

fast charge transfer with coupled chemical reactions.^{19,20} The ac findings complement the dc findings with respect to the "reversibility" of the electron transfer steps and have been particularly informative in studying the reversible reduction steps for Zn(OEt-SacSac)₂. The very large wave widths at half peak height (Table IV) together

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with the asymmetric nature of the peaks confirm that all electrode processes apart from those due to the reduction of the zinc complex are quite irreversible and are undoubtedly complicated by complex chemical reactions and adsorption phenomena in many instances.

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Solute Structuring in Aqueous Copper(II) Chloride Solutions¹

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Abstract: The predominant solute species in aqueous CuCl₂ solutions of 3.18 and 4.35 M are similar as measured by X-ray diffraction. In each case the average Cu(II) has six nearest neighbors, and extensive sharing of chlorides by adjacent Cu(II) species is observed. The extent of chloride vs. oxygen occupation of the nearest neighbor sites as well as the extent of solute association depends upon the solution composition. The mean species are *ca.* Cu₃Cl₆·(H₂O)₈ and *ca.* Cu₈Cl₁₀(H₂O)₁₂ in the 3.18 and the 4.35 M solutions. For each species the average Cu–O and Cu–Cl bond distances are measured to be 1.93 (±0.03) and 2.43 (±0.01) Å. The former is indicative of Cu–O contacts for oxygens occupying equatorial coordination sites, and the latter is indicative of chlorides occupying both axial and equatorial sites about Cu(II).

Of the crystalline metal halide complexes, none have been investigated more thoroughly than the chloro complexes of copper(II). Particular interest in these complexes has been related to examination of the Jahn–Teller effect and also toward the extent of "direct" Cu(II)–Cu(II) bonding.²

In chloro and chloroaquo complexes of Cu(II), the tendency for Cu(II) to fit into interstitial "octahedral" holes has been well established. Furthermore, the chain formation either by dichloro bridges between adjacent Cu(II) ions,^{3–8} by mono halo bridges between adjacent cations,⁹ by dihydroxy bridges between adjacent cations,¹⁰ or by chloro-aquo bridges^{11,12} have been found. In each of these cases the coordination geometry about Cu(II) is distorted octahedral with the bridging ligands occupying equatorial coordination sites. Discrete units of [CuCl₄(H₂O)₂]^{2–} are found in K₂CuCl₄·2H₂O.¹³ The existence of Cu₂Cl₆^{2–} dimers,

where Cu(II) has four equatorial chloride and two axial chloride neighbors, has also been well documented.^{14–16}

On the other hand, in Cs₂CuCl₄ crystals, Cu(II) has a distorted tetrahedral coordination environment.¹⁷ Distorted CuCl₄^{2–} tetrahedra also exist in crystals when the cations are complex ammonium species,^{18,19} large organic species,²⁰ or a substituted phosphonium oxide.²¹ "Square-planar" complexes of copper(II) chloride with dimethyl sulfoxide have been reported.²² In this complex the axial coordination sites about Cu(II) are apparently unoccupied.

X-Ray studies²³ of an aqueous CuCl₂ solution of composition CuCl₂·25H₂O suggest that Cu(II) has four oxygen (water) nearest neighbors and two chloride nearest neighbors at this concentration range. The X-ray studies have been interpreted to indicate that Cu(II) has an anisotropic electron density distribution, *i.e.*, the Jahn–Teller distortion.

Extensive magnetic,²⁴ electrometric,²⁵ spectral,^{27–30}

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epr,³¹ and viscosity³² measurements of aqueous and nonaqueous CuCl₂ solutions have yielded somewhat ambiguous structural details regarding the nearest neighbor environment about Cu(II) in such solutions.

Because of our interest in the coordination details and in the solute-solvent interactions of first-row transition metal halides in hard solvents,³³⁻³⁸ we have extended our X-ray studies to include aqueous solutions of CuCl₂. The objectives of this study are to determine the following: (a) the mean Cu-O and/or Cu-Cl bond distance(s) in each solution, (b) the mean coordination geometry about Cu(II) in each solution, (c) the influence of solute concentration on items (a) and (b), (d) the reportedly extensive Cu-Cu interactions in similar complexes of Cu(II).

Experimental Section

The solutions were prepared by weight from predried anhydrous CuCl₂ and distilled water. Densities were measured with a specific gravity bulb. The solution compositions are shown in Table I.

Table I. Solution Compositions

Solution	Molarity	Mole fraction				Density, g/ml
		Cu	Cl	O	H	
A	4.35	0.028	0.056	0.305	0.611	1.462
B	3.18	0.020	0.040	0.313	0.617	1.343

Each solution was loaded into a Teflon sample holder, which had the window consisting of 1.0-mil Mylar film, and an X-ray diffraction pattern was obtained utilizing our X-ray diffractometer. Scattered intensities were collected as a function of scattering angle increments in the scattering angle of 0.03° from $s = 0.3$ to $s = 13.5 \text{ \AA}^{-1}$ ($s = 4\pi\lambda^{-1} \sin \theta$). At least four runs over the entire angular range were made for each solution. The average intensity at each scattering point investigated was utilized in subsequent calculations.

The scattered radiation was corrected for background (*ca.* 3 cpm), polarization,³⁹ sample penetration,⁴⁰ multiple scattering,⁴¹ and Compton scattering.⁴² The resultant scattering was scaled to $\sum x_i f_i^2(s)$ constructed for each solution from the appropriate atomic scattering factors⁴³ by the methods of Lawrence and Kruh.⁴⁴

Atomic radial-distribution functions (ARDF's) were calculated as outlined in our previous papers³³⁻³⁸ at increments in Δr of 0.01, 0.05, and 0.10 Å with a damping of 0.015. The resultant ARDF's are shown in Figure 1.

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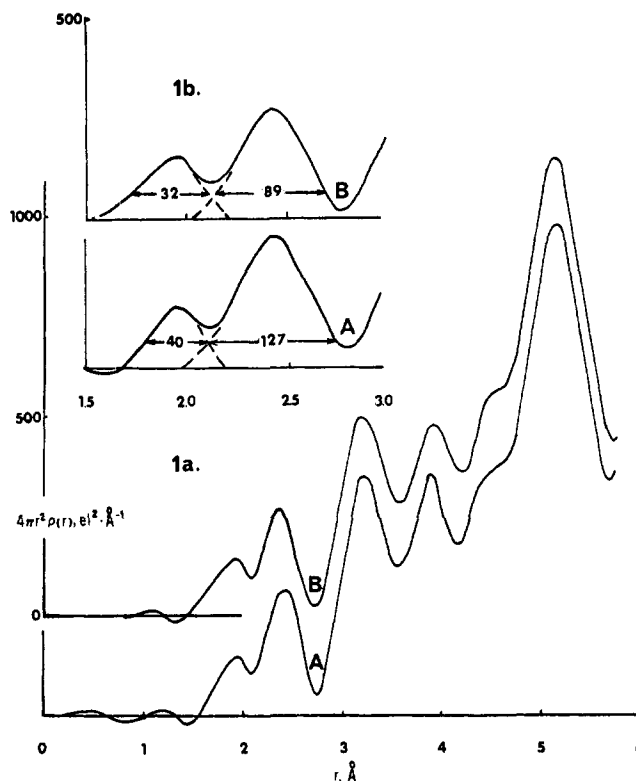


Figure 1. The ARDF's; $b = 0.015$. Shown in Figure 1a are the ARDF's for solutions A and B from $r = 0$ to $r = 6 \text{ \AA}$. Shown in Figure 1b is an enlargement of each ARDF in the region $r = 1.5$ to $r = 3.0 \text{ \AA}$.

The area under the first peak in each ARDF was determined *via* repeated integration by graphical techniques. Subsequent deviation from the mean was $<2\%$ of the mean area of each peak.

For each solution the area due to one Cu-Cl and to one Cu-O contact was calculated by the ideal peak (IP) method of Waser and Schomaker⁴⁶ and was evaluated by graphical integration. For solution A, the IP area due to one Cu-Cl bond is $35.2 e^2$, and the IP area due to one Cu-O bond is $16.5 e^2$. For solution B, the IP areas due to one Cu-Cl pair and to one Cu-O pair are 27.0 and $12.1 e^2$, respectively.

Results and Discussion

Aside from the area under the first peak in the ARDF's of solutions A and B, these ARDF's are quite similar, as seen in Figure 1.

The ARDF's of both aqueous solutions show a double primary peak. In each case, the total peak may be resolved into a small initial peak with its maximum at $1.90\text{--}1.95 \text{ \AA}$ and a larger secondary peak at 2.43 \AA . Other peaks occur at 3.2 , at 3.8 , and at 5.1 \AA in each ARDF. A clearly discernible shoulder at *ca.* 4.4 \AA is noted in each ARDF as well.

In the ARDF of solution A, the area under the initial peak is *ca.* $40 e^2$ and the area under the second peak is *ca.* $127 e^2$. For solution B, the areas under the initial and second peaks are *ca.* 32 and *ca.* $89 e^2$.

If it is assumed that the first peak, centered at $1.90\text{--}1.95 \text{ \AA}$, is due to Cu-O bonding and that the second peak is due to Cu-Cl bonding in each ARDF, then Cu(II) has the following nearest neighbor environment in these aqueous solutions.⁴⁶

Solution	Chloride neighbors	Oxygen neighbors
A	3.6	2.4
B	3.3	2.7

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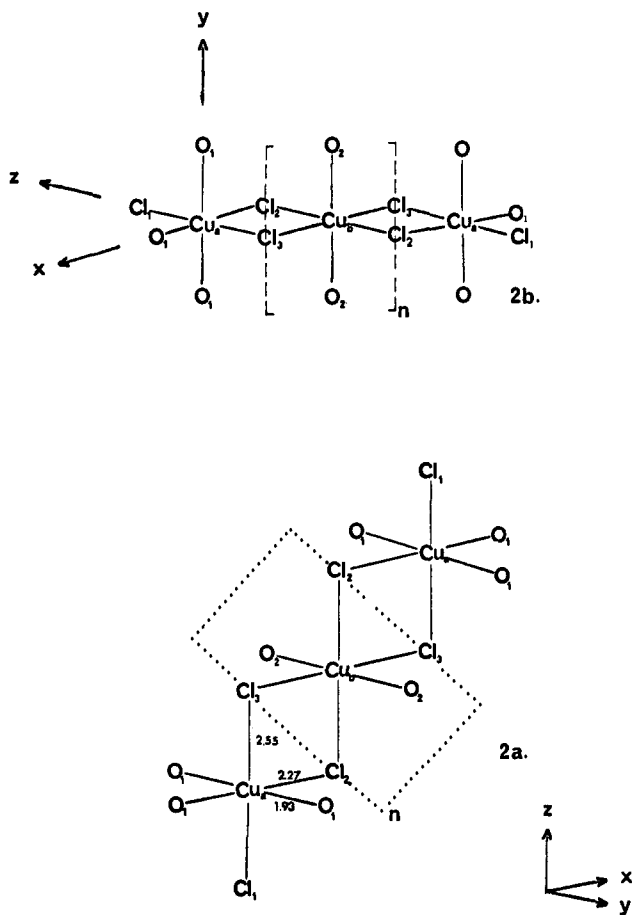


Figure 2. Model(s) of mean solution species in the aqueous copper(II) chloride solutions. For solution A, $n = 3$; for solution B, $n = 1$.

Thus, in these solutions, as well as in numerous crystals, Cu(II) clearly has sixfold nearest neighbor coordination.³⁻¹⁶ Further, that the *average* Cu-O contact distance is 1.90–1.95 Å indicates the oxygen nearest neighbors occupy equatorial coordination positions exclusively in the mean species in these solutions. Such interactions are similar to those occurring in $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$,^{11,12} in $\text{CuCl}_2 \cdot \text{DMSO}_2$,²² and in $\text{K}_2\text{CuCl}_4 \cdot 2\text{H}_2\text{O}$.¹³ For oxygens occupying axial sites, the Cu-O_{ax} distance is 2.3–2.6 Å.^{6,10}

Extensive solute association is present in these solutions since the average Cu(II) has more than two chloride nearest neighbors. The model which is consistent with (a) the chloride:Cu(II) stoichiometry (*i.e.*, 2:1), (b) the nearest neighbor environment of Cu(II) as viewed in the ARDF's, and (c) the fact that the nearest neighbor oxygens occupy equatorial coordination sites is shown in Figure 2. For solution A, the mean species is *ca.* $[\text{CuCl}_2(\text{H}_2\text{O})_2]_5 \cdot 2\text{H}_2\text{O}$ and, for solution B, the mean species is *ca.* $[\text{CuCl}_2(\text{H}_2\text{O})_2]_3 \cdot 2\text{H}_2\text{O}$.

Since oxygens (waters) occupy more than half of the equatorial coordination sites about Cu(II) in each solution, extensive occupation of axial as well as equatorial coordination sites by chlorides is necessary. The location of the second peak in each ARDF is consistent

(46) The mean number of Cu-O pairs per Cu in solution A is calculated by dividing the area under the "Cu-O peak" (40 e²) by the area per Cu-O pair for that solution (16.5 e²). Analogous calculations have been utilized to determine the average number of Cu-O pairs per Cu(II) in solution B and the average number of Cu-Cl pairs per Cu(II) in each solution.

with this interpretation; *i.e.*, the second peak is composed of both Cu-Cl_{ax} and Cu-Cl_{eq} contacts, and the peak maximum in each ARDF represents an averaging of these two interaction distances. The location of this peak in the ARDF's cannot be correlated exclusively with Cu-Cl_{eq} contacts because Cu-Cl_{eq} bond distances are significantly shorter, *e.g.*, 2.26–2.34 Å, depending upon whether the equatorial chloride is functioning as a bridging^{3-6,8,11,12,14-16} or as a terminal^{6,7,9,13-16,22} ligand. That the dichloro bridges are not exclusively in the equatorial planes is not without precedent in the crystal stereochemistry of chloro-copper(II) complexes. Rather, structures similar to the model proposed in Figure 2 have been found in $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ ^{11,12} and in $\text{LiCuCl}_3 \cdot 2\text{H}_2\text{O}$ ⁶ and numerous other species with more complicated ligands.

If it is assumed that the mean Cu-Cl_{eq} distance is 2.27 Å, as it is in $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$,^{11,12} in $\text{LiCuCl}_3 \cdot 2\text{H}_2\text{O}$,⁶ or in the $\text{Cu}_2\text{Cl}_6^{2-}$ dimers,¹⁴⁻¹⁶ the Cu-Cl_{ax} bond distance may be calculated by the formula $D_{\text{ax}} = [2(n+2)]^{-1} [N\langle D \rangle - 2(n+1)(D_{\text{eq}})]$. Here $\langle D \rangle$ is the mean Cu-Cl distance as measured in the ARDF, *i.e.*, 2.43 Å, n is the number of $-\text{CuCl}_2(\text{H}_2\text{O})_2-$ units in the species, D_{ax} is the average Cu(II)-Cl_{ax} bond distance, D_{eq} is taken to be 2.27 Å, and N is the number of Cu-Cl bonds contained in the average species in that solution. Though this relationship contains inherent uncertainties with regard to the Cu-Cl_{eq} distance being exactly 2.27 Å and with regard to the *exact* location of the maximum in each ARDF, the average Cu(II)-Cl_{ax} distance, 2.55 Å, is certainly correct to within ± 0.05 Å for each solution. A previous study of a more dilute aqueous solution of CuCl_2 suggests that the Cu-Cl_{ax} distance is 2.5 Å.²³

Substantiation of the model proposed in Figure 2 is offered by a comparison of the atom-pair interaction distances requisite with the model and the ARDF's obtained from the X-ray study of these solutions. This comparison is shown in Table II. Included under

Table II. A Comparison of the Atom-Pair Interaction Distances Requisite with the Coordination Model and the ARDF's

	Requisite atom-pair interactions	Model distance, Å	Maximum ARDF, Å
Cis	O-O	2.72	3.2
	O-Cl ₂	3.00	
	O-Cl ₁	3.17	
	Cl ₁ -Cl ₂	3.14	
Cis	Cu _a -Cu _b	3.44	3.9
	Trans	O-O	
Trans	Cu _a -O ₂	3.94	
	Cu _b -O ₁	3.94	
	Cu _a -Cl ₃	4.04	
Trans	O ₁ -Cl ₂	4.23	
	Cl ₃ -Cl ₃	4.54	
Trans	Cl ₂ -Cl ₂	5.10	5.1
	Cl ₁ -Cl ₃	5.10	
Trans	Cu _a -Cl ₂	5.19	

the peak in each ARDF at 3.2 Å are the nonbonded cis ligand-ligand interactions, the ever present Cl-O hydrogen bonded interaction,^{33-37,44,45,47-50} and prob-

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ably the Cu-Cu interaction. The well defined maximum at 3.9–4.0 Å in each ARDF includes trans O–O, “secondary” Cu–O, and Cu–Cl interactions. The shoulder at *ca.* 4.4 Å may be related to trans O–Cl and trans Cl–Cl interactions. The well defined peak at 5.0–5.1 Å in each ARDF is due to trans Cl–Cl as well as to tertiary Cu–Cl interactions. No other model will account for the peaks observed in the ARDF’s.

Conclusions

Cu(II), with an ionic potential between that of Co(II) and Zn(II), behaves in a fashion similar to neither with regard to the resultant complexes in concentrated aqueous solutions of the metal(II) halides. CoCl₂ dissociates completely to form Co(H₂O)₆²⁺ even in 3.6 M aqueous solutions,³⁵ whereas in the corresponding aqueous solutions of CuCl₂, solute association is the predominant solution feature. At similar concentrations ZnCl₂ neither associates nor dissociates significantly, and ZnCl₂(H₂O)₂ is the mean species in aqueous

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solutions of ZnCl₂.^{37,47} While Cu(II) has a greater tendency toward solute association than does the harder Zn(II) or the softer Co(II) in the concentrated metal(II) halide solutions, it is not clear whether these data indicate that Cu(II) prefers to bond to chloride to a greater extent than does Zn(II) or whether the inherent tendency of Cu(II) to achieve the tetragonally distorted octahedral ligand environment is the principal driving force in these processes. However, the basic electrostatics of the hard-soft metal-ligand interactions are contradicted by Cu(II), since, under comparable conditions, the softer Co(II) strongly prefers oxygens to chlorides and the harder Zn(II) shows no marked preference toward oxygens or chlorides.

The ligand stereochemistry about Cu(II) in these aqueous solutions is significantly similar to the wide variety of stereochemistries reported for Cu(II) in crystals. The mean Cu–O and Cu–Cl distances are 1.90–1.95 and 2.43 Å, respectively, in these solutions. Based upon our model and subsequent calculations, the Cu–Cl_{ax} distance is 2.55 Å, if it is assumed that the Cu–Cl_{eq} distance is 2.27 Å as in various chloroquo complexes of Cu(II) in crystals.

Role of the Five-Coordinate Intermediate in the Stereochemistry of Dissociative Reactions of Octahedral Compounds

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Abstract: Compound topological graphs have been presented which allow the systematic analysis of the stereochemical aspects of any substitution or stereoisomerization reaction of an octahedral six-coordinate compound which proceeds *via* a five-coordinate intermediate capable of rearranging according to the Berry pseudorotation mechanism. Examples are given of a substitution reaction of a complex with monodentate ligands and intramolecular isomerization reactions of tris bidentate chelates.

Five-coordinate intermediates or transition states have often been implicated in the substitution and isomerization reactions of octahedral coordination complexes.¹ In such a case, the stereochemical aspects of the reaction are strongly related to the stereochemical fate of the five-coordinate species. The most general and economical way to depict these relationships is through the use of a compound topological graph relating the six-coordinate potential energy surface to the five-coordinate potential energy surface. This type of approach has been used very elegantly for the study of the reactions *via* five-coordinate intermediates of tetrahedral four-coordinate phosphorus² and sulfur³ com-

pounds. Qualitative mechanistic features (including the operation of the principle of microscopic reversibility) are rendered quite obvious, and even quantitative activation considerations can be facilitated.²

The General Complex Containing Monodentate Ligands. The most general six-coordinate complex is one in which all six ligands are distinguishable, M(L₁L₂L₃L₄L₅L₆). For an octahedral structure, there are 30 possible stereoisomers, and the six-coordinate surface can be visualized as a regular pentagonal dodecahedral graph where the 30 edge midpoints represent the stereoisomers.⁴ Removal of ligand number six generates the intermediate five-coordinate species M(L₁L₂L₃L₄L₅). Direct determination of the structure of such a transient species is often difficult if not impossible; so one employs the assumption that the structural propensities of this intermediate are similar to those of stable five-coordinate compounds which are overwhelmingly in favor of the trigonal bipyramid

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