Spectrophotometric and X-Ray Diffraction Studies of Structure of Copper(II) Dichloride Aqueous Solutions Saturated with the Dihydrate Crystals

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Abstract

The solute structures of copper(II) dichloride aqueous solutions saturated with the dihydrate crystals have been investigated by spectrophotometric at 25, 40, 55 and 70°C and by the X-ray scattering methods at 25°C. The spectra did not indicate the formation of tetrahedral or square-planar complexes with an increase in the saturated temperature. The X-ray data was analyzed by using the model complex of the elongated octahedron, in which the equatorial positions are occupied by 1.8 chloride ions ($Cu - Cl_{eq}$ = 225 pm) and 2.2 water molecules ($Cu - O_{eq}$ = 197 pm), and two water molecules are located at the axial positions ($Cu - O_{ax}$ = 260 pm).

1. Introduction

The structures of aqueous solutions saturated with crystals have drown special attention in the field of crystal growth. Recently, the solution structures of $MnCl_2$, $CoCl_2$, and $NiCl_2$ saturated with the corresponding hydrate crystals have been successfully

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carried out by the X–ray scattering (Waizumi, 1999). On the other hands, X–ray scattering studies on chloro–complexes of Cu^{2+} in aqueous solutions meets with great difficulty, because complexes of Cu^{2+} with d^9 electronic structures have the Jahn–Teller distortion. Thus, the results reported previously were contradictory, i. e. Bell et al. reported that the mean species in the 3.18 M and 4.35 M $CuCl_2$ aqueous solution were polymeric $Cu_3Cl_5(H_2O)_8$ and $Cu_5Cl_{10}(H_2O)_{12}$, respectively, although Magini asserted that the complexes of Cu^{2+} in the 2.95 M solution were, as average, the elongated octahedral complexes of $Cu[Cl_{1.2}(H_2O)_{1.8}]_{eq}(H_2O)_{2,ax}$ where the subscript eq and ax denote the equatorial and axial positions, respectively. In addition, thermodynamic quantities for the formation of chloro complexes of Cu^{2+} in such concentrated aqueous solutions have not been also reported with reliable certainties in the literature.

In the present work, in order to clarify whether complexes of Cu^{2+} in concentrated $CuCl_2$ aqueous solutions are polymerized or not, the spectrophotometric and X–ray scattering studies have been carried out to the $CuCl_2$ aqueous solutions saturated with the dihydrate crystals. The spectra were used to check significant formation of tetrahedral or square–planar complexes of Cu^{2+}, which were compared with those of the Mn^{2+}, Co^{2+} and Ni^{2+} solutions. The X–ray scattering data obtained from the $CuCl_2$ solution saturated with the dihydrate at 25ºC was preliminary analyzed on the basis of model complexes of Cu^{2+} with elongated octahedral geometry.

2. Experimental

2.1. Spectrophtometric measurements for Mn^{2+}, Co^{2+}, Ni^{2+} and Cu^{2+} dichloride aqueous solutions

Each of the divalent transition–metal dichloride hydrate crystals of a reagent grade was used without further purification. Each samples of solutions were prepared by

mixing a distilled water with the hydrate crystals and by saturating at 25, 40, 55, and 70°C. The compositions and densities of the sample solutions were determined using the solubility data, respectively (Sohnel, 1985).

Electronic spectra of the solutions were measured on a spectrophotometer (Shimadzu UV–3100) in 10.0 mm quartz cell for Mn^{2+}, and 0.05 mm demountable quartz cells for Co^{2+}, Ni^{2+}, and Cu^{2+}. The temperatures were controlled by a constant-temperature bath circulator.

2.2. X-ray Scattering Measurements

Copper dichloride dihydrates of reagent grade were used without further purification. Solution was prepared by mixing water with the respective hydrate crystals and was saturated at 25°C. Composition of the sample solution determined by using a liquid chromatography was 4.861 M, and the density of 1.530 g cm^{-3} was measured by using a pycnometer.

X-ray scattering measurements were made on the reflection geometry by using a JEOL θ–θ diffractometer. The Mo Kα (λ =71.07 pm) line was used, and the X–rays scattered from the free surface of a sample solution were monochromatized by a Johansson type LiF (200) crystal. The range of the scattering angle (2θ) was 2 – 140°, which corresponds to an s range of 0.003 to 0.16 pm^{-1} (s = 4 π (sinθ) / λ). The intensity below 1° was extrapolated to zero at θ = 0°. Ten thousands counts at each discrete angle (2θ) were accumulated over the whole scan range. The measurements were scanned three times and the data sets obtained at each scan agreed with each other within 2%. Details of measurements and data collections were described in the literature (Ohtaki, 1974)

Corrections for background, absorption, polarization, multiple scattering, incoherent scattering, and subsequent scaling of the corrected scattering intensities to electron units were carried out as usual manner.

The structure function $i(s)$ was obtained by subtracting the independent scattering intensities of all atoms in the sample solutions from the scaled intensities $I(s)$:

$$i(s) = I(s) - \Sigma x_i f_i(s)^2 \tag{1}$$

where x_i is the number of the i-th atom in the stoichiometric volume V containing one M atom and $f_i(s)$ is the coherent scattering factor corrected for the real and imaginary parts of the anomalous dispersion.

The radial distribution function (RDF), $D(r)$, and the correlation function, $G(r)$, are calculated by the Fourier transform of the structure function:

$$D(r) = 4\pi r^2 \rho_0 + (2r / \pi) \int_0^{s_{max}} si(s)M(s)\sin(sr)ds \tag{2}$$

$$G(r) = D(r) / 4\pi r^2 \rho_0 = 1 + (1 / 2\pi^2 r \rho_0) \int_0^{s_{max}} si(s)M(s)\sin(sr)ds \tag{3}$$

where ρ_0 and s_{max} denote the average electron density and the maximum s value attained in the measurement, respectively. A modification function, $M(s)$, was introduced in the form

$$M(s) = [f_i(0)^2 / f_i(s)^2] \exp(-100s^2) \tag{4}$$

The synthetic structure function based on a model is obtained by

$$i(s)_{syn} = \sum_i \sum_j x_i n_{ij} f_i f_j (\sin(sr_{ij}) / sr_{ij}) \exp(-b_{ij}s^2) \tag{5}$$

Equation (5) includes the interatomic distance, r_{ij}, the temperature factor, b_{ij}, and the number of interactions, n_{ij}, for atom pairs $i - j$. All the calculations were carried out by means of the program KURVLR (Johansson, 1973).

3. Results and discussion

3.1. Spectrophotometric study

The experimental spectra measured are presented in Figs. 1–4, where (A), (B), (C), and (D) represent the spectra for saturated solutions at 25, 40, 55, and 70℃, respectively.

The peak positions (λ_{max}/nm) and heights (ε_{max} / 10mol^{-1}dm^2) of the obtained spectra are listed in Table I–IV, together with those of the hexaaqua and tetrachloro complexes.

For MnCl$_2$ (Fig 1), with an increase in the saturated temperature the spectra shift and its intensity increase in both cases. However, these spectra are significantly different from the spectrum of the tetrachloro complex which has the tetrahedral structure. This implies that it is difficult to form the tetrachloro complex of Mn^{2+} within the present experimental conditions. The shift of peak positions and increase of the intensities should be due to sucsessive formation of higher chlorinated octahedral complexes such as [MnCl(H$_2$O)$_5$]$^+$ and [MnCl$_2$(H$_2$O)$_4$]. Existance of such complexes was also suported by the X–ray scattering study (Waizumi, 1999).
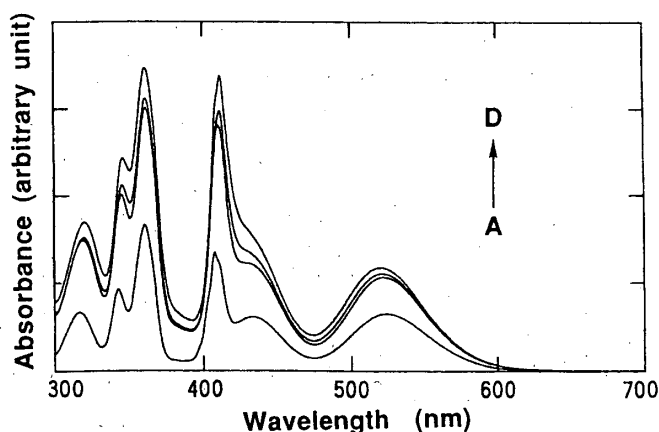

Fig. 1. Absorption spectra of MnCl$_2$ saturated aqueous solutions at 25°C (A), 40°C (B), 55°C (C), and 70°C (D).

Table I. Comparison with Absorption spectra of Mn^{2+} ions in chloride solutions

	λ_{max} / nm	ε_{max}/ 10mol^{-1}dm^2
A(25°C)	523.5	0.0254
	432.6	0.0214
	407.5	0.0521
	360.5	0.0645
	342.5	0.0359
	316.5	0.0260
B(40°C)	521.5	0.0371
	411.0	0.0988
	361.0	0.1047
	344.5	0.0702
	319.0	0.0517
C(55°C)	521.0	0.0332
	411.0	0.0890
	361.0	0.0935
	345.0	0.0636
	319.5	0.0454
D(70°C)	520.0	0.0325
	411.5	0.0931
	361.0	0.0936
	345.5	0.0636
	320.0	0.0467
[Mn(H$_2$O)$_6$]$^{2+}$ [a]	530	0.0183
	433	0.0152
	357	0.0214
	336	0.0217
	303	0.0145
[MnCl$_4$]$^{2-}$ [b]	444	1.29

a) Heidt, 1957. b) Cotton, 1962.

It is well known that tetrahedral complexes of Co^{2+} can form in aqueous solutions. As shown in Fig 2, the spectra are divided into two broad bands of about 400–600 and 600–750 nm, which have been ascribed to spectra of octahedral and tetrahedral species, respectively (Cotton, 1972). The apparent absorbance of the both bands increased according as the saturation temperature become higher, and the absorbance of tetrahedral species remarkably increased, compared with that of octahedral ones. On the assumption that the molar absorbances of any octahedral and tetrahedral complexes are close to those of $[Co(H_2O)_6]^{2+}$ and $[CoCl_4]^{2-}$, repsectively, the concentration ratio of octahedral to tetrahedral species can be estimated: it was found to be approximately 120:1, 30:1, 10:1, and 7:1 for the solutions of A(25°C), B(40°C), C(55°C), and D(70°C), respectively. The ratio for B(40°C), C(55°C), and D(70°C) are in good agreement with those of 31:1, 11:1, and 7:1, respectively, obtained by the X–ray scattering measurements (Waizumi, 1999).
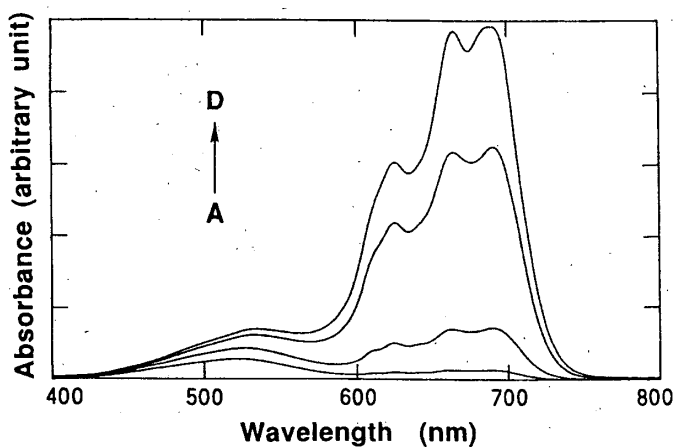
Table II. Comparison with Absorption spectra of Co^{2+} ions in chloride solutions

	λ_{max} / nm	ε_{max}/ $10mol^{-1}dm^2$
A(25°C)	689.6	6.77
	664.0	6.72
	624.6	5.10
	522.0	14.19
B(40°C)	691.0	30.87
	663.6	30.06
	625.2	21.61
	526.4	18.21
C(55°C)	690.8	111.64
	664.0	109.76
	624.6	75.86
	531.8	21.13
D(70°C)	690[c]	163[c]
	664[c]	161[c]
	624.4	103.22
	535.0	23.38
$[Co(H_2O)_6]^{2+, a)}$	514	4.55
$[CoCl_4]^{2-, b)}$	690	590

a) Jorgensen, 1954. b) Bjerrum, 1975. c) Estimated value.

Fig. 2. Absorption spectra of $CoCl_2$ saturated aqueous solutions at 25°C (A), 40°C (B), 55°C (C), and 70°C (D).

In the case of $NiCl_2$ (Fig. 3), no significant spectra originated from tetrahedral species could be seen within the experimental conditions, i. e. tetrahedral complexes of Ni^{2+} also hardly form even in such the concentrated solutions. The shift of peak positions and increase of the intensities should also be due to sucsessive formation of higher chlorinated octahedral complexes such as $[NiCl(H_2O)_5]^+$ and $[NiCl_2(H_2O)_4]$. The higher chlorinated complexes were also proved in our previous work by the X-ray scattering methods (Waizumi, 1999).

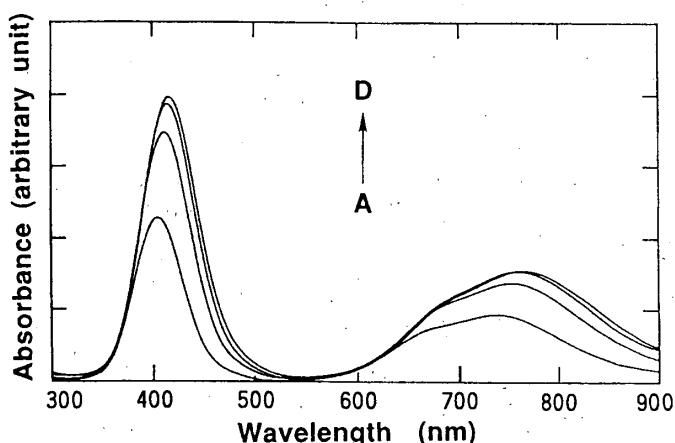
Fig. 3. Absorption spectra of NiCl₂ saturated aqueous solutions at 25°C (A), 40°C (B), 55°C (C), and 70°C (D).

Table III. Comparison with Absorption spectra of Ni^{2+} ions in chloride solutions

	λ_{max} / nm	ε_{max}/ $10mol^{-1}dm^2$
A(25°C)	733.0	4.33
	404.0	10.70
B(40°C)	750.5	5.57
	410.5	14.50
C(55°C)	752.5	5.95
	413.5	15.30
D(70°C)	766.0	5.67
	415.0	14.80
$[Ni(H_2O)_6]^{2+, a)}$	740	1.8
	395	5.2
$[NiCl_4]^{2-, b)}$	705	206
	658	200

a) Jorgensen, 1954. b) Nash, 1964.

In Fig 4, for $CuCl_2$, with increasing the saturation temperature the near-infrared spectra show a shift of the absorption maximum from 867.0 to 882.0 nm, and its intensity increase from 89.6 to 108.6 (units : mol^{-1} dm^3 cm^{-1} = 10 mol^{-1} dm^2). The tetrachlorocuprate(II) has been found to exist as a square-planar or in a flattened tetrahedron structure. The form of a square-planar structure presents the maximum of absorption at about 1000 nm (Khan, 1989). The form of a flattened tetrahedron, on the other hand, presents several d–d transition bands between 1100 and 2200 nm (Elleb,

1980). The spectra obtained here show no peaks around 1000 nm for a square-planar complex and around 1200 nm for a flattened tetrahedron. The shift of absorption maximum from 790 nm for $[Cu(H_2O)_6]^{2+}$ to 882.0 nm as well as the increase of extinction coefficient from 13.6 $mol^{-1} dm^3 cm^{-1}$ for $[Cu(H_2O)_6]^{2+}$ to approximately 108.6 / 10 $mol^{-1} dm^2$ would be considered as effects of formation of higher chlorinated octahedral complexes such as $CuCl(H_2O)_5$ and $CuCl_2(H_2O)_4$, as well as the cases of Mn^{2+} and Ni^{2+} as shown above.

Although the determination of the concentration of the individual complexes such as $[MCl(H_2O)_5]^+$ and $[MCl_2(H_2O)_4]$ (M = metal ion) in the solutions were attempted by the spetrophotometric data, it failed in such high concentrated ones at the present stage.
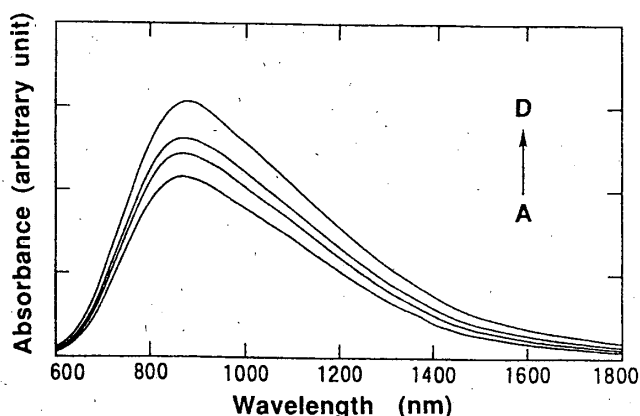

Fig. 4. Absorption spectra of CuCl₂ saturated aqueous solutions at 25°C (A), 40°C (B), 55°C (C), and 70°C (D).

Table IV.   Comparison with Absorption spectra of Cu^{2+} ions in chloride solutions

	λ_{max} / nm	ε_{max} / $10mol^{-1}dm^2$
A(25°C)	867.0	89.6
B(40°C)	871.0	94.6
C(55°C)	871.0	97.2
D(70°C)	882.0	108.6
$[Ni(H_2O)_6]^{2+,}$ [a]	790	13.6
$[NiCl_4]^{2-}$ square planar[b]	1000	122
flattened tetrahedron[c]	1200	120

a) Bjerrum, 1954. b) Khan, 1989. c) Elleb, 2699.

3.2. X-ray scattering study

3.2.1. Model Fittings

According to the suggestion reduced from the spectrophotometric measurements, elongated octahedral complexes of Cu^{2+} were assumed in the analysis of the X–ray diffraction data. The first coordination shell of the octahedral complexes consists of water molecules and Cl^- ions and is characterized with their interatomic distances r_{ij},

temperature factors b_{ij}, and number of interactions n_{ij}. We assumed that chloride ions preferentially occupy the axial position. The interligand interactions of O•••O, Cl•••O, and Cl•••Cl pairs within the first sphere were also take into account. The distances and the number of the interligand interactions were calculated from those of Cu–O and Cu–Cl pairs by assuming an elongated octahedral geometry of the complexes. It is hardly believed that such concentrated aqueous solutions retain a structure of a bulk water and Cl⁻ ions form some rigid polyhedral structure with water molecules. However, the first neighbor O•••O and Cl•••O interactions must exist to some extent even in the saturated solutions, and thus, the interactions were taken into account at model fittings. The O–H and H–H interatomic distances in water were fixed at the values found in the gas phase by taking into account the temperature factor b reported previously (Narten, 1968).

3.2.2. Obtained Structures

The $G(r)$ curves are presented in Fig. 5, where the dots show experimental values, the solid lines represent theoretical values calculated by using the parameters given in Table VI, and the dashed lines indicate residual values obtained after subtraction of the calculated curves (solid lines) from the observed curves (dots). The residual curves in $G(r)$ did not show significant peaks in the gentle slope, which means the model well reproduce the experimental $G(r)$ curves with the range under consideration.
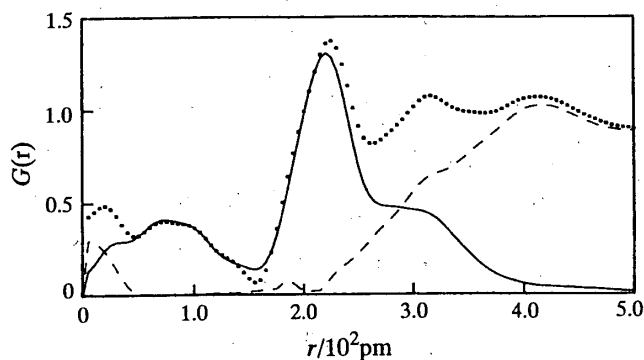

Fig. 5. The $G(r)$ curve of the saturated aqueous solution of CuCl₂ at 25°C. The residual curve (– –) is obtained after subtraction of the calculated $G(r)$ curve (——) from observed $G(r)$ one (•••••).

Table V. Selected distance of atom pair interaction, r (pm), and the number of the interaction, n, in the elongated octahedral Cu²⁺ complexes used for model calculations

		This work		Magini[a]
Cu – O$_{eq}$	r	197	r	195.4
	n	2.2	n	2.8
Cu – Cl$_{eq}$	r	225	r	225.0
	n	1.8	n	1.2
Cu – O$_{ax}$	r	260	r	262.6
	n	2.0	n	2[b]

a) Magini, 1981. b) Fixed value.

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The atom pair distances obtained are in good agreement with the previous results reported by Magini (Magini, 1981) as listed in Table VI. The n–value of Cl_{eq} interactions became larger than unity in the solutions, which may be caused by the existence of $Cu[Cl_2(H_2O)_2]_{eq}(H_2O)_{ax}$ complexes. If we assume that the elongated octahedral complexes of $Cu(H_2O)_{4,eq}(H_2O)_{2,ax}$ and $Cu[Cl_2(H_2O)_2]_{eq}(H_2O)_{aq}$ as dominant species in the solution, the concentration ratio of former to the latter is roughly calculated to be 1 : 9, which value is significantly larger than that of 1 : 1 estimated by Magini (Magini, 1981) for the solution of 2.95M. However, the larger value estimated here is understandable concerning the higher concentration, 4.86 M of the present solition.

Polymerization of Cu^{2+} complexes suggested by Bell, et al. (Bell, 1973) is not needed in our solution, although the concentration of 4.86 M of our solution is higher than those of 4.35 M and 3.18 M used by them. However, sharing of chloride ions between two Cu^{2+} ions may be possible in solutions with much higher concentration. Further work could be of help in the elucidation of this point.

4. Acknowledgments

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