769. *The Stereochemistry of* B *Subgroup Metals. Part II.*[1] *The Inert Pair.*

By L. E. ORGEL.

The mixing of *s* and *p* orbitals on a central ion in non-cubic environments which lack a centre of symmetry is shown to account for the stereochemical influence of inert pairs of electrons on the chemistry of Tl^+, Pb^{++}, and related ions.

MANY B subgroup metals exhibit a stable valency two smaller than the group valency. This tendency is most pronounced for thallium, lead, and bismuth and is also important for many lighter elements such as tin and antimony. The stereochemistry of molecules and solids containing ions in these unusual valencies is very often complicated.

The free ions corresponding to the lower valencies all have electron configurations consisting of closed shells followed by a pair of *s* electrons; 6*s* for Tl^+, Pb^{++}, and Bi^{+++}; 5*s* for In^+, Sn^{++}, and Sb^{+++}, etc. It is generally recognized that the unusual stereochemistry of these ions is connected with the pair of electrons outside a closed shell, but various views have been expressed as to the precise way in which the unshared electrons exert their influence. We shall develop the method suggested for d^{10} ions in a previous paper.[1]

We consider first a metal ion with an *s* electron pair at the centre of an octahedron of anions. A symmetrical displacement of the ligands can only mix the orbital containing the unshared *s* electrons with other *s* or *d* orbitals.* Since these are all energetically very highly excited such mixing is unlikely to be important. A displacement of an antisymmetrical kind, however, can mix the top filled *s* orbital with the *p* orbitals of the same subshell, which are known from spectroscopic evidence to be separated from the *s* orbital by only 5—6 ev in typical ionic solids.[2] If the *s* and *p* orbitals were initially degenerate the octahedron would be bound to be distorted, but in view of the actual energy separation between *s* and *p* orbitals it is a quantitative matter to decide whether distortion should occur or not.[1]

We make a very rough estimate of the energy contributed by polarization of the cation in a distorted configuration by adopting a point-charge model. Let us suppose that the anions along the *Z* axis of an octahedral complex are displaced a distance *z* in the same direction. The polarization energy is readily shown to be † $E_p = z^2(8\alpha Q^2/R^6) = \gamma_z{}^2$ where

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* This is an example of a very general quantum-mechanical argument which shows that if a system has a centre of symmetry, *g* and *u* states, that is even and odd states, can be mixed by an antisymmetric perturbation while two even or two odd states can be mixed by a symmetric perturbation.

† The field acting on the central ion is $Q\{[1/(R + z)^2] - [1/(R - z)^2]\}$, of which the most important term is $4zQ/R^3$. The polarization energy is $\frac{1}{2}\alpha(4zQ/R^3)^2$.

[1] Orgel, *J.*, 1958, 4186.

[2] Jørgensen, to be submitted for publication.

α is the polarizability of the cation, Q is the charge on the anion and R is the interionic distance.

Ions with an inert *s* electron pair are undoubtedly much more polarizable than ions of similar atomic number but with filled shells. Experimental values do not seem to be available, but Pauling has calculated the polarizabilities of Al^+ and Si^{++} to be $41{\cdot}2 \times 10^{-25}$ and $20{\cdot}6 \times 10^{-25}$ cm.^{3} compared with values of $1{\cdot}79 \times 10^{-25}$ and $0{\cdot}94 \times 10^{-25}$ cm.^{3} for Na^+ and Mg^{++}. The polarizabilities of Cs^+, Ba^{++}, and La^{+++} are $25{\cdot}2 \times 10^{-25}$, $15{\cdot}5 \times 10^{-25}$, and $10{\cdot}4 \times 10^{-25}$ cm.^{3}, respectively,[3] suggesting that the polarizabilities of Tl^+, Pb^{++}, and Sb^{+++} are in the range from 100×10^{-25} to 500×10^{-25}. In Table 1 we have collected some typical values for γ, reasonable values for R and α being assumed. It will be seen that γ is of the order of 10^5 dyne/cm., which is just the order of the force constants in typical oxides.[4] Thus, if we compare a stable regular octahedrally co-ordinated oxide of an A subgroup element with a corresponding B subgroup oxide, the difference in polarizability due to the inert pair is sufficient to loosen the metal ion at the centre of the octahedron or even to lead to instability.

TABLE 1. *Values of γ for various choices of α, R, and z.*

α	$R = 2$ Å; $z = 1$	$R = 2$ Å; $z = 2$	$R = 3$ Å; $z = 1$	$R = 3$ Å; $z = 2$
100×10^{-25}	$2{\cdot}875 \times 10^5$	$11{\cdot}50 \times 10^5$	$0{\cdot}25 \times 10^5$	$1{\cdot}01 \times 10^5$
500×10^{-25}	$14{\cdot}37 \times 10^5$	$57{\cdot}50 \times 10^5$	$1{\cdot}26 \times 10^5$	$5{\cdot}05 \times 10^5$

FIG. 1. *The structures obtained by the distortion of a regular octahedron along* (a) *a fourfold axis,* (b) *a twofold axis,* (c) *a threefold axis.*

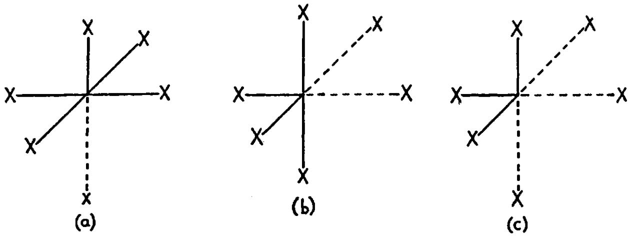


FIG. 2. *The structure obtained by distorting a cube about a fourfold axis.*

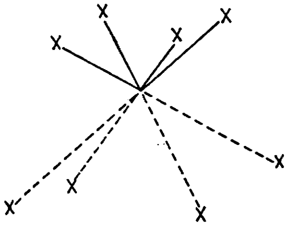
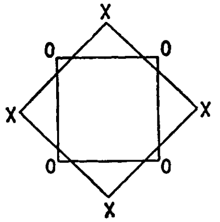


FIG. 3. *The structure obtained by distorting a square antiprism about a fourfold axis. The* 0*'s represent atoms above the plane and the* ×*'s atoms below the plane.*



It should be noted that the stabilization energies increase rapidly as R decreases so that in so far as their origin is electrostatic these distortions can be expected to be most evident in oxides and fluorides and less so in sulphides, chlorides, etc.* This is exactly the opposite conclusion to that which is reached if covalent influences are supposed to be dominant. We shall see that in fact this distance effect does seem to be important in some, if not all, classes of compound, *e.g.*, SnS and PbO are strongly distorted while PbS, PbSe, and PbTe, although presumably more covalent, have the sodium chloride structure.

* This assumes that the restoring force constants k are less sensitive than is γ to changes in R.

[3] Landolt-Börnstein, " Zahlenwerte und Functionen," Vol. I, Part I, Springer, Berlin, 1950.

[4] Herzberg, " Infra-red and Raman Spectra," 1945, van Nostrand, New York.

We now consider the environments of metal ions which can be derived from regular co-ordination if antisymmetric distortions are present. We start with a regular octahedron and consider the displacements which are symmetric about four-, two-, and three-fold axes, respectively. They lead to the configurations shown in Fig. 1. Each of these is encountered among the complexes and binary compounds of many ions with s^2 ground states. Starting from a cubic environment there are again three simple types of distortion, as shown in Fig. 2. Only the first is easily recognized, for example among the compounds of the larger ions, Pb^{++} and Bi^{+++}. Finally starting with a square antiprism the most symmetrical distortion is to the configuration shown in Fig. 3 and again is found most often for the larger ions, Pb^{++} and Bi^{+++}. We must emphasize that structures which are not closely related to cubic co-ordination may occur when the stereochemical influence of the inert pair is great, and that they should all lack even an approximate centre of symmetry.

Structural Evidence.—We have shown that ions with an s^2 outer electron configuration should often occur in environments lacking a centre of symmetry. An interesting comparison is thus possible between compounds of B subgroup elements for which a sodium chloride or cæsium iodide structure might be expected if distortions were absent. We have already seen that mercuric sulphide in the form of cinnabar can be considered to have a strongly distorted sodium chloride structure which nearly retains its centre of symmetry and that mercuric oxide also has a centro-symmetric structure based on a very distorted octahedral co-ordination.[1] Now stannous sulphide also has a deformed sodium chloride structure but one pair of opposite bonds have lengths of 2·62 Å and 3·39 Å, respectively, while the remaining four bonds occur in two opposed pairs each consisting of one short (2·68 Å) and one long (3·27 Å) bond.[5] Stannous and plumbous oxide are dimorphic, but the form whose structure is known most certainly can be considered to have a very strongly distorted cæsium iodide structure while the other form has a very unsymmetrical octahedral environment about the metal atom.[5] We have noted that PbS, PbSe, PbTe, and SnTe, which are presumably more covalent than the compounds discussed so far, all have undistorted sodium chloride structures.[5]

We can select only a few compounds containing s^2 ions from the many complex halides, oxides, and sulphides which have been studied. Many more are catalogued.[5] The five-co-ordinated structure (Fig. 1) occurs for example in K_2SbF_5,[6] and $KSbF_4$;[7] the four-co-ordinated structure (Fig. 1) in the $Sb_8O_8(OH)_4^{4+}$ ion[8] and the three-co-ordinated structure (Fig. 1) for example in GeO, As_2O_3, and Sb_2O_3.[5] The four-co-ordinated structure shown in Fig. 1a occurs in SnO,[5] PbO,[5] and $BiSbO_4$.[9] The square antiprism (Fig. 3) occurs in $Pb_2Cu(OH)_4Cl_2$.[10] The Cu^{++} ion shows the usual Jahn–Teller distorted 4 + 2 co-ordination but the lead atom is surrounded by four close oxygen atoms on a square, and four more-distant chloride ions completing an antiprism.

The distribution of more-distant neighbours in these compounds is interesting. When the distortion is along the four-fold axis of a cube or the three-fold axis of an octahedron both the short and the long bonds can often be recognized, for example in PbO, GeO, and Sb_2O_3. When, however, the distortion is along the four-fold axis there is usually no unique sixth group completing the octahedron. The case of distortion along a two-fold axis is intermediate. This can be most easily understood by considering the charge density distribution of the unshared pair after polarization. In the case of five-fold co-ordination these electrons are in an orbital pointing directly at the sixth position so an arrangement such as that in Fig. 4 is preferred. However, in the case of three close groups the unshared pair points along a three-fold axis of the original octahedron so that the remaining vertices of that octahedron are still the most favourable positions for weak attachments. The

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[5] Landolt-Börnstein, "Zahlenwerte und Functionen," Vol. I, Part IV, Springer, Berlin, 1950.
[6] Byström and Wilhelmi, *Arkiv Kemi*, 1951, **3**, 461.
[7] Byström, Backlund, and Wilhelmi, *Arkiv Kemi*, 1952, **4**, 175.
[8] Edstrand, *Arkiv Kemi*, 1955, **8**, 257.
[9] Aurivillius, *Arkiv Kemi*, 1951, **3**, 153.
[10] Byström and Wilhelmi, *Arkiv Kemi*, 1950, **2**, 397.

same argument shows that four next-nearest neighbours should be recognizable in the case of displacement along the four-fold axis of a cube or square antiprism.

The occurrence of phase transitions between structures of cubic symmetry and distorted structures has been recognized among the oxides with the perovskite structure containing the Pb^{++} ion. Megaw[11] has shown that at least in a few cases the distortions must in large measure be attributed to the stereochemical irregularities of the Pb^{++} ion.

The Polarizability of Undistorted Structures and Ferroelectricity.—We have suggested that the possibility of *s–p* mixing causes a tendency to instability to antisymmetric distortions in a cubically co-ordinated ion with an unshared *s* electron pair. This leads to the prediction that even if the cubic structure is stable it should be particularly susceptible to atom polarization by a static electric field, since the restoring force opposing ionic displacements should be reduced. In fact, thallium chloride and bromide, which have the cæsium iodide structure, have extremely large dielectric constants—much larger than can be accounted for even when the large electron polarizability of the Tl^+ ion is allowed for. This situation can be compared with that in titanium dioxide, which for different reasons is very unstable to antisymmetric displacement of the Ti^{4+} ions and so has a very large dielectric constant.[12]

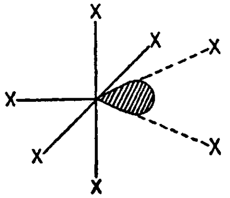

FIG. 4. *An electrostatically favourable arrangement of next-nearest neighbours about a five co-ordinated metal ion.*

In other compounds of Tl^+, Pb^{++}, etc., the distortions accompanying *s–p* mixing may be responsible for the often large dielectric constants. On the other hand, mercuric compounds based on octahedral co-ordination should not show this anomalous behaviour since the distortions characteristic of these ions do not lead to net dipole moments and indeed their polarizabilities are not abnormal. This suggests that among oxides, etc., ferroelectric compounds will be found most often if metal ions are present which are stabilized by antisymmetric distortions.

Relation to Previous Theories of Bond Type.—The account of the stereochemical influence of the inert pair which we have obtained by considering the mixing of *s–p* orbitals is closely related to the conventional electrostatic theory.[13] It amplifies this latter theory by:

(*a*) Giving a very simple explanation of the differences between the deviations from ionic packing found with d^{10} and $d^{10}s^2$ ions.

(*b*) Showing that the unusual stereochemical properties observed in certain discrete molecules and complex ions represent the extreme examples of a much more general phenomenon. The occurrence of minor distortions from cubic symmetry, for example in stannous compounds, and the appearance of a high static dielectric constant, for example in thallium chloride, do not seem to have been recognized as consequences of the " stereochemical properties " of the inert pair.

(*c*) Providing the basis for calculations of the paramagnetic contribution to the susceptibility and the chemical shifts observed in the nuclear magnetic resonance spectra of Tl^+, Pb^{++}, compounds, etc.[14]

It is more difficult to assess the relevance of this approach to the nature of the bonding in crystals containing Pb^{++} ions, etc. Undoubtedly the metal ion in a distorted complex has an electron distribution which is far from spherically symmetrical. The electron

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[11] Megaw, " Ferroelectricity in Crystals," Methuen, London, 1957.

[12] Orgel, *Discuss. Faraday Soc.*, 1958, No. 26, 138.

[13] Wells, " Structural Inorganic Chemistry," 2nd edn., Oxford University Press, 1951.

[14] Orgel, *Mol. Physics*, 1958, **1**, 322.

affinity is consequently much greater in the direction of the shorter bonds than it would be in a symmetrical environment and these bonds are therefore stronger, and in this sense more covalent. However, as in transition-metal chemistry, the stereochemistry is determined in large measure by the electronic structure of the ground and the lowest excited states of the free ion and not by the tendency of the ligands to form covalent bonds. It is for this reason that oxides and fluorides show a greater tendency to distortion (and hence possibly a greater deviation from ionic bonding) than sulphides and other halides.

The electrostatic crystal-field theory and the molecular-orbital theory lead to similar qualitative conclusions in problems of transition-metal stereochemistry.[15,16] An extension of these arguments to the stereochemistry of the inert pair is quite straightforward, and if we had been interested in molecules such as Ph_2TeCl_2 we could have used the molecular-orbital approach instead of an electrostatic theory. For example, in a covalent tetrahedral molecule such as silicon tetrachloride the main bonding is due to the combination of *s* and *p* orbitals on the metal with orbitals on the chlorine atoms. This gives rise to four bonding and four antibonding orbitals, the former of which are filled and the latter empty. In a molecule such as sulphur tetrachloride the two *s* electrons would have to go into a strongly antibonding orbital if the molecule were to remain tetrahedral. However, a distortion from tetrahedral symmetry allows the use of *s*, *p*, and *d* orbitals for bonding and leaves an almost non-bonding *sp* hybrid orbital to accommodate the extra electrons. If the gain in bonding energy compensates for the promotion energy from *s* to *p* and *d* orbitals then the regular tetrahedral molecule must be unstable. This shows very clearly why the extent of distortion depends on the *s*–*p* separation.

Considerations of this sort lead to the same qualitative conclusions about stereochemistry as the electrostatic arguments advanced in greater detail. They are capable of considerable elaboration to take into account π bonding, the use of *d* orbitals in bonding, etc. It follows, therefore, that stereochemistry alone gives little information about the covalent or ionic character of the bonding.

UNIVERSITY CHEMICAL LABORATORY, CAMBRIDGE. [*Received, January* 23*rd*, 1959.]

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[15] Ballhausen and Moffitt, *Ann. Rev. Phys. Chem.*, 1956, **7**, 107.
[16] Griffith and Orgel, *Quart. Rev.*, 1957, **11**, 318.