X-Ray Diffraction Studies of the Structures of Hydrated Divalent Transition-Metal Ions in Aqueous Solution*

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X-ray scattering measurements have been carried out for concentrated aqueous solutions of divalent transition–metal perchlorates of manganese(II) to zinc(II). The radial distribution curves showed that each central metal ion was octahedrally surrounded by six water molecules at the distances of 2.20 Å for Mn^{2+}–OH_2, 2.12 Å for Fe^{2+}–OH_2, 2.08 Å for Co^{2+}–OH_2, 2.04 Å for Ni^{2+}–OH_2, and 2.08 Å for Zn^{2+}–OH_2. The results from the radial distribution curves were confirmed by the direct analysis of reduced intensities. Concentrated aqueous solutions of copper(II) and zinc(II) sulfates have also been measured. The bond distances of 1.94 Å for the Cu^{2+}–OH_2 (equatorial), 2.38 Å for the Cu^{2+}–OH_2 (axial) and 2.08 Å for Zn^{2+}–OH_2 were consistent with those obtained for the perchlorate solutions. No evidence for the contact ion pairs of metal and sulfate ions was found by the present X-ray measurements. The bond energies between metal ions including copper ion[26] were discussed by application of the Garrick model with a slight modification.

In crystals, divalent transition-metals of various salts are coordinated by 2 to 6 water molecules and the vacant apices of the octahedral structure of the metal ions are occupied by other ligands. The bond distance between a central metal ion and a water molecule is affected by counter-anions.

The manganese(II) ion in the $Mn(NH_4)_2(SO_4)_2\cdot 6H_2O$ crystal combined with water molecules at the distance of 2.18 Å.[1] For iron(II) salts the Fe^{2+}–OH_2 distance varied from 1.96 Å to 2.15 Å[2–6] depending on anions in salts. The Co^{2+}–OH_2 distance in crystals changed over the range of 2.08 Å to 2.23 Å,[7–10] which was longer than the Ni^{2+}–OH_2 distance; the latter was found to be 2.04—2.07 Å.[10–14] In copper salts were found two different Cu^{2+}–OH_2 bond lengths due to the Jahn–Teller distortion. The shorter bond length was in the order of 1.97 Å[15–19] except the bond within $Cu(H_2O)_6(ClO_4)_2$ in which the length was 2.125 Å,[20] and the longer one was about 2.3—2.8 Å.[15–20] The zinc(II) ion had a regular octahedral structure and the Zn^{2+}–OH_2 distance was about 2.08—2.10 Å.[10,21,22]

In contrast to a number of crystallographic studies of divalent transition-metal salts, only a few studies by X-ray diffraction have been reported on the structures of hydrated divalent transition-metal ions in solution. According to Shapovalov *et al.* who measured X-ray scatterings of sulfate solutions,[23,24] divalent transition-metals were hydrated with six water molecules and the bond lengths were about 2.15 Å independent of the metal ions except the Mn^{2+}–OH_2 distance of 2.20 Å and the longer Cu^{2+}–OH_2 distance of 2.5 Å. Bol *et al.* reported shorter bond lengths for hydrated Co^{2+}, Ni^{2+}, and Zn^{2+} ions in nitrate solutions[25] than those by Shapovalov *et al.* Our previous results for a copper perchlorate solution[26] showed that the Cu^{2+}–OH_2 distance in the equatorial position was 1.94 Å and that in the axial position was 2.43 Å, both of them being shorter than the distances reported by Shapovalov and Radchenko[23] in a sulfate solution.

In the present investigation we aim at determining the structures of a series of divalent transition-metal ions from Mn^{2+} to Zn^{2+} in aqueous perchlorate solutions by means of X-ray diffraction and discussing the change in the M^{2+}–OH_2 bond length with varying metal ions. The structures of hydrated copper(II) and zinc(II) ions in sulfate solutions are also determined in order to examine if the bond distances of metal and water molecules would really be affected by anions even in solutions.

Preparation and Analysis of Sample Solutions

Mn(II), Co(II), and Ni(II) Perchlorate Solutions. Manganese, cobalt, and nickel perchlorates were prepared by dissolving the metal chlorides (Wako reagent grade), which had been recrystallized twice from water, in dilute perchloric acids. Hydrochloric acid formed in solution was removed by repeated evaporation. After recrystallizing twice from water, crystals thus obtained were dissolved in water to prepare sample solutions. The concentrations of these metal ions were determined by two different methods; gravimetry as pyrophosphate $Mn_2P_2O_7$ and titration with EDTA for Mn^{2+}, electrogravimetry and titration with EDTA for Co^{2+}, and electrogravimetry and gravimetry as the dimethylglyoximate for Ni^{2+} ions.

Fe(II) Perchlorate Solution. A stoichiometric amount of $Ba(ClO_4)_2$ crystals (Wako reagent grade) was dissolved into an aqueous solution of $FeSO_4\cdot 7H_2O$ (Wako reagent grade) containing perchloric acid and then either $Ba(ClO_4)_2$ or sulfuric acid solution was added dropwise from burets to attain the exact stoichiometric ratio of Ba^{2+} to SO_4^{2-} ions in the mixture. The equivalent point was detected by the naked eye. A solution of iron (II) perchlorate was obtained by removing the $BaSO_4$ precipitates through G4 glass filters and No. 5C filter papers. All the treatments were performed under an atmosphere of nitrogen gas. The sample solution thus prepared was tested for Ba^{2+} and SO_4^{2-} ions by the addition of drops of sulfuric acid and a $Ba(ClO_4)_2$ solution, respectively. A check for Fe^{3+} ion with a KSCN aqueous solution was negative. The content of Fe^{2+} was determined by titration with a $KMnO_4$ solution.

Zn(II) Perchlorate Solution. Zinc perchlorate crystals were prepared by dissolving zinc oxide (Wako reagent grade)

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TABLE 1. COMPOSITIONS OF THE SAMPLE SOLUTIONS (in g-atoms·dm^{-3})

	$Mn(ClO_4)_2$	$Fe(ClO_4)_2$	$Co(ClO_4)_2$	$Ni(ClO_4)_2$	$Cu(ClO_4)_2$[26]	$Zn(ClO_4)_2$	$CuSO_4$	$ZnSO_4$
M	2.612	2.173	2.672	2.491	3.550	2.886	1.368	2.797
S	—	—	—	—	—	—	1.371	2.809
Cl	5.818	4.499	5.710	5.430	7.357	6.179	—	—
O	65.93	64.10	66.66	66.61	69.86	67.65	60.51	64.87
H	85.48	92.36	88.00	90.23	81.12	86.27	110.1	107.1

in a hot perchloric acid and recrystallizing twice from water. A solution of the zinc perchlorate was prepared by dissolving the crystals in water. The content of Zn^{2+} was determined both by gravimetry as $ZnHg(SCN)_4$ and by titration with EDTA.

The amounts of perchlorate and hydrogen ions in the solutions were determined as described in the previous papers.[26,27]

Cu(II) and Zn(II) Sulfate Solutions. Copper and zinc sulfate crystals (Wako reagent grade) were recrystallized once from water. The content of Cu^{2+} in the copper sulfate sample solution was determined by electrogravimetric analysis and by titration with EDTA. The concentration of zinc in the sample was analyzed by the same method as used for the zinc perchlorate solution. The content of SO_4^{2-} ions in the solutions was determined gravimetrically as $BaSO_4$.

The results of analysis for metal ions made by two different methods agreed each other within 0.2%. A small amount of perchloric or sulfuric acid was added to all the sample solutions in order to prevent the hydrolysis of the metal ions.

The density of the solutions was determined pychnometrically.

The compositions of the solutions investigated are given in Table 1, together with that of the $Cu(ClO_4)_2$ solution previously reported.[26]

X-Ray Scattering Measurements

X-Ray scattering measurements were carried out on a θ-θ X-ray diffractometer (JEOL Co., Tokyo) in a room thermostated at 25 ± 1 °C. In the case of the iron(II) perchlorate solution, the measurements were carried out under an atmosphere of nitrogen gas in order to prevent the oxidation of the iron(II) ion by air.

Mo$K\alpha$ radiation ($\lambda=0.7107$ Å) was diffracted at the sample solution and then monochromatized by reflection on a curved surface of an LiF crystal. A Philips PW 210500 X-ray tube was employed. The observed range of scattering angles (2θ) was 2° to 140°, corresponding to the range 0.31 Å$^{-1}<s<16.6$ Å^{-1} ($s=4\pi\sin\theta/\lambda$). Times required to accumulate 40000 counts at each angle were recorded. The whole angle range was scanned twice. The details of the measurements are described elsewhere.[26,27]

Symbols

$D(r)$	The radial distribution function
ρ_0	The bulk electron density in the stoichiometric unit volume
$s_{\max}$	The maximum value of s accessible in the experiments
$i(s)$	The reduced intensity
$M(s)$	The modification function
$I(s)$	The scaled intensities after correction for background, polarization, and absorption in the sample
n_i	The number of atom "i" in the stoichiometric volume containing one metal atom
$f_i(s)$	The scattering factor for atom "i" corrected for the real part of the anomalous dispersion
$\Delta f_i''$	The imaginary part of the anomalous dispersion correction for atom "i"
$\Phi(s)$	The fraction of the total incoherent scattering reaching the counter
$I_i^{\mathrm{inco}}(s)$	The incoherent scattering of atom "i"
k	The damping factor
r_{ij}	The distance between the atoms "i" and "j"
b_{ij}	The temperature factor of the atoms "i" and "j"

Treatment of Intensity Data

The measured intensities were corrected for background, polarization,[28] and absorption in the sample,[28] and then scaled to absolute intensities by the conventional methods.[26,29,30] The coherent scattering factors used for Mn, Fe, Co, Ni, Cu, Zn, Cl, S, and O were those given by Cromer and Waber.[31] The values for H were those given by Stewart *et al.*[32] The incoherent scattering factors cited from Cromer[33] for Fe, Co, Ni, O, S, and Cl, from Cromer and Mann[34] for Mn, Cu, and Zn, and from Compton and Allison[35] for H were corrected for the Breit–Dirac factors. Values of anomalous dispersion corrections for all atoms were taken from Cromer and Lieberman.[36]

The radial distribution functions $D(r)$ were calculated by means of the Fourier transform according to Eq. 1:

$$D(r) = 4\pi r^2\rho_0 + 2r\pi^{-1}\int_0^{s_{\max}} si(s)M(s)\sin(rs)\mathrm{d}s \tag{1}$$

where the reduced intensities $i(s)$ are written as[26,27]

$$i(s) = I(s) - \sum_i n_i(f_i^2(s) + (\Delta f_i'')^2 + \Phi(s)I_i^{\mathrm{inco}}(s)) \tag{2}$$

and the modification function $M(s)$ used in this study was $(\sum_i n_i f_i^2(0)/\sum_i n_i f_i^2(s))\exp(-ks^2)$ with the damping factor k of 0.015 Å^2 except the $CuSO_4$ case for which $k=0.01$ Å^2 was used.

Spurious peaks below 1 Å which appeared in the $D(r)$ curve were corrected since these spurious peaks did not correspond to any interatomic distances.[26,27] The reduced intensities $i(s)$ multiplied by s and the $D(r)$ curves thus deduced are shown in Figs. 1 and 2, respectively, for all the solutions, those for $Cu(ClO_4)_2$ solution previously reported[26] being also included.

Theoretical intensities due to interatomic interactions were calculated according to Eq. 3:

$$i(s)_{\mathrm{calc}} = \sum_i\sum_j n_i f_i(s) f_j(s) \frac{\sin(r_{ij}s)}{r_{ij}s}\exp(-b_{ij}s^2) \tag{3}$$

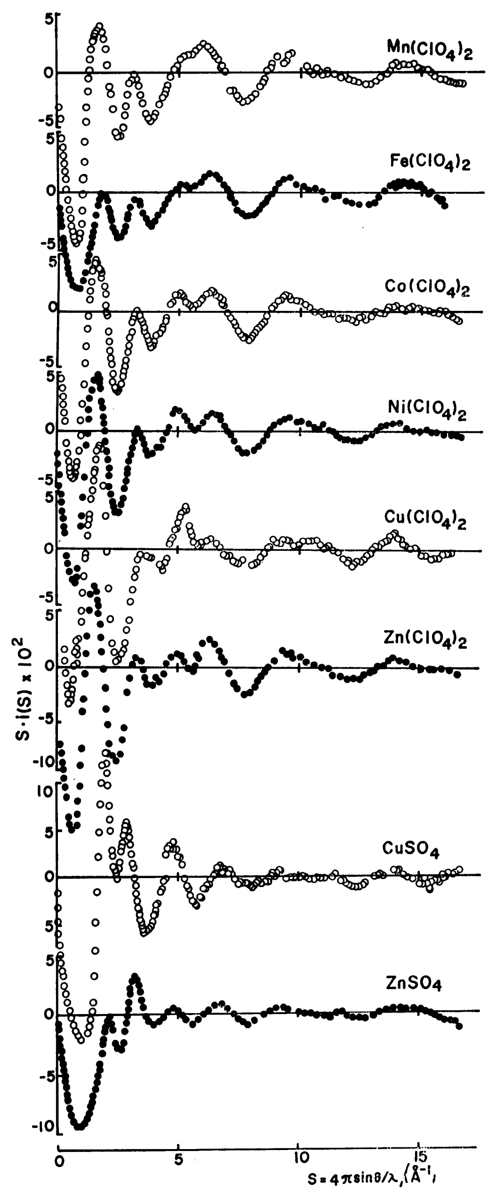

Fig. 1. Observed $s \cdot i(s)$ values of the solutions.

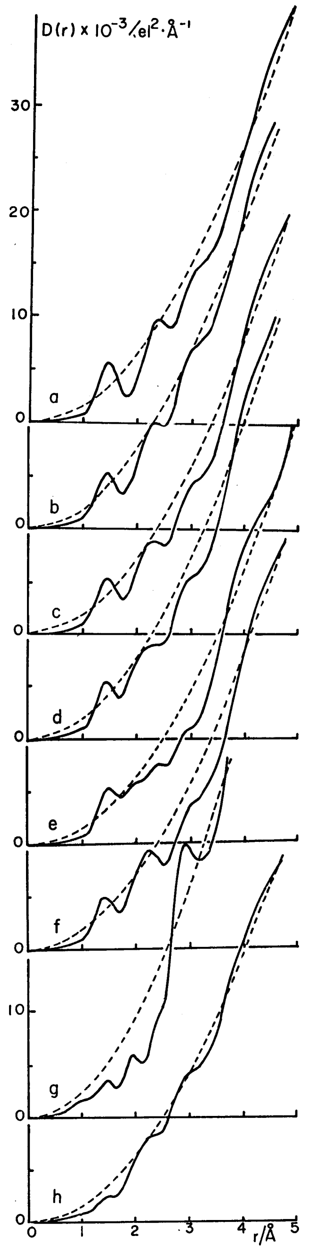

Fig. 2. Radial distribution curves $D(r)$'s (solid line) and $4\pi r^2 \rho^0$ (dashed line) for the solutions. a. $Mn(ClO_4)_2$, b. $Fe(ClO_4)_2$, c. $Co(ClO_4)_2$, d. $Ni(ClO_4)_2$, e. $Cu(ClO_4)_2$, f. $Zn(ClO_4)_2$, g. $CuSO_4$, h. $ZnSO_4$.

All calculations were carried out on a HITAC 8700 computer at the Computer Center of our Institute by means of the KURVLR program.[37]

Analysis of Intensity Data and Results

a) Solutions of Manganese, Iron, Cobalt, Nickel, and Zinc Perchlorates. The $D(r)$ curves for these solutions are shown in Fig. 2 (a, b, c, d, and f); the $D(r)$ curve (Fig. 2e) for the $Cu(ClO_4)_2$ solution reported in the previous paper[26] being also contained for comparison. The $D(r)$ curves represented the first peak at around 1.4 Å, which corresponded to the Cl–O distance within the ClO_4^- ion according to previous investigations.[26,27] The second peak appeared in the region 2.0—2.2 Å which was expected to correspond to both the distance between the metal ions and neighboring water molecules and the O–O distance ($\simeq 1.4$ Å $\times \sqrt{8/3} = 2.3$ Å) within the ClO_4^- ion which is known to form a regular tetrahedron. In order to deduce the peaks corresponding to the distances between metal ions and water molecules, the contributions from the Cl–O bond and the O–O

TABLE 2. PARAMETER VALUES FOR THE Cl–O, O–O ATOM PAIRS WITHIN ClO_4^-, THE S–O, O–O ATOM PAIRS WITHIN SO_4^{2-}, AND THE O–H ATOM PAIR WITHIN H_2O

		r_{ij}/Å	b_{ij}/Å²	n_{ij}
ClO_4^-	Cl–O	1.43	0.001	4
	O–O	2.34	0.002	6
SO_4^{2-}	S–O	1.47	0.001	4
	O–O	2.40	0.002	6
H_2O	O–H	1.01	0.001	2

interactions within the ClO_4^- ion were theoretically subtracted from the $D(r)$ curves. Calculations of these contributions were carried out according to Eqs. 1 and 3. Values of parameters attributed to the structure of the ClO_4^- ion used for the calculations are listed in Table 2.[38] Theoretical peak shapes thus calculated are shown in Fig. 3 with a special reference to the zinc perchlorate solution. The distance between the metal ion and water molecules was obtained from the residual peak shown in Fig. 3a. The number of water molecules bonded to the metal ion was roughly estimated from the peak area (shown by the dotted line in Fig. 3a) according to procedures described in a previous paper.[27] Final values for the structure of the aqua complex were determined by the method of trial and error so that the subtraction of the calculated peak due to the $M-OH_2$ bond from the $D(r)$ curve led to a smooth background curve with no indication of residual intramolecular interaction. (Fig. 3b).

The distances between metal ions and water molecules were found to be 2.20 Å for Mn^{2+}, 2.12 Å for Fe^{2+}, 2.08 Å for Co^{2+}, 2.04 Å for Ni^{2+}, and 2.08 Å for Zn^{2+}, and the numbers of water molecules in the first hydration sphere and the temperature factors were about 6 and 0.004 Å^2, respectively, for all the solutions.

In order to confirm the results obtained by the analysis of $D(r)$ curves, the distances, the temperature factors, and the frequency factors for the hydrated metal ions as well as for the perchlorate ions were refined by a least squares method in which the minimum of the function $U=\sum s^2(i(s)-i(s)_{\text{calc}})^2$ was sought. Various subsets of the reduced intensities from different s regions were used in order to check experimental errors in the data and errors in the parameter values introduced by contributions from intermolecular interactions which largely contribute to the reduced intensities at low s regions. The calculations were carried out by the use of the program NLPLSQ, which is a modified program of the algorithm described by Marquardt.[39]

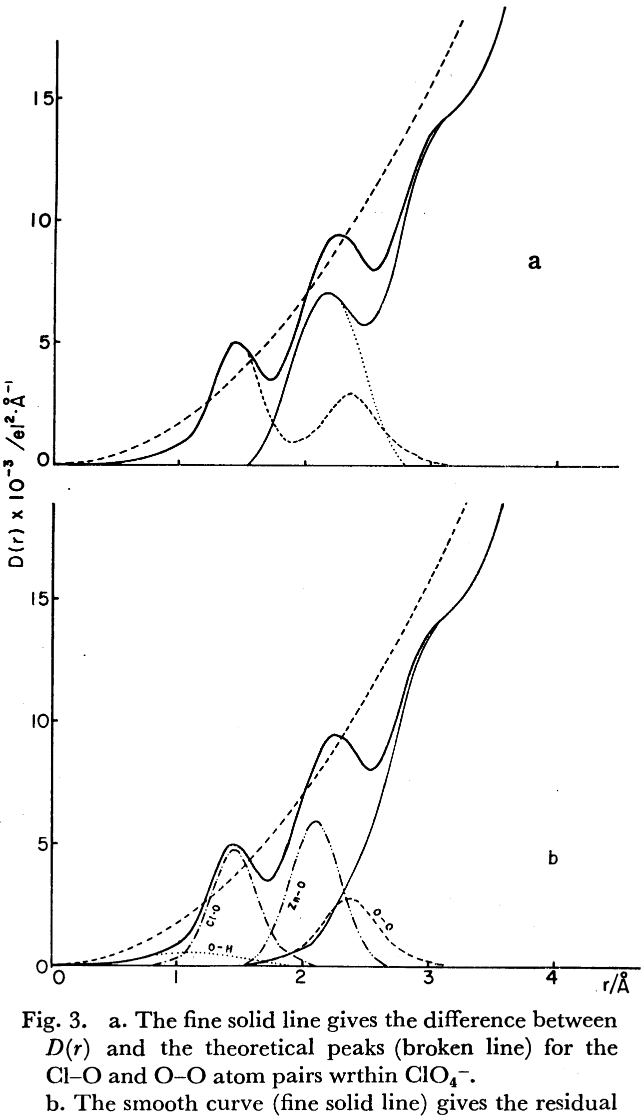

Fig. 3. a. The fine solid line gives the difference between $D(r)$ and the theoretical peaks (broken line) for the Cl–O and O–O atom pairs wrthin ClO_4^-.
b. The smooth curve (fine solid line) gives the residual distribution function obtained after subtraction of the peak shapes of the O–H, Cl–O, O–O, and $Zn-OH_2$ atom pairs from the $D(r)$ curve.

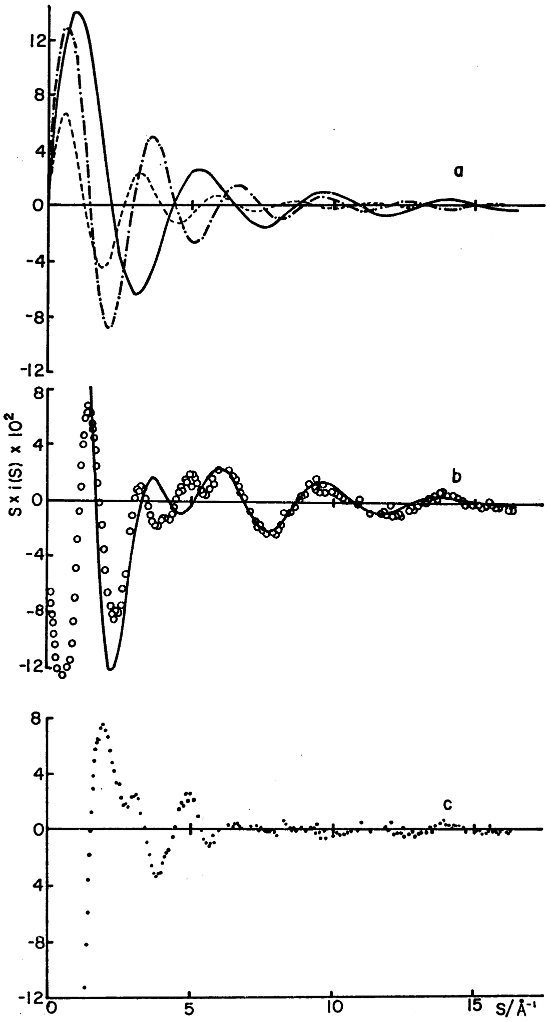

Fig. 4. Observed and calculated $s\cdot i(s)$ values for the $Zn(ClO_4)_2$ solution.
a. Each contribution of the Cl–O(—), O–O (···), and $Zn-OH_2$ (–·–) atom pairs.
b. Comparison between observed $s\cdot i(s)$ (circle) and the calculated $s\cdot i(s)$ (solid line) for the atom pairs considered using the refined parameter values given in Table 3.
c. Difference between observed and calculated $s\cdot i(s)$ values.

TABLE 3. THE RESULTS OF LEAST SQUARES REFINEMENTS OF THE $Zn(ClO_4)_2$ SOLUTION BY PROGRAM NLPLSQ. The units of r and b are Å and Å², respectively. Standard deviations are listed in parentheses.

	$3.22<s/\text{Å}^{-1}<14.95$	$6.01<s/\text{Å}^{-1}<14.95$	$10.70<s/\text{Å}^{-1}<14.95$
r_{Zn-O}	2.083(4)	2.081(2)	2.080(6)
b_{Zn-O}	0.0047(3)	0.0042(1)	0.0043(2)
n_{Zn-O}	5.84(4)	5.92(6)	5.7(2)
r_{Cl-O}	1.427(2)	1.430(1)	1.428(2)
b_{Cl-O}	0.0008(2)	0.0010(1)	0.0010(1)
n_{Cl-O}	4.06(3)	3.98(3)	4.07(7)
r_{O-O}	2.376(1)	2.339(7)	2.338(1)
b_{O-O}	0.0025(7)	0.0013(3)	0.0013(4)
n_{O-O}	5.97(1)	6.3(2)	6.8(4)
U	0.126×10^7	0.101×10^6	0.409×10^5

The results calculated in various s ranges are shown in Table 3 with a reference to the $Zn(ClO_4)_2$ solution. The refined parameter values of a given hydrated metal ion were almost the same for different s regions, and did not differ significantly from the values estimated from the $D(r)$ curve. The $s\cdot i(s)_{calc}$ values are compared with the values of $s\cdot i(s)$ in Fig. 4 for the $Zn(ClO_4)_2$ solution as an example. From Fig. 4 it is seen that the agreement is good except at a low s region where various interactions including intermolecular interactions, which are not taken into account in the present refinements, significantly contribute to the $s\cdot i(s)$values.

b) Copper Sulfate Solution. The $D(r)$ curve for the copper sulfate solution (Fig. 2g) showed three peaks at 1.5 Å, 1.95 Å, and 2.9 Å and shoulders at about 1 Å and 2.4 Å. The shoulder at 1 Å was ascribed to the intramolecular O–H interaction within H_2O. The peak at 1.5 Å could be identified as being due to the S–O bond within the SO_4^{2-} ion.[40–42]

TABLE 4. PARAMETER VALUES OF THE HYDRATED COPPER ION

	$r_{ij}/\text{Å}$	$b_{ij}/\text{Å}^2$	n_{ij}
$Cu-O_{eq}$	1.94	0.002	4
$Cu-O_{ax}$	2.38	0.004	2
cis-$O_{eq}-O_{eq}$	2.70	0.01	4
$O_{eq}-O_{ax}$	3.05	0.01	8

The distances and the numbers of equatorial and axial $Cu^{2+}-OH_2$ bonds were determined by the same procedures as those made for the copper perchlorate solution[26] after subtraction of interactions of the S–O and O–O bonds within the SO_4^{2-} ion and the O–H bond of H_2O from $D(r)$. Calculations are illustrated in Fig. 5a. Figure 5b shows the difference curve $(D(r)-4\pi r^2\rho_0)$ on which the peaks are better distinguishable. Values for the structure of the SO_4^{2-} ion given in Table 2 were used.[38] From the peak positions of the residual curve (Fig. 5a, b), it was found that the distance of the equatorial $Cu^{2+}-OH_2$ bond was 1.94 Å and that of the axial $Cu^{2+}-OH_2$ bond was 2.38 Å. The area for $Cu^{2+}-OH_2$ interaction in the equatorial position was found to correspond to four $Cu^{2+}-OH_2$ bonds by an analogous calculation to that in the perchlorate systems. Interactions within the hydrated copper ion which formed a distorted octahedron were calculated using the values listed in Table 4 and are shown in Fig. 5a. The subtraction of these interactions from the residual curve in Fig. 5a led to a smooth curve, which showed no dominant peak in the region below 2.8 Å (Fig. 5c). The sharp peak at 2.9 Å may be due to both adjacent O–O interactions of bulk water[43] and the interaction between water molecules and the oxygen atom of the SO_4^{2-} ion.[41]

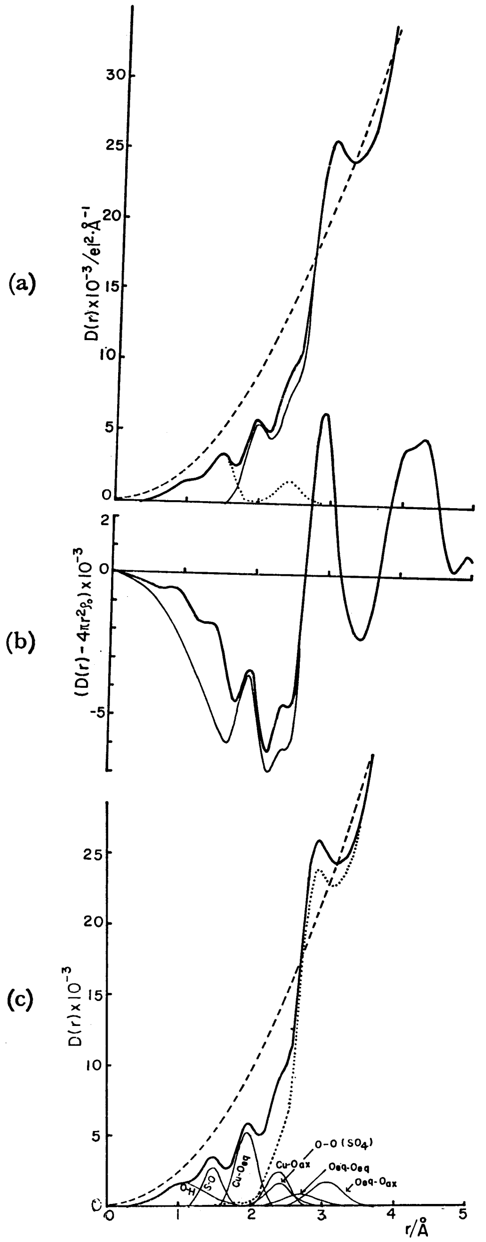

Fig. 5. a. The residual curve (fine solid line) obtained after subtraction of the theoretical peak(dotted line) of the S–O, O–O atom pairs within SO_4^{2-} and the O–H atom pair within H_2O from $D(r)$.
b. $D(r)-4\pi r^2\rho_0$ curve (upper) and the residual curve given in $a-4\pi r^2\rho_0$ (lower).
c. The smooth curve (dotted line) obtained by subtraction of theoretical peak shapes from $D(r)$.

c) Zinc Sulfate Solution. The $D(r)$ curve in Fig. 2h showed three peaks at around 1.5 Å, 2.1 Å, and 3 Å.

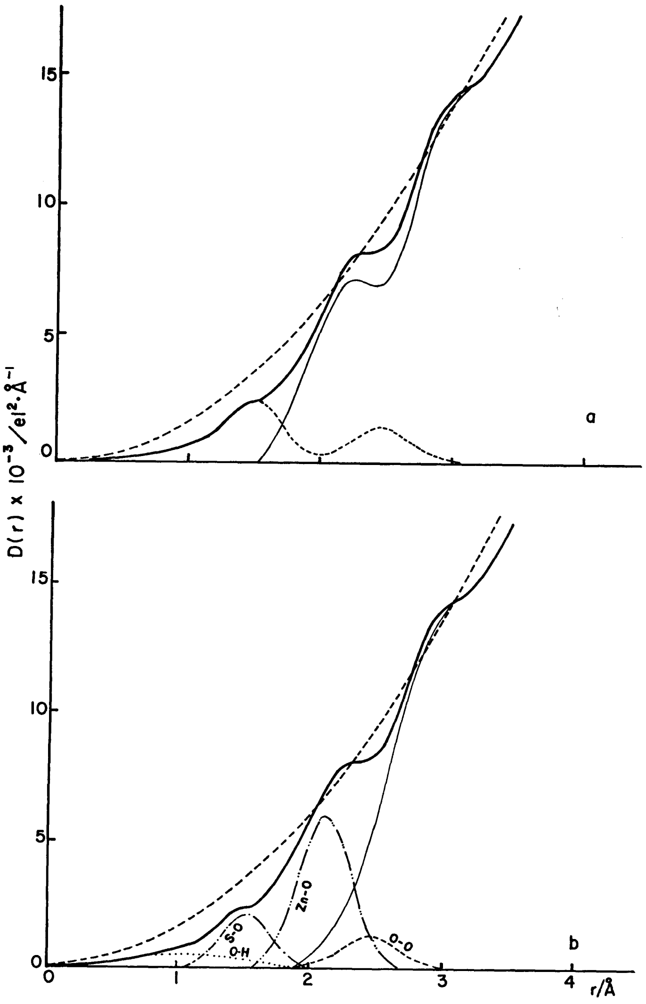

Fig. 6. a. The residual curve (fine solid line) obtained by subtraction of the theoretical peak (broken line) of the S–O and O–O atom pairs within SO_4^{2-} from $D(r)$. b. The smooth curve(fine solid line) gives the residual distribution function obtained after subtraction of the S–O, O–O, and Zn–OH_2 atom pairs from $D(r)$.

The peak at 1.5 Å corresponded to the S–O distance within the SO_4^{2-} ion. The second peak at around 2.1 Å was due to both Zn^{2+}–OH_2 and O–O interactions within the SO_4^{2-} ion. Parameter values for the Zn^{2+}–OH_2 bond within the hydrated Zn^{2+} ion were estimated according to the same procedures as those in the perchlorate system after subtraction of the contributions from the S–O and O–O interactions within the SO_4^{2-} ion from the $D(r)$ curve. These procedures are illustrated in Fig. 6. From the analysis, the Zn^{2+}–OH_2 distance was found to be 2.08 Å, and the number of the Zn^{2+}–OH_2 bonds was about 6, and the corresponding temperature factor was estimated to be 0.004 Å².

Discussion

In the aqueous perchlorate solutions of divalent transition-metal ions, Mn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, and Zn^{2+}, the M–OH_2 bond distances were found to be 2.20 Å, 2.12 Å, 2.08 Å, 2.04 Å, and 2.08 Å, respectively, and all the metal ions were octahedrally hydrated with six water molecules. The measurements for interatomic distances of zinc and copper sulfate solutions resulted in the same values as those obtained in the perchlorate solutions. Values of the cation–water distances obtained in this study are summarized in Table 5, along with those reported in the literature.[23–25] As is seen in Table 5, the present results were in excellent agreement with those found by Bol *et al.* in the metal nitrate solutions.[25] The distance of the longer Cu^{2+}–OH_2 bond in the copper sulfate solution differed slightly from that in the copper perchlorate solution, but this difference in the distance could not be significant in view of uncertainties in the present investigation. From the results obtained in this work and those reported by Bol *et al.*,[25] we concluded that the anions cause no change in the bond distances between cation and water molecules. This conclusion agreed with that obtained by Andreev *et al.*[44] and by Holmes and McClure[45] from the visible and ultraviolet spectra of the transition-metals in aqueous solution, who reported that the atmosphere around central metal ions was not affected by anions such as sulfate and nitrate ions. Values by Shapovalov *et al.*[23,24] are too large for the distances between transition-metal ions and neighboring water molecules.

In metal sulfate solutions, metal ions tend to form complexes with the sulfate ion. From infrared spectrophotometric measurements of divalent transition-metal ions in aqueous sulfate solutions, Larsson[46] estimated that the degree of inner-sphere complexity was about 10%. On the contrary, Hester and Plane[47] reported, using the Raman spectroscopy, that there was no evidence for the contact ion-association between transition-metal ions and sulfate ions in aqueous solution. According to the association constants reported in aqueous solution[48] of as high an ionic strength as of the sample solution, about 50% of the sulfate ions in our sample solutions were estimated to be bound as complexes. If 50% of the sulfate ions were directly coordinated to the metal ions through the M–OSO_3

Table 5. The distances between the metal ions and water molecules

	Anion	Mn^{2+}	Fe^{2+}	Co^{2+}	Ni^{2+}	Cu^{2+}	Zn^{2+}	
r_{M-OH_2}/Å	Perchlorate	2.20	2.12	2.08	2.04	1.94 2.43	2.08	This work
	Sulfate	—	—	—	—	1.94 2.38	2.08	This work
	Sulfate	2.20	—	2.15	2.15	2.15 2.50	2.15	Shapovalov *et al.*[23,24]
	Nitrate	—	—	2.06	2.06	—	2.09	Bol *et al.*[25]

bond, the peaks ascribed to the M–O bond in the sulfate solutions would become broader and more or less asymmetrical compared with those in the perchlorate solutions, because it is expected that the M-OSO_3 bond within metal sulfate compounds is a little shorter than the M-OH_2 bond.[49] However, such evidence could not be observed in both copper and zinc sulfate solutions. Therefore, we concluded that the association of copper and zinc ions with sulfate ions was solvent-separated and the hydration sphere of the ions was not affected by the associated sulfate ions in the outer-sphere.

Estimation of the M–OH_2 Bond Energies. Bond energies for aqua complexes with the regularly symmetric configuration have so far been calculated on the basis of several models.[50–52] However, no calculation for the hydrated copper(II) ion has been carried out, because of its asymmetric structure due to the Jahn–Teller effect.

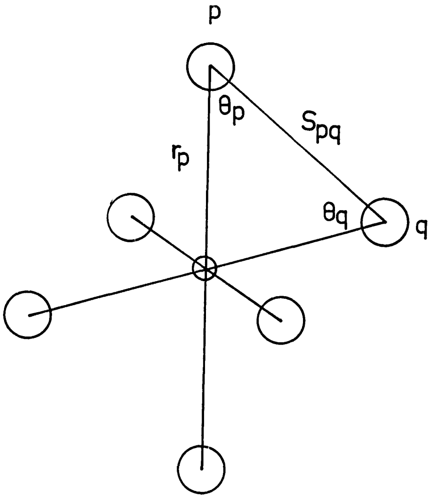

Fig. 7. The model of octahedral hydration.

We calculated the bond energies for the hydrated divalent transition-metal ions by application of the electrostatic model proposed by Garrick[52] and Basolo and Pearson[53] with a modification for a distorted octahedral structure. The bond energy in vacuum $-\Delta H_{\text{bond}}$ for a model of the octahedral hydration (Fig. 7) may be written as follows.

$$-\Delta H_{\text{bond}} = U_{\text{ed}} + U_{\text{dd}} + U_{\text{id}} + U_{\text{vw}} \tag{4}$$

Here subscripts ed, dd, id, and vw refer to the interaction between the ion and the dipole, that between the dipole and dipole, polarization of ligands to form induced dipoles, and the van der Waals repulsion. Each energy term is given as follows.

$$U_{\text{ed}} = -\sum_{p=1}^{N}(ze)(\mu_0+\mu_{\text{i}.p})/r_p{}^2 \tag{5}$$

$$U_{\text{dd}} = 1/2\sum_{p=1}^{N}\sum_{q=1}^{N}(\mu_0+\mu_{\text{i}.p})(\mu_0+\mu_{\text{i}.q}) \times (\sin\theta_p \sin\theta_q + 2\cos\theta_p \cos\theta_q)/s_{pq}^3 \tag{6}$$

$$U_{\text{id}} = \sum_{p=1}^{N}\mu_{\text{i}.p}^2/2\alpha \tag{7}$$

$$U_{\text{vw}} = \sum_{p=1}^{N}B_p/r_p{}^9 \tag{8}$$

where r_p denotes the distance between a central metal ion and a water molecule p, ze the charge of the central metal ion, μ_0 the permanent dipole moment of the water molecule (1.85×10^{-18} esu·cm), $\mu_{\text{i}.p}$ and $\mu_{\text{i}.q}$ the induced dipole moments of the water molecules p and q at a distance s_{pq}, α the polarizability of water (1.48 Å^3), and N the hydration number which is 6 in this case. The dipole moment of the water molecule p induced by another water molecule q was calculated by Eq. 9.

$$\mu_{\text{i}.p} = \frac{\mu_0 + (ze)/r_p}{1+\sum_{q=1}^{N-1}\alpha s_{pq}^{-3}(\sin\theta_p \sin\theta_q + 2\cos\theta_p \cos\theta_q)} - \mu_0 \tag{9}$$

The constant B_p in the repulsion term was estimated according to the procedures proposed by Basolo and Pearson[53] on the assumption of spherical hydrated ions. For a copper ion both $B_{p.\text{eq}}$ and $B_{p.\text{ax}}$ were estimated on the assumption of spherically hydrated ions having radii of $r_{p.\text{eq}}$ and $r_{p.\text{ax}}$. This approximation may be acceptable in calculating the interaction energies because of the relatively small value of van der Waals repulsion energies.

Each interaction energy calculated by the use of Eqs. 4—9 is tabulated in Table 6 and the total bond energies for the hydrated metal ions ($-\Delta H_{\text{bond}}$) thus calculated are graphically represented in Fig. 8, together with the experimental values of the enthalpy change of hydration ($-\Delta H_{\text{h}}$) of these ions in solution.[54]

The curves of $-\Delta H_{\text{bond}}$ and $-\Delta H_{\text{h}}$ were parallel and the maxima of both curves appeared at Cu^{2+}. The differences between the two curves were about 150 kcal·mol^{-1} independent of the ions, which was approximately equal to the sum of the free energy change in transfer of one mole of a hydrated divalent ion with an ionic radius of about 3.5 Å ($\simeq$ an average $r_{\text{M-OH}_2}+$ the radius of a water molecule) and the energy change of vaporization of six moles of water. The dotted lines show the enthalpy change expected after the correction

Table 6. The bond energies ($-\Delta H_{\text{bond}}$) calculated by the use of the Garrick model[52] and the enthalpy change of hydration ($-\Delta H_{\text{h}}$)[54] for the hydrated divalent transition-metal ions (in kcal·mol^{-1})

Ion	$r_{\text{M-OH}_2}$/Å	U_{ed}	U_{dd}	U_{id}	U_{vw}	$-\Delta H_{\text{bond}}$	$-\Delta H_{\text{h}}$
Mn^{2+}	2.20	+617.4	−124.8	−89.4	−95.4	+307.8	+459.0
Fe^{2+}	2.12	+676.2	−144.0	−96.0	−102.0	+334.2	+480.0
Co^{2+}	2.08	+708.6	−155.4	−99.6	−105.6	+348.0	+503.1
Ni^{2+}	2.04	+743.4	−167.4	−102.6	−109.2	+364.2	+518.6
Cu^{2+}	1.94 2.43	+586.8 +151.8	−157.2	−89.2 −18.8	−79.6 −27.2	+366.6	+519.5
Zn^{2+}	2.08	+708.6	−155.4	−99.6	−105.6	+348.0	+506.6

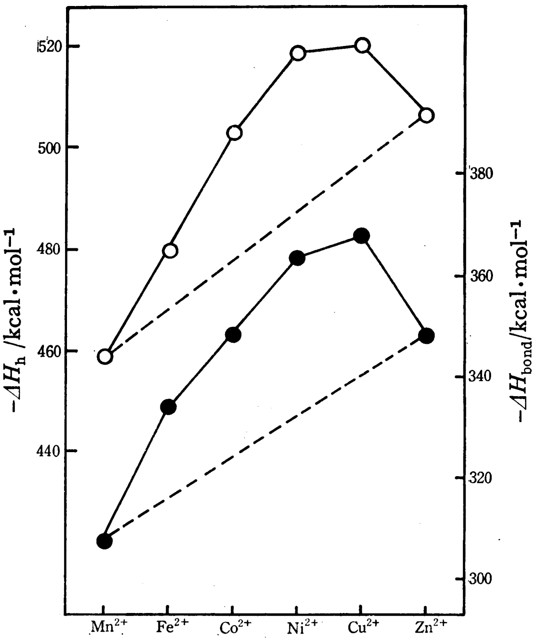

Fig. 8. $-\Delta H_{bond}$ (full circle) and $-\Delta H_h$ (open circle) for Mn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, and Zn^{2+}. The dashed line shows the enthalpy change expected after correction of the crystal field stabilization.

for the effect of the crystal field. From these results we see that the crystal field largely contributes to the bond distances between a central metal ion and ligands in complexes.

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