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An X-Ray Diffraction Study of the Structure of Hydrated Copper(II) Ion in a Copper(II) Perchlorate Solution

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The structure of hydrated copper(II) ion was determined by means of the X-ray diffraction of a 3.55 M copper(II) perchlorate solution. The radial distribution curve showed that the copper(II) ion has a distorted octahedral structure with six water molecules. Four water molecules occupy the equatorial sites of the octahedron at a distance of 1.94±0.02 Å from the Cu(II) ion and the other two water molecules at the axial sites are 2.43±0.03 Å distant from the central ion.

A number of X-ray investigations have been carried out on crystal structures of various copper(II) complexes, and anisotropic electron distributions of copper(II) have been observed in many complexes of Cu(II).1–3)

X-Ray crystal studies of copper(II) hydrates disclosed the fact that the Cu^{2+} ion coordinated to six water molecules possesses a distorted octahedral configuration. Four water molecules are located at the equatorial positions with the Cu–O bond distance of 1.94—2.16 Å, and the other two water molecules are at the axial positions with the Cu–O distance of 2.2—2.5 Å.4–8)

The distortion in the structure of hydrated copper(II) ion has also been observed in aqueous solution by Shapovalov and Radchenko,9) who carried out X-ray diffraction measurements of an aqueous copper(II) sulfate solution, and determined that the Cu^{2+} ion is surrounded by six water molecules, four of which lie at a distance of 2.15 Å from the central ion and the other two occupy the opposite ends of the axis of the octahedron at a distance of 2.5 Å from the ion.

The present paper deals with an X-ray diffraction study of a copper(II) perchlorate solution, and the results are compared with those obtained for the sulfate solution.9)

Experimental

Preparation and Analysis of Copper(II) Perchlorate Aqueous Solution. Copper(II) perchlorate was prepared by dissolving copper(II) oxide of p.a. quality (Wako Pure Chemicals Co.) in a hot perchloric acid and was recrystallized twice from water. A copper(II) perchlorate solution was prepared by dissolving the copper(II) perchlorate crystals in water containing a small amount of perchloric acid in order to prevent the hydrolysis of Cu^{2+} ion.

The concentration of Cu^{2+} ion in the sample solution was determined by means of electrodeposition of copper on a platinum gauze electrode. The amount of perchlorate ion was determined by an acid-base titration of a perchloric acid effluent obtained by passing an aliquot of the solution through a cation-exchanger column (Dowex 50W–X12) of the H$^+$ form. The concentration of hydrogen ion was determined from the relation, $[H^+]=[ClO_4^-]-2[Cu^{2+}]$. The density of the solution was measured with a pycnometer. The composition of the sample solution is given in Table 1.

Measurements and Treatment of X-Ray Diffraction Intensities. X-Ray diffraction measurements were carried out with an X-ray diffractometer (JEOL Co., Tokyo).10)

TABLE 1. COMPOSITION OF THE SAMPLE SOLUTION (in g atoms/l)

Cu	3.550
Cl	7.357
O	69.86
H	81.12

The surface of the solution thermostated at 25±1 °C was irradiated with a divergent beam of MoKα radiation (λ= 0.7107 Å) emitted from a Philips PW210500 Mo X-ray tube.

The diffraction was measured at discrete points between θ=1 and 70°, where θ is half the scattering angle. Three different slit combinations, with divergent slits 1/12°, 1/4°, and 1°, were used. The diffracted intensities were measured as times used for preset 40000 counts (which contain a statistical error of 0.5%) at angular intervals of 0.125° in the low angle range θ=1—6° with a combination of a 1/12° divergent slit, 0.25° in the intermediate range θ=3—20° with a 1/4° divergent slit, and 0.5° in the high angle range θ=16—70° with a 1° divergent slit. The whole angle range was scanned twice in order to examine the reproducibility of the results. The intensities measured at the same angle usually agreed within 2%.

The measured intensities with the three different slit combinations were corrected for background radiation and were normalized to the intensities obtained with a 1° divergent slit by comparing them with those measured in the overlapping regions. The normalized intensities were corrected for absorption in the solution and polarization in the solution and in the monochromator and then scaled to absolute intensities in such a way that the asymptote became equal to the sum of the calculated coherent and incoherent intensities at high scattering angles (θ>50°). The scaling factor thus calculated agreed with that calculated by the method of Krogh-Moe11) and Norman12) within less than 1% accuracy.

Intensities $i(s)$ due to combinations of any pairs of atoms were evaluated from the scaled intensities $I(s)$ after correction of the independent atom- and incoherent-scattering according to the equation

$$i(s) = I(s) - \sum_i n_i[(f_i(s)+\Delta f_i')^2 + (\Delta f_i'')^2 + \Phi(s)\cdot I_i^{\mathrm{inco}}(s)] \qquad (1)$$

where s denotes $4\pi\sin\theta/\lambda$ (λ=0.7107 Å), n_i the number of atom i, $f_i(s)$ the scattering factor of atom i at angle s, $\Delta f_i'$ and $\Delta f_i''$ the real and imaginary parts, respectively, of the anomalous dispersion, and $\Phi(s)$ the fraction of the incoherent radiation reaching the counter. The reduced intensities $i(s)$ thus evaluated are shown in Fig. 1 in the form of $s\cdot i(s)$ *vs.* s.

The coherent scattering factors of Cu, Cl, and O were taken from Cromer and Waber,13) and those of H from the

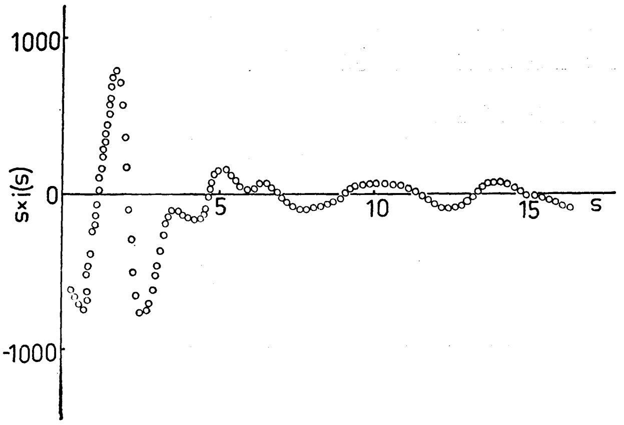

Fig. 1. The reduced intensities $i(s)$ multiplied by s as a function of s. For clarity not all of the experimental points are shown.

International Tables.[14] The incoherent scattering factors for Cu were those given by Cromer and Mann,[15] those for Cl and O by Cromer[16] and those for H by Compton and Allison.[17] The incoherent scattering factors were corrected by the Breit-Dirac factors. The values used for anomalous dispersion were taken from Cromer and Lieberman.[18]

Results and Discussion

The radial distribution curve $D(r)$ was calculated from the reduced intensity data $i(s)$ according to Eq. (2). The calculations were carried out with the help of the computer program KURVLR specially written for the analysis of X-ray diffraction data in solution.[19]

$$D(r) = 4\pi r^2\rho_0 + 2r\pi^{-1}\int_0^{s_{\max}} s\cdot i(s)\cdot M(s)\cdot\sin(sr)\,\mathrm{d}s \qquad (2)$$

Here ρ_0 denotes the average scattering density of the solution in electron unit and the modification function $M(s)$ was chosen to be

$$\sum_i n_i f_i(0)^2 / \sum_i n_i f_i(s)^2 \exp(-0.01s^2).$$

The $D(r)$ function thus calculated showed spurious peaks in the range less than 1 Å, which has no relation with any interatomic distance. These spurious peaks were eliminated by the Fourier inversion of the $D(r)$ function below 1 Å on the assumption that the $D(r)$ function below 1 Å consisting of contributions only from the O–H bonds within H_2O and the Cl–O bonds within ClO_4^-.

Figure 2(a) shows the final radial distribution function $D(r)$ thus calculated. It shows four peaks at around 1.4, 1.95, 2.4, and 3 Å. The peak at around 1.4 Å is due to the Cl–O bonds within ClO_4^-, that at 1.95 Å can be attributed to the bonds between Cu and O at an equatorial position within the hydrated Cu^{2+} ion, and the one at 2.4 Å is due to both the axial Cu–O bond within the hydrated Cu^{2+} ion and the O–O contact within ClO_4^-.

The distances and the numbers of equatorial and axial Cu–O bonds were determined from the residual peaks after subtraction of the contributions from the Cl–O and O–O contacts at 1.43 and 2.43 Å, respectively, within ClO_4^- ion and the O–H bond at 1.01 Å within H_2O. The theoretical peak shapes for the Cl–O, O–O, and O–H contacts were evaluated as follows.

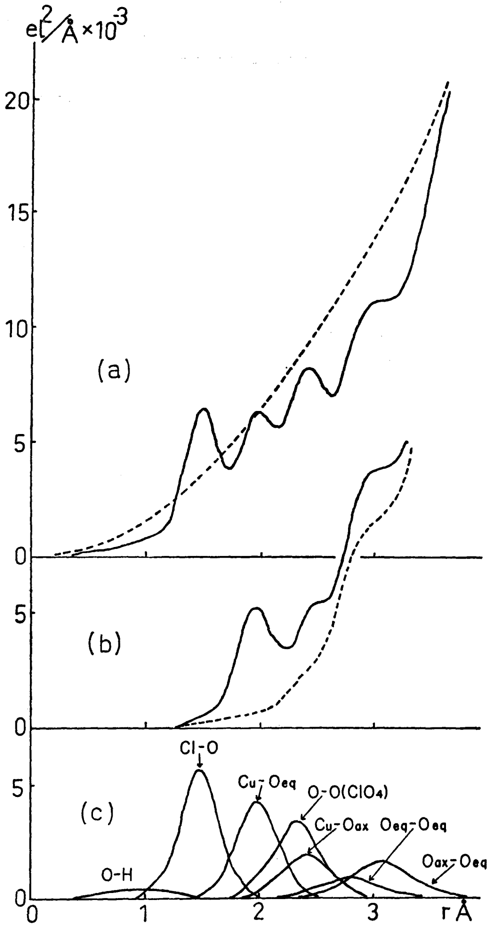

Fig. 2. (a) The radial distribution curve. The broken curve denotes $4\pi r^2\rho_0$. (b) The full curve gives the difference between $D(r)$ and the calculated peak shapes for the Cl–O and O–O atom pairs within ClO_4^-, and the broken curve the residual distribution function obtained by subtraction of the theoretical peak shapes shown in (c) from the $D(r)$ curve. (c) The calculated peak shapes with the parameters given in Table 2.

Theoretical intensities caused by any i–j atom pair can be calculated by

$$i(s) = \sum_i\sum_j n_{ij} f_i(s) f_j(s) \frac{\sin(r_{ij}s)}{r_{ij}s}\exp(-b_{ij}s^2) \qquad (3)$$

where n_{ij}, r_{ij}, and b_{ij} represent the frequency factor, the distance, and the temperature factor, respectively, of the interaction between any atoms i and j.

The values of r, b, and n for the Cl–O and O–O pairs[10] and those for the O–H bond are given in Table 2.

The theoretical intensities thus calculated were converted into atomic pair distribution functions by means of the Fourier integration with Eq. (2). The calculated functions are reproduced in Fig. 2(c). Figure 2(b) gives the residual radial distribution curve (full line) obtained by subtracting these peaks from the $D(r)$ curve. Three peaks still remain at the positions 1.94, 2.43, and 3 Å. The area under the peak at 1.94 Å was estimated with a planimeter. The number of

TABLE 2. FINAL PARAMETER VALUES FOR THE COPPER(II) ION COORDINATED TO SIX WATER MOLECULES, PERCHLORATE ION, AND WATER MOLECULE

	r(Å)	b	n
$Cu(H_2O)_6^{2+}$			
Cu–O_{eq}	1.94	0.002	4
Cu–O_{ax}	2.43	0.005	2
cis–O_{eq}–O_{eq}	2.74	0.01	4
O_{ax}–O_{eq}	3.11	0.01	8
ClO_4^-			
Cl–O	1.43	0.001	4
O–O	2.34	0.002	6
H_2O			
O–H	1.01	0.001	2

water molecules around Cu was evaluated to be about four, which corresponds to the number of Cu–O bonds in an equatorial plane. The area under the peak at 2.43 Å, which may correspond to the number of bonds between Cu and water molecules at the axial coordination sites, was difficult to estimate, since contributions from atom pairs at longer distances were overlapped. The broad peak ranging from 2.7 to 3.2 Å is ascribable to both the equatorial O–O contacts at *cis*-position and the contacts between axial and equatorial oxygens within the distorted octahedron of the hydrated copper(II) ion.

From the results, it was assumed that the Cu^{2+} ion is bound by six water molecules and the length of four Cu–O bonds in the plane is 1.94 Å and that of the other two along the axis is 2.43 Å. The values of r, b, and n were evaluated for four kinds of atom pairs (the equatorial Cu–O, the axial Cu–O, the *cis*-contacts of the equatorial O–O and the equatorial O–axial O) within $Cu(H_2O)_6^{2+}$. They are given in Table 2, together with the values for the Cl–O and O–O pairs within ClO_4^- and for the O–H pair within H_2O.

In order to see if the proposed structure and the values of the parameters given in Table 2 can satisfactorily explain the experimental data, the theoretical peaks were calculated with the parameters according to Eqs. (3) and (2) (the calculated peaks for the interactions within $Cu(H_2O)_6^{2+}$ are shown in Fig. 2(c)). The peaks were subtracted from the residual curve (full line, Fig. 2(b)) which had been obtained by subtraction of the contributions of ClO_4^- from the $D(r)$ curve. The curve thus obtained (broken line, Fig. 2(b)) gives a smooth curve with no dominant peak in the region less than 2.8 Å. The broad peak remaining at around 2.9 Å may be due to the contacts between oxygen atoms of water molecules and oxygen atoms of ClO_4^-.[10,20,21]

It is thus concluded that the copper(II) ion, which is coordinated to six water molecules in the first coordination sphere, has a distorted octahedral structure with the values of the parameters given in Table 2.

Shapovalov and Radchenko[9] obtained 2.15 and 2.5 Å as the distances from Cu to O occupying an equatorial and an axial site, respectively, in the sulfate solution. These distances are greater than the corresponding ones, 1.94±0.02 Å and 2.43±0.03 Å, we found in the perchlorate solution. The uncertainties of the distances were estimated from the shape of the distribution curve in Fig. 2(b).

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