**Stereochemically Inactive Lone Pairs**

In Chapter 7, titled Structure, a significant section deals with the structures of main group element compounds according to the rules of Valence Shell Electron Pair Repulsion (VSEPR) Theory. For compounds EX*n*Z*m* (where E is the central element surrounded by *n* X groups and *m* lone pairs, Z), the rules of VSEPR operate with very few exceptions for compounds where the total number of electron pairs, *n* + *m*, is less than or equal to six.1 For compounds with seven electron pairs, the situation is less clearly defined principally because a number of polyhedra are possible which have very similar energies, for example a pentagonal bipyramid, a mono-capped octahedron and a mono-capped trigonal prism.

For compounds EX7, such as IF7, [TeF7]– and [IOF6]–, these are observed to be pentagonal bipyramidal whilst those of the type EX5Z2 containing two lone pairs, such as [XeF5]– and [IF5]2–, are pentagonal planar with the two lone pairs occupying mutually *trans* positions in the two axial sites. The predicted or expected structures for compounds of the type EX6Z with six bond pairs and one lone pair are more problematic, however. A pentagonal pyramidal structure in which a lone pair occupies one of the axial sites in a pentagonal bipyramid is only rarely observed, an example being [IOF5]2– as noted on page 123. Instead, structures including regular octahedra and various distorted octahedra are found in which the lone pair is either stereochemically inactive in regular octahedra or active, even if only partially, in distorted octahedra. It is compounds of this type, EX6Z, that are the subject of this addendum which was prompted by a recent (2022) paper on the structures of the anions [BrF6]– and [IF6]–.2 There are no examples of compounds of the type EX4Z3.

Perhaps the archetypal compound of the EX6Z class is XeF6 which is known to have a distorted octahedral structure, specifically a C*3v* distortion, although calculations indicate a regular octahedral geometry of O*h* symmetry is only slightly higher in energy. Although XeF6 is the sole example of a neutral compound of this class, a large number of halo-anions are known many of which are collected in Table 1. The associated counterions include Group 1 and ammonium cations as the most common, but the precise nature of the cation does influence the structure of the anion to some extent as noted below.

**Table 1**. Anionic Compounds of the p-Block Elements of the Type EX6Z.a

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| --- | --- | --- | --- | --- | --- |
| Group 18 | [XeOF5]– |  |  |  |  |
| Group 17 | [ClF6]– | [BrF6]– | [IF6]– |  |  |
| Group 16 | [SeF6]2– | [SeCl6]2– | [SeBr6]2– | [TeCl6]2– | [TeBr6]2– |
| Group 15 | [SbCl6]3– | [SbBr6]3– | [BiBr6]3– | [BiI6]3– |  |
| Group 14 | [SnCl6]4– | [SnBr6]4– | [PbCl6]4– | [PbBr6]4– |  |

a [SbCl6]3– and [TeCl6]2– are mentioned briefly on page 123.

With regard to the details of the work described in ref. 2, the [BrF6]– anion is observed to be slightly distorted from O*h* symmetry in the solid state (with cations K+, Rb+, Cs+) although a regular octahedral structure with O*h* symmetry is computed to be lowest in energy. [ClF6]– is also known to be octahedral, but a distorted structure of C*1* symmetry is computed to be the energy minimum for the anion [IF6]–.

Concerning whether a compound adopts a symmetric or distorted octahedral structure, a general trend is observed in which those compounds with the heaviest E and X, such as [BiI3]3–, are found to exhibit undistorted octahedral structures whereas those with lighter E and X, such as [SbCl6]3–, are more often found to be distorted from idealised octahedral symmetry although as noted above, whether or not the structure is distorted, and by how much, can be dependent on the cation. The question which demands an answer, therefore, is what factors determine whether any particular compound is likely to exhibit a regular octahedral structure or a distorted structure, with a secondary consideration being the nature or symmetry of the distortion itself.

Several explanations have been offered which have been summarized in ref. 2. Thus, Christe has proposed that stereochemical activity of a lone pair will be observed if space exists within the coordination sphere of the central element and that whether or not this space exists can be judged from the known maximum coordination number, for a given attached atom, of the element concerned.3 In the case of bromine, observed coordination numbers, where the bromine is attached to fluorine, do not exceed six such that in [BrF6]–, it is argued that there is simply no room for a stereochemically active lone pair, and a regular octahedral geometry is therefore observed. Iodine, however, can accommodate eight fluorines, as seen in the anion [IF8]–, so that in [IF6]–, there is space for a lone pair and a distorted structure is found. This is fundamentally a steric argument which is also the basis of Gillespie’s reasoning that in a molecule such as [BrF6]–, the fluorines are essentially close-packed which means that they cannot be forced any closer together consequent with a lone pair being stereochemically active. Gillespie’s general point, therefore, is that according to the size of the central element and the atoms to which it is bonded, a stereochemically active lone pair will be expected if the attached atoms are not close-packed but not if they are.3

In contrast, Seppelt has offered an electronic argument and proposed that in [BrF6]–, the 4s electrons are strongly bound (or low in energy) as a result of the preceding 3d row. Thus, the 4s electrons effectively form part of the bromine core such that the bonding to the fluorines in [BrF6]– is exclusively through the three bromine 4p orbitals for which a regular octahedral geometry would be expected.3 In fact, Seppelt goes a little further and argues that the octahedral structure of [BrF6]– cannot primarily be due to steric factors since the Br–F bond distance in [BrF6]– is the same as the Xe–F bond length in XeF6 for which a distorted structure is observed. Furthermore, the presence of a lone pair in a pure bromine 4s orbital is consistent with the longer Br–F bond lengths in [BrF6]– (about 1.86±0.01 Å) compared with the Br–F bond lengths in the cation [BrF6]+ of 1.67 Å which has two fewer electrons. Moreover, the calculated contribution of the bromine 4s orbital to the Br–F bonds is 37% for the cation but only 3% for the anion.2

An electronic argument of a more general nature has also been advanced based on a second order Jahn-Teller distortion which is considered in the main text for trigonal pyramidal species EX3Z on pages 125-128.4 For the EX6Z case, distortions which can lower the energy of the system are allowed which reduce the symmetry from O*h* to C*4v*, C*2v* or C*3v* that are associated with the lengthening of, respectively, one E–X bond, two *cis*-E–X bonds and three *fac*-E–X bonds. Additionally, for the C*2v* distortion there is an increase in the angle between the two lengthened *cis* bonds whilst for the C*3v* distortion, there is an increase in the X–E–X angles between the three lengthened *fac* E–X bonds. In geometrical terms, the C*2v* and C*3v* distortions therefore result in an expansion of one edge and one face of the octahedron respectively. These three distortions are represented diagrammatically in Fig. 1 which also illustrates the localisation of the lone pair in the region of the distortion.



**Fig. 1**. Allowed second order Jahn-Teller distortions for an octahedral compound of O*h* symmetry. (a) A C*4v* distortion which lengthens one E–X bond, (b) a C*2v* distortion which lengthens two *cis* E–X bonds and (c) a C*3v* distortion which lengthens three *fac* E–X bonds. Dotted lines indicate the lengthened bonds and in (b) also highlight the expanded edge and in (c), the expanded face. The site of localisation of the lone pair is shown in each case.

The most commonly observed distortion in the example compounds considered above is a C*3v* type distortion in which the lone pair is becoming localised in one face of the octahedron. Full localisation, however this is defined, would result in a mono-capped octahedral geometry in which the lone pair occupies the capped site, but structures are observed at all stages along this distortion coordinate. Where the distortions are small, this is sometimes described in terms of an incipient lone pair.

In addition to any symmetry requirements necessary for a second order Jahn-Teller distortion to occur, the energies of the relevant orbitals must be sufficiently close and the closer they are, the greater the extent of the expected distortion. In general, the key orbitals in the more symmetric structure are often the HOMO and the LUMO although calculations for a range of EX6Z species indicate that it is the energies of some of the lower energy filled orbitals that are rather more important in these examples.4 Moreover, these calculations confirm that the relevant orbital energies for the EX6Z species generally become closer together for the heavier E and X species and that it is for these examples that the greatest distortions should be expected to occur as is indeed observed.

So far, the examples examined have all been for symmetrical molecular species. Similar distortions have been observed for many less symmetric molecular species, but it is important to also consider the stereochemical activity of lone pairs in related solid-state materials. Fig. 6.8 on page 113, along with the relevant text on that page, highlights the trend in the structures of the Group 15 tri-iodides: AsI3, SbI3 and BiI3. In all cases, the Group 15 element resides in an octahedral site within a close-packed lattice of iodines, symmetrically so in the case of Bi but becoming increasingly asymmetric for Sb and As. This asymmetry or distortion is of C*3v* local symmetry and is therefore closely related to the distortion of the molecular species discussed above. It is interesting to note, however, that in [EX6]3–, for example, a C*3v* distortion opens a face of the octahedron and lengthens the corresponding E–X bonds consistent with localisation of the lone pair at that site but as a result of the constraints of a solid-state EX3 structure, the E–X angles between the lengthened E–X bonds decrease rather than increase.

Another important category of solid-state materials relevant to this topic are the so-called binary IV-VI compounds, AB, where A is a Group 14 element and B is a Group 16 element, some of which are noted in Chapter 8 (IV and VI refer to an older Group numbering scheme but are still often used in this context). Examples include SnS, SnSe, SnTe, PbS, PbSe and PbTe. Of these, all of the Pb compounds and SnTe adopt the NaCl structure in which the Group 14 element, which is formally in oxidation state (II) with a lone pair, resides in a site of regular octahedral symmetry. In contrast, SnS and SnSe have distorted structures with incipient localisation of the Sn lone pair. It is therefore the materials with the lighter elements that are observed to have the distorted structures, in line with the molecular examples outlined above, and these can be understood in terms of a Peierls distortion which is the solid-state analogue of a Jahn-Teller distortion.

A more general analysis of the structures of solid-state materials, including oxides, in which the element cation has an s2 pair of electrons has been provided by Egdell and Watson and co-workers who propose what they refer to as a Revised Lone Pair (RLP) model.5 Specifically, for a range of compounds A*x*B*y* where A is the cation (which has an s2 pair) and B is an anion from Group 16 (more generally, where B is more electronegative than A in compounds which are not ionic), the relative energy of the cation s and anion p orbitals is critical in determining whether the s2 lone pair is stereochemically active or not. Thus, for the oxides of the elements Sn, Pb, Sb, Bi and Po, the *n*s orbitals are close but lower in energy than the O 2p orbitals which allows a stabilisation of the element–O antibonding interaction through mixing with the element *n*p orbitals but, for symmetry reasons, only when a distortion to lower symmetry from a regular octahedral geometry occurs. This is illustrated in Fig. 2 which shows, for PbO, an interaction between the Pb 6s pair and an O 2p orbital and the resulting stabilisation of the antibonding orbital by a Pb 6p orbital which becomes allowed in a lower symmetry geometry. Since the S 3p, Se 4p and Te 5p orbitals are higher in energy than O 2p (Fig. 2), any such stabilisation is reduced, and distorted structures become less likely. As a result, in the structures of SnO, PbO, Sb2O3, Bi2O3 and PoO2 the cation geometry is distorted from regular octahedral such that the s2 pair becomes stereochemically active but whilst Bi2S3 also exhibits a stereochemically active Bi(III) lone pair, Bi2Se3 and Bi2Te3 do not. For the antimony compounds in which Sb 5s is higher in energy than the Bi 6s, for Sb2X3 (X = O, S, Se, Te), only Sb2Te3 is undistorted. Similarly, as noted in the previous paragraph, SnS and SnSe are distorted whilst SnTe is not consistent with Sn 5s being higher in energy than Pb 6s.6 Thus, for these solid-state materials, the relationship between whether a structure is distorted or not as a function of relative orbital energies is the same as that observed for the molecular species discussed earlier. Finally, as the authors of ref. 5, make clear, this topic is of more than academic interest since many of these solid-state compounds have useful properties, the precise nature of which is critically dependent on the structure and the extent of any distortion.



**Fig. 2**. An orbital interaction diagram showing, for PbO, the interaction between Pb 6s and O 2p orbitals. The stabilisation of the antibonding orbital allowed by mixing with Pb 6p when the symmetry is reduced from regular octahedral is shown in blue. Higher energy S 3p, Se 4p and Te 5p orbitals are shown on the right. This diagram is adapted from ref. 5.

Finally, although stereochemically inactive lone pairs are most commonly encountered for six-coordination, a stereochemically inactive lone pair is present in [XeF8]2– which has a regular square antiprismatic structure, perhaps not unexpectedly for eight coordination. Also, the anion [Bi{Co(CO)4}4]– adopts a regular tetrahedral rather than a disphenoidal structure, this being the only example of an EX4Z compound with a stereochemically inactive lone pair presumably due to the large Co(CO)4 groups.

***References***

1. The focus will be on compounds in which the X groups are singly bonded to the E centre. For those examples which contain an oxygen atom bonded to E, it is therefore easiest in the present context to consider the bonding as E+–O– (as outlined in the marginal note on page 121) rather than as E=O.

2. *Bromine Pentafluoride BrF5, the Formation of [BrF6]– Salts, and the Stereochemical (In)activity of the Bromine Lone Pair*. M. Möbs, T. Graubner, K. Eklund, A. J. Karttunen and F. Kraus, *Chem. Eur. J*., 2022, e202202466 (1-15).

3. References to the relevant work of Christe, Gillespie and Seppelt can be found in ref. 2.

4. For details of the second order Jahn-Teller distortion proposed for these EX6Z species, see *Stereochemically Active or Inactive Lone Pair Electrons in Some Six-Coordinate, Group 15 Halides*. R. A. Wheeler and P. N. V. Pavan Kumar, *J. Am. Chem. Soc*., 1992, **114**, 4776-4784.

5. *Stereochemistry of Post-Transition Metal Oxides: Revision of the Classical Lone Pair Model*. A. Walsh, D. J. Payne, R. G. Egdell and G. W. Watson, *Chem. Soc. Rev*., 2011, **40**, 4455-4463.

6. The lower energy of the 6s orbital compared with the 5s orbital for the 6p and 5p elements considered here is a direct consequence of relativistic effects described on pages 36-38.