mechanisms involving the formation of intermediate products with the solvent or with an added catalyst have been proposed.

While these mechanisms may apply to the reaction in the specified environment, they certainly do not describe the behavior of the compound in the dry state. A direct unimolecular exchange of positions between the amino halogen and nuclear hydrogen seems to be the simplest assumption in connection with the photochemical rearrangement of the pure, dry crystals.

Summary

The ultraviolet absorption spectrum of acetylchloro-aminobenzene and of its rearrangement product, *p*-chloro-acetanilide, has been plotted.

The rearrangement is caused by heat alone at comparatively low temperatures. The reaction is completed within two hours at 100°.

The rearrangement occurs in the absence of solvents and without the appearance of a liquid phase when solid crystals of acetylchloro-aminobenzene are exposed to the radiation of a mercury-vapor lamp.

Mechanisms involving intermediate products cannot apply to the solid phase reaction.

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[CONTRIBUTION FROM THE GATES CHEMICAL LABORATORY, CALIFORNIA INSTITUTE OF TECHNOLOGY, NO. 134]

THE CRYSTAL STRUCTURES OF AMMONIUM, POTASSIUM AND RUBIDIUM CUPRIC CHLORIDE DIHYDRATES

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Introduction

The low crystallographic symmetry of most salt hydrates and ammoniates has prevented the study of such compounds by x-ray methods. In an effort to comprehend more fully the geometrical relationship of water to the other components of such compounds we have studied the alkali cupric chloride dihydrates, $R_2CuCl_4.2H_2O$ (where R represents ammonium, potassium or rubidium). These compounds form an apparently isomorphous series crystallizing in the ditetragonal bipyramidal class of the tetragonal system.[1] The axial ratios and observed densities of these compounds are given in Table I.

Large crystals, showing development of (111) and (100), were grown from aqueous solutions containing cupric chloride and the alkali chloride in the correct stoichiometrical quantities. Great caution was used in selecting crystals for the x-ray photographs, since twinning on (111)

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[1] Groth, "Chemische Krystallographie" Engelmann, Leipzig, 1906, vol. I, pp. 355–356.

TABLE I

AXIAL RATIOS AND DENSITIES OF THE ALKALI CUPRIC CHLORIDE DIHYDRATES

Compound	Axial ratio $a:c$ Goniometric	Axial ratio $a:c$ X-ray	Density Obs.	Density Calcd.
$K_2CuCl_4.2H_2O$	1:0.7525	1:0.7405	2.410	2.41
$(NH_4)_2CuCl_4.2H_2O$	1:0.7417	1:0.7415	2.01 (1.963)	1.98
$Rb_2CuCl_4.2H_2O$	1:0.7441	1:0.7250	2.895	2.80

was common. The investigation was carried out by the use chiefly of Laue and spectral photographs interpreted with the aid of the theory of space groups.[2]

The Structure of Potassium Cupric Chloride Dihydrate

The Unit of Structure.—Spectral data for $K_2CuCl_4.2H_2O$ are listed in Table II, and for the ammonium and rubidium salts in Tables III and IV, respectively. Col. 1 gives the crystallographic indices of the face under consideration; those without subscript refer to the original crystallographic axes, while indices with the subscript s. g. refer to the axes of the unit of structure. The angles of reflection, θ, of molybdenum K lines are given in Col. 4. For potassium cupric chloride dihydrate the smallest unit compatible with these spectral data has its a axis rotated 45° from the original crystallographic axis, and has $d_{100} = d_{010} = 7.45$ Å. and $d_{001} = 7.88$ Å. It contains 2.00 $K_2CuCl_4.2H_2O$. The method described by Kirkpatrick and Dickinson[3] was used in making this restriction. No Laue data were found requiring a larger unit.

TABLE II

SPECTRAL DATA FROM $K_2CuCl_4.2H_2O$

hkl	Order	Line (a)	Angle of reflection	*d/n*	Obs. intensity	Calcd. structure factor
(111)	n (= 1)	Mo$K\beta$	2°53′	5.420	m. w.	69
$(101)_{s.g.}$	n	α	3°15′	5.420	s.	
	$2n$	γ	5°40′	5.418	w.	
	$2n$	β	5°47.5′	5.404	m.	162
	$2n$	α	6°32.5′	5.395	v. s.	
	$3n$	β	8°44′	5.391	v. v. w.	73
	$3n$	α	9°48.5′	5.410	w.-m. w.	
	$4n$	γ	11°26′	5.395	v. w.	
	$4n$	β	11°37.5′	5.413	m. w.	225
	$4n$	α_1	13°5′	5.410	m. s.	
	$4n$	α_2	13°12.5′	5.407	m.	
(001)	n (= 2)	β	3°58′	3.899	m. w.	
$(001)_{s.g.}$	n	α	4°28.5′	3.938	s.	94
	$2n$	γ	7°47′	3.948	w.-v. w.	

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[2] For a detailed description of the experimental methods see Wyckoff, "The Structure of Crystals," The Chemical Catalog Co., New York, **1924**, pp. 109–116, 161–164.

[3] Kirkpatrick and Dickinson, THIS JOURNAL, **48**, 2327 (1926).

TABLE II (*Concluded*)

hkl	Order	Line (a)	Angle of reflection	d/n	Obs. intensity	Calcd. structure factor
	$2n$	β	7°57′	3.945	m.	
	$2n$	α_1	8°58′	3.931	v. s.	264
	$2n$	α_2	9°1′	3.935	m. s.	
	$3n$	β	12°0′	3.932	v. v. w.	
	$3n$	α_1	13°28′	3.943	w.	84
	$3n$	α_2	13°35′	3.940	v. w.	
	$4n$	β	16°3′	3.944	v. v. w.	
	$4n$	α_1	18°4.5′	3.945	m.-m. w.	234
	$4n$	α_2	18°10′	3.955	w.	
(110)	n (= 2)	β	4°13′	3.706	v. w.	52
$(100)_{s.g.}$	n	α	4°46′	3.699	m. w.	
	$2n$	γ	8°16.5′	3.715	w.	
	$2n$	β	8°24′	3.731	m.	256
	$2n$	α	9°29.5′	3.726	v. s.	
(100)	n (= 1)	α	3°25′	5.156	w.	29
$(110)_{s.g.}$	$2n$	γ	5°51′	5.241	w.	
	$2n$	β	5°58′	5.241	s.	283
	$2n$	α	6°42′	5.270	v. s.	
	$3n$	α	10°5′	5.270	w.	73
	$4n$	γ	11°50′	5.218	v. w.	
	$4n$	β	11°57′	5.260	w.	225
	$4n$	α_1	13°26′	5.270	m.	
	$4n$	α_2	13°32′	5.270	m. w.	

In the tables concerning the spectral data the following abbreviations and simplifications are used: (a) Mo$K\beta$ = 0.6311 Å.; $K\gamma$ = 0.6178 Å.; $K\alpha_1$ = 0.7078 Å.; Kα_2 = 0.7120 Å.; K_α, mean of K_{α_1} and K_{α_2}, 0.710 Å.; (b) v. v. w. = very, very weak; v. w. = very weak; w. = weak; m. w. = medium weak; m. = medium; m. s. = medium strong; s. = strong; v. s. = very strong.

TABLE III

SPECTRAL DATA FROM $(NH_4)_2CuCl_4.2H_2O$

hkl	Order	Line	Angle of reflection	d/n	Obs. intensity	Calcd. structure factor
(111)	n (= 1)	β	3°15′	5.565	v. w.	69
$(101)_{s.g.}$	n	α	3°40.5′	5.539	m.	
	$2n$	γ	6°28′	5.500	v. w.	
	$2n$	β	6°34′	5.519	m.	132
	$2n$	α_1	7°23′	5.505	s.	
	$2n$	α_2	7°24.5′	5.520	m.	
	$3n$	β	9°56.5′	5.481	v. w.	13
	$3n$	α	11°9.5′	5.505	w.	
	$4n$	γ	13°2.5′	5.491	v. w.	
	$4n$	β	13°17.5′	5.490	m. w.	168
	$4n$	α_1	14°56′	5.514	s.	
	$4n$	α_2	15°15′	5.493	m.	
(001)	n (= 2)	γ	4°27′	3.994	v. w.	
$(001)_{s.g.}$	n	β	4°31.5′	3.999	w.	126
	n	α	5°6.5′	3.990	m. s.	
	$2n$	γ	8°57.5′	3.981	v. w.	

Table III (*Concluded*)

hkl	Order	Line	Angle of reflection	*d/n*	Obs. intensity	Calcd. structure factor
	$2n$	β	9°7.5′	3.981	m.	232
	$2n$	α_1	10°15.5′	3.978	s.	
	$2n$	α_2	10°18.5′	3.980	m.	
	$3n$	β	13°46′	3.980	v. w.	
	$3n$	α_1	15°29′	3.978	w.	116
	$3n$	α_2	15°35.5′	3.978	v. w.	
(100)	n (= 1)	β	3°19′	5.360	v. w.	61
$(110)_{s.g.}$	n	α	3°45′	...	m.	
	$2n$	γ	6°37.5′	5.370	w.	
	$2n$	β	6°44′	5.380	m. s.	251
	$2n$	α	7°36.5′	5.364	v. s.	
	$3n$	β	10°11.5′	5.358	v. w.	
	$3n$	α_1	11°26.5′	5.355	m.	107
	$3n$	α_2	11°29′	5.371	w.	
	$4n$	β	13°37′	5.361	v. w.	
	$4n$	α_1	15°17.5′	5.365	m.	193
	$4n$	α_2	15°24′	5.370	w.	

Table IV

Spectral Data from $Rb_2CuCl_4.2H_2O$

hkl	Order	Line	Angle of reflection	*d/n*	Obs. intensity	Calcd. structure factor
(111)	n (= 1)	β	3°17.5′	5.494	v. v. w.	69
$(101)_{s.g.}$	n	α	3°43′	5.488	v. w.	
	$2n$	γ	6°31′	5.465	v. v. w.	
	$2n$	β	6°37′	5.485	w.-v. w.	236
	$2n$	α_1	7°24′	5.494	m.	
	$2n$	α_2	7°27.5′	5.483	w.	
	$3n$	..	....	...	abs.	13
	$4n$	β	13°15.5′	5.500	v. w.	
	$4n$	α_1	14°53′	5.503	m. w.	282
	$4n$	α_2	14°59′	5.503	w.	
(100)	n (= 1)	..	....	...	abs.	43
$(110)_{s.g.}$	$2n$	γ	6°27′	5.515	v. v. w.	
	$2n$	β	6°34′	5.520	v. w.	355
	$2n$	α_1	7°22′	5.520	m.	
	$2n$	α_2	7°26′	5.515	w.	
	$3n$	..	....	...	abs.	1
	$4n$	β	13°13.5′	5.520	v. w.	
	$4n$	α_1	14°51.5′	5.520	m. w.	297
	$4n$	α_2	14°57.5′	5.520	w.	
(001)	n (= 2)	..	....	...	abs.	22
$(001)_{s.g.}$	$2n$	γ	8°53.5′	4.010	v. w.	
	$2n$	β	9°5′	3.995	m.	336
	$2n$	α_2	10°11′	4.002	v. s.	
	$2n$	α_1	10°15′	4.000	s.	

The Lattice and Space Group.—The observation that a Laue photograph made with the x-ray beam normal to (001) shows a fourfold axis and four planes of symmetry requires the structure to be isomorphous with point group V_d, C_{4v}, D_4 or D_{4h}. The presence of reflections in the first order from planes with $h + k + l$ both odd and even as well as with $h + k$ both odd and even requires the lattice to be the simple tetragonal one Γ_t. The following space groups based on this lattice and isomorphous with one of the above point groups are eliminated for the reasons given.[4]

TABLE V

LAUE PHOTOGRAPHIC DATA FROM $K_2CuCl_4.2H_2O$, USED IN SPACE-GROUP DETERMINATION

Photograph 1

Plane	d_{hkl} Å.	$n\lambda$ Å.	Estimated intensity
$\bar{2}\bar{3}0$	2.065	0.37	0.8
401	1.815	.42	.0
$\bar{4}\bar{1}0$	1.807	.36	4.0
331	1.712	.41	0.15
051	1.465	.45	2.5
061	1.225	.33	0.0
$0\bar{7}1$	1.055	.35	1.5
$\bar{5}\bar{5}1$	1.045	.48	0.10
702	1.025	.31	.0
$\bar{8}01$	0.925	.43	.0
	Photograph 2		
$10\bar{4}$	1.907	.475	0
$0\bar{1}\bar{4}$	1.907	.380	0
$01\bar{7}$	1.112	.360	1.0
$20\bar{7}$	1.077	.324	0
$0\bar{2}\bar{7}$	1.077	.250	0
$\bar{1}08$	0.976	.332	0
650	.953	.340	0.10
$30\bar{8}$	.916	.366	0
$0\bar{3}\bar{8}$	.916	.302	0
209	.852	.260	0
$0\bar{2}9$	.852	.392	0
$40\bar{9}$	.792	.265	0
$05\bar{9}$	.756	.380	0.17

D_{4h}^8, D_{4h}^{11}, D_{4h}^{13}, D_{4h}^{16}, C_{4v}^8, D_4^3, D_4^4, D_4^7 and D_4^8, since these space groups do not have positions for two copper atoms.

D_{4h}^3, D_{4h}^4, D_{4h}^7, D_{4h}^8, D_{4h}^{11}, D_{4h}^{12}, D_{4h}^{15} and D_{4h}^{16}, since these require the absence in odd orders of $(hk0)$ with $(h + k)$ odd; yet $(\bar{4}\bar{1}0)$, $(\bar{2}\bar{3}0)$, (650) were observed to be present in the first order.

D_{4h}^3, D_{4h}^5, D_{4h}^{11}, D_{4h}^{13}, C_{4v}^2, C_{4v}^8 require the absence in odd orders of $(0kl)$ if k is odd; $(0\bar{7}1)$, (051), $(05\bar{9})$ and $(01\bar{7})$ were observed in the first order.

D_{4h}^2, D_{4h}^8, D_{4h}^{10}, D_{4h}^{16}, C_{4v}^3, C_{4v}^5, require the absence in odd orders of $(0kl)$ if l is odd; $(0\bar{7}1)$, (051), $(05\bar{9})$, $(01\bar{7})$ were observed in the first order.

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[4] Astbury and Yardley, *Phil. Trans.*, **224A,** 221 (1924).

D_{4h}^{2}, D_{4h}^{4}, D_{4h}^{6}, D_{4h}^{8}, D_{4h}^{9}, D_{4h}^{11}, D_{4h}^{13}, D_{4h}^{15}, C_{4v}^{5}, C_{4v}^{6}, C_{4v}^{7}, C_{4v}^{8}, V_{d}^{2} and V_{d}^{4} require the absence of odd order reflection form (*hhl*) with *l* odd; (331) and ($\overline{55}1$) were observed in the first order.

D_{4}^{3}, D_{4}^{4}, D_{4}^{7} and D_{4}^{8} require the absence of (001) in even orders not multiples of four; the second and sixth orders were observed.

Space groups not eliminated by the above considerations require the following general absences of reflection in odd orders: D_{4h}^{1}, D_{4}^{1}, C_{4v}^{1}, V_{d}^{1} none; D_{4h}^{14}, C_{4v}^{4}, (0*kl*) with $(k + l)$ odd; V_{d}^{3}, D_{4}^{2}, D_{4}^{6}, (100), D_{4}^{5}, (001). The types of absences of first-order reflections required by D_{4}^{5}, V_{d}^{3}, D_{4}^{2}, and D_{4}^{6} are special cases of those required to be absent by D_{4h}^{14} and C_{4v}^{4}, that is, reflection in the *odd* orders from planes of the type (0*kl*) with $(k + l)$ odd. No such planes were found to reflect. Reflections in odd orders were found to be absent from the following planes: (100), (001), ($\bar{8}01$), ($\bar{1}08$), (061), (702), (401), ($10\bar{4}$), ($30\bar{8}$), ($20\bar{7}$), ($40\bar{9}$), ($0\bar{2}9$). Examination of the coördinate positions in space groups D_{4h}^{1}, D_{4}^{1}, C_{4v}^{1}, V_{d}^{1}, V_{d}^{3}, D_{4}^{2}, D_{4}^{6} and D_{4}^{5} showed that this criterion could be satisfied in a few special cases, but that the absence of reflection would be dependent on a relationship involving relative reflecting powers and parameters defining atomic positions. While such a relationship might be satisfied for one member of the isomorphous series, it probably would not give a satisfactory answer for another member, the postulate being made that great changes in structure do not take place between different members of this isomorphous series. Accordingly D_{4h}^{14} and C_{4v}^{4}, which have the same general criteria, alone remain. On account of the difficulty of treating C_{4v}^{4} further, the remainder of the investigation has been confined to the more symmetrical space group D_{4h}^{14}. The justification for this is that D_{4h}^{14} is in accord with such crystallographic evidence as we possess and leads to a structure in agreement with our x-ray data.

The Atomic Arrangement.—The following are all the special arrangements[5] occurring in D_{4h}^{14}; the general arrangement possesses 16 equivalent positions and does not concern us here.

D_{4h}^{14}	Two equiv. positions	(a)	$000;\ \frac{1}{2}\frac{1}{2}\frac{1}{2}$	(b)	$00\frac{1}{2};\ \frac{1}{2}\frac{1}{2}0$
	Four equiv. positions	(c)	$0\frac{1}{2}0;\ 0\frac{1}{2}\frac{1}{2};\ \frac{1}{2}0\frac{1}{2};\ \frac{1}{2}00$		
		(d)	$0\frac{1}{2}\frac{1}{4};\ 0\frac{1}{2}\frac{3}{4};\ \frac{1}{2}0\frac{3}{4};\ \frac{1}{2}0\frac{1}{4}$		
		(e)	$00w;\ 00\bar{w};\ \frac{1}{2},\frac{1}{2},w+\frac{1}{2};\ \frac{1}{2},\frac{1}{2},\frac{1}{2}-w$		
		(f)	$uu0;\ \bar{u}\bar{u}0;\ \frac{1}{2}-u,u+\frac{1}{2},\frac{1}{2};\ u+\frac{1}{2},\frac{1}{2}-u,\frac{1}{2}$		
		(g)	$vv\frac{1}{2};\ \bar{v}\bar{v}\frac{1}{2};\ \frac{1}{2}-v,v+\frac{1}{2},0;\ v+\frac{1}{2},\frac{1}{2}-v,0$		
	Eight equiv. positions	(h)	$0\frac{1}{2}u;\ \frac{1}{2}0u;\ \frac{1}{2},0,u+\frac{1}{2};\ 0,\frac{1}{2},u+\frac{1}{2};$ $0\frac{1}{2}\bar{u};\ \frac{1}{2}0\bar{u};\ \frac{1}{2},0,\frac{1}{2}-u;\ 0,\frac{1}{2},\frac{1}{2}-u$		
		(i)	$uv0;\ vu0;\ v+\frac{1}{2},\frac{1}{2}-u,\frac{1}{2};\ u+\frac{1}{2},\frac{1}{2}-v,\frac{1}{2}$ $\bar{u}\bar{v}0;\ \bar{v}\bar{u}0;\ \frac{1}{2}-v,u+\frac{1}{2},\frac{1}{2};\ \frac{1}{2}-u,v+\frac{1}{2},\frac{1}{2}$		
		(j)	$uuv;\ uu\bar{v};\ u+\frac{1}{2},\frac{1}{2}-u,\frac{1}{2}-v;\ u+\frac{1}{2},\frac{1}{2}-u,v+\frac{1}{2};$ $\bar{u}\bar{u}\bar{v};\ \bar{u}\bar{u}v;\ \frac{1}{2}-u,u+\frac{1}{2},v+\frac{1}{2};\ \frac{1}{2}-u,u+\frac{1}{2},\frac{1}{2}-v.$		

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[5] Wyckoff, *Carnegie Inst. Pub.*, **318**, p. 97 (1922).

The completion of the structure determination requires the allocation of 2 Cu, 4 alkali, 8 Cl and 4 H_2O among the above coördinates, and the determination of the parameters involved. The large number of possible combinations of these coördinates makes this task at first sight hopeless. Fortunately, however, we have found a general characteristic of the reflections from one class of planes, which greatly simplifies the problem. This observation is that first-order reflections from planes with $h + k + l$ odd and l odd (designated Class 1a) are always of comparatively very small intensity while those from planes having $h + k + l$ odd and l even (designated Class 1b) are not, and this observation holds good not only for the potassium salt but also for the ammonium and rubidium salts.

TABLE VI

PARAMETER VALUES FOR WHICH D_{4h}^{14} STRUCTURE FACTORS, S, VANISH WHEN $h = k = l$ IS ODD

Arrangement	No. of equiv. pos.	Parameter values		
		h odd, k even, l even	h odd, k odd, l odd	h even, k even, l odd
(a)	2	S always zero	S always zero	S always zero
(b)	2	S always zero	S always zero	S always zero
(c)	4	S always zero	S always zero	S always zero
(d)	4	S always zero	S always zero	S always zero
(e)	4	S always zero	S always zero	S always zero
(f)	4	$u = \frac{1}{4}$	No solution	$u = \frac{1}{4}$
(g)	4	$u = \frac{1}{4}$	No solution	$u = \frac{1}{4}$
(h)	8	S always zero	S always zero	S always zero
(i)	8	$u = 0$ or $\frac{1}{2}$; v unrestricted or $v = 0$ or $\frac{1}{2}$; u unrestricted	$u = 0$ or $\frac{1}{2}$; v unrestricted or $v = 0$ or $\frac{1}{2}$; u unrestricted	$u = 0, \frac{1}{4}, \frac{1}{2}$ or $\frac{3}{4}$; v unrestricted or $v = 0, \frac{1}{4}, \frac{1}{2}$ or $\frac{3}{4}$; u unrestricted
(j)	8	$u = \frac{1}{4}$; v unrestricted	$v = \frac{1}{4}$; u unrestricted	$u = \frac{1}{4}$; v unrestricted or $v = \frac{1}{4}$; u unrestricted

We have given in Table VI all of the values of the parameters (exclusive of those which lead to identical arrangements or coincidence of two atoms) for which that part of the structure factor due to each of the above arrangements becomes zero whatever may be the values of h, k and l, subject to the restrictions given at the head of each column. We may, without loss of generality, place the two copper atoms at (a); the copper atoms then contribute nothing to first orders from planes with $h + k + l$ odd. The presence of such reflections shows that some of the positions (f), (g), (i) and (j) must be occupied by alkali, chlorine or water, or some combination of them. This occupancy cannot be by one kind of atom alone in any *single* arrangement except (j), for only here can a parameter value (namely, v near $\frac{1}{4}$) be found which will make reflections of Class

1a weak without making those of Class 1b weak also. No other arrangement gives a solution common to Cols. 4 and 5 but not Col. 3 of Table VI. Only the 8 chlorine atoms can occupy (j). On the other hand, if more than one of the positions (f), (g), (i) and (j) are occupied, one of these positions cannot be occupied by an alkali atom, for then weakness of reflection in Class 1a would have to be ascribed to a suitable interference between alkali and chlorine or oxygen (or both). Such destructive interference in the case of the ammonium salt could hardly remain on substitution of potassium or the much heavier rubidium. The possibility that such interference occurs between chlorine and water likewise seems remote. There remains only the possibility that the chlorine atoms are non-equivalent, four being at (f) and four at (g). With this arrangement Class 1a and not Class 1b can become weak and, in general, only when u is nearly equal to v. We conclude, therefore: (1) that the alkali atoms are at (c), (d) or (e); (2) that the chlorine atoms are either all equivalent at (j) with v near $\frac{1}{4}$, or that they are two groups of four at (f) and (g) with u nearly equal to v.

The spectral data (Tables II, III, IV) show that with all three salts the second order from (001) was much weaker than the fourth, and that the second was relatively weakest from the rubidium salt, being of almost vanishing intensity in this case. The alternative chlorine positions which remain place the chlorine atoms either [(f) and (g)] equally in basal planes with the copper atoms, or (j) in basal planes practically half way between them. Simple calculations of the basal plane structure factors for the second and fourth orders make it evident that with the chlorine at (j) the alkali atoms must be at (c) in order to make the second order of the rubidium salt reasonably weak; and that with the chlorine at (f) and (g) the alkali atoms must be at (d), or at (e) with w near $\frac{1}{4}$. These conclusions require only the approximate use of atomic numbers or electron numbers and are not markedly dependent upon the position of the water molecule. The positions (e) for the alkali atoms involves placing three positive atoms in a line in a distance of 8 Å. and placing an alkali at about 2 Å. from a copper atom; this is regarded as so improbable that it has not been treated further. We are thus left with two main alternatives: (1), 2Cu at (a), 8Cl at (j) with v near $\frac{1}{4}$, 4 alkali at (c), $4H_2O$ at (d), (e), (f) or (g); (2), 2Cu at (a), 4Cl at (f) and 4Cl at (g) with u nearly equal to v, 4 alkali at (d), $4H_2O$ at (c), (e), (f) or (g).

A piece of evidence against Arrangement (j) for a chlorine atom is the strength of the fourth order from (101) as compared with the second; in the case of the ammonium compound the fourth was practically as strong as the second, thus requiring a larger structure factor for the fourth order. Neglecting water, the structure factors given by the arrangement involving (j) are

$$n = 2 \quad S = 2\overline{\mathrm{Cu}} + 4\overline{\mathrm{alk}} + 8\overline{\mathrm{Cl}} \cos 4\pi u \cos 4\pi v$$

$$n = 4 \quad S = 2\overline{\mathrm{Cu}} + 4\overline{\mathrm{alk}} + 8\overline{\mathrm{Cl}} \cos 8\pi u \cos 8\pi v$$

For the values $u = \frac{1}{4}$, $v = \frac{1}{4}$, these both reduce to $2\overline{\mathrm{Cu}} + 4\overline{\mathrm{alk}}. + 8\overline{\mathrm{Cl}}$. The effect of changing the parameter values away from $\frac{1}{4}$ is to reduce the 8Cl term for all values of u or v near $\frac{1}{4}$, and to reduce it more in the fourth than in the second order (the only values of u and v compatible with other data are sufficiently near to $\frac{1}{4}$ for this to apply). Hence, the only way in which the fourth can be made greater than the second is by water; it is regarded as doubtful whether the scattering power of water is great enough to account for the observed difference. On the other hand, the arrangement with (Cl) at (f) and (g) leads with parameter values determined below to a much larger structure factor for the fourth than for the second order even when water is omitted.

A similar piece of simple evidence comes from powder photographs of the potassium and of the ammonium salt made with molybdenum $K\alpha$ radiation in a General Electric Company cassette. The strong line due to (110) second order was stronger than that due to (101) second order occurring at a slightly smaller angle. As the number of coöperating planes for (110) is only half that for (101), the structure factor must be the greater for (110). Arguments similar to those used above again favor chlorine at (f) and (g) rather than at (j).

Other data which again eliminate (j) are the Laue photographic comparisons: (551) > (351); (151) > (241); (632) > (542). These have the disadvantage of involving only small intensity differences, but the advantage of not involving relative reflecting powers.

Finally, the alternative involving (f) and (g) as chlorine positions remains to be considered. In this case the possibility of water also being at (f) and (g) is removed by the chemical improbability of such a structure, by the necessary close approach of the chlorine and copper atoms and the water molecule, and also by the fact that planes having $h + k + l$ odd and l odd are uniformly weak no matter what the interplanar distance is.

Evaluation of the Parameters.—In order that the spectral data from $(101)_{\mathrm{s.\,g.}}$ shall be satisfied, u and v must be in the region 0.18 to 0.32. The following comparisons from Photograph 2 restrict the parameters to the region (0.21, to 0.23); (418) > (652), (652) > (643), (652) > $(\bar{1}28)$. This region could not be further restricted by intercomparisons not involving assumptions concerning relative reflecting powers. The near equalities of the intensities of reflections $(\bar{3}\bar{8}6) \geqslant (4.1.10)$ and (652) > $(\bar{1}2\bar{8})$, together with the required separation of the two parameters, suggest $u = 0.213$ and $v = 0.217$, or vice versa, as the most probable values.[6] A consideration of other data is necessary to distinguish between u and v.

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[6] The values $u = \frac{1}{2} - \beta$ and $v = \frac{1}{2} - \alpha$ lead to the same structures as the values $u = \alpha$ and $v = \beta$ and hence do not require separate consideration.

The following observed inequalities of reflections, (473) > (471), (653) > (651), (387) > (385), between planes having $h + k + l$ even and l odd, require oxygen to be at (e), with a value of w between 0.250 to 0.333; these comparisons do not involve the assumption of numerical relative reflecting powers. A closer restriction of w can be made by comparisons affected by the value of the chlorine parameter; (149) > (167), (219) > (651) require w to be between 0.315 and 0.333. We have taken 0.32 as an approximate value.

TABLE VII

LAUE PHOTOGRAPHIC DATA FROM POTASSIUM CUPRIC CHLORIDE DIHYDRATE

Incident Beam 8° from normal to $(110)_{s.g.}$

				S for u = 0.213 v = 0.217 w = 0.318	
hkl	d_{hkl}, Å.	$n\lambda$, Å.	Estimated intensity	Atomic numbers[a]	50% increase for Cu over atomic number
123	2.064	0.33	3.0	5.06	5.86
114	1.842	.40	0.80	1.24	0.44
234	1.425	.40	0.50	2.68	2.68
334	1.357	.32	0.20	1.91	2.71
433	1.295	.40	1.20	5.15	5.95
017	1.112	.36	1.0	3.58	4.38
542	1.102	.36	0.30	2.78	2.78
362	1.067	.44	1.15	6.10	6.10
217	1.066	.45	1.10	3.43	4.23
255	1.038	.40	0.38	1.40	2.20
436	0.983	.42	.65	4.85	4.85
643	.962	.45	.00		
650	.953	.34	.10	3.48	3.48
651	.947	.31	.07	2.83	3.63
128	.944	.34	.09	3.30	3.30
		.36	.10		
471	.929	.35	.08	2.67	3.47
652	.927	.35	.10	3.49	3.49
653	.896	.35	.09	5.58	6.38
527	.879	.41	.30	3.36	4.16
473	.867	.33	.10	5.42	6.22
418	.865	.36	.30	6.00	6.00
219	.847	.31	.10	4.45	5.25
167	.828	.46	.30	3.58	4.38
419	.788	.44	.37	4.50	5.30
385	.763	.38	.09	2.04	2.84
059	.756	.38	.17	4.62	5.42
386	.726	.47	.16	6.17	6.17
4.1.10	.721	.45	.16	6.00	6.00
1.5.10	.692	.41	.37	9.61	10.41
3.8.7	.689	.44	.09	4.01	4.81
1.6.10	.662	.45	.15	7.54	7.54
9.6.4	.655	.38	.02	3.12	3.12
7.3.10	.613	.43	.20	8.30	9.10

[a] Cl is to be taken as unity.

The only remaining undetermined factor is whether u = 0.213, v = 0.217, or the reverse. This question can be answered only by a consideration of data from all types of planes—it will depend upon relative reflecting powers as well as the usual assumptions of the methods of analysis of Laue photographs. The final tabulation of Laue data as given in Table VII, compiled from Photograph 2, shows the agreement obtained with u = 0.213 and v = 0.217. The structure factors have been calculated, first using atomic numbers and then using a reflecting power of copper increased by 50%. No data either from Laue photographs or spectral photographs were obtained in disagreement with these parameter values.

The Crystal Structure of Ammonium and Rubidium Cupric Chloride Dihydrates

The analysis of the data obtained from Laue and spectral photographs of these two compounds leads to conclusions similar to those given above. The values of the parameters were determined under the assumption that u_{Cl} and v_{Cl} did not differ by more than 0.015 (the value found in the case of potassium cupric chloride dihydrate being 0.004). The agreement between the observed intensities and calculated structure factors for spectral data is evident by reference to Tables III and IV. Table VIII gives a summary of the results obtained from the three compounds.

Table VIII

A Summary of Parameter Values, Unit Distances and Atomic Distances in the Compounds $R_2CuCl_4.2H_2O$ (R = NH_4, K or Rb)

Compound	$d_{100} = d_{010}$, Å.	d_{001}, Å.	u_{Cl}	v_{Cl}	w_O
$(NH_4)_2CuCl_4.2H_2O$	7.58	7.96	0.217	0.221	0.320
$K_2CuCl_4.2H_2O$	7.45	7.88	.213	.217	.318
$Rb_2CuCl_4.2H_2O$	7.81	8.00	.213	.217	.330

	Atomic distances, Å.					
Compound	Cu to nearest oxygen	Cu to nearest Cl at (f)	Cu to nearest Cl at (g)	Cu to nearest R	R to nearest Cl at (f)	R to nearest Cl at (g)
$(NH_4)_2CuCl_4.2H_2O$	2.55	2.44	3.14	4.28	3.28	3.35
$K_2CuCl_4.2H_2O$	2.51	2.37	3.15	4.21	3.32	3.31
$Rb_2CuCl_4.2H_2O$	2.64	2.41	3.20	4.38	3.43	3.42

Discussion of the Structure

Geometrical and Chemical Significance of the Structure.—The unit of structure containing two $R_2CuCl_4.2H_2O$ is shown in Fig. 1. In this structure each copper atom is immediately surrounded by two oxygen atoms and four chlorine atoms, two of the chlorine atoms being at a distance different from the other two. The average copper to chlorine distance is 0.75 Å. greater in one case than in the other (see Table VIII).

Each alkali atom is surrounded by four oxygen atoms, four copper atoms and eight chlorine atoms. In this case, although the eight surrounding chlorine atoms are not all equivalent, they are practically equidistant from the alkali atom. The small difference in distance is necessary so that the Laue data can be satisfied (see next section). The average alkali to chlorine distance in these compounds is *ca.* 0.14 Å. greater than that of the corresponding alkali halides having the sodium chloride type of structure.

In the case of potassium chlorostannate K_2SnCl_6[7] and of $NiCl_2.6NH_3$[8] a group of six chlorines or ammonias is equidistantly placed around the central metal atom, the geometrical association being quite definite. Similarly in the case of the alkali cupric chloride dihydrates, each chlorine or water has one copper atom which is nearer to it than any other copper atoms are; and if the chlorine or water be regarded as associated with this copper atom, and the process repeated for all chlorine and water, the result is an array of cupric chloride dihydrate groups. These groups are all alike and are octahedral in shape, but not regular. However, any physical unity or stability cannot be attributed to these groups on such purely geometrical grounds. Indeed, in view of the considerable inequality in the two copper to chlorine distances, it is natural to assume that the forces exerted by the copper on the surrounding chlorine atoms are quite unequal. This inequality may well correspond to a lack of stability of the coördination group, which would be in agreement with the behavior of the substance in solution as a double salt rather than as a complex salt.

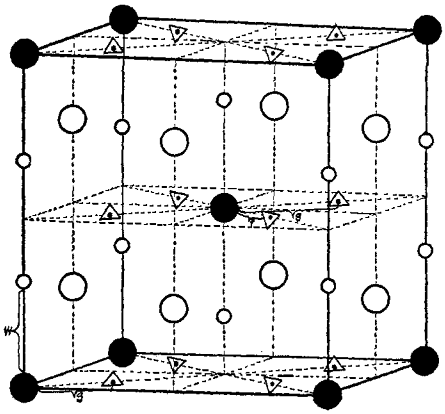

Fig. 1.—The unit of structure of the alkali cupric chloride dihydrates. ▽, Cl at (*f*); △, Cl at (*g*); ○, Cu; ●, NH_4, K or Rb; ◯, 0.

These compounds represent a new structural type. Although they have the same space-group symmetry as magnesium fluoride, they are not related to magnesium fluoride in the simple manner in which potassium chlorostannate is related to calcium fluoride.

Discussion of the Method of Analysis

In making use of absences of reflections from planes in positions to reflect, in order to determine the correct space group, it is desirable to examine combinations of special positions in the eliminated space groups

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[7] Dickinson, This Journal, **44,** 276 (1922).

[8] Wyckoff, *ibid.*, **44,** 1239 (1922).

in order to be certain that the observations could not be accounted for by giving particular values to the parameters. In the present case such a method reduces the number of space groups to two, C_{4v}^4 and D_{4h}^{14}. Since C_{4v}^4 can approximate arrangements from D_{4h}^{14} as closely as desired, we have made the *assumption* that the crystallographically assigned symmetry is correct. Such an assumption has proved to be incorrect in some cases (penta-erythritol, sodium periodate, etc.).

An observation of great value to us in the structure determination was the presence of weak reflections from planes with $h + k + l$ odd and l odd. It is conceivable that these reflections appear only because of a dissymmetry in a particular kind of atom, chlorine for instance. However, when two such planes reflected at the same wave length, and the one with the smaller interplanar distance was the more intense, its structure factor, with a separation of the value of u and v not exceeding (0.03) in case of chlorine (f) and (g), was always found to be the greater of the two. This is of further interest since arrangements with chlorine at (j) could not account for such an observation.

The elimination of the arrangement with chlorine at (j) is not as straightforward as one might wish. It is based upon rather close Laue comparisons, and a general disagreement with the spectral data. Reflections for which chlorine at (j) and at (f) and (g) would lead to considerably different intensities require some knowledge of reflecting powers in their treatment.

The determination of the chlorine parameters has been made independently of relative reflecting powers; but our determination of which value represents u and which v is not a very good one. The difference between the two is, however, very small.

It is not probable that oxygen reflects strongly enough to be a factor governing markedly the intensity of the Laue spots. Small intensity differences in our data require a parameter for oxygen, however. The parameter determination in the case of oxygen at (e) is of approximate character only. The data, without assumptions concerning relative reflecting powers, could not be explained by placing oxygen at (c) or (d). This elimination of (c) and (d) is based on several comparisons, all of which are necessarily close.

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Summary

The structures of crystals of ammonium, potassium and rubidium cupric chloride dihydrates have been investigated by means of Laue and spectral photographs interpreted with the aid of the theory of space groups. The unit of structure, based on a simple tetragonal lattice,

contains two $R_2CuCl_4.2H_2O$. The space-group symmetry is probably D_{4h}^{14} with 2Cu at (a), 4 alkali at (d), 4Cl at (f), 4Cl at (g) and $4H_2O$ at (e). The compounds seem to have "double salt" characteristics.

PASADENA, CALIFORNIA

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF STANFORD UNIVERSITY]

THE CONDUCTIVITY OF ACIDS AND SALTS IN LIQUID AMMONIA[1]

BY FRANCIS A. SMITH

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In the course of the development of the system of compounds derived from liquid ammonia as a solvent, by Franklin[2] and his associates, it was desired to know the extent to which certain acids and salts would ionize when dissolved in liquid ammonia. This information was designed to indicate whether or not metallic salts of acids derived from the ammonia system, when dissolved in liquid ammonia, would ionize to a greater extent than their respective acids. This conspicuous property of salts of aquo-acids in water solution would thus serve to test the validity of the classification of the former as true salts.

Also it was hoped that such information would be a useful addition to existing knowledge of the properties of substances dissolved in liquid ammonia.

Some of the data obtained by Franklin[3] and by Franklin and Kraus[4] are made use of for purposes of comparison.

Treatment and Expression of Results

The following notation has been used to express the designated quantities: R, measured resistance; C, cell constant; v, dilution, in liters per mole; Λ, molecular conductivity; Λ_∞, the value approached by Λ as the dilution increases; K, the ionization or equilibrium constant.

The conductivity curves of the substances measured, with some of the curves of Franklin and of Franklin and Kraus, have been plotted together in Fig. 1 for comparison.

The graphical methods of Kraus and Bray[5] have been used, where applicable, to evaluate Λ_∞ and K, and these values are given in Tables I and II.

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[1] From a thesis presented to the Department of Chemistry and the Committee on Graduate Study of Stanford University in 1925 in partial fulfilment of the requirements for the degree of Doctor of Philosophy. The work herein described was done under the direction of Dr. E. C. Franklin.

[2] Franklin, "Liquid Ammonia as a Solvent," A. C. S. Monograph in preparation.

[3] Franklin, *Z. physik. Chem.*, **69**, 270 (1909).

[4] (a) Franklin and Kraus, *Am. Chem. Jour.*, **23**, 277 (1900); (b) THIS JOURNAL, **27**, 191 (1905).

[5] Kraus and Bray, THIS JOURNAL, **35**, 1315 (1913).