895. *The Stereochemistry of Five-co-ordination. Part I. Non-transition Elements.*

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The stereochemistry of five-co-ordination in molecules of the non-transition elements is discussed in terms of the theory of valency-shell electron-pair repulsions. It is shown that this theory provides a better explanation for the observed bond lengths and bond angles in both trigonal-bipyramidal and square-pyramidal molecules than does the conventional theory of directed valency based on hybrid orbitals. The discussion includes a consideration of molecules with a doubly bonded oxygen atom as one of the ligands, *e.g.*, SOF_4, trigonal-bipyramidal transition states, and pseudorotation in trigonal-bipyramidal molecules.

FIVE-CO-ORDINATED molecules have been found to have either a trigonal-bipyramidal or a square-pyramidal shape. In terms of the familiar valence-bond theory of directed orbitals the bonding in a five-co-ordinated molecule may be described in terms of a set of five sp^3d hybrid orbitals. If the d_{z^2} orbital is used, the hybrid orbitals are directed towards the corners of a trigonal bipyramid but if the $d_{x^2-y^2}$ orbital is chosen the set of hybrid orbitals are directed towards the corners of a square pyramid. Since there appears to be no reasonable way of deciding whether the d_{z^2} or the $d_{x^2-y^2}$ orbital should be chosen this theory cannot provide a satisfactory explanation for the general shape of any particular five-co-ordinated molecule. Moreover, it does not explain various details of these two shapes, such as the greater length of the axial than of the equatorial bonds in trigonal-bipyramidal molecules and the distortion of the "ideal" shape of square-pyramidal molecules, such as BrF_5, in which the bromine atom lies below the base of the square pyramid formed by the fluorine atoms.

It is the purpose of this paper to amplify and extend a previous discussion of the shapes of five-co-ordinated molecules of the non-transition elements,[1] and to show that all the important features of the shapes of five-co-ordinated molecules of these elements can be accounted for satisfactorily in terms of the repulsions between the electron pairs in the valency shell of the central atom. In the following paper the discussion is extended to the transition elements.

It had been shown previously that the general shape of a molecule AX_nE_m, where A is a non-transition element, is determined by $n + m$, the sum of the number of ligands X

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[1] Gillespie, *Canad. J. Chem.*, 1961, **39**, 318.

and the number of non-bonding or lone electron pairs E, and is a consequence of the mutual interactions of these bonding and non-bonding electron pairs.[2-4] Similar interactions exist between the non-bonding electron pairs on different X atoms, but because it is believed that this interaction diminishes very rapidly with increasing separation of the electron pairs [4] the repulsions between the non-bonding electron pairs on different X atoms will, in general, be much smaller than the interactions between the electron pairs in the same valency shell. Thus the point of view on which the discussion in this paper is based differs fundamentally from that given in a recent discussion of molecular shape,[5] in which it is considered that the repulsive interactions between non-bonded atoms is the most important factor in determining molecular shape. Obviously, for sufficiently bulky groups and in special steric situations these interactions may be of importance, but the present discussion is based on the assumption that they are generally less important in determining molecular shape than the repulsions between the electron pairs in the same valency shell.

The preferred arrangement of five electron pairs may be shown to be the trigonal bipyramid.[4] It is assumed that the five electron pairs are at the same average distance from the nucleus (they may for convenience be regarded as points on the surface of a sphere) and that their mutual interactions may be expressed in terms of a potential of the form $1/r^n$ where r is the distance between any two electron pairs. Then, for the case where n approaches infinity the most stable arrangements are those which maximize the least distance between any two pairs, and these are the trigonal bipyramid and the square pyramid with equal edges (Fig. 1, a and b). For values of n smaller than infinity the square pyramid is distorted, so that the basal plane moves below the central atom (Fig. 1c), but in all cases this is now somewhat less stable than the trigonal bipyramid. For $n = 8$—12, the angle α in the most stable square-pyramidal arrangement is ~100° and this is about 8% less stable than for the trigonal bipyramid. Thus it seems reasonable to assume that in a case where some special steric situation prevents the adoption of a trigonal-bipyramidal arrangement, then a square pyramid with an angle of ~100° between the axial and the basal bonds might be expected. In general, however, the preferred arrangement of five electron pairs is the trigonal bipyramid and it may similarly be shown that the preferred arrangement of six electron pairs is the octahedron.[1,4] Thus, AX_5 molecules have the trigonal-bipyramidal shape (I), and AX_5E molecules have the square-pyramidal shape (II).[1]

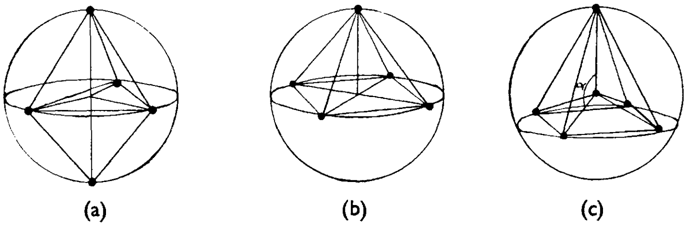
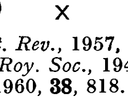
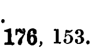


FIG. 1. Equilibrium arrangements for electron pairs on the surface of a sphere repelling each other according to a force law of the form $1/r^n$.
(a) and (b) are the most stable arrangements for $n = \infty$. (c) is the form of the square-pyramidal configuration for $n < \infty$.



$$\begin{array}{c} X \\ | \\ X-A\begin{smallmatrix}<X\\<X\end{smallmatrix} \\ | \\ X \end{array}$$

(I)



$$\begin{array}{c} X \\ | \\ \begin{smallmatrix}X>\\X>\end{smallmatrix}\underset{\cdot\cdot}{A}\begin{smallmatrix}<X\\<X\end{smallmatrix} \end{array}$$

(II)

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[2] Gillespie and Nyholm, *Quart. Rev.*, 1957, **9**, 339.
[3] Sidgwick and Powell, *Proc. Roy. Soc.*, 1940, *A*, **176**, 153.
[4] Gillespie, *Canad. J. Chem.*, 1960, **38**, 818.
[5] Bartell, *J. Chem. Phys.*, 1960, **32**, 827.

Trigonal Bipyramid AX_5 *Molecules.—Bond lengths.* The repulsions between the electron pairs in a valency shell are of such a nature that they are negligibly small when the orbitals occupied by the two electron pairs do not overlap appreciably, but they increase rapidly when the average distance between the electron pairs decreases so that their orbitals begin to overlap to a significant extent.[1,4,6] Thus in the trigonal-bipyramidal arrangement of five electron pairs it is a reasonable approximation to consider only the interactions between the pairs of electrons that make an angle of 90° to each other at the nucleus, and to neglect the interaction between electron pairs that make angles of 120° with each other. In this case it may be seen that each of the three equatorial pairs interacts with only two axial pairs at angles of 90°, while each axial pair interacts with three equatorial pairs at 90° (Fig. 2). Evidently it is impossible to have a stable arrangement with all the electron pairs at the same distance from the nucleus. If they were all at the same average distance from the nucleus, the axial electron pairs would be subject to a greater repulsion than the equatorial pairs, hence the equilibrium arrangement must be one in which the two axial pairs are at a slightly greater distance from the nucleus than the equatorial pairs; or, in other words, the radius of the central atom should be greater in the axial than in the equatorial direction. In all the fifteen cases that have so far been studied with sufficient accuracy, including molecules where one or two of the five electron pairs are non-bonding pairs (*i.e.*, AX_4E and AX_3E_2 molecules), the axial radius of the central atom has been found to be larger than the equatorial radius, with $r_{ax}/r_{eq} = 1{\cdot}1$—$1{\cdot}2$.[1] For example, in a recent determination of the structure of SF_4 by microwave spectroscopy it was found that the equatorial bonds have a length of 1·545 Å while the axial bonds have a length of 1·646 Å.[7]

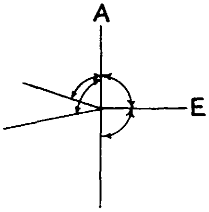

FIG. 2. Diagram illustrating the three 90° interactions of the axial electron pair A and the two 90° interactions of the equatorial electron pair E.

It is sometimes stated that the familiar valence-bond description of the trigonal-bipyramidal structure in terms of $sp^3d_{z^2}$ orbitals accounts for the greater length of the axial than of the equatorial bonds, but this is not so. The hybrid orbitals on the central atom may be represented by the functions:

$$\Psi_{eq^1} = \left(\frac{1}{\sqrt{3}} \sin \alpha\right)s + \frac{\sqrt{2}}{\sqrt{3}} p_x - \left(\frac{1}{\sqrt{3}} \cos \alpha\right)d_{z^2}; \quad . \quad . \quad . \quad . \quad . \quad (1)$$

$$\Psi_{eq^2} = \left(\frac{1}{\sqrt{3}} \sin \alpha\right)s - \frac{1}{\sqrt{6}} p_x + \frac{1}{\sqrt{2}} p_y - \left(\frac{1}{\sqrt{3}} \cos \alpha\right)d_{z^2}; \quad . \quad . \quad (2)$$

$$\Psi_{eq^3} = \left(\frac{1}{\sqrt{3}} \sin \alpha\right)s - \frac{1}{\sqrt{6}} p_x - \frac{1}{\sqrt{2}} p_y - \left(\frac{1}{\sqrt{3}} \cos \alpha\right)d_{z^2}; \quad . \quad . \quad (3)$$

$$\Psi_{ax^1} = \left(\frac{1}{\sqrt{2}} \cos \alpha\right)s + \frac{1}{\sqrt{2}} p_z + \left(\frac{1}{\sqrt{2}} \sin \alpha\right)d_{z^2}; \quad . \quad . \quad . \quad . \quad . \quad (4)$$

$$\Psi_{ax^2} = \left(\frac{1}{\sqrt{2}} \cos \alpha\right)s - \frac{1}{\sqrt{2}} p_z + \left(\frac{1}{\sqrt{2}} \sin \alpha\right)d_{z^2}, \quad . \quad . \quad . \quad . \quad . \quad (5)$$

where α is a convenient mixing parameter. According to Pauling, the strength of a bond formed by a hybrid orbital is proportional to the maximum value of the angular part

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[6] Gillespie, *J. Amer. Chem. Soc.*, 1960, **82**, 5978.
[7] Tolles and Gwinn, *J. Chem. Phys.*, 1962, **36**, 1119.

of the wave function.[8] Duffey[9] has shown that the total covalent bond energy of an AX_5 molecule is maximized for $\cos \alpha = 0{\cdot}5424$, in which case the bond-forming power of equatorial bonds is 2·249 and of axial bonds 2·937 on the scale adopted by Pauling according to which the bond-forming power of an *s* orbital is taken to be unity. According to this theory, therefore, the equatorial bonds are expected to be weaker and therefore presumably longer than the axial bonds.

The hybrid-orbital description can be reconciled with the observed bond lengths, with the Pauling criterion of bond strength, only if it is assumed that the equatorial bonds are largely *sp* in character while the axial bonds are largely pd_{z^2} in character, *i.e.*, that $\cos \alpha \longrightarrow 0$. Since, however, this is an arbitrary assumption that cannot be justified, it merely provides a possible description of, but certainly not an explanation for, the actual electron distribution.

An alternative possibility is that the difference between the axial and equatorial bond lengths is due to a difference in double-bond character. However, we may note, following Kimball,[10] that only the d_{xz} and the d_{yz} orbitals are available for strong double-bond formation. These could give rise to bonds of order 2·0 in the axial directions, but to bond orders of only 1·66 in the equatorial directions. Thus again it would be expected that the equatorial bonds would be longer than the axial bonds.

The Pauling criterion of bond strength has, however, been criticized and it is certainly not valid for bonds formed by carbon in the sp, sp^2, and sp^3 hybridization states. In this case, and probably generally, the magnitude of the overlap integral is probably a more satisfactory measure of the bond strength.[11,12] Cotton[13] has recently shown, using Slater-type orbitals, that, if the total overlap integral between the $sp^3d_{z^2}$ orbitals of a phosphorus atom and the *s* or *p* orbitals of five fluorine or chlorine atoms situated at the same distance from the phosphorus atom and at the corners of a trigonal bipyramid, is maximized by varying the parameter α in equations 1—5, then the overlap for an equatorial bond is greater than for an axial bond. He therefore concludes that the axial bonds should be weaker than the equatorial bonds. It is tempting to conclude further that the axial bonds would also, therefore, be longer than the equatorial bonds, but this is not possible because the method initially assumes that the axial and the equatorial bond lengths are the same. Indeed it might be argued that there would be a tendency for the axial bonds to decrease in length to increase the overlap in these bonds.

In an earlier paper Craig *et al.*[14] avoided the initial assumption of equal axial and equatorial bond lengths and, by making certain rather arbitrary assumptions concerning the effective nuclear charges of the atoms involved, showed that maximum overlap of ligand orbitals with an equatorial orbital of the central atom may occur at a slightly smaller internuclear distance than for an axial orbital and that therefore the axial bonds may be slightly longer than the equatorial bonds. However, this explanation does not have the simplicity or the generality of the explanation based on electron-pair repulsions and in view of the assumptions involved it is certainly no more quantitative.

Pseudorotation. A particularly interesting feature of trigonal-bipyramidal molecules is the possibility of internal exchange of atoms, or pseudorotation, as described by Berry.[15] A consideration of the repulsions between the bonding electron pairs makes this seem very plausible. The repulsive interactions between the equatorial bonding electron pairs are very weak because they make angles of 120° with each other and the repulsions between electron pairs in the valency shells of phosphorus, sulphur, and other second-row elements

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[8] Pauling, " Nature of the Chemical Bond," Cornell Univ. Press, Ithaca, 3rd edn., 1961.
[9] Duffey, *J. Chem. Phys.*, 1949, **17**, 196.
[10] Kimball, *J. Chem. Phys.*, 1940, **8**, 188.
[11] Maccoll, *Trans. Faraday Soc.*, 1950, **46**, 369.
[12] Mulliken, *J. Amer. Chem. Soc.*, 1950, **72**, 4493.
[13] Cotton, *J. Chem. Phys.*, 1961, **35**, 228.
[14] Craig, Maccoll, Nyholm, Orgel, and Sutton, *J.*, 1954, 332.
[15] Berry, *J. Chem. Phys.*, 1960, **32**, 933.

do not become of importance until they are at an angle of approximately 90° to each other.[6] Even for first-row elements these repulsions are important only for angles approaching 109°. Evidently, then, there will be little resistance to the motion of the equatorial electron pairs 1 and 3 in the directions shown in Fig. 3 until they make angles of approximately 90° with pair 2 in the rotated form *b*. The movement of electron pairs 1 and 3 can be accompanied by the corresponding movement of 4 and 5 with essentially no change in their repulsive interactions with neighbouring electron pairs.

In contrast to the expected ready internal exchange, or pseudorotation, for a trigonal-bipyramidal molecule it may be noted that a similar internal motion of an octahedral molecule involving, for example, the conversion of a molecule AX_4Y_2 from a *cis*- to a *trans*-form would involve a transition state with angles between electron pairs considerably smaller than 90°. In view of the strong repulsions that would be involved such an internal motion is very unlikely.

The ^{19}F nuclear magnetic resonance (n.m.r.) spectrum of phosphorus pentafluoride is a widely separated doublet due to P–F spin–spin coupling that shows no indication of separate signals or spin–spin coupling arising from non-equivalent axial and equatorial fluorine atoms.[16] It has therefore been concluded that either the chemical shifts and P–F coupling constants are identical for both the axial and the equatorial atoms and that the F_{ax}–F_{eq} coupling constant is very small, or that some rapid exchange process makes the fluorine atoms equivalent in an n.m.r. measurement.[16,17] This exchange cannot be intermolecular because of the observation of P–F coupling; hence it is probable that it is the pseudorotation discussed above.

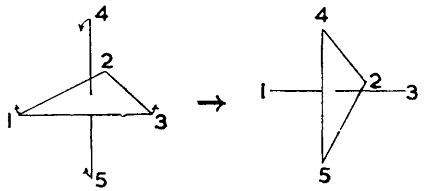

FIG. 3. Pseudorotation of the trigonal bipyramid. The numbers indicate the positions of bonding electron pairs or ligand atoms.

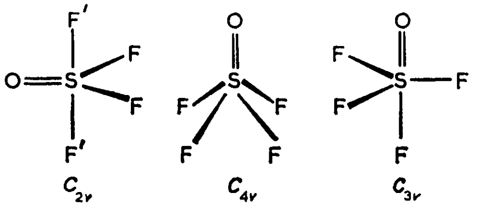

FIG. 4. Possible structures for the SOF_4 molecule.

Transition states. The same stereochemical considerations that apply to stable molecules can also be applied to transition states. The author pointed out some years ago that the transition state of an S_N2 substitution at a saturated carbon atom can be regarded as containing a five-covalent carbon atom and that the bonding could be described by using trigonal-bipyramidal hybrid orbitals involving the $3d_{z^2}$ orbital of the carbon atom.[18] In such a transition state there are evidently five electron pairs in the valency shell of the carbon atom and, according to the present ideas, these will adopt a trigonal-bipyramidal configuration. However, five electron pairs will cause very considerable crowding in the valency shell of a carbon atom and therefore the lengthening of the axial compared with the equatorial bonds will be considerably greater than in stable trigonal-bipyramidal molecules. These long bonds are, of course, those formed by the entering and the leaving group and this is in accord with the generally accepted picture of such a transition state.[19] The long bonds can be very approximately described as being formed from $2p3d_{z^2}$ orbitals on the carbon atom.

[16] Gutowsky, McCall, and Slichter, *J. Chem. Phys.*, 1953, **21**, 279.

[17] Muetterties and Phillips, *J. Amer. Chem. Soc.*, 1959, **81**, 1084; Mahler and Muetterties, *J. Chem. Phys.*, 1960, **33**, 636.

[18] Gillespie, *J.*, 1952, 1002.

[19] Ingold, " Structure and Mechanism in Organic Chemistry," Cornell Univ. Press, Ithaca, 1953, p. 403.

Trigonal-bipyramid AOX_4 *Molecules.*—Molecules of this type are of interest because of the presence of a doubly bonded oxygen atom.[20] Since a double bond contains two pairs of electrons, the corresponding orbital (in this case a four-electron orbital) will be necessarily larger than a two-electron or single-bond orbital. Hence it will overlap more with neighbouring orbitals and exert a stronger repulsion on neighbouring electron pairs. In an AOX_4 molecule the oxygen atom would, therefore, be expected to occupy an equatorial position in order that the interactions of the two double-bond electron-pairs with other electron pairs are minimized. This conclusion is in agreement with the results of a recent investigation of the vibrational spectrum of SOF_4 which show that the molecule has the expected C_{2v} symmetry, and not the C_{4v} or C_{3v} symmetry of possible alternative structures (Fig. 4).[21] The extra repulsion exerted by the double bond should cause the F′SF angles to be slightly smaller than the ideal value of 90° and the FSF angles to be somewhat smaller than the ideal value of 120°. Similar deviations from the regular trigonal-bipyramidal arrangement of five electron pairs as a consequence of the greater repulsion exerted by a lone pair have been observed in sulphur tetrafluoride and related molecules.[1,7] A determination of details of the structure of SOF_4 would obviously be of interest.

It is interesting that, although there are two non-equivalent pairs of fluorine atoms in this structure, only one line has been observed in the fluorine n.m.r. spectrum [22] at room temperature, whereas two signals of equal intensity each with a fine-structure of the A_2B_2 type due to spin–spin coupling would be expected, as has been observed at low temperatures in the spectrum of SF_4.[23] It seems probable that the molecule undergoes intramolecular exchange or pseudorotation of the type discussed above.

Square-pyramidal AX_5E *Molecules.*—This shape results from the octahedral arrangement of six electron pairs in a valency shell. Six equivalent electron pairs would have a regular octahedral arrangement, but the arrangement of five bonding and one lone pair will depart from the regular octahedron because of the greater repulsion exerted by the lone pair. The four electron pairs in the base of the pyramid will be repelled upwards and outwards from their " ideal " positions causing the bond angles at the central atom to be slightly less than 90° and the bonds in the base of the pyramid to be slightly longer than the axial bond (Fig. 5). This distortion has been observed in $SbCl_5^{2-}$ and BrF_5.[24,25] The same square-pyramidal structure is found in a number of polymeric fluorides and sulphides of antimony(III). It has been pointed out by Grdenic and Scavnicar [26] that the same distortion of the ideal structure is observed in all these cases, the antimony atom being below the base of the square pyramid formed by the five ligands. In the SbF_5^{2-} ion the angle between the axial and the basal fluorine atoms is 82°, as expected, but it is reported that the axial bond is longer (2·08 Å) than the basal bonds (2·02 Å).[24] The reason for this observation is not clear, and SbF_5^{2-} and related structures merit further study. It has been suggested [27] that the difference in the lengths of the axial and the basal bonds in bromine pentafluoride can be explained either by assuming the axial bond to be a *pd* hybrid and the basal bonds to be sp^2d hybrids, or by assuming that the axial bond is formed from an *sp* hybrid and the basal bonds from p^2d^2 hybrids. Actually, only the description in which the axial bond has predominately *sp* character and the basal bonds considerable p^2d^2 character would be consistent with the observed bond lengths, but in any case that can only be regarded as a convenient description of the bonding electrons and not as a satisfactory explanation of the observed bond lengths.

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[20] Wells, " Structural Inorganic Chemistry," Oxford Univ. Press, 1962, 3rd edn., p. 434.

[21] Goggins, Roberts, and Woodward, *Trans. Faraday Soc.*, 1961, **57**, 1877.

[22] Dudley, Shoolery, and Cady, *J. Amer. Chem. Soc.*, 1956, **78**, 568.

[23] Cotton, George, and Waugh, *J. Chem. Phys.*, 1958, **28**, 994; Muetterties and Phillips, *J. Amer. Chem. Soc.*, 1959, **81**, 1084; Bacon, Gillespie, and Quail, *Canad. J. Chem.*, 1963, **41**, 1016.

[24] " Interatomic Distances," ed. by L. E. Sutton, *Chem. Soc. Special Publ.* No. 11, 1958.

[25] Burbank and Bensey, *J. Chem. Phys.*, 1957, **27**, 982.

[26] Grdenic and Scavnicar, *Proc. Chem. Soc.*, 1960, 147.

[27] Wiebenga, Havinga, and Boswijk, *Adv. Inorg. Chem. Radiochem.*, 1961, **3**, 133.

An alternative explanation attributes the difference in bond lengths to double-bond character in the axial bond.[25] However, no adequate explanation has been given for why only the axial and not the basal fluorine atoms are involved in double bonding since all five fluorine atoms have opportunities for double bonding by using the d_{xy}, d_{yz}, and d_{xz} orbitals.

Square-pyramidal AOX_4E *Molecules.*—There appears to be only one complex of the type AOX_4E of known structure, namely, $SeOCl_2,2C_5H_5N$. This has the expected square-pyramidal structure shown in Fig. 6.[28] In this case both the lone pair and the two pairs of the double bond exert greater repulsions than the single bond pairs and hence they take up *trans*-positions in the octahedron. Moreover, the four-electron orbital of the double bond appears to exert a slightly greater repulsion than the lone pair and hence in this case the square pyramid is slightly distorted in the opposite sense from that in the AX_5E molecules, so that the selenium atom comes a little above the base of the square pyramid formed by the ligands. The strong repulsions exerted on the four single-bond pairs by the double-bond quartet and the lone pair is reflected in the lengths of these bonds. The Se–N bonds are 0·33 Å longer than the calculated single bond length of 1·87 Å, and the mean Se–Cl bond length is similarly greater by 0·32 Å than the calculated value of 2·16 Å.

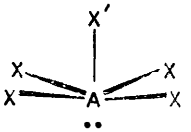

FIG. 5.

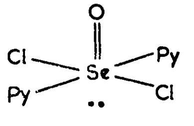

FIG. 6.

FIG. 5. Structure of AX_5E molecules. $r_{AX} > r'_{AX}$, $\angle X'AX < 90°$.

FIG. 6. Structure of $SeOCl_2,2C_5H_5N$.

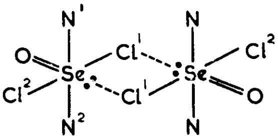

FIG. 7. Structure of the $SeOCl_2,2C_5H_5N$ dimer.

$\angle Cl^1SeO$ 95·1°; $\angle Cl^2SeO$ 99·7°; $\angle N^1SeO$ 90·9°; N^2SeO 92·8°.

Se–N 2·19 Å; Se–Cl^1 2·57 Å; Se–Cl^2 2·39Å.

An interesting feature of the crystal structure is that the molecules appear to be held together in pairs by a very weak interaction between a chlorine on one and the lone pair on the other (Fig. 7). The bond from selenium to this chlorine atom is considerably longer than that to the non-bridging chlorines. It appears that the strong repulsions between the seven electron pairs in the valency shell of the selenium cause the lone pair to be delocalized slightly into a vacant 3*d* orbital on the chlorine atom of the adjacent molecule which thus acts as a very weak acceptor. That chlorine can exhibit such weak acceptor properties is shown by the existence of the rather unstable Cl_3^- ion.[27]

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[28] Lindqvist and Nahringbauer, *Acta Cryst.*, 1959, **12**, 638.