BASIC SALTS

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OUR knowledge of the structure of inorganic compounds has increased enormously during the past thirty years. This has been due chiefly to the application of X-ray diffraction methods to the study of crystalline solids.[1] Before this method was developed chemists endeavoured to deduce the structure of inorganic compounds from studies of gases, liquids, and solutions, assuming that indications so obtained were applicable directly to the solid compound from which the gas, liquid, or solution was obtained. This method works well with organic compounds but for relatively very few inorganic ones. We know now that this is because the majority of organic compounds are composed of discrete molecules even in the solid state, whereas very few inorganic compounds are so composed. For that small number the old methods are satisfactory up to a point, but for the majority of inorganic compounds they are of little help. Even for compounds, either organic or inorganic, composed of discrete molecules the older methods of study gave information only about single molecules and told little or nothing about their arrangement in the crystals. That arrangement existed only in the crystal and was destroyed on vaporisation, fusion, or solution, but insofar as the same molecules were present in all four physical states, the compound could be said to exist in all these states.

The study of *inorganic* crystals by X-ray methods has made it quite clear that the majority of these compounds exist only in the crystalline state (or in several crystalline states). In the majority of cases no molecules can be distinguished in the crystals, which are built up of atoms or ions arranged in a comparatively limited number of patterns. On vaporisation, fusion, or solution the crystal structure breaks down into atoms, ions, or molecules.

The only similarity to the original solid lies, as a rule, in the proportion of the various atoms or ions being the same in the new physical state as it was in the original solid. Even this similarity is often absent when, for example, a solid on heating gives a mixture of a gas and a new solid. With few exceptions, therefore, the study of the structure of inorganic compounds had to wait until methods were available for studying crystals in the solid state. The case of the silicates is, of course, classical in this connection. There had been little progress in the understanding of this complex group of compounds in a structural sense until a systematic study of the diffraction of X-rays by silicate minerals had been made, largely by W. L. Bragg and

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[1] W. H. and W. L. Bragg, "X-Rays and Crystal Structure", 1st edn., 1915.

his school.[2] That work gave an enormous impetus to the similar study of other compounds, and very many inorganic compounds of all types have been investigated by *X*-ray methods during the last twenty years. The basic salts form one group of compounds upon which much light has been shed by such methods.

Views as to the nature of the interatomic links in the compounds of the metals have undergone a considerable change as a result of these *X*-ray studies, more particularly in regard to the differentiation between ionic and covalent links. Such work has shown that there is no sharp line of division between compounds which are truly ionic in nature and those which are entirely covalent. There appears to be every shade between these two extremes. When a structure is fully ionised the constituent atoms (or, in some cases, groups of atoms forming a complex ion) are held together by electrostatic forces and the charge on each atom can be regarded as being uniformly dispersed. If linkages are covalent then the charges become localised and the links are directional. This difference has an important effect on the type of packing of the atoms in the crystal. In the ionic structure the ions pack together as closely and in such a manner as is determined chiefly by their relative sizes. An ionic crystal tends therefore to have a close-packed lattice. Where the links are covalent and directed, this is not usually the case. Thus when covalent links are present an oxygen atom cannot have more than four neighbours in a tetrahedral configuration, whereas, if the linkages are ionic with close packing, six neighbours may be present in an octahedral arrangement. The co-ordination of the atoms in a lattice (*i.e.*, the number of atoms surrounding another atom) is a very important criterion in assessing the types of linkage present.

Comparison of ionic radii with covalent radii or metallic radii shows that a positive ion is appreciably smaller than the neutral atom of the same element, owing to the excess of nuclear charge over that of the orbital electrons, whereas the radius of a negative ion is much larger than the covalent radius :

Li	1·52 A.	Cl^-	1·81 A.
Li^+	0·60 A.	Cl	0·99 A.

The interatomic distance in a covalent link is longer than that of an ionic link for the same pair of elements. Thus for a covalent link between Li and Cl the distance would be 2·51 A., while for an ionic link it would be 2·41 A. For a covalent link between Si and O the distance would be 1·91 A., while for an ionic link it would be 1·81 A. For Al–O the covalent link is 2·00 A. and the ionic link 1·90 A. Now in a covalent crystal the individual links are longer than in an ionic crystal and these linkages are directed, whereas in an ionic crystal the atoms are much more close-packed. For these reasons a crystal formed by covalent links has a more open structure, and sometimes a much more open structure, than one formed only by ionic links.

X-Ray observations enable the interatomic distances and relative arrangements of the atoms in a crystal to be deduced. The decision as to

[2] " The Structure of Silicates ", 2nd edn., 1932 ; *Trans. Faraday Soc.*, 1929, **25**, 291.

whether a given structure is covalent or ionic, or to what extent it has either characteristic, is based mainly on such determinations.

The links between metal atoms and oxygen or fluorine appear to be essentially ionic. As one goes from fluorine to iodine the links between metal and halogen become increasingly more covalent in character though even the iodides, especially of the more electropositive metals, are mainly ionic. Even in the case of silicon and oxygen the links appear to be about 50% ionic. At one time it was thought that a link must be either ionic or covalent, and the experimental evidence that this is not the case has been accounted for by the principle of resonance. The binding of atoms is a very complex process and is brought about by the interaction of the valency electrons of the combining atoms (or their corresponding orbitals). Several different types of link could originate, as a rule, between any two atoms, according to just how these interactions took place. These several types of link are compounded by resonance into the one which actually occurs, which is of higher stability than any of the possible types individually. This recalls the well-known case of benzene, where the distance between each pair of carbon atoms is not that characteristic of either a single (1·54 A.) or a double (1·34 A.) bond but has an intermediate value (1·39 A.) less than the mean of the two.

It is easy to see that covalent linkages can lead to crystal lattices showing either isolated groups of atoms, or to chain, band, sheet, or meshwork structures. It is not so readily appreciated that similar types of structure can occur in ionic crystals. If an ionic crystal has a layer structure then the oppositely charged ions in the layers will be held together by strong electrical forces, each ion with its appropriate co-ordination number. These layer structures are built up into crystals by much weaker van der Waals forces. The more purely ionic the linkages in a crystal the more close-packed its structure and the more this corresponds to a three-dimensional meshwork. Formation of sheet and chain structures is generally an indication of increasing covalency of the atomic linkages, but a three-dimensional meshwork is not necessarily a closely packed or an ionic one and this is true of the silicate meshworks.

The presence of hydroxyl groups or ions in a crystal leads to other complications due to the formation of what are known as hydroxyl bonds. As these bonds are largely responsible for the formation and peculiarities of many, though not all, basic salts, a short account of their nature is here given.

The Hydroxyl Bond.[3]—Abnormally short O–O distances in certain acid salts arise from the presence of an H atom between two O atoms. Such short hydrogen bonds –O–H–O–, of length about 2·55 A., are symmetrical, owing to resonance between the extremes –O–H . . . O– and –O . . . H–O–. The H atom is not attached preferentially to either of the O atoms, as is shown by the infra-red absorption spectra. The absorption band at 3 μ, characteristic of the OH group, is absent in the spectrum of H_2SO_4 and of

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[3] Cf. A. F. Wells, " Structural Inorganic Chemistry ", Clarendon Press, 1945, pp. 350, 351.

compounds with intra-molecular H bonds such as salicylaldehyde. Bonds of a somewhat similar nature are formed between hydroxyl groups. In this case, as distinct from the above, there is an H atom attached to each O atom and, in some cases at least, there is good evidence that the H atoms of these longer " hydroxyl " bonds (2·7—2·8 A.) remain associated with their own O atoms. In other words, the hydroxyl group retains its identity when forming an hydroxyl bond so that compounds with such bonds still give the absorption band at 3 μ. The packing of the OH group in certain hydroxides indicates that directed bonds are formed between OH groups attached to different metal atoms, leading to a more open packing of these groups than is found for the halogen atoms in the corresponding halides. Since the OH groups concerned are attached on one side to metal atoms, the bond between the OH groups cannot be any simple dipole attraction, since similar ends of the dipole would be in contact. J. D. Bernal and H. D. Megaw [4] therefore suggested that in a suitable environment the oxygen atom of the OH group develops the same tetrahedral character as in the water molecule. In the OH group the H atom lies about 1 A. from the centre of the O atom, the effective radius of which ranges from 1·3 to 1·8 A., and we may assume a similar position for the H in the OH ion. The O–H bond is polar, so we may picture the OH ion as a dipole with a charge of about 1·5e near the centre of the O atom and a charge of $+\frac{1}{2}e$ at the H atom. This ion has cylindrical polar symmetry. In the vicinity of the more highly charged positive ions, however, the electron distribution is distorted. Bernal suggests that the OH ion passes through the following stages. If the polarisation is small, the group retains its cylindrical symmetry and merely increases its dipole moment. Further distortion leads to a separation of charges arranged tetrahedrally. The negative charge on one O can attract the H atom attached to another, forming a hydroxyl bond. With still further polarisation the H atom can leave the O and migrate to a neighbouring O atom. This corresponds to our picture of the short H bond, for the two states of the system have identical energies and the H may be regarded as belonging equally to both atoms. This final stage in the polarisation of the OH group will occur only in oxy-acids and acid salts. In hydroxides such a transfer of H would lead to the formation of a water molecule.

The old view of basic salts was that they resulted when some only of the hydroxyl groups or oxygen atoms of a polybasic hydroxide or oxide reacted with acid. In this way such basic salts as Cd(OH)Cl or BiOCl were formed. They were regarded as the opposite of acid salts such as $NaHCO_3$ or $CaHPO_4$. Simple compounds of this kind could be readily explained in this way, but it was more difficult to account for more complex basic salts, such as $CuCl_2,3Cu(OH)_2$, of which many were known. A. Werner attempted to deal with some of these in terms of his co-ordination theory [5] by supposing that they contained complex kations in which molecules of the metal hydroxide were co-ordinated through the hydroxyl groups to the metal ion in much

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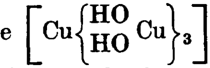
[4] *Proc. Roy. Soc.*, 1935, *A*, **151**, 384.

[5] " Neuere Anschauungen auf dem Gebiete der Anorganischen Chemie ", Zurich, 1st edn., 1905; 2nd edn., 1908.

the same way as water molecules in hydrated salts, so that $CuCl_2,3Cu(OH)_2$ became  $\left[Cu\left\{\begin{matrix}HO\\HO\end{matrix}Cu\right\}_3\right]Cl_2$, in which a copper ion was at the centre of an octahedron with three $Cu(OH)_2$ molecules straddling three edges. This view was supported by G. T. Morgan[6] and N. V. Sidgwick.[7] There were many basic salts known, however, especially among minerals, which could not be accounted for in such ways.

Basic salts will be defined, for the purposes of this article, as " salts in which the proportion of base to acid is greater than in the normal salts ". This includes a small number of compounds such as BiOCl which are excluded by an alternative definition which only includes those compounds, coming under the above general definition, which contain OH groups.

The majority of metal oxides and hydroxides are either very insoluble or only sparingly so, so it is not surprising that basic salts, and especially the very basic ones, tend to be very insoluble even when the corresponding normal salts are easily soluble in water. This makes the study of basic salts by phase-rule methods rather difficult. Each basic salt is generally stable only in contact with very dilute solutions and often over only a very short range. For these reasons basic salts are often difficult to prepare in a pure state or well crystallised. *X*-ray examination is of great help in sorting out the various basic salts in such cases, quite apart from any attempts at determinations of structure.

Many well-crystallised basic salts occur as minerals, and many of these, as well as others not known as minerals, have been prepared artificially. Some of them crystallise with surprising readiness, but rather special conditions are frequently necessary. The flocculent precipitates first obtained by adding alkali to heavy-metal salt solutions are, as a rule, basic salts. Prepared in this way, they may look amorphous but may give an *X*-ray diagram characteristic of a crystalline solid. Further action of alkali will convert them into the metal hydroxide. In some cases metal hydroxide is readily converted into basic salt by the action at room temperature of a solution of the normal salt.

Possible Types of Basic Salts

I. *Salts derived from Poly-acid Bases in which only some of the* O *or* OH *Groups have reacted with Acid and in which the Remainder are covalently attached to the Metal.*—Uranyl chloride, UO_2Cl_2, appears definitely to contain the bivalent UO_2 ion. It is noteworthy that this and the nitrate, sulphate, and acetate are all readily soluble and stable towards water and probably the UO_2 kation is present in all these compounds. The complete elucidation of their crystal structure may be a matter of great difficulty, however.[8] It does not follow that all uranyl compounds are of the same character, and

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[6] " A Survey of Modern Inorganic Chemistry ", p. 47 ; Institute of Chemistry Lecture, 1933.

[7] " Electronic Theory of Valency ", 1927 (Clarendon Press).

[8] Cf. the case of $[UO_2][NO_3]_2,6H_2O$: L. Pauling and R. G. Dickinson, *J. Amer. Chem. Soc.*, 1924, **46**, 1615.

in the case of the mineral *autunite*, $Ca[(UO_2)_2(PO_4)_2],nH_2O$,[9] the structure recalls that of the micas inasmuch as PO_4 and UO_2 groups are linked together into two-dimensional sheet anions. The three atoms of the UO_2 group form a line perpendicular to the plane of the linked PO_4 groups, and the uranium atoms are large enough to cause an oxygen atom of the UO_2 groups to project alternately above and below the PO_4 plane. These projecting oxygen atoms form cavities between the planes in which are situated the calcium ions which hold the anionic sheets together and the water of hydration. This water is zeolitic in character and the calcium also, as it is readily replaceable by other metals by the action of salt solutions (see Fig. 1).[9a]

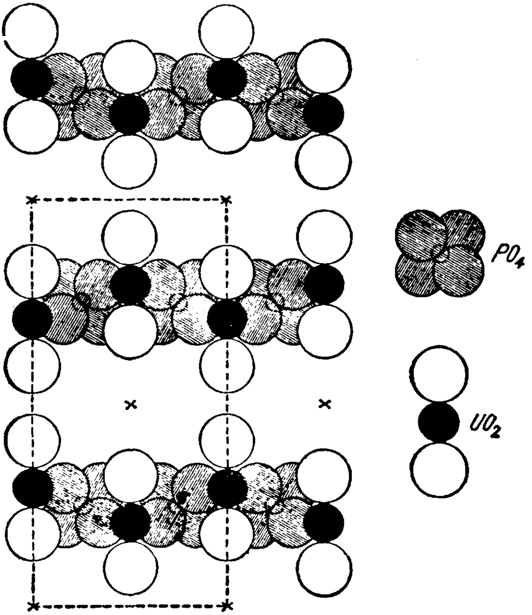


FIG. 1

Elevation of the structure of autunite, $Ca(UO_2)_2(PO_4)_2,nH_2O$ (*after Beintema*).

(*Reproduced by permission from Wells's " Structural Inorganic Chemistry ".*)

So far as the *X*-ray evidence goes, autunite is to be regarded as a salt of a complex uranic–phosphoric acid, and this shows how artificial is the division of salts into basic, normal, complex, etc. So much depends upon the sizes of the atoms and how they can be packed together. Even aluminium, which occurs as kations in most of its solid compounds, can enter readily into very stable complex anions as is well known to all students of chemistry. It is by no means necessary that metals behaving in this way should be of an " acidic " nature, though it is especially those of low electro-affinity which tend to form negative complexes. For instance, in salts containing the OsO_2

[9] J. Beintema, *Rec. Trav. chim.*, 1938, **57**, 155.

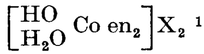
[9a] J. G. Fairchild, *Amer. Min.*, 1929, **14**, 265.

or osmyl group the latter is usually present as part of a complex negative ion, as is the case with $K_2[OsO_2,Cl_4]$. In the crystals of this compound the two $K^{\cdot}$ ions and the complex $[OsO_2Cl_4]''$ ion are arranged in a manner closely similar to that of the two F' and the $Ca^{\cdot\cdot}$ ions in fluorite.[10]

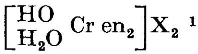
It is clear that all salts containing negative complex ions composed partly of metal–oxygen groups can be regarded as a special type of basic salt, but it is customary and usually more convenient to regard such compounds as salts of substituted oxy-acids. There are a few compounds at the other end of the scale which, although they contain no metal, have some claim to be regarded as a kind of basic salt. Some of the nitrosyl compounds—such as $(NO)ClO_4$ and $(NO)BF_4$ [11]—have been shown to have similar structures to the corresponding ammonium salts, so that they probably contain $(NO)^{\cdot}$ kations. Formally, at least, the $NO^{\cdot}$ kation is basic just as $UO_2^{\cdot\cdot}$ although nitrosyl salts are not generally thought of from this angle.

Several basic salts seem to have kations of the Werner co-ordination pattern with covalently attached hydroxyl groups, though here also the *X*-ray evidence is either incomplete or entirely lacking at present. The simplest of these is the least basic of the basic aluminium sulphates, $Al_2O_3,2SO_3,11H_2O$. This is well crystallised, and readily soluble in cold water (with slow further hydrolysis), and the *X*-ray evidence, though not yet completed, shows that it probably is to be regarded as $[Al(OH)(H_2O)_5]^{\cdot\cdot}[SO_4]''$.[12]

Werner prepared a very large number of cobaltic and chromic salts in which the $Cr^{\cdot\cdot\cdot}$ or $Co^{\cdot\cdot\cdot}$ ions were co-ordinated to a variety of groups in octahedral complex kations. A number of these were found to exist in two forms, in agreement with the geometrical requirements of an octahedral configuration which required the existence of *cis-* and *trans*-isomers in certain cases. A few of the compounds occurring in *cis-* and *trans*-forms were basic salts inasmuch as an OH group was present in the complex ion. Examples of these are :



$$\left[\begin{matrix}HO\\H_2O\end{matrix}Co\,en_2\right]X_2$$ [13]



$$\left[\begin{matrix}HO\\H_2O\end{matrix}Cr\,en_2\right]X_2$$ [14]

The one form, in each case, was readily converted into an oxalato-compound $[C_2O_4Co(or\ Cr)\,en_2]X$ and was therefore considered to be the *cis*-form. This form readily yields the diol on heating :

Di-cobaltic salts
Di-chromic ,,

$$\left[(NH_3)_4Co\begin{matrix}OH\\OH\end{matrix}Co(NH_3)_4\right]X_4$$ [15]

or

$$\left[en_2\,Co\begin{matrix}OH\\OH\end{matrix}Co\,en_2\right]X_4$$ [16]

$$\left[en_2\,Cr\begin{matrix}OH\\OH\end{matrix}Cr\,en_2\right]X_4$$ [17]

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[10] J. L. Hoard and J. D. Grenko, *Z. Krist.*, 1934, **87**, 100.

[11] L. J. Klinkenberg, *Rec. Trav. chim.*, 1937, **56**, 749.

[12] H. Bassett, work not yet published.

[13] A. Werner, *Ber.*, 1907, **40**, 272 ; J. Meisenheimer and E. Kiderlen, *Annalen*, 1924, **438**, 252 (en = ethylenediamine ; X = univalent negative ion).

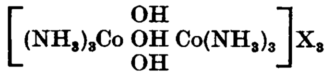
[14] P. Pfeiffer, *Z. anorg. Chem.*, 1907, **56**, 279.

[15] A. Werner, *Ber.*, 1907, **40**, 4434.

[16] *Idem*, *Annalen*, 1910, **375**, 83.

[17] P. Pfeiffer, W. Vorster, and R. Stern, *Z. anorg. Chem.*, 1908, **58**, 272.

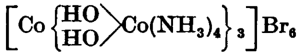
Compounds claimed to have the structure



$$\left[(NH_3)_3Co\begin{matrix}OH\\OH\\OH\end{matrix}Co(NH_3)_3\right]X_3$$

have also been prepared.[18]

The still more complex compound



$$\left[Co\left\{\begin{matrix}HO\\HO\end{matrix}\!\!>\!Co(NH_3)_4\right\}_3\right]Br_6$$

is an important one in the history of stereochemistry. It was prepared by Werner and resolved by him into its optically active isomers, being about the first compound containing no carbon whatever to be so resolved.[19]

It was the existence of compounds of this type which led Werner to the view that in the basic salts of other metals such as copper, zinc, etc., the metal hydroxide was co-ordinated to the kation of the normal salt.

The stereochemical evidence quoted is strongly in favour of these compounds having essentially the structures assigned to them by Werner.

Many other closely related basic complex salts of Co, Cr, and Pt have been prepared, but there is not always much stereochemical evidence in support of their supposed structures.

The fact that no cases of polynuclear kations linked together by hydroxyl groups appear to have been found among the numerous basic salts which have been examined by X-rays makes the need for such examination of the cobalt and chromium complexes all the more urgent.

II. *Basic Salts with an Infinite Three-dimensional Lattice of an Ionic Type.*—Many basic salts are best regarded as a special type of double salt containing O'' or OH' anions in addition to typical anions of the acidic type (F', Cl', SO_4'', etc.). This group of basic salts is probably a large one and contains some well-known and important minerals.

Lanthanum oxyfluoride,[20] LaOF, prepared by heating a finely powdered mixture of La_2O_3 and LaF_3 to 900° for 36 hours in a high vacuum, is the simplest fully ionic basic salt known. It is cubic and has the fluorite structure. It is able to take a large amount of LaF_3 into solid solution (up to about 62 mols. %). This is because LaF_3 also has a lattice closely related to that of fluorite. Up to about 2 mols. % of La_2O_3 can go into solid solution in the LaOF, the smaller proportion in this case being due to the fact that the crystal structure of La_2O_3 differs considerably from that of LaOF. This capacity for solid-solution formation is a characteristic of many basic salts and helps to make their study more difficult.

The well-crystallised minerals *libethinite* [21] $Cu_2(OH)PO_4$, *olivenite* [22] $Cu_2(OH)AsO_4$, and *adamite* [23] $Zn_2(OH)AsO_4$ are isomorphous and all have three-dimensional structures of the ionic type. Half of the metal ions are surrounded, approximately octahedrally, by four oxygen atoms of AsO_4 (or PO_4) ions and by two OH ions, while the other half are surrounded by

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[18] A. Werner, *Ber.*, 1907, **40**, 4834.
[19] *Idem*, *Ber.*, 1914, **47**, 3087.
[20] W. Klemm and H. A. Klein, *Z. anorg. Chem.*, 1941, **248**, 167.
[21] H. Heritsch, *Z. Krist.*, 1939, **102**, 1.
[22] H. Strunz, *ibid.*, 1936, **94**, 60.
[23] P. Kokkoros, *ibid.*, 1937, **96**, 417.

four oxygen atoms of AsO_4 (or PO_4) ions and one OH ion, the five oxygens being at the corners of a deformed trigonal bipyramid (see Fig. 2). There is a possibility of hydroxyl bonds between the OH ions and the oxygen atoms of the PO_4 or AsO_4 ions, but any effect of this is so small as to have little influence on the packing of the ions. It is thus found that the structure of the orthosilicate *andalusite*[24] $Al_2(O)SiO_4$ is essentially the same as that of olivenite, etc. The other two polymorphic forms of $Al_2(O)SiO_4$ have closely related structures. In *sillimanite* half the Al ions are 6 co-ordinated and the other half 4 co-ordinated, while in *cyanite*[25] they are all 6 co-ordinated, in all cases to oxygen. The density of these three polymorphic forms increases with increase in the co-ordination number of the Al ions. *Higginsite* $CaCu(OH)AsO_4$ and *descloisite* $(Pb,Zn)Pb(OH)VO_4$ probably have similar structures to adamite, with the Cu in higginsite and half the Pb in descloisite in the 5 co-ordinated condition referred to above, but *tilasite* $CaMg(OH,F)AsO_4$ appears to have the same structure as *titanite* (*sphene*) $CaTi(O)SiO_4$ in which both Ca and Ti have the usual octahedral co-ordination.[26]

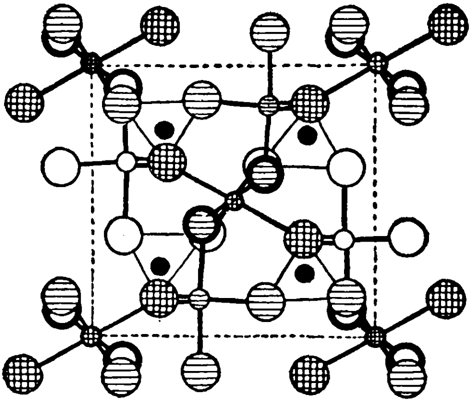

FIG. 2

Plan of the structure of $Cu_2(OH)AsO_4$ (*olivenite*). *Large circles represent* O (*light*) *or* OH (*heavy*), *small shaded circles* Cu, *and small black circles* As. *Shading indicates height above the plane of the paper ; unshaded atoms are at height* 0, *those shaded horizontally at height* $c/2$, *and those shaded horizontally and vertically at heights* $c/4$ *and* $3c/4$. *The 6 co-ordinated* Cu *atoms are those at the corners and centre of the unit cell.*

(Reproduced by permission from Wells's "Structural Inorganic Chemistry".)

Durangite[27] $NaAlFAsO_4$ also has the same structure as titanite. When it is found that F' can replace OH' isomorphously, as in the *apatites*, or O'' as in the durangite–titanite pair, this can be taken as strong presumptive evidence that the OH or O is ionic and that, for example, in titanite one has $Ti^{\cdot\cdot\cdot\cdot}$ and O'' ions and not $(TiO)^{\cdot\cdot}$. This deduction depends upon the fact that, in its compounds with metals, fluorine is almost always ionised.

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[24] W. H. Taylor, *ibid.*, 1929, **71**, 203.

[25] S. Náray-Szabo, W. H. Taylor, and W. W. Jackson, *ibid.*, p. 117.

[26] H. Strunz, *ibid.*, 1937, **96**, 7.

[27] P. Kokkoros, *ibid.*, 1938, **99**, 39.

Topaz [28] $Al_2(F,OH)_2SiO_4$ also contains individual SiO_4 tetrahedra and has in a general sense a structure somewhat similar to that of the above minerals. Each Al ion is at the centre of an octahedron composed of four oxygen atoms of SiO_4 ions and two F or OH ions.

Linarite $CuPb(OH)_2SO_4$ possibly belongs to this type of basic salt also.

Malachite [29] $Cu_2(OH)_2CO_3$ is another important mineral with a structure similar to that of olivenite in the sense that some of the copper ions are 6 co-ordinate, being surrounded by two oxygens of CO_3 ions and four OH ions, while the others are 5 co-ordinate and surrounded by three oxygens of CO_3 ions and two OH ions.

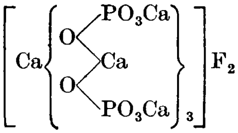
The anhydrous aluminium silicates are very important in connection with refractories and they have been studied considerably. If the formulæ of *sillimanite* Al_2O_3,SiO_2 and *mullite* $3Al_2O_3,2SiO_2$ are written in this way, they suggest that mullite is a much more basic aluminium silicate than is sillimanite.

Optical and *X*-ray data show that the two minerals must have almost identical structures. We have seen that sillimanite is $Al_2{}^{6+}O^{2-}(SiO_4)^{4-}$, and it seems fairly certain that mullite differs from this in having one quarter of the silicon replaced by aluminium. This requires either the provision of one extra positive charge for every Si so replaced or, what comes to the same thing, the removal of one negative charge. Mullite [29a] can then be written

$$[Al_2{}^{6+}O^{2-}(SiO_4)^{4-}]_6\left[\begin{matrix}Al_2{}^{6+} & \multirow{2}{*}{O^{2-}} & (AlO_4)^{5-}\\ Al_2{}^{6+} & & (AlO_4)^{5-}\end{matrix}\right]$$

The mullite lattice is then similar to that of sillimanite with one oxygen ion position vacant and a quarter of the (SiO_4) ions replaced by (AlO_4) ions. Looked at from this angle, mullite is actually less basic than sillimanite since it contains a smaller proportion of oxygen ions and its greater Al_2O_3 content is due to the presence of much of this in the complex negative ions. Such replacement of silicon by aluminium gives rise to compounds which are often called " more basic " by the mineralogists. Thus *anorthite* $Ca^{2+}[Al_2Si_2O_8]^{2-}$ is commonly called a more basic felspar than *albite* $Na^{+}[AlSi_3O_8]^{-}$ with which it is isomorphous. This use of the term " basic " must not be confused with the use made of it in the present review. From the view point of the latter both anorthite and albite are " normal " salts.

Hydroxyapatite is generally written as $[Ca_3(PO_4)_2]_3,Ca(OH)_2$. As a mineral this is of minor importance in comparison with the isomorphous *fluorapatite* $[Ca_3(PO_4)_2]_3,CaF_2$. Biologically, hydroxyapatite is of great importance, as it is the major constituent of bone. A. Werner [30] considered apatite to have the structure



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[28] J. Leonhardt, *ibid.*, 1923, **59,** 216 ; N. A. Alston and J. West, *Proc. Roy. Soc.*, 1928, *A*, **121,** 358 ; *Z. Krist.*, 1928, **69,** 149 ; L. Pauling, *Proc. Nat. Acad. Sci.*, 1928, **14,** 603.

[29] H. Brasseur and J. Toussaint, *Bull. Soc. roy. sci. Liège*, 1938, 213.

[29a] W. H. Taylor, *Z. Krist.*, 1928, **68,** 503.

[30] *Ber.*, 1907, **40,** 4447.

with a very complex kation, but without the slightest evidence. Only quite recently has the structure been fully elucidated,[31] although the new results agree in all important points with the older determination by S. Náray-Szabo.[32] The structure is a three-dimensional ionic complex of a remarkable type. Along each of the three-fold axes is a chain of Ca ions ½ of the *c*-axis apart, each of which is bonded to its neighbours above and below by means of three oxygen atoms thus forming a continuous chain -Ca-3O-Ca-3O-Ca-. Each Ca is also linked to three oxygens almost at the same level on the *c*-axis as itself, so that each Ca ion in the chain is surrounded by 9 oxygens. All these oxygens belong to PO_4 ions, and the P atoms link the chains together, producing a hexagonal network with channels running down the *c*-axis of the prism. In the walls of these channels are six hollows per unit length, three at one level and three at another, and into these six other calcium ions fit with just enough room in the centre of each group of three for one F or OH ion to fit. This gives a very unusual planar arrangement of three calcium ions at the corners of an equilateral triangle around the central fluorine or hydroxyl ion. These planar Ca_3F groups are arranged one above the other in the hexagonal channels in such a way that the Ca ions of alternate planes are directly above one another, while those in two adjacent planes form a six-fold arrangement. An interesting feature of this arrangement is that the OH ions of hydroxyapatite are adjacent to one another, which seems remarkable in view of the fact that a temperature of about 1200° is needed for complete expulsion of the water. It is true that they are some distance apart (3·4 A.).

Similar proximity of hydroxyl ions and difficulty in expelling water is found in other cases such as *topaz* and especially in basic complex silicates such as the *amphiboles*, including *asbestos* and *micas*, and may be usual. It is possibly associated with great stability of the lattice structure as a whole and the fact that this must collapse when water is driven off. The stability of the lattice as a whole, the exact distance apart of the OH ions or groups, the presence or absence of hydroxyl bonds, and the extent of the ionic character of the OH in any given case must all affect the ease with which elimination of water will occur on heating. The ionic strength is perhaps very important as judged from the relative behaviour of the members of the series NaOH or KOH, LiOH, $Ca(OH)_2$, $Mg(OH)_2$, $Zn(OH)_2$, where the ease of elimination of water increases greatly with decrease in ionic character.

All the indications appear to be that the apatite structure is highly ionic. It should, of course, be written $Ca_5F(PO_4)_3$ or $Ca_5(OH)(PO_4)_3$ and not in the conventional manner $[Ca_3(PO_4)_2]_3CaF_2$ or $[Ca_3(PO_4)_2]_3Ca(OH)_2$ which suggests that $Ca_3(PO_4)_2$, CaF_2, and $Ca(OH)_2$ are present in the compounds. The simplest formula which gives the chemical composition should be used for all double salts.

$Pb_5(OH)(PO_4)_3$ is said to show great similarity to calcium hydroxyapatite and presumably has a similar structure.[33]

[31] C. A. Beevers and D. B. McIntyre, *Min. Mag.*, 1946, **27**, 254.

[32] *Z. Krist.*, 1930, **75**, 387.

[33] R. Klement, *Z. anorg. Chem.*, 1938, **237**, 161.

III. *Basic Salts with Layer Lattices of the Ionic Type and without Hydroxyl.*—The majority of metal oxyhalides which have had their structures fully determined are less fully ionic than LaOF. An indication of this is given by their layer-lattice structures.

FeOCl [34] and *lepidocrocite* γ-FeO·OH are both orthorhombic and have essentially the same structure in the individual layers of which the crystal lattices are composed. The Fe ions are at the centres of somewhat distorted octahedra of oxygen and OH ions, or of oxygen and chlorine ions in the case of FeOCl. These octahedra are linked together in such a way that each Cl or OH ion is common to two octahedra, while each oxygen ion is shared by four octahedra. An electrically neutral layer structure results which has a series of ridges and valleys with OH or Cl ions at the tops of each ridge. The ridges are alternately on the one side or the other of the layer. In FeOCl the outermost atoms on both sides of the layers are chlorine, and the layers are stacked in the crystal so that there is close-packing of the chlorine ions—the ridges on one layer fit into the valleys in the next. In γ-FeO·OH, the OH ions are outermost on both sides of the layers. These cannot fit together so as to give close-packing of the oxygen atoms owing to the intervention of hydroxyl bonds. These result in directed links of a tetrahedral nature between the hydroxyl groups of neighbouring layers and a rather more open structure in which the outer oxygen atoms of one layer lie directly upon those of the layer below, instead of fitting in between two oxygens of the lower layer.

The bismuth oxyhalides, BiOCl, BiOBr, and BiOI, are tetragonal.[35] They, too, form layer lattices with the halogen ions on both sides of the layers. The covalent character of the linkages becomes more marked as the atomic weight of the halogen increases. This is shown by the cleavage parallel to the plane of the layers becoming more and more marked. It is also shown by the distortion of the halogen ions due to the small bismuth ions. In the case of the oxychloride and oxybromide this distortion or polarisation is more marked along the *c*-axis, *i.e.*, between contiguous layers, than along the *a*-axis. In both compounds the distance between two halogen atoms in contiguous layers is somewhat less than the theoretical diameter of the halogen atom, but distances between halogen atoms in the same layer indicate no compression. In the case of the oxyiodide there is marked compression in both directions ; the distance between two iodine atoms in the same layer is 4·01 A., and in contiguous layers 4·17 A., as compared with the theoretical diameter 4·40 A. The red colour of the oxyiodide is also an indication of marked polarisation.

IV. *Basic Salts with Layer Lattices of the Ionic Type and containing Hydroxyl.*—A great deal of work has been carried out on the basic salts of bivalent metals, especially magnesium, zinc, and cadmium, which belong to this category. The salts examined have been mainly halides, but some nitrates, sulphates, phosphates, etc., have also been dealt with. Apart from

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[34] S. G. Goldsztaub, *Compt. rend.*, 1934, **198,** 667 ; *Bull. Soc. franç. Min.*, 1935, **58,** 6.

[35] F. A. Bannister and M. H. Hey, *Min. Mag.*, 1935, **24,** 49.

the fluorides, which are fully ionic with either the fluorite or rutile structure, the halides and hydroxides of these metals form similar layer-lattice structures. Each metal ion is surrounded octahedrally by six halogen or hydroxyl ions, each of which is common to three octahedra, which are thus linked together into an infinite layer or sheet which is electrically neutral. In the case of zinc the individual layers of both hydroxide and halide are similar, but in the hydroxide the layers are held together by hydroxyl bonds instead of by van der Waals forces as in the halide. Hydroxyl bonds are not present in the hydroxides of the other bivalent metals with the exception of beryllium, so that in those cases the structures of hydroxide and halides differ much less. The basic magnesium chlorides [36] seem to be well defined and interesting: Mg(OH)Cl has the $MgCl_2$ structure with statistical distribution of the OH and Cl in the octahedral arrangement of ions around each magnesium ion. There are also compounds $MgCl_2,3Mg(OH)_2$ and $MgCl_2,5Mg(OH)_2$ which exist in the water-free form and also as 3, 5, and 7 hydrates. The water-free forms have the $Mg(OH)_2$ layer structure, but in the hydrates with 5 and $7H_2O$ these layers have been broken up into bands, the crystals being built up of these bands separated by bands or chains of H_2O molecules.

In the case of zinc and cadmium some rather ill-defined hydroxyfluorides are said to exist.[37] The hydroxy-chlorides, -bromides and -iodides of zinc are well crystallised and of two types $ZnX_2,Zn(OH)_2$ and $ZnX_2,4Zn(OH)_2$.[38] There is also a basic nitrate $Zn(NO_3)_2,4Zn(OH)_2$.[38] All these compounds have layer-lattice structures very similar to that of α-$Zn(OH)_2$ [$Zn(OH)_2$ is dimorphic]. The structure of $ZnX_2,Zn(OH)_2$ [Zn(OH)Cl] differs most from that of α-$Zn(OH)_2$. The chief difference in the other cases is due to an expansion along the *c*-axis as OH is replaced by the larger halogen ions.

Although much work has been done on the corresponding cadmium compounds, only two of these seem to be really well established, namely, Cd(OH)Cl [39] and $CdCl_2,4Cd(OH)_2$.[40] There are probably a number of others [41] but the cadmium compounds appear to be less soluble and to crystallise less readily than the zinc compounds. This and the small differences in the *X*-ray diagrams make results difficult to interpret, especially as, even when definite compounds clearly exist, as in the case of zinc, there are indications that intermediate solid solutions (possibly metastable) may appear. This is perhaps due to some random replacement of OH by halogen in the hydroxide layers and is most likely to occur when the basic salt is rapidly prepared, as by precipitation.

The structure of Cd(OH)Cl differs in an interesting way from that of Mg(OH)Cl. The crystals are made up of layers having the empirical

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[36] W. Feitknecht and F. Held, *Helv. Chim. Acta*, 1944, **27**, 1480.

[37] W. Feitknecht and H. Bucher, *ibid.*, 1943, **26**, 2177, 2196.

[38] W. Feitknecht, *ibid.*, 1930, **13**, 22; W. Feitknecht and H. Weidmann, *ibid.*, 1943, **26**, 1560, 1564.

[39] J. L. Hoard and J. D. Grenko, *Z. Krist.*, 1934, **87**, 110; W. Feitknecht and W. Gerber, *ibid.*, 1937, **98**, 168.

[40] *Idem, Helv. Chim. Acta*, 1937, **20**, 1344.

[41] *Idem, loc. cit.*; W. Feitknecht, *Experientia*, 1945, **1**, 230; *Helv. Chim. Acta*, 1945, **28**, 1444.

composition Cd(OH)Cl in which every Cd ion is surrounded octahedrally by three OH and three Cl ions in such a manner that the OH ions lie all to one side of the plane of Cd ions and the Cl ions to the other side. All the OH and Cl ions of an octahedron are shared by two other octahedra, and in consequence every Cl has three Cd ions to one side of it and three OH to the other in an octahedral arrangement, while the OH ions are similarly surrounded by three Cd and three Cl ions (see Fig. 3). The layers in the crystals are held together merely by van der Waals forces, for there is no possibility of hydroxyl bonds since the hydroxyl ions of one layer face chlorine ions of the next layer. Now $Mg(OH)_2$ and $Cd(OH)_2$ both crystallise with the same lattice and so do $MgCl_2$ and $CdCl_2$ and the general arrangement of ions in the lattices of Mg(OH)Cl and Cd(OH)Cl is fundamentally similar. Why is the distribution of OH and Cl random in the case of the magnesium compound but fixed in a very definite way in the cadmium compound ?

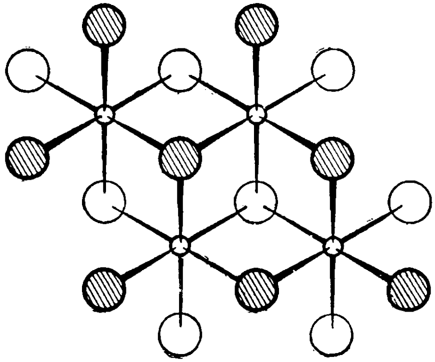

FIG. 3

Portion of one layer of Cd(OH)Cl. *The* OH *groups (shaded) lie above, and the* Cl *atoms below, the plane of the metal atoms.*

(Reproduced by permission from Wells's " Structural Inorganic Chemistry ".)

It may mean that the linkages in Cd(OH)Cl have sufficient covalent character to fix the OH and Cl in some favoured position while those in the magnesium structure cannot do this because of their rather more ionic character.

Some basic sulphates form layer-lattice structures : $CoSO_4,3Co(OH)_2$ is one of these.[42] It forms microscopic hexagonal leaflets built up of alternate layers of hydroxide and normal sulphate ; about 4 mols. of zeolitic water are normally present. This blue basic salt is converted by concentrated aqueous $CoSO_4$ into a violet salt $2CoSO_4,3Co(OH)_2,5H_2O$ in which the water is also held zeolitically.

It is stated,[43] on the other hand, that $CdSO_4,3{\cdot}5Cd(OH)_2$ forms hexagonal plates and that it has a simple layer-lattice structure formed from that of $Cd(OH)_2$ by replacing every eighth OH by SO_4. The interesting mineral

[42] W. Feitknecht and G. Fischer, *ibid.*, 1935, **18**, 40.

[43] W. Feitknecht and W. Gerber, *ibid.*, 1945, **28**, 1454.

hemimorphite [44] is one of the very small number of silicates containing the $Si_2O_7^{6-}$ ion. Its behaviour on dehydration and its crystal structure show it to be $Zn_4(OH)_2(Si_2O_7),H_2O$. It has a layer lattice.

It is evident that a very large number of basic salts have a layer-lattice type of structure in which layers of hydroxide alternate with layers of normal salt. This appears to be due to the fact that many normal salts and many hydroxides have layer-lattice structures and that the kations in both salt and hydroxide are surrounded octahedrally by oxygen, hydroxyl, or halogens. The structures of the layers of many salts and hydroxides are so similar for this reason that they are often able to key together and form very strong composite layers, the composite structure being a basic salt. It is evident that the number of layers of normal salt and of metal hydroxide so bound

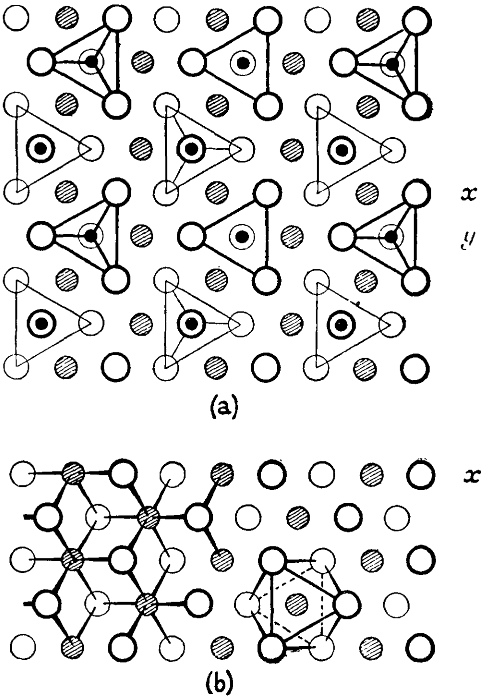

Fig. 4

Plans of the structures of (a) Mg_2SiO_4 *and* (b) $Mg(OH)_2$. *Small black circles represent* Si, *shaded circles* Mg, *and open circles* O *atoms. In* (a) *light and heavy lines are used to distinguish between* SiO_4 *tetrahedra at different heights. To the left in* (b) *the* Mg–OH *bonds are shown, and to the right an octahedral co-ordination group is outlined.*

Repeat unit :

xxy :	*norbergite,*	$Mg_2SiO_4,Mg(OH)_2$.
xy, xxy :	*chondrodite,*	$2Mg_2SiO_4,Mg(OH)_2$.
xy, xy, xxy :	*humite,*	$3Mg_2SiO_4,Mg(OH)_2$.
xy, xy, xy, xxy :	*clinohumite,*	$4Mg_2SiO_4,Mg(OH)_2$.

(*Reproduced by permission from Wells's " Structural Inorganic Chemistry ".*)

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[44] T. Ito and J. West, *Z. Krist.*, 1932, **82**, 1.

may be expected to depend upon various factors and to vary considerably, although there may well be certain proportions of hydroxide and normal salt which are more stable than others. In the case of zinc, as we have seen, the basic salts tend to have 4 mols. of $Zn(OH)_2$ combined with one of zinc halide (or nitrate), but in the case of numerous cupric salts one finds $3Cu(OH)_2$ for each mol. of normal salt [*atacamite*, $CuCl_2,3Cu(OH)_2$; *brochantite*, $CuSO_4,3Cu(OH)_2$; $Cu(NO_3)_2,3Cu(OH)_2$]. In all these cases several layers of hydroxide separate each layer of normal salt. The opposite type of structure in which one hydroxide layer is divided from the next by several layers of the normal salt also occurs and is found in the well-known *chondrodite* series of basic orthosilicate minerals. At one end of this series is the mineral *brucite* $Mg(OH)_2$, and at the other *olivine* Mg_2SiO_4. The intermediate stages are *norbergite* $Mg_2SiO_4,Mg(OH)_2$ which has single layers of Mg_2SiO_4 and $Mg(OH)_2$ alternating, *chondrodite* $2Mg_2SiO_4,Mg(OH)_2$ where two layers of Mg_2SiO_4 alternate with one of $Mg(OH)_2$, *humite* $3Mg_2SiO_4,Mg(OH)_2$, and *clinohumite* $4Mg_2SiO_4,Mg(OH)_2$ (see Fig. 4). Some of the hydroxyl groups are generally replaced by fluorine as is so often the case with naturally occurring basic salts. This is an indication of the ionic character of the hydroxyls.

Staurolite has a similar type of structure which can be regarded as composed of layers of cyanite interleaved with ferrous hydroxide layers. It can be written $2Al_2SiO_5,Fe(OH)_2$.

V. *Basic Salts containing Complex Silicate and Aluminosilicate Anions.*—The majority of the minerals belonging to the more complex types of silicate structures appear to be somewhat basic. This does not apply to the *pyroxenes*, which contain simple chain anions $(SiO_3)_n^{2-}$. The members of this group, such as *enstatite* $MgSiO_3$ and *diopside* $CaMg(SiO_3)_2$, appear to be non-basic.

The *amphiboles* with the more complex band ions $(Si_4O_{11})_n^{6-}$ all seem to be basic and usually to the extent indicated by the formula $(OH)_2Ca_2Mg_5(Si_4O_{11})_2^{6-}$ of *tremolite*. The $(Si_4O_{11})_n^{6-}$ band anions are bound together by the metal ions. There can be wide variation in the nature of these kations, the number of which depends upon the extent to which any of the silicon atoms in the Si_4O_{11} have been replaced by aluminium, for every aluminium atom taking part in such replacement necessitates one more positive valency among the kations. In *hornblende*, the best-known of the amphiboles, the anion has the composition $[Si_6Al_2O_{22}]^{14-}$. The more such replacement of Si by Al has occurred the more tightly the anions are held together, as the kations are then more numerous. In other cases the links are relatively weak and the crystals tend to break into long fibres; asbestos is an amphibole. Hydroxyl bonds have little, if anything, to do with the behaviour of the amphiboles. This is not the case with *chrysotile asbestos* which is very closely related to the amphiboles. Its formula is $(OH)_6Mg_6(Si_4O_{11})^{6-},H_2O$. The magnesium ions lie between the oxygen atoms of the Si_4O_{11} anions and OH anions so that it is chiefly the bonds between the OH groups of adjacent bands which hold the latter together. These are much weaker than the more ionic bonds of the less basic true amphiboles. The crystals of this mineral split into fine fibres particularly easily.

If the band ions of the amphiboles are linked together, endless sheet anions result. These usually contain hexagonal rings, linked together as in a honeycomb, formed from six SiO_4 tetrahedra, but rings formed from 4, or 8, SiO_4 groups are also found in a few minerals. Among the minerals containing these sheets of hexagonal rings [representable as $(Si_2O_5)_n$] are the clay minerals (*kaolinite, dickite, nacrite,* etc.), the *micas* and the *chlorites.* All of these are basic salts and they are so important technically in connection with agriculture and all the industries in which clay or clay products are used that a special "Clay Minerals Group" of the Mineralogical Society has been formed recently for their study. Similar groups exist in France and other countries.

It is possibly of some importance in connection with the structures of the clay minerals, *vermiculites, chlorites,* etc., that in some cases at least they have arisen by degradation of mica and other silicates formed at high temperatures. Silicic acid sheet structures may well have survived from the mica structures or have been formed from the three-dimensional structures of the felspar. The clay minerals and related compounds could have been built up from such silicic acid sheets at ordinary low temperatures. This mode of formation would help to explain the fact that, though crystalline, the crystallites of those clays which have been formed from felspars are extremely minute, as a rule, whereas crystals of the vermiculites which have been formed from micas are often quite large. They are pseudomorphs of the original mica but not in the usual sense of being polycrystalline aggregates. The silica skeleton of the original mica seems to have been retained almost intact.

All the minerals of this group, *viz.*, clays, vermiculites, chlorites, etc., owe their formation essentially to the fact that in the silica sheet of the mica type all the vertices of the SiO_4 tetrahedra point towards the same side of the silica sheet, and that the distance apart of the O atoms at these vertices in the hexagonal rings is very closely the same as the distance between the OH ions of the hexagonal rings in the layer structures of *hydrargillite* $Al(OH)_3$ and *brucite* $Mg(OH)_2$. This enables the silica sheets and the hydroxides to bond together in layer structures. J. W. Gruner [45] is especially responsible for the suggested structures of the resulting minerals and these have stood the test of time very well. *Halloysite,* $Al_2O_3,2SiO_2,4H_2O$, was considered by Gruner to have the simplest structure and to consist of sheets of silicic acid and aluminium hydroxide held together merely by hydroxyl bonds

$$\left[\begin{array}{l} \ldots\ O_4Si_2(OH)_2\ \ldots \\ \ldots\ (OH)_3Al_2(OH)_3\ \ldots \end{array}\right]$$

Although the structure of this mineral is still under dispute, the indications appear to be that it is essentially similar to that of kaolinite but with disordered stacking of the layers. In the typical clay minerals (kaolinite, dickite, nacrite) interaction has occurred between the OH of the silica and

[45] *Z. Krist.*, 1934, **88,** 412; *Amer. Min.*, 1934, **19,** 557; 1935, **20,** 475.

alumina layers so that there is actual chemical bonding with formation of $[Al_2(OH)_4Si_2O_5]_n$. These double layers are neutral and only held together by hydroxyl bonds in the crystals. These links are easily broken, which accounts for the swelling and other physical properties of the clays.

By coupling a second silica sheet on to the other side of the aluminium hydroxide layer there results the triple-layer compound *pyrophyllite* $[Al_2(OH)_2Si_4O_{10}]_n$ which is also a neutral structure. In this case the hydroxyl groups are right in the middle of the triple layer and quite close together (cf. the remarks on p. 256), so that in the crystals the triple layers are only held together by weak van der Waals forces. *Talc* is the corresponding triple-layered magnesium compound $[Mg_3(OH)_2Si_4O_{10}]_n$: no magnesium compound corresponding to kaolinite is known.

Montmorillonite,[46] the chief constituent of fuller's earth and *bentonite*, is derived from pyrophyllite by the intercalation of an indefinite amount of water between the triple layers of the latter, but there has always been some replacement of Al by Mg or of Si by Al (or both) together with the intercalation between the layers of exchangeable, zeolitic, kations needed by such replacement (see the section on micas).

The *vermiculites* [47] have a structure which seems to be related to that of both the bentonites and chlorites. Owing to the macro-crystalline nature of the vermiculites their general physical character seems very different from that of the bentonites with their submicroscopic crystals but the intercalated layer of water molecules (probably with a regular orderly arrangement) is present, all the same, as is shown by the enormous swelling and exfoliation which occurs on heating. The *c*-spacing in the crystals is quite characteristic and differs from that of the bentonites.

The true micas [47] differ from pyrophyllite or talc in having one in four of the silicon atoms replaced by aluminium. This necessitates the presence of an ion having one positive charge for every silicon atom so replaced. In both *muscovite* $K_n^{\bullet}[Al_2(OH)_2(Si_3AlO_{10})]_n'$ (the mica derived from pyrophyllite) and *phlogopite* $K_n^{\bullet}[Mg_3(OH)_2(Si_3AlO_{10})]_n'$ (mica derived from talc) these positive charges are provided by potassium ions. These are located between the triple-layer anionic structures which are thereby held much more tightly together than in pyrophyllite or talc. The electrostatic forces are still moderate, however, so that cleavage remains excellent. In the so-called brittle micas half the Si atoms have been replaced by Al, so that twice as many positive charges are required as in muscovite. Margarite is $Ca_n^{\bullet\bullet}[Al_2(OH)_2(Si_2Al_2O_{10})]_n''$ and the sheet anions are now held together so strongly that cleavage is much less good and the mineral is much harder.

The *chlorites* [48] provide the last variant of these structures containing siliceous sheets. They are derived from talc by replacing some of the silicon atoms by Al, and the triple anionic sheets range in composition between $[Mg_3(OH)_2(AlSi_3O_{10})]_n^-$ and $[Mg_2Al(OH)_2(Al_2Si_2O_{10})]_n^-$, the greater replace-

[46] J. W. Gruner, *loc. cit.* ; S. B. Hendricks and M. E. Jefferson, *Amer. Min.*, 1938, **23**, 863 ; F. A. Bannister, *Ann. Reports*, 1938, **35**, 190.

[47] L. Pauling, *Proc. Nat. Acad. Sci.*, 1930, **16**, 453.

[48] L. Pauling, *ibid.*, p. 578.

ment of silicon in the second case being made up for by some replacement of Mg by Al. The negatively charged infinite sheets arising in this way are held together in the crystals, not by simple positive ions as in the micas, but by other positively charged infinite sheets derived from layers of the *brucite* $Mg(OH)_2$ structure by replacement of one-third of the Mg by Al. *Chlorite* may be written as $[Mg_2Al(OH)_6]_n^+[Mg_3(OH)_2(AlSi_3O_{10})]_n^-$.

Silicates with three-dimensional network anions may also be basic; thus the important mineral *epidote* may be written as $Ca_2(OH)[(Al,Fe)_3Si_3O_{12}]$. Although the complex negative structures of the silicates have been called anions and considered to be held together by covalencies in the above discussion, yet it has to be remembered that the Si–O link has some ionic character. This may be considerable in respect of some of the links, especially those involving Mg and Al in octahedral co-ordination in the brucite and hydrargillite portions of the complex sheet structures of the pyrophillites, micas, chlorites, etc.

VI. *Basic Salts with Discrete Molecules*.—The only basic salts which come into this category appear to be the remarkable basic beryllium acetate $Be_4O(CO_2CH_3)_6$ and the similar compounds $Be_4O(CO_2R)_6$ (where R = ethyl, propyl, *iso*propyl or *tert.*-butyl). The beryllium atoms in the acetate are arranged tetrahedrally around the central oxygen, and the six acetate groups straddle the six edges of the tetrahedron. The structure is truly molecular, and the links essentially covalent.[49] The basic acetate crystallises in the cubic system, but a completely symmetrical arrangement of the acidic groups along the tetrahedral edges is only possible in the case of the acetate (and formate). A great decrease in symmetry is found in the basic propionate, which is monoclinic. Apart from this difference in symmetry the general arrangement in the molecules of all the above compounds is, no doubt, very much the same.

In conclusion, the writer wishes to acknowledge the great help he has received in preparing this review from A. F. Wells's " Structural Inorganic Chemistry ". He also thanks Dr. Wells and the Clarendon Press for permission to reproduce the four figures, and Dr. Max Hey for helpful advice.

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[49] W. H. Bragg and G. T. Morgan, *Proc. Roy. Soc.*, 1923, *A*, **104**, 437; L. Pauling and J. Sherman, *Proc. Nat. Acad. Sci.*, 1934, **20**, 340; G. D. Preston and J. Trotter, *Nature*, 1943, **151**, 166; C. A. Beevers, *ibid.*, 1943, **152**, 447.