

## INORGANIC STEREOCHEMISTRY

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DURING the past few years there have been several developments in theoretical chemistry which have led to a much better understanding of the factors responsible for the shapes of inorganic molecules. These developments have also made it clear that some apparently different approaches to stereochemistry can be integrated and, indeed, shown to be complementary. This Review attempts to bring together these approaches and to apply them to elements over the whole of the Periodic Table. Perhaps the most important result emerging from this unification is the conclusion that the simple qualitative Sidgwick-Powell<sup>1</sup> theory of electron-pair repulsions is of great value in accounting for the stereochemistry of practically all inorganic compounds.

In early applications of the valence-bond method to stereochemistry only the  $\sigma$ -bond electrons were considered, the stereochemistry being inferred from the bonding orbitals they were presumed to occupy. Later, consideration in addition of non-bonding lone pairs generally gave a better approximation to the actual shape of molecule. Sidgwick and Powell<sup>1</sup> assumed that lone pairs of electrons and bonding pairs were of equal importance and that they arranged themselves symmetrically so as to minimise the repulsions between them. The ligand(or crystal)-field theory is concerned with the influence of the non-bonding electrons upon the arrangement of the ligands which are assumed to be negative ions or dipoles surrounding a central metal atom. Recently the influence of covalent binding has also been considered. These various theories are in fact closely related and an attempt has been made in this Review to integrate them. It appears that the simple theory of electron-pair repulsions receives considerable justification from quantum-mechanics and when refined to take into account differences between the repulsions between lone pairs and bonding pairs of electrons provides a very satisfactory theory of the stereochemistry of inorganic molecules.

### A simple electrostatic theory

**The Arrangement of Electron Pairs in Valency Shells.**—Sidgwick and Powell<sup>1</sup> pointed out in 1940 that the arrangements in space of the covalencies of multivalent atoms are very simply related to the size of the valency shell of electrons. The pairs of electrons in a valency shell, irrespective of whether they are shared (*i.e.*, bonding) pairs or unshared (*i.e.*, non-bonding) pairs, are always arranged in the same way which depends *only* on their number. Thus two pairs are arranged linearly, three pairs

<sup>1</sup> Sidgwick and Powell, *Proc. Roy. Soc.*, 1940, **A**, 176, 153.

in the form of a plane triangle, four pairs tetrahedrally, five pairs in the form of a trigonal bipyramid, and six pairs octahedrally. Table I and Fig. 1 give the various possible molecular shapes that can arise from these different electron arrangements. These arrangements appear to hold without exception for the non-transitional elements, *i.e.*, those which do not use inner *d* orbitals for bond formation. To these we can add a further arrangement, namely that of seven electron pairs in a pentagonal-bipyramid. Valency shells containing more than seven electron pairs are very rare among the non-transitional elements.

These regular shapes are only obtained if all the electron pairs are forming bonds with the same kind of atom or group. If some of the electrons are lone pairs, or if there are two or more different kinds of attached atom or group, deviations from these regular structures are to be expected and are discussed later.

In certain cases (marked \* in Table I, and Fig. 1 on pp. 341 and 342) there are alternative positions for the one or more lone pairs and therefore alternative molecular shapes. The choice has been made on grounds discussed later. For example, we cannot say at this stage of the argument whether  $\text{ClF}_3$  would be planar T-shaped with  $90^\circ$  bond angles (I), planar and symmetrical with  $120^\circ$  bond angles (II), or pyramidal (III).

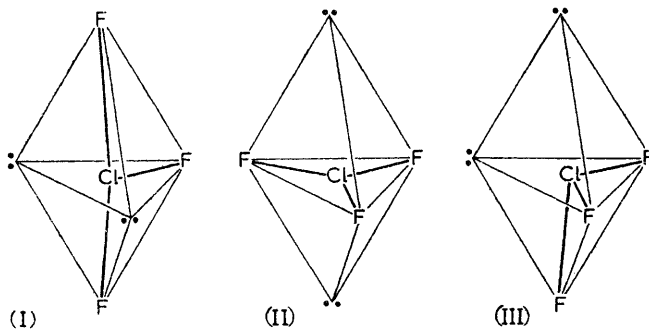


Table I includes all the known shapes of molecules of the non-transitional elements. The pentagonal-bipyramidal arrangement of six bonding pairs and one lone pair is the only one that is at all uncertain. Its only example so far investigated is the  $[\text{SbBr}_6]^{3-}$  ion, which was reported<sup>2</sup> in 1933 to have a regular, and not an irregular, octahedral structure as suggested in the Table.

The arrangements of electron pairs giving the molecular shapes in Table I are just those predicted if it is assumed that the electron pairs repel each other so that they arrange themselves as far apart as possible. Thus methane, ammonia, and water should all have bond angles of  $109^\circ 28'$ , compared with the experimental values of  $109^\circ 28'$ ,  $106^\circ 7'$ , and  $104^\circ 27'$ .

The shapes of molecules containing double and triple bonds can be similarly predicted if it is assumed that the two pairs of electrons in a double

<sup>2</sup> Hoard and Dickenson, *Z. Krist.*, 1933, **84**, 436.

bond and the three pairs in a triple bond together occupy only one of the positions in the various arrangements given in Table 1. In this way the shapes given in Table 2 can be predicted.

**Deviations from Regular Shapes.**—This simple theory can be considerably improved qualitatively by assuming that electrostatic repulsions between the electron pairs in a valency shell decrease in the order: lone-pair-lone-pair > lone-pair-bond-pair > bond-pair-bond-pair. This can be

FIG. 1

*Shapes of molecules (non-transitional elements).*

The numeral following the description of the shape is the number of lone pairs of electrons.

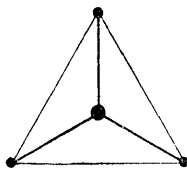
No. of electron  
pairs

2

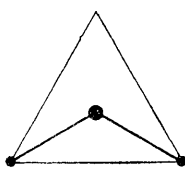


Linear (0)

3

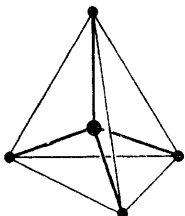


Triangular-plane (0)

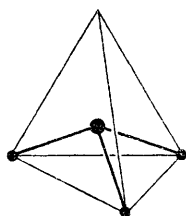


V-shape (1)

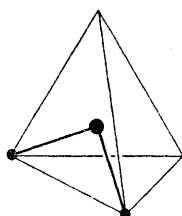
4



Tetrahedron (0)

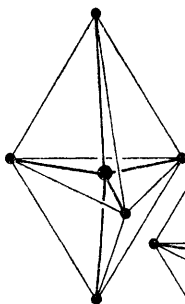
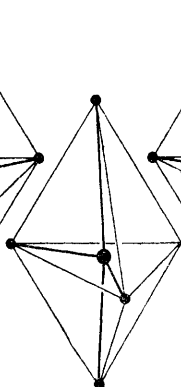
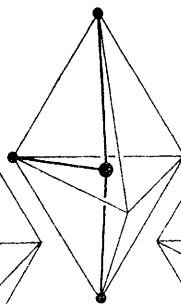


Trigonal-pyramid (1)

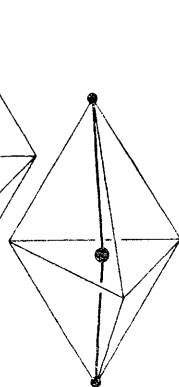


V-shape (2)

5

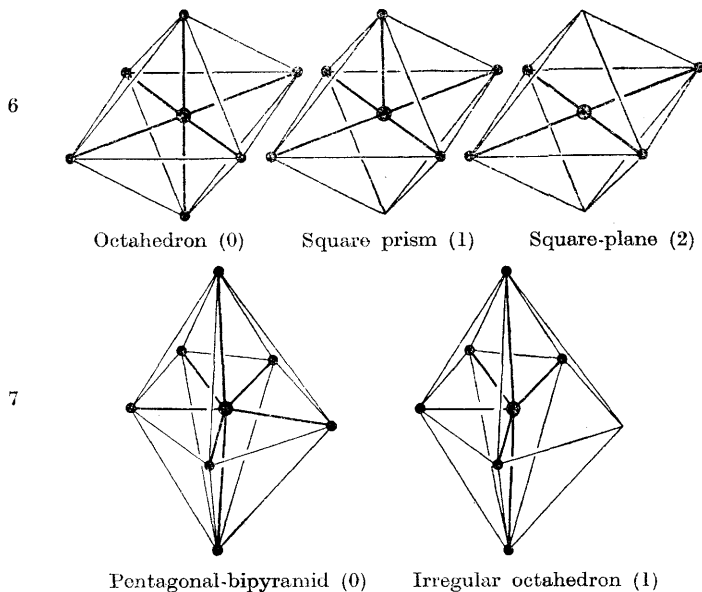
Trigonal-  
bipyramid (0)Irregular  
tetrahedron (1)

T-shape (2)



Linear (3)

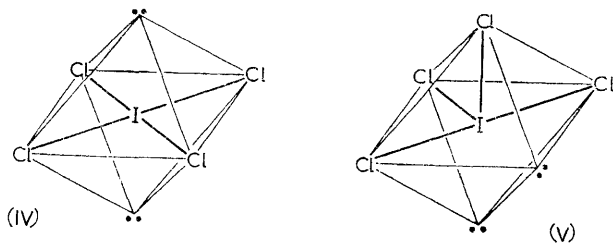
[FIG. 1 continued overleaf

FIG. 1.—*continued*

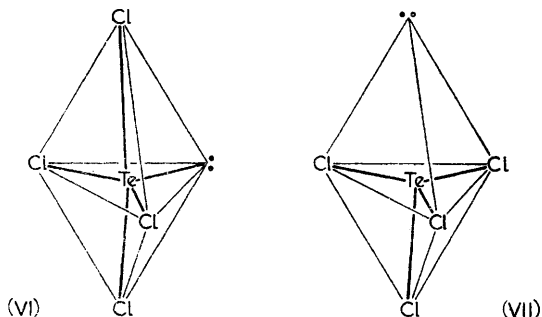
understood by picturing the lone pairs as being closer to the nucleus than the bonding pairs, which may be imagined pulled out to some extent by the other nucleus with which they are forming a bond. Thus the lone pairs will be closer to each other than the bonding pairs and so will repel each other more strongly. This assumption enables one to give a qualitatively correct account of the decrease of the bond angles in a series such as methane, ammonia, and water and to understand better the shapes of those molecules that could not be predicted unambiguously in Table 1.

On passing from methane to ammonia, we replace a bonding pair by a lone pair, which repels the remaining three bond pairs somewhat more than the original bond pair, so causing the bond angle to decrease from the tetrahedral value of  $109^\circ 28'$ . On passing from ammonia to water we replace another bond pair by a lone pair and the bond angle decreases further.

In  $[\text{ICl}_4]^-$  it might appear that the two lone pairs could be either at an angle of  $180^\circ$  (IV) or  $90^\circ$  (V). Repulsions between the lone pairs will evidently be minimised in (IV), however, and this is the structure observed.



In tellurium tetrachloride,  $\text{TeCl}_4$ , there is only one lone pair and it is necessary to consider the lone-pair-bond-pair repulsions. In structure (VI) the lone pair is at an angle of  $90^\circ$  to two of the bonding pairs, but in structure (VII) it is at an angle of  $90^\circ$  to three of the bond pairs. The lone-pair-bond-pair repulsion should be less in the former than in the latter, and the former is, in fact, the observed structure.



In the case of chlorine trifluoride there are three possible structures, (I), (II), and (III), in which the two lone pairs are at angles of  $120^\circ$ ,  $180^\circ$ , and  $90^\circ$  respectively. Considering only the lone-pair-lone-pair repulsion, we predict that the planar structure (II) should be preferred to (I) or (III). The actual structure is, however, (I), so that it appears that lone-pair-bond-pair repulsions must also be taken into account. In structure (II) there are six lone-pair-bond angles, all of  $90^\circ$ , whereas in (I) two of these angles are  $120^\circ$ , and only four of them are  $90^\circ$ . This reduction in the lone-pair-bond-pair repulsions seems more than to offset the increased lone-pair-lone-pair repulsion caused by decreasing the angle between them from  $180^\circ$  to  $120^\circ$ . As the two bond angles in the molecule are actually only  $87^\circ 29'$ , the angles between the lone pairs and the fluorine atoms are slightly greater than  $90^\circ$ , which would be expected if lone-pair-lone-pair repulsions are greater than bond-pair-bond-pair repulsions.

The variations in the bond angle in series of related molecules can be satisfactorily interpreted by a slight extension of these ideas. Thus, in the following two series of molecules, the bond angles decrease:  $\text{NH}_3$   $106^\circ 45'$ ,  $\text{PH}_3$   $93^\circ 50'$ ,  $\text{AsH}_3$   $91^\circ 35'$ ,  $\text{SbH}_3$   $91^\circ 30'$ ; and  $\text{H}_2\text{O}$   $104^\circ 27'$ ,  $\text{H}_2\text{S}$   $92^\circ 20'$ . This can be attributed to the decreasing electronegativity of the central atom in both series, which allows the bonding pairs to be drawn further away from the central nucleus by the hydrogen atoms, thereby increasing their distance apart and decreasing the repulsions between them.<sup>3</sup> A similar effect is obtained by replacing hydrogen by the more electronegative fluorine:  $\text{NF}_3$   $102^\circ 9'$ ,  $\text{OF}_2$   $101^\circ 30'$ . This substitution decreases the bond angle. Similarly the decrease in the bond angle in the series  $\text{CF}_4$   $109^\circ 28'$ ,  $\text{CHF}_3$   $108^\circ 48'$ ,  $\text{CH}_2\text{F}_2$   $108^\circ$  can be attributed to the fact that the replacement of fluorine by hydrogen enables the electrons in the remaining C-F bonds to move further out towards the fluorine atoms.

<sup>3</sup> Linnett and Mellish, *Trans. Faraday Soc.*, 1954, **50**, 657.

TABLE 1. *The arrangements of electron pairs in valency shells and the shapes of molecules (non-transitional elements).*

Total no. of electron pairs in valency shell	Arrangement of electron pairs	Corresponding hybrid orbitals	No. of bonding pairs	No. of non-bonding (lone) pairs	Shape of molecule	Examples
2 . . . .	Linear	$sp$	2	0	Linear	$\text{HgCl}_2$ $[\text{Ag}(\text{CN})_2]^-$
3 . . . .	Triangular-plane	$sp^2$	3	0	Triangular-plane	$\text{BCl}_3$
4 . . . .	Tetrahedron	$sp^3$	4	0	Tetrahedron	$\text{SnCl}_4$ ( <i>gas</i> )
			3	1	Trigonal-pyramid	$\text{CH}_4$ $\text{NH}_3$
5 . . . .	Trigonal-bipyramid	$sp^3d_{z^2}$	2	2	V-shape	$\text{H}_2\text{O}$ $\text{F}_2\text{O}$
			5	0	Trigonal-bipyramid	$\text{PCl}_5$
			4	1	Irregular * tetrahedron	$\text{TeCl}_4$
			3	2	T-shape *	$\text{ClF}_3$
			2	3	Linear *	$[\text{Cl}_2]^-$
6 . . . .	Octahedron	$sp^3d_x d_y d_z^2 \dots y^2$	6	0	Octahedron	$\text{SF}_6$ $[\text{PCl}_6]^-$
			5	1	Square-pyramid	$\text{IF}_5$
			4	2	Square *	$[\text{Cl}_4]^-$
7 . . . .	Pentagonal-bipyramid	$sp^3d_x^2 d_e$	7	0	Pentagonal-bipyramid	$\text{IF}_7$
			6	1	Irregular octahedron *	$[\text{SbBr}_6]^{3-}$

TABLE 2. *The shapes of molecules containing double bonds.*

Total no. of bonds and lone pairs	Arrangement	No. of bonds	No. of lone pairs	Shape of molecule	Examples
2 . . .	Linear	2	0	Linear	O:C:O H-C≡N
3 . . .	Triangular	3	0	Triangular-plane	
	Plane	2	1	V-shape	
4 . . .	Tetrahedral	4	0	Tetrahedral	
		3	1	Triangular-pyramid	
		2	2	V-shape	
5 . . .	Trigonal	5	0	Trigonal-bipyramid	
		4	1	Irregular tetrahedron	
6 . . .	Octahedron	6	0	Octahedron	

### The exclusion principle and molecular shape

The distribution of electrons in atoms and molecules can only be correctly described by means of quantum mechanics. Exact calculations are not possible even for simple molecules and the approximate calculations that can be made are lengthy and difficult. Some very important conclusions can, however, be reached simply by considering the fundamental property of electrons expressed in the exclusion principle, as a consequence of which electrons having the same spin tend to avoid each other as far as possible and, in particular, if all the electrons in a system have the same spin their most probable distribution is that in which they are all as far apart as possible.<sup>4</sup> Pauli originally stated the exclusion principle in the form that two electrons with the same spin cannot have the same space wave function, that is, occupy the same orbital. A more exact and general statement

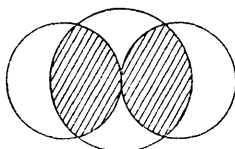
<sup>4</sup> Lennard-Jones, *Adv. Sci.*, 1954, **51**, 136.

which leads to the above conclusion that electrons with the same spin avoid each other, is that the complete wave function  $\psi$  for a system must be antisymmetrical to electron interchange.

**The Most Probable Configurations of Electrons in Atoms: Hybrid Orbitals.**—Let us consider, as an example, the beryllium atom in the configuration  $(1s)^2(2s)(2p)$  and in which the spins of the two unpaired electrons are the same. The probability that the two electrons will be found simul-

FIG. 2

“Overlap” (shaded area) of  $s$  and  $p$  atomic orbitals.



taneously with any given co-ordinates is given by the square of the wave function,  $\psi^2$ . As a consequence of the exclusion principle the actual probability distribution of the electrons will differ considerably from what may be called the “classical” distribution in which the electrons are regarded as occupying one each of the atomic orbitals  $\psi(2s)$  and  $\psi(2p)$  quite independently, because they will tend to avoid coming as close together as the “classical” distribution allows.<sup>5</sup> Thus the probability of finding the two electrons in the same region of overlap\* of the two orbitals in which they will be close together will be low. Since these two orbitals have a considerable region of overlap the actual distribution will differ considerably from the “classical” distribution—it differs by the “exchange” contribution to the probability distribution which is proportional to the extent of overlap of the two orbitals. Calculation of the maximum value of  $\psi^2$  shows that the electrons have a maximum probability of being found on opposite sides of the nucleus on a straight line passing through the nucleus, *i.e.*, at an angle of  $180^\circ$  (Fig. 3). If however we replace the atomic orbitals  $\psi(2s)$  and  $\psi(2p)$  by the equivalent  $sp$  hybrid orbitals

$$\psi(sp: 1) = (1/\sqrt{2})[\psi(2s) + \psi(2p)] \text{ and } \psi(sp: 2) = (1/\sqrt{2})[\psi(2s) - \psi(2p)]$$

which leaves the complete wave function  $\psi^2$  for the system unchanged, we can see (Fig. 4) that they give a clearer picture of the actual electron distribution than do the atomic orbitals  $\psi(2s)$  and  $\psi(2p)$ : the directions

FIG. 3

The most probable arrangement of two electrons with the same spin in the configuration  $(2s)(2p)$ .



<sup>5</sup> Lennard-Jones and Pople, *Proc. Roy. Soc.*, 1950, A, **202**, 166.

\* *I.e.*, a region in which the product of orbitals  $\psi_A\psi_B$  is substantially different from zero. We do not use the term “overlap” to mean “overlap integral” which in many of the cases discussed is zero.

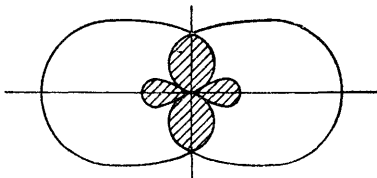


of the maxima of these orbitals correspond to the directions in which there is a maximum probability of finding the two electrons. This is because these hybrid orbitals have a much smaller region of overlap than the atomic orbitals and thus the exchange contribution to the distribution is small and the actual distribution differs only slightly from the "classical" distribution.

For the configuration  $(1s)^2(2s)^2(2p_x)(2p_z)$  of the carbon atom, Zimmerman and van Rysselberghe<sup>6</sup> have shown, as a consequence of the exclusion principle, that the most probable arrangement of the four  $p$  electrons, if they all have the same spin, is at the vertices of a regular tetrahedron.

FIG. 4

*Region of overlap (shaded area) and shape of  $sp$  hybrid orbitals.*



Similarly, in the configuration  $(1s)^2(2s)(2p_x)(2p_y)$  of the boron atom, in which the unpaired electrons all have the same spin, the most probable arrangement is at the vertices of an equilateral triangle. Electron-probability distributions in these two cases are given well by a "classical" interpretation of their distributions in the tetrahedral  $sp^3$  and the trigonal  $sp^2$  hybrid orbitals respectively.

**The Most Probable Configurations of Electrons in Molecules: Valency- or Bond-orbitals.**<sup>7</sup>—We now pass to a consideration of systems with equal number of electrons of opposite spin, in particular valency shells of atoms that have been completed in molecule formation. In the neon atom there are four electrons of one spin and four of opposite spin in the configuration  $(2s)^2(2p_x)^2(2p_y)^2(2p_z)^2$  and Lennard-Jones<sup>4</sup> has shown that the exclusion principle leads to the conclusion that the most probable arrangement of each set of four electrons of the same spin is at the vertices of a tetrahedron, but there is no correlation between these two sets of opposite spin, which therefore have an equal probability of being found in any relative orientation. In a molecule such as methane the eight valency-shell electrons of the carbon atom might be expected to have the same most probable arrangement. However, the attractions of the hydrogen nuclei for these electrons will cause the two tetrahedra to come into register with each other, so that there will be in effect four pairs of electrons arranged tetrahedrally. The same arrangement will also be found in all other molecules with four pairs of electrons in the valency shell of the central atom, such as, for example, ammonia and water. Thus solely as a consequence of the exclusion principle the most probable arrangement of four pairs of electrons in

<sup>6</sup> Zimmerman and van Rysselberghe, *J. Chem. Phys.*, 1949, **17**, 598.

<sup>7</sup> See, for example, Coulson, "Valence", Oxford Univ. Press, 1952, p. 108.

a valency shell proves to be at the corners of a tetrahedron—just the arrangement that was given in Table 1.

Each of the four pairs of electrons in the valency shell of, for example, the methane molecule can be regarded as occupying a localised valency- or bond-orbital, that is, a linear combination of one of the  $sp^3$  hybrid orbitals of the carbon atom and the  $1s$  orbital of a hydrogen atom. There will be four such equivalent bond orbitals in methane.

Similarly, the water molecule can be described, to a first approximation, in terms of two bond orbitals, each containing two electrons of opposite spin and being a linear combination of one of the hybrid  $sp^3$  orbitals on the oxygen atom and a hydrogen  $1s$  atomic orbital, and two lone-pair orbitals, each containing two electrons, which are the two remaining hybrid  $sp^3$  orbitals. Such a description of the water molecule in terms of localised orbitals is equivalent to the molecular- (non-localised) orbital description<sup>8</sup> but, because of the smaller overlap of the localised orbitals, it gives a clearer picture of the electron distribution in the molecule in terms of classical ideas than does the molecular-orbital description. Similarly it can be shown that the most probable disposition of the two pairs of electrons in molecules such as beryllium chloride,  $BeCl_2$ , is at an angle of  $180^\circ$  and that of three pairs in molecules such as boron trichloride,  $BCl_3$ , is in a plane at angles of  $120^\circ$ . Again these are the arrangements that were given in Table 1.

Another important advantage of the use of hybrid orbitals in describing atoms and molecules can be illustrated by the results of Lennard-Jones and Pople's calculation<sup>5</sup> on the two valency electrons of the beryllium atom in the configuration  $(1s)^2(2s)(2p)$ . They used Slater-type  $2s$  and  $2p$  functions and calculated the interaction energy for both the atomic-orbital and the hybrid-orbital description of the atom. The total interaction energy of the electrons is the same for both descriptions, of course, and can be expressed as the sum of terms which can be described as "classical" Coulomb repulsion-energy terms and non-classical or "exchange" energy terms. The magnitude of the latter depends on the overlap of the component orbitals, and thus they are greater for the atomic-orbital than for the hybrid-orbital description. Lennard-Jones and Pople<sup>5</sup> found that, whereas for atomic orbitals the exchange energy was 28% of the total interaction energy, for hybrid orbitals it was only 2.4%. Thus, if the electrons are described in terms of hybrid orbitals, their interaction energy can reasonably be regarded entirely as electrostatic repulsion.

In general, whenever electrons are described in terms of localised orbitals (*i.e.*, hybrid or bond orbitals) their energy of interaction is almost entirely classical electrostatic repulsion energy between charge-clouds corresponding to the localised orbitals.<sup>5</sup> This justifies our earlier treatment of the interaction energy between pairs of electrons simply in terms of the electrostatic repulsions between them.

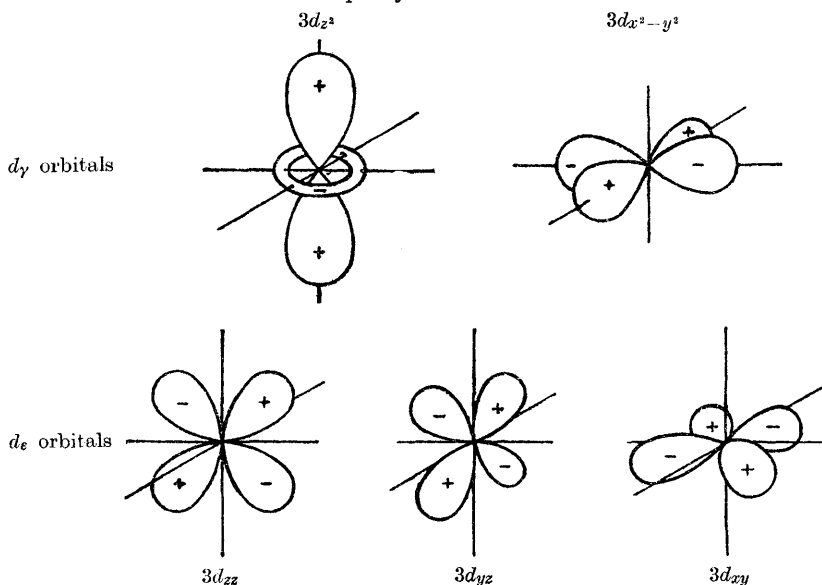
We may summarise by saying that because of the exclusion principle

<sup>8</sup> See, for example, Walsh in "Progress in Stereochemistry", Butterworths, London, 1954, vol. 1.

the unpaired electrons in an atom having the same spin tend to keep as far apart as possible, and that the electrons in the valency shell of any atom in a molecule are distributed in pairs which tend to keep as far apart as possible. These electrons are most conveniently regarded as occupying localised orbitals which in atoms are hybrid orbitals and in molecules are hybrid orbitals or bond orbitals formed by taking a linear combination of a hybrid orbital on the central atom and a suitable unoccupied orbital on the combining atom. Because such localised orbitals only overlap slightly a "classical" interpretation of the distribution of the electrons in such orbitals is a good approximation to the truth. Moreover their interaction energy can reasonably be regarded as the classical electrostatic repulsion energy between charge clouds corresponding to the hybrid orbitals.

**Valency Shells containing more than Eight Electrons :  $d$  Orbitals.**—In valency shells containing more than eight electrons,  $d$  orbitals are used. These have properties that differ in some important respects from those of  $p$  orbitals. Unlike  $p$  orbitals, they have not all the same shape, or the same relative orientation in space. Thus the  $d_{z^2}$  orbital differs in shape from the four equivalent  $d_{x^2-y^2}$ ,  $d_{xy}$ ,  $d_{xz}$ , and  $d_{yz}$  orbitals and the  $d_{z^2}$  and the  $d_{x^2-y^2}$  orbitals are directed along the same  $x$ ,  $y$ , and  $z$  orbitals as the  $p$  orbitals, whereas the  $d_{xy}$ ,  $d_{yz}$ , and  $d_{xz}$  orbitals have their nodes in between the directions of these axes (Fig. 5). The difference in the relative orientation of the  $d$  orbitals is most important for stereochemistry and, following the usual practice in ligand-field theory, we shall sometimes find it convenient

FIG. 5

Shapes of  $d$  orbitals.

[Reproduced, with permission, from "Progress in Stereochemistry", Butterworths, London, 1957, Vol. 2, p. 277]

to refer to the  $d_{x^2-y^2}$  and the  $d_{z^2}$  orbitals as  $d_y$  orbitals and the  $d_{xy}$ , etc., orbitals as  $d_e$  orbitals. The arrangements of the electron pairs in valency shells and the shapes of molecules depend on the particular  $d$  orbitals that are used for bond formation, as well as on the number that are used.

It will be convenient here to distinguish between the transitional and non-transitional elements, and for the moment to discuss only the latter, which use in bond formation only  $d$  orbitals with the same principal quantum number as the highest  $s$  and  $p$  orbitals, these  $d$  orbitals being of higher energy than the last two. Thus  $d$  orbitals are only used *in addition to* the  $s$  and the three  $p$  orbitals and one, two, and three  $d$  orbitals are used in five-, six-, and seven-co-ordinated molecules respectively.

When only one  $d$  orbital is used in bond formation it is most likely to be a  $d_y$  orbital. Linnett and Mellish<sup>9</sup> have shown that because of the exclusion principle the most probable arrangement of five electrons with the same spin in the configuration  $(s)(p)^3(d_{z^2})$  is at the corners of a pentagonal-bipyramid. The corresponding hybrid orbitals are the  $sp^3d_{z^2}$  pentagonal-bipyramidal orbitals. The most probable arrangement for the configuration  $(s)(p)^3(d_{x^2-y^2})$  is the square-pyramid.<sup>9</sup> The corresponding hybrid orbitals are the four planar  $sp^2d_{x^2-y^2}$  orbitals together with the "unhybridised"  $p_z$  orbital. Linnett and Mellish found that the probability of the trigonal-bipyramidal arrangement is slightly greater than that of the square-pyramidal arrangement. By an argument similar to that applied to methane, it can be concluded that, in any molecule in which there are five pairs of electrons in the valency shell of a non-transitional element, these pairs will be at the corners of a trigonal-bipyramid. The trigonal-bipyramid and structures derived from it (see Table 1) are the only structures yet observed for molecules of the non-transitional elements with ten electrons in their valency shells.

When two  $d$  orbitals are used for bond formation, they are most likely to be the two  $d_y$  orbitals. Linnett and Mellish<sup>9</sup> showed that the most probable arrangement of six electrons with the same spin in the configuration  $(s)(p)^3(d_{x^2-y^2})(d_{z^2})$  is at the corners of an octahedron. Similarly in any molecule in which there are six pairs of electrons in the valency shell of an atom of a non-transitional element the pairs of electrons will be arranged octahedrally. The corresponding orbitals are the  $sp^3d_y^2$  octahedral orbitals; the octahedron and structures derived from it (see Table 1) are the only structures yet observed for molecules of the non-transitional elements with twelve electrons in their valency shells.

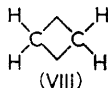
When three  $d$  orbitals are used for bond formation, it seems most likely that these will be the two  $d_y$  orbitals and one of the  $d_e$  orbitals. The most probable arrangement of seven electrons with the same spin in the configuration  $(s)(p)^3(d_y)^2(d_e)$  or of seven electrons pairs has not been previously discussed but it can be shown to be the pentagonal-bipyramid. The corresponding  $sp^3d_y^2d_e$  pentagonal-bipyramidal hybrid orbitals have been discussed by Duffey.<sup>10</sup> In the only known example of a seven-co-ordinated

<sup>9</sup> Linnett and Mellish, *Trans. Faraday Soc.*, 1954, **50**, 665.

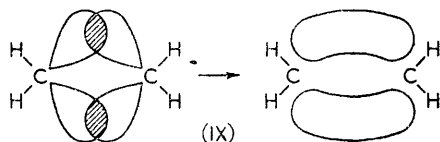
<sup>10</sup> Duffey, *J. Chem. Phys.*, 1950, **18**, 943.

molecule of a non-transitional element, iodine heptafluoride, a pentagonal-bipyramidal structure was observed. The probability that the ion  $[\text{SbBr}_6]^{3-}$  also has a structure based on the pentagonal-bipyramid has been discussed earlier.

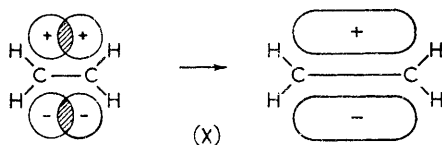
**Double and Triple Bonds.**—We mentioned earlier that if the two or three electron pairs of a double or a triple bond are regarded as occupying only one of the positions in the various arrangements shown in Fig. 1 the molecular shapes in Table 2 can be predicted. The most probable arrangement of the electron pairs of an atom forming double or triple bonds is the same, at least to a first approximation, as if it was forming only single bonds. In the case of the carbon atom for example, this is the tetrahedral arrangement of four electron pairs. Thus, the bonds in the ethylene molecule can be pictured as in (VIII), each carbon atom forming four tetrahedral bonds. The pairs of electrons can most conveniently be regarded as occupying bond orbitals formed from the four tetrahedral  $sp^3$  hybrid orbitals of the carbon atom. The two orbitals forming the double bond must be "bent" or "banana-shaped" bonds (IX).



It is customary, however, and sometimes more convenient, to describe double and triple bonds in a different, although entirely equivalent,<sup>11</sup> manner in terms of  $\sigma$  and  $\pi$  orbitals. Thus, in ethylene for example, each



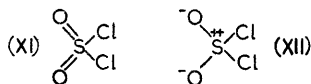
carbon atom is regarded as forming a  $\sigma$  bond to each of the three atoms to which it is bonded. Each of the  $\sigma$  bonds is formed from a trigonal  $sp^2$  orbital on the carbon atom, by "end-on" overlap with a suitable orbital on the other atom. In addition there is a  $\pi$  bond between the two carbon atoms formed by "sideways" overlap of a  $p$  orbital on each carbon atom (X).



Because the  $\pi$  orbital is relatively delocalised and overlaps the  $\sigma$  orbital appreciably this description of the double bond does not give such a good picture of the most probable distribution of the electrons as does that given in structure (IX); nevertheless, it has become common practice to use this description. The stereochemistry of an atom that is forming double bonds can be regarded as being determined only by the number of pairs of  $\sigma$  electrons in the valency shell and the  $\pi$ -electron pairs can be ignored.

<sup>11</sup> See, for example, Pitzer, "Quantum Chemistry", Prentice-Hall, New York, 1953, p. 165.

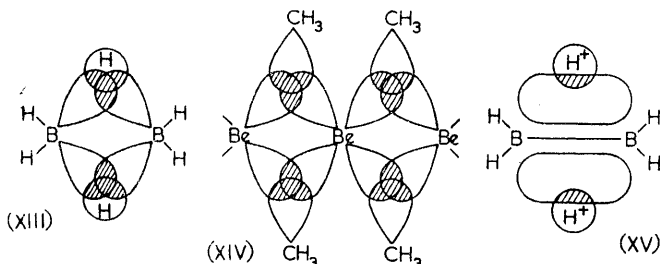
Thus carbon dioxide  $O=C=O$  has a linear structure based on the most probable arrangement of two  $\sigma$  electron pairs and carbonyl chloride  $Cl_2C=O$  has a planar-triangular structure based on the most probable arrangement of three  $\sigma$  electron pairs. In many molecules some bonds are neither pure single nor pure double bonds, but have an intermediate character as, for example, in sulphuryl chloride,  $SO_2Cl_2$ , which may be described as a resonance hybrid of (XI) and (XII).



It is, however, not necessary to know the extent of the double-bond character of the sulphur-oxygen bonds to predict that the molecule will be tetrahedral since this is determined solely by the tetrahedral arrangement of the four  $\sigma$ -bonding pairs in the valency shell of the sulphur atom. Since a double bond contains two electron pairs the electrostatic repulsions between two double bonds would be expected to be greater than that between a double bond and a single bond which, in turn, would be greater than that between two single bonds. Thus we would expect the angles between the double bonds formed by an atom in any molecule to be greater than the angles between its single bonds, and this is generally found to be so. A number of examples are discussed later.

**Multicentre Bonds.**—Although a single electron pair normally binds two atoms it can in some cases unite three or more. Such bonds are conveniently called multicentre bonds. Examples are found in electron-deficient molecules such as  $B_2H_6$  and  $[Be(CH_3)_2]_n$ . These bonds can be described in at least two different but essentially equivalent ways:

They may be considered as being formed by the overlap of three atomic or hybrid orbitals as in structures (XIII) and (XIV). If this type of description is used the foregoing conclusions concerning the arrangements of electron pairs in valency shells apply equally well to this type of molecule.



Thus in  $B_2H_6$  there is a tetrahedral arrangement of four electron pairs around each boron atom. Similarly in  $[Be(CH_3)_2]_n$  there is a tetrahedral arrangement of four electron pairs around both the beryllium and carbon atoms.

Alternatively these bonds can be regarded as formed by the overlap of a  $\pi$ -type bond orbital containing a pair of electrons with an empty atomic

or hybrid orbital. This type of formulation was first suggested for  $B_2H_6$  by Pitzer<sup>12</sup> who described it as a "protonated double bond" (XV).

**Transition Metals.**—That lone pairs or non-bonding electrons are very important in determining the shapes of molecules is not necessarily so for transition metals, which can use inner  $d$  orbitals for bond formation and also often have non-bonding electrons in such inner  $d$  orbitals. Thus, for example,  $[Fe(CN)_6]^{4-}$  is octahedral, although the iron atom has nine pairs of electrons in its valency shell. This can be understood by considering the most probable arrangement of nine electrons with the same spin in the configuration  $(d)^5(s)(p)^3$  which has been shown to have six electrons at the corners of an octahedron and the remaining three with an equal probability of being at the mid-points of each of the three sets of four co-planar edges of the octahedron.<sup>9</sup> The six electrons at the vertices of the octahedron can be described as occupying  $d_{\gamma}^2sp^3$  hybrid orbitals, and the three remaining electrons as occupying the three "unhybridised"  $d_e$  orbitals, which have maxima directed towards the mid-points of the edges of the octahedron. Similarly the eighteen electrons in the valency shell of the iron atom in  $[Fe(CN)_6]^{4-}$  can be regarded as occupying the same orbitals in pairs. In this ion the six bonding pairs can be described as occupying localised bond orbitals that are linear combinations of one of the hybrid  $d_{\gamma}^2sp^3$  orbitals and a singly-occupied orbital on the carbon atom of the CN group; the three lone pairs then occupy the  $d_e$  orbitals. Because of the symmetry of the set of three doubly-filled  $d_e$  orbitals repulsions between them and the bond electrons cannot affect the shape of the molecule. The same conclusion holds for the configuration  $(d)^7(s)^2(p)^6$  and quite well for the configurations  $(d)^9(s)^2(p)^6$ ,  $(d)^8(s)^2(p)^6$ ,  $(d)^6(s)^2(p)^6$ , and  $(d)^5(s)^2(p)^6$ . Because of the shape and orientation of the  $d_e$  orbitals, the effects of electrostatic repulsions between non-bonding electrons in them, even if they are incompletely occupied, and the bonding pairs will be only slight and cannot lead to any deviations from the  $90^\circ$  bond angles of the octahedron, and could only cause two of the bonds to be slightly longer or slightly shorter than the other four (see p. 360).

If only five of the pairs of electrons in a completed shell with the configuration  $(d)^{10}(s)^2(p)^6$  are bonding pairs, then they, together with one of the non-bonding pairs, will be arranged at the corners of an octahedron, giving a square pyramidal structure for the molecule, and the other three lone pairs will be in the  $d_e$  orbitals. Configurations in which the  $d_e$  orbitals are incompletely occupied will also have the same arrangement of bonding pairs. In the molecule  $NiBr_3 \cdot 2PEt_3$  the valency shell of the nickel atom has the configuration  $(d)^9(s)^2(p)^6$  and, in agreement with the above ideas, dipole-moment measurements<sup>13</sup> suggest that it has the square-pyramidal structure. The iron atom in iron pentacarbonyl,  $Fe(CO)_5$ , has the configuration  $(d)^{10}(s)^2(p)^6$ , and this molecule should therefore have the square-pyramidal structure, a conclusion which agrees with its finite dipole moment<sup>14</sup>

<sup>12</sup> Pitzer, *J. Amer. Chem. Soc.*, 1945, **67**, 1126.

<sup>13</sup> Jensen and Nygaard, *Acta Chem. Scand.*, 1949, **3**, 474.

<sup>14</sup> Bergmann and Engel, *Z. phys. Chem.*, 1931, **13**, B, 232.

but not with the results of its electron-diffraction,<sup>15</sup> which indicated a trigonal-bipyramidal structure. The structure of this molecule would evidently merit further study.

If only four of the pairs of electrons in a completed shell with the configuration  $(d)^{10}(s)^2(p)^6$  are bonding, then the five non-bonding pairs will completely occupy the  $d$  orbitals and will therefore have an overall spherical symmetry; hence they will not affect the orientation of the four bonding pairs, which will therefore be arranged at the corners of a tetrahedron. The ligand-field theory has been valuable in the understanding of the stereochemistry of transition metal complexes and a qualitative discussion of the basic ideas of this theory now follows.

### The ligand-field theory

This theory<sup>16</sup> deals with the relation of the behaviour of the non-bonding electrons in the valency shell of an atom to the symmetry and strength of the electric field arising from the attached atoms (*i.e.*, ligands in a complex ion). Ligand-field theory thus interests the chemist in connection with (a) valency problems, (b) stereochemistry, and (c) the magnetic behaviour, and (d) absorption spectra of compounds (especially those of the transition metals). After the enunciation of the principles of the theory<sup>17</sup> it was used by Penney and Schlapp<sup>18</sup> to interpret the magnetic behaviour of rare-earth and transition-metal compounds and was applied to valency problems by Van Vleck.<sup>19</sup> Chemists, however, rather neglected it until about five years ago, but have since applied it extensively to the interpretation of spectra and magnetic behaviour, mainly in compounds of the transition metals and to a lesser extent those of the lanthanides and actinides.

Ligand-field theory is based in the first instance on an ionic model in which a central metal ion is considered as being surrounded by charges, *i.e.*, ligands which may be ions (*e.g.*,  $\text{Cl}^-$ ) or electric dipoles (*e.g.*,  $\text{H}_2\text{O}$ ). In the simple model covalent binding between the metal ion and the ligand is neglected although, of course, some charge transfer from the ligand to the metal\* occurs in actual molecules and the bond has some covalent character. We shall deal with two aspects of the theory in relation to stereochemistry, namely (i) the way in which the general shape (*i.e.*, octahedral, tetrahedral, etc.) is determined by the number of non-bonding  $d$  electrons and the orbitals they occupy, and (ii) the extent to which the disposition of these electrons in possible  $d$  orbitals causes departures from

<sup>15</sup> Ewens and Lister, *Trans. Faraday Soc.*, 1939, **35**, 681.

<sup>16</sup> The literature is now so extensive that the following papers only are quoted. They give full references to earlier works:—(a) Orgel, *J.*, 1952, 4756; (b) Jørgensen, Report to the 10th Solvay Council, Brussels, 1956, p. 355; (c) Orgel, *idem*, p. 289; (d) Nyholm, *idem*, p. 225; (e) Moffitt and Balhausen, *Ann. Rev. Phys. Chem.*, 1956, **7**, 107; (f) Griffith and Orgel, *Quart. Rev.*, 1957, **11**, 381.

<sup>17</sup> Bethe, *Ann. Physik*, 1929, **3**, 133; *Z. Physik*, 1930, **60**, 218.

<sup>18</sup> Penney and Schlapp, *Phys. Rev.*, 1932, **41**, 194; 1932, **42**, 666; 1933, **43**, 486.

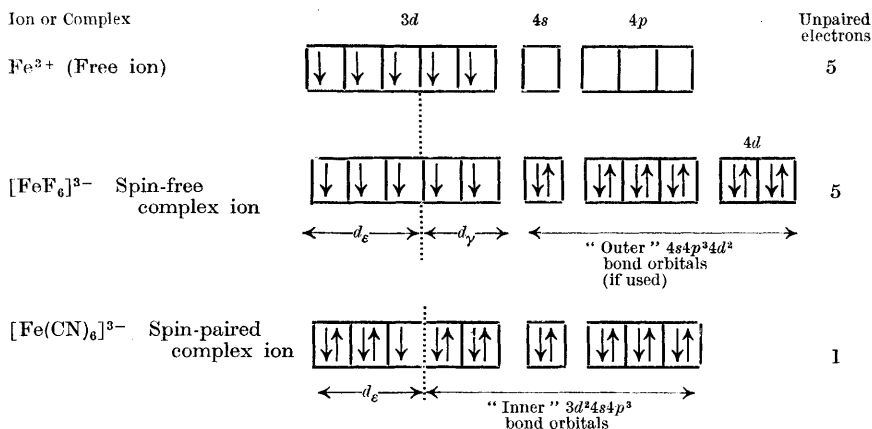
<sup>19</sup> Van Vleck, *Ibid.*, 1932, **41**, 208; *J. Chem. Phys.*, 1935, **3**, 807.

\* Charge transfer from the metal to the ligand may also occur if  $d_{\pi} \rightarrow d_{\pi}$  or  $d_{\pi} \rightarrow p_{\pi}$  binding is present; see ref. 20.



perfect stereochemical arrangement (*i.e.*, distortion of a regular tetrahedron or octahedron). It is convenient to discuss first how five singly-occupied  $d$  orbitals, which are degenerate in a field-free ion, are affected by bringing up six negatively-charged ligands to form a regular octahedron. We consider first the  $[\text{FeF}_6]^{3-}$  ion, in which there are five unpaired  $3d$  electrons. In this complex ion the number of unpaired electrons is the same as in the field-free  $\text{Fe}^{3+}$  ion and hence we refer to  $[\text{FeF}_6]^{3-}$  as a "spin-free" complex ion (for a discussion of this nomenclature see ref. 16*e*). We shall then pass to the  $[\text{Fe}(\text{CN})_6]^{3-}$  ion which contains only *one* unpaired electron, being an example of a "spin-paired" complex ion. We represent the

FIG. 6



electron arrangement in the  $[\text{FeF}_6]^{3-}$  ion diagrammatically in Fig. 6. In Fig. 7 we show the position of the six ligands (*i.e.*,  $\text{F}^-$  ions) along the  $x$ ,  $y$ , and  $z$  axes in relation to the two  $d_y$  orbitals ( $d_{z^2}$  and  $d_{x^2-y^2}$ ) which point along the  $z$  and  $x-y$  axes respectively. The  $d_e$  orbitals ( $d_{xy}$ ,  $d_{yz}$ , and  $d_{zx}$ ) however point *in between* the  $x$ ,  $y$ , and  $z$  axes in the  $xy$ ,  $yz$ , and  $xz$  planes respectively, only the  $d_{xy}$  orbital being shown.

As the fluoride ligands approach along  $x$ ,  $y$ , and  $z$  axes the repulsion exerted by the ligand on the electron in the  $d_{z^2}$  and  $d_{x^2-y^2}$  orbitals exceeds that experienced by an electron in a  $d_e$  orbital and in consequence the  $d_y$  orbitals become of higher energy (less stable) than the  $d_e$  orbitals, as shown in Fig. 8. Now if the energy separation  $\Delta$  between these  $d_e$  and  $d_y$  levels becomes large enough all *five*  $d$  electrons are accommodated in  $d_e$  orbitals, with electron-pairing which leaves only one ( $d_e$ ) electron unpaired. This occurs, for example, in the  $[\text{Fe}(\text{CN})_6]^{3-}$  complex ion (see Fig. 8). The two main factors which are believed to lead to spin-paired complexes are (i) a readily polarisable electron pair on the donor atom, and (ii) ability of the donor atom to form  $d_\pi \rightarrow p_\pi$  or  $d_\pi \rightarrow d_\pi$  bonds by receiving electrons back from the (transition) metal atom. Physically one might picture this in an octahedral complex as a strong polarisation of the donor electron

FIG. 7

$[\text{FeF}_6]^{3-}$  Ion, showing  $d_\gamma$  orbitals and one  $d_\epsilon$  orbital.

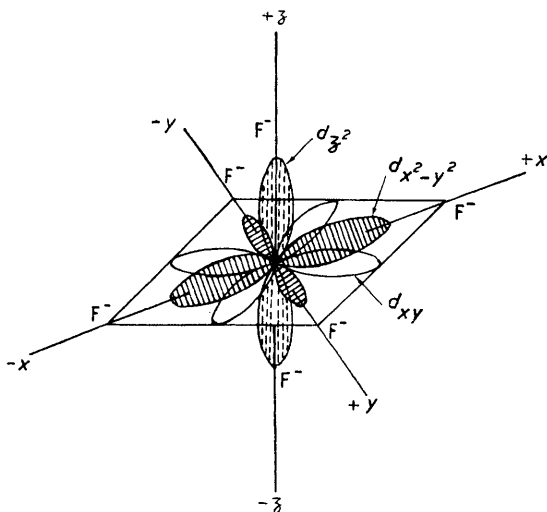
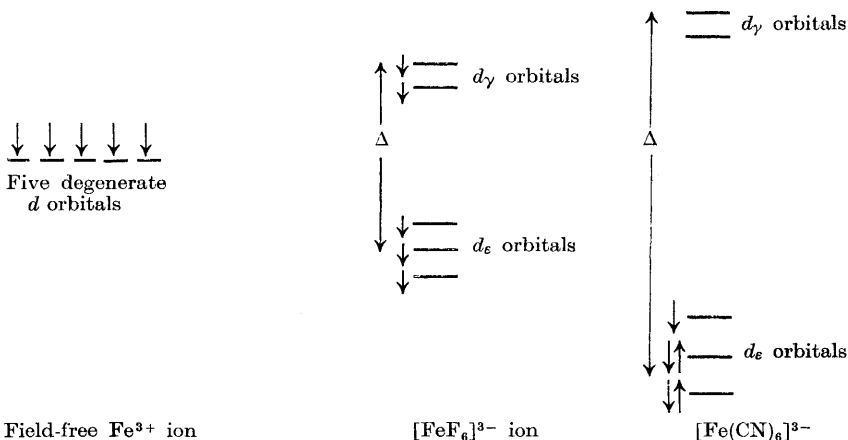


FIG. 8

Energy levels of  $d$  orbitals.

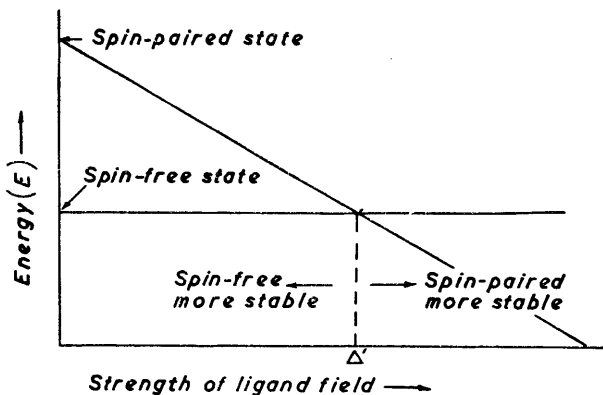


pair by the metal atom and the consequent overlap with the  $d_\gamma$  orbitals forcing any non-bonding electron(s) in these orbitals to pair off in the  $d_\epsilon$  orbitals. Any double-bond character tends to strengthen and shorten the metal-ligand bond by increasing the overlap and by restoring the charge distribution between metal atom and donor atom which, in turn, strengthens the  $\sigma$  bond.

The octahedral complexes in which electron pairing occurs to leave the

two  $d_{\gamma}$  orbitals available for  $\sigma$  bond formation are Pauling's "covalent" complexes, the bond orbitals in the  $[\text{Fe}(\text{CN})_6]^{3-}$  ion, for example, being  $3d_{\gamma}^2 4s 4p^3$ . On the other hand, those spin-free complexes in which the number of non-bonding  $d$  electrons exceeds three clearly cannot have two vacant  $d_{\gamma}$  orbitals for bond formation and hence these complexes, if they involve bonding orbitals at all, must utilise "outer"  $d$  orbital hybrids, *i.e.*,  $4s 4p^3 4d^2$  orbitals. It has been customary to use magnetic measurements to distinguish between the two kinds of metal complex, the spin-free being originally called "ionic" and the spin-paired "covalent". As pointed out by Orgel,<sup>16a</sup> however, the change in magnetic behaviour simply means that the electric field due to the ligands has become so strong that a certain critical energy separation ( $\Delta$ ) between  $d_e$  and  $d_{\gamma}$  orbitals has been exceeded. If this critical energy separation is exceeded it is energetically more feasible to pair electrons in the  $d_e$  orbitals than to lift them into  $d_{\gamma}$ ,

FIG. 9



orbitals. How the change from the spin-free to spin-paired state arises is shown diagrammatically in Fig. 9; when the ligand field exceeds  $\Delta'$  the spin-paired complex is the more stable. It should be stressed that ligand-field theory tells us nothing as to what orbitals—if any—are occupied by the lone pairs of electrons of the ligands in spin-free complexes. We consider, however, that it is convenient to refer to the occupation of "outer" orbitals which give the required stereochemistry, especially since overlap calculations<sup>20</sup> support the view that these orbitals may be at least partially occupied. On this view (see Fig. 6) we can conveniently regard both the  $[\text{FeF}_6]^{3-}$  and the  $[\text{Fe}(\text{CN})_6]^{3-}$  ions as covalent, the former making some use of  $4s 4p^3 4d_{\gamma}^2$  orbitals and the latter  $3d_{\gamma}^2 4s 4p^3$ .

If the arrangement of the ligands about a metal ion is to be that of a regular octahedron the electric field arising from the non-bonding  $d$  electrons of the metal atom must have cubical symmetry. This symmetry is expected for the  $d^0$ ,  $d_e^3$ ,  $d_e^3 d_{\gamma}^2$ ,  $d_e^8 d_{\gamma}^2$ , and  $d^{10}$  configurations. Two types

<sup>20</sup> Craig, Maccoll, Nyholm, Orgel, and Sutton, *J.*, 1954, 332.

of deviation from octahedral symmetry are expected according to whether the  $d_e$  or the  $d_y$  sub-shell is asymmetrical. If the electric field arising from the non-bonding  $d$  electrons is not cubically symmetrical this may be due to either an unsymmetrical  $d_e$  sub-shell or an unsymmetrical  $d_y$  sub-shell. In the first instance the effect on the stereochemistry would be very small because the  $d_e$  orbitals point between the directions of the octahedral bonds. No deviation from the octahedral shape which can be attributed to this effect *alone* appears to have been reported. The second case is much more important and arises in spin-free complexes with  $d_y^1$  and  $d_y^3$  configurations—in which there is necessarily a difference between the number of electrons in the  $d_{x^2-y^2}$  and  $d_{z^2}$  orbitals. In some spin-paired complexes a difference between the two  $d_y$  orbitals of *two* electronic charges is possible, *i.e.*, in  $d_e^6 d_y^2$  complexes. Chromium(II) and manganese(III) hexicovalent complexes should fall into the  $d_e^3 d_y^1$  category and have been discussed by Orgel; <sup>16c</sup>  $\text{MnF}_3$ , for example, has two long coaxial bonds as expected.<sup>21</sup> The  $d_e^6 d_y^3$  type are exemplified by copper(II) complexes. There are many examples which show that copper(II) tends to form compounds with four bonds in the plane and two longer ones normal to this plane. Wells<sup>22</sup> listed many of these; the subject is discussed in greater detail by Dunitz and Orgel.<sup>23</sup> A good illustration is the complex  $[\text{Cu en}_2][\text{Hg}(\text{SCN})_4]$  investigated by Scouladi.<sup>24</sup> Here there are four coplanar copper–nitrogen bonds to the ethylenediamine groups and two longer bonds to the nitrogen atoms of two thiocyanate groups. The effect of having *two* electrons in a  $d_{z^2}$  orbital of a  $d_e^6 d_y^2$  complex is expected to lead to repulsion of the ligands attached normal to the plane. This has been observed<sup>25</sup> in  $[\text{PdI}_2(\text{diarsine})_2]$  which is an octahedral complex with two *trans*-Pd–I distances of 3.52 Å, which is much greater than the expected Pd–I distance (2.65 Å). Four square-coplanar Pd–As bonds complete the octahedron.

If the repulsion were strong enough, the two ligands might be lost from the two *trans* positions of the octahedron leading to the formation of a square complex. This has not been observed yet with a  $d^4$  spin-free complex but may well occur for certain chromium(II) complexes. However,  $d^7$  and  $d^8$  (both spin-paired) and  $d^9$  configurations can give rise to square complexes; these are exemplified severally by square cobalt(II), nickel(II), and copper(II) complexes.

Finally we must enquire in what circumstances a tetrahedral arrangement is likely and what deviations from perfect symmetry are to be expected. The most usual co-ordination number in the transition series is six; even the square complexes can be regarded as arising from the octahedral type of co-ordination with one or more  $d_y$  electrons occupying the fifth and the

<sup>21</sup> Hepworth, Jack, and Nyholm, *Nature*, 1957, **179**, 211.

<sup>22</sup> Wells, "Structural Inorganic Chemistry", Oxford Univ. Press, 1950, 2nd edn. p. 624.

<sup>23</sup> Dunitz and Orgel, *Nature*, 1957, **179**, 462.

<sup>24</sup> Scouladi, *Acta Cryst.*, 1953, **6**, 651.

<sup>25</sup> Harris, Nyholm, and Stephenson, *Nature*, 1956, **177**, 1127.

sixth position of the octahedron. To prepare a tetrahedral compound there are *two* requirements : (i) a ligand which is readily polarised, thereby tending to make a sexicovalent complex relatively less stable than a quadricovalent one because the negative charge transferred from the ligand to the metal may be excessive, and (ii) a non-bonding electron shell which is symmetrical with respect to the four tetrahedrally disposed ligands. Now in a tetrahedral complex it is the electrons in  $d_e$  orbitals which point more towards the ligands than the  $d_\gamma$  orbitals and they will therefore suffer most repulsion. Indeed the diagram shown in Fig. 8 is *inverted* for a tetrahedral complex, the two  $d_\gamma$  orbitals becoming the more stable. Hence the electronic arrangements likely to give rise to a spherically symmetrical non-bonding shell and consequently favour stable tetrahedral arrangements are  $d^0$ ,  $d_\gamma^2$ ,  $d_\gamma^2 d_e^3$ ,  $d_\gamma^4$  (spin-paired),  $d_\gamma^4 d_e^3$  (spin-free), and  $d^{10}$ . These are exemplified severally by  $\text{TiCl}_4$ , the  $[\text{FeO}_4]^{2-}$  ion, and perhaps some vanadium(III) complexes,  $[\text{FeCl}_4]^-$ ,  $[\text{CoCl}_4]^{2-}$ , and  $[\text{ZnCl}_4]^{2-}$  complexes.

It must be emphasised that these configurations refer to *regular* tetrahedral arrangements. By the operation of the Jahn-Teller effect, an unsymmetrical  $d_e$  shell (*e.g.*,  $d_\gamma^4 d_e^4$  as in  $\text{Ni}^{II}$ ) is expected to give rise to an *irregular* tetrahedron, that is, if one can prepare quadricovalent complexes. In forced configurations a regular tetrahedron may occur, but then the shape is being decided mainly by the environment and not by the symmetry of the non-bonding shell.

Before leaving the ligand-field theory we must stress that these deductions concerning bond lengths and molecular shapes assume that (i) the electron configuration is predominantly that of the ground state, (ii) other ions and ligands not directly attached to the metal atom have a negligible effect upon stereochemistry, (iii) lattice forces are negligible, and (iv) atomic vibrations do not "smooth out" small differences in bond lengths. In some cases one or more of these assumptions may not be justified. Thus the ion  $[\text{Ni en}_2]^{2+}$  may be para- or dia-magnetic according to the anion,<sup>26</sup> that is, its stereochemistry is apparently affected by packing considerations in the crystal.

The stereochemistry expected from the ligand theory is shown in Table 4.

### Stereochemistry and the Periodic Table<sup>27</sup>

Although the valency of a central atom in a series of complexes is fixed, the number of attached ligands—the co-ordination number—may vary from one compound to another and from one element to another in the same vertical column of the Periodic Table. Thus, whereas boron never has a co-ordination number greater than four (*e.g.*, in  $\text{KBF}_4$ ), aluminium displays both four (in gaseous  $\text{Al}_2\text{Cl}_6$ ) and six (in  $\text{Na}_3\text{AlF}_6$ ). Similarly

<sup>26</sup> Nyholm, *Chem. Rev.*, 1953, **53**, 263.

<sup>27</sup> Detailed references are not given in this section. References to the original determinations of the structure and bond angles discussed are given in: Wells, "Structural Inorganic Chemistry", Oxford Univ. Press, 1950; Sidgwick, "The Chemical Elements", Oxford Univ. Press, 1950; Walsh, "Progress in Stereochemistry", Butterworths, London, 1953, Vol. 1; Allen and Sutton, *Acta Cryst.*, 1950, **3**, 46.

TABLE 4. *Stereochemistry expected from ligand-field theory. First transition series.*

No. of non-bonding $d$ electrons	Shape expected, with example †	
$d^0$ * . .	Regular octahedron ( $K_2TiCl_6$ ) or regular tetrahedron ( $TiCl_4$ )	
$d^1$ . .	Octahedron, possibly with slight distortion ( $d_e^1$ ) $\{[Ti(H_2O)_6]^{3+}\}$	
$d^2$ . .	Octahedron, possibly with slight distortion ( $d_e^2$ ) $\{V(H_2O)_6\}^{3+}$ or regular tetrahedron ( $d_\gamma^2$ ) $\{[FeO_4]^{2-}\}$	
$d^3$ . .	Regular octahedron ( $d_e^3$ ) $\{[Cr(NH_3)_6]^{3+}\}$	
	Spin-free	Spin-paired
$d^4$ . .	Square-planar ( $d_e^3d_\gamma^1$ ) (? $CrCl_2 \cdot 4H_2O$ ) or octahedron with two long coaxial bonds ( $d_e^3d_\gamma^1$ ) (? $CrSO_4 \cdot 7H_2O$ )	Octahedron with very slight distortion ( $d_e^4$ ) $[K_4Cr(CN)_6]$ or regular tetrahedron ( $d_\gamma^4$ ) (? $[ReCl_4]^-$ )
$d^5$ * . .	Regular octahedron ( $d_e^3d_\gamma^2$ ) $\{[FeF_6]^{3-}\}$ or regular tetrahedron ( $d_\gamma^3d_e^2$ ) $\{[FeCl_4]^-$	Octahedron ( $d_e^5$ ) with very slight distortion $\{[Fe(CN)_6]^{3-}\}$
$d^6$ . .	Octahedron ( $d_e^4d_\gamma^2$ ) with very slight distortion $\{[Fe(H_2O)_6]^{2+}\}$	Regular octahedron ( $d_e^6$ ) $\{[Co(NH_3)_6]^{3+}\}$
$d^7$ . .	Octahedron ( $d_e^5d_\gamma^2$ ) with very slight distortion $\{[Co(H_2O)_6]^{2+}\}$ or regular tetrahedron ( $d_\gamma^4d_e^3$ ) $\{[CoCl_4]^{2-}\}$	Octahedron ( $d_e^6d_\gamma^1$ ) with two longer coaxial bonds $\{?[Co(NO_2)_6]^{4-}\}$ or square-planar ( $d_\gamma^2d_e^5$ ) $\{?[Co(diarsine)_2]^{2+}\}$ or square-pyramid ( $d_e^6d_\gamma^1$ ) (? $NiBr_3 \cdot 2Et_3P$ )
$d^8$ . .	Regular octahedron ( $d_e^6d_\gamma^2$ ) $\{[Ni(H_2O)_6]^{2+}\}$	Octahedron ( $d_e^6d_\gamma^2$ ) with two long coaxial bonds $[PdI_2(diarsine)_2]$ or square-planar ( $d_\gamma^2d_e^6$ ) $(NiCl_2 \cdot 2Et_3P)$ or square-pyramid ( $d_e^6d_\gamma^2$ ) (? $NiBr_2 \cdot triarsine$ )
$d^9$ . .	Octahedron ( $d_e^6d_\gamma^3$ ) with two long coaxial bonds [copper(II) complexes generally] or square-planar ( $d_\gamma^2d_e^6d_\gamma^1$ ) ( $Cu^{II}$ )	
$d^{10}$ * . .	Regular octahedron ( $d_e^6d_\gamma^4$ ) $\{[Zn(NH_3)_6]^{2+}\}$ or regular tetrahedron ( $d_\gamma^3d_e^6$ ) $[Zn(acetylacetonate)_2]$	

\* It might be mentioned that since  $d^0$ ,  $d^5$ , and  $d^{10}$  configurations represent spherically-symmetrical non-bonding shells (being empty, half-full, and full respectively) the stereochemistry for co-ordination numbers 2–7 is expected to follow from Table 1.

† The compound quoted in each case is an example of the  $d$ -electron configuration, for in certain cases—where indicated—the stereochemistry expected has not yet been confirmed experimentally.

with trivalent iron, fluorine gives the sexicovalent  $[\text{FeF}_6]^{3-}$  ion and chlorine the quadricovalent  $[\text{FeCl}_4]^-$  ion. The failure of boron to give hexacoordination is readily understood; the first-row elements have no  $d$  orbitals in the second quantum shell. Aluminium and iron, however, have an adequate number of  $d$  orbitals and the greater stability of  $[\text{FeCl}_4]^-$  than of  $[\text{FeCl}_6]^{3-}$  is presumably attributable to the effect of charge distribution. The Pauling electroneutrality principle<sup>28</sup> suggests that charges on atoms are usually near zero or at least between  $+e$  and  $-e$ . If one tries to replace the difficultly polarisable fluoride ion in  $[\text{FeF}_6]^{3-}$  by chloride in an attempt to make  $[\text{FeCl}_6]^{3-}$  more negative, charge will be passed to the  $\text{Fe}^{\text{III}}$  atom. This is apparently more than can be accepted for the resulting compound to be stable. Examination of complexes of the first transition series suggests that the polarisability of the ligands is the major factor which decides the number of ligands attachable to a metal atom *unless*  $\pi$  bonding ( $d_\pi-d_\pi$  or  $d_\pi-p_\pi$ ) can occur and negative charge be returned from the metal to the ligand. Thus with cobalt(II), the ligands  $\text{H}_2\text{O}$ ,  $\text{NH}_3$ , and ethylenediamine (all uncharged) form sexicovalent complexes whereas the more readily polarisable  $\text{Cl}^-$ ,  $\text{Br}^-$ , and  $(\text{C}_2\text{H}_5)_3\text{P}$  (in  $\text{CoCl}_2 \cdot 2\text{Et}_3\text{P}$ ) form quadricovalent tetrahedral compounds as the more stable species.

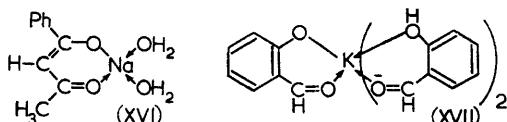
To understand the change in preferred co-ordination number of the metals in any vertical column we suggest that a knowledge of the electronegativity of the metal as well as the tendency to reach electrical neutrality is important. Electronegativity measures the extent to which charge from the electron pair of the ligand is transferred to the metal atom. Thus let us assume that in the complexes of copper(I), silver(I), and gold(I) the unipositive metal ion attaches ligands until it acquires a charge of zero. The first ionisation potentials for copper, silver, and gold are respectively 7.72, 7.57, and 9.22 v, as for gold there is more charge transfer in *each* bond from ligand to metal than for copper or silver. This should cause gold to acquire zero charge with a smaller number of ligands than do copper and silver, so this hypothesis explains the fact that although two is the preferred co-ordination number for univalent gold, it is four for silver and copper. The principles can be similarly applied to bivalent zinc, cadmium, and mercury, the first two of which form a hexammine whereas the last gives only a tetrammine.

Important as steric factors undoubtedly are on occasions in deciding the stability of complexes we believe that they are frequently overemphasised. Thus although one might be tempted to explain the tendency of iron(III) not to form  $[\text{FeF}_6]^{3-}$  but only an  $[\text{FeCl}_4]^-$  ion purely in terms of size of the halide ion, such an explanation seems unlikely when one recalls that stable sexicovalent complexes of iron-(II), -(III), and -(IV) can be prepared in which four arsenic atoms and two chlorine atoms are fitted around the iron atom.

**Alkali Metals and Alkaline-earth Metals.**—*Alkali metals.* The univalent alkali metals generally form ionic compounds. Some neutral quadri- and sexi-

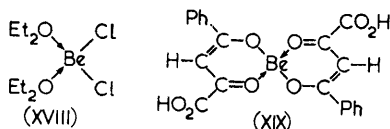
<sup>28</sup> Pauling, "Nature of the Chemical Bond", Cornell Univ. Press, 1945, p. 252; *J.*, 1948, 1461,

covalent chelate compounds are, however, known [*e.g.*, (XVI) and (XVII)],

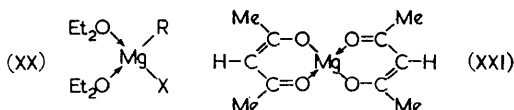


and these complexes would be expected to be tetrahedral and octahedral respectively. The bonds in both no doubt have some covalent character, and are formed from  $sp^3$  hybrid orbitals in the tetrahedral complexes and from  $sp^3d_{z^2}$  hybrid orbitals in the octahedral complexes. It is noteworthy that the covalency of lithium never exceeds four, which is consistent with the fact that it has no  $d$  orbitals available for bonding.

*Alkaline-earth metals.* The bivalent alkaline-earth metals generally form ionic compounds. A few bivalent compounds are probably formed by beryllium (*e.g.*,  $\text{BeCl}_2$  in the gas phase at high temperatures) but nothing is known about their structure. As such molecules would have two pairs of electrons in their valency shells they should be linear. (Some well-established examples of this shape are, however, found among the compounds of metals of Group IIB, *i.e.*, zinc, cadmium, and mercury; see p. 374.) Beryllium tends very strongly to complete its valency shell by forming tetra-co-ordinated complexes, which, because of the small size and double charge of the beryllium ion are probably predominantly covalent in character. Nearly all the beryllium salts form a tetrahydrate as their highest hydrate and crystal-structure determinations have confirmed the expected tetrahedral arrangement of the water molecules around the central beryllium atom. Similar complexes with ammonia, *e.g.*,  $\text{BeCl}_2 \cdot 4\text{NH}_3$ , and with amines, *e.g.*, ethylendiamine  $[\text{Be en}_2]^{2+}\text{Cl}_2^-$  are known and would be expected to be tetrahedral. The complex fluoride ion  $[\text{BeF}_4]^{2-}$  has been shown to be tetrahedral. Various quadricovalent complexes are also known [such as (XVIII) and (XIX)]. The complex (XIX) is optically active in agreement with the expected tetrahedral arrangement of the beryllium valencies in it.



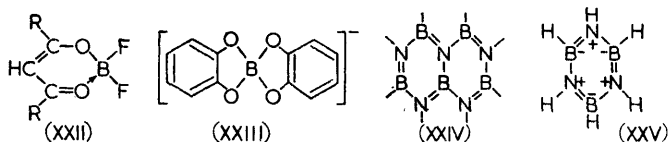
No bivalent compounds of the other alkaline-earth metals are known. Magnesium forms a few quadricovalent neutral complexes such as the Grignard reagents (XX) and an acetylacetonone complex (XXI). Calcium,



strontium, and barium also form quadricovalent neutral acetylacetonone complexes and also dihydrates of these that are presumably sexicovalent and octahedral.



“Light” Elements (Boron to Fluorine).—In its tricovalent compounds boron has three electron pairs in its valency shell, so these molecules should be planar and triangular. Examples of established structures are  $\text{BF}_3$ ,  $\text{BCl}_3$ ,  $\text{BBr}_3$ ,  $\text{B}(\text{CH}_3)_3$ , and  $\text{B}(\text{CH}_3)_2\text{F}$ . Like beryllium, boron tends very strongly to complete its valency shell, as is shown by the very large number of co-ordination compounds formed by boron trifluoride. The boron valencies have the expected tetrahedral arrangement in one of these,  $\text{Me}_2\text{O}^+-\text{B}-\text{F}_3$ . Other quadricovalent complexes include the ions  $[\text{BH}_4]^-$ ,  $[\text{BF}_4]^-$ , and  $[\text{BF}_3(\text{OH})]^-$ , and chelate complexes [such as (XXII) and



(XXIII)]. Some quadricovalent molecules in which one of the bonds formed by the boron is a double bond are known. These include boron nitride (XXIV) and borazole (XXV) and its derivatives. The shapes of these molecules are determined by the trigonal-planar arrangement of the three  $\sigma$ -bonding pairs of electrons in the valency shell of the boron, the fourth  $\pi$ -bonding pair having no effect on the stereochemistry. These molecules are therefore planar and the boron and nitrogen atoms are arranged in regular hexagonal rings. The very strong tendency of boron to complete its octet is also evident in the boron hydrides. As mentioned earlier (p. 352), in diborane, for example, there are two three-centre bonds and both boron atoms are surrounded by four tetrahedrally arranged pairs of electrons.

*Carbon.* In its stable compounds, carbon always has four pairs of tetrahedrally-arranged electrons in its valency shell. Thus molecules containing single bonds are always tetrahedral. The shapes of molecules containing double and triple bonds can also be derived from this tetrahedral arrangement of the four pairs of electrons in the valency shell as shown earlier (p. 345).

However, it is generally more convenient to describe double and triple bonds in terms of  $\sigma$  and  $\pi$  bonds. The shapes of molecules containing double and triple bonds from a carbon atom are then based on the trigonal-planar arrangement of three bonding pairs and the linear arrangement of two  $\sigma$ -bonding pairs as shown in Table 5.

*Nitrogen.* This always has four pairs of electrons in its valency shell. In its tricovalent molecules (*e.g.*, ammonia), three of these are bonding pairs and one is non-bonding. In quadricovalent molecules (*e.g.*,  $\text{NH}_4^+$ ) all four pairs are bonding. Thus tricovalent single-bonded molecules are pyramidal, and quadricovalent are tetrahedral. The shapes of molecules containing double bonds are based on the trigonal-planar arrangement of three  $\sigma$ -pairs (either bonding or lone pairs) and the linear arrangement of two  $\sigma$ -bonding pairs. The various shapes are summarised in Table 6. The decrease in the bond angle on passing from  $\text{NH}_3$  to  $\text{NF}_3$  may be attributed to the fluorine's withdrawing the bonding pairs from the nitrogen, on account

TABLE 5

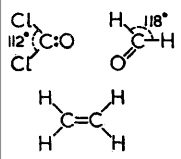
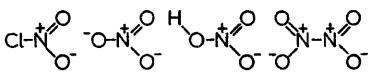
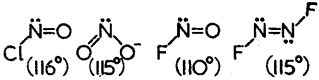
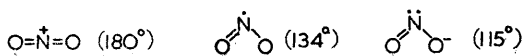
No. of $\sigma$ -bonding pairs	No. of $\pi$ -bonding pairs	Corresponding hybrid orbitals	Shape	Examples
4 . . . . .	0	$sp^3$	Tetrahedral	$\text{CH}_4$ $\text{CCl}_4$ $\text{C}_2\text{H}_6$
3 . . . . .	1	$sp^2$	Trigonal Plane	
2 . . . . .	2	$sp$	Linear	$\text{O}:\text{C}:\text{O}$ $\text{H}:\text{C}:\text{N}$ $\text{H}_2\text{C}:\text{C}:\text{CH}_2$

TABLE 6

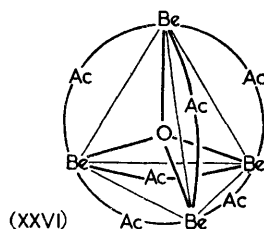
No. of $\sigma$ -pairs (bonding and lone pairs)	No. of $\pi$ -bonding pairs	Corresponding hybrid orbitals	No. of lone pairs	Shape	Examples
4 . . .	0	$sp^3$	0	Tetrahedral	$\text{NH}_4^+$ $\text{N}(\text{CH}_3)_4^+$ $(\text{CH}_3)_3\text{N}^+\text{O}^-$
			1	Trigonal-pyramid	$\text{NH}_3$ ( $106^\circ 45'$ ) $\text{N}(\text{CH}_3)_3$ ( $108^\circ$ ) $\text{NF}_3$ ( $102^\circ 30'$ )
3 . . .	1	$sp^2$	0	Trigonal-plane	
			1	Angular	
2 . . .	2	$sp$	0	Linear	$\text{O}=\text{N}=\text{O}$ $\left\{ \begin{array}{l} \text{N}=\text{N}=\text{O} \\ \text{N}=\text{N}=\text{O}^- \end{array} \right\} \left\{ \begin{array}{l} \text{H}-\text{N}=\text{N}=\text{N} \\ \text{H}-\text{N}=\text{N}=\text{N} \end{array} \right\}$

of its greater electronegativity, and thus decreasing the repulsions between them. The fact that the observed bond angle in the angular molecules such as  $\text{ClNO}$  is less than  $120^\circ$  is consistent with the greater repulsions between lone pairs and bond pairs than between bond pairs themselves. The decrease of the bond angle in the series



is of interest. It shows that the two pairs of  $\sigma$ -bonding electrons which are collinear in  $\text{NO}_2^+$  are forced together when a single electron is added to give  $\text{NO}_2$  and are forced still closer together when another electron is added to give  $\text{NO}_2^-$ . Thus one sees, as expected, that the repulsions between a single non-bonding electron and bonding electron pairs are smaller than those between a non-bonding pair and bonding electron pairs.

*Oxygen.* In all its compounds, oxygen has four pairs of electrons in its valency shell. In its bivalent compounds (e.g.,  $\text{H}_2\text{O}$ ) there are two bonding pairs and two lone pairs, and these are therefore angular. In its trivalent molecules (e.g.,  $\text{H}_3\text{O}^+$ ) there are three bonding pairs and one lone pair, so these are pyramidal. The ozone molecule contains a double bond and its shape is based on the planar-triangular arrangement of three  $\sigma$ -pairs of electrons. In basic beryllium acetate,  $\text{Be}_4\text{O}(\text{COCH}_3)_6$ , and related compounds oxygen appears to be quadricovalent and the arrangement of the four bonds around the central oxygen is tetrahedral (XXVI). (See Table 7.) The bonds no doubt have an appreciable ionic character, because otherwise the oxygen would have an excessively large positive charge. The crystal structure of ice in which each oxygen atom takes part in four tetrahedrally directed hydrogen bonds provides further confirmation of the tetrahedral arrangement of the pairs of electrons in the valency shell



of the oxygen atom. A few compounds are known in which an oxygen atom appears to form two collinear bonds,<sup>29, 30</sup> e.g.,  $[\text{Cl}_5\text{Ru}-\text{O}-\text{RuCl}_5]^{4-}$  and  $(\text{SiH}_3)_2\text{O}$ . The bonds formed by oxygen in these molecules are believed to have considerable double-bond character and these structures are

TABLE 7

No. of $\sigma$ -pairs (bonding and lone pairs)	No. of $\pi$ -electron pairs	Corresponding hybrid orbitals	No. of lone pairs	Shape	Examples
4 . . .	0	$sp^3$	0	Tetrahedral	$\text{Be}_4\text{O}(\text{CH}_3\text{-CO}_2)_6$
			1	Pyramidal	$\text{H}_3\text{O}^+$
			2	Angular	$\text{H}_2\text{O}$ (104° 27') $\text{F}_2\text{O}$ (101° 30') $\text{H}_2\text{O}_2$ (101° 5')
3 . . .	1	$sp^2$	1	Angular	$\text{O}_3$ (117°)
2 . . .	2	$sp$	0	Linear	$(\text{SiH}_3)_2\text{O}$ $[\text{Cl}_5\text{RuORuCl}_5]^-$

<sup>29</sup> Mellor, Mathieson, and Stephenson, *Acta Cryst.*, 1952, **5**, 185.

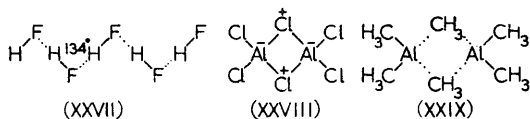
<sup>30</sup> Lord, Robinson, and Schumb, *J. Amer. Chem. Soc.*, 1956, **78**, 1327.

therefore based on the linear arrangement of two  $\sigma$ -pairs of electrons, *e.g.*,  $\text{H}_3\text{Si}=\overset{+}{\text{O}}=\overset{-}{\text{Si}}\text{H}_3$ . The decrease in the bond angle from that in water obtained by replacing hydrogen by hydroxyl and fluorine to give hydrogen peroxide and fluorine oxide ( $\text{F}_2\text{O}$ ) is consistent with the greater electronegativity of these groups. That chlorine monoxide ( $\text{Cl}_2\text{O}$ ) has a larger bond angle must be attributed presumably to repulsions between the lone pairs of the large chlorine atoms. The bond angle in ozone is slightly less than  $120^\circ$  which is consistent with the fact that the valency shell of the central oxygen has a lone pair of electrons.

*Fluorine.* The arrangement of the four electron pairs in the valency shell of the fluorine atom should be tetrahedral but as fluorine is almost without exception univalent no evidence for this can be obtained.  $[\text{H}_2\text{F}]^+$  possibly exists but its structure is not known. However, in the crystal of ammonium fluoride each fluoride ion forms four tetrahedrally arranged hydrogen bonds with neighbouring ammonium ions, strongly suggesting that the four lone-pairs of the fluoride ion are in fact tetrahedrally arranged. In solid hydrogen fluoride the molecules are arranged in zig-zag chains joined by hydrogen bonds and the angle between the two bonds formed by each fluorine atom is  $134^\circ$ . If the hydrogen bonds were linear this angle should be the tetrahedral angle of  $109\frac{1}{2}^\circ$ . Presumably the relatively weak hydrogen bond is fairly easily bent and thus the bond angle is increased by repulsions between the lone pairs of alternate fluorine atoms (XXVII).

**Group III (Aluminium, Gallium, Indium, and Thallium).**—These elements are trivalent and should form molecules with three electron pairs in their valency shells and should therefore be planar with  $120^\circ$  bond angles. However, because they have a strong tendency to complete their valency shells they generally form quadricovalent complexes that are tetrahedral. There are very few examples of tercovalent molecules and none whose structure has been determined. The alkyl derivatives of aluminium are associated but those of gallium, indium, and thallium are monomeric in the vapour state and presumably therefore have planar triangular structures. These trialkyls form very stable addition compounds, *e.g.*,  $(\text{CH}_3)_3\text{Ga}-\overset{-}{\text{N}}\overset{+}{\text{H}}_3$ , that are presumably tetrahedral.

The fluorides are all ionic but the other halides give dimeric molecules (XXVIII, XXIX) in the vapour state in which the metal atom forms four tetrahedrally disposed covalent bonds. Some of these halides appear to

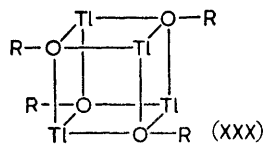


dissociate to monomers at high temperatures and, although they are presumably planar like boron trichloride, their structures are not known. The halides also form numerous quadricovalent and presumably tetrahedral addition compounds, *e.g.*,  $\text{Cl}_3\text{Al}-\overset{-}{\text{O}}\overset{+}{\text{Et}}_2$ .

The dimeric aluminium alkyls also have similar bridge structures (XXIX) with three-centre bonds.

Because of the availability of *d* orbitals these elements, unlike boron, also form sexicovalent octahedral complexes. Thus complex ions such as  $[\text{Al}(\text{OH})_6]^{3-}$ ,  $[\text{Al}(\text{H}_2\text{O})_6]^{3+}$ , and  $[\text{AlF}_6]^{3-}$  have all been found to have an octahedral structure by X-ray determinations of the structures of their salts. Other complex fluorides with formulæ such as  $\text{Ti}_2\text{AlF}_5$  and  $\text{TiAlF}_4$  also contain octahedral  $\text{AlF}_6$  groups in which two corner fluorine atoms are shared, giving linear complexes with the empirical formula  $[\text{AlF}_5]^{2-}$  in which all four fluorine atoms in one plane are shared giving an infinite planar complex with the empirical formula  $[\text{AlF}_4]^-$ . The other metals also form complex ions but not many of their structures have been determined. The ions  $[\text{InCl}_5\text{H}_2\text{O}]^{3-}$  and  $[\text{TiCl}_6]^{3-}$  are octahedral. The salt  $\text{Cs}_3\text{Ti}_2\text{Cl}_9$  contains the binuclear complex ion  $[\text{Ti}_2\text{Cl}_9]^{3-}$  in which two  $\text{TiCl}_6$  octahedra share three chlorine atoms. It is noteworthy that the chloride and bromide complexes of aluminium all have the general formula  $\text{MAiX}_4$  and presumably contain tetrahedral complex ions  $[\text{AlX}_4]^-$ . This may be because the relatively electronegative aluminium would then acquire too much charge from six polarisable chlorine or bromine atoms. Indium and thallium on the other hand form no complex fluorides and their complex chlorides and bromides contain octahedral complex ions of the type  $[\text{TiCl}_6]^{3-}$ . They are presumably too weakly electronegative to form bonds with appreciable covalent character with the very weakly polarisable fluorine, although they can do so with the more polarisable chlorine and bromine without acquiring too great a negative charge, as would aluminium.

The thalloses alkoxides are of interest. They appear to be tetrameric in solution and it has been suggested that they have a cubic structure (XXX), in which each oxygen atom is quadricovalent, as in basic beryllium acetate, and each thallium atom has a valency shell of three shared pairs of electrons and one lone pair which would therefore be expected to be arranged tetrahedrally (see Table 8).



**Group IV (Silicon, Germanium, Tin, and Lead).**—These elements are

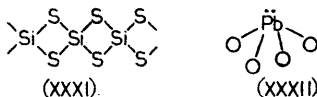
TABLE 8

No. of $\sigma$ -pairs (bonding and lone pairs)	Corresponding hybrid orbitals	No. of lone pairs	Shape	Examples
3 . . .	$sp^2$	0	Trigonal-plane	$\text{Ga}(\text{CH}_3)_3$ ?
4 . . .	$sp^3$	0	Tetrahedral	$\text{Al}_2\text{Cl}_6$ $\text{AlCl}_3\text{NH}_3$
		1	Pyramidal	$[\text{TiOR}]_4$
6 . . .	$sp^3d_2$	0	Octahedral	$[\text{AlF}_6]^{3-}$ $[\text{TiCl}_6]^{3-}$ $[\text{Al}(\text{H}_2\text{O})_6]^{3+}$

quadrivalent and form a large number of molecules with a tetrahedral arrangement of four bonds, their valency shells containing four tetrahedrally arranged pairs of electrons.

A large number of simple molecules such as the tetramethyls, *e.g.*,  $\text{Ge}(\text{CH}_3)_4$ ,  $\text{Sn}(\text{CH}_3)_4$ , and the tetrahalides  $\text{SiF}_4$  and  $\text{PbCl}_4$ , have been shown to be tetrahedral by electron-diffraction. In unsymmetrical molecules such as  $\text{Sn}(\text{CH}_3)_2\text{Cl}_2$  deviations from the exactly tetrahedral structure are expected and found, although they appear to be slight.

The same tetrahedral arrangement of four bonds is found for example in silica ( $\text{SiO}_2$ ), the silicates, and silicones and in silicon disulphide,  $\text{SiS}_2$ , which contains linear chains with the structure (XXXI). All these ele-



ments form sexicovalent complexes and all those investigated have the expected octahedral structures, *e.g.*,  $[\text{SiF}_6]^{2-}$ ,  $[\text{GeF}_6]^{2-}$ ,  $[\text{SnI}_6]^{2-}$ ,  $[\text{PbCl}_6]^{2-}$ ,  $[\text{Sn}(\text{OH})_6]^{2-}$ , and  $[\text{Pb}(\text{OH})_6]^{2-}$ .

Both tin and lead have stable lower valencies of two. The simple halides (*e.g.*,  $\text{SnCl}_2$  and  $\text{SnBr}_2$ ) have angular structures in the gas phase as expected from the size of their valency shells, which contain three electron pairs. In lead monoxide,  $\text{PbO}$ , each lead atom has the configuration (XXXII) and each oxygen atom is surrounded tetrahedrally by four lead atoms. If the bonds are regarded as having at least some covalent character the lead has ten electrons in its valency shell—four bonding pairs and one lone pair—and these should have a trigonal-bipyramidal arrangement. The observed arrangement can be regarded as the trigonal-bipyramidal arrangement distorted by the greater repulsions between the lone pair and the bonding pairs than between the bonding pairs themselves (see Table 9).

TABLE 9

No. of $\sigma$ -pairs (bonding and lone pairs)	Correspond- ing hybrid orbitals	No. of lone pairs	Shape	Examples
3 . . .	$sp^2$	1	Angular	$\text{SnCl}_2$ $\text{PbCl}_2$
4 . . .	$sp^3$	0	Tetrahedral	$\text{SiCl}_4$ $\text{Sn}(\text{CH}_3)_4$ $\text{SiHCl}_3$
5 . . .	$sp^3d_z^2$	1	$\text{TeCl}_4$ structure	$\text{PbO}$
6 . . .	$sp^3d_{\gamma}^2$	0	Octahedral	$[\text{SiF}_6]^{2-}$ $[\text{Sn}(\text{OH})_6]^{2-}$ $[\text{PbCl}_6]^{2-}$

**Group V (Phosphorus, Arsenic, Antimony, and Bismuth).**—These elements have five valency electrons. They can either complete their octets of four tetrahedrally arranged pairs of electrons by forming three covalent bonds

which thus have a trigonal-pyramidal arrangement or they can use all their valency electrons to form five bonds with a trigonal-bipyramidal arrangement. In addition they form tetrahedral tetraco-ordinated and octahedral hexaco-ordinated complexes and probably penta- and hepta-co-ordinated complexes also. They also form a number of molecules containing one double bond to an oxygen atom. Thus a variety of different shapes is possible for the molecules of these elements and they are summarised in Table 10. The simple trico-ordinated molecules such as phosphorus trichloride and arsenic trichloride have the expected trigonal-pyramidal shape. The observed bond angles are slightly less than the tetrahedral angle because the lone-pair-bond-pair repulsions are greater

TABLE 10

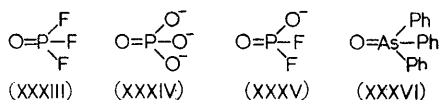
No. of $\sigma$ -pairs of electrons	Corresponding hybrid orbitals	No. of $\pi$ -pairs of electrons	No. of lone pairs	Shape	Examples
3 . . .	$sp^2$	1	1	V	$O=SbCl$ ?
4 . . .	$sp^3$	0	0	Tetrahedron	$[PH_4]^+$ $[PCl_4]^+$ $[As(Ph)_4]^+$
		0	1	Trigonal-pyramid	$PCl_3$ $AsCl_3$ $P_4O_6$
5 . . .	$sp^3d_{z^2}$	0	0	Trigonal-bipyramid	$PCl_5$ $PF_5$ $PF_3Cl_2$
		0	1	Distorted-tetrahedron	$[SbF_4]^-$ ?
		1	0	Tetrahedron	$POCl_3$ $PO_4^{3-}$ $PO_2F_2^-$
6 . . .	$sp^3d_{\gamma^2}$	0	0	Octahedron	$[PCl_6]^-$ $[Sb(OH)_6]^-$
		0	1	Square-pyramid	$[SbCl_5]^{2-}$ ?
		1	1	Square-pyramid	$[O-Sb(Cat)_2]^-$ ?
7 . . .	$sp^3d_{\gamma^2}d_e$	0	0	Pentagonal-bipyramid	$[SbF_7]^{2-}$ ?
		0	1	Distorted octahedron	$[SbBr_6]^{3-}$ ?
8 . . .	$sp^3d^4$	1	0	?	$[O=Sb(Cat)_3]^{3-}$

Cat =  $o-C_6H_4(OH)O^-$

than the bond-pair-bond-pair repulsions (*e.g.*,  $\text{PF}_3$   $104^\circ$ ,  $\text{PCl}_3$   $100^\circ$ ,  $\text{AsF}_3$   $102^\circ$ ,  $\text{AsCl}_3$   $98\frac{1}{2}^\circ$ ,  $\text{SbCl}_3$   $99\frac{1}{2}^\circ$ ). The hydrides however have bond angles considerably less than the tetrahedral angle ( $\text{PH}_3$   $93^\circ 30'$ ,  $\text{AsH}_3$   $92^\circ 0'$ ,  $\text{SbH}_3$   $91^\circ 30'$ ). It thus appears that in these molecules the lone-pair-bond-pair repulsions are much greater than the repulsions between the bond pairs themselves. The latter are in fact almost as close together as is possible if they occupy only *s* and *p* orbitals and not *d* orbitals. A possible reason for this is that the electrons in an A-H bond are free to move around the hydrogen atom and are therefore not so localised as the electron pairs of other A-B bonds which are kept localised in the region of the bond by the repulsions of the other electron pairs on the atom B. Hence it might be expected that the repulsions between A-H bonds would be less than between other bonds. In non-hydride molecules repulsions between lone pairs of non-bonded atoms may also sometimes be important. It is noteworthy that such small bond angles approaching  $90^\circ$  in molecules whose central atom has a valency shell of four electron pairs are only found in the hydrides.

The 'onium complexes ( $\text{PH}_4^+$ ,  $\text{PCl}_4^+$ , etc.) have the expected tetrahedral shape. The pentaco-ordinated molecules such as phosphorus pentachloride and arsenic pentachloride have trigonal-bipyramidal structures based on this arrangement of five electron pairs. Various tetraco-ordinated complexes are known {*e.g.*,  $[\text{SbF}_4]^-$  and  $\text{Et}_2\text{O}^+ \text{---} \text{SbF}_3$ } but their structures have not been investigated; they should be based on the trigonal-bipyramidal arrangement with a lone pair occupying one of the positions. Apparently pentaco-ordinated complexes such as  $[\text{SbCl}_5]^{2-}$  have also been prepared. They should be square-pyramidal with a lone pair occupying the sixth octahedral position. Hexaco-ordinated complexes have been more extensively studied and several of them, *e.g.*,  $[\text{PCl}_6]^-$  and  $[\text{Sb}(\text{OH})_6]^-$ , have been shown to have the expected octahedral shape. The hexaco-ordinated complex ion  $[\text{SbBr}_6]^{3-}$  has also been reported to be octahedral but since there are seven pairs of electrons in the valency shell of the antimony atom the shape of the molecule should be based on the pentagonal-bipyramidal arrangement of seven electron pairs. If the lone pair occupies an equatorial position the shape would be that of a slightly distorted octahedron. The structure of the heptaco-ordinated complex ion  $[\text{SbF}_7]^{2-}$  has not been studied: it should have the shape of a pentagonal-bipyramid.

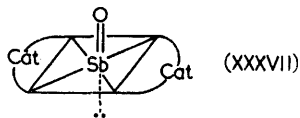
Compounds containing a doubly-bonded oxygen atom are fairly numerous. Many of these have been shown to have the expected tetrahedral shape arising from the tetrahedral arrangement of four  $\sigma$ -bonding pairs of electrons [*e.g.*, (XXXIII)-(XXXVI)]. In all the cases investigated the bond angles



have approximately the tetrahedral value. In molecules of the type  $\text{POX}_3$ ,  $\angle \text{XPX}$  has always been found to be less than the tetrahedral angle (*e.g.*,



$\text{POF}_3$   $102\frac{1}{2}^\circ$ ,  $\text{POCl}_3$   $103\frac{1}{2}^\circ$ ,  $\text{PSF}_3$   $100^\circ$ ,  $\text{PSCl}_3$   $100\frac{1}{2}^\circ$ ), in accordance with the idea that the double bond repels the single bonds more than the latter repel each other. Various antimonyl complexes with catechol have been described, *e.g.*,  $[\text{O}=\text{Sb}(\text{Cat})_2]^-$ . This has five  $\sigma$ -bonding pairs and one lone pair of electrons as well as one  $\pi$ -bonding pair. It should therefore be square-pyramidal with a lone pair occupying the sixth octahedral position (XXXVII).



**Group VI (Sulphur, Selenium, Tellurium, and Polonium).**<sup>31</sup>—These elements can form molecules in which they have four, five, and six pairs of electrons in their valency shells. In their singly-bonded molecules these give rise to an angular shape based on the tetrahedral arrangement of two bonding pairs and two lone pairs of electrons, to a distorted tetrahedral shape based on the trigonal-bipyramidal arrangement of four bonding and one lone pair of electrons, and to an octahedral shape based on that arrangement of six bonding pairs. Selenium, tellurium, and polonium also form a number of hexaco-ordinated complex ions. In addition a number of molecules containing double bonds, mainly to oxygen, are known. The wide variety of possible shapes of the molecules of these elements is summarised in Table 11. All the singly-bonded dico-ordinated molecules studied have the expected angular shape [*e.g.*,  $\text{SCl}_2$ ,  $\text{S}(\text{CF}_3)_2$ ,  $\text{S}_8$ ]. The observed bond angles are slightly less than the tetrahedral angle, being in the range  $100$ – $109^\circ$ , owing to the greater repulsions between the lone pairs than between the bond pairs.

The hydrides are exceptional in having rather small bond angles approaching  $90^\circ$ , *i.e.*,  $\text{H}_2\text{S}$   $92^\circ 20'$ ,  $\text{H}_2\text{Se}$   $91^\circ$ . The explanation must be the same as that for the similar small bond angles found in phosphine, etc. (p. 343). It has been suggested,<sup>32</sup> in order to account for these small bond angles, that the central atom uses *d* orbitals as well as *s* and *p* orbitals for bond formation. It is not clear, however, why this only occurs in bonds to hydrogen or why the bond angle apparently decreases to a limiting value of  $90^\circ$  when smaller bond angles are possible if *d* orbitals are used.

The singly-bonded tetraco-ordinated molecules of these elements [*e.g.*,  $\text{SeF}_4$ ,  $\text{TeCl}_4$ , and  $(\text{CH}_3)_2\text{TeCl}_2$ ] all have the same distorted tetrahedral structure based on the trigonal-bipyramidal arrangement of five electron pairs one of which is a lone pair. The hexaco-ordinated molecules (*e.g.*,  $\text{SF}_6$ ) have the expected octahedral structure.

A large number of sulphur compounds contain double bonds. These include the dioxide with a bond angle of  $119^\circ 33'$  whose structure is determined by the planar-triangular arrangement of three  $\sigma$ -pairs of electrons, one of which is a lone pair. The planar-triangular structure of the trioxide is based on the same arrangement of three  $\sigma$ -pairs of electrons which in this case are all bonding pairs. The thionyl halides  $\text{SOX}_2$ ,  $\text{SeOCl}_2$ ,  $\text{H}_2\text{SeO}_3$ , and  $\text{SeO}_2$  all have trigonal-pyramidal structures based on the tetrahedral

<sup>31</sup> Abraham, *Quart. Rev.*, 1956, **10**, 407.

<sup>32</sup> Burrus and Gordy, *Phys. Rev.*, 1953, **92**, 274.

TABLE II

No. of $\sigma$ -pairs of electrons	Corresponding hybrid orbitals	No. of $\pi$ -pairs of electrons	No. of lone pairs	Shape	Examples
3 . . .	$sp^2$	2	1	V	$SO_2$
		3	0	Triangular-plane	$SO_3$
4 . . .	$sp^3$	2	0	Tetrahedron	$SO_2Cl_2$ $H_2SeO_4$
		1	1	Trigonal-pyramid	$SOCl_2$ $(CH_3)_2SO$ $SeO_2$
		0	2	V	$H_2S$ $Cl_2S$ $S_8$ $Ph_2S$
5 . . .	$sp^3d_{z^2}$	0	1	Distorted tetrahedron	$TeCl_4$ $Cl_2Se(C_6H_4 \cdot Me)_2$
6 . . .	$sp^3d_{\gamma^2}$	0	0	Octahedron	$SF_6$ $SeF_6$ $Te(OH)_6$ $S_2F_{10}$
		0	1	Square-pyramid	$[CH_3TeI_4]^-$ ?
7 . . .	$sp^3d_{\gamma^2}d_i$	0	1	Distorted octahedron	$Cl_4Te(NMe_2Ph)_2$

arrangement of four  $\sigma$ -bonding pairs of electrons, one of which is a lone pair. In agreement with the idea that a double bond repels single bonds more than they repel each other it is found in the molecules  $X_2S=O$  that  $\angle XSO$  is greater than  $\angle XSX$  (Table 12).

TABLE 12

Compound	$\angle XSO$	$\angle XSX$
$F_2SO$ . . . .	$106.8^\circ \pm 0.1^\circ$	$92.8^\circ \pm 0.1^\circ$
$Br_2SO$ . . . .	$108 \pm 2$	$96 \pm 2$
$(CH_3)_2SO$ . . . .	$107 \pm 5$	$100 \pm 5$
$(C_6H_5)_2SO$ . . . .	$106.2 \pm 0.7$	$97.3 \pm 1.0$

The molecules  $H_2SO_4$ ,  $SO_2X_2$ ,  $(SO_3)_3$ , and others similar all have the tetrahedral structure to be expected from the four  $\sigma$ -pairs of electrons in the valency shell of the sulphur atom in them. The bond angles should decrease in the order  $\angle OSO > \angle OSX > \angle XSX$  as is so in sulphonyl fluoride and di-*p*-bromophenyl sulphoxide.

The complex ions  $[SeCl_6]^{2-}$  and  $[TeCl_6]^{2-}$  are analogous to  $[SbBr_6]^{3-}$

and should have the same distorted octahedral structure. The compound  $(\text{PhMe}_2\text{N})_2\text{TeCl}_4$  should have a similar structure.

**Group VII (Chlorine, Bromine, and Iodine).**—In their neutral molecules these elements exhibit valencies of 1, 3, 5, and 7 corresponding to valency shells containing 8, 10, 12, and 14 electrons respectively. They also form complex negative ions in which they may be di-, tetra-, or hexa-co-ordinated. Iodine also forms complex positive ions in which it is dico-ordinated. Double bonds with oxygen occur in a number of molecules and ions. A variety of molecular shapes are therefore possible and they are summarised in

TABLE 13

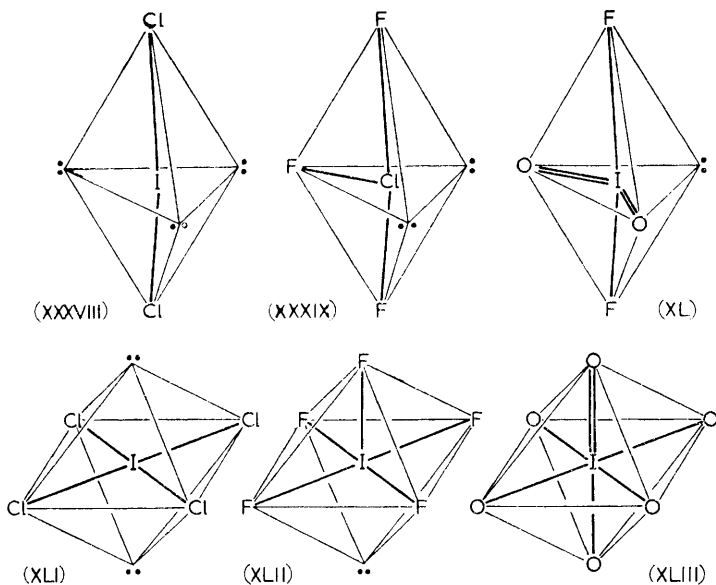
No. of $\sigma$ -electron pairs	Corresponding hybrid orbitals	No. of $\pi$ -electron pairs	No. of lone electron pairs	Shape	Examples
4 . . . .	$sp^3$	0	2	V	$[\text{IR}_2]^+ ?$
		1	2	V	$[\text{ClO}_2]^-$
		2	1	Trigonal-pyramid	$[\text{ClO}_3]^-$ $[\text{BrO}_3]^-$ $\text{HIO}_3$
		3	0	Tetrahedron	$[\text{ClO}_4]^-$ $[\text{IO}_4]^-$
5 . . . .	$sp^3d_{z^2}$	0	3	Linear	$[\text{ICl}_2]^-$ $[\text{I}_3]^-$ $[\text{BrICl}]^-$
		0	2	T-shape	$\text{ClF}_3$
		1	1	Distorted tetrahedron	$[\text{IO}_2\text{F}_2]^-$
6 . . . .	$sp^3d_{\gamma^2}$	0	2	Square-plane	$[\text{Cl}_4]^-$
		0	1	Square-pyramid	$\text{IF}_5$
		1	0	Octahedron	$[\text{IO}_6]^{5-}$
7 . . . .	$sp^3d_{\gamma^2}d_{\delta}$	0	0	Pentagonal-bipyramid	$\text{IF}_7$

Table 13. The shapes of most of the oxyanions are based on the tetrahedral arrangement of four  $\sigma$ -pairs of electrons. Thus  $[\text{ClO}_2]^-$  is angular,  $[\text{ClO}_3]^-$ ,  $[\text{BrO}_3]^-$ , and  $[\text{IO}_3]^-$  are pyramidal, and  $[\text{ClO}_4]^-$  and  $[\text{IO}_4]^-$  are tetrahedral.

The shapes of the molecules that contain five electron pairs in their valency shells are interesting: they are all based on the trigonal-bipyramid. Thus  $[\text{ICl}_2]^-$  (XXXVIII) and  $[\text{I}_3]^-$  are linear with three lone pairs in the

equatorial positions,  $\text{ClF}_3$  is planar T-shaped (XXXIX) with two lone pairs in the equatorial position and  $[\text{IO}_2\text{F}_2]^-$  (XL) has a distorted tetrahedral structure, like  $\text{SeF}_4$ , with one lone pair in an equatorial position.

Those molecules and ions in which the halogen has six electron pairs in its valency shell have structures based on the expected octahedral arrangement of these electron pairs. Thus  $[\text{ICl}_4]^-$  (XLI) has a square-planar



structure with two lone pairs occupying opposite positions.  $\text{IF}_5$  (XLII) is a square-pyramid with a lone pair occupying the sixth octahedral position, and  $[\text{IO}_6]^{5-}$  (XLIII) is octahedral.

Iodine heptafluoride is interesting as the only known example of a pentagonal-bipyramidal structure based on this expected arrangement of seven electron pairs.

**Transition Metals.**—*Co-ordination number two.* This appears to be restricted to compounds in which the metal atom has a  $d^0$  or  $d^{10}$  non-bonding configuration. For both cases we have a symmetrical non-bonding shell and hence for bicovalency a linear arrangement is expected. Examples of  $d^0$  complexes include the linear uranyl  $(\text{UO}_2)^{2+}$ ,  $[\text{VO}_2]^+$ , and  $[\text{MoO}_2]^{2+}$  cations. The univalent Group IB complexes and bivalent Group IIB compounds illustrate the  $d^{10}$  configurations. Thus wherever structural data are available on complex ions like  $[\text{Ag}(\text{NH}_3)_2]^+$  or  $[\text{AuCl}_2]^-$  or compounds such as mercuric chloride a linear arrangement is observed.

*Co-ordination number three.* It is difficult to find examples of simple covalent compounds of the transition metals in which the co-ordination number is three. Monomeric ferric chloride in the gas phase is presumably an example, however, and since the ferric ion has a  $d^5$  configuration the molecule is expected to be a triangular-plane.

Few well-established complex compounds of the transition metals with the co-ordination number three are known. Ahrlund and Chatt<sup>33</sup> recently described complexes of the type  $\text{AgX}_2\text{R}_3\text{P}$  for which molecular-weight (and other) data indicate a tricovalent metal atom. Cass, Coates, and Hayter<sup>34</sup> obtained similar evidence. The electronic arrangement in these complexes is  $d^{10}s^2p^4$  which is again that required for a triangular-plane.

*Co-ordination number four.* Tetra- and hexa-co-ordination are the most frequently occurring valencies among the transition metals—and indeed the whole Periodic Table; most metals give rise to *both* quadricovalent tetrahedral and sexicovalent octahedral arrangements, but the latter are the more common. The influence of non-bonding electrons is greater in de-stabilising the quadricovalent tetrahedral arrangement than the octahedral one. The former is found most readily in spin-free compounds when the non-bonding  $d$  shell is empty ( $d^0$ , e.g.,  $\text{Ti}^{\text{IV}}$ ), half-full ( $d^5$ , e.g.,  $\text{Fe}^{\text{III}}$ ) with  $d_y$  full and  $d_z$  half-full, i.e.,  $d_y^4d_z^3$  (e.g.,  $\text{Co}^{\text{II}}$ ), or full ( $d^{10}$ , e.g.,  $\text{Cu}^{\text{I}}$ ); it is expected also in  $d_y^2$  compounds. Of the spin-paired type only the configuration  $d_y^4$  is expected to give a tetrahedral rearrangement. Many quadricovalent compounds with a  $d^0$  non-bonding configuration are known, e.g., titanium tetrachloride, which is a regular tetrahedron. With the  $d_y^1$  non-bonding configuration quadricovalent vanadium(IV) halides are known, e.g.,  $\text{VCl}_4$ , for which electron-diffraction indicates a regular tetrahedron. It is surprising that the single  $d_y$  electron does not distort the regular tetrahedron. As possible examples of a  $d_y^2$  non-bonding configuration there are the tetrahalides of chromium, molybdenum, and tungsten. Molybdenum tetrachloride is a brown powder which forms a yellow vapour when heated and hence is apparently covalent. If paramagnetic it is presumably tetrahedral, but no structural data are available. Quadricovalent compounds with three  $d$  non-bonding electrons are exemplified by rhenium tetrafluoride which melts at  $124^\circ$  and sublimes at  $500^\circ$ , but its structure is unknown. The  $d^4$  configuration would occur in quadricovalent complexes of chromium(II) and manganese(III).<sup>16c, 21</sup> There is some evidence of quadricovalency in the former, e.g., in the formation of the tetrahydrate  $\text{CrCl}_2 \cdot 4\text{H}_2\text{O}$ . The configuration  $d_z^3d_y^1$  favours the formation of a square complex because the electron in the  $d_z$  orbital is expected to destabilise an octahedral complex owing to repulsion of two *trans* ligands on the  $z$  axis.

The  $d^4$  non-bonding configuration occurs in  $\text{K}[\text{ReCl}_4]$ , the weak paramagnetism of which suggests that the two  $d_y$  levels lie lowest and accommodate the four electrons with full pairing. The structure of the ion  $[\text{ReCl}_4]^-$  is not available; if it is tetrahedral no distortion is expected. Quadricovalent  $d^5$  complexes are well known with trivalent iron, e.g., the tetrahedral  $[\text{FeCl}_4]^-$  ion. No quadricovalent compound with the  $d^6$  configuration appears to have been described. The  $d^7$  configuration marks the point of transition from tetrahedral to square-planar quadricovalent complexes. In spin-free complexes the tetrahedral arrangement is favoured by the symmetrical  $d_y^4d_z^3$  arrangement but in spin-paired complexes one

<sup>33</sup> Ahrlund and Chatt, *Chem. and Ind.*, 1955, 96.

<sup>34</sup> Cass, Coates, and Hayter, *ibid.*, 1954, 1485.

obtains a  $d_e^6 d_y^1$  configuration. The  $d_y$  electron can be regarded either as repelling ligands from the two *trans* positions of an octahedral complex or as utilising one  $d$  orbital, hence leaving  $d_y sp^2$  orbitals for square bond formation. Quadricovalent  $d^8$  and  $d^9$  complexes are known and in all cases they are square-planar, e.g.,  $[\text{PtCl}_4]^{2-}$  and  $[\text{Cu}(\text{NH}_3)_4]^{2+}$ . The  $d^{10}$  configuration gives rise once more to quadricovalent tetrahedral complexes.

*Co-ordination number five.* Several non-complex compounds with five bonds to the metal atom are known. Where the number of non-bonding  $d$  electrons is small the molecules which have been studied have a trigonal-bipyramidal shape, e.g.,  $d^0$ ,  $\text{NbCl}_5$  and  $d^1$ ,  $\text{MoCl}_5$  (no distortion by the single  $d_e$  electron was reported). The compounds  $\text{ReF}_5$  ( $d^2$ ) and  $\text{RuF}_5$  ( $d^3$ ) have not yet been investigated. One expects the trigonal-bipyramidal shape in each case. A few quinquovalent complexes are known; they occur mainly with  $d^7$ ,  $d^8$ , and  $d^9$  configurations but are formed by certain elements at the beginning of the series, also, for example, in  $\text{TiCl}_4 \cdot \text{Et}_3\text{N}$ . Practically no structural data are available but the complexes of the later elements can be regarded as derived from the square arrangement together with the use of the vacant  $p$  orbital normal to the plane of the square. This should lead to a square-pyramid arrangement. Thus,  $d^7$  complexes of the type  $\text{CoI}_2 \cdot \text{triarsine}$  are known; the latter is probably square-pyramidal.<sup>35</sup>  $d^8$  is illustrated by  $\text{NiI}_2 \cdot \text{triarsine}$ <sup>35</sup> and  $\text{NiBr}_3 \cdot 2\text{Et}_3\text{P}$ <sup>13</sup> and in certain gold(III) and palladium(II) di(tertiary arsine) complexes of the type  $[\text{Pd}^{\text{II}}(\text{diarsine})_2\text{Hal}]\text{ClO}_4$ —at least in nitrobenzene solution.<sup>25, 36</sup>  $d^9$  Quinquovalent complexes of copper(II) have also been reported, e.g.,  $[\text{Cu}(\text{dipyridyl})_2\text{I}]\text{ClO}_4$ ; the large orbital contribution to the magnetic moment suggests a trigonal-bipyramidal shape for reasons discussed elsewhere.<sup>16d</sup> Earlier in the transition series compounds of the  $d^0$  type such as  $\text{TiCl}_4 \cdot \text{Et}_3\text{N}$  are presumably bipyramidal since the arrangement of five bonding pairs of electrons, in the absence of any non-bonding  $d$  electrons, is expected to give this shape.

*Co-ordination number six.* The arrangement of six bonds in a  $d^0$  configuration leads to a perfect octahedral arrangement and is exemplified by compounds such as  $\text{K}_2\text{TiF}_6$ ,  $\text{KVF}_6$ , and  $\text{MoF}_6$ . In  $d^1$  and  $d^2$  complexes the effect of the non-bonding  $d_e$  electrons is expected to be small and hence the arrangement shows no significant difference from a perfect octahedron. The  $d_e^3$  complexes form regular octahedra. Examples of these include:  $d^1$ ,  $(\text{NH}_4)_3\text{TiF}_6$ ;  $d_e^2$ ,  $\text{M}_3^{\text{I}}\text{VF}_6$ , and  $\text{M}_2^{\text{I}}\text{VF}_5 \cdot \text{H}_2\text{O}$ ;  $d_e^3$ ,  $[\text{Cr}(\text{NH}_3)_6]\text{Cl}_3$  and  $\text{K}_3\text{Cr}(\text{C}_2\text{O}_4)_3$ . When we pass to  $d^4$  complexes two possibilities arise depending upon whether spin-pairing occurs, giving  $d_e^4$ , or not, in which case  $d_e^3 d_y^1$  is the electronic configuration. Sexicovalent complexes of the spin-paired type are few but include  $\text{K}_4\text{Cr}(\text{CN})_6$ ,  $\text{K}_3\text{Mn}(\text{CN})_6$ , and  $[\text{Cr}^{\text{I}}(\text{dipyridyl})_3]\text{Br}_2$ . No crystal-structure data are available but significant departure from perfect octahedral symmetry is not expected. In the spin-free case the electron in the  $d_y$  ( $d_{z^2}$ ) orbital is expected to cause two *trans* bonds in the octahedron to be longer than the other four; complexes in this category

<sup>35</sup> Barclay and Nyholm, *Chem. and Ind.*, 1953, 378.

<sup>36</sup> Harris and Nyholm, *J.*, 1956, 4375; 1957, 63.

include  $[\text{Mn}^{\text{III}}(\text{acetylacetonate})_3]^0$  but no crystal-structure data are available.\* The  $d^5$  configuration, if spin-free (*i.e.*,  $d_e^3d_\gamma^2$ ), should be perfectly symmetrical as in  $[\text{Fe}^{\text{III}}(\text{acetylacetonate})_3]^0$  or  $\text{K}_3\text{Fe}(\text{C}_2\text{O}_4)_3$ . Even when spin-paired (*i.e.*,  $d_e^5$ ) the departure from perfect octahedral symmetry should be negligible; examples include  $\text{K}_3\text{Fe}(\text{CN})_6$ . The  $d^6$  complexes if spin-free will have a configuration  $d_e^4d_\gamma^2$  and no significant departure from the perfect octahedron is expected, *e.g.*,  $[\text{Fe}(\text{H}_2\text{O})_6]\text{SO}_4 \cdot \text{H}_2\text{O}$  and  $[\text{Fe}(\text{NH}_3)_6]\text{Cl}_2$ ; spin-paired  $d_e^6$  complexes have filled  $d_e$  sub-shells and form perfect octahedra, for example complex cyanides of iron(II)  $[\text{K}_4\text{Fe}(\text{CN})_6]$  and cobalt(III)  $[\text{K}_3\text{Co}(\text{CN})_6]$ . The  $d^7$ ,  $d^8$ , and  $d^9$  arrangements are of particular interest, especially in spin-paired complexes, and we shall deal with  $d^7$  and  $d^8$  together. In spin-free  $d^7$  complexes the configuration is  $d_e^5d_\gamma^2$  and no significant deviation from the perfect octahedron is expected, *e.g.*,  $[\text{Co}(\text{NH}_3)_6]\text{Cl}_2$ . Similarly  $d^8$  complexes form a symmetrical shell of the type  $d_e^6d_\gamma^2$  and a regular octahedron is to be expected, *e.g.*,  $[\text{Ni}(\text{NH}_3)_6]\text{Cl}_2$ . In the spin-paired complexes, however, we obtain the electronic configurations  $d_e^6d_\gamma^1$  and  $d_e^6d_\gamma^2$  respectively—if it is assumed that no promotion of the electrons from the  $d_\gamma$  orbital takes place. The  $d^7$  and  $d^8$  spin-paired complexes are exemplified by cobalt(II), *e.g.*,  $\text{M}_2\text{M}^{\text{II}}[\text{Co}(\text{NO}_2)_6]$  and by palladium(II), *e.g.*,  $[\text{Pd}(\text{diarsine})_2\text{I}_2]^0$ , respectively. In the latter case there are two Pd-I *trans* bonds much longer than expected, and this may be attributed to repulsion by the electron pair in the  $d_\gamma$  (*i.e.*,  $d_{z^2}$ ) orbital.<sup>25</sup> No exact crystal structure data on cobalt(II) complexes of this type are available but it is significant that attempts to prepare  $\text{K}_4\text{Co}(\text{CN})_6$  yield the pentacyanide  $\text{K}_3\text{Co}(\text{CN})_5$ ; Dwyer<sup>37</sup> has shown that in solution it is the  $[\text{Co}^{\text{II}}(\text{NO}_2)_6]^{3-}$  ion and *not* the  $[\text{Co}^{\text{II}}(\text{NO}_2)_6]^{4-}$  ion which is formed. It is noteworthy that in a spin-paired  $d^8$  complex there are not two vacant  $d_\gamma$  orbitals available to form octahedral  $(n-1)d_\gamma^2 nsp^3$  bonds. A convenient way of looking at these complexes is to imagine that four  $(n-1)d_\gamma nsp^2$  bonds are formed in a plane and two longer coaxial bonds normal to this plane are formed by  $npnd$  [or  $np(n+1)s$ ] hybrids.

The  $d^9$  configuration is restricted to nickel(II) and copper(II) complexes but hexicovalent compounds of the latter only are known. These usually involve two coaxial bonds longer than the other four—a picture consistent with the idea that in the configuration  $d_e^6d_\gamma^3$  one of the  $d_\gamma$  electrons is in the plane of four ligands in a  $d_{x^2-y^2}$  orbital whereas the other pair are in a  $d_{z^2}$  orbital normal to this plane and exert a greater repulsion on the two ligands along this direction. Many copper(II) complexes are known in which this arrangement occurs; there are four bonds in a plane and two longer ones normal to this plane.

**Lanthanide and Actinide Elements.**—The lanthanides are a group of elements having the electronic configuration  $1s2s \dots 4d^{10}4f^n5s^25p^65d^16s^2$ . The important electrons are underlined. The usual behaviour in forming compounds is to lose the three  $5d^16s^2$  electrons to form *tervalent* ions or complexes except when the loss or gain of an electron by the  $4f$  shell leads to an empty ( $f^0$ ), half filled ( $f^7$ ), or filled ( $f^{14}$ ) sub-shell. This occurs for

<sup>37</sup> Dwyer, personal communication, 1956.

\* As mentioned earlier, however,<sup>21</sup>  $\text{MnF}_3$  does show this hexagonal distortion.

example with cerium(IV) ( $f^0$ ) and with europium(II) ( $f^7$ ). The sum of the three ionisation potentials of the actinides is relatively small (La $^{3+}$ , 36.2 v; cf. Al $^{3+}$ , 53.2 v; Tl, 56.3 v). As a result they are fairly basic, that is, have low electronegativities and tend to form complexes only with the more electronegative ligands, such as oxygen in water and in oxyacids. As the (relatively) deep-seated  $4f^n$  electrons are shielded from the valency shell the stereochemistry is unaffected by them and the complexes are usually octahedrally co-ordinated. With quadrivalent cerium an apparently octaco-ordinated complex [Ce(acetylacetonate) $_4$ ] $^0$  has been described but nothing is known of the stereochemistry.

The actinide elements are similar in electronic configuration to the lanthanides except that (a) the screening of the outer (valency) electrons is greater and valencies higher than 3 are common, (b) the  $5f$  and  $6d$  levels are closer together in energy and the ground states in certain valency states are less definite. The stereochemistry of the trivalent compounds is similar to that of the lanthanides and (presumably) octahedral compounds of the type [MCl $_6$ ] $^{3-}$  are found. In the quadrivalent state, e.g., Cs $_2$ PuCl $_6$ , octahedral co-ordination is also observed since this compound is isomorphous with Cs $_2$ GeCl $_6$ . For the quinquevalent state, e.g.,  $\alpha$ - and  $\beta$ -uranium pentafluoride, both sexi- and septa-covalency are observed. The uranium atom in  $\alpha$ -uranium pentafluoride is octahedrally co-ordinated, a polymeric structure being obtained containing bridges of fluorine atoms.<sup>38</sup> However, in the  $\beta$ -compound each uranium atom is apparently septavalent but the actual arrangement is uncertain. In the hexivalent state octahedral co-ordination is observed in uranium hexachloride and hexafluoride but there is a very marked tendency for uranium—and indeed the remaining actinide elements—to form linear [O=M=O] $^{n+}$  ions having one or two positive charges according as M is quinque- or sexi-valent. This may remain as a unit in which the M atom is bicovalent or it may attach five more ligands in a plane making a pentagonal-bipyramid. Examples of this are K $_3$ [U $^{VI}$ O $_2$ F $_5$ ] and K $_3$ UF $_7$ . As pointed out by Zachariasen,<sup>38</sup> [MO $_2$ ] $^{2+}$  ions are also formed by plutonium, americium, and neptunium and [MO $_2$ ] $^{+}$  ions by plutonium and americium.

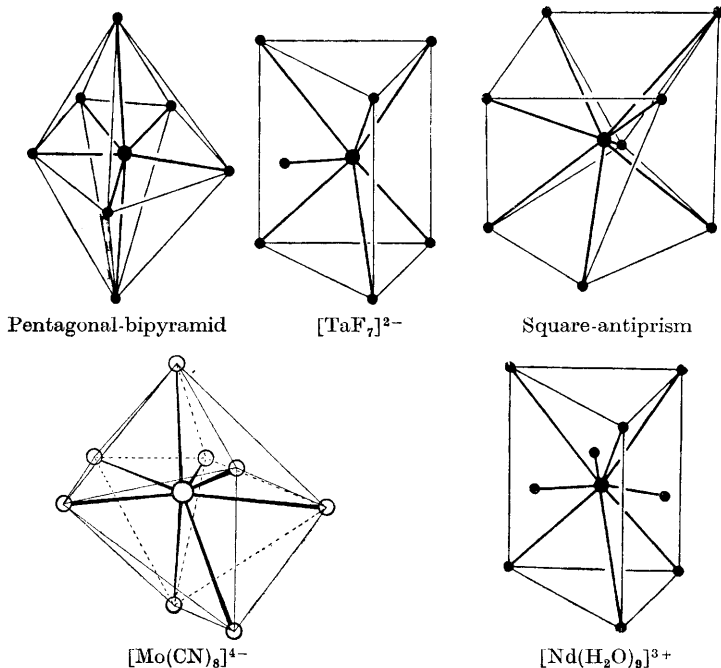
**Co-ordination Numbers Greater than Six.**—The most probable arrangement of seven bonding pairs of electrons in the configuration  $(d_e)^2(d_\nu)^4(s)^2(p)^6$  is the pentagonal-bipyramid. Recently, Zachariasen<sup>38</sup> has shown that [ZrF $_7$ ] $^{3-}$ , which had previously been reported to have a distorted octahedral structure with an additional bond at the centre of one of the triangular faces, has a pentagonal-bipyramidal structure, as also have [UO $_2$ F $_5$ ] $^{3-}$  and [UF $_7$ ] $^{3-}$ . However [TaF $_7$ ] $^{2-}$ , which like [ZrF $_7$ ] $^{3-}$  also has 14 electrons in its valency shell, apparently has the structure of a distorted trigonal-prism (Fig. 10) with an extra bond at the centre of one of the rectangular faces. In [ZrF $_7$ ] $^{3-}$ , the two remaining  $d_e$  orbitals are empty, although in heptaco-ordinated molecules with larger valency shells it would be possible for these  $d_e$  orbitals to contain non-bonding electrons without affecting the shape of the molecule.

<sup>38</sup> Zachariasen, *Acta Cryst.*, 1954, 7, 792; and earlier references therein.



FIG. 10

Some shapes of molecules with co-ordination numbers greater than six.



Two structures have so far been observed for octaco-ordinated molecules: the square-antiprism as found in  $[\text{TaF}_8]^{3-}$  and  $[\text{Sr}(\text{H}_2\text{O})_8]^{2+}$  and the  $[\text{Mo}(\text{CN})_8]^{4-}$  structure. The former arises from the configuration  $(d_z)^6(d_x)^2(s)^2(p)^6$  and the latter from the configuration  $(d_z)^4(d_x)^4(s)^2(p)^6$ . In  $[\text{TaF}_8]^{3-}$  and  $[\text{Sr}(\text{H}_2\text{O})_8]^{2+}$  the  $d_z$  orbital is empty, but in  $[\text{Mo}(\text{CN})_8]^{4-}$  a  $d_z$  orbital is occupied by a non-bonding pair which, because of its symmetrical situation with respect to the bonding pairs, will not have any appreciable effect on their arrangement. Distortions in complex fluorides can be understood if we bear in mind the highly polar nature of the metal-fluorine bond. If we regard the fluorine atom as behaving somewhat like an  $\text{F}^-$  ion, then repulsions of ion-ion type may be comparable with electron-pair repulsions.

It is interesting to note that, provided  $f$  electrons are not involved, there is only one possible configuration for the electrons of nonaco-ordinated molecules, namely  $(d)^{10}(s)^2(p)^6$ , and their structures are likely to be based on the most probable arrangement of nine electron pairs in this configuration. Duffey<sup>39</sup> has pointed out that several bond arrangements are possible with this electron configuration and has suggested that the most likely is that shown in Fig. 10, *i.e.*, a trigonal-prism with an atom at each corner and one in the middle of each rectangular face. Nonaco-ordinated neodymium is found in the compound  $[\text{Nd}(\text{H}_2\text{O})_9]^{3+}(\text{BrO}_3^-)_3$  in which the

<sup>39</sup> Duffey, *J. Chem. Phys.*, 1951, **19**, 553.

nine water molecules do have this arrangement. The complex ion  $[\text{OsF}_9]^-$  has been claimed but its structure has not been determined.

The same arrangement of nine bonds is found in a number of other crystals, *e.g.*,  $\text{UCl}_3$ ,  $\text{LaCl}_3$ ,  $\text{CeCl}_3$ ,  $[\text{UF}_6]^-$ ,  $[\text{ThF}_6]^-$ ,  $[\text{LaF}_4]^-$ ,  $[\text{CeF}_4]^{4-}$ , and  $[\text{Sr}(\text{H}_2\text{O})_6]^{2+}$ , although none of these contains discrete molecules or complex ions, at least some of the ligands being shared between two metal atoms. Nevertheless, it is likely that the bonds in all these cases have some covalent character.

### Summary

The stereochemistry of an atom in any particular molecule depends on the number of pairs of electrons in its valency shell. It is convenient to distinguish three types of electron pairs: (1) non-bonding or lone pairs, (2)  $\sigma$ -bonding pairs, (3)  $\pi$ -bonding pairs. The general arrangement of the valencies around any atom is determined by the fact that the lone pairs and the  $\sigma$ -bonding pairs of electrons arrange themselves as far apart as possible. To a first approximation the  $\pi$ -bonding pairs can be ignored.

A more detailed and exact description of the shapes of molecules can be given if it is assumed (1) that a lone pair repels other electron pairs more than a bonding pair of electrons, (2) that a double bond repels other bonds more than a single bond; (3) that the repulsion between bonding pairs depends to some extent on the electronegativity of the ligand and decreases as the latter increases.

The tendency of the electron pairs in a valency shell to keep apart is mainly due to the exclusion principle. Such relatively localised electron pairs are most conveniently described in terms of localised molecular orbitals or bond orbitals constructed from appropriate hybrid orbitals on the central atom and a suitable singly-occupied orbital on the ligand. When they are thus described by suitable localised orbitals the energy of interaction of the electron pairs is largely electrostatic, the non-classical or "exchange" part of the interaction energy being relatively small.

When some of the electrons in a valency shell occupy  $d$  orbitals it is necessary to distinguish between the different  $d$  orbitals. It is often convenient to divide the  $d$  orbitals into two types,  $d_{\nu}$  and  $d_{\sigma}$  orbitals; when one kind is used for bonding, non-bonding electrons of the *same* kind are equally as important as the bonding electron pairs in determining the shape of a molecule but electrons of the *other* kind have only a small effect on the stereochemistry.

The ligand-field theory shows that the degeneracy of the five  $d$  orbitals is removed by the electric field of the ligands and that they split into two or more groups depending on the symmetry of the ligand field. It thus emphasises the necessity of distinguishing between the different types of  $d$  orbitals when discussing the stereochemistry of an atom which has valency-shell electrons in  $d$  orbitals. When the ligand-field theory is combined with the idea that valency-shell electrons described by suitably localised orbitals have a predominantly electrostatic interaction energy, then a detailed understanding of the shapes of transition-metal complex ions is possible.