

CHAPTER 9

*Problems of Inorganic Structures**

by Linus Pauling

In June 1913 a leading American physical chemist, H. C. Jones, in his book *A New Era in Chemistry*, pointed out how little was known about the solid state. He said 'We do not know what is the formula of rock salt, or of ice; and we have no reliable means at present of finding out these simplest matters about solids. Our ignorance of solids is very nearly complete.'

June of 1913 was about the last time when such a statement could be made. Already on 17 April 1913 W. H. Bragg and W. L. Bragg had read a paper before the Royal Society of London on the reflection of X-rays by crystals, in which they pointed out that they had obtained strong evidence from their X-ray studies for supposing that the atoms in rock salt are arranged in what we now call the sodium chloride arrangement. Their paper was published in the *Proceedings of the Royal Society* in the fall of 1913. A detailed description of the sodium chloride structure, the fluorite structure, the sphalerite structure, and the pyrite structure was presented before the Royal Society by W. L. Bragg on 27 November 1913, and published early in 1914. A powerful and reliable method for determining the structure of crystals had thus become available, and during the past 50 years it has been principally responsible for the development of a powerful and extensive theory of structural inorganic chemistry, and has also, of course, contributed greatly to other fields of chemistry.

9.1. Simple Inorganic Structures

The English mathematician and astronomer Thomas Harriot, who was tutor to Sir Walter Raleigh and who travelled to Virginia in 1585,

* Contribution No. 2574 of the Gates and Crellin Laboratories of Chemistry.

apparently knew about the structure representing closest packing of spheres; he said that the bodies with greatest density are those in which every atom touches twelve surrounding atoms, whereas those with least density have only six contacts. The crystallographers such as Haüy did not make as much use of crystallographic information as they might have, because instead of attempting to account for the forms of crystals in terms of aggregates of spherical atoms, they in general represented the fundamental unit as a polyhedron.

The structure of diamond was determined by W. H. and W. L. Bragg in 1914, and recognized at once as corresponding to the theory of the tetrahedral carbon atom that had been proposed by Van 't Hoff and LeBel just forty years before and that had become one of the important principles underlying the structure theory of organic chemistry. It seems to me astounding that in this period of forty years, between 1874 and 1914, no scientist had suggested that the diamond crystal has the diamond structure.* In this period a number of investigators (W. Barlow, W. J. Pope, W. J. Sollas, F. M. Jaeger) had attempted to discover reasonable arrangements of atoms in space and to assign them to various crystals on the basis of the available information about the properties of the crystals. Barlow was the most successful of these investigators. In 1883 he suggested five 'very symmetrical' structures, the sodium chloride, cesium chloride, and nickel arsenide arrangements, cubic closest packing, and hexagonal closest packing. He was strongly criticized by L. Sohncke, who pointed out that Barlow seemed not to know what the adjective symmetrical meant. This criticism apparently stimulated Barlow to make a study of symmetry, and led to his independent development of the 230 space groups during the following decade. Barlow and Pope assigned copper, silver, and gold to the cubic closest packed arrangement, and pointed out that magnesium and beryllium had the correct symmetry and axial ratio to correspond to hexagonal closest packing. However, their discussion of diamond was incorrect: they assigned diamond to the cubic closest-packed arrangement.

After the discovery of X-ray diffraction rapid progress was made in the determination of simple structures. By January 1915, when W. H. and W. L. Bragg sent the manuscript of their book *X-Rays and*

* This statement may not be formally correct because the true diamond structure was reportedly predicted by A. Nold in 1891 on the ground of tetravalency (I have, however, been unable to trace the paper). That this prediction found no acceptance is excusable because the remainder of about a dozen structures of elements, proposed on similar principles, makes no sense whatever (cf. P. P. Ewald, *Kristalle und Röntgenstrahlen*, pg. 96 and 316, J. Springer, Berlin, 1923).

Crystal Structure to the publisher, they were able to report complete structure determinations representing nine structure types: sodium chloride (NaCl, KCl, KBr, KI, PbS), diamond, sphalerite (ZnS), wurtzite (ZnO, CdS), cesium chloride (NH₄Cl), cubic closest packing (Cu), fluorite (CaF₂), pyrite (FeS₂, MnS₂, CoAsS), and calcite (CaCO₃, MgCO₃, MnCO₃, FeCO₃, ZnCO₃, NaNO₃). They had also made good progress toward the determination of the cuprite structure, the hematite structure, and the spinel structure, and had made studies of a number of other crystals. Other investigators, too, had already become active.

The hexagonal closest-packed arrangement was discovered by A. W. Hull in 1917, when he carried out his powder studies of magnesium, and at the same time he discovered the body-centered arrangement, in his investigation of lithium and potassium metals. The rutile and anatase structures were discovered by Vegard in 1916; the third structure for titanium dioxide, brookite, was not determined until 1928. The nickel arsenide arrangement was determined by Aminoff in 1923. The first layer structure was discovered in 1922: the cadmium iodide structure, by Bozorth.

An important consequence of the determination of the structures of the alkali halogenide crystals and the recognition that they could be described in a reasonable way as a packing of cations and anions was the development of a simple theory of ionic crystals, especially by E. Madelung, W. Kossel, M. Born, and F. Haber.

Most of the structures of binary compounds were seen to involve a packing of 4, 6 or 8 non-metal atoms about the metal atoms, at the corners of a tetrahedron, an octahedron, or a cube, respectively. Molybdenite (1923) was found to constitute an exception: in it the six sulfur atoms that surround a molybdenum atom are arranged at the corners of a trigonal prism, with axial ratio close to unity. This coordination polyhedron is, however, rare. The great majority of structures of inorganic substances that have been determined during recent decades can be described in terms of the three simple coordination polyhedra, the tetrahedron, octahedron, and cube. Some others, which occur less often, are described in the following section.

As more and more structures were determined, the possibility of systematizing them through principles arrived at in part by induction and in part by deduction from the laws of electrostatics was recognized. V. M. Goldschmidt made two great contributions in the second decade of the X-ray diffraction period. One was to add greatly to the body of structural information by synthesizing a large number of binary

compounds and determining their structures. The other was to classify substances on the basis of structure type and interatomic distances. W. L. Bragg had attempted to formulate a system of atomic radii. His efforts were extended by Goldschmidt, who divided substances into two classes, ionic and atomic (covalent, including metals), and formulated two sets of radii, ionic radii and atomic radii. He then developed a system of classification and explanation of crystal types in relation to the sizes of atoms and ions.

This method of interpreting structural information has been highly developed and found to be of much value. A description of some of the structural principles is given in the following section.

Structure determinations have now been made for hundreds of binary compounds, and the structural chemist is tempted to feel that he understands them. He is, in fact, often able to predict in a reasonably reliable way not only the structure of a substance but also the interatomic distances, usually to within about 0.05 Å. But it is difficult to make reliable predictions for substances more complicated than binary compounds, and even the binary compounds sometimes offer puzzles.

For example, in 1924 Dickinson and Friauf found that lead monoxide forms tetragonal crystals involving layers in which the oxygen atoms lie in one plane and the lead atoms lie in adjacent planes, above and below the oxygen plane. In most layer structures the metal atoms are at the center of the layer, and the nonmetal atoms are on the two sides of the layer. No very convincing explanation of the stability of the observed structure for lead oxide, rather than, for example, the sphalerite structure, has been given.

The structural principles for crystals such as the silicate minerals in which oxygen is the principal non-metal have been well worked out. The corresponding compounds of sulfur and its congeners are as yet not thoroughly understood. The sphalerite and wurtzite structures are, of course, simple ones that can be described in terms of tetrahedral coordination of atoms about one another. Chalcopyrite (CuFeS_2), enargite (Cu_3AsS_4), and many other sulfides have structures that represent superstructures of sphalerite and wurtzite, or are capable of similar interpretation in terms of covalent bonds arranged either tetrahedrally or otherwise in accordance with a reasonable electronic structure. But many of these substances have surprising and unexplained structures. An example is sylvanite, Cu_3VS_4 . This cubic crystal has a structure in which the sulfur atoms are arranged in the same way as in sphalerite, and the copper atoms occupy the positions occupied by three of the four zinc atoms, per unit cube, in sphalerite; but the vanadium atom,

instead of occupying the fourth tetrahedral position, is in another place, where it is still surrounded by four sulfur atoms but also is close to six copper atoms. Each sulfur atom, instead of being surrounded by three copper atoms and one vanadium atom in a tetrahedral arrangement (as, in enargite, it is surrounded by three copper atoms and one arsenic atom) is, instead, in a one-sided relationship with its environment: it forms three bonds with copper atoms, at tetrahedral angles, and a fourth bond, with vanadium, in the same direction, midway among the three bonds to copper.

Many sulfide structures, especially structures of sulfide minerals, have now been determined. It is possible that the amount of structural information available is already great enough to permit the induction of a significant set of structural principles, but there is also the possibility that the interactions in these crystals are so complex that additional structure determinations will be needed before this problem can be attacked with success. I think that it is likely that the next ten years will see the formulation of a sound set of structural principles for the metal sulfides, comparable in its significance to the set of principles that was formulated over 30 years ago for the oxides.

9.2. *Inorganic Complexes*

The first inorganic complex to have its structure determined by X-ray diffraction was the carbonate ion. When W. H. and W. L. Bragg carried out their study of calcite and isomorphous minerals in 1914 they found that the carbonate ion is planar and that the three oxygen atoms are equivalently related to the carbon atom. This information required that the chemists abandon the conventional valence-bond structure for the carbonate ion, in which one of the oxygen atoms is attached to the carbon atom by a double bond and the other two are attached by single bonds. During the following fifteen years two proposals about the structure were made: one, that the carbon atom forms only three bonds, and has only three electron pairs in its valence shell, and the second, that the carbon atom forms four bonds, and shares four electron pairs with the oxygen atoms, but with the structure a resonance hybrid of the three possible conventional structures, such as to make the three oxygen atoms equivalent. The discovery of the configuration of the carbonate ion in calcite thus contributed in an important way to the development of chemical structure theory during the period between 1914 and 1934.

The discovery that pyrite contains two sulfur atoms only 2.08 Å apart, also made in 1914, did not have much influence on the development of chemical structure theory, in part because the disulfide complex is so simple as not to introduce any serious theoretical problems and in part because in the decade following 1914 there was not great understanding of the significance of interatomic distances, and the sulfur-sulfur distance was at that time not necessarily interpreted as corresponding to a single covalent bond between the two sulfur atoms. On the other hand, the next complex ion found by X-ray diffraction, the dichloriodide ion in the rhombohedral crystal cesium dichloriodide that was studied by Wyckoff and reported in his first published paper in 1920, represented a significant contribution to the body of information underlying chemical structure theory. Wyckoff found that the dichloriodide ion is linear, with the two chlorine atoms equidistant from the iodine atom. The number of valence electrons is such that no electronic structure of the classical type (with shared electron pairs for the bonds and with no atom having a larger number of electrons associated with it than the number for the next noble gas) can be assigned to the complex. Even now, after more than forty years, there is some uncertainty about the best way of describing the electronic structure of the dichloriodide ions and of the many other complex ions formed by the halogens with one another that have been investigated in recent years, especially by Rose Slater and O. Hassel. There is no doubt that an extension of existing valence theory will be needed to encompass these complexes. The linear sequences of iodine atoms along the axis of a helical shell formed by starch molecules, as discovered by Rundle, also come in this category.

In 1921 Dickinson and, independently, Bijvoet and Kolkmeijer reported the structures of sodium chlorate and sodium bromate. The pyramidal configurations of the ions, in agreement with the theory of electronic structure that had been developed five years earlier by G. N. Lewis, provided strong support for this theory.

The years 1921 and 1922 were important ones for the Werner coordination theory of inorganic complexes. In 1921 Wyckoff and Posnjak reported their structure determination of ammonium hexachloroplatinate, verifying the octahedral arrangement of the six chlorine atoms about the platinum atom in the hexachloroplatinate ion that had been postulated by Werner twenty years before. The octahedral configuration was also verified within a year for the hexachlorostannate ion in the potassium and ammonium salts by Dickinson, for the hexafluorosilicate in the ammonium salt by Bozorth,

for the hexachloroplatinate ion in the potassium salt by Scherrer and Stoll, and for the nickel hexammoniate cation in the chloride, bromide, iodide, and nitrate by Wyckoff. Wyckoff in 1922 also showed that the hexahydrated zinc ion in zinc bromate hexahydrate has the octahedral configuration.

The surprising discovery by Werner, on the basis of studies of isomerism, that the tetraligated complexes of bipoisitive palladium and platinum have a square planar configuration was also verified by X-ray diffraction by Dickinson in 1922, through his determination of the structures of K_2PtCl_4 , K_2PdCl_4 , and $(NH_4)_2PdCl_4$. Dickinson found that the bond lengths in these square planar complexes are the same as in the corresponding octahedral complexes of the metal atoms with oxidation number greater by + 2. Ten years later, on the basis of theoretical considerations, it was pointed out (Pauling, 1931) that certain diamagnetic crystalline compounds of nickel should contain square planar complexes, and this prediction was soon verified by X-ray diffraction studies of many crystals.

The square planar configuration about bipoisitive copper in $K_2CuCl_4 \cdot 2H_2O$ was reported in 1927 by Hendricks and Dickinson, and a similar configuration was found in cupric chloride dihydrate by Harker. In these crystals the copper atom forms bonds that are indicated by the interatomic distances to be strong with two chlorine atoms and two oxygen atoms of water molecules, at the corner of a planar rhomb, and also forms two weaker bonds with chlorine atoms at the two remaining corners of an octahedron. This arrangement of four strong bonds and two weak bonds about the copper atom still constitutes something of a challenge to theoretical chemists, thirty years after its discovery.

During recent years some hundreds of crystals containing complexes have been investigated by X-ray diffraction, often with surprising and unusually interesting results. An outstanding example showing the power of the X-ray diffraction technique was the study of duodecitungstophosphoric acid, $H_3PW_{12}O_{40} \cdot 29H_2O$ by Keggin in 1934. Many complexes in which the ligancy of the metal atom is not four or six have also been investigated. An interesting example is the molybdenum octacyanide ion in $K_4Mo(CN)_8 \cdot 2H_2O$, the structure of which was determined by Hoard and Nordsieck in 1939.

9.3. *Inorganic Molecular Crystals*

The first inorganic crystal to be found to contain discrete molecules was tin tetraiodide, the structure of which was reported by Dickinson in 1923 (cubic, 8 SnI_4 per unit cube). In the same year Dickinson and A. L. Raymond reported the structure of the first organic compound, hexamethylenetetramine, and Bozorth reported his determination of the structure of pentoxides of arsenic and antimony, and showed that the crystals contain discrete molecules As_4O_6 and Sb_4O_6 .

9.4. *Metals and Other Crystals involving Metal-metal Bonds*

Although Barlow and Pope correctly assigned copper, silver, and gold to the cubic closest-packed arrangement and magnesium and beryllium to the hexagonal closest-packed arrangement, this assignment had little impact on science because their evidence was not convincing. A great part of the present understanding of the nature of metals and alloys is the result of X-ray investigations, beginning with the determination of the structure of copper by W. L. Bragg in 1914. Most of the metals were found to have simple structures, cubic or hexagonal closest packing or the cubic body centered arrangement; but the discovery of the structure of white tin by Bijl and Kolkmeijer in 1919, in which the atoms have ligancy six, was followed in a few years by the determination of the complex structures of alpha manganese and beta manganese by Bradley and, independently, Westgren and Phragmén, in 1925.

The first intermetallic compounds to be investigated were found to have simple structures. Then in 1927 Friauf determined the structures of MgCu_2 and MgZn_2 (the Friauf phases), and Bradley as well as Westgren and Phragmén investigated the gamma alloys. In all of these complex structures, including alpha manganese and beta manganese, the smaller atoms are surrounded by larger atoms at the corners of an icosahedron, and the larger atoms have ligancy greater than twelve. Many other structures of the icosahedral type, such as the structures of the sigma alloys, have been investigated in recent years. The nature of the interatomic interactions leading to the stability of these very complex structures has not yet been thoroughly elucidated, but it seems likely that the coordination polyhedra whose faces consist only of triangles are more stable than those involving squares, which occur in the simple structures, because the repulsion of atoms separated by the

diagonal of a square leads to instability. In metals and intermetallic compounds, as well as other substances, we may hope that a thorough analysis of the extensive information about interatomic distances will in the course of time provide a much greater understanding of the structures than exists now.

The extreme complexity and variety in the structure of chemical substances has been brought to light largely by X-ray techniques. An interesting early example is silver subfluoride, Ag_2F , investigated by Ott and Seyfarth in 1928. This crystal was found to have pairs of hexagonal layers of silver atoms with single layers of fluorine atoms interleaved between them. The bonds between the two silver layers in juxtaposition are closely similar to those between silver atoms in metallic silver, whereas the bonds between silver and fluorine seem to be essentially as in silver fluoride, AgF . Since then many other crystals in which there are metal-metal bonds as well as metal-nonmetal bonds have been investigated.

One of the first complexes to be studied in which evidence was found for a metal-metal bond was the ditungsto-enneachloride ion, $\text{W}_2\text{Cl}_9^{--}$, found in the crystal $\text{K}_3\text{W}_2\text{Cl}_9$, by Brosset in 1935. The complex has the configuration of two WCl_6 octahedra sharing a face, and the two tungsten atoms are only 2.41 Å apart, much less than in metallic tungsten (2.74 Å). This fact provides evidence that there is a strong tungsten-tungsten bond in this complex. Many other complexes have been found through X-ray investigation of the crystals to have metal atoms bonded together. Interesting examples of these complexes are $(\text{Mo}_6\text{Cl}_8)^{++++}$ (Brosset, 1945), and $(\text{Nb}_6\text{Cl}_{12})^{++}$, $(\text{Ta}_6\text{Cl}_{12})^{++}$, and $(\text{Ta}_6\text{Cr}_{12})^{++}$ (P. A. Vaughan and coworkers, 1950). In these complexes the metal atoms lie at the corners of an octahedron, with the halogen atoms out from the centers of the faces or the edges of the octahedron. The interatomic distances for the molybdenum complex are close to the single-bond value and for the other complexes close to the value corresponding to bond number 2/3.

The carbonyl complexes provide an interesting problem in structural chemistry that has been in large part solved by the methods of X-ray diffraction of crystals and electron diffraction of gas molecules. The first significant step in the solution of this problem was the investigation of crystals of diiron-enneacarbonyl, $\text{Fe}_2(\text{CO})_9$, by R. Brill in 1927. In this molecule each iron atom is surrounded octahedrally by carbon atoms, and the octahedra share a face. The three bridging carbon atoms are at distances from the iron atom corresponding to the formation of two single bonds with these atoms (and a double bond

with the attached oxygen atom), whereas the other six carbon atoms form essentially double bonds with the adjacent iron atom. (The discovery that the interatomic distances in carbonyls correspond to double bonds between carbon and metal was made for nickel tetracarbonyl by L. O. Brockway and P. C. Cross in 1935.) The two iron atoms in diiron-eneacarbonyl are 2.46 Å apart, corresponding to the formation of a bond between them. During recent years many complex metal carbonyls and related substances have been investigated, and found to involve metal-metal bonds, bridging carbonyl groups, and other carbonyl groups attached to metal atoms by double bonds, as in diiron-eneacarbonyl.

The amount of accurate and detailed structural information about complexes has now become very great, exceeding the bounds of chemical theory. It is likely that the extensive information about interatomic distances and bond angles in these complexes will be used at some time in the future as the basis for the development of a more penetrating theory of electronic structure and chemical bonding in these complexes than is now available. Other powerful methods of studying complexes, such as electron spin magnetic resonance and nuclear magnetic resonance and the Mössbauer effect, have become available and are also providing information that will need to be taken into consideration in the formulation of a more powerful theory of complexes.

9.5. *Other Problems*

The discovery of antiferromagnetism and ferrimagnetism has stimulated structural investigations of oxides and other crystals with these properties. In magnetite, Fe_3O_4 , for example, it has been found by neutron diffraction that the octahedrally coordinated metal atoms have their magnetic moments pointed in one direction and the tetrahedrally coordinated metal atoms have the opposite orientation of their magnetic moments. In manganous fluoride, which has the rutile structure, the magnetic moments of the manganese atoms have parallel orientation for a string of octahedra that share edges with one another and the opposite orientation for the surrounding strings of octahedra. These and other magnetic superstructures that have been discovered by neutron diffraction indicate that in these crystals the bonds between the metal atoms and the non-metal atoms are one-electron bonds, rather than the usually assumed electron-pair bonds with some partial ionic character.

The hydrogen bond is a structural feature that has received recognition largely through the X-ray diffraction studies of crystals. Although the discovery of the hydrogen bond by Latimer and Rodebush in 1920 was not based to any significant extent on crystal-structure results, a large part of the knowledge now existing about the properties of this bond has resulted from X-ray studies. Among the interesting results of these studies is the recognition of the existence of hydrogen-bonded clathrate compounds, by Powell and his coworkers, and in particular the clathrate hydrates, such as chlorine hydrate. The importance of the hydrogen bond in living organisms, as in protein molecules and deoxyribonucleic acid molecules, has been recognized in large part because of the knowledge about these bonds obtained through X-ray studies.

The boranes and metallocenes provide interesting examples of substances with structures not compatible with simple valence-bond theory. In ferrocene, for example, the iron atom is equidistant from ten carbon atoms, in the two cyclopentadienyl rings. Both the observed interatomic distance and theoretical considerations indicate strongly that the iron-carbon bonds are not single covalent bonds, but are instead fractional bonds. No really satisfactory theory of substances of this sort has been developed as yet. I think that we may expect that during the next few years much progress will be made in the development of a more powerful theory of the chemical bond than exists at present, and also in the interpretation of the experimentally determined bond lengths, and that the method of X-ray diffraction, in collaboration with other methods of investigating the structure of molecules and crystals, will lead to additional great progress in our understanding of the nature of molecules and crystals.

It is, of course, impossible to answer the question as to how the field of inorganic structures would have developed if the discovery of X-ray diffraction had been delayed. The almost complete lack of progress in the decades before 1913 and the great progress thereafter show clearly that the development of this field resulted from Laue's brilliant discovery and the Braggs' effective application of it. Despite the great progress that has been made, there are many problems in structural inorganic chemistry still awaiting solution, and X-ray diffraction will no doubt contribute to their solution during the coming years.