symmetry which has a two-fold axis and a mirror plane. The octahedron groups are connected with each other with hydrogen bonds (broken lines in Fig. 6);

$$Cl(1)\cdots O(2) = 3.176(2)\ \text{Å} \text{ and } O(1)\cdots O''_{II}(2) = 2.767(4)\ \text{Å},$$

and the length of the hydrogen bonds are also in good agreement with those of the typical Cl···O and O···O hydrogen-bonds,[26] respectively.

Table 5. Bond Lengths/Å and Angles/° for $CoCl_2\cdot 6H_2O$[c)]

Co-Cl	2.445(2)	Co-O(1)	2.081(5)
Cl-Co-O(1)	89.39(14)	Cl-Co-O′(1)	89.39(14)
Cl-Co-O″(1)	90.61(14)	Cl-Co-O‴(1)	90.61(14)
Cl′-Co-O(1)	90.61(14)	Cl′-Co-O′(1)	90.61(14)
Cl′-Co-O′′(1)	89.39(14)	Cl′-Co-O‴(1)	89.39(14)
Cl-Co-Cl′	180		
O(1)-Co-O′(1)	93.24(17)	O(1)-Co-O″(1)	180
O(1)-Co-O‴(1)	86.76(17)	O′(1)-Co-O″(1)	86.76(17)
O′(1)-Co-O‴(1)	180	O″(1)-Co-O‴(1)	93.24(17)

c) Symmetry code: O′(1): −*x*, *y*, −*z*; O″(1), Cl′: −*x*, −*y*, −*z*; O‴(1): *x*, −*y*, *z*.

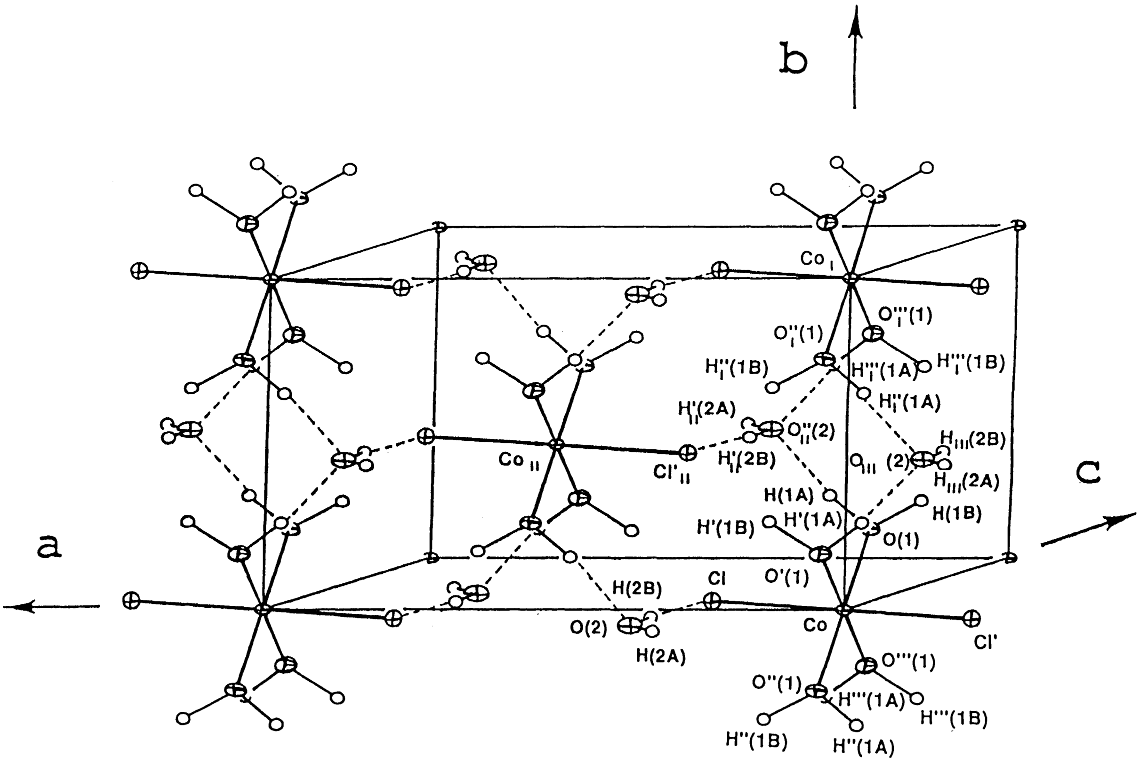


Fig. 6. An ORTEP drawing of the crystal structure for $CoCl_2\cdot 6H_2O$ with thermal ellipsoids scaled at 30% probability level.[21] H atoms are represented by small circles with 0.1 Å radius.

Discussion

The phase diagram of $CoCl_2$ hydrates is shown in Fig. 1. The solubility curve reported by Benrath$^{12)}$ (marked by solid lines) bounds the region where the thermodynamically stable chemical compounds exist, while the dashed curve reported by Etard$^{11)}$ can be considered to be the boundaries for $CoCl_2 \cdot 6H_2O$ and $CoCl_2 \cdot 2H_2O$ as metastable compounds in a stable region of $CoCl_2 \cdot 4H_2O$. The observed transformation under a microscope seems to follow the solubility curve proposed by Etard and dotted line in Fig. 1. As described in a previous section, the dihydrate crystals grew along the dotted curve when temperature was decreased to a supercooling temperature and the tetrahydrate crystals do not form in the cooling process. The hexahydrates formed at about 47 °C, which is slightly lower than the temperature given for the transition in the phase diagram. When we heated a solution equilibrated with the hexahydrate crystals, the crystals gradually dissolved and the dihydrate crystals formed. The hexahydrates could not exist at a higher temperature than about 50 °C as expected from the peritectic temperature reported by Etard.$^{11)}$ No crystal of the tetrahydrate was observed in the course of the temperature change of the solution. Hydrogen bonds in the $CoCl_2 \cdot 6H_2O$ crystal may be broken due to thermal vibrations of atoms and dihydrate crystals formed under the present experimental conditions. Crystals of $CoCl_2 \cdot 4H_2O$ might be formed when the temperature would be changed much slowly.

The molecular structures for $CoCl_2 \cdot 6H_2O$ and $CoCl_2 \cdot 4H_2O$ are shown in Fig. 4, together with that for $CoCl_2 \cdot 2H_2O$. In the $CoCl_2 \cdot 2H_2O$ crystal, four chloride ions in the square plane and two water molecules along the axis are octahedrally coordinated to a cobalt ion to form the $[CoCl_4(H_2O)_2]$ unit. The chloride ions are shared between the adjacent cobalt(II) ions to form polymeric chains along the *c* axis. The Co-Cl and Co-O bond lengths for hexa-, tetra-, and dihydrate complexes are in the order as follows:

For the Co-Cl bond length, di-(equatorial, 2.450, 2.478 Å) ≈ hexa-(axial, 2.445 Å) >tetra-(equatorial, 2.422 Å) ≈ the median value (2.417 Å) in the literature$^{23)}$ >tetrahydrate(axial, 2.406 Å);

For the Co-O bond length, tetra-(equatorial, 2.123, 2.115, 2.107 Å) >tetra-(axial, 2.094 Å) ≈ the median value (2.090 Å) in the literature$^{23)}$ ≈ hexa-(equatorial, 2.081 Å) >dihydrate(axial, 2.040 Å).

The order indicates that the hexahydrate has an axially elongated octahedral form, whereas the di- and tetrahydrates are axially compressed octahedral one. In the hexahydrate, the two water molecules out of the octahedron may pull the axial Cl^- ions by hydrogen bonding to elongate the axial bond length. On the other hand, four Cl^- ions at the equatorial position are shared by the adjacent cobalt(II) ions to form an infinite polymeric chain and thus the two water molecules at the axial position may be more attracted toward Co^{2+} ion. In the tetrahydrate, Cl···H-O hydrogen bonds may be responsible for the formation of the uniquely distorted form of the octahedron.

The complex species to be formed in the solution have been reported to be $[Co(H_2O)_6]^{2+}$, $[CoCl(H_2O)_5]^+$, $[CoCl_2(H_2O)_4]$, $[CoCl_3(H_2O)]^-$ and $[CoCl_4]^{2-}$.$^{4-10)}$

From the present in-situ observation under a microscope, it was seen that $CoCl_2 \cdot 4H_2O$ can hardly form in solutions compared with $CoCl_2 \cdot 6H_2O$ and $CoCl_2 \cdot 2H_2O$. The reason for the difficulty of crystallization of $CoCl_2 \cdot 4H_2O$ can be considered from the X-ray results as follows: In solution the aqua complex $[CoCl_2(H_2O)_4]$ exists as a minor component,$^{4-10)}$ which may have the trans-configuration because the trans-form should be more stable than the cis-form according to the consideration of steric repulsion between two chloride ions. However, the $CoCl_2 \cdot 4H_2O$ unit in the crystal has a cis-form, which may be stabilized in the crystal by the formation of hydrogen bonds between Cl^- ions and H_2O molecules. Thus the formation of $CoCl_2 \cdot 4H_2O$ should accompany the structural change from the trans-form (in the case of $CoCl_2 \cdot 6H_2O$ the two Cl^- ions are in the trans position) to the cis-form. The kinetics of the formation of $CoCl_2 \cdot 4H_2O$ crystals should be related to the concentration of $[CoCl_2(H_2O)_4]$ in solution and the activation energy of the cis-trans configurational change of the complex, as well as the ordering velocity of the units to form the hydrogen bonding network at crystallization. Although we can not conclude which process plays the major role in the kinetics of crystallization of the $CoCl_2 \cdot 4H_2O$, it is suggested that the structure of ionic species in solution may play an important role in the process of the crystal formation.

The complete F_o-F_c data are deposited as Document No. 9088 at the Office of the Editor of Bull. Chem. Soc. Jpn.

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