

### 332. *The Crystal Structure of CsCuCl<sub>3</sub> and the Crystal Chemistry of Complex Halides ABX<sub>3</sub>.*

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The crystal structure of CsCuCl<sub>3</sub> is determined. The crystals are hexagonal,  $a = 7.20$ ,  $c = 18.00$  Å.; space-group  $C6_32$ , with 6 molecules of CsCuCl<sub>3</sub> per cell. There are infinite chain ions of composition  $(CuCl_3)_2^{2-}$  formed by planar CuCl<sub>3</sub> groups joined up by sharing two adjacent chlorine atoms, these ions being in the form of spirals around the six-fold screw axes. They are held together laterally by the caesium ions. The crystal chemistry of complex halides ABX<sub>3</sub> is discussed.

THE structure of the compound CsCuCl<sub>3</sub> is of interest both in connection with the stereochemistry of copper and also because of its close relation to a number of other halides ABX<sub>3</sub>, in which the A and X atoms together are close-packed. Except for the hydrated compounds CuCl<sub>2</sub>·2H<sub>2</sub>O (Harker, *Z. Krist.*, 1936, **93**, 136; MacGillavry and Bijvoet, *ibid.*, 1936, **94**, 231) and K<sub>2</sub>CuCl<sub>4</sub>·2H<sub>2</sub>O (Chrobak, *ibid.*, 1934, **88**, 35), little is known of the structures of cupric halides, simple or complex. The crystal structures of the cupric halides themselves are not known, and only the unit-cell dimensions and space-groups of the compounds KCuBr<sub>3</sub> (Silberstein, *Compt. rend.*, 1939, **209**, 540) and Cs<sub>2</sub>CuCl<sub>4</sub> (Mellor, *Z. Krist.*, 1939, **101**, 160) have been determined. A note on CsCuCl<sub>3</sub> was published recently (Klug and Sears, *J. Amer. Chem. Soc.*, 1946, **68**, 1133) but the authors were unable to determine its crystal structure.

In the Periodic Table the elements around copper which exhibit bivalency are :

|    |    |    |    |         |    |
|----|----|----|----|---------|----|
| Mn | Fe | Co | Ni | Cu      | Zn |
|    |    |    |    | Pd (Ag) | Cd |

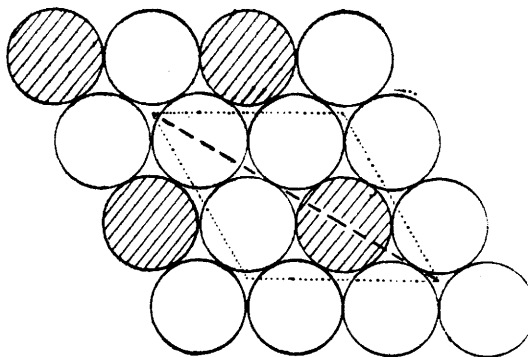
As regards its crystal chemistry Cu<sup>II</sup> appear to be most closely related to Pd<sup>II</sup>. For instance, the monoxides MnO, FeO, CoO, NiO, and CdO have the rock-salt structure, ZnO the wurtzite and the zinc-blende structure, but CuO a quite different structure, very similar to that of PdO, in which there is square co-ordination of the metal atoms by oxygen. The difluorides MnF<sub>2</sub>, FeF<sub>2</sub>, CoF<sub>2</sub>, NiF<sub>2</sub>, and ZnF<sub>2</sub> have the rutile structure, and CdF<sub>2</sub> the fluorite structure. CuF<sub>2</sub> apparently has neither of these structures (v. Wartenberg and Laves, *Z. anorg. Chem.*, 1939, **281**, 381); that of PdF<sub>2</sub> is unknown. The dichlorides of Mn, Fe, Co, Ni, Zn, and Cd all crystallise with the cadmium chloride structure, in which a metal atom forms six octahedral bonds, but crystalline PdCl<sub>2</sub> is built up of infinite chains in which each Pd forms four planar bonds. The bonds formed by the former elements in complex halides are discussed later. It will be shown in this paper that in CsCuCl<sub>3</sub> copper forms four planar bonds, again resembling Pd<sup>II</sup> rather than the other elements mentioned above. The relation of the structure of CsCuCl<sub>3</sub> to that of CsAuCl<sub>3</sub> and other halides ABX<sub>3</sub> will be discussed later.

*Determination of the Crystal Structure.*—Crystals of CsCuCl<sub>3</sub> are readily grown from an aqueous solution containing caesium chloride and an excess of cupric chloride. The garnet-red crystals are hexagonal prisms {10 $\bar{1}$ 0} terminated by bipyramids, or, if grown slowly, essentially bipyramids {10 $\bar{1}$ 1}. They are uniaxial and exhibit dichroism, the colour transmitted being brownish-red for vibrations along  $c$  and yellowish for vibrations perpendicular to  $c$ . No pyro-electric effect has been detected. The cell dimensions,  $a = 7.20$  Å.,  $c = 18.00$  Å., are in good agreement with the values given by Klug and Sears (*loc. cit.*). The density, 3.65 g./c.c., indicates that the unit cell contains 6 CsCuCl<sub>3</sub> molecules.  $X$ -Ray photographs (Cu- $K_\alpha$  radiation) show that the Laue symmetry is  $6/mmm$ . The only systematic absences observed were in the orders 000 $l$ , which appear only for  $l = 6n$ , indicating the space-group  $C6_32$  (or  $C6_32$ ). The crystal class 62 is consistent with the face development.

The cell dimensions are closely related to those of Cs<sub>3</sub>Tl<sub>2</sub>Cl<sub>9</sub> (Powell and Wells, *J.*, 1935, 1008; Hoard and Goldstein, *J. Chem. Physics*, 1935, **3**, 199), for which  $a = 12.82$  ( $=\sqrt{3} \times 7.40$ ),  $c = 18.27$  Å., and suggest that the structure of CsCuCl<sub>3</sub> also consists essentially of six close-packed (CsCl<sub>3</sub>) layers of the type shown in Fig. 1. In the investigation of Cs<sub>3</sub>Tl<sub>2</sub>Cl<sub>9</sub> it was found that lamellar twinning, leading to a higher apparent symmetry, usually occurred. Crystals of CsCuCl<sub>3</sub> were therefore grown both very rapidly and very slowly, and their  $X$ -ray photographs compared. No differences were detected, and it was assumed that twinning of the type encountered in the thallium compound was not occurring in this compound. In Cs<sub>3</sub>Tl<sub>2</sub>Cl<sub>9</sub> the thallium atoms are arranged in pairs of adjacent octahedral holes between the close-packed layers. Since an octahedral environment of 6 Cl (at about 2.5 Å.) would not be unreasonable for copper, it was decided first to try all the possible arrangements of copper atoms in octahedral

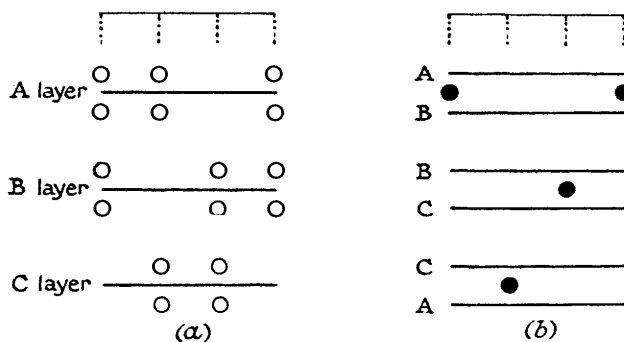
holes. For any structure consisting of six close-packed layers, which contain all the Cs and Cl atoms, the orders of  $000l$  with  $l \neq 6n$  will occur only (1) if the layers are displaced from their ideal heights,  $c/6$  apart, or (2) if the Cu atoms are placed in such positions as to contribute to these orders. The survey of possible structures based on octahedrally co-ordinated copper was therefore not restricted to those containing  $6_1$  (or  $6_2$ ) axes, but was carried out in the most exhaustive way in order to eliminate such structures conclusively.

FIG. 1.

Close-packed  $\text{CsCl}_3$  layer (caesium ions represented by shaded circles).

The problem is to determine the possible structures built of six close-packed layers, each of composition  $\text{CsCl}_3$ , held together by 6 Cu placed in octahedral holes between sets of 3 Cl in adjacent layers. Adopting the conventional nomenclature, each layer may be an A, B, or C layer (*i.e.*, the Cs is at  $\frac{2}{3}, \frac{1}{3}$  or 00), with the provisos that similar layers may not be adjacent, and the repeat unit along the  $c$  axis must not exceed 6 layers. It is necessary to place one Cu between each pair of layers, for the following reason. The possible positions for Cu atoms lie on the lines  $00z$ ,  $\frac{1}{3}\frac{2}{3}z$  or  $\frac{2}{3}\frac{1}{3}z$ , but on either side of a layer of a given type only two of these positions are possible. Representing the long diagonal of the base of the unit cell (the broken line in Fig. 1) as a horizontal line, we may indicate these possibilities as in Fig. 2*a*, so that between

FIG. 2.

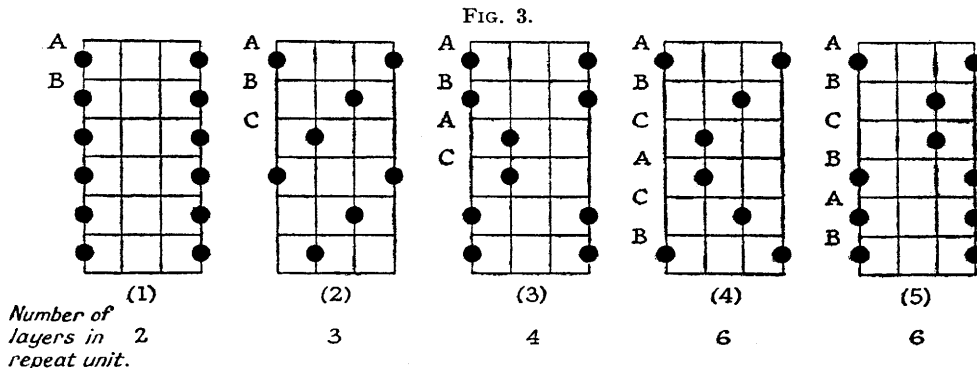


Possible positions of Cu atoms : (a) on either side of an A, B, or C layer ; (b) between AB, BC, or CA layers.

layers AB, BC, CA the only possible positions for Cu are those shown at (b), Fig. 2. The various sequences of layers lead to five possible structures. These are summarised diagrammatically in Fig. 3 as elevations on  $(11\bar{2}0)$  of one unit cell.

If a layer is represented by  $h$  when the two surrounding layers are of the same type, and by  $c$  if they are of different types, then the sequences of close-packed layers in these structures are (1)  $h$ , (2)  $c$ , (3)  $hc$ , (4)  $hcc$ , (5)  $hhhchc$ . Of these the first four are well known as the four simplest types of close-packing. In the first two, hexagonal and cubic close-packing respectively, all the spheres are equivalent; in the second two there are two kinds of non-equivalent spheres. The fifth structure is of a more complex type, and contains four kinds of non-equivalent spheres—

it is interesting as the only one of the six-term set with a repeat unit of only six layers.\* In structure (1) there are infinite chains of octahedra formed by sharing opposite faces. Structure (2) is the perovskite structure. The only structures to be tested are (4) and (5), both of which contain infinite 3-dimensional  $(\text{MX}_3)$  ions formed by  $\text{MX}_6$  octahedra sharing all their X atoms with other octahedra. The mode of linking of the octahedra is discussed later. Both these structures can be built up to conform to the space-group  $C\bar{6}m2$ , but a comparison of intensities calculated on the basis of either of these structures with those observed for  $\text{CsCuCl}_3$  shows that neither is the structure of this compound. In  $C\bar{6}m2$  the only variable  $x$  parameters are those of the chlorine atoms, and no small modification of the ideal structures could possibly account for the observed intensities. For example, they both give  $F_{600} = F_{000}$  and  $F_{601} = 0$ , whereas 600 is quite weak and  $601 > 600$ . It is therefore concluded that  $\text{CsCuCl}_3$  does not possess a structure in which Cu is octahedrally co-ordinated by six chlorine atoms.



Possible structures for a complex halide  $\text{CsMCl}_3$ , assuming octahedral co-ordination of M atoms (diagrammatic).

To account for the general nature of the  $h00$  and  $hk0$  intensities it is necessary to shift the close-packed layers relative to one another. Starting with structure (1), with hexagonal close-packing of  $(\text{Cs} + 3\text{Cl})$  and Cu atoms with six octahedral neighbours at about 2.5 Å., it is possible by suitable translations of the layers relative to one another to give each Cu four nearest Cl neighbours at about 2.3 Å. and two more distant neighbours. The relation between a pair of adjacent layers is that shown in Fig. 4. In order to fit this new arrangement into the space-group  $C6_12$  the three chlorine atoms in any layer are no longer equivalent, and the centre of the (distorted) octahedron of chlorine atoms now lies off the line  $00z$ . The Cu atoms are therefore arranged around the screw axis in a spiral arrangement. Slight movements from the positions in the ideal close-packed layer of Fig. 1 were necessary to improve the agreement between observed and calculated intensities, and the following parameters were finally chosen as giving the best overall agreement :

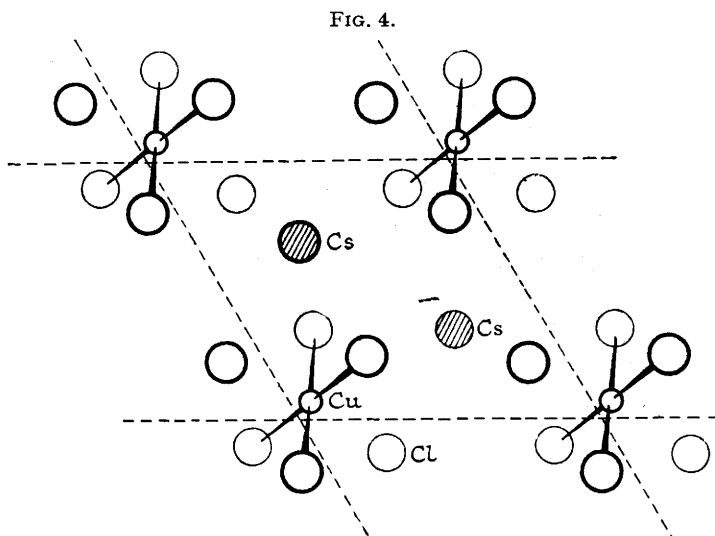
Cu :  $6(a)$ ,  $x00$ , etc.,  $x = 0.07$   
Cs :  $6(b)$ ,  $x$ ,  $2x$ ,  $\frac{1}{2}$ , etc.,  $x = 0.345$

$\text{Cl}_1$  :  $6(b)$ ,  $x$ ,  $2x$ ,  $\frac{1}{2}$ , etc.,  $x = 0.90$   
 $\text{Cl}_2$  :  $12(c)$ ,  $xyz$ , etc.,  $x = 0.35$ ,  $y = 0.22$ ,  $z = 0.25$

\* The simplest close-packed arrangements are tabulated below, together with the numbers of layers in a repeat unit. Certain of these, containing only two types of non-equivalent atom, have recently been discussed by Hägg (*Arkiv Kemi, Min. Geol.*, 1942, **16**, B, No. 3), in connection with the structures of the cadmium halides.

| Symbol.   | No. of layers<br>in repeat unit. | Symbol. | No. of layers<br>in repeat unit. |
|-----------|----------------------------------|---------|----------------------------------|
| $\bar{h}$ | 2                                | $hhcc$  | 5                                |
| $c$       | 3                                | $hhcc$  | 10                               |
|           |                                  | $hchc$  | 10                               |
| $hc$      | 4                                | $hccc$  | 10                               |
|           |                                  | $chc$   | 15                               |
| $hcc$     | 6                                | $hhhc$  | 15                               |
| $chh$     | 9                                |         |                                  |
|           |                                  | $hhhhc$ | 6                                |
| $hhc$     | 8                                | $hhhhc$ | 12                               |
| $ccch$    | 8                                | $hcccc$ | 12                               |
| $cchh$    | 12                               | $hhccc$ | 12                               |
|           |                                  | $hhcch$ | 12                               |
|           |                                  | $hhhhc$ | 18                               |
|           |                                  | $hhccc$ | 18                               |
|           |                                  | $ccchc$ | 18                               |

It will be seen that there are five parameters in the basal plane which can be varied independently. The structure is not centro-symmetrical, and owing to its nature there is no simple way of refining the parameters. Further work on such a structure would be very tedious and not very profitable, for the only bond length of special interest is Cu-Cl, and this structure would not be chosen for an accurate determination of this bond length. Intensity relationships between pairs of  $h00$  and  $hk0$  reflexions of similar spacing were used to obtain the  $x$  and  $y$  parameters given above. The only variable  $z$  parameter is that of the 12-fold chlorine position. This was assumed to be 0.25, thus keeping all the groups of chlorine atoms coplanar with the caesium atoms at heights  $1/12, 1/4, 5/12$ , etc. There are so many striking intensity relationships, particularly in series of  $h0l$  reflexions, which are all accounted for at least qualitatively, that the structure can certainly be accepted as essentially correct. The intensities of 67 reflexions, of all



*Relation between pairs of adjacent close-packed layers in  $CsCuCl_3$ .*

kinds, calculated as proportional to  $F^2(1 + \cos^2 2\theta/\sin 2\theta)$ , are compared with the observed intensities in Table I. The  $f$ -curves used were those for  $Cu^{2+}$ ,  $Cs^+$ , and  $Cl^-$  given in the "International Tables for the Determination of Crystal Structures". Since the copper is certainly not present as cupric ions, this is not very satisfactory, but this difficulty always arises

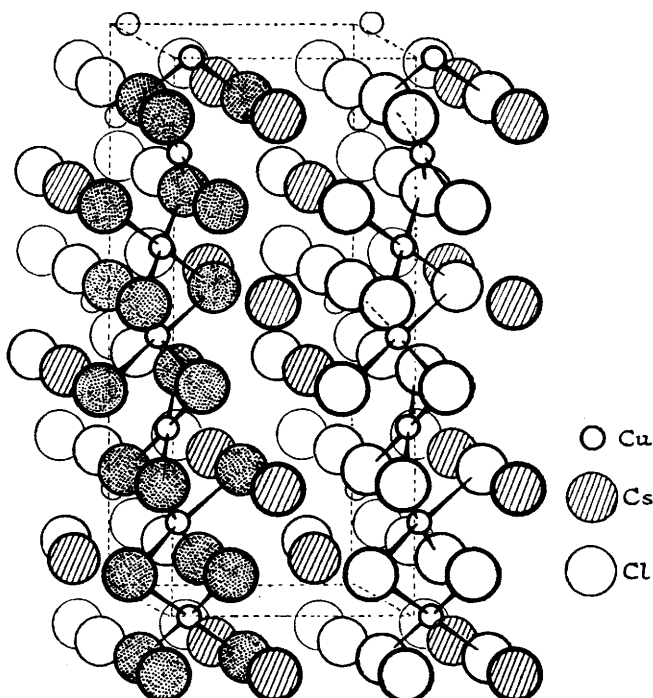
TABLE I.

| $hkl$          | $I$ , calc. | $I$ , obs. | $hkl$          | $I$ , calc. | $I$ , obs. | $hkl$          | $I$ , calc. | $I$ , obs. |
|----------------|-------------|------------|----------------|-------------|------------|----------------|-------------|------------|
| 10 $\bar{1}$ 0 | 29          | w          | 21 $\bar{3}$ 2 | 3           | —          | 31 $\bar{4}$ 3 | 45          | ms         |
| 10 $\bar{1}$ 1 | 7           | —          | 11 $\bar{2}$ 6 | 33          | w          | 31 $\bar{4}$ 4 | 1           | —          |
| 10 $\bar{1}$ 2 | 0           | —          | 21 $\bar{3}$ 3 | 64          | m          | 22 $\bar{4}$ 5 | 12          | w          |
| 10 $\bar{1}$ 3 | 202         | s          | 20 $\bar{2}$ 6 | 159         | s          | 22 $\bar{4}$ 6 | 80          | ms         |
| 10 $\bar{1}$ 4 | 3           | —          | 21 $\bar{3}$ 4 | 2           | —          | 31 $\bar{4}$ 5 | 6           | w          |
| 11 $\bar{2}$ 0 | 493         | vs         | 30 $\bar{3}$ 0 | 130         | s          | 4040           | 31          | m          |
| 11 $\bar{2}$ 1 | 16          | w          | 30 $\bar{3}$ 1 | 10          | m          | 00012          | 345         | vs         |
| 11 $\bar{2}$ 2 | 0           | —          | 30 $\bar{3}$ 2 | 7           | w          | 31 $\bar{4}$ 6 | 72          | m          |
| 10 $\bar{1}$ 5 | 8           | —          | 21 $\bar{3}$ 5 | 26          | w          | 32 $\bar{5}$ 0 | 10          | vw         |
| 20 $\bar{2}$ 0 | 45          | m          | 30 $\bar{3}$ 3 | 2           | —          | 41 $\bar{5}$ 0 | 31          | m          |
| 20 $\bar{2}$ 1 | 16          | w          | 30 $\bar{3}$ 4 | 0           | —          | 50 $\bar{5}$ 0 | 9           | vw         |
| 11 $\bar{2}$ 3 | 0           | —          | 21 $\bar{3}$ 6 | 50          | m          | 33 $\bar{6}$ 0 | 23          | m          |
| 0006           | 515         | vs         | 22 $\bar{4}$ 0 | 181         | s          | 42 $\bar{6}$ 0 | 5           | —          |
| 20 $\bar{2}$ 2 | 44          | ms         | 22 $\bar{4}$ 1 | 75          | ms         | 51 $\bar{6}$ 0 | 5           | —          |
| 11 $\bar{2}$ 4 | 9           | —          | 30 $\bar{3}$ 5 | 3           | —          | 60 $\bar{6}$ 0 | 14          | w          |
| 20 $\bar{2}$ 3 | 312         | vs         | 22 $\bar{4}$ 2 | 14          | w          | 43 $\bar{7}$ 0 | 2           | —          |
| 10 $\bar{1}$ 6 | 111         | ms         | 22 $\bar{4}$ 3 | 1           | —          | 52 $\bar{7}$ 0 | 24          | w          |
| 20 $\bar{2}$ 4 | 13          | m          | 30 $\bar{3}$ 6 | 26          | w          | 61 $\bar{7}$ 0 | 15          | w          |
| 11 $\bar{2}$ 5 | 5           | —          | 31 $\bar{4}$ 0 | 10          | vw         | 44 $\bar{8}$ 0 | 18          | w          |
| 20 $\bar{2}$ 5 | 41          | m          | 31 $\bar{4}$ 1 | 4           | —          | 70 $\bar{7}$ 0 | 26          | w          |
| 21 $\bar{3}$ 0 | 5           | —          | 31 $\bar{4}$ 2 | 11          | w          | 53 $\bar{8}$ 0 | 8           | vw         |
| 21 $\bar{3}$ 1 | 0           | —          | 22 $\bar{4}$ 4 | 4           | —          | 62 $\bar{8}$ 0 | 20          | m          |
|                |             |            |                |             |            | 71 $\bar{8}$ 0 | 5           | —          |

in a structure in which the bonds differ appreciably in amount of ionic character. Absorption of Cu- $K_{\alpha}$  radiation by this crystal is appreciable, necessitating the use of a very small equidimensional crystal. A temperature factor has not been incorporated into the calculated intensities, nor has allowance been made for absorption, the effect of which may be appreciable for some reflexions.

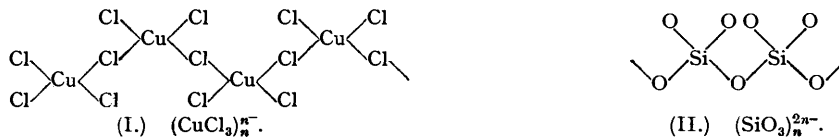
*Description of the Structure.*—The structure, which is illustrated in Fig. 5, consists essentially of close-packed layers of composition  $(\text{CsCl}_3)_n$  arranged approximately in hexagonal close-packing, with the copper atoms between the layers surrounded by four chlorine atoms in a square planar configuration. The next nearest neighbours of a copper atom are two more chlorine atoms,

FIG. 5.

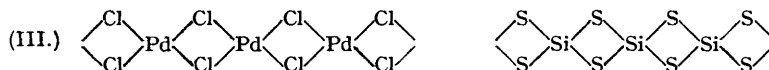


Unit cell of the crystal structure of  $\text{CsCuCl}_3$ . The stippled circles represent chlorine atoms forming part of one  $(\text{CuCl}_3)_n^{2-}$  ion.

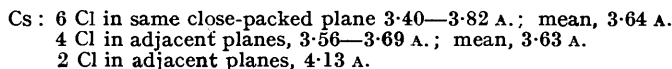
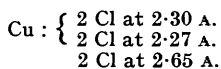
forming with the other four a somewhat distorted octahedron. The square  $\text{CuCl}_4$  groups are arranged in a spiral around six-fold screw axes and are joined up, by sharing two adjacent corners, to form infinite chains of composition  $(\text{CuCl}_3)_n^{2-}$ . The structure may therefore alternatively be regarded as consisting of infinite chain ions  $(\text{CuCl}_3)_n^{2-}$  held together laterally by  $\text{Cs}^+$  ions. This chain ion (I) is the analogue, for 4-square co-ordination, of the  $(\text{SiO}_3)_n^{2-}$  ion in diopside (II), in which tetrahedral  $\text{SiO}_4$  groups are joined up by sharing corners. The infinite



linear molecules in  $\text{PdCl}_2$ , formed by planar  $\text{PdCl}_4$  groups sharing opposite edges, are related in a similar way to the infinite chain molecules in  $\text{SiS}_2$ , which contains tetrahedral  $\text{SiS}_4$  units (III).



From the parameters given above the following interatomic distances are calculated :



The Cu-Cl bond length is, to within the probable accuracy, the same as that found in  $K_2CuCl_4 \cdot 2H_2O$  and  $CuCl_2 \cdot 2H_2O$ .

*Discussion.*—The adoption of this structure by  $CsCuCl_3$  emphasises the point made in the introduction, that in its crystalline compounds bivalent copper tends to resemble  $Pd^{II}$  rather than the elements Co, Ni, or Zn. It has been shown that there are several possible structures for  $CsCuCl_3$  containing 6-co-ordinated cupric ions with Cu-Cl about 2.5 Å., with an equally satisfactory packing of  $Cs^+$  and  $Cl^-$  ions. In preference to these, however,  $CsCuCl_3$  adopts a structure with a distorted Cs-Cl packing in order that the copper atoms shall have only four nearest neighbours arranged at the corners of a square.

It is worth while considering briefly the general nature of the structures shown in Fig. 3, as this is of interest in connexion with the stability of complex halides  $CsMCl_3$ . In the perovskite structure,  $ABX_3$ , every  $BX_6$  octahedron shares its corners with 6 other such octahedra, while in structure (1), Fig. 3, the octahedra are joined together into chains by sharing opposite faces. This type of complex ion has so far not been found, and may well be unstable owing to the close approach of the two B atoms. The linking of such octahedral co-ordination groups by sharing faces is not known to proceed beyond the formation of the ion  $(B_2X_9)$ , in  $Cs_3Ti_2Cl_9$ , etc. In such an ion the repulsion of the B atoms does lead to some distortion of the  $BX_6$  octahedra, a type of distortion which is not possible if the linking of octahedra proceeds further. The remaining three structures in Fig. 3, *viz.*, (3), (4), and (5), are, as regards the mode of linking of the  $BX_6$  octahedra, intermediate in nature between structures (1) and (2). In structure (3) all the  $BX_6$  octahedra are equivalent and share three corners with other octahedra and the remaining three (a face) with a fourth octahedron. In structures (4) and (5), however, the  $BX_6$  octahedra are no longer all equivalent. In (4), two-thirds share a face and three corners, one-third six corners, while in (5) two-thirds share a face and three corners and the remainder two faces. It seems probable, therefore, that all the structures (1), (3), (4), and (5) in Fig. 3 would be less stable than (2), the perovskite structure, so that we should expect halides  $KMF_3$  or  $CsMCl_3$  containing octahedrally co-ordinated atoms, if they are formed at all, to have that structure. Now, although the simple halides  $MCl_2$  of Fe, Co, Ni, and Zn all crystallise with a structure in which the metal atom is surrounded by six chlorine atom at about 2.5 Å., stable complex halides  $CsMCl_3$  are rare. Moreover, in the complex halides they do form they exhibit, in the compounds so far studied, a lower co-ordination number than in the simple halide. (It should be remarked that cadmium behaves differently from the above elements and retains 6-co-ordination in its complex halides, which are therefore different structurally, and also often in formula type, from those of  $Fe^{II}$ , Co, Ni, and Zn.)

TABLE II.

Complex chlorides of the type  $A_mBCl_n \cdot xH_2O$ .

| Co-ordination of B by Cl. | $Fe^{II}$ ,<br>?  | $Co^{II}$ ,<br>4,<br>tetra-<br>hedral. <sup>1</sup>     | Ni,<br>?                   | $Cu^{II}$ ,<br>4,<br>planar. <sup>2</sup> | Zn,<br>4,<br>tetra-<br>hedral. <sup>3</sup>            | Cd,<br>6,<br>octa-<br>hedral. <sup>4</sup>                       |
|---------------------------|---|---|----------------------------|---|--|--|
| <i>n</i> .                |   |   |                            |   |  |  |
| Na                        | None  | None  | ?                          | None                                      | ?  | ?  |
| K                         | 3 $KFeCl_3 \cdot 2H_2O$<br>4 $K_2FeCl_4 \cdot 2H_2O$          | None<br>—   | $KNiCl_3 \cdot 5H_2O$<br>— | $KCuCl_3$<br>$K_2CuCl_4 \cdot 2H_2O$      | $KZnCl_3 \cdot 2H_2O$<br>$K_2ZnCl_4$ (and<br>$2H_2O$ ) | $KCdCl_3 \cdot H_2O$<br>$K_2CdCl_4$                              |
|                           | 5   | —   | —                          | —   | —  | [ <i>n</i> = 6 :<br>$K_4CdCl_6$ ]                                |
| Rb                        | 3 ?<br>4 —<br>5 —   | $RbCoCl_3 \cdot 2H_2O$<br>$Rb_2CoCl_4 \cdot 2H_2O$<br>— | ?<br>—<br>—                | ?<br>—<br>—                               | ?<br>—<br>—  | $RbCdCl_3$<br>$Rb_2CdCl_4$<br>[ <i>n</i> = 6 :<br>$Rb_4CdCl_6$ ] |
| Cs                        | 3 $CsFeCl_3 \cdot 2H_2O$<br>4 $Cs_2FeCl_4 \cdot 2H_2O$<br>5 — | $CsCoCl_3 \cdot 2H_2O$<br>$Cs_2CoCl_4$<br>$Cs_3CoCl_5$  | $CsNiCl_3$<br>—<br>—       | $CsCuCl_3$<br>$Cs_2CuCl_4$<br>—           | —<br>$Cs_2ZnCl_4$<br>$Cs_3ZnCl_5$                      | $CsCdCl_3$<br>$Cs_2CdCl_4$<br>—                                  |

<sup>1</sup> Established in  $Cs_3CoCl_5$  (Powell and Wells, *J.*, 1935, 359).

<sup>2</sup> Established in  $CsCuCl_3$ .

<sup>3</sup> Established in  $(NH_4)_2ZnCl_5$  (Klug and Alexander, *J. Amer. Chem. Soc.*, 1944, 66, 1056).

<sup>4</sup> Established in  $RbCdCl_3$  (MacGillavry, Nijveld, Dierdorp, and Karsten, *Rec. Trav. chim.*, 1939, 58, 193).

Table II gives a general, though rather incomplete, picture of the types of complex chloride formed by these elements which can be isolated from aqueous solution at 25°. Of the elements Fe<sup>II</sup>, Co, Ni, and Zn, apparently only Ni forms a halide of the type CsMCl<sub>3</sub> (Campbell, *Amer. J. Sci.*, 1894, **48**, 418; *Z. anorg. Chem.*, 1895, **8**, 126). The salt CsNiCl<sub>3</sub> is obtained by evaporating a concentrated solution containing 12 CsCl : 1 NiCl<sub>2</sub>, and it is immediately decomposed by water. Its structure is not known. In the case of iron and cobalt, the dihydrates are obtained. It would seem that the compounds CsFeCl<sub>3</sub>, etc., are on the borderline as regards stability towards water, and that while CsNiCl<sub>3</sub> can just be prepared from aqueous solution in the presence of a very large excess of CsCl, the others take up 2H<sub>2</sub>O, presumably between the chains as in K<sub>2</sub>SnCl<sub>4</sub>·H<sub>2</sub>O. With the smaller rubidium and potassium ions hydration is more frequent and often occurs also in the salts M<sub>2</sub>FeCl<sub>4</sub>·2H<sub>2</sub>O, etc., while sodium salts are in general not obtainable at all. This effect is well illustrated by the complex caesium-cobalt chlorides (see Table II) and by the alkali-copper halides :

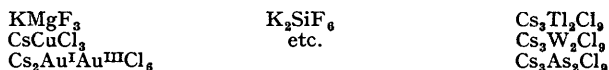
| Cs.  | Rb | K.  | Na.  | Li.                                    |
|--|----|---|------|--|
| CsCuCl <sub>3</sub>                                    | ?  | KCuCl <sub>3</sub>                                  | —    | LiCuCl <sub>3</sub> ·2H <sub>2</sub> O |
| Cs <sub>2</sub> CuCl <sub>4</sub>                      | —  | —   | None | —                                      |
| (Cs <sub>2</sub> CuCl <sub>4</sub> ·2H <sub>2</sub> O) | —  | K <sub>2</sub> CuCl <sub>4</sub> ·2H <sub>2</sub> O | —    | —                                      |

Whereas CsCuCl<sub>3</sub> is a stable salt, KCuCl<sub>3</sub> is unstable in moist air, decomposing to a mixture of two hydrated salts (CuCl<sub>2</sub>·2H<sub>2</sub>O and K<sub>2</sub>CuCl<sub>4</sub>·2H<sub>2</sub>O), and KCuBr<sub>3</sub> is very hygroscopic. The appearance of a hydrated lithium salt, in contrast to the non-existence of sodium salts, is presumably due to the fact that an entirely different type of structure becomes possible for the very small, tetrahedrally co-ordinated lithium ion. Similar variations in degree of hydration and stability towards water are found in many other series of complex halides, e.g., the dichloroiodides, hexachloroplatinates, etc.

This question, why certain compounds are formed by one element and not by others, is obviously of great interest in chemistry. The direct approach would involve the calculation of the lattice energies of all possible structures for the hypothetical compound, but this exhaustive treatment is not likely to be possible in many cases. In general, it is not possible even to deduce all the reasonable structures for a given compound, so that in the most favourable cases we should only be able to say that one or more specified structures would be unstable, without being sure that there are no other structures the compound could adopt.

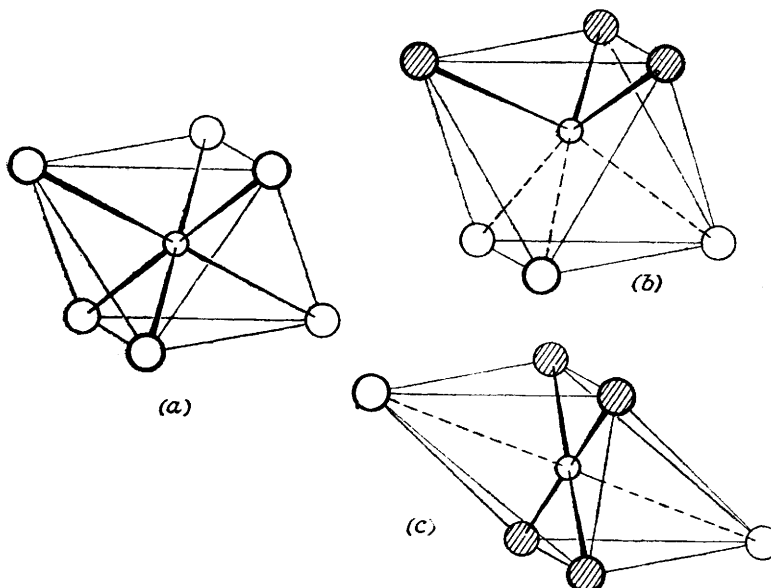
In the case of halides CsMCl<sub>3</sub> (where M = Mn, Fe, Co, Ni) it would seem that the perovskite structure should be the most stable, it being assumed (1) that the Cs and Cl will be essentially close-packed, and (2) that structures of the type adopted by the larger Cd, containing "band" ions (CdCl<sub>3</sub>)<sub>n</sub><sup>n-</sup>, are not possible for these elements. The instability of these compounds would therefore suggest that the perovskite structure, with linear M-Cl-M bonds, is not stable for chlorides. [It has been stated that CsCdCl<sub>3</sub> (Ferrari and Baroni, *Atti R. Accad. Lincei*, 1927, **6**, 418) and CsHgCl<sub>3</sub> (Natta, *ibid.*, 1927, **5**, 1003) crystallise with this structure, though the compounds were not studied in any detail. A regular octahedral arrangement of 6 Cl around Hg would be very surprising, but unfortunately the precise location of the relatively light Cl atoms would in any case be very difficult.] The fact that the simple halides MnCl<sub>2</sub>, etc., have the CdCl<sub>2</sub> structure with octahedral co-ordination of the metal atoms shows that it is not the requirement of 6-co-ordination which prevents the complex halides adopting the perovskite structure, but it is significant that in the CdCl<sub>2</sub> structure the chlorine bonds are non-linear. In complex oxides the ideal perovskite structure (with linear -O- bonds) is by no means as common as was once thought (Megaw, *Proc. Physical Soc.*, 1946, **58**, 133). We conclude therefore that the instability of these halides CsMCl<sub>3</sub> is due to the fact that the perovskite structure is stable only for the essentially ionic fluorides and oxides of the more electropositive elements. For chlorides it is far less stable than for fluorides, so that instead of CsCoCl<sub>3</sub> we find CsCoCl<sub>3</sub>·2H<sub>2</sub>O, with presumably either infinite chain ions (CoCl<sub>3</sub>)<sub>n</sub><sup>n-</sup>, containing tetrahedrally co-ordinated cobalt and H<sub>2</sub>O molecules between the chains, or (less probably) infinite aquo-ions or bands as in NH<sub>4</sub>CdCl<sub>3</sub> with H<sub>2</sub>O between the "band" ions.

The structures of complex halides ABX<sub>3</sub> in which the ratio of halogen to alkali-metal atoms is 3 : 1 are of special interest because for this ratio the X and A atoms together can form a close-packed array, provided they are of about the same size. The conditions for forming such structures are particularly favourable for K and F and for Cs and Cl, so that in all the following compounds the alkali and halogen atoms are close-packed :



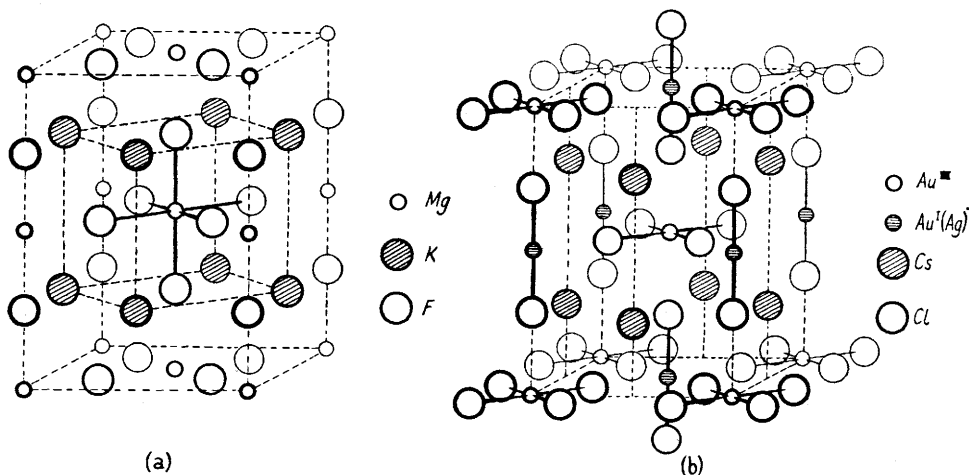
From the geometrical standpoint, the structures of  $\text{KMgF}_3$ ,  $\text{K}_2\text{SiF}_6$ , and  $\text{Cs}_2\text{Tl}_2\text{Cl}_9$  differ only in the proportions and arrangement of octahedral holes which are occupied by the more highly charged positive ions, leading in the last two cases to finite  $(\text{SiF}_6)^{2-}$  and  $(\text{Tl}_2\text{Cl}_9)^{3-}$  ions respectively. In the perovskite structure of  $\text{KMgF}_3$  no discrete complex ions exist; it is to be regarded as an

FIG. 6.



Two modes of distortion of an octahedral co-ordination group  $\text{BX}_6$ , (a), to give (b) a pyramidal molecule  $\text{BX}_3$ , and (c) a planar  $\text{BX}_4$  group.

FIG. 7.

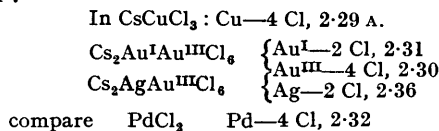


(a) The perovskite structure of  $\text{KMgF}_3$ , with octahedral  $\text{MgF}_6$  co-ordination groups; (b) the structure of  $\text{Cs}_2\text{Au}^{\text{I}}\text{Au}^{\text{II}}\text{Cl}_6$  with linear  $\text{Au}^{\text{I}}\text{Cl}_2$  and planar  $\text{Au}^{\text{II}}\text{Cl}_4$  groups.

infinite 3-dimensional array of  $\text{K}^+$ ,  $\text{Mg}^{2+}$  and  $\text{F}^-$  ions. For atoms which do not form six octahedral bonds these simple close-packed structures are not possible, and we find interesting variants for  $\text{Cs}_3\text{As}_2\text{Cl}_9$  (Hoard and Goldstein, *J. Chem. Physics*, 1935, **3**, 117),  $\text{CsCuCl}_3$ , and  $\text{CsAuCl}_3$ . These illustrate three different ways of distorting an octahedral co-ordination group to give less than six nearest neighbours (Figs. 6 and 7), viz., 3 pyramidal (in  $\text{Cs}_3\text{As}_2\text{Cl}_9$ ), 4 planar (in  $\text{CsCuCl}_3$ ), and 4-planar or 2 linear neighbours (in  $\text{Cs}_2\text{Au}^{\text{I}}\text{Au}^{\text{II}}\text{Cl}_6$ ). In  $\text{CsCuCl}_3$  all the  $\text{Cu}^{\text{II}}$



atoms are equivalent and are surrounded by 4 Cl in a plane. The gold compound, although having a similar empirical formula, is of a different kind, containing Au<sup>I</sup> and Au<sup>III</sup> atoms in equal numbers. Just as CsCuCl<sub>3</sub> adopts a distorted version of an idealised hexagonal close-packed structure, so the gold compound has a distorted version of the perovskite structure (Elliott and Pauling, *J. Amer. Chem. Soc.*, 1938, **60**, 1846). The distortion is of such a nature as to give Au<sup>I</sup> two nearest neighbours (linear Au<sup>I</sup> bonds) and Au<sup>III</sup> four nearest neighbours (4 square Au<sup>III</sup> bonds), as shown in Fig. 7, (a) and (b). The mixed halide Cs<sub>2</sub>AgAu<sup>III</sup>Cl<sub>6</sub> has the same structure. The bond lengths in the (CuCl<sub>4</sub>), (Au<sup>I</sup>Cl<sub>2</sub>), (Au<sup>III</sup>Cl<sub>4</sub>), and (AgCl<sub>2</sub>) groups in these closely related structure are very similar:



We may summarise the crystal chemistry of these complex halides in the scheme below.

*Crystal structures of complex halides ABX<sub>3</sub> with close-packed A and X atoms.*

|  |   |  |
|--|---|--|
|  |   | <i>Distorted perovskite structure.</i>   |
|  | BX <sub>6</sub> regular octahedral co-ordination  | Cs <sub>2</sub> Au <sup>I</sup> Au <sup>III</sup> Cl <sub>6</sub> $\left\{ \begin{array}{l} \text{Au}^{\text{I}}\text{Cl}_2 \text{ linear} \\ \text{Au}^{\text{III}}\text{Cl}_4 \text{ planar.} \end{array} \right.$               |
| <i>Cubic close-packing</i>                   | K <sub>2</sub> SiF <sub>6</sub> structure<br><i>Perovskite structure</i><br>KMgF <sub>3</sub> | BX <sub>3</sub> pyramidal<br>Cs <sub>3</sub> As <sub>2</sub> Cl <sub>9</sub> structure   |
|  | Fig. 3, structures<br>(3), (4), (5)   |  |
| <i>(More complex types of close-packing)</i> | intermediate between perovskite structure and structure (1), below                            |  |
| <i>Hexagonal close-packing</i>               | Structure (1), Fig. 3   | BX <sub>6</sub> octahedral but slightly distorted owing to formation of B <sub>2</sub> X <sub>9</sub> ion<br>Cs <sub>3</sub> W <sub>2</sub> Cl <sub>9</sub> structure<br>Cs <sub>3</sub> Tl <sub>2</sub> Cl <sub>9</sub> structure |
|  |   | BX <sub>4</sub> planar<br>CsCuCl <sub>3</sub> structure  |

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