The substantial lowering of the conductivity of aqueous solutions of dodecylammonium chloride by the addition of long-chain non-electrolytes indicates that the latter are incorporated into the associated particles formed by the electrolyte. The shift in the critical point toward a lower concentration of electrolyte lends further support to this assumption. The effect of the non-electrolytes upon the conductivity of aqueous solutions of dodecylammonium chloride manifests itself at concentrations much lower than the critical concentration. This supports the contention that associated particles are present in very dilute solutions of this electrolyte.

Summary

The equivalent conductivities of aqueous solutions of mixtures of dodecyl- and octadecylammonium chlorides and of hexyl- and octadecylammonium chlorides have been determined. In the former mixtures the micelles are apparently composed of both components. Although the conductivity values of the latter mixtures are intermediate between those of their components the concentration of octadecylammonium chloride at the critical point is not influenced by the presence of hexylammonium chloride. This indicates that hexylammonium chloride is not included in the micelles.

The presence of long-chain non-electrolytes lowers the conductivity and also the critical concentration of aqueous solutions of dodecylammonium chloride, thus suggesting that such non-electrolytes are included in the micelles.

CHICAGO, ILLINOIS RECEIVED NOVEMBER 25, 1946

The Crystal Structure of Anhydrous Cupric Bromide

BY LINDSAY HELMHOLZ[1]

Introduction

The crystal structure of anhydrous cupric bromide has been determined on part of a program having as its object the correlation of absorption spectra of solids with their structures. The color of this solid resembles that of its solution containing excess bromide ion so closely that a determination of the environment of the metal ion in the solid was undertaken in the hope that this information would aid in the interpretation of both solid and solution spectra. The existence of square coördination about cupric ion has been established in many compounds.[1a-5] It seems likely that the coördination in $CuSO_4 \cdot 5H_2O$ is essentially square covalent also.[6] It was consequently thought of interest to determine whether the preference of bivalent copper for square over tetrahedral coördination would persist if the coordinating ions were larger so that steric interference became important.

It has been found that solid cupric bromide is made up of "strings," with composition $(CuBr_2)_n$ formed by the sharing of edges of the squares of bromine surrounding the copper atoms. The structure is, in this respect, similar to that of palladous chloride[7]; however, a tendency in the case of the copper salt to form fifth and sixth bonds leads to different packing of the "strings." This has the effect of changing the symmetry of the structure from tetragonal (palladous chloride) to monoclinic (cupric bromide).

Experimental

Crystals of cupric bromide were prepared by slow evaporation of a water solution at room temperature. They resembled iodine in luster and color, appearing reddish to brown by transmitted light. The crystals were deposited both as needles and thin plates. Some large crystals were formed but these were found always to be so thoroughly twinned as to be useless for X-ray work and so soft that breaking up the twins without distortion was impossible.

For reasons of convenience the needles were chosen for investigation. Laue photographs were taken in directions normal to the needle axis. Nine out of ten showed twinning of varying degrees of complexity. Three samples, in all cases very small crystals, were found which showed the Laue symmetry C_{2h}, and were apparently untwinned. Series of photographs were taken with *b*- and *c*-axes vertical using a crystal of dimensions 0.03 × 0.015 mm. perpendicular to the needle axis. The Laue photograph showed that the *b*-axis makes an angle of 64° with the needle axis, the $[01\bar{1}]$ direction. This meant that the orientation of the needle with *b* vertical in the X-ray beam was not a favorable one to give an easily calculated absorption correction. The fact that no systematic discrepancies attributable to neglect of absorption are apparent in the agreement between calculated and observed F-values has led me to neglect this effect entirely and to assign rather larger limits of errors to the parameter values than would ordinarily be done.

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[1] Present address: Washington University, St. Louis, Missouri.

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Determination of Structure.—The size of the unit cell was determined roughly using layer line measurements and more accurately after indexing equatorial reflections of the two sets of pictures. The magnitude of the angle β was determined from the difference between θ for pairs of reflections such as ($60\bar{2}$) and (602). The cell dimensions are as follows

$$a_0 = 7.14 \pm 0.02\ \text{Å}.$$
$$b_0 = 3.46 \pm 0.01\ \text{Å}.$$
$$c_0 = 7.18 \pm 0.01\ \text{Å}.$$
$$\beta = 121°\,15' \pm 15'$$

Laue photographs showed no reflections requiring a larger unit.

No reflections with $k + l$ odd were found on any photographs. This observation indicated C_2^3 or C_{2h}^3 as probable space group and the following atomic positions:

for C_2^3-A2
2 Cu 000, 0 $^1/_2$ $^1/_2$, + 0y0
4 Br 000, 0 $^1/_2$ $^1/_2$, + xyz, $\bar{x}y\bar{z}$
for C_{2h}^3-A2/m
the same as above with $y = 0$ or $^1/_2$.

The special positions of C_{2h}^3 which place two atoms in the unit along the b-axis must be excluded since the spacing in this direction (3.46 Å.) will not accommodate two atoms.

The values of the z and x parameters may clearly be determined from the ($h0l$) reflections independently of the choice of space group. This was done in the usual manner by calculating relative intensities as functions of x and z and eliminating values for which decided intensity discrepancies occurred. Since it seems certain that the essential nature of the structure would not be altered by a slight change in parameters and the bond distance is not of primary interest at present, no attempt was made to correct for absorption. This fact has probably led to errors of as much as 50% in the observed values of F_{h0l} and to a correspondingly large uncertainty in the parameter values. The effect of temperature vibrations was taken into account by multiplying the Pauling–Sherman f-values by $e^{-2.0(\sin/\lambda)^2}$. The agreement between observed and calculated intensities could be improved somewhat if an anisotropic factor were used for the copper atoms, assuming the copper to have a larger amplitude of vibration perpendicular to the coördination square than parallel to it. This is probably the case but the correction has not been made since the approximate nature of the data does not seem to warrant it. The "best" values of x and z are

$$x = 0.240 \pm 0.01$$
$$z = 0.015 \pm 0.005$$

Calculated values of F_{hkl} are compared with those observed in Table I. The observed relative intensities were obtained by visual estimation using the multiple film technique[8] and the values of F_{hkl} obtained from the intensities by dividing the square root of the intensities by the square root of the Lorentz, polarization and time factors.

TABLE I

(hkl)	Obs.	Calcd.	(hkl)	Obs.	Calcd.
100	2.2	2.8	$40\bar{2}$	5.6	5.3
102	1.3	1.4	404	2.3	2.3
$10\bar{2}$	4.8	3.6	$40\bar{4}$	5.3	4.5
104	abs	0.05	$40\bar{6}$	3.5	3.0
$10\bar{4}$	3.5	3.2	$40\bar{8}$	2.0	1.5
106	abs	0.35	500	2.2	2.0
$10\bar{6}$	2.4	2.4	502	1.15	1.0
$10\bar{8}$	1.2	1.5	$50\bar{2}$	2.8	2.9
200	3.3	3.0	$50\bar{4}$	3.5	3.3
202	1.9	2.4	$50\bar{6}$	3.0	3.0
$20\bar{2}$	4.1	2.9	$50\bar{8}$	2.5	2.1
204	1.9	1.8	600	1.7	1.5
$20\bar{4}$	2.7	1.9	602	1.4	1.2
206	1.4	1.0	$60\bar{2}$	2.0	1.5
$20\bar{6}$	2.0	1.30	$60\bar{4}$	1.0	1.1
$20\bar{8}$	0.7	0.6	$60\bar{6}$	0.8	0.7
300	1.0	1.0	$60\bar{8}$	0.5	0.3
302	0.9	1.2	700	< .43	.27
$30\bar{2}$	<0.3	0.2	$70\bar{2}$	0.8	.60
304	1.0	1.1	$70\bar{4}$	1.0	1.0
$30\bar{4}$	0.5	0.6	$70\bar{6}$	0.7	1.1
$30\bar{6}$	0.7	1.1	$70\bar{8}$	1.0	..
400	5.0	5.0	$80\bar{2}$	2.0	1.8
402	3.7	3.7	$80\bar{4}$	2.0	1.8

The parameters by themselves indicate that there exist in the structure separate chains of bromine atoms parallel to the b-axis. These chains are made up of approximately square arrangements of bromine atoms sharing edges. The copper atoms are located on the axis of these chains and their position in the center of the squares seems by far the most likely. Any deviation would show up in disagreement between observed and calculated F's for planes with k not equal to 0. Placing the copper atom in the center of the bromine square gives the parameters:

$$z_{\mathrm{Br}} = 0 \quad \text{or } z_{\mathrm{Br}} = {}^1/_2$$
$$z_{\mathrm{Cu}} = {}^1/_2 \text{ or } z_{\mathrm{Cu}} = 0$$

Table II gives the values of calculated and observed F's for some further X-ray reflections. The agreement is such that there can be no doubt as to the essential correctness of the choice of z-parameters, and serious structural arguments could be raised against any other values.

Discussion of the Structure.—A drawing of the structure is shown in Fig. 1 in which atoms with centers lying outside the unit cell are included as dotted circles to show the complete coördination of one copper atom. The structure is seen to consist of chains of composition

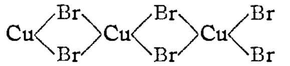

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TABLE II

(*hkl*)	Obs.	Calcd.	(*hkl*)	Obs.	Calcd.
040	3.2	2.2	431	1.1	1.2
140	0.9	0.6	43$\bar{1}$	1.2	1.4
240	1.4	1.2	531	0.4	0.1
11$\bar{1}$	1.5	1.4	531	0.5	0.2
21$\bar{1}$	5.7	7.2	631	1.8	1.9
211	5.2	5.7	042	2.4	2.0
311	2.2	1.8	142	0.9	0.8
31$\bar{1}$	3.2	2.9	242	2.1	1.1
411	2.3	2.1	313	4.0	3.4
41$\bar{1}$	2.7	2.1	413	1.5	1.5
511	abs	0.2	413	2.35	1.8
511	abs	0.2	315	4.4	3.5
611	2.4	2.5	415	1.5	1.3
61$\bar{1}$	2.8	3.0	515	0.95	1.1
71$\bar{1}$	2.1	1.6	615	3.45	2.6
031	2.75	1.9	017	1.1	0.9
131	1.9	1.0	117	0.5	0.7
13$\bar{1}$	1.4	0.5	217	1.9	2.0
231	4.1	3.2	317	2.0	2.3
231	4.8	3.5	417	1.8	1.3
331	0.9	0.9	517	1.0	1.1
33$\bar{1}$	1.9	1.7	617	2.0	1.6

arranged parallel to the *b*-axis and so rotated that two bromine atoms from the next neighboring chains are brought close to the copper atom in the chain between them, completing an irregular coördination octahedron about this atom. These contacts are only loosely bonded, as may be seen from the distance 3.18 Å., 0.78 Å. greater than the bonded distance 2.40 Å. The arrangement of bromine atoms is slightly distorted from a square: the angles between the diagonals are 87°30′ in the *b* direction and 92°30′ perpendicular to this. The bromine–bromine contacts within the chain are 3.46 Å. along the chain, and 3.30 Å. at right angles to this direction. Both these distances are considerably smaller than the sum of the van der Waals radii (approximately 3.90 Å.) and suggest that the preference of copper for square coördination must be very great to overcome the greater repulsive energy of the square arrangement relative to a tetrahedral arrangement. In view of this result and the other known structures containing cupric ion, it appears likely that in all complexes cupric ion forms square rather than tetrahedral or octahedral bonds, and that the saturated complex ion in bromide solution is $CuBr_4^=$, probably with two water molecules occupying the vacant coördination positions of an octahedron but only loosely held.

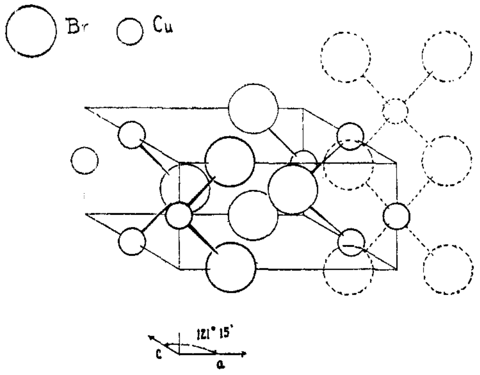


Fig. 1.—Unit cell of anhydrous cupric bromide. The atoms belonging to the unit cell are shown as full-line circles. One copper and six bromine atoms lying outside the unit cell are shown as dashed circles to illustrate the nature of the $(CuBr_2)_n$ chains. These chains are planar and lie very nearly in the (001) face.

A comparison of this structure with that of palladous chloride is instructive. The principal factor governing the formation of chains of coördinated metal atoms is the same for both crystals. A secondary factor for cupric bromide seems to be the formation of a weak bond from the copper to fifth and sixth bromine atoms (ions) somewhat in the same way as in dehydrated cupric chloride. This does not occur to any extent in palladous chloride where neither the symmetry nor the distance indicate a tendency to an irregular though higher coördination. This difference in behavior between the copper and palladium salts may be due to the difference in electronic structure of the planar groups. It seems likely that the palladium chain can be described by a combination of ionic and covalent structures which leave the palladium and halogen atoms nearly neutral so that the tendency for coulomb interaction between the chains is small. The results of this determination would lead to the assignment of a structure to the cupric bromide chains in which the contribution of ionic terms to the ground state is relatively large, so that the electrical attraction is appreciable.

For cupric bromide the ratio of non-bonded to bonded copper–bromine distance is 1.33, this ratio is 1.68 in palladous chloride and the non-bonded distance is apparently determined by the bromine–bromine repulsion rather than palladium–bromine attraction.

The environment of the atoms in copper bromide is given in Table III.

TABLE III

Atom	No. of neighbors	Kind of neighbor	Distance
Cu	4	Br	2.40
	2	Br	3.18
	2	Cu	3.46
Br	2 Cu		2.40
	1 Cu		3.18
	1 Br		3.30 perpendicular to chain
	1 Br		3.46 parallel to chain
	2 Br		3.90
	1 Br		3.86

The structure may be thought of as made up of layers similar to those in the cadmium iodide structure but in which two of the octahedral bonds have lengthened. The superposition of these layers unlike that of cadmium iodide is such that the anion packing is distorted cubic rather than hexagonal close packing. The layers have triangular arrangements of bromine atoms as surfaces, two of the sides of the triangle being equal (3.90 Å.) and corresponding to bromine–bromine contacts between chains and a short side (3.46 Å.) corresponding to contacts within a chain. The arrangement of one layer on another is such that all bromine–bromine contacts are equal within the limits of error of the determination. As might be expected the crystal shows good cleavage in the direction parallel to (100).

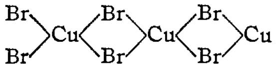
Since the forces orienting one layer over another are relatively weak, the existence of twinning on the (100) face might be expected. This was the most frequent type of twinning found and occurred in almost all crystals of dimensions greater than 0.1 mm.

The fact that the habit of the crystal does not correspond to the X-ray symmetry is disturbing, but the observance of this phenomenon is not limited to this crystal. Attempts to find X-ray evidence for lower symmetry have been unavailing. It is not apparent why the structure as determined should lead to growth in the observed habit

I should like to express my appreciation to the John Simon Guggenheim Foundation for the opportunity to pursue this research, and to the Chemistry Department of the California Institute of Technology for permitting me to use their laboratories.

Summary

The crystal structure of cuprous bromide has been determined and found to be made up of parallel packing of chains having the arrangement



The arrangement of these chains is such that the copper atoms have two more Br atoms in their coördination sphere but these are at considerably greater, "non-bonded," distances.

The structure is discussed in relation to the similar $PdCl_2$ structure and the arrangement in copper complex ions.

ST. LOUIS, MISSOURI RECEIVED OCTOBER 21, 1946

[CONTRIBUTION NO. 587 FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF PITTSBURGH]

The Heats of Dilution of Aqueous Solutions of Four Amino Butyric Acids at 25°[1]

BY L. S. MASON AND A. L. ROBINSON

The physiological importance of amino acids[2] and the theoretical significance of their dipolar ionic character in aqueous solution[3] have led to a considerable interest in the properties of solutions of such substances. Precise thermochemical data, however, are not extensive. Prior to 1940, the literature contains measurements of the heats of dilution of solutions of glycine[4] at three concentrations from 1.0 to 0.1 *M*, and of eleven amino acids[5] (from one to ten concentration intervals) down to 0.5 *m* for eight acids, and to 0.1 *m* for glycine, *dl*-alanine and *dl*-valine. More precise results for glycine[6,7,8] and for α- and β-alanine[9] have been reported.

Using a simplified structural model, Scatchard and Kirkwood[10] examined the activity of zwitterions in salt solutions from the standpoint of the Debye–Hückel theory and concluded that zwitterions behave more like highly polar non-electrolytes than real ions in salt solutions of low ionic strength. The influence of the dielectric constant of the solvent, in addition to the effect of salts, upon the activity of a spherical ion having a complex charge distribution has been studied[11] for the case corresponding to zwitterions in which the net charge is zero and the dipole moment is large. It has been shown[12] for spherical molecules containing point dipoles at the centers that there is a linear limiting relationship between the function, j,[13] and the concentration; a linear relationship between the partial molal heat capacity and the concentration was also derived. The latter relationship appears to be corroborated experimentally[14] for glycine, α- and β-alanine. Dependency of ΦL_2, the relative apparent molal heat content, upon the first power of the molality, *m*, seems to be indicated in the case of the amino acids for

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[1] The generous support of the Buhl Foundation in this study is acknowledged.

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