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Simple Calculations of Bond Lengths and Bond Angles in Certain Oxides, Fluorides or Oxide Fluorides of Sb^{3+}, Te^{4+} and Pb^{2+}

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There are a fair number of cases in compounds with AX_4E polyhedra known, where E stands for one unshared electron pair on atom A. The structure of such a polyhedron has often been described as a trigonal bipyramid with sp^3d orbitals, with the unshared pair occupying one of the equatorial orbitals. The ideal angles, axial X–A–X and equatorial X–A–X would then be 180 and 120°, respectively. Large deviations from these values occur, and Gillespie and Nyholm have suggested that this is due to lone pair–bonding pair repulsion (*1*).

The stereochemistry of five configurations has been discussed by Gillespie (*2*) and the distortions such as they are found among the structures of molecules. Cation–anion distances are shortest in the equatorial plane, due to competition between the forces that operate to level out these distances and anion repulsion forces, and it was convenient to define two different radii for the central atom, one equatorial and one axial, so that $r_{ax}/r_{eq} = 1.1$–1.2 (*2*).

For certain solid oxides or oxide fluorides of Sb^{3+}, Pb^{2+} and Bi^{3+}, it was shown that the volume of the lone pair and its cation is of the same size as that of an anion (*3*). Also, the center of the volume of the lone pair could be localized to a position, which is normally occupied by an anion or a large cation. The distance between the center of the volume of the lone pair and its cation was found to be approximately 1 Å (*3*).

The trigonal bipyramid polyhedron is easily recognized in hexagonally closest packing (*hcp*) as being two tetrahedra sharing faces. In such a trigonal bipyramid with all edges of the same length, the equatorial center–corner distances are naturally smaller than the corresponding axial distances. When this five configuration occurs in transition metal chemistry, the trigonal bipyramid polyhedron is also considerably distorted. However, when one of the equatorial corners of the trigonal bipyramid is occupied by a lone pair, the cation is off-center so that the lone–pair cation distance is only about 1 Å. This off-centering means of course that such a trigonal bipyramid can be very close to the ideal one occurring in *hcp*. Using simple packing considerations it is then easy to calculate the cation–anion distances, the anion–anion distances and the equatorial and axial angles within such a AX_4E polyhedron. Instead of assuming two different radii for the same cation we distort the trigonal bipyramid with two different anion–anion (or lone pair) distances a_1 and a_2, which are simply related to the radius r of the anion, and a constant K:

$$\frac{a_1}{2K} = r, \quad \text{and} \quad \frac{a_2 \cdot K}{2} = r;$$

From a number of structures we find K to be 1.025 and we assume that the atomic radii r for high coordination numbers for O^{2-} and F^- are 1.42 and 1.33 Å (*4*). The a_1:*s* are the anion–anion (lone pair) distances in the equatorial plane and the a_2:*s* are all other anion–anion (lone pair) distances in the polyhedron.

Cation radii are derived from structures with cations in three configurations with a stereochemically active lone pair completing a nearly ideal tetrahedron. Such structures are SbF_3 (*5*), orthorhombic Sb_2O_3 (*6*), α-$TeVO_4$ (*7*) and Pb_3O_4 (*8*). These radii are defined by the geometry given in Fig. 1 and are thus identical with the radii observed for Sb^{5+}, Te^{6+} and Pb^{4+}.

In Table I we summarize the constants used in the calculations.

A close-packed arrangement of two anions, *A* and *B*, and one lone pair *C*, is drawn in Fig. 1 and the triangle *ABC* is then the equatorial plane of a trigonal bipyramid. *E* is the center of two other anions, situated in a *hcp* arrangement (the layers *aba*) above and below the equatorial plane, and completing the trigonal bipyramid polyhedron. It then follows that

$$a_1 = AB = AC = BC,$$
$$a_2 = AE = EC = EB,$$

D is the center of the cation and

$$d_1 = AD = BD \text{ (equatorial distance)}$$

and

$$d_2 = DE \text{ (axial distance).}$$

Half the equatorial anion–cation–anion angle $\beta/2$ is indicated in Fig. 1, and the corresponding axial angle $\alpha/2$ is shown in Fig. 2, which is a clinographic projection of the trigonal bipyramid polyhedron.

It is easy to show that $\tan(\alpha/2)$ is a function of d_1, a_1 and a_2, d_2 is a function of a_1, d_1 and a_2, and $\sin(\beta/2)$ is simply $a_1/2d_1$.

TABLE I

K	1.025
$r(F^-)$	1.33 Å
$r(O^{2-})$	1.42 Å
$r(Sb^{3+})$	0.58 Å
$r(Te^{4+})$	0.49 Å
$r(Pb^{2+})$	0.78 Å

a_1, a_2 and d_1 are obtained from Table I, and in Table II we have calculated a_1, a_2, d_1, d_2, α and β for a number of structures. The agreement between observed and calculated values is surprisingly good, showing that the stereochemistry of this configuration is more a result of simple packing than anything else.

The agreement is best in the structures with AX_4E polyhedra joined or partly joined to other polyhedra with corner-sharing, as for example in KSb_2F_7, $CsSb_2F_7$, TeO_2, $TiTe_3O_8$ and $SbPO_4 \cdot 2H_2O$. In β-Sb_2O_4 of the $BiSbO_4$structure type (*9*), and $SbNbO_4$, edge-sharing occurs, which naturally distorts the polyhedra in well-known ways. In L-SbOF and M-SbOF oxygens and fluorines are ordered so that in the configuration of four anions of Sb^{3+}, there is always only one which is fluorine. Furthermore, in M-SbOF there are two independent Sb^{3+} and the values given in Table II are averages. Angles

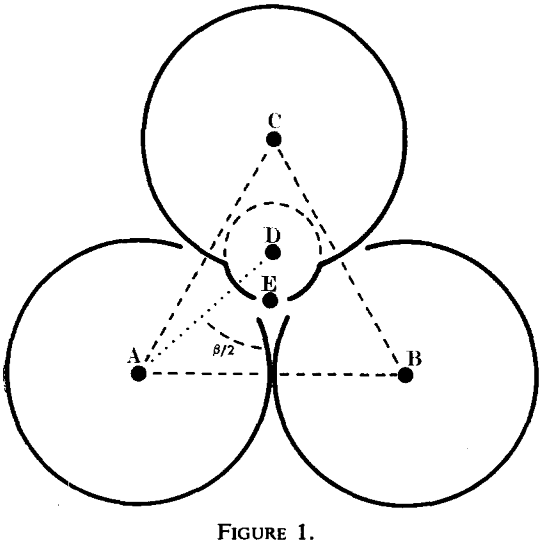

FIGURE 1.

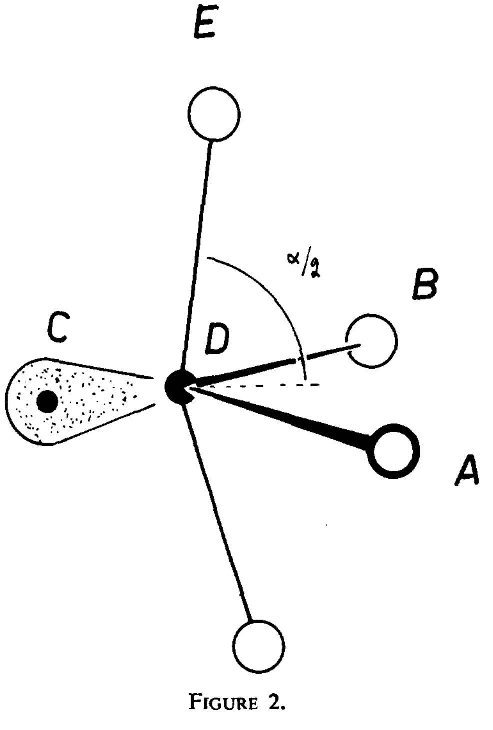

FIGURE 2.

TABLE II

	Pb^{2+}		Sb^{3+}						
	Calc oxides	Obs PbO(orth) (13)	Calc oxides	$SbNbO_4$ (14)	Obs β-Sb_2O_4 (15)	$SbPO_4 \cdot 2H_2O$ (16)	$SbPO_4$ (17)	Calc fluorides	Obs KSb_2F_7 (18)
a_1	2.91	3.15	2.91	—	—	2.89	—	2.73	2.73
a_2	2.77	3.00	2.77	—	—	2.75	—	2.63	2.60
d_1	2.20	2.22	2.00	2.02	2.02	1.97	2.01	1.91	1.92
d_2	2.34	2.49	2.27	2.23	2.22	2.22	2.18	2.14	2.07
α	140.0	147.5	153.4	150.7	148.1	156.0	164.8	150.2	155.2
β	82.6	90.4	93.6	92.1	87.9	94.4	87.9	91.3	90.4

	Sb^{3+} (cont.)			Te^{4+}						
							Obs $Zn_2Te_3O_8$ (22)			
	$CsSb_2F_7$ (19)	Obs L-SbOF (10)	M-SbOF (11)	Calc oxides	TeO_2 (20)	TeO_2 (21)	Te_1	Te_2	$TiTe_3O_8$ (23)	UTe_3O_9 (24)
a_1	—	2.93	2.91	2.91	2.90	2.96	2.92	2.88	2.88	2.82
a_2	—	2.63	2.67	2.77	2.70	2.74	2.75	2.73	2.65	2.68
d_1	1.94	1.97	2.00	1.91	1.92	1.90	1.83	1.91	1.85	1.90
d_2	2.11	2.16	2.19	2.22	2.09	2.08	2.10	2.20	2.12	2.16
α	151.6	142.9	145.0	159.8	163.9	168.5	174.7	156.1	158.6	156.6
β	90.5	95.9	93.7	99.4	98.3	102.1	106.2	98.2	102.2	95.8

have not been calculated for these two structures with mixed anions in the configuration shells of the cations, as a rather complex edge-sharing distorts the polyhedra as well, but there is good general agreement with oxides or fluorides of Sb^{3+}. These two structures will be discussed elsewhere (*10, 11*).

The distances between the lone pair center and the cation center in the various structures with this particular polyhedron have been calculated to be 1.00 Å for Pb^{2+}, 1.03 Å for Sb^{3+} in KSb_2F_7, 1.17 Å for Sb^{3+} in the oxides and 1.32 for Te^{4+}. This seems to indicate that for divalent cations with a lone pair, this pair would have less stereochemical activity and indeed, the two forms of PbF_2 are reported to have the CaF_2 and the $PbCl_2$ structures, and also, SnO has been reported to transform to the wurtzite structure type at elevated pressure (*12*).

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