333. *The Crystal Structure of Anhydrous Cupric Chloride, and the Stereochemistry of the Cupric Atom.*

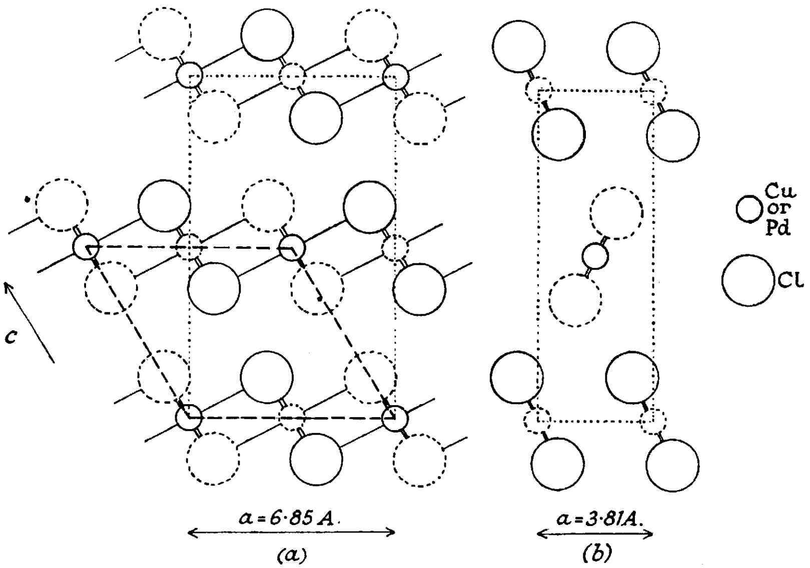
By A. F. Wells.

Anhydrous cupric chloride is monoclinic: $a = 6{\cdot}85$, $b = 3{\cdot}30$, $c = 6{\cdot}70$ A., $\beta = 121°$; space-group $C2/m$, with Cu at 000, $\frac{1}{2}\frac{1}{2}0$, and 4 Cl at $x0z$, etc., $x \approx \frac{1}{2}$, $z \approx \frac{1}{4}$. The structure contains infinite chain molecules formed by planar $CuCl_4$ groups sharing opposite edges, as in $PdCl_2$. The packing of these chains is different from that found in $PdCl_2$, apparently in order to give Cu^{II} two next nearest neighbours at about 3 A. completing a distorted octahedral co-ordination group. The stereochemistry of the cupric atom is discussed.

Cupric chloride is one of the few halides of the commoner elements which has not previously been studied by the methods of *X*-ray crystallography. Its structure is of interest in view of the planar configuration of four bonds from a cupric atom, already established in a number of crystalline salts and co-ordination compounds. Since the length of a Cu^{II}–Cl bond is the same ($2{\cdot}30 \pm 0{\cdot}03$ A.) as that of Pd^{II}–Cl, one might expect cupric chloride to have the same crystal structure as palladous chloride (Wells, *Z. Krist.*, 1938, **100**, 189), in which planar $PdCl_4$ groups are joined up by sharing opposite edges to form infinite chain molecules. In fact, it is found that the structure of $CuCl_2$, although closely related to that of $PdCl_2$, differs from that structure in a significant way. This point will be discussed later in more detail in a survey of the crystal structures of certain cupric compounds.

Determination of the Crystal Structure of Cupric Chloride.—Cupric chloride is hygroscopic, and is normally obtained from aqueous solution as the dihydrate. The anhydrous salt is readily prepared by heating the dihydrate to a moderate temperature in a stream of hydrogen chloride, being obtained as brown pseudomorphs of the needles of the blue dihydrate. This material is very poorly crystalline, as judged by its powder photograph, and attempts to index the latter unambiguously were not successful. Single crystals of cupric chloride were therefore prepared by melting this material in a hard-glass tube (when some decomposition takes place), allowing it to cool, and breaking up the cooled melt. The crystals are sufficiently stable on a dry day to permit microscopic examination and the selection of suitable crystals which can then be sealed up in short lengths of thin-walled capillary tube. The crystals are thin laths (001) or needles, elongated along the b axis. There is perfect (001) cleavage, and moreover, the slightest pressure on a (001) plate causes it to split along its length (b) into a bundle of fibres, looking much like asbestos. By reflected light the crystals appear brown. They exhibit striking pleochroism, the light transmitted being yellowish-green for vibrations perpendicular to b and reddish-brown for vibrations along b, a colour change quite similar to that of $CsCuCl_3$ (preceding paper). X-Ray examination (Cu-K_α radiation) shows the crystals to be monoclinic: $a = 6{\cdot}85$, $b = 3{\cdot}30$, $c = 6{\cdot}70$ A., $\beta = 121°$. Owing to the physical weakness of the crystals, which are easily bent and split, the accuracy of these figures is probably no greater than $\pm$ 1%. The density was not determined, but since by analogy with the structure of $PdCl_2$ the above cell contains 2 $CuCl_2$, the calculated density is 3·44 g./c.c.

Fig. 1.



Projections of the crystal structures of (a) $CuCl_2$ *and* (b) $PdCl_2$ *on* (010), *showing the differences in packing of the chains. Atoms at* $y = 0$ *and* $y = \frac{1}{2}$ *are represented by full and dotted circles respectively. In* (a) *the broken lines enclose the monoclinic unit cell, and the dotted lines indicate the pseudo-rhombic cell.*

The halvings observed are those characteristic of a c face-centred lattice. Since there is no evidence of lower symmetry the space-group is assumed to be $C2/m$. The strong absorption of light vibrating along b and the fact that the length of the b axis is the same as for $PdCl_2$ suggest a chain structure closely related to that of $PdCl_2$. In fact it is found that the photographs about the b axis can be indexed on the basis of a pseudo-rhombic all face-centred cell with dimensions: $a = 6{\cdot}85$, $b = 3{\cdot}30$, $c = 11{\cdot}4$ A., containing 4 $CuCl_2$. The spacings of the $h0l$ planes show also that the projection of the structure on (010) is pseudo-hexagonal. The cell dimensions of $PdCl_2$ (orthorhombic, space-group $Pnmn$) are: $a = 3{\cdot}81$, $b = 3{\cdot}34$, $c = 11{\cdot}0$ A., *i.e.*, very similar to those of $CuCl_2$ except that the a axis is nearly doubled in the case of the latter. This increased a dimension is clearly due to the interposition of a chain related by a translation of $b/2 + a/2$ between alternate chains along the a axis. Since the lattice is known to be c face-centred monoclinic, the only possible way of packing the chains is that shown in Fig. 1(a), the chain length (b) being normal to the plane of the paper. The corresponding projection of the structure of $PdCl_2$ is shown in Fig. 1(b). It will be seen that this way of packing the $CuCl_2$ chains accounts for the pseudo-hexagonal nature of the b axis and for the pseudo-rhombic all face-centred unit cell corresponding to the true orthorhombic cell of the palladium compound.

Considerations of packing show that the planes of the $CuCl_4$ groups must lie approximately in (100). The structure is then defined as follows, the space-group nomenclature of the International Tables being used :

Cu in 2 (a) : 000, $\frac{1}{2}\frac{1}{2}0$ Cl in 4 (i) : $x0z$, etc., $x \approx \frac{1}{2}$, $z \approx \frac{1}{4}$

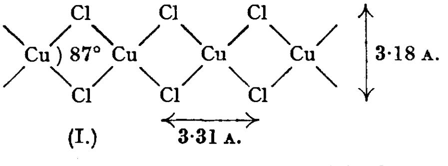
Owing to the fact that the parameters x and z have, at least approximately, the special values $\frac{1}{2}$ and $\frac{1}{4}$ respectively, striking intensity relationships are observed, for all the structure factors have one of the three values, $2f_{\text{Cu}}$, $2f_{\text{Cu}} + 4f_{\text{Cl}}$ or $2f_{\text{Cu}} - 4f_{\text{Cl}}$. Because of the small size of the unit cell, comparatively few reflexions are observed for copper radiation, and the only practicable way of determining the parameters accurately would be to project the structure on (010), using a shorter radiation and, if possible, avoiding the use of a capillary tube. Since it is not likely that better intensity data will be obtainable in the near future, it was considered desirable to publish the present paper as this establishes the structure within close limits and raises an interesting point about the stereochemistry of the cupric atom.

The calculated and observed intensities given in Table I are sufficient to prove the essential correctness of the structure. The intensities are calculated as proportional to $F^2(1 + \cos^2 2\theta/2 \sin 2\theta)$ the f-curves used being those for Cu and Cl atoms given in the International Tables (Vol. II). The planes are arranged in order of increasing sin θ, and include only those with $k = 0$ or 1.

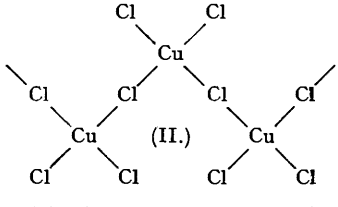
TABLE I.

hkl.	*I*, calc.	*I*, obs.	*hkl.*	*I*, calc.	*I*, obs.	*hkl.*	*I*, calc.	*I*, obs.
001	202	vs	$31\bar{2}$	112	s	$31\bar{4}$	0	—
$20\bar{1}$	97	s	$11\underline{2}$	106	s	$11\underline{3}$	11	w
200	309	vs	$11\bar{3}$	26	w	$11\bar{4}$	0	—
$20\bar{2}$	0	—	$40\bar{2}$	0	—	004	45	ms
110	0	—	310	0	—	203	10	w
$11\bar{1}$	74	s	$31\bar{3}$	22	w	$20\bar{5}$	10	w
002	0	—	$20\underline{2}$	0	—	$40\underline{1}$	10	w
111	44	ms	$20\bar{4}$	87	ms	$40\bar{5}$	10	w
$11\bar{2}$	185	vs	$40\bar{1}$	20	w	$51\bar{2}$	39	m
201	40	m	$40\bar{3}$	20	w	$51\bar{3}$	10	w
$20\bar{3}$	40	m	400	47	ms	$31\underline{2}$	38	m
003	30	mw	$40\bar{4}$	47	ms	$31\bar{5}$	9	w
$31\bar{1}$	27	w	311	11	w			

Description of the Structure.—The structure is illustrated in Fig. 2, which shows three unit cells. The Cu and Cl atoms are joined together to form infinite chains in which each Cu is surrounded by 4 Cl in a plane and each Cl is attached to 2 Cu. From the similarity in the lengths of the b axes in $CuCl_2$ and $PdCl_2$ it may be concluded that the structure of a chain is very similar to that in $PdCl_2$, *viz.*, (I), though this small distortion of the $CuCl_4$ groups has not been established in the present case. The length of the Cu–Cl bond is the same (2·3 A.) as that in $CsCuCl_3$, $K_2CuCl_4,2H_2O$, and $CuCl_2,2H_2O$. It has been shown (preceding paper) that in $CsCuCl_3$ exactly similar planar $CuCl_4$ groups are joined together to form infinite chain ions of the type (II).



(I.)

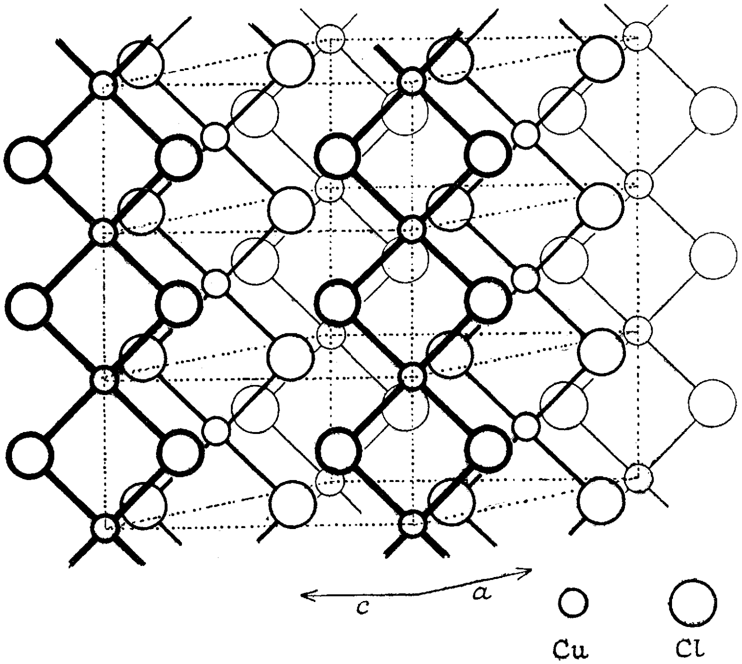


(II.)

The configuration of the $CuCl_2$ chain being assumed to be that shown above, the shortest distance between chlorine atoms of different chains is 3·5 A. The next nearest neighbours of a copper atom are two more Cl (in adjacent chains related by the c face-centring) at 2·95 ± 0·05 A. These weak Cu–Cl bonds, discussed below, are shown as light full lines in Fig. 1(a), and they complete the distorted octahedral arrangement of six bonds from each Cu atom. Taking account of this weak additional binding, the chains form sheets parallel to (001), though, of course, by far the strongest bonds are those within the individual chains, which run parallel to [010]. A somewhat analogous state of affairs is found in the structure of mercuric bromide (Verweel and Bijvoet, *Z. Krist.*, 1931, **77**, 122), in crystals of which each Hg atom has a distorted octahedral environment, with two of the six Br much closer than the other four. Having regard only to the strongest bonds, the structure contains linear molecules $HgBr_2$, but taking into account also the weak secondary bonds from a Hg atom to its four next nearest neighbours, the structure is seen to be a layer structure. In $PdCl_2$, on the other hand, there is no such suggestion of secondary bonds linking the chains laterally into layers, and the mode of packing of the infinite chains is much more like that of non-polar chain molecules such as long-chain hydrocarbons.

The structure clearly accounts for the strong absorption of light vibrating along the *b* axis, this being the direction of the infinite chain molecules. The structure also explains the perfect (001) cleavage, and the remarkable tendency to split into fibres is obviously due to the secondary cleavage parallel to (100). The *X*-ray photographs of some crystals show additional reflexions due to twinning, the possibilities of which are considerable. Rotational twinning (about *b*) is possible because of the pseudo-hexagonal packing of the chains. Also, if the set of chains shown (in projection) in the lower part of Fig. 1(*a*) is sheared in the direction of the *a* axis in the plane (001), they can rearrange by sliding over one another to take up the alternative orientation related to the first by reflexion across the plane (20$\bar{1}$).

FIG. 2.



The crystal structure of anhydrous cupric chloride (three unit cells).

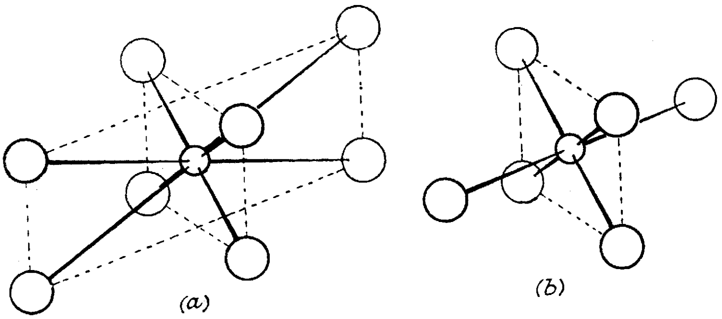
The Stereochemistry of the Cupric Atom.—Perhaps the most interesting result of this study is the demonstration that the structure of $CuCl_2$ is *different* from that of $PdCl_2$. It was known previously that the lengths of the Cu^{II}–Cl and the Pd^{II}–Cl bonds are the same to within the accuracy to which they are known, and the present work confirms this. Both compounds form exactly the same type of infinite chain molecule, yet the chains are packed in different ways in the crystals of $CuCl_2$ and $PdCl_2$. It is worth while enquiring why this should be so. In $PdCl_2$ the next nearest chlorine neighbours of a Pd atom (*i.e.*, after the four coplanar neighbours) are four more (at 3·85 A.) arranged at the corners of a rectangle, the plane of which is perpendicular to that of the $PdCl_4$ group [see Fig. 3(*a*)]. In $CuCl_2$, on the other hand, neighbouring chains along [100] are displaced relative to one another in such a way that the next nearest neighbours of a Cu atom are *two* more Cl atoms of neighbouring chains. These complete a distorted octahedron of Cl atoms around the Cu atom [Fig. 3(*b*)], and they are at a distance of only about

2·95 A. It might appear fanciful to suppose that the different packing of the chains is adopted in order to give Cu^{II} this distorted octahedral environment, particularly as it is at present difficult to say what type of binding a bond of this length would indicate, were it not for the fact that Cu^{II} has precisely this environment in a number of other crystalline salts. The structures (and stabilities) of certain crystalline cupric salts present a number of striking features to which attention does not appear to have been drawn. The facts are as follows.

(1) *Potassium cupric halides.* The only potassium cupric halide stable in the presence of water at ordinary temperatures is the blue-green hydrated salt $K_2CuCl_4,2H_2O$. (The red $KCuCl_3$ can be prepared from concentrated solution but is rapidly converted by moist air into a mixture of $CuCl_2,2H_2O$ and $K_2CuCl_4,2H_2O$.) Palladous chloride on the other hand forms the stable anhydrous K_2PdCl_4. In crystalline K_2PdCl_4 the $PdCl_4^{2-}$ ions are stacked vertically above one another, so that the next nearest Cl neighbours of a Pd atom (apart from those of other $PdCl_4^{2-}$ ions coplanar with the one under consideration) are 8 Cl at distances of more than 4 A. In contrast to this, $K_2CuCl_4,2H_2O$ does not contain planar $CuCl_4^{2-}$ ions at all, but each Cu has, as nearest neighbours, 2 O (of H_2O) at 1·97 A., 2 Cl at 2·32 A., and 2 more Cl at 2·95 A., the whole set forming a distorted octahedral group around the Cu (Chrobak, *Z. Krist.*, 1934, **88**, 35; "Strukturbericht", 1936, **4**, 104). In $Pd(NH_3)_4Cl_2,H_2O$ we find Pd with $4NH_3$ as nearest neighbours at 2·02 A., with 8 Cl as next nearest neighbours, arranged at the corners of a cube, at 4·27 A. (Dickinson, *Z. Krist.*, 1934, **88**, 281).

(2) *Cupric chloride dihydrate.* Here again we might have expected to find 4 Cl around Cu at about 2·30 A. Instead, we find exactly the same arrangement of atoms as in $K_2CuCl_4,2H_2O$, *viz.*, 2 O at 2·01 A., 2 Cl at 2·31 A., and 2 Cl at 2·98 A. (Harker, *ibid.*, 1936, **93**, 136). It may be argued that the displacement of two of the four possible chlorine atoms by 2 H_2O (to give 2 H_2O and 2 Cl as nearest neighbours instead of 4 Cl) is connected with the strong tendency of Cu^{II} to form bonds to oxygen—witness the numerous "basic" salts of copper (actually hydroxy-salts)—but this does not account for the persistent 4 + 2 co-ordination of Cu^{II} which also occurs in *anhydrous* $CuCl_2$ and $CsCuCl_3$. The comparison of the stereochemistry of Cu^{II} and of Pd^{II} will be more complete when two more structures are known, those of $PdCl_2,2H_2O$ and Cs_2CuCl_4. It will be interesting to know whether the former adopts the same structure as $CuCl_2,2H_2O$ or whether, as seems more likely, Pd will retain 4 Cl as its immediate neighbours. A knowledge of the structure of the latter salt (or some similar compound) is required because the existence of discrete $CuCl_4^{2-}$ ions has not so far been proved in any crystal.

FIG. 3.



The environment of (a) Pd *in* $PdCl_2$ *and* (b) Cu *in* $CuCl_2$ (*small circles represent metal atoms*).

The above considerations suggest that the statement that Cu^{II} forms four coplanar bonds may require modification, in the sense that the analogy with Pd^{II} or Pt^{II} is not so close as that statement would imply. There is, of course, no reason why Cu^{II} should form exactly the same number and arrangement of directed bonds as Ni^{II}, Pd^{II}, or Pt^{II}, and careful comparative studies may indicate more subtle differences between the stereochemical behaviour of atoms which form essentially the same number and arrangement of *strongest* bonds. It is supposed that, when Cu^{II} forms four planar bonds (dsp^2), the 35 valency electrons are distributed among the available orbitals as follows :

$$\begin{array}{ccccccc} & & 3s & 3p & 3d & 4s & 4p \\ 2 & 8 & 2 & 6 & \multicolumn{3}{c}{8 + \underbrace{2 \qquad 2 \qquad 4}_{\text{shared}} + 1} \end{array}$$

the odd electron occupying a $4p$ orbital. In the case of Ni^{II} forming four dsp^2 bonds the electronic arrangement is similar except that there is no odd electron. It seems possible that this electron may have some bonding power and might be responsible for two additional weak bonds perpendicular to the plane of the four strong dsp^2 bonds.

RESEARCH LABORATORIES, IMPERIAL CHEMICAL INDUSTRIES LTD.,
HEXAGON HOUSE, MANCHESTER 9.

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