

## Coordination of Copper(II). Evidence of the Jahn-Teller Effect in Aqueous Perchlorate Solutions

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Two concentrated copper(II) perchlorate aqueous solutions have been examined by X-ray diffraction techniques. The analysis of the distribution functions leads, in an apparently unique way, to the determination of the structural configuration of the  $\text{Cu}^{2+}$  ions in solution. Such a configuration consists of six water molecules arranged around the copper ions in a tetragonally distorted octahedron. The structural parameters of the aquocopper(II) ion have been determined by directly comparing—through a least-squares procedure—the experimental structure functions with those calculated by solution models.

### Introduction

It is well-known that the  $d^9$  electronic configuration of Cu(II) makes it subject to Jahn-Teller distortion when placed in an environment of cubic symmetry. When hexacoordinate, the typical distortion is an elongation along one fourfold axis: four normal bonds lie in a square-planar configuration (equatorial positions = eq) and two long bonds occur above and below the plane (axial positions = ax). The arrangement is described as "distorted" octahedral (4 + 2). As a limiting case, when the two axial positions are much longer than the equatorial ones, the distorted octahedral and square coordination cannot be sharply differentiated. Square-planar (4) and distorted pyramidal (4 + 1) coordinations, in fact, are also common configurations for the  $\text{Cu}^{2+}$  ion.<sup>1</sup>

The case we are now interested in is that of  $\text{CuL}_6$  complexes, i.e., complexes with equal ligands in the six positions. Structural determinations in crystalline solid compounds indicate that the more common distortion is the tetragonal one with the four Cu-L short bonds equivalent or approximately equivalent.<sup>2-6</sup> Rhombic distortion has been found in  $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ <sup>7</sup> and in Tutton's salt.<sup>8</sup> An apparent regular octahedron, due to a dynamic Jahn-Teller effect (i.e., the resultant of three mutually perpendicular tetragonal distortions), has been reported to occur in the two isomorphous  $\text{K}_2\text{MCu}(\text{NO}_2)_6$  (M = Pb, Ba) salts.<sup>9</sup> Later it has been evidenced that the hexanitocuprate salts are subject to a dynamic-static Jahn-Teller effect in the sense that a temperature lowering will produce the classic static tetragonal distortion.<sup>10</sup>

In previous work on a  $\text{CuCl}_2$  solution,<sup>11</sup> the occupancy of equatorial copper sites has been successfully described by the configuration  $\text{Cu}(\text{H}_2\text{O})_{2.8}\text{Cl}_{1.2}$ , which is an average of the various Cu(II) complexes present in this solution. On the other hand, the axial positions were not unambiguously determined. The presence of two kinds of equatorial sites (Cu-OH<sub>2</sub> at ~2 Å and Cu-Cl at ~2.3 Å) and the large contribution from

$\text{Cl}(\text{H}_2\text{O})_6^-$  ions (at ~3.1 Å) did not allow for a unique determination of the axial positions.

These complications should not arise in copper perchlorate solutions where only water molecules are expected to enter the metal inner coordination sphere. Further,  $\text{ClO}_4^-$  anions will contribute to the total scattered intensities in a much more definite way—which we can easily account for—than the  $\text{Cl}^-$  ions. Thus copper(II) perchlorate seems suitable to substantiate the Jahn-Teller distortion in aqueous solutions. An aqueous copper(II) perchlorate solution has already been examined by Ohtaki et al.<sup>12</sup> and distorted octahedral coordination around the  $\text{Cu}^{2+}$  ions was found in that case. However, in order to give a more detailed picture of the solute structure, we felt it useful to further examine these solutions. The analysis of the scattering data has not been limited, in the present work, to an improved analysis of the distribution curve. Direct comparison between experimental data and data calculated through a solution model has been performed as well, so that a quantitative description of the dominant species occurring in solution, by sets of structural parameters, has been obtained.

### Experimental Details and Data Treatment

**Solutions.** The copper(II) perchlorate salt was prepared by dissolving copper(II) oxide in concentrated perchloric acid and recrystallizing twice from water. Analysis of the dried salt gave the formula  $\text{Cu}(\text{ClO}_4)_2 \cdot 6.2\text{H}_2\text{O}$ . Two copper solutions were prepared by dissolving weighed amounts of the crystalline salt in doubly distilled water. The copper contents were determined by direct titration with standard EDTA or after cation exchange on a cationic resin (Dowex 50W-X8). The densities were obtained by a digital precision densimeter. The compositions of the solutions and their symbols are reported in Table I.

**Data Treatment.** The  $\theta$ - $\theta$  X-ray diffractometer and the procedure of data collection and reduction have been previously described.<sup>13</sup> The radial distribution curves were calculated from the structurally sensitive part of the scattering data,  $i(s)$ , by a Fourier transformation according to

$$D(r) = 4\pi r^2 \rho_0 + \frac{2r}{\pi} \int_{s_{\min}}^{s_{\max}} i(s) M(s) \sin(rs) ds \quad (1)$$

where  $\rho_0$  is the average electronic bulk density and  $M(s)$  a modification function of the form  $[\sum_i n_i f_i(0)]^2 / [\sum_i n_i f_i(s)]^2 \exp(-0.005s^2)$  used to minimize the truncation errors. Spurious peaks below 1 Å in the  $D(r)$  curves were eliminated.<sup>14</sup>

For direct comparison between experimental and calculated data, a theoretical structure function was obtained from

$$i_{\text{calcd}}(s) = i_{\text{intra}}(s) + i_{\text{inter}}(s) \quad (2)$$

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Table I. Compositions of the Copper Perchlorate Solutions (Cu-2, Cu-3) in Moles per Liter<sup>a</sup>

solution	[M <sup>2+</sup> ]	[ClO <sub>4</sub> <sup>-</sup> ]/[M <sup>2+</sup> ]	[H <sub>2</sub> O]/[M <sup>2+</sup> ]	<i>d</i> , g cm <sup>-3</sup>	<i>V</i> , Å <sup>3</sup>	ρ <sub>0</sub> , e <sup>2</sup> Å <sup>-3</sup>
Cu-2	1.94 <sub>s</sub>	2.0	25.13	1.391	853.69	167.84
Cu-3	2.92	2.0	15.39	1.576	568.64	139.01
Co-3	2.93 <sub>s</sub>	2.0	14.99	1.549	565.74	135.78

<sup>a</sup> *d* is the density, *V* the stoichiometric volume used for data reduction, and ρ<sub>0</sub> the average electronic bulk density. The composition of a cobalt(II) solution (Co-3), isomorphous with Cu-3, is also given.

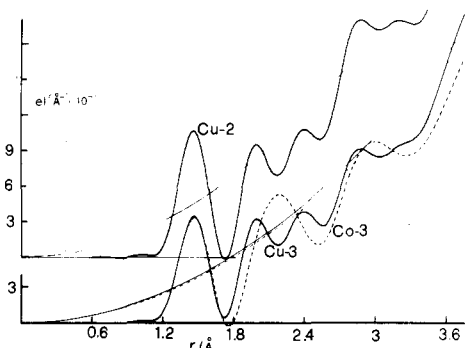


Figure 1. Radial distribution functions, in the  $D(r)$  form, shown by solid lines, in the 0–3.5-Å interval, for the investigated copper solutions (Cu-2 and Cu-3). The distribution curve of a 3 M cobalt perchlorate solution (Co-3) is also shown by dashes for comparison (see text). The parabolic curves (weak lines and dashes) are the respective  $4\pi r^2 \rho_0$  functions.

where  $i_{\text{intra}}(s)$  refers to intramolecular interactions between all atom pairs "pq" within the  $n_j$  molecular complexes or specific interactions

$$i_{\text{intra}}(s) = \sum_j n_j \sum_p \sum_q f_p f_q \sin(sr_{pq}) / (sr_{pq}) \exp(-b_{pq}s^2) \quad (3)$$

with  $r_{pq}$  being the average distance separating atoms p and q and  $b_{pq}$  the associated temperature factor. The intermolecular interactions are accounted for by assuming that each atom of the solution is surrounded by an even-electron distribution beyond a structured hole of radius  $R_j$

$$i_{\text{inter}}(s) = \frac{-4\pi R_j^3}{3V} \frac{3(\sin(sR_j) - s \cos(sR_j))}{(sR_j)^3} \exp(-B_j s^2) \sum n_j f_j \sum n_i f_i \quad (4)$$

where  $V$  is the stoichiometric volume and the summations are extended over the number of atoms in the stoichiometric unit. Least-squares refinements of model parameters were performed in a search of the minimum, in a selected  $s$  range, for the function

$$U = \sum w(s) [i_{\text{obsd}}(s) - i_{\text{calcd}}(s)]^2 \quad (5)$$

with  $w(s) = s^4$  being the weight given to each experimental point.

## Results and Discussion

**Distribution Curves Analysis.** The Fourier-transformed data of the two copper solutions, reported in Figures 1 and 2, allow for the following preliminary considerations: (a) The two sharp peaks at 1.5 and 2.4 Å are due to Cl–O and O–O nonbonded interactions within the perchlorate anion. (b) 2-Å peak is due to Cu–OH<sub>2</sub> interactions within the first copper coordination shell. We will later see how many neighbors are represented by this peak. (c) Two other significant peaks occur at 2.8 and ~4 Å. They do not warrant special attention: it is here assumed, as usual, that they represent H<sub>2</sub>O–H<sub>2</sub>O interactions of various kinds and secondary interactions from second cations' neighbors, respectively.<sup>15</sup> (d) Two other peculiar peaks, probably relevant in an understanding of copper coordination, are noticed: a clear small one occurring at ~3.2 Å (see Figure 1) and a pronounced shoulder at ~4.4 Å (see Figure 2). The 3.2-Å peak would agree with (H<sub>2</sub>O)<sub>eq</sub>–(H<sub>2</sub>O)<sub>ax</sub>

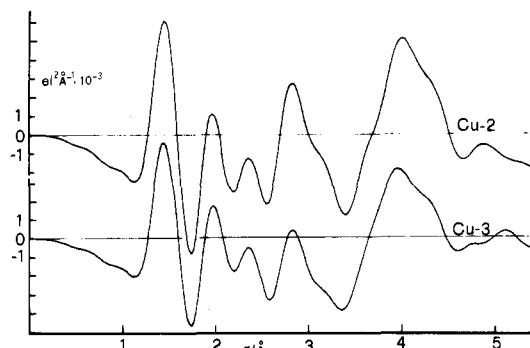


Figure 2. Differential form,  $D(r) - 4\pi r^2 \rho_0$ , of the distribution curves in the 0–5-Å interval for the copper solutions.

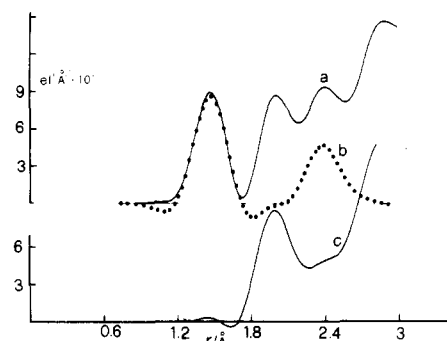


Figure 3. Subtraction of the contribution due to the ClO<sub>4</sub><sup>-</sup> anion (dots, curve b) from the total distribution curve of solution Cu-3 (curve a). The difference (curve c) is shown separately. The negative areas in the calculated curve b are due to termination errors in the Fourier integral.

interactions within distorted octahedral Cu(H<sub>2</sub>O)<sub>6</sub><sup>2+</sup> ions and the ~4, ~4.4 Å peaks should represent Cu–OH<sub>2</sub> distances from water molecules bonded either to (H<sub>2</sub>O)<sub>eq</sub> or to (H<sub>2</sub>O)<sub>ax</sub>.

If the preliminary suggestions about the existence of a distorted octahedron in our solutions are true, then the Cu–(OH<sub>2</sub>)<sub>ax</sub> should be evident in the distribution curves. The occurrence, at the expected distance, of O–O interactions from the perchlorate group masks the presence of such copper–water interactions. The ClO<sub>4</sub><sup>-</sup> anion, however, is structurally well-known, and its contribution may be subtracted from the total distribution function. Figure 3 shows such an operation for solution Cu-3. The residual distribution curve (curve c of Figure 3) clearly shows a distinct hump at 2.3–2.4 Å: i.e., O–O distances from the anions alone do not explain the 2.4-Å peak, which then contain, very likely, also the expected Cu–(OH<sub>2</sub>)<sub>ax</sub> distances. A similar conclusion is reached for solution Cu-2.

The definite answer to the existence of well-defined distorted Cu(H<sub>2</sub>O)<sub>4,eq</sub>(H<sub>2</sub>O)<sub>2,ax</sub> octahedra in perchlorate copper solutions is obtained by a useful comparison described as follows. In Figure 1 the distribution curve of Cu-3 is compared with the curve of an *isomorphous* cobalt(II) perchlorate solution in which a regular octahedral coordination of six water molecules around the Co<sup>2+</sup> ions has been found to occur.<sup>16</sup> It is already

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evident, from the shape of the curves, that the  $\text{Co}-\text{OH}_2$  peak is much greater than the  $\text{Cu}-\text{OH}_2$  peak (six neighbors at 2.1 Å instead of four at 2 Å). The absence of the 3.2-Å peak, in cobalt solution, is also evident. The comparison may be extended by using the semiquantitative treatment first used by Johansson et al.<sup>17</sup> and here assumed with minor modifications.

A total theoretical structure function (eq 2) is obtained by assuming the existence, in solution, of definite molecular species or characteristic interactions (eq 3) and assuming an even distribution of atoms beyond the structured holes (eq 4). A theoretical distribution function can be then obtained, in a transformation of eq 3 and 4 by eq 1, and compared with the experimental one

$$D(r) - 4\pi r^2 \rho_0 = (\sum n_j P_j)_{\text{intra}} + (\sum n_i P_i)_{\text{inter}} + P_{\text{cor}} \quad (6)$$

where  $n_j$  is the number of the assumed structural units and  $n_i$  is the stoichiometry of the atoms in solution (metal, Cl, O, and  $\text{H}_2\text{O}$ ).  $P_j$  is then the "peak shape" of a given structural unit and is the Fourier transform of every term of eq 3.  $P_{\text{cor}}$  represents residual differences between experimental (right-hand side of eq 6) and calculated (left-hand side of the same equation) distribution functions. Referring eq 6 to our metal perchlorate solutions, we have

$$\text{DIFF} = D(r) - 4\pi r^2 \rho_0 = (n_M P_M + n_{\text{ClO}_4} P_{\text{ClO}_4} + n_{\text{ww}} P_{\text{ww}})_{\text{intra}} + (\sum n_i P_i)_{\text{inter}} + P_{\text{cor}} \quad (7)$$

where  $P_{M,\text{intra}}$  describes the immediate surrounding of the metal ion.

The two solutions compared in Figure 1 are *isomorphous*; i.e., they have the same analytical compositions and contain cations having approximately the same ionic radius. This fact allows for the following assumptions: (a) Intramolecular interactions from  $\text{ClO}_4^-$  anions will contribute in a similar way in the two solutions. (b)  $P_{\text{ww}}$  accounts for several kinds of  $\text{H}_2\text{O}-\text{H}_2\text{O}$  contacts (either from remaining "free" water or from "specific"  $(\text{H}_2\text{O})_{\text{I}}-(\text{H}_2\text{O})_{\text{II}}$  distances of two subsequent cations' shells<sup>15</sup>), and it is reasonable to assume that it will not drastically differ in the two solutions. (c) The "continuums" seen by every atom in the two solutions should only differ slightly from each other. Physically speaking, intermolecular interactions come from packing of the atoms around the main species. Since the two solutions contain equal amounts of each "atom" and the two cations have similar ionic radii, we expect similar intermolecular interactions in the two solutions. (d)  $P_{\text{cor}}$  values are small residual differences between calculated and experimental values. They show the same trend in isomorphous solutions, and their difference from copper to cobalt solution is certainly negligible.

Now, with the assumptions explained above and from the known solute structure in cobalt solution,<sup>16</sup> information is drawn on the structuring of water molecules around the  $\text{Cu}^{2+}$  ion. In fact, applying eq 7 to our solutions, we have

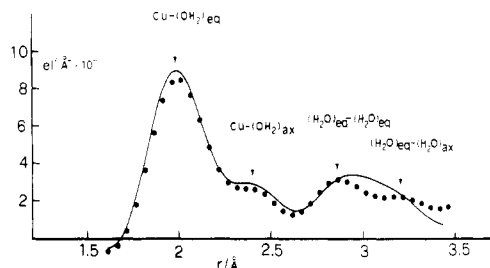
$$\text{DIFF}_{\text{Cu}} - \text{DIFF}_{\text{Co}} = n_{\text{Cu}} P_{\text{Cu,intra}} - n_{\text{Co}} P_{\text{Co}(\text{H}_2\text{O})_6,\text{intra}} \quad (8)$$

or, since  $n_{\text{Cu}} = n_{\text{Co}} = 1$

$$P_{\text{Cu,intra}} = (\text{DIFF}_{\text{Cu}} - \text{DIFF}_{\text{Co}}) + P_{\text{Co}(\text{H}_2\text{O})_6,\text{intra}} \quad (9)$$

where  $P_{\text{Cu,intra}}$  is now the "peak shape" of copper ion extracted from all the other overlapping contributions to the experimental distribution function, provided the assumptions made above are valid.

The dotted line in Figure 4 shows the peak shape obtained for the copper ion with use of eq 9. The sequence of the peaks, indicated by arrows on the figure, is that expected if distorted octahedral units were occurring in solution. The sizes of the



**Figure 4.** Shape function of  $\text{Cu}^{2+}$  ions derived with eq 9 (see text) is shown by dots. The continuous line has been calculated for an octahedral tetragonally distorted  $\text{Cu}((\text{H}_2\text{O})_{\text{eq}})_4((\text{H}_2\text{O})_{\text{ax}})_2$  unit with use of the following parameters:  $r_{\text{Cu}-(\text{OH}_2)_{\text{eq}}} = 1.96 \text{ \AA}$ ;  $r_{\text{Cu}-(\text{OH}_2)_{\text{ax}}} = 2.30 \text{ \AA}$ ;  $b_{\text{Cu}-(\text{OH}_2)_{\text{eq}}} = 0.0025 \text{ \AA}^2$ ;  $b_{\text{Cu}-(\text{OH}_2)_{\text{ax}}} = 0.01 \text{ \AA}^2$ .

**Table II.** Parameter Values ( $r, R =$  Distances (Å);  $b, B =$  Temperature Factors (Å<sup>2</sup>);  $n =$  Frequency Factors) and Computed Standard Deviations (in Parentheses) Obtained from Least-Squares Refinements

source of interactions	parameters	solution	
		Cu-3	Cu-2
Dominant Interactions			
$\text{Cu}(\text{H}_2\text{O})_{4,\text{eq}}(\text{H}_2\text{O})_{2,\text{ax}}$	$r_{\text{Cu}-(\text{OH}_2)_{\text{eq}}}$	1.979 (1)	1.976 (1)
	$b_{\text{Cu}-(\text{OH}_2)_{\text{eq}}}$	0.0025 (1)	0.0014 (1)
	$r_{\text{Cu}-(\text{OH}_2)_{\text{ax}}}$	2.392 (5)	2.339 (4)
	$b_{\text{Cu}-(\text{OH}_2)_{\text{ax}}}$	0.0074 (6)	0.0047 (5)
	$b_{(\text{H}_2\text{O}-\text{H}_2\text{O})_{\text{cis}}}$	0.009 (2)	0.009 (2)
$\text{ClO}_4^-$	$r_{\text{Cl}-\text{O}}$	1.453 (1)	1.449 (1)
	$b_{\text{Cl}-\text{O}}$	0.0031 (1)	0.0023 (1)
	$b_{\text{O}-\text{O}}$	0.0042 (3)	0.0024 (3)
$(\text{H}_2\text{O})_{\text{I}}-(\text{H}_2\text{O})_{\text{II}}$ (per metal atom)	$r$	2.799 (8)	2.728 (4)
	$b$	0.0015 (8)	0.0026 (4)
	$n$	11.1 (2)	11.6 (4)
Less Relevant Interactions			
$\text{Cu}-(\text{H}_2\text{O})_{2,\text{nd}}$	$r$	3.96 (1)	3.95 (1)
	$b$	0.075 (3)	0.056 (3)
Cu	$R$	4.75 (2)	4.89 (7)
	$B$	0.014 (7)	0.12 (5)
Cl	$R$	2.95 (4)	2.75 (5)
	$B$	0.02 (1)	0.01
O	$R$	3.59 (3)	3.46 (5)
	$B$	0.09 (2)	0.14 (3)
$\text{H}_2\text{O}$	$R$	3.25 (2)	3.22 (3)
	$B$	0.07 (1)	0.12 (2)

peaks are also consistent with such units. The continuous line in Figure 4, in fact, is a peak shape calculated (but not least-squares refined) with the unit  $\text{Cu}(\text{H}_2\text{O})_{4,\text{eq}}(\text{H}_2\text{O})_{2,\text{ax}}$ , and it is seen that the sequence of both positions and sizes of the peaks is consistent with the dotted line. In a reversion of the flow of argument, i.e., a start with the assumption of the existence of the distorted octahedral unit in our solution, Figure 4 is an "a posteriori" proof of the validity of the procedure and of the assumptions illustrated above.

**Direct Fitting of the Structure Functions.** The final step is to obtain, for the coordination of copper ion, a set of quantitative parameters, and this can be done through a least-squares procedure. In this way experimental and calculated data are compared (eq 5) until best fits are obtained, with an assumed model, by varying the structural parameters. The model introduced, of course, contains all the relevant structural parameters, not only those related to the  $\text{Cu}(\text{II})$  coordination. The complete model needed has already been illustrated for  $\text{Co}(\text{II})$  and  $\text{Ni}(\text{II})$  perchlorate solutions,<sup>16</sup> and it has been here assumed with the only difference that the coordination around  $\text{Cu}^{2+}$  ions is now tetragonally distorted; i.e., it is described by two main distances while the geometry has been kept constant.

The final fits are given in Figure 5 and the parameters reported in Table II. Nonnegligible deviations are present in the innermost part of the  $i(s)$  function (mostly Cu-2 solu-

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Table III. Distorted Octahedral Coordination Displayed by  $\text{Cu}^{2+}$  Ions and Six Equivalent Ligands<sup>a</sup>

compd (or solution)	basic unit <sup>b</sup>	Cu- $X_{\text{eq}}$ , Å	Cu- $X_{\text{ax}}$ , Å	ref
Crystalline Compounds				
$\text{Cu}(\text{NH}_3)_6\text{X}_2$ (X = Cl, Br, I)	$\text{Cu}[(\text{NH}_3)_4](\text{NH}_3)_2$	~2.1	~2.6	2
$\text{CuSiF}_6 \cdot 6\text{H}_2\text{O}$	$\text{Cu}[(\text{H}_2\text{O})_4](\text{H}_2\text{O})_2$	1.97	2.37	3
$\text{Cu}_3(\text{ZrF}_7)_2 \cdot 16\text{H}_2\text{O}$	$\text{Cu}[(\text{H}_2\text{O})_4](\text{H}_2\text{O})_2$	1.95/1.98	2.35	4
$\text{Cu}_2\text{ZrF}_8 \cdot 12\text{H}_2\text{O}$	$\text{Cu}[(\text{H}_2\text{O})_4](\text{H}_2\text{O})_2$	1.94/2.01	2.41	5
$\text{K}_2\text{Cu}(\text{ZrF}_6)_2 \cdot 6\text{H}_2\text{O}$	$\text{Cu}[(\text{H}_2\text{O})_4](\text{H}_2\text{O})_2$	1.97/2.02	2.33	6
$\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$	$\text{Cu}[(\text{H}_2\text{O})_4](\text{H}_2\text{O})_2$	2.09/2.16	2.28	7
$\text{Cu}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$	$\text{Cu}[(\text{H}_2\text{O})_4](\text{H}_2\text{O})_2$	1.96/2.10	2.22	8
Compounds in Solution				
copper(II) sulfate	$\text{Cu}[(\text{H}_2\text{O})_4](\text{H}_2\text{O})_2$	2.15	2.50	20
copper(II) perchlorate, 3.5 M	$\text{Cu}[(\text{H}_2\text{O})_4](\text{H}_2\text{O})_2$	1.94	2.43	12
2 M	$\text{Cu}[(\text{H}_2\text{O})_4](\text{H}_2\text{O})_2$	1.97	2.34	this work
3 M	$\text{Cu}[(\text{H}_2\text{O})_4](\text{H}_2\text{O})_2$	1.98	2.39	this work

<sup>a</sup> The distortion is tetragonal for all systems except  $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$  and  $\text{Cu}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ . <sup>b</sup> Equatorial ligands are in brackets and axial ligands in parentheses.

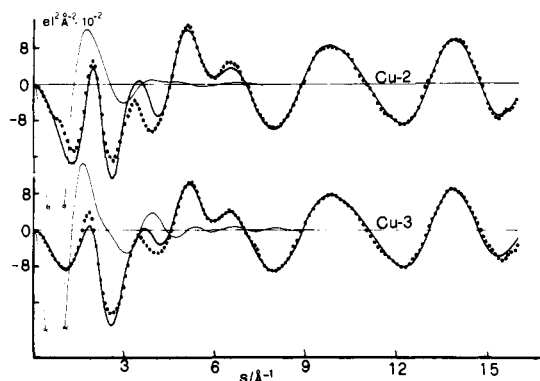


Figure 5. Experimental structure functions, in the  $s^2 i(s)$  form, shown by dots. The solid strong lines have been calculated with the parameters given in Table II. Contributions of the "continuum" are shown by weak solid lines.

tion), showing model inadequacy. This fact, however, does not affect at all the accuracy of the structural parameters obtained for the dominant interactions (upper part of Table II). These parameters, in fact, have been refined in the outermost parts of the  $i(s)$  curves where dominant intramolecular frequencies are easily separated from the remaining contributions.<sup>18</sup>

### Comments and Conclusions

The structural behavior of copper(II) perchlorate solutions differs from that of nickel(II) perchlorate and cobalt(II) perchlorate solutions only in the primary coordination of the cations. Therefore the structure of the perchlorate anion, the existence of preferred  $(\text{H}_2\text{O})_{\text{I}}-(\text{H}_2\text{O})_{\text{II}}$  interactions between water molecules belonging to two subsequent coordination shells of the cations, the role of "free" water, and second-order distances around cations and anions, already illustrated for cobalt and perchlorate nickel perchlorate solutions, will not be repeated here.

On the other hand, some comments on the coordination of  $\text{Cu}(\text{II})$  are needed. The existence of a distorted arrangement

of six water molecules around the  $\text{Cu}^{2+}$  ions has been proved, in an unambiguous way, by both distribution curves and structure functions. We must conclude, therefore, that the occupancy of axial positions is assured also in solution where, in contrast with what happens in the crystalline networks, the solvent can play a crucial role in determining the final configuration of the  $\text{Cu}^{2+}$  ion. Owing to the impossibility of defining the axial positions in copper(II) chloride solutions,<sup>11</sup> we could not exclude, in that case, the existence of square-planar copper complexes. We argued that the more weakly bonded ligands could prefer the stabilization due to the solvent effect rather than occupy the axial sites. We can now exclude a "solvent effect" when water molecules occupy the axial sites, but the question is still open if the sites were to be occupied by a larger ligand—i.e., a weaker  $\text{Cu-L}$  bond—such as the  $\text{Cl}^-$  ion.

Table III summarizes some examples of  $\text{CuL}_6$  complexes present as building blocks in crystalline solid compounds. The most common distortion is the tetragonal one. The solid  $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$  crystalline salt, i.e., the starting material of our solutions, however, shows a rhombic distortion. Three  $\text{Cu-OH}_2$  distances, almost equispaced, occur. We have often noticed<sup>15,19</sup> that the solution complexes retain memory of the units present in the starting material. Though the general shapes of the distribution curves and the derived shape function of Figure 4 would exclude such an arrangement in our solutions, the rhombic distortion has been tested anyway by direct least-squares analysis. The minimum-error-squares sum obtained (eq 5), considerably higher than that of tetragonal distortion, ruled out such a possibility. Structural parameters obtained in solution are also given in Table III. Shapovalov's<sup>20</sup> distances, equatorial and axial, are evidently too large as shown by the comparison with distances present in crystals. However, our results substantially confirm those previously obtained by Ohtaki et al.<sup>12</sup> in a 3.5 M copper(II) perchlorate solution.

Registry No.  $[\text{Cu}(\text{H}_2\text{O})_6](\text{ClO}_4)_2$ , 15333-31-0;  $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ , 19296-06-1.

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