

THE CRYSTAL STRUCTURES OF SALT HYDRATES AND COMPLEX HALIDES

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Introduction

At different stages in the development of chemistry various compounds or groups of compounds have appeared to be anomalous, as regards either their formulæ or properties. When the appropriate advance has been made in, say, the theory of interatomic forces, or when a new technique has led to further information about the relative positions of atoms, it has become evident that the "anomalies" were simply indications of an inadequate understanding of the structures of the compounds, in the widest meaning of the word structure.

We propose to discuss here two groups of compounds, salt hydrate and complex halides, the formulæ of many of which were for a long time difficult to understand. Examples of such "anomalous" compounds were listed by Sidgwick,^{1a} and many others could have been added. In order to see why it was difficult to formulate these compounds it will be necessary to indicate briefly the ideas about the structures of inorganic compounds which were current some thirty years ago. We shall then outline the present state of our knowledge of the structures of some of these compounds.

Werner's Co-ordination Theory.—During the first quarter of the present century discussion of the structures of complex inorganic compounds was dominated by the co-ordination theory of Alfred Werner. This was first put forward in 1891 and developed more fully in 1893 and later in "Neuere Anschauungen auf dem Gebiete der anorganischen Chemie" (1st edition, Vieweg, Brunswick, 1905). It had been known for a long time that ammonia, ethylenediamine, and other molecules unite with many metallic salts to form compounds which in some cases are extraordinarily stable. Two features of this type of combination are: (1) the molecule combining with the salt is itself a stable molecule, and (2) various numbers of, for example, ammonia molecules can combine with cobaltic chloride, platinum chloride, etc., to give series of well-defined amines. Platinum chloride combines in this way with six, five, four, three, or two ammonia molecules to give a series of compounds $\text{PtCl}_4 \cdot n\text{NH}_3$. Werner formulated these compounds in the following way: $[\text{Pt}(\text{NH}_3)_6]\text{Cl}_4$, $[\text{Pt}(\text{NH}_3)_5\text{Cl}]\text{Cl}_3$, $[\text{Pt}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}_2$, $[\text{Pt}(\text{NH}_3)_3\text{Cl}_3]\text{Cl}$, and $\text{Pt}(\text{NH}_3)_2\text{Cl}_4$, grouping six atoms or groups around the metal atom in the first "co-ordination sphere" and the remainder in the second sphere. Measurements of molecular conductivity

¹ (a) Sidgwick, "Electronic Theory of Valency", Clarendon Press, Oxford, 1927; (b) Lewis, *J. Amer. Chem. Soc.*, 1916, **38**, 762; (c) Pfeiffer, "Organische Molekulverbindungen", 2nd edn., Enke, Stuttgart, 1927.

showed that in the case of the first four compounds the chlorine in the second sphere ionises leaving ions $[\text{Pt}(\text{NH}_3)_n\text{Cl}_{6-n}]^{2-n}$, and that the last compound is a non-electrolyte.

The fundamental feature of Werner's theory was the grouping of a number of atoms or groups, usually four or six, around the central atom, these being attached by non-ionisable linkages. The charge on the complex ion depends on the number of neutral molecules (ammonia, water, etc.) in the co-ordination group. In $\text{PtCl}_4\cdot 6\text{NH}_3$ all six ammonia molecules are in the first co-ordination group and the ion $[\text{Pt}(\text{NH}_3)_6]^{4+}$ carries a charge equal to the valency of the platinum in the original salt. As ammonia is replaced by chlorine in the co-ordination group so the charge on the complex ion falls until the non-ionisable $\text{Pt}(\text{NH}_3)_2\text{Cl}_4$ is reached. Further replacement of ammonia by chlorine gives the anions $[\text{Pt}(\text{NH}_3)\text{Cl}_5]^-$ and $[\text{PtCl}_6]^{2-}$. The co-ordination number of the metal atom bears no relation to its periodic group, being six not only for platinum(IV) and cobalt(III) but also for chromium or aluminium.

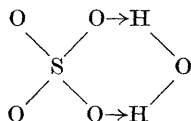
As to the stereochemistry of the co-ordination complexes, Werner assumed that six groups would be arranged in the most symmetrical way possible, at the apices of an octahedron, an arrangement which was consistent with the resolution into optical isomers of an ion such as $[\text{Co}(\text{C}_2\text{O}_4)_3]^{3-}$. The arrangement of four atoms around carbon was known to be tetrahedral and this was a likely arrangement also in many co-ordination complexes, though Werner showed that in the four-co-ordinated complexes of bivalent platinum the existence of two geometrical isomers of compounds $\text{Pt}a_2b_2$ indicated a square planar rather than a tetrahedral configuration.

The Early Electronic Theory of Valency.—The next step towards an understanding of co-ordination compounds was the suggestion that both the electrons for an electron-pair bond could come from one of the atoms (Lewis,^{1b} 1916). Provided that one of the atoms possessed one or more pairs of unshared electrons and that the valency group of the "acceptor" atom could expand, then a co-ordinate link could be formed. The number of such bonds was not determined, like that of ordinary covalent bonds, by the periodic group to which the element belonged. Sidgwick was then led to enunciate his "covalency rule", which expressed the fact that the size of the valency group (or the number of covalent bonds which an atom can form) is subject to limits which depend on its position in the periodic table but not on the group to which it belongs. He concluded that these maximum covalencies were: hydrogen, 2; elements of the first short period, 4; elements of the second short period, 6; heavier elements (rubidium onwards), 8.

The evidence for the two-covalency of hydrogen was the association of water and hydroxy-compounds generally, the association of hydrogen fluoride, and the formation of the $(\text{HF}_2)^-$ ion. All such cases are now described in terms of hydrogen bonds (bridges). Sidgwick observed that "there is no indication of any limit in the periodic table to the odd as there is to the even covalencies", that even covalencies are much more frequent than odd ones, and that in Werner co-ordination compounds even co-ordination

numbers were to be expected. While it was possible to formulate satisfactorily a very large number of compounds, some presented difficulty. Examples are :

Hydrates.—(a) *Containing odd numbers of molecules of water of crystallisation.* Werner noted the frequent occurrence of tetra- and hexa-hydrates, but it was difficult to understand the formation of, for example, $\text{BaCl}_2 \cdot \text{H}_2\text{O}$, $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$, $\text{LiClO}_4 \cdot 3\text{H}_2\text{O}$, $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, and so on. Sidgwick suggested that hydration of the anion was the reason for the odd numbers of molecules of water of crystallisation in the formulæ of some hydrated metallic sulphates,



the water forming a six-membered ring, but it was obviously difficult to account for all "odd" hydrates in this way. (b) *Containing too many molecules of water of crystallisation to permit formulation as a normal Werner co-ordination compound.* Sidgwick observed that although the formulæ of the great majority of hydrated salts "do not contain more water than is compatible with the covalency rule, if we allow for the hydration of certain anions" there is nevertheless a considerable number of salts which contain more water molecules than can be accounted for in this way. Instead of admitting co-ordination numbers of 8 and 12, as Pfeiffer^{1c} had done, Sidgwick preferred Werner's view that either the water molecules associated in pairs and that each pair occupied only one co-ordination position, or that there were crystalline aggregates composed of two or more molecules. He concluded that "the occurrence of double water molecules attached by single covalencies to the cation is at least probable", and the following are examples of octa- and dodeca-hydrates which could then be reconciled with the covalency rule: $[\text{Be}(\text{H}_2\text{O})_8]\text{PtCl}_6$; $[\text{Mg}(\text{H}_2\text{O})_{12}]\text{Cl}_2(\text{ClO}_3)_2$; $[\text{Mg}(\text{H}_2\text{O})_8]\text{Cl}_2$; $[\text{Zn}(\text{H}_2\text{O})_{12}](\text{ClO}_3)_2$. By assuming hydration of the anion, further hydrates could be formulated: $[\text{Mg}(\text{H}_2\text{O})_8](\text{Br}, \text{H}_2\text{O})_2$ for $\text{MgBr}_2 \cdot 10\text{H}_2\text{O}$ and $[\text{Al}(\text{H}_2\text{O})_{12}]_2(\text{SO}_4, \text{H}_2\text{O})_3$ for $\text{Al}_2(\text{SO}_4)_3 \cdot 27\text{H}_2\text{O}$.

While we may say that these ideas are no longer acceptable we should add that very little more is known today of the structures of these groups of compounds than was known twenty-five years ago. (c) *Of the metallic fluorides.* The almost invariable hydration of fluorides, even when the cation is one which is not normally hydrated (e.g., $\text{KF} \cdot 2\text{H}_2\text{O}$ and $\text{AgF} \cdot 2\text{H}_2\text{O}$ or $\text{AgF} \cdot 4\text{H}_2\text{O}$) seemed to suggest hydration of the fluoride ion. This appeared anomalous because hydration was regarded as being due to formation of covalent (co-ordinate) links, and the small, electronegative fluorine should show less tendency than the other halogens to form covalent bonds. Now that we associate hydration with the formation of hydrogen bonds which are essentially electrostatic in nature the hydration of fluorides presents no difficulty.

Complex Halides.—Here again we should expect to find many compounds which could be formulated as simple co-ordination compounds, and in fact

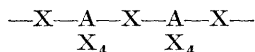
the number of complex halides of the types $A_m[BX_4]_n$ and $A_p[BX_6]_q$ which are known must be very large. As in the case of hydrates, however, there are many complex halides with apparently anomalous formulæ, *e.g.*, $KHgI_3$, Cs_3CoCl_5 , K_4RuCl_7 , and so on. Sidgwick regarded the compound $KHgI_3$ as intermediate between HgI_2 and K_2HgI_4 , containing a complex $[HgI_3]^-$ in which mercury is forming three covalent bonds. He was, however, careful to point out that "it cannot always be assumed that a 'double salt' really contains a complex molecule" and suggested that a salt like $K_{15}TaF_{20}$, for example, could well be a "crystalline aggregate" of, say, $K_3[TaF_8]$ and $12KF$.

Before proceeding to the description of the structures of salt hydrates and complex halides it will be convenient to make some more general observations about the meaning of the empirical formulæ of crystalline solids.

The Chemical Formulæ of Crystalline Solids

Three factors have had a profound effect on the development of structural chemistry; the importance of the study of gases in the early years of modern chemistry, the successful development of structural organic chemistry, and the fact that the study of the solid state became possible only in recent times. As a result chemists became accustomed to thinking in terms of finite groups of atoms, the molecules and complex ions which had been studied intensively for a century before the discovery of the diffraction of X-rays by crystals. After chemical analysis had established the relative numbers of atoms of different kinds in a substance and the molecular weight had been determined in solution or in the vapour state, the next stage was to visualise the arrangement of appropriate numbers of atoms of different elements in a finite group.

The results of the study of atomic arrangement in crystals emphasised the importance of infinite as well as finite groups of atoms. A molecule or complex ion with the empirical composition AX_5 is not necessarily a finite group of six atoms, for this composition may arise in other ways: (a) octahedral AX_6 groups joined into infinite linear arrangements by sharing two X atoms:



(b) equal numbers of AX_4 and AX_6 groups, (c) AX_4 groups and an equal number of X atoms (ions).

Similar considerations apply to any grouping AX_n , and in general the number of ways of realising a particular ratio of X to A atoms is greater the smaller the value of n . The composition AX_3 , for example, can arise not only in a variety of finite groups but also from arrangements extending indefinitely in one, two, or three dimensions. Some of these are set out on page 385 and illustrated in Fig. 1. We shall refer later to some of these examples.

It will now be evident that the chemical formula of a crystalline compound should not be discussed without reference to the crystal structure.

In the examples below the composition AX_3 results from atomic arrangements in which the A atom is attached to three, or two and four, or four, or six X atoms. It is therefore not profitable to discuss the electronic

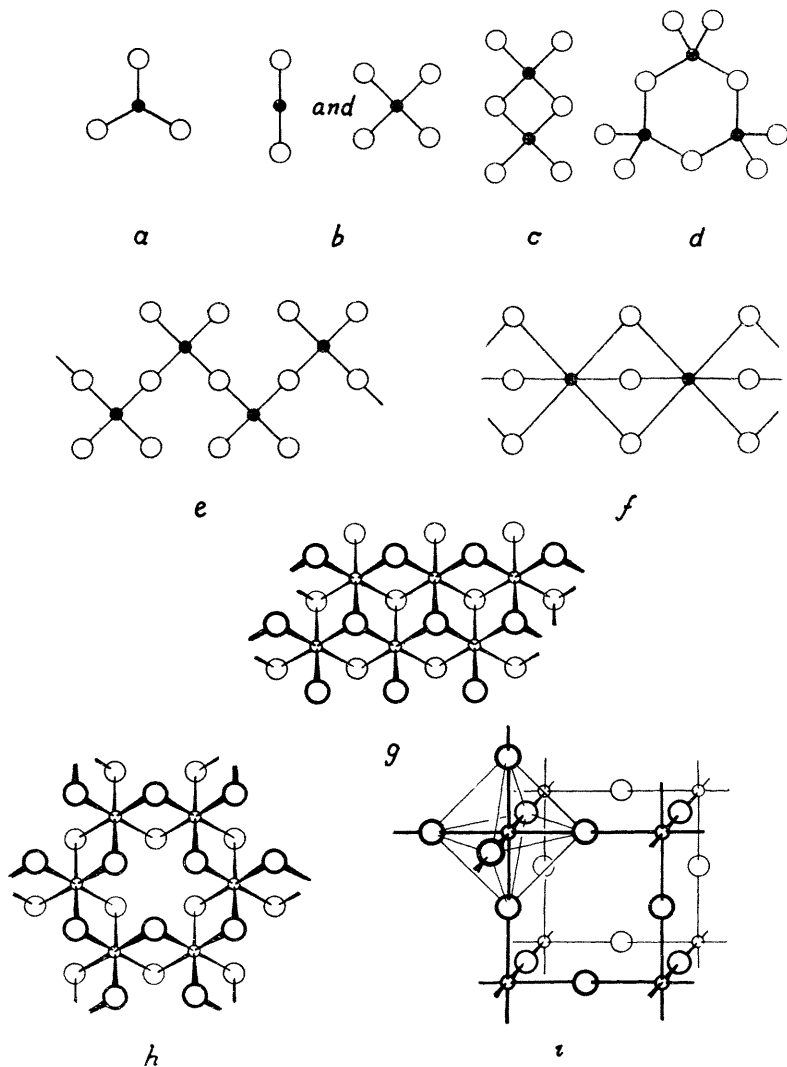


FIG. 1

Some ways of realising a ratio of $3X:A$ in finite or infinite groupings of atoms.

structure of an atom A in a group AX_3 until we know how many X atoms are actually attached to A. This simple geometrical analysis also shows that odd values of n in AX_n can arise from atomic arrangements in which either odd or even numbers of X atoms are attached to each A atom, and

<i>Type of complex</i>	<i>Examples</i>
(a) Finite group AX_3	BO_3^{3-} and other ions
(b) Equal numbers of AX_2 and AX_4	$AuCl_2^-$ and $AuCl_4^-$ in $CsAuCl_3$
(c) Finite group A_2X_6	Au_2Br_6 , Al_2Cl_6 , Fe_2Cl_6
(d) Cyclic systems of AX_4 groups	S_3O_9 , $Si_3O_9^{6-}$ in $CaSiO_3$
(e) Infinite linear systems of AX_4 groups sharing $2X$	$CuCl_3^-$ in $CsCuCl_3$, SiO_3^{2-} in $CaSiO_3$
(f) Infinite linear systems of octahedral AX_6 groups sharing a pair of opposite faces	$Li(H_2O)_3$ system in $LiClO_4 \cdot 3H_2O$
(g) Infinite double row of octahedra AX_6	$CdCl_3^-$ in NH_4CdCl_3
(h) Infinite two-dimensional system of octahedra AX_6 sharing three edges	$CrCl_3$ layer structure
(i) Infinite three-dimensional structure formed from AX_6 octahedra each sharing corners with six others	ReO_3 structure

it suggests that many of the supposedly anomalous formulæ appeared anomalous only because these geometrical points were not taken into account.

We are now in a position to review the structures of crystalline salt hydrates and complex halides. It is interesting to note, in passing, that many of the compounds mentioned by Sidgwick as having "awkward" formulæ (including those with excessive hydration that have already been listed) have not yet been examined by the X-ray crystallographer, though sufficient is now known of these groups of compounds to establish the general principles underlying their structures.

The Crystal Structures of Salt Hydrates

The Behaviour of the Water Molecule in Crystals.—The behaviour of water in many crystals can be understood in terms of the simple electrostatic model of the water molecule described by Bernal and Fowler in 1933.² Spectroscopic studies of the vapour show that the O-H bond length is 0.958 \AA and that the angle \widehat{HOH} is $104^\circ 31'$. The infra-red and Raman spectra of water vapour and ice show that the vibration frequencies of the water molecule vary very little with change of state and since the O-O distance in ordinary ice is 2.76 \AA we may assign to the water molecule a radius of 1.38 \AA , the hydrogen nuclei being at distances of about 1 \AA from the centre of the molecule. Bernal and Fowler accounted for the dipole moment of the molecule and for the heat of vaporisation of ice by assuming the presence of net effective charges of $+\frac{1}{2}e$ on each hydrogen atom and $-e$ on the oxygen atom. Since each water molecule in ice is surrounded tetrahedrally by four others it may be regarded as having a tetrahedral charge distribution as shown in Fig. 2.

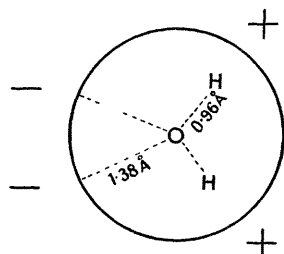


FIG. 2

The structure of the water molecule.

This picture of the water molecule is consistent with its environment in

² Bernal and Fowler, *J. Chem. Phys.*, 1933, 1, 515.

many crystals. Not only can water molecules be linked to other water molecules by hydrogen bonds, which are essentially electrostatic in nature, to form in the limit the various types of ice³ and the ice-like hydrates of the rare gases, but they can attach themselves to the cations of the more electro-positive elements by electrostatic bonds and also to fluoride ions or the oxygen atoms of oxy-ions by hydrogen bonds. There is accordingly a number of possibilities for the environment of a water molecule in a crystal ranging from (a), Fig. 3, where it is surrounded entirely by water molecules, through (b), where it is surrounded partly by water molecules and partly by cations or anions, to (c), where its neighbours are all of the latter sort. In Fig. 3 a shaded circle represents either a singly-charged OH^- or F^- ion or an

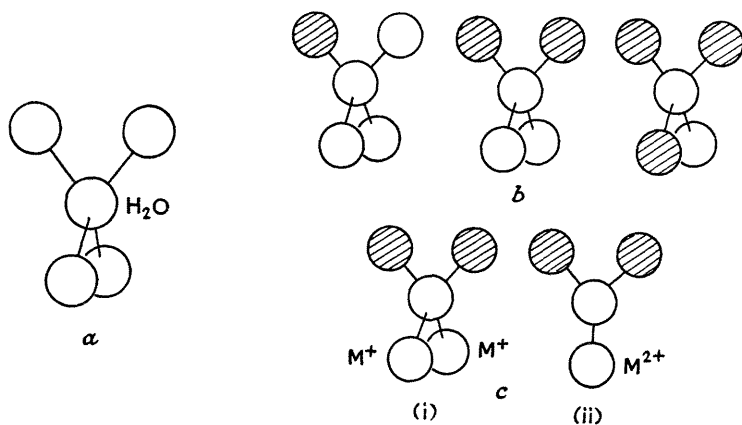


FIG. 3

Environments of water molecules in crystals. Shaded circles represent oxygen atoms of oxy-ions, or OH^- or F^- ions.

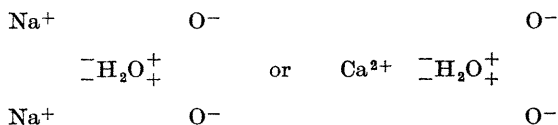
oxygen atom of an oxy-ion, this being either a finite ion (SO_4^{2-} , NO_3^- , etc.) or one of the 1-, 2-, or 3-dimensional oxy-ions such as occur in, for example, silicates or aluminosilicates.⁴ It must be supposed that one of the positive regions of a water molecule is directed towards a negative ion (or the negative region of an adjacent water molecule) and the negative regions towards neighbouring positive ions or the positive regions of adjacent water molecules.

The limit of the linking of SiO_4 tetrahedra, when each is joined to four others by sharing all its oxygen atoms, is reached in the polymorphs of silica itself. If some of the silicon atoms are replaced by aluminium three-dimensional charged frameworks are possible (three-dimensional oxy-ions), and the positive ions necessary for electrical neutrality are accommodated in the holes in the frameworks. Some framework silicates [*e.g.*, feldspars,

³ Owston, *Quart. Reviews*, 1951, **5**, 344.

⁴ Bragg, "The Atomic Structure of Minerals", Cornell Univ. Press and Oxford Univ. Press, 1936.

KAlSi_3O_8 , $\text{CaAl}_2\text{Si}_2\text{O}_8$] are anhydrous ; others [*e.g.*, zeolites $\text{NaAlSi}_2\text{O}_6 \cdot \text{H}_2\text{O}$, $\text{BaAl}_2\text{Si}_3\text{O}_{10} \cdot 4\text{H}_2\text{O}$] are hydrated. In the latter the water molecules take up definite positions within the frameworks so that each has an environment consistent with its tetrahedral charge distribution, for example :



the O^- ions being oxygen atoms of the $(\text{Si,Al})_n\text{O}_{2n}$ framework.

At the other end of the scale we have the ice-like hydrates formed by the inert gases, chlorine, carbon dioxide, methyl chloride, and many other molecules.⁵ The structure of ice-I represents one of the simplest ways of linking water molecules so that each is linked, by hydrogen bonds, to four others, and the structure is relatively compact. There is, however, an indefinite number of more complex four-connected frameworks,⁶ of which the (Si,Al) frameworks of aluminosilicates are examples. Provided that these can be realised with tetrahedral interbond angles they also represent possible ways of linking up water molecules to form more open "ice-like" structures which, however, will not be stable unless the voids (or some of them) are occupied. The structures proposed for the hydrates with formulæ approximating to $\text{M},6\text{H}_2\text{O}$ or $\text{M},8\text{H}_2\text{O}$ and $\text{M},17\text{H}_2\text{O}$ are of this kind. In the first structure there are 46 water molecules in the unit cell, which contains two small and six rather larger holes. If all the voids are filled, as is probably the case with argon and small molecules like H_2S , this corresponds to $46/8 = 5\frac{3}{4}$ water molecules per molecule M ; in chlorine hydrate only the larger holes are occupied, giving the formula $\text{Cl}_2 \cdot 7\frac{2}{3}\text{H}_2\text{O}$. In the second structure the much larger unit cell contains 136 water molecules and in this cell also there are holes of two sizes, sixteen smaller and eight larger. Filling of the larger holes only gives a ratio of $136/8 =$ seventeen water molecules per molecule of methyl iodide, chloroform, etc., but it appears that molecules of two quite different sizes can be accommodated, each in the holes of appropriate size, accounting for the existence of mixed hydrates such as $\text{CHCl}_3 \cdot 2\text{H}_2\text{S} \cdot 17\text{H}_2\text{O}$. This structure is illustrated in Fig. 4.

The cases set out in Fig. 3, (b) and (c), are typical of the environment of water molecules in crystals of hydrated oxy-salts and $\text{KF} \cdot 2\text{H}_2\text{O}$. (The only other hydrated simple fluoride which has been studied is $\text{AlF}_3 \cdot \frac{1}{2}\text{H}_2\text{O}$ —see p. 394.) As regards its immediate environment, the behaviour of the water molecule in hydrated chlorides is less easy to interpret, and we shall therefore deal separately with these compounds.

We should perhaps mention that it is possible to adopt a purely geometrical classification of hydrates,⁷ grouping them according to whether the water

⁵ Stackelberg, *Naturwiss.*, 1949, **36**, 327 ; *J. Chem. Phys.*, 1951, **19**, 1319 ; Claussen, *ibid.*, p. 259, 662, 1425 ; Pauling and Marsh, *Proc. Nat. Acad. Sci.*, 1952, **38**, 112.

⁶ Wells, *Acta Cryst.*, 1954, **7**, 545.

⁷ Bernal, *J. Chim. phys.*, 1953, **50**, C1.

molecules are (i) discrete water molecules or forming parts of isolated co-ordination groups, (ii) arranged along lines, (iii) situated in layers, or (iv) forming a continuous three-dimensional system extending throughout the crystal. This classification is not entirely satisfactory if we wish to discuss the behaviour of the water molecule. For example, $\text{LiClO}_4 \cdot 3\text{H}_2\text{O}$ is then described as an example of (ii) since there are columns of water molecules arranged around the lithium ions. However, the tetrahedral charge distribution of a water molecule is satisfied by an environment of the type of Fig. 3 (c) and not by attractions to other water molecules in the $(\text{Li}, 3\text{H}_2\text{O})$ columns (see p. 391). In $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ the water molecules are arranged in

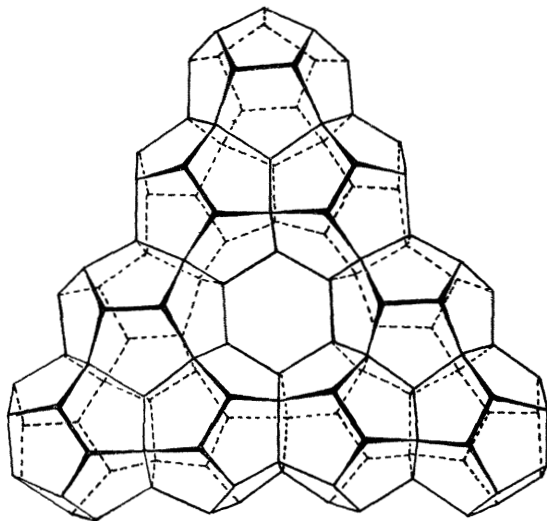


FIG. 4

Part of the water framework in the structure proposed for a hydrate $\text{M}, 17\text{H}_2\text{O}$, shown as a packing of pentagonal dodecahedra. At the centre can be seen part of one of the larger holes.

layers, placing this crystal in class (iii), but there are no $\text{H}_2\text{O}-\text{H}_2\text{O}$ interactions within the "layers" of water molecules, the immediate environment of which is again of the type of Fig. 3 (c). The genuine cases intermediate between (i) and (iv) would be structures in which water molecules were linked by two or three O-H-O bonds to other water molecules to form aquo-chains or -layers. The water layers in some hydrated clay minerals may be of the latter type, but among the hydrates of simple inorganic salts there are no examples of extended systems of water molecules linked by hydrogen bonds.

Hydrates of Oxy-salts.—It is perhaps unnecessary to remark that the presence of H_2O in the formula of a compound does not necessarily imply the presence of water molecules. It has been known for a long time that the "monohydrate" of alumina is actually $\text{AlO}(\text{OH})$, but X-ray studies are still leading to the reformulation of compounds originally thought to be hydrates

of meta- or pyro-salts. Examples are :

$\text{Na}_2\text{H}_2\text{Sb}_2\text{O}_7 \cdot 5\text{H}_2\text{O}$	is ⁸	$\text{Na}[\text{Sb}(\text{OH})_6]$
$\text{Mg}(\text{SbO}_3)_2 \cdot 12\text{H}_2\text{O}$	is ⁹	$\text{Mg}[\text{Sb}(\text{OH})_6]_2 \cdot 6\text{H}_2\text{O}$
$\text{LiSbO}_3 \cdot 3\text{H}_2\text{O}$	is	$\text{Li}[\text{Sb}(\text{OH})_6]$
$\text{Cu}(\text{NH}_3)_3(\text{SbO}_3)_2 \cdot 9\text{H}_2\text{O}$	is	$[\text{Cu}(\text{NH}_3)_3(\text{H}_2\text{O})_3][\text{Sb}(\text{OH})_6]_2$
$\text{NaBO}_2 \cdot \text{NaCl} \cdot 2\text{H}_2\text{O}$	is ¹⁰	$\text{Na}_2\text{B}(\text{OH})_4\text{Cl}$

In a crystalline anhydrous oxy-salt the metal ions are necessarily surrounded entirely by oxygen atoms of oxy-ions. It might have been expected that in hydrates $\text{M}_x\text{R}_y \cdot n\text{H}_2\text{O}$ (where R is an oxy-ion) the nature of the co-ordination group around M would depend in a simple way on the value of n , and that three cases would be recognisable : (i) if n is less than the co-ordination number of M, M surrounded partly by H_2O , partly by oxygen atoms of oxy-ions, (ii) n is equal to the co-ordination number of M, M surrounded entirely by water molecules, and (iii) n is greater than the co-ordination number of M, all M ions fully hydrated and additional water held between $\text{M}(\text{H}_2\text{O})_m$ groups and oxy-ions. When the ratio of the number of water molecules to cations is equal to the co-ordination number of M (case (ii)) the structures are in fact particularly simple, the crystal being an assembly of $\text{M}(\text{H}_2\text{O})_m$ groups and oxy-ions. In (i), however, the situation is not as simple as stated above. First, it is possible for the metal ions to be completely surrounded by water molecules when n is less than the co-ordination number of M if water molecules are shared between two M ions. This has been illustrated in Fig. 1 (f) for $\text{LiClO}_4 \cdot 3\text{H}_2\text{O}$, to which we refer shortly. Secondly, even when n is less than the co-ordination number of M all the water molecules do not necessarily congregate around the M ions, but some may be accommodated like the "excess" of water in (iii).

As regards the behaviour of the water molecules we may therefore recognise two classes of the water salt hydrate :

Class I : all water molecules attached to at least one metal ion, as in Fig. 3 (c). For lower hydrates the co-ordination group around the cation may be composed partly of water and partly of oxygen atoms of oxy-ions, or it may (as in $\text{LiClO}_4 \cdot 3\text{H}_2\text{O}$) consist entirely of water molecules ; this depends on the geometry of the cation-water complex. When the ratio of water molecules to M ions equals the co-ordination number of M there is sufficient water to surround the M ions completely, forming discrete $\text{M}(\text{H}_2\text{O})_m$ groups.

Class II : some water molecules are not adjacent to M ions but are held between oxy-ions and other water molecules. This class necessarily includes those hydrates in which the ratio of water molecules to M ions exceeds the co-ordination number of M but it also includes hydrates such as $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ and $\text{CdSO}_4 \cdot 2\frac{2}{3}\text{H}_2\text{O}$.

We shall now illustrate these points by referring briefly to the main

⁸ Schrewelius, *Z. anorg. Chem.*, 1938, **238**, 241.

⁹ Beintema, *Rec. Trav. chim.*, 1937, **56**, 931.

¹⁰ Fornaseri, *Periodica mineral.*, Rome, 1949, **18**, 103 (Structure Reports, 1949, **12**, 263).

features of the structures of the following hydrates : $\text{LiOH}\cdot\text{H}_2\text{O}$, $\text{Na}_2\text{CO}_3\cdot\text{H}_2\text{O}$, $\text{CaSO}_4\cdot 2\text{H}_2\text{O}$, $\text{LiClO}_4\cdot 3\text{H}_2\text{O}$, $\text{BeSO}_4\cdot 4\text{H}_2\text{O}$, $\text{CuSO}_4\cdot 5\text{H}_2\text{O}$, $\text{NiSO}_4\cdot 6\text{H}_2\text{O}$, $\text{NiSO}_4\cdot 7\text{H}_2\text{O}$ and $\text{Nd}(\text{BrO}_3)_3\cdot 9\text{H}_2\text{O}$.

Class I : All water molecules attached to at least one M ion

(a) n is less than the co-ordination number of M. As examples of monohydrates we have chosen those of lithium hydroxide¹¹ and sodium carbonate.¹² In the former each structural unit, Li^+ , OH^- , and H_2O , has four

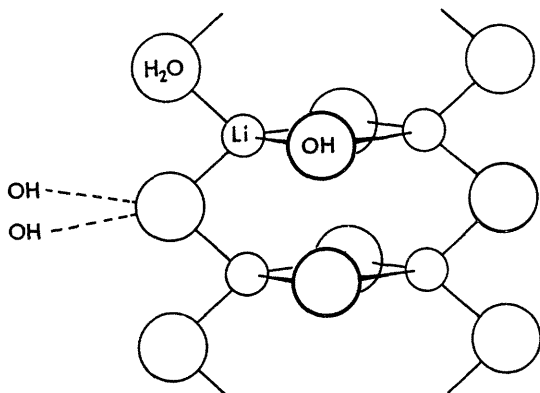


FIG. 5

Portion of one double chain in crystalline $\text{LiOH}\cdot\text{H}_2\text{O}$ (diagrammatic).

nearest neighbours. The lithium ions are surrounded by two hydroxyl ions and two water molecules and these tetrahedral co-ordination groups share an edge and two corners to form double chains (Fig. 5) which are held together laterally by hydrogen bonds between OH^- and H_2O . Each water molecule has four neighbours arranged approximately tetrahedrally, these being 2Li^+ and 2OH^- ions of (different) neighbouring chains.

The larger Na^+ ion is usually surrounded octahedrally by six neighbours

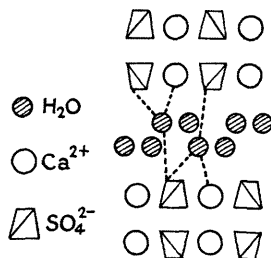


FIG. 6

The crystal structure of gypsum (diagrammatic).

in oxy-salts. In $\text{Na}_2\text{CO}_3\cdot\text{H}_2\text{O}$ the cations fall into two groups, half being surrounded by one water molecule and five oxygen atoms and half by two

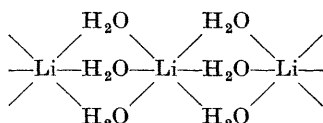
¹¹ Pepinsky, *Z. Krist.*, 1939, **102**, 119.

¹² Harper, *ibid.*, 1936, **95**, 266.

water molecules and four oxygen atoms of carbonate ions. Again the water molecule has four tetrahedral neighbours, two Na^+ ions and two oxygen atoms of carbonate ions.

In gypsum, $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$,¹³ the Ca^{2+} and SO_4^{2-} ions are packed in layers between which are arranged the water molecules. The attractive forces between the layers are hydrogen bonds between water molecules and sulphate ions (Fig. 6), each water molecule having as nearest neighbours one calcium ion and two oxygen atoms of sulphate ions. The relative weakness of the inter-layer bonding results in the good cleavage parallel to the plane of the layers.

A feature of the crystal structure of $\text{LiClO}_4 \cdot 3\text{H}_2\text{O}$ is the presence¹⁴ of columns of water molecules composed of octahedral groups sharing pairs of opposite faces. There is a lithium ion at the centre of each octahedral group and the perchlorate ions are situated between the columns. In Fig. 7 we show (in projection) one such column of composition $[\text{Li}(\text{H}_2\text{O})_3]_n^{n+}$:



and its three neighbouring ClO_4^- ions. All the atoms drawn as heavy circles are at the same height (0 and c), those drawn lightly are at $\pm c/2$, and the Li^+ ions are at $c/4$ and $3c/4$ above a reference plane. The tetrahedral charge distribution of the water molecule is again in evidence, each being in

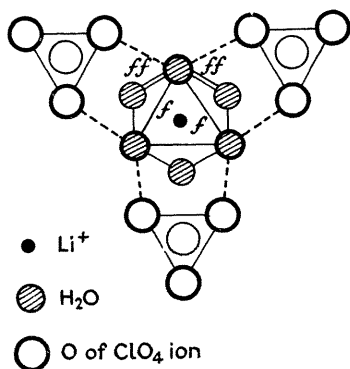


FIG. 7

Portion of the crystal structure of $\text{LiClO}_4 \cdot 3\text{H}_2\text{O}$, showing one $[\text{Li}(\text{H}_2\text{O})_3]_n^{n+}$ chain, viewed end-on, and three neighbouring ClO_4^- ions.

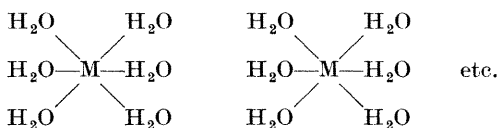
contact with two lithium ions (at 2.15 \AA) and with two oxygen atoms of ClO_4^- ions (at 2.94 \AA), these four neighbours being arranged tetrahedrally. It is also evident that each water molecule has six water molecules as neighbours (at 2.88 — 3.18 \AA) within a $[\text{Li}(\text{H}_2\text{O})_3]$ column (the contacts marked f in Fig. 7), but these are clearly not contacts between oppositely charged regions

¹³ Wooster, *Z. Krist.*, 1936, **94**, 375.

¹⁴ West, *ibid.*, 1934, **88**, 198.

of different water molecules. As shown by its immediate environment, which is of the type of Fig. 3 (c), the water molecule is behaving in the same way in $\text{LiClO}_4 \cdot 3\text{H}_2\text{O}$ as in $\text{LiOH} \cdot \text{H}_2\text{O}$ and in $\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$.

If instead of placing ions M^+ in all the octahedral holes in a water column we place ions M^{2+} in alternate holes we have the sequence



with discrete $[\text{M}(\text{H}_2\text{O})_6]^{2+}$ groups, and the compound is now a hexahydrate. The compounds $\text{M}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ (where M is Mg, Mn, Fe, Co, Ni, or Zn) have a structure¹⁵ related in this way to that of $\text{LiClO}_4 \cdot 3\text{H}_2\text{O}$, and it is interesting to note that the fluoroborates are isomorphous with the perchlorates.

(b) *n* is equal to the co-ordination number of M. Here the structural principles are very simple. The structure is a packing of discrete units of two kinds, M ions, surrounded by a complete shell of water molecules, and the oxy-ions. In $\text{BeSO}_4 \cdot 4\text{H}_2\text{O}$ the tetrahedral $[\text{Be}(\text{H}_2\text{O})_4]^{2+}$ and SO_4^{2-} ions are arranged¹⁶ in much the same way as the ions in the caesium chloride structure. Each water molecule is in contact with oxygen atoms of two sulphate ions so that its environment is of the type of Fig. 3 (c) (ii). In $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ ¹⁷ and in $\text{Zn}(\text{BrO}_3)_2 \cdot 6\text{H}_2\text{O}$ ¹⁸ there are octahedral $[\text{M}(\text{H}_2\text{O})_6]^{2+}$ groups, and in $\text{Nd}(\text{BrO}_3)_3 \cdot 9\text{H}_2\text{O}$ ¹⁹ the co-ordination group around M^{3+} is composed of six water molecules at the apices of a trigonal prism with three others beyond the mid-points of the three rectangular prism faces. [The octahydrates of SrO_2 and $\text{Sr}(\text{OH})_2$ presumably also fall into this class, but the published structures of these compounds are not entirely satisfactory and would repay further study.]

Class II : Some water molecules not attached to M^{n+} ions.—The simplest type of structure arises when *n* is greater than the co-ordination number of M, as in $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$.²⁰ Here there are octahedral $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$ groups, as in the hexahydrate, the seventh water molecule being held between these and the sulphate ions. The actual contacts made by the "odd" water molecule are three to water molecules of other $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$ groups and one to an oxygen atom of a sulphate ion.

In $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ ²¹ the metal ion is six-co-ordinated as in the hydrates of nickel sulphate, but although there are only five water molecules the fifth is not attached to a cation. Instead, the co-ordination group around the cupric ion is composed of four water molecules and two oxygen atoms of sulphate ions, and the fifth water molecule is held between water molecules attached to cations and oxygen atoms of sulphate ions (Fig. 8).*

¹⁵ West, *Z. Krist.*, 1935, **91**, 480.

¹⁶ Beevers and Lipson, *ibid.*, 1932, **82**, 297.

¹⁷ *Idem*, *ibid.*, 1932, **83**, 123.

¹⁸ Yü and Beevers, *ibid.*, 1936, **95**, 426.

¹⁹ Helmholz, *J. Amer. Chem. Soc.*, 1939, **61**, 1544.

²⁰ Beevers and Schwartz, *Z. Krist.*, 1935, **91**, 157.

²¹ Beevers and Lipson, *Proc. Roy. Soc.*, 1934, *A*, **146**, 570.

* Figs. 8, 10, 11, 12, and 13 are from the author's "Structural Inorganic Chemistry", 2nd edn., Clarendon Press, Oxford, 1950.

Our last example in this class is $\text{CdSO}_4 \cdot 2\frac{2}{3}\text{H}_2\text{O}$.²² The crystal structure of this hydrate is necessarily somewhat complex because of the unusual ratio of water to salt. There are two kinds of cadmium ions with slightly different environments, but all are octahedrally surrounded by two water molecules and four oxygen atoms of sulphate ions. There are four kinds of crystallographically non-equivalent water molecules and, of these, three-quarters

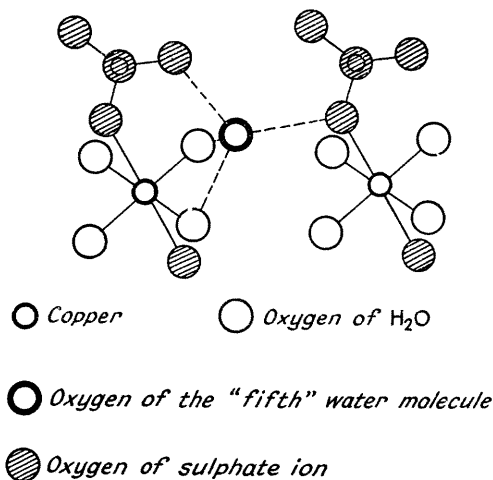
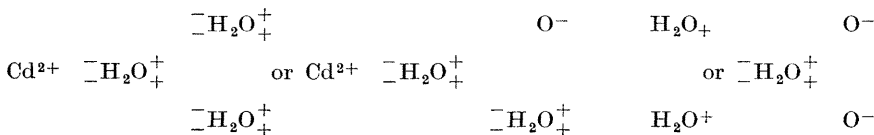


FIG. 8

Environment of the fifth water molecule in $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$.

are attached to a cation. The remaining water molecules have no contact with a metal ion, but have four neighbours, two other water molecules and two oxygen atoms of oxy-ions. It appears that the important point is the provision of three or four neighbours, which can be



It is well to remember that in the present state of our knowledge we are far from understanding why a hydrate with a formula so extraordinary as $\text{CdSO}_4 \cdot 2\frac{2}{3}\text{H}_2\text{O}$ should form at all; its structure and therefore its chemical formula represent a compromise between the requirements of Cd^{2+} , SO_4^{2-} and H_2O .

Hydrated Fluorides.—The fluorides of an element often differ from the other halides as regards their tendency to hydrate. In some cases the fluoride is anhydrous while the other halides form hydrates, as, for example, calcium fluoride and calcium chloride hexahydrate; in other cases the fluoride

²² Lipson, *Proc. Roy. Soc.*, 1936, A, 156, 462.

is the only hydrated halide at ordinary temperatures, for example, $\text{KF}\cdot 2\text{H}_2\text{O}$, $\text{AgF}\cdot 2\text{H}_2\text{O}$, and $\text{AgF}\cdot 4\text{H}_2\text{O}$, the other halides being anhydrous. Very little is known of the crystal structures of hydrated fluorides. It is stated that $\text{AlF}_3\cdot 3\frac{1}{2}\text{H}_2\text{O}$ loses water in stages on heating and that the last $\frac{1}{2}\text{H}_2\text{O}$ is removed only at red heat. As the result of an early X-ray study²³ a structure was proposed for AlF_3 and positions were suggested for these very firmly-held water molecules, but further study of this system would appear desirable.

The dihydrate of potassium fluoride has a simple structure²⁴ in which each potassium or fluoride ion is surrounded by two water molecules and four

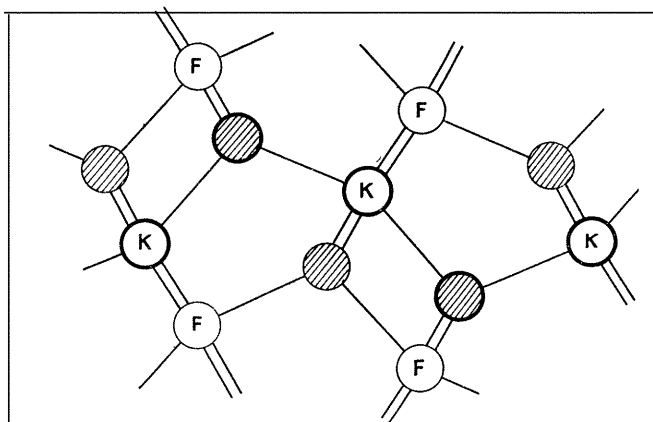


FIG. 9

Projection of the crystal structure of $\text{KF}\cdot 2\text{H}_2\text{O}$. Heavy circles represent atoms lying in the plane of the paper, light circles atoms lying in planes 2 Å above and below that of the paper. Shaded circles represent water molecules

ions of opposite sign at the apices of a slightly distorted octahedron, and each water molecule has two K^+ and two F^- neighbours, arranged tetrahedrally. A projection of the structure is shown in Fig. 9.

Hydrated Chlorides.—Owing to the small size and extreme electro-negativity of fluorine the structural chemistry of this halogen is very different from that of the other members of the family. Many crystalline fluorides are typical ionic structures while the chloride and other halides form layer or chain structures, and a similar difference is found between complex halides, as we shall see shortly. The differences between the hydrates of fluorides and other halides which have been noted above are due to the ability of fluorine, alone among the halogens, to form strong hydrogen bonds with water molecules. It is not possible to compare the crystal structures of the corresponding hydrates of fluorides and chlorides because in no case are the structures of such a pair of hydrates known. In the rather rare case where both the fluoride and the chloride of an element form hydrates there appear to be few pairs hydrated to the same degree, but there are a few such

²³ Ketelaar, *Z. Krist.*, 1933, **85**, 119.

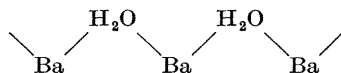
²⁴ Anderson and Lungafelter, *Acta Cryst.*, 1951, **4**, 181.

cases and it would be interesting to know the structures of, for example, $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ and $\text{FeF}_2 \cdot 4\text{H}_2\text{O}$ and of $\text{CoF}_2 \cdot 2\text{H}_2\text{O}$ to compare with that of $\text{CoCl}_2 \cdot 2\text{H}_2\text{O}$ (see p. 396).

In hydrated fluorides the tetrahedral character of water is expected to show itself, as it does in $\text{KF} \cdot 2\text{H}_2\text{O}$, but in hydrated chlorides the behaviour of water is less simple. The compounds stable at ordinary temperatures range from those of the more electropositive metals such as the alkaline earths to those of transition elements such as copper which form essentially covalent bonds with chlorine. In the first group the structure is an assembly of M^{2+} and Cl^- ions and H_2O molecules, and the forces holding these together in the crystal are essentially electrostatic. The water molecule is therefore surrounded by positive and negative ions and has an environment like it has in a hydrated fluoride or oxy-salt (cf. $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$, below). In the second group, where the metal-chlorine bonds have appreciable covalent character, the polarity of the water molecule as judged by its environment is less in evidence. Unfortunately, very few hydrated halides have been studied by the methods of X-ray crystallography, and we can only note here the main features of the crystal structures of a small number of these compounds. A satisfactory account of the crystal chemistry of this interesting group of compounds will not be possible until more structures have been determined.

As in the case of hydrated oxy-salts the simplest structures arise when each M^{n+} ion is completely hydrated and the structure is built of $[\text{M}(\text{H}_2\text{O})_n]$ groups and anions. Examples are $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ ²⁵ and $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$.²⁶ If the only factor determining the structure was the size of $[\text{Mg}(\text{H}_2\text{O})_6]^{2+}$ relative to that of Cl^- then we should expect $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ to adopt the fluorite structure, and in this structure each water molecule would be in contact with four chloride ions. In fact, the corresponding ammine, $\text{MgCl}_2 \cdot 6\text{NH}_3$, does crystallise with the fluorite structure, but the hydrate has a less symmetrical structure in which each water molecule is in contact with only two chloride ions. There is a somewhat similar difference between the structures of $\text{Al}(\text{NH}_3)_6\text{Cl}_3$ and $\text{Al}(\text{H}_2\text{O})_6\text{Cl}_3$. The former has the simple ionic YF_3 structure but the hexahydrate adopts a much more complex structure in which again every water molecule is adjacent to only two chloride ions. In these compounds the water molecule is clearly exhibiting its tetrahedral character.

Three hydrates of alkaline earth chlorides have been studied; they provide interesting examples of extended cation-water complexes. In barium chloride monohydrate, which has been studied by electron diffraction,²⁷ there are zig-zag chains



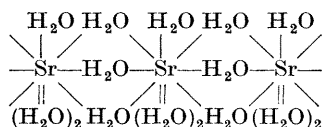
surrounded by chloride ions in such a way that the neighbours of a barium ion are seven chloride ions and two water molecules. It would appear that

²⁵ Andress and Gundermann, *Z. Krist.*, 1934, **87**, 345.

²⁶ Andress and Carpenter, *ibid.*, p. 446.

²⁷ Vajnštejn and Pinsker, *Zhur. Fiz. Khim.*, 1949, **23**, 1058 (Structure Reports, 1949, **12**, 160).

the water molecules are surrounded in a similar way by two barium ions and seven chloride ions, the nine neighbours being arranged in the same way as the nine water molecules around Nd^{3+} in $\text{Nd}(\text{BrO}_3)_3 \cdot 9\text{H}_2\text{O}$. There is a similar arrangement of nearest neighbours around the strontium ion in $\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$ ²⁸ but here the infinite cation-water complex is of the type



so that all nine neighbours of the strontium ion are water molecules.

Infinite two-dimensional cation-water complexes occur in the dihydrates of barium chloride ²⁹ and of strontium chloride. ³⁰ These hydrates have

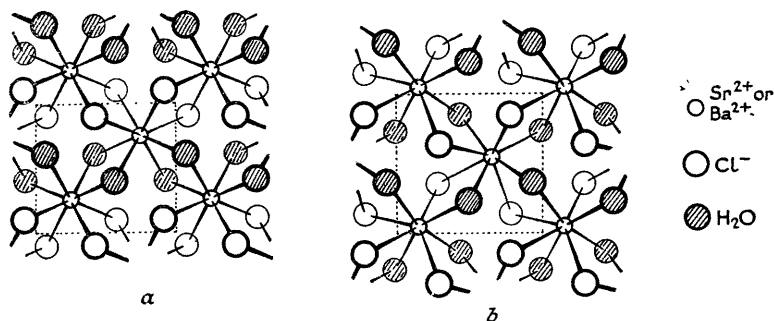
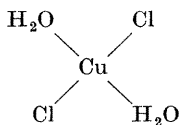


FIG. 10

Plans of layers in the crystal structures of (a) $\text{SrCl}_2 \cdot 2\text{H}_2\text{O}$ and (b) $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$. Atoms above or below the plane of the metal ions are shown as heavy or light circles respectively.

layer structures in which the metal ions are surrounded by four chlorine ions and four water molecules, though there is a somewhat different arrangement of nearest neighbours in the two structures (Fig. 10).

The structures of two hydrated halides of our second group have been studied, namely $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ ³¹ and $\text{CoCl}_2 \cdot 2\text{H}_2\text{O}$. ³² In the former there are discrete square planar groups with the *trans*-configuration



which are packed together in much the same way as the (non-polar) molecules in a crystal of, for example, naphthalene. The actual neighbours of a water molecule are the copper atoms of its own complex and four chlorine atoms of

²⁸ Jensen, *Kgl. Danske Videnskab. Selsk.*, 1940, **17**, Nr. 9.

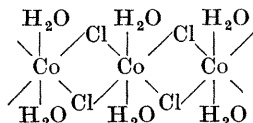
²⁹ *Idem, ibid.*, 1943, **20**, Nr. 5.

³⁰ *Idem, ibid.*, 1945, **22**, Nr. 3.

³¹ Harker, *Z. Krist.*, 1936, **93**, 136.

³² Vajnštejn, *Doklady Akad. Nauk S.S.S.R.*, 1949, **68**, 301 (Structure Reports, 1949, **12**, 161).

neighbouring groups. In $\text{CoCl}_2 \cdot 2\text{H}_2\text{O}$ there is linking of Co, Cl, and H_2O to form infinite linear groupings which also pack as separate units in the crystal :



Here again the nearest neighbours of a water molecule are the metal atom of its own complex and four chlorine atoms of neighbouring chains (in addition, of course, to four other chlorine atoms of its own octahedral $[\text{CoCl}_4(\text{H}_2\text{O})_2]$ co-ordination group. The same sort of environment of water is found in certain hydrated complex halides, suggesting that in compounds in which the metal-halogen bonds have appreciable covalent character the water molecule is not behaving in the same way as in the essentially ionic crystals such as $\text{KF} \cdot 2\text{H}_2\text{O}$ or $[\text{Mg}(\text{H}_2\text{O})_6]\text{Cl}_2$.

To sum up : we see that the attempt to formulate hydrates with finite aquo-complexes suggested by the analogy with Werner co-ordination compounds fails because in a crystalline material there is the possibility of cation-water complexes extending indefinitely in one, two, or three dimensions. Further, water can be held between such complexes and oxy-ions, so that it is not only unnecessary but erroneous to postulate the hydration of anions.

The Crystal Structures of Complex Halides

A great deal could be written on this subject, but our immediate concern here is to indicate how crystallographic studies have led to an understanding of the formulæ of these compounds, which exist only in the crystalline state. In this brief survey we shall deal first with complex fluorides and then with complex chlorides. This division into two classes is convenient for a number of reasons. The fluorides *in general* have structures different from those of complex chlorides, bromides, and iodides, and are typical ionic structures in which one (or both) of the ions has a high co-ordination number. We shall mention the structures of some complex fluorides formed by the alkali metals (and ammonium and thallium) with the following elements :

Al	Ti	V	Fe	Co	Ni	Mg
Y	Zr	Nb				Zn
La	Hf	Ta				

and the lanthanons and actinides (which contain incomplete *4f* and *5f* shells respectively) *i.e.*, we are concerned for the most part with elements of the A sub-groups, the first Group VIII triad, and the lanthanons and actinides.

Our second group will consist of complex chlorides of the alkali metals with those of B sub-group elements and certain of the heavier elements of Group VIII :

	Cu			
Pd	Ag	Cd		Sn
Pt	Au	Hg	Tl	Pb

Again generalising, we may say that those elements of the first group which form numerous stable complex fluorides do not form many stable complex

chlorides, and, conversely, the elements of the second group form few complex fluorides. The stability of complex halides appears to fall rapidly as we pass from chloride to bromide or iodide, relatively few of these last two classes of compounds being known to exist at ordinary temperatures.

One particular group of complex halides, namely A_2BX_6 , occupies a rather special position in that compounds of this type are formed by a considerable number of elements drawn from both the above groups. Moreover, these compounds adopt one (or both) of two closely related structures and although one structure is favoured by fluorides and the other by chlorides there is some overlap; in particular, K_2SiF_6 and $(NH_4)_2SiF_6$ are dimorphic.

K_2SiF_6 structure	. . .	$A_2BF_6(9)$, $A_2BCl_6(1)$
K_2PtCl_6 structure	. . .	$A_2BF_6(8)$, $A_2BCl_6(28)$, $A_2BBr_6(3)$, $A_2BI_6(2)$

The numerals in parentheses are the numbers of compounds known to crystallise with these structures.

These structures are very simple, consisting ideally of layers of composition AX_3 arranged in hexagonal or cubic close-packing with B atoms occupying one-half of the octahedral holes between six X atoms so that discrete BX_6 groups can be distinguished in the structure. The details of these structures are of more crystallographic than chemical interest and will not be discussed further, but we mention these compounds here because they form a link between our two classes of complex halide.

Complex Fluorides.—It will be convenient to deal with these in five groups.

(a) *Complex fluorides with structures geometrically the same as those of simple halides.* In crystalline CaF_2 (fluorite structure) each calcium ion is surrounded by eight fluoride ions situated at the corners of a cube, and each fluoride ion by four calcium ions arranged tetrahedrally. It is possible for pairs of other cations having approximately the same radii to form the same structure, and there are two ways in which these ions could be arranged. They could occupy the Ca^{2+} positions in a regular way or at random. In the complex oxide $ZnSb_2O_6$ the Zn^{2+} and Sb^{5+} ions form a superlattice of the rutile (TiO_2) structure, the so-called trirutile structure, but so far no examples of this kind of regular replacement have been found in complex halides. In $KLaF_4$ and α - K_2UF_6 the metal ions occupy at random the Ca^{2+} positions of the fluorite structure,³³ while $BaUF_6$ and $BaThF_6$ have random LaF_3 structures.³⁴ It is interesting to note that $NaLaF_4$ has a different structure, the β_2 - Na_2UF_6 structure which is mentioned on p. 400.

(b) *Complex fluorides with the perovskite structure.* A series of closely related structures are found for complex halides $A_mB_nX_p$ in which $p = 3m$. The common structural feature is the close packing of the A and X ions, which must be comparable in size. The structures are built of close-packed layers with composition AX_3 of the type shown in Fig. 11 (a). These layers can be packed together in hexagonal, cubic, or more complex kinds of closest

³³ Zachariasen, *J. Amer. Chem. Soc.*, 1948, **70**, 2147.

³⁴ *Idem*, *Acta Cryst.*, 1949, **2**, 388.

packing, as shown in Fig. 11 (b), so that there are holes between the layers which can be occupied by the B ions. The latter are then surrounded octahedrally by six X ions. According to whether all, two-thirds, or one-half of these positions are occupied, the formula of the resulting complex halide

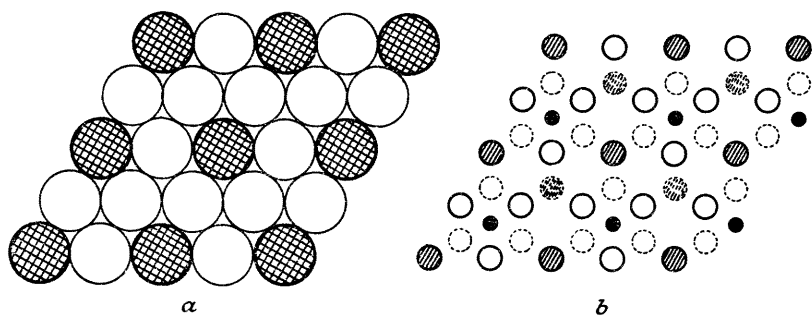


FIG. 11

(a) Close-packed layer of composition AX_3 ; (b) two adjacent layers (full and dotted circles) showing the positions, midway between the layers, for metal atoms (small black circles) within octahedra of X atoms.

is ABX_3 , $A_3B_2X_9$, or A_2BX_6 . Since the radii of A and X must be very similar these structures occur for compounds in which A is K^+ and X is F^- (radii 1.33 and 1.36 Å respectively) or A is Cs^+ and X is Cl^- (radii 1.69 and 1.81 Å respectively).

Not only is there the possibility of different layer sequences (*i.e.*, different kinds of close-packing) but there is also a number of ways in which a given

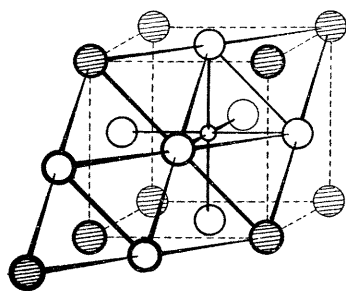


FIG. 12

The perovskite structure of $KMgF_3$ showing a Mg^{2+} ion (small circle) surrounded by six F^- ions. A layer of close-packed K^+ and F^- ions (large shaded and open circles respectively) is emphasised [cf. Fig. 11 (a)].

proportion of the octahedral holes can be occupied. For each type of complex halide, therefore, say ABX_3 or A_2BX_6 , there is a series of possible structures with, respectively, hexagonal, cubic, or more complex types of close-packing of the A and the 3X ions. The compounds $KMgF_3$, $KZnF_3$, and $KNiF_3$, for example, have the perovskite structure (Fig. 12) in which

there is cubic close-packing of the larger ions, while in CsCuCl_3 (see p. 401) there is a different type of close-packing (hexagonal) and also a different arrangement of the B atoms. The structures for A_2BX_6 compounds with respectively hexagonal and cubic close-packing are the K_2SiF_6 (Cs_2PuCl_6) and K_2PtCl_6 structures to which we have already referred (p. 398).

(c) *Some complex fluorides of uranium and thorium.* In recent years a series of complex fluorides of quadrivalent uranium and thorium have been characterised, such as NaUF_5 , Na_2UF_6 , Na_3UF_7 , Na_4ThF_8 , and KTh_2F_9 . Their structures^{33, 35} are interesting as showing how different types of chemical formulæ can arise. For example, the Na_3UF_7 structure is closely related to that of calcium fluoride. The U^{4+} ions occupy, in a regular way, one-quarter of the cation positions of that structure, the remainder being occupied by Na^+ , and one-eighth of the F^- positions are unoccupied. Both Na^+ and U^{4+} are seven-co-ordinated. The fluoride Na_2UF_6 is polymorphic; one form (γ) has a slightly distorted fluorite structure in which both ions are eight-co-ordinated. In another form (β_2) there is six-co-ordination of Na^+ and nine-co-ordination of U^{4+} , while in the closely related β_1 - K_2UF_6 structure there is nine-co-ordination of the larger K^+ and also of the U^{4+} ions.

(d) *Complex fluorides of groups IVA and VA elements.* Here also we find fluorides and oxyfluorides with unusual formulæ, and in particular a preference for forming compounds of the type A_mBF_7 . Niobium shows a marked tendency to form oxyfluoro-ions, the ion $(\text{NbOF}_5)^{2-}$ being more stable than simple NbF_n ions, but the salt K_2NbF_7 can be prepared from $\text{K}_2\text{NbOF}_5 \cdot \text{H}_2\text{O}$ and hydrofluoric acid and Rb_2NbF_6 can be made by crystallisation of Rb_2NbOF_5 from hydrofluoric acid. In all the salts K_2NbF_7 ,³⁶ K_2TaF_7 ,³⁶ and $(\text{NH}_4)_3\text{ZrF}_7$,³⁷ there are MF_7 complexes, but in $(\text{NH}_4)_3\text{SiF}_7$,³⁸ there are octahedral SiF_6^{2-} and discrete F^- ions. Octahedral $(\text{NbOF}_5)^{2-}$ ions occur in $\text{K}_2\text{NbOF}_5 \cdot \text{H}_2\text{O}$ ³⁹ and also, together with linear $(\text{HF}_2)^-$ ions, in K_3HNbOF_7 ,³⁹ which should preferably be formulated $\text{K}_3(\text{HF}_2)(\text{NbOF}_5)$.

(e) *Complex fluorides of aluminium.* In addition to the well-known mineral cryolite, Na_3AlF_6 , there is a number of other complex fluorides of aluminium which illustrate the linking of octahedral AlF_6 groups to form complexes extending indefinitely in one or two dimensions. In Na_3AlF_6 and $\text{Na}_3\text{Li}_3\text{Al}_2\text{F}_{12}$ the fluorine : aluminium ratio shows that there are discrete $(\text{AlF}_6)^{3-}$ ions. It should be emphasised that in classifying these compounds according to the way in which the AlF_6 octahedra are linked together we do not necessarily imply any difference in character between the Al-F and the Na-F bonds; in fact, $\text{Na}_3\text{Li}_3\text{Al}_2\text{F}_{12}$ ⁴⁰ has the same structure as $\text{Al}_2\text{Ca}_3(\text{SiO}_4)_3$, showing that its formula could alternatively be written $\text{Al}_2\text{Na}_3(\text{LiF}_4)_3$.

In Ti_2AlF_5 ⁴¹ each AlF_6 octahedron shares two fluorine atoms with other

³⁵ Zachariasen, *Acta Cryst.*, 1948, **1**, 265.

³⁶ Hoard, *J. Amer. Chem. Soc.*, 1939, **61**, 1252.

³⁷ Hampson and Pauling, *ibid.*, 1938, **60**, 2702.

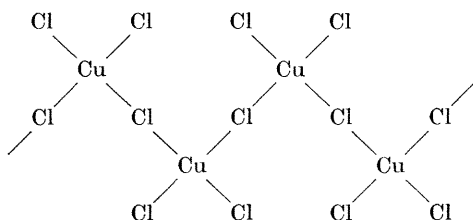
³⁸ Hoard and Williams, *ibid.*, 1942, **64**, 633.

³⁹ Hoard and Martin, *ibid.*, 1941, **63**, 11.

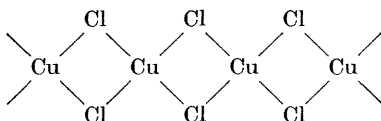
⁴⁰ Menzer, *Z. Krist.*, 1930, **75**, 265.

⁴¹ Brosset, *Z. anorg. Chem.*, 1937, **235**, 139.

columns throughout the crystal. There is also a small translation of each close-packed layer relative to its neighbours to give each copper atom only four nearest neighbours (at 2.30 Å) instead of six, the remaining two being appreciably farther away (2.65 Å). In the crystal we may distinguish chain ions $(\text{CuCl}_3)_n^{n-}$ of the type



This ion may be regarded as intermediate between the finite $(\text{CuCl}_4)^{2-}$ ion which exists in salts such as the lemon-yellow Cs_2CuCl_4 and the infinite chain molecule



which is the structural unit in crystalline cupric chloride.⁴⁶ The complex ion⁴⁷ in the cuprous and argentous compounds K_2CuCl_3 and Cs_2AgCl_3 is built of chains formed by tetrahedral MCl_4 groups sharing two corners.

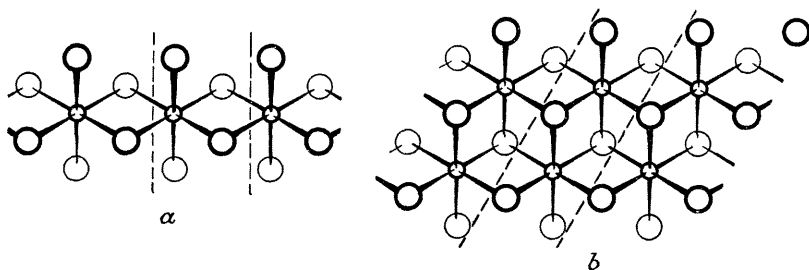


FIG. 13

Infinite single and double chains formed by the linking of octahedral AX_6 groups. The broken lines mark off the repeat units, of compositions (a) AX_4 and (b) AX_3 .

The CdCl_3^- ion in NH_4CdCl_3 is of a different kind.⁴⁸ In its halides, in the crystalline state, cadmium forms bonds to six halogen atoms. We have already noted that octahedral AX_6 groups can be linked up by sharing two opposite corners (X atoms) to form infinite chains of composition AX_5 or by sharing two opposite edges to give chains AX_4 [Fig. 13 (a)]. Such chain

⁴⁶ Wells, *J.*, 1947, 1670.

⁴⁷ Brink and MacGillavry, *Acta Cryst.*, 1949, **2**, 158.

⁴⁸ Brasseur and Pauling, *J. Amer. Chem. Soc.*, 1938, **60**, 2886; MacGillavry, Nijveld, Dierdorp, and Karsten, *Rec. Trav. chim.*, 1939, **58**, 193.

ions occur in $K_2HgCl_4 \cdot H_2O$ ⁴⁹ and $K_2SnCl_4 \cdot H_2O$. ⁵⁰ If two such AX_4 chains are joined up along their length to form the double chain of Fig. 13 (b) the composition becomes AX_3 . This is the configuration of the infinite complex ion in NH_4CdCl_3 . Further lateral linking of octahedral chains leads ultimately to the AX_2 layers of crystalline cadmium chloride.

We mentioned that the complex fluoride $(NH_4)_3SiF_7$ contains octahedral $(SiF_6)^{2-}$ and discrete F^- ions, and we have noted $Cs_2(AuCl_2)(AuCl_4)$ as a complex chloride containing two types of anion. In Cs_3CoCl_5 ⁵¹ and $(NH_4)_3ZnCl_5$ ⁵² there are tetrahedral $(CoCl_4)^{2-}$ and $(ZnCl_4)^{2-}$ ions respectively in addition to Cl^- ions. It is likely that further studies of crystalline complex halides will provide additional examples of structures of this kind, but this short account should suffice to show how structural studies have led to an understanding of the empirical formulæ of many solid compounds.

⁴⁹ MacGillavry, De Wilde, and Bijvoet, *Z. Krist.*, 1938, **100**, 212.

⁵⁰ Brasseur and Rassenfosse, *ibid.*, 1939, **101**, 389.

⁵¹ Powell and Wells, *J.*, 1935, 359.

⁵² Klug and Alexander, *J. Amer. Chem. Soc.*, 1944, **66**, 1056.