JOURNAL OF SOLID STATE CHEMISTRY **11**, 214–233 (1974)

Bond Valence as an Aid to Understanding the Stereochemistry of O and F Complexes of Sn(II), Sb(III), Te(IV), I(V) and Xe(VI)

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Received October 2, 1973

The calculation of bond valences (S) from the bond lengths (R) observed in 63 different crystals using the relation $s = s_0(R/R_0)^{-N}$ allows a direct quantitative comparison of the bonding in a variety of different complexes formed between A and X atoms where A = Sn(II), Sb(III), Te(IV), I(V) and Xe(VI) and X = 0 and F. The environment of A is usually an octahedron which has been distorted so that the weak bonds occur opposite strong bonds and bonds of intermediate strength occur opposite each other. The possible environments form a continuous series from one having 2 strong, 2 intermediate, and 2 weak bonds ($\mathscr{A}$) through one having 3 strong and 3 weak bonds ($\mathscr{C}$) to one having 1 strong, 1 weak and 4 intermediate bonds ($\mathscr{E}$). The particular environment observed is related to the ratio of the valences of A and X, a ratio of 2 leading to a configuration close to $\mathscr{A}$, 3 close to $\mathscr{C}$ and 5 close to $\mathscr{E}$. Specific bond valences can be associated with strong, intermediate and weak bonds for each pairs of atoms A–X and the angles between any 2 strong bonds is equal to $(73 + 17 < s >)$ degrees where $< s >$ is their average bond valence. These principles lead to a natural explanation of the O and F bridges frequently found in these complexes and the influences such bridges have on the detailed environment of A.

Introduction

The atoms Sn(II), Sb(III), Te(IV), I(V) and Xe(VI) characteristically show very irregular coordination in their crystalline complexes. This behaviour has been rationalised by Gillespie and Nyholm, (*1*) who suggest that the lone pair of electrons in the valence shell occupy one of the positions normally occupied by a ligand. Thus, for example, XeF_5^+ has fluorine atoms arranged at 5 of the corners of an octahedron and IO_3^- has the oxygen atoms arranged at 3 of the corners of a tetrahedron. However, this approach has little to say about the 3 or 4 additional weak bonds which are almost invariably found occupying the vacant position in the coordination sphere. The coordination of I in IO_3^- can, for example, be just as easily considered as octahedral with the I atom displaced off center along the threefold axis. For example, both NH_4IO_3 (*2*) and $RbIO_3$ (*3*) have a distorted perovskite structure with I in pseudooctahedral interstices.

The correct treatment of the long bonds has presented some difficulty in the discussion of these compounds. Alcock (*4*) refers to them as secondary interactions but sometimes they are described as nonbonding distances (*5, 6*). In this paper it is shown that the bond strength or bond valence approach provides a quantitative method of treating these long bonds and of understanding the stereochemistry of these atoms.

Bond Valence Theory

The valence of an atom is sometimes defined as the number of bonds formed by that atom, but this is also the definition of the coordination number. The ambiguity lies in the ambivalent use of the word "bond." In bond valence theory we define a bond as an attractive (i.e., bonding) interaction between 2 atoms. Such a bond may be relatively strong (e.g., the C–C bond in acetylene) or relatively weak (e.g., the Na–Cl bond, 6 of which surround each atom in NaCl). The total number of these bonds formed by an atom is defined as the coordination number. The valence is taken to be the formal oxidation state or ionic charge of an atom and can be regarded as its potential for bonding. Where an atom forms many bonds, this potential must be shared between them. We can define, following Pauling (*7*), the average bond strength, or average bond valence, as being equal to the atom valence divided by the coordination number. Where the bonds are all equivalent (e.g., in NaCl) the individual bond valences will be equal to the average. In other cases, the valence may be unequally shared between the various bonds and in such cases the individual bond valence is the amount of an atom's potential for bonding that is associated with a particular bond. A number of workers (e.g., *8–10*) have shown that the length of a bond is inversely related to its bond valence and Brown and Shannon (*10*)[1] have used the principle that "the sum of the bond valences around each atom must be equal to the atom valence", to determine empirical bond valence (S)-bond length (R) curves for bonds between O and the atoms in the first 3 rows of the periodic table. Calculating bond valences from the observed bond lengths with the relation

$$S = S_0(R/R_0)^{-N} \qquad (1)$$

where S_0, R_0 and N are constants for a given pair of ions, they found that the sums of the bond valences came within 4% of the atomic valence in the large number of crystal structures they examined. Thus using bond lengths determined by X-ray or neutron diffraction, one can examine quantitatively the way in which the valence of the atom is distributed between the bonds it forms. A prior knowledge of the ionic or covalent character of a bond is not necessary to calculate the bond valence; indeed, Brown and Shannon (*10*) suggest that this character can be determined from the bond valence itself: the larger the bond valence, the larger the covalent character.[2]

The underlying principle of bond valence theory, (i.e., that the valence of an atom is distributed among the bonds it forms) is essentially the same as Pauling's electrostatic valence rule (*7*) derived from an ionic model, but the value of the bond valence is very close to the bond order derived from covalent bonding theories. In either case, one valence unit corresponds to the bonding power of two electrons; in the ionic extreme these are both found on the anion, in the covalent extreme they are arranged symmetrically in the bond.

TABLE I

Parameters for Bond Valence–Bond Length Curves

	Bonds to O			Bonds to F		
	S_o	R_o	N	S_o	R_o	N
Sn(II)	0.5	2.17	4.5	0.4	2.26	3.5
Sb(III)	1.0	1.91	4.5	0.5	2.137	3.7
Te(IV)	1.333	1.813	4.5	1.0	1.779	3.5
I(V)	1.0	1.967	4.5	1.0	1.81	3.5
Xe(VI)	1.0	1.971	4.5	1.0	1.838	3.33

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[1] Brown and Shannon use the term bond strength rather than bond valence. The latter term (cf. Donaay and Allmann (*9*)) is used here to avoid confusion with the thermodynamic term bond strength.

[2] For convenience, the ionic nomenclature (e.g., anion, cation) will often be used in discussing weak bonds ($S \lesssim 0.4$ v.u.). The term "ionic charge" is synonymous with "atomic valence."

The bond valence approach is complementary to the valence bond, molecular orbital and valence shell electron pair theories and provides a quantitative method for comparing the strength of ionic and covalent bonds. It is particularly suitable for studying compounds with very distorted atomic environments such as are found around atoms of the lower valence states of Sn, Sb, Te, I and Xe.

Procedure

Values of the constants S_0, R_0 and N in Eq. (1) were chosen, using the procedure of Brown and Shannon (*10*), for each of the atom pairs A–X (A = Sn(II), Sb(III), Te(IV), I(V), and Xe(VI); X = O(II) and F(I)), so that the bond valence sums around each atom were as close as possible to the atom valence in the 63 structures listed in the appendix. The values obtained are given in Table I and the curves for Sn–F, Xe–F, Sn–O and Xe–O are illustrated in Fig. 1. The agreement between the bond valence sums and the atom valences is within 0.06 v.u. or experimental error, whichever is the greater. In practice the summation is usually restricted to bonds with $S \gtrsim 0.08$ v.u. (equivalent to about 3.1 Å in the present case). This is the point at which cation–cation distances begin appearing in the coordination sphere. Longer bonds normally make only a small contribution to the bond valence sums and they can generally be ignored.

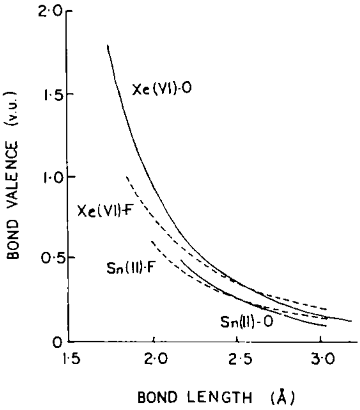

FIG. 1. Bond valence vs bond length. Curves for Sb(III), Te(IV) and I(V) lie between the Sn(II) and Xe(VI) extremes.

Discussion

In order to allow a thorough study in the time available, the following discussion is restricted to complexes formed between the isoelectronic series Sn(II), Sb(III), Te(IV), I(V) and Xe(VI) (=A) and O(II) and F(I) (=X) although some of the comments made may have application to other valence states of these atoms or to other atoms. However, the lowest valence states of these atoms show different configurations from those discussed here and the atoms of the next row (e.g., Pb(II)) are much larger, allowing coordination numbers greater than 6. It follows that most of the ideas developed here are applicable only to the complexes listed in the title.

The irregularity of the coordination around atoms with stereoactive lone pairs has been treated by Gillespie (*11*). He identifies a number of ideal geometries in which one of the bonding positions of an otherwise regular polyhedron is occupied by the lone pair, thus preventing bonding in this direction and, incidentally, forcing the other bonds closer together. Many of the oxy- and fluoro complexes discussed here show one of these geometries (Fig. 2): 5 coordination based on an octahedron (AX_5E, called configuration ℰ here), 3 coordination based on a tetrahedron (AX_3E, configuration 𝒞), and 4 coordination based on a trigonal bipyramid (AX_4E, configruation 𝒜). In almost all cases there are also a number (2–4) of longer bonds arranged around the lone pair direction and it is the treatment of these bonds that has given rise

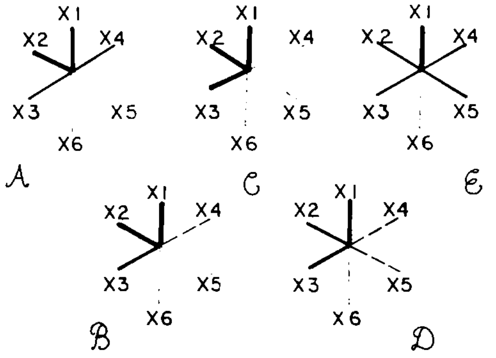

FIG. 2. Arrangements of X(=O.F) found around Sn(II), Sb(III), Te(IV), I(V) and Xe(VI).

to difficulties. Although Gillespie and Nyholm's approach is widely used in discussing the stereochemistry of these atoms, it implies the occurrence of several coordination numbers (4, 5 and 6 counting the lone pair). However, the ratios of the ionic radii (*12*, *13*) of the central (A) atom to the ligand (X) for all these atoms lie between 0.5 and 0.7 indicating that they should all be 6 coordinate. In this paper the environment of the central atom is assumed to be an octahedron[3] which has been distorted by a lengthening of some of the bonds on one side.

In none of the complexes discussed here is a regular octahedron found (although it does occur in $TeCl_6^{2-}$ (*15*) and $TeBr_6^{2-}$ (*15A*)). The distortion takes the form of the lengthening of one or more of the A–X bonds (Fig. 2). At the same time, it is observed in all these complexes that the bond *trans* to the one that is lengthened is shortened so that the sums of the valences of each *trans* pair are approximately equal.[4] The $\mathscr{E}$ configuration (Fig. 2e) is achieved by the lengthening of one bond (A–X6) and the strengthening of the bond (A–X1) *trans* to it. For reasons discussed below the trans bond in this case is normally only slightly strengthened and the weak bond is replaced by 3 or 4 weak bonds, but the 5 stronger bonds remain close to the octahedral configuration. Weakening a second bond (A–X5, necessarily *cis* to the first weak bond) leads to 2 strong *cis* bonds (*trans* to the weak bonds) and 2 bonds of intermediate strength (*trans* to each other) (Fig. 2a). This is the arrangement referred to by Gillespie (*11*) as AX_4E and denoted as $\mathscr{A}$ here. When a third bond (A–X4, 1 of the 2 intermediate bonds of the $\mathscr{A}$ configuration) is weakened an arrangement of 3 mutually *cis* strong bonds and 3 weak bonds results. This is Gillespie's AX_3E configuration ($\mathscr{C}$) (Fig. 2c). Weakening 1 of the remaining 3 strong bonds to produce an AX_2E arrangement necessarily results in the strengthening of the weak bond *trans* to it so that the resulting configuration is the same as $\mathscr{A}$ (Fig. 2a). In fact the $\mathscr{A}$ configuration with its 2 strong, 2 intermediate and 2 weak bonds corresponds to 2, rather than 4, coordination, as will be shown below.

Between these 3 ideal geometries ($\mathscr{A}$, $\mathscr{C}$, and $\mathscr{E}$) there are transitional geometries: the partial lengthening of one of the intermediate bonds in $\mathscr{A}$ leads to an arrangement ($\mathscr{B}$) transitional between $\mathscr{A}$ and $\mathscr{C}$, and the partial strengthening of 2 of the weak bonds in $\mathscr{C}$ leads to an arrangement ($\mathscr{D}$) transitional between $\mathscr{C}$ and $\mathscr{E}$. Since the transitional arrangements can cover the whole range between the limiting ideal geometries, as has been pointed out by Zemann (*16*) and Pertlik and Zemann (*16A*), the set of configurations $\mathscr{A} \leftrightarrow \mathscr{B} \leftrightarrow \mathscr{C} \leftrightarrow \mathscr{D} \leftrightarrow \mathscr{E}$ form a continuous series. It is significant that no examples of a transitional state between $\mathscr{A}$ (2 coordination) and $\mathscr{E}$ (5 coordination) have been found.[5]

Factors Affecting the Geometry Around A

The formation of 2, 3 or 4 strong bonds by the central atom is determined by its valence relative to the valence of its ligands. The contributions of N strong bonds of bond valence S_s to the valence of the central atom is NS_s but each ligand only receives a contribution of S_s from this source. Since NS_s will be only slightly less than V_A (the valence of A), and S_s will normally be only slightly less than V_X (the valence of X), we may assume that

$$N = NS_s/S_s \sim V_A/V_X \tag{2}$$

providing that the S_S represents the major contribution to the valence of X.[6] Thus we find the 5 coordinate arrangement ($\mathscr{E}$, Fig. 2) with the fluorides of Sb, Te, I and Xe ($V_A/V_X = 3$, 4, 5 and 6, respectively); the 3 co-

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[3] $(NO)_2XeF_8$ (*14*) has a coordination based on a square antiprism and will not be discussed further here.

[4] The tendency for weak bonds to appear opposite strong bonds has been noted by Alcock (*4*) in his comprehensive survey of compounds with stereoactive lone pairs.

[5] It is possible that Te in UTe_3O_9 (*17*) might have this configuration, but the poor agreement between the atomic valence and the bond valence sums suggests that bond distances are not reliable.

[6] This result may seem trivial if the valence is assumed to be the number of bonds formed by an atom. It is not trivial in terms of the definition of valence used here. Equation (3) applies only to the complexes discussed here; it does not apply, for example, to NaCl or S_3O_9.

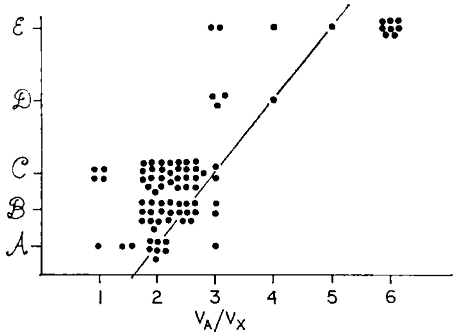

FIG. 3. Configurations observed in the compounds listed in the appendix plotted as a function of V_A/V_X.

ordinate arrangement (𝒞) with the fluorides of Sn and Sb ($V_A/V_X = 2$, $2\frac{1}{2}$, 3, respectively), and the 2 coordinate arrangement (𝒜) with the fluorides of Sn and Sb ($V_A/V_X = 2$ and 3, respectively) and the oxides of Sn, Sb and Te ($V_A/V_X = 1$, $1\frac{1}{2}$ and 2, respectively). In these cases it is convenient to treat the compounds as containing the discrete groups AX_5, AX_3 or AX_2 weakly linked to the rest of the structure.

The transitional geometry 𝒟 linking the 3 and 5 coordinate geometries corresponds to 4 coordination and is found in fluorides of Sb and Te ($V_A/V_X = 3$ and 4, respectively), but since this arrangement does not contain four well defined strong bonds, there are no clearly identifiable SbF_4^- and TeF_4 units so that 4 coordination is anomolous. The particular structures adopted by TeF_4 and SbF_4^- are discussed in more detail below. Fig. 3 shows the distribution of observed configurations as a function of V_A/V_X.

Observed Bond Valences

The observed values of the bond lengths in 63 compounds have been used with Eq. (1) to calculate bond valences and these, together with the observed bond angles, are listed in the appendix. From these values it is possible to derive a series of typical structures, one for each configuration and each pair of atoms. These are shown in Figs. 4–6. In most cases the deviations between the actual structures and the typical structures are within experimental error[7] (see appendix) although the transitional structures (ℬ and 𝒟) can cover the whole range between the 2 extremes. It is useful for the purposes of the following discussion to classify the bonds into 3 categories, strong, intermediate, and weak defined such that weak bonds occur *trans* to strong bonds and intermediate bonds occur *trans* to intermediate bonds. The actual

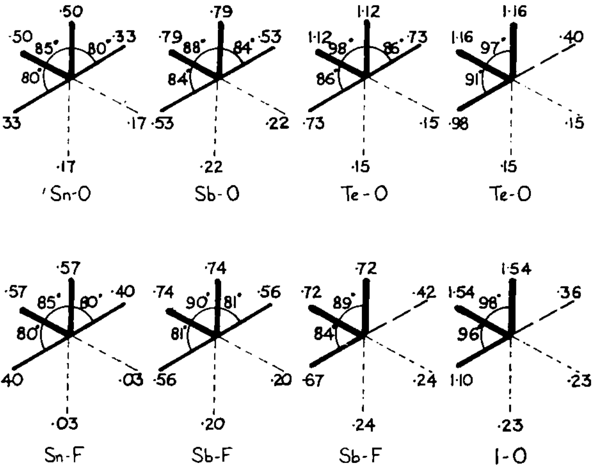

FIG. 4. Typical bond valences and angles found for 𝒜 and ℬ configurations.

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[7] The experimental errors in the determination of individual bond valences are of the order of 6% and result from the difficulty of making accurate measurements of the A–X bond lengths using X-ray diffraction when A and X have very different atomic numbers.

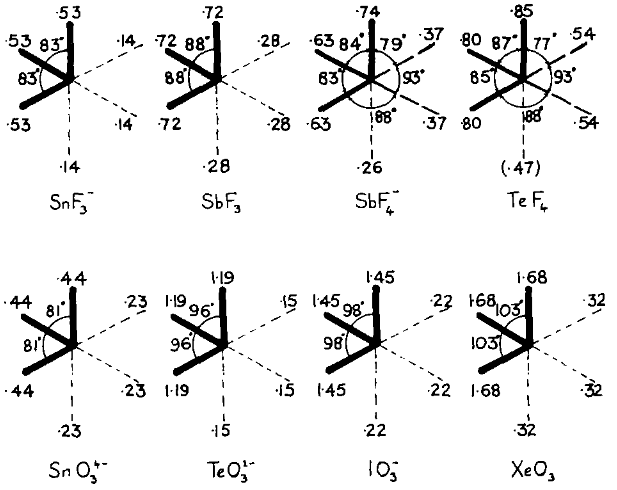

FIG. 5. Typical bond valences and angles found for $\mathscr{C}$ and $\mathscr{D}$ configurations.

valence of the strong and intermediate bonds will depend on the 2 atoms forming the bond and, in those compounds showing transitional geometries, the classification will not always be unambiguous. Typical bond valences for each class of bond are given in Table II.

Since in the $\mathscr{C}$ configuration (Fig. 2c) there are only strong and weak bonds present and since the weak bonds in most cases are about 0.2 v.u., the valence (S_s) of the strong bonds should be given by the equation

$$V_A = 3\ (S_s + 0.2)\ \text{v.u.} \qquad (3)$$

where, as before, V_A is the valence of A. By a similar argument the valence (S_I) of the intermediate bonds should be given by

$$V_A = 6S_I. \qquad (5)$$

These relationships hold well for the oxides

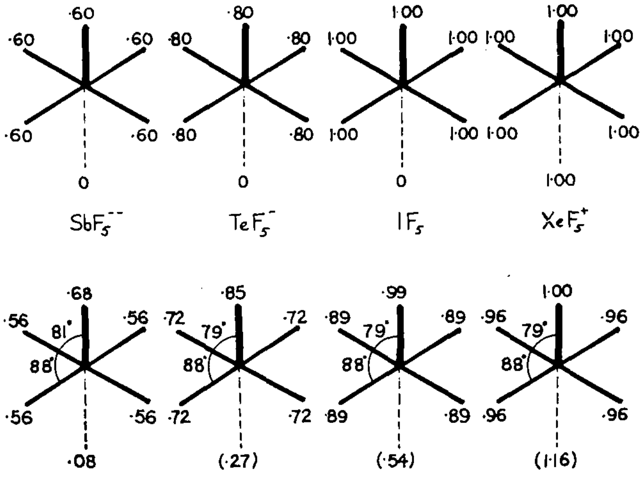

FIG. 6. Bond valences and angles found for $\mathscr{E}$ configuration. Top line: Ideal structure obtained by dividing the valence of A equally between 5 bonds. Bottom line: typical observed structures. Valences in parentheses are divided between several weak bonds.

TABLE II

VALENCES OF STRONG, INTERMEDIATE, AND WEAK BONDS

	Strong		Intermediate		Weak	
	Valence (v.u.)	Distance (Å)	Valence (v.u.)	Distance (Å)	Valence (v.u.)	Distance (Å)
Sn–F	0.55	2.06	0.40	2.20	0.1	3.36
Sb–F	0.72	1.94	0.56	2.07	0.2	2.74
Te–F	0.85	1.86	0.72	1.95	0.2	2.82
I–F	1.00	1.81	0.89	1.87	0.2	2.87
Xe–F	1.00	1.84	0.96	1.86	0.3–0.5	2.64–2.26
Sn–O	0.45	2.22	0.30	2.43	0.2	2.66
Sb–O	0.79	2.02	0.53	2.21	0.2	2.75
Te–O	1.15	1.87	0.73	2.07	0.2	2.76
I–O	1.50	1.80	(0.8)	2.07	0.2	2.81
Xe–O	1.68	1.76	(1.0)	1.97	0.2	2.82

but not for the fluorides since no bond to F can be more than 1.0 v.u. Consequently, when V_A is large, the strong and intermediate A–F bonds have similar strengths and as a result the weak fluorine bonds have to become stronger and more numerous in order to satisfy the total valence of the central atom. This explains why several weak bonds are found in fluorides with configuration $\mathscr{E}$ (TeF_5^-, IF_5 and XeF_5^+) and why there is so little difference in strength between the strong apical and intermediate strength equatorial bonds. It is noteworthy that in IOF_4^- (*18*) the apical I–O bond has a strength of 1.83 v.u. while the equatorial I–F bonds have a strength of only 0.75 v.u.

Angles

Although the environment of the central A atoms is roughly an octahedron, the angles deviate significantly from 90°. As has been observed in other strongly (i.e., covalently) bonded complexes, the stronger the bonds the larger are the angles between them (*19–21*). The origin of this effect is not clear but may well be related to ligand–ligand repulsion when the ligands are tightly bound (see for example Andersson *et al.* (*22*)). The present series of complexes shows a good correlation between bond angle (θ) and average valence ($<s>$) of the 2 defining bonds when these bonds are strong or intermediate in character. Figure 7 shows the correlation between θ and $<s>$ for the typical structures (Figs. 4–6), together with the line representing the equation

$$\theta = 73 + 17 <s> \text{ deg.} \qquad (5)$$

The only notable deviations from Eq.(5) are the F (apical)–A–F(equatorial) angles of the

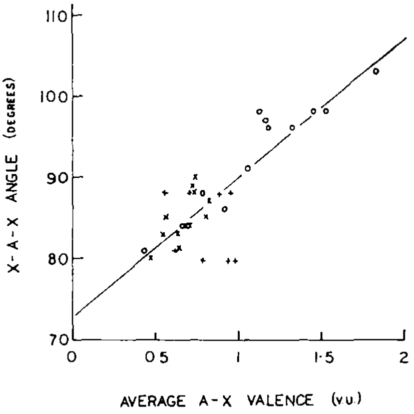

FIG. 7. Bond angle vs average valence of the 2 defining bonds. ○ = oxygen complexes, + = fluorine complexes with $\mathscr{E}$ configuration, × = other fluorine complexes.

$\mathscr{E}$ configuration. The low values (79°) found for these angles can be attributed to the presence of 3 or 4 rather than 1 weak bond, causing a crowding in the axial direction.

AX_5 Ions ($\mathscr{E}$ Configuration)[8]

There are 4 different ions or molecules which possess the $\mathscr{E}$ configuration. XeF_5^+ is represented by 8 examples, IF_5 and TeF_5^- by 1 each and SbF_5^{2-} by 2 examples. All of these groups have a square pyramidal arrangement of F atoms with F(apical)–A–F (equatorial) angles of 79° and F(equatorial)–A–F (equatorial) angles of 88° so that A is slightly below the base of the pyramid. Each group contains 5 almost equally strong bonds (since the strong and intermediate bonds have similar strengths) and a number of weak bonds (all to F atoms in the examples considered) in the vacant position of the octahedron.

The extent to which the strength of an A–F bond falls below 1.0 v.u. is the extent to which the F atom must form bonds to other atoms in the structure, since the total bond valence around each F atoms must be 1.0. The group thus bonds to other atoms in the crystal either through its F atoms or through its central atom. Two extreme ideal bond valence structures can thus be written and these are exemplified by XeF_5^+ and SbF_5^{2-} (Fig. 6, top line). The XeF_5^+ ion is expected to have 5 fully saturated Xe–F bonds[9] and to form additional Xe-anion bonds totalling 1 v.u. corresponding to the ionic charge of +1. On the other hand, the Sb–F bonds are unsaturated and the ionic charge of −2 is manifest in the bonds formed from the F atoms to the cations in the crystal. In these 2 cases the observed structures (Fig. 6, bottom line) are very close to the ideal ones, the XeF_5^+ ion exhibiting an external valence of about 1 and SbF_5^{2-} exhibiting an external valence of close to 2 as expected from the formal ionic description.

TABLE III

Effective Valences of $AX_5^{-V_f}$ Ions

	Formal valence (V_f)	Effective valence (V_{eff})
XeF_5^+	1	1.32
IF_5	0	0.99
TeF_5^-	1	1.54
SbF_5^{2-}	2	2.16

On the other hand, IF_5 and TeF_5^- show a larger external valence than is suggested by the ionic description. Both these groups form weak bonds from the central atom to other F atoms as well as bonds from F to other cations in the structure. As a result the A–F bonds are weaker than expected and the external F cation bonds stronger. By summing the total strength of the external bonds formed in these two cases it is seen that TeF_5^- has an effective valence of 1.54 v.u. (cf. ideal valence = 1.0 v.u.) and IF_5 has an effective valence of 0.99 v.u. (cf. ideal valence = 0). Thus we observe a tendency for the effective valency of the asymmetric AX_5 groups to be greater than the formal valence when the formal valence is small[10] (see Table III). It is interesting to compare this result with the traditional views of the association of IF_5 molecules into a solid below 9°C. In one view, the F atoms are regarded as electron donors and the I atoms as electron acceptors so that intermolecular electron donor–acceptor bonds can be formed. An alternative view is that the bonding results from the permanent dipole moment of the lopsided molecule. This causes an electrostatic attraction between the negatively charged F atoms on one molecule and the positively charged I atoms on the next. This weak associative bonding can be described as ionic where each molecule functions as both the anion and cation e.g., ${}^{1/2+}IF^{1/2-}$. The bond valence theory is complementary to these views allowing the strength of the weak intermolecular interaction to be quantified and compared directly with the bonding within

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[8] The discussion in the next few sections is limited to groups where the ligands are either all F or all O. Examples with mixed O and F ligands are discussed at the end of the paper.

[9] The "ideal" structures proposed here are obtained by dividing the valence of the central atom equally between the 5 strong and intermediate bonds.

[10] A similar argument can be applied to the asymmetric H_2O molecule. Its effective valence is 0.80 v.u. even though its ideal valence is zero.

TABLE IV

EFFECTIVE VALENCE OF $AX_3^{-V_f}$ IONS

	Formal valence (V_f)	Effective valence (V_{eff})
SbF_3	0	1.68
SnF_3^-	1	1.83
XeO_3	0	1.92
IO_3^-	1	2.31
TeO_3^{2-}	2	2.88
SnO_3^{4-}	4	5.37

the molecule. Furthermore, using the correlation between bond valence and covalent character (*10*), one expects the weak bonds (0.14 v.u.) between molecules to have about 80% ionic character and the strong bonds within the molecule to be predominantly covalent, in agreement with the qualitative predictions of the traditional theories.

AX_3 Ions ($\mathscr{C}$ Configuration)

The AX_3 groups are represented by determinations of 13 TeO_3^{2-} ions, 13 IO_3^- ions as well as determinations of the SnF_3^- and SnO_3^{4-} ions and the XeO_3 and SbF_3 molecules.

The effective valence of these groups can be calculated in the same way as with the AX_5 groups and the same trends are found (Table IV). In this case the difference between the formal valence and the effective valence is much larger than in the AF_5 groups, the result of the higher valence of the atoms and the larger amount of space available for bonding to the central atom. The increase in the angles with increasing valence is most apparent in this series (see Fig. 5).

TABLE V

EFFECTIVE VALENCE OF $AX_2^{-V_f}$ IONS

	Formal valence (V_f)	Effective valence (V_{eff})
SbF_2^+	1	2.04
SnF_2	0	1.72
TeO_2	0	3.53
SbO_2^-	1	3.92
SnO_2^{2-}	2	4.00

AX_2 Ions ($\mathscr{A}$ Configuration)[11]

The $\mathscr{A}$ configuration is found for Sn and Sb fluorides as well as Sn, Sb and Te oxide complexes (Fig. 4). Since it corresponds to 2 coordination (Eq. (2)), both the intermediate and weak bonds contribute to the effective valence (Table V). The extremely large effective valences of the oxides should be compared with the effective valence of 5.33 v.u. that Sn(IV)O_2 has in the regular octahedral rutile structure. Large effective valences indicate a strong association between the ion and the crystal and hence a tendency towards a regular lattice structure.

Summary

The stereochemistry of the oxygen and fluorine complexes of Sn(II), Sb(III), Te(IV), I(V) and Xe(VI) is governed by the following considerations.

1. The environment of the central atom can usually be viewed as a distorted octahedron.
2. The distortion is such that strong bonds occur opposite weak bonds and intermediate strength bonds occur opposite each other, i.e., the sums of the valences of *trans* pairs of bonds are approximately equal within any octahedron.
3. The environments found around the central atom form a continuous series from $\mathscr{A}$ (2 strong, 2 intermediate, and 2 weak bonds) through $\mathscr{C}$ (3 strong and 3 weak bonds) to $\mathscr{E}$ (1 strong, 4 intermediate and 1 weak bond).
4. Which particular environment is expected depends on the ratio of the valences of the central atom (A) to the ligand (X). Configuration $\mathscr{A}$ is found when this ratio is near 2, $\mathscr{C}$ when it is near 3 and $\mathscr{E}$ when it is near 5.

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[11] Andersson, Åstrom, Galy and Meunier (*22*) have discussed this configuration in terms of hard sphere ions treating the lone pair as a spherical ion. They are able to predict bond lengths and angles using this model with fair accuracy.

5. Deviations from the above rules occur for fluorides of large valence atoms since the valence of the strong bonds saturates at 1.0 v.u. In these cases strong and intermediate bonds have a similar strength and the additional valence has to be absorbed by the weaker bonds. This situation is only found in the $\mathscr{E}$ configuration where the strong and intermediate bonds have similar strengths and the single weak bond is replaced by 3 or 4 weak bonds.

Applications

The following sections illustrate how the above rules can be used in understanding the stereochemistry of these compounds.

Polyions

Many of these elements form polyions with formula A_MX_N or form single AX_N groups which are linked into infinite chains. By recognizing that a bridging F atom will form two bonds of 0.5 v.u., it is possible to examine the ways in which the AX_N groups can be linked. Bridging bonds formed between Sn and F will be intermediate to strong bonds (see Table II). Those between Sb and F will be intermediate to weak bonds while those between Xe and F will be weak. Similarly, O will bridge with bonds of 1.0 v.u. corresponding to strong bonds for Sb, and Te and strong to intermediate bonds for I.

Strong bridges, i.e., bridges formed by strong A–X bonds, are found in the ions $Sn_2F_5^-$ (*23*), $Te_2O_5^-$ (*24*), and the molecule I_2O_5 (*25*) (Fig. 8c), in which two AX_3 groups share a common X atom. In each of these cases the bridging bond is slightly weaker than the ideal and the configuration around the central atoms has distorted from $\mathscr{C}$ to $\mathscr{B}$. In cubic Sb_2O_3 (senarmontite) (*26*) the strong bonds are again expected to be bridging. The correct stoichiometry is achieved by the formation of the Sb_4O_6 group with Td symmetry (Fig. 8b). Each Sb atom forms three strong bonds to O ($\mathscr{C}$ configuration) and each O forms 2 strong bonds to Sb. Unfortunately, the accuracy of this structure determination does not warrant a detailed discussion of bond valences and angles. The structure of orthorhombic Sb_2O_3 (Valentinite) (*27*) is different but is not known in detail.

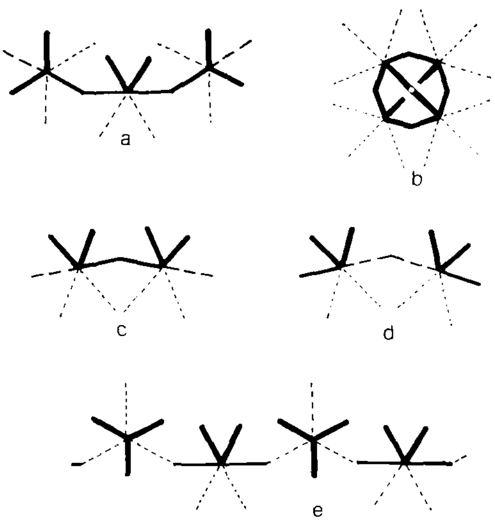

FIG. 8. Bridges based on the $\mathscr{A}$ and $\mathscr{C}$ configurations. *a* strong-intermediate, *b* strong (tetramer), *c* strong (dimer), *d* intermediate–weak (symmetrical dimer), *e* intermediate–weak (asymmetric polymer).

The bridges based upon strong bonds tend to be symmetric but those based upon intermediate or weak bonds can be either symmetric or asymmetric. An example of the former is found in $CsSb_2F_7$ (*28*) in which the Sb atoms have the $\mathscr{B}$ configuration and are bonded through the intermediate weak bond to form the $Sb_2F_7^-$ ion (Fig. 8d). On the other hand, an asymmetric bond occurs in KSb_2F_7 (*29*) so that alternating SbF_4 ($\mathscr{A}$ configuration) and SbF_3 ($\mathscr{C}$ configuration) groups are linked to form a continuous chain (Fig. 8e). A useful formal description of weak or intermediate bridges is to consider them as being formed by F^- or O^{2-} ions and AX_N groups. The symmetric $Sb_2F_7^-$ ion can then be written as

$$(SbF_3 - F^- - SbF_3)$$[12]

---

[12] Note that the valence of F^- is used entirely in forming the bridge and the "ionic charge" shown formally on the bridging F is transferred to the terminal F atoms which actually form the bonds to the cations. Retention of the F^- symbol makes it easier to compute the formal charge (i.e., the external valence) of the complex ion.

and the asymmetric arrangement found in KSb_2F_7 as

$$-SbF_2{}^+-F^--SbF_3-F^--SbF_2{}^+-F^--$$

The advantage of such a description is that it gives the ideal configuration expected around Sb (i.e., $SbF_2{}^+$ has $\mathscr{A}$ configuration and SbF_3 has $\mathscr{C}$) and a consideration of the relative bond valences will indicate whether this ideal configiration will be altered to a transitional form. A similar asymmetric bridge is also found in $Sn_3F_{10}^{4-}$ (*30*) which can be written

$$(SnF_3{}^--F^--SnF_2-F^--SnF_3{}^-)$$

A particularly interesting example of intermediate to weak bridging is found in TeF_4 (*31*) which can be formulated as

$$-TeF_3{}^+-F^--TeF_3{}^+-F^--$$

with the configuration around Te altered from $\mathscr{C}$ to $\mathscr{D}$ in order to provide the right strength for the bridge.

Strong to intermediate bonds are required for Te–O bridges so that, in addition to $Te_2O_5{}^-$ mentioned above, the triple ion (Fig. 8a)

$$(TeO_3^{2-}-TeO_2-TeO_3^{2-})$$

is known (*32*).

Bridged polyions based on the $\mathscr{E}$ configuration are expected only for fluoride complexes of Sb, Te, I, and Xe. For the former 3, the bridging bonds must be intermediate to weak and will involve a distortion of geometry from $\mathscr{E}$ to $\mathscr{D}$. This is just the arrangement found in TeF_4 discussed above and similar chains are found for $SbF_4{}^-$ in $NaSbF_4$ (*33*). The same type of bonding is used in the cyclic tetraantimonate ion found in $KSbF_4$ (*34*) (Fig. 9a). With Xe it is necessary to use weak bonds for bridging and 2 examples of this are found in $Xe_2F_{11}^+$ ($=XeF_5{}^+-F^--XeF_5{}^+$) (*35*) and in XeF_6 (*36*) which forms tetramers $(XeF_5{}^+F^-)_4$ and hexamers $(XeF_5{}^+F^-)_6$ (Figs. 9b, c) in which the bridging F forms 2 and 3 weak bonds to Xe, respectively. In all these cases the configuration around Xe is $\mathscr{E}$.

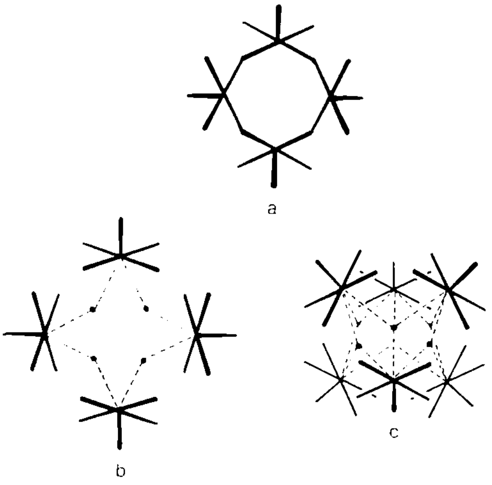

FIG. 9. Bridges based on the $\mathscr{E}$ configuration. *a* intermediate (tetramer), *b* weak (tetramer), *c* weak (hexamer).

Table VI summarizes the kinds of bridged polyions expected. There are many possible polyions that can be built on these principles involving discrete linear ions (e.g., Sn_2F_5, Sn_3F_{10}), infinite chains (e.g., TeF_4), cyclic polyions based on these chains (e.g., Sb_4F_{16}) and cluster polyions (e.g., XeF_6, Sb_2O_3).

Neutral Fluoride Molecules

The series of neutral fluoride molecules should possess a geometry corresponding exactly to the coordination number calculated by Eq. (2) and this is found to be the case. The effective valences and configurations for the molecules are given in Table VII. The second column gives the observed configuration and the third the values of the effective valence expected for an ion with this ideal geometry (see Figs. 4–6). The fourth column gives the values actually observed. There is a tendency for the effective valence to increase as the valence and coordination number decrease but TeF_4 and XeF_6 have anomolously high effective valences. In the former case this is the result of the $\mathscr{D}$ conformation not having 4 clear strong bonds, and in the latter case it results from the absence of a suitable distorted octahedral configuration with 6 strong bonds. As discussed above, these 2 substances can best be formulated as the complex cation fluorides $TeF_3{}^+F^-$ and $XeF_5{}^+F^-$.

Since the effective valence of a molecule measures the strength of its association with other molecules one would expect an approximate relationship between effective valence

TABLE VI (a)

TYPES OF FLUORINE BRIDGE[a]

A	Expected configuration (Eq. (2))	Type of bond used in bridge	Possible ions	Actual configuration	Comments	Fig.
Sn	$\mathcal{A}$	Strong-intermediate	$Sn_2F_5^-$	$\mathcal{C}$	$NaSn_2F_5$(23)	8c
			$(SnF_3^- - F^- - SnF_2 - F^- - SnF_3^-)$	$\mathcal{A},\mathcal{C}$	$Na_4Sn_3F_{10}$(30)	8e
Sb	$\mathcal{C}$	Intermediate-weak	$(Sb_3 - F^- - Sb_3)$	$\mathcal{B}$	$CsSb_2F_7$(28)	8d
			$-SbF_3 - F^- - SbF_2^+ - F^- -$	$\mathcal{A},\mathcal{B}$	KSb_2F_7(29)	8e
			$-SbF_3 - F^- - SbF_3 - F^- -$	$\mathcal{D}$	$NaSbF_4$(33)	9a
			Sb_4F_{16}	$\mathcal{D}$	$KSbF_4$(34)	9a
Te	$\mathcal{D}$	Intermediate-weak	$-TeF_3^+ - F^- - TeF_3^+ - F^- -$	$\mathcal{D}$	TeF_4(31)	9a
I	$\mathcal{E}$	Intermediate-weak	$-IF_3^{2+} - F^- - IF_3^{2+} - F^- -$	$\mathcal{D}$	Not known	
Xe	$\mathcal{E}$	Weak	$(XeF_5^+ - F^- - XeF_5^+)$	$\mathcal{E}$	$Xe_2F_{11}AuF_6$(35)	9b
			$-XeF_5^+ - F^- - XeF_5^+ - F^- -$	$\mathcal{E}$	XeF_6(36)	9b & c

[a] A–F–A bonds have an expected valence of 0.5 v.u.

and melting point. This is shown for a number of materials in Fig. 10. A linear relation of the form

$$T_{(mp)} = 290\ V_{eff}\ ^{\circ}K$$

gives a reasonable fit. All molecules that form solids at room temperature are expected to have an effective valence greater than 1.0 v.u.

Mixed O, F Complexes

One can apply the same principles to the mixed complexes that apply to the pure O and pure F complexes. However, there is now a new element of flexibility. When V_A is large (i.e., for I and Xe), so that a strong A–F bond has the same valence as an intermediate bond,

TABLE VI (b)

TYPES OF OXYGEN BRIDGE[a]

A	Expected configuration (Eq. (2))	Type of bond used in bridge	Possible ions	Actual configuration	Comments	Fig.
Sn	$\mathcal{A}$(?)	All bonds too weak for symmetric bridges. The bonding is likely to be dominated by stronger bonds to other cation (e.g., P, S)				
Sb	$\mathcal{A}$	Strong	Sb_4O_6	$\mathcal{C}$	cubic Sb_2O_3(26)	8b
Te	$\mathcal{A}$	Strong-intermediate	$Te_2O_5^-$	$\mathcal{B}$	$CuTe_2O_5$(24), Mackayite (37) $Fe_2Te_4O_{11}$(38)	8c
			$(TeO_3^{2-} - TeO_2 - TeO_3^{2-})$	$\mathcal{A},\mathcal{B}$	$Zn_2Te_3O_8$(32)	8a
I	$\mathcal{A},\mathcal{C}$	Strong-intermediate	I_2O_5	$\mathcal{B}$	I_2O_5(25)	8c
			$-IO_2^+ - IO_3^- - IO_2^+ - IO_3^- -$	$\mathcal{A},\mathcal{C}$	Not known	8a
Xe	$\mathcal{C}$	Intermediate	$-XeO_3 - O^{2-} - XeO_3 - O^{2-} -$	$\mathcal{D}$	Not known	
			$-XeO_2^{2+} - O^{2-} - XeO_2^{2+} - O^{2-} -$	$\mathcal{A}$	Not known	
			$-XeO_3 - O^{2-} - XeO_2^{2+} - O^{2-} -$	$\mathcal{A},\mathcal{D}$	Not known	8e
			$(XeO_3 - O^{2-} - XeO_3)$	$\mathcal{B}$	Not known	8d

[a] A–O–A bonds have an expected valence of 1.0 v.u.

TABLE VII

EFFECTIVE VALENCES OF NEUTRAL MOLECULES

	Configuration	Expected	Observed	Melting points	
SnF_2	$\mathscr{A}$	1.72			
SbF_3	$\mathscr{C}$	1.68	1.42(5)	292°	SbF_3(39)
TeF_4	$\mathscr{D}$	1.94	1.74(9)	subl. >97°	TeF_4(31)
IF_5	$\mathscr{E}$	.99	1.16(1)	9.6°	XeF_2IF_5(40)
XeF_6	$\mathscr{E}$		1.29+	47.7°	(Average calculated from 6 nearest neighbours in XeF_6) (36)

configurations are favored in which A–O can from a strong bond and A–F an intermediate bond. Thus IOF_4^- (*18*) has the $\mathscr{E}$ configuration with O in the strong apical position, and XeO_2F_2 (*41*) and $IO_2F_2^-$ (*42*), in spite of being 4 coordinate, have the $\mathscr{A}$ rather than the $\mathscr{D}$ configuration. Here the O atoms form the strong equatorial bonds and the F atoms the intermediate axial bonds. In contrast the XeO_3F^- (*43*) ions shows the expected 4 coordinate $\mathscr{D}$ configuration with 3 strong Xe-O and 2 moderately weak Xe-F bonds providing bridges to form an infinite polyion of the form

$$-F^--XeO_3-F'-XeO_3-F^--$$

SbOF should be 2 coordinate with the $\mathscr{A}$ configuration. Assigning 1 strong bond each to O and F leaves enough valence on O to provide both axial bonds, linking the molecules into the chains found in L–SbOF (*44*). On the other hand, M–SbOF (*45*) has a more complex structure based upon the $\mathscr{C}$ configuration with strong O bridges.

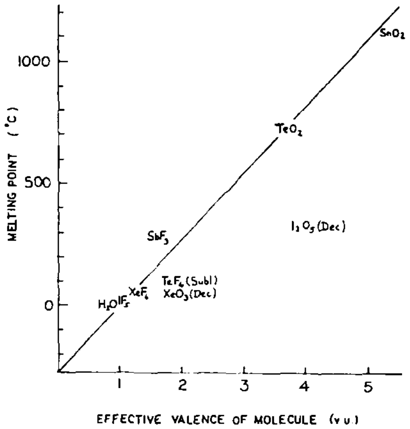

FIG. 10. Melting point of various molecules as a function of their effective valence. Subl. = Sublimation temperature, Dec. = decomposition temperature.

Note added in proof. The structure of Valentinite has just been published by C. Svensson *Acta Cryst.* **B30**, 458, (1974). The Sb atoms have the $\mathscr{C}$ configuration and are linked by strong oxygen bridges into ladder-like double chains.

Acknowledgments

I wish to thank Dr. R. J. Gillespie, Prof. J. Zemann, Dr. C. Calvo, and Dr. C. J. L. Lock for helpful discussion, and the National Research Council of Canada for a research operating grant.

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Appendix

The appendix lists the structures used in this study according to the configuration ($\mathscr{A}$–$\mathscr{E}$) and within each configuration according to the atoms forming the bonds of interest (Sn, Sb, Te, I and Xe, and F and O). Since the 5 configurations $\mathscr{A} \leftrightarrow \mathscr{B} \leftrightarrow \mathscr{C} \leftrightarrow \mathscr{D} \leftrightarrow \mathscr{E}$ form a continuous series, it is not always possible to classify a particular environment unambiguously, a structure showing a $\mathscr{B}$ configuration may differ only slightly from one with an $\mathscr{A}$ configuration (cf. $NaVTeO_5$ listed under $\mathscr{A}$ and β-TeO_2 listed under $\mathscr{B}$).

Each entry contains the formula or name of the compound, the bond valences (upper line), bond lengths (lower line), bond valence sums and bond angles found around the A atom. The number in parenthesis after the bond valence sum is the standard error in the last figure quoted calculated from the standard errors in the bond length (this has been estimated where not given in the original paper). The numbering of the ligands is shown in Fig. 2. For each class of structure the typical values (see Figs. 4–6) are also given.

In general crystal structures published before 1950 have been omitted as too unreliable for quantitative work, but the accuracy of the structure determinations used varies considerably (see the standard errors in the bond valence sums). The following structures were omitted for the reasons shown.

$Te_4O_8HNO_3$	(*82*)	$\mathscr{A}$ or $\mathscr{B}$ configuration. Bond valence sums indicate that the structure is probably wrong.
SnF_2	(*83*)	Probably $\mathscr{C}$ configuration. Structure inadequately described.
SnO	(*84*)	Possibly $\mathscr{A}$ configuration, structure probably wrong (short O–O distance).
Zemannite	(*85*)	$\mathscr{C}$ configuration, compositional and positional disorder.
MTe_3O_8(M = T, Sn, Hf, Zr)	(*86*)	$\mathscr{A}$ configuration, high symmetry structure of a kind that frequently leads to poor bond valence sums.
UTe_3O_9	(*17*)	Possibly $\mathscr{A}$ configuration, structure gives poor bond valence sums.

The following symbols are used in the bond valence columns: – no weak bond in this position; × two weaker bonds in this position; ★ three weaker bonds in this position; + four weaker bonds in this position; ( ) This bond valence is usually distributed between two or more bonds.

A configuration

		bond to						bond valence sum	X-A-X bond angles								Ref.
		X1	X2	X3	X4	X5	X6		X1-X2	X1-X3	X2-X3	X1-X4	X2-X4	X3-X4	X2-X5	X1-X6	
Sn-F																	
typical	v.u.	0.57	0.57	0.40	0.40	0.03	0.03	2.00	85°	80°	80°	80°	80°	155°			
	Å	2.04	2.04	2.26	2.26	4.74	4.74										
$Na_4Sn_3F_{10}$(2)	v.u.	0.57	0.57	0.40	0.40	-	-	1.94(3)	86°	79°	85°	85°	79°	159°	-	-	(30)
	Å	2.04	2.04	2.26	2.26												
Sb-F																	
typical	v.u.	0.74	0.74	0.56	0.56	0.20	0.20	3.00	90°	81°	81°	81°	81°	155°			
	Å	1.92	1.92	2.07	2.07	2.74	2.74										
KSb_2F_7(2)	v.u.	0.76	0.72	0.58	0.55	0.14	X	2.94(1)	90°	81°	82°	80°	81°	155°	158°	-	(29)
	Å	1.91	1.93	2.05	2.08	3.02											
Sn-O																	
typical	v.u.	0.50	0.50	0.33	0.33	0.17	0.17	2.00	85°	80°	80°	80°	80°				
	Å	2.17	2.17	2.38	2.38	2.76	2.76										
α-$SnWO_4$	v.u.	0.49	0.49	0.32	0.32	0.15	0.15	1.92(3)	85°	82°	78°	78°	82°	120°	150°	156°	(46)
	Å	2.18	2.18	2.40	2.40	2.83	2.83										
Sb-O																	
typical	v.u.	0.79	0.79	0.53	0.53	0.21	0.21	3.00	88°	84°	84°	84°	84°	164°			
	Å	2.01	2.01	2.20	2.20	2.70	2.70										
β-Sb_2O_4	v.u.	0.78	0.78	0.51	0.51	?	?		88°	?	?	?	?	148°	?	?	(47)
	Å	2.03	2.03	2.22	2.22												
	(insufficient information is given to recalculate the distances and angles)																
$SbPO_4$	v.u.	0.84	0.75	0.55	0.55	0.15	0.13	3.12(3)	88°	84°	85°	84°	85°	165°	150°	142°	(48)
	Å	1.98	2.04	2.18	2.18	2.94	3.07										
	(Sb-O5 is replaced by two bonds with the characteristics shown)																
Te-O																	
typical	v.u.	1.12	1.12	0.73	0.73	0.15	0.15	4.00	98°	86°	86°	86°	86°	169°			
	Å	1.90	1.90	2.09	2.09	2.97	2.97										
α-TeO_2	v.u.	1.12	1.12	0.74	0.74	0.17	0.17	4.08(9)	102°	88°	85°	85°	88°	169°	172°	182°	(49)
	Å	1.90	1.90	2.08	2.08	2.88	2.88										
$NaVTeO_5$	v.u.	1.03	1.03	0.80	0.65	0.21	0.18	3.92(14)	94°	90°	88°	79°	86°	167°	161°	147°	(54)
	Å	1.93	1.94	2.05	2.15	2.75	2.84										
Te_2O_5	v.u.	1.15	1.09	0.76	0.75	0.11	0.23	3.98(2)	91°	86°	86°	87°	82°	166°	110°	152°	(51)
	Å	1.89	1.91	2.07	2.08	3.16	2.71										
$H_2Te_2O_6$	v.u.	1.24	1.03	0.77	0.71	0.18	0.18	4.12(2)	91°	89°	87°	87°	84°	172°	158°	150°	(52)
	Å	1.86	1.94	2.06	2.11	2.85	2.84										
$Zn_2Te_3O_8$(1)	v.u.	1.33	1.33	0.72	0.72	-	-	4.10(10)	106°	93°	84°	84°	93°	175°	-	-	(32)
	Å	1.83	1.83	2.10	2.10												
$Te(O_2C_6H_4)$	v.u.	0.94	0.94	0.88	0.70	0.26	0.10	3.80(9)	98°	85°	81°	81°	80°	154°	154°	77°	(53)
	Å	1.98	1.98	2.01	2.11	2.64	3.28										
	(The small value of the valence for Te-O1 and Te-O2 arises from the fact that the strong O-C bonds are expected to have a valence of 1 v.u.)																
Mixed ligands																	
		O	F	O	O		F										
L-SbOF	v.u.	0.83	0.68	0.57	0.57	X	0.15	3.08(3)	96°	73°	85°	73°	85°	143°	-	180°	(44)
	Å	1.99	1.96	2.16	2.16		3.01										
		O	O	F	F	O	F										
KIO_2F_2	v.u.	1.12	1.06	0.72	0.70	0.20	0.18	3.98(31)	95°	90°	92°	89°	.88°	180°	162°	170°	(42)
	Å	1.92	1.94	1.99	2.00	2.81	2.89										
	(The errors in this early determination are large. It is likely that I-O(1) and I-O(2) are 0.1Å too large, giving a valence 0.5 v.u. too small)																
		O	O	F	F	O	O										
XeO_2F_2	v.u.	1.88	1.88	0.90	0.90	0.20	0.20	5.96(7)	105°	92°	92°	92°	92°	174°	?	? -	(41)
	Å	1.71	1.71	1.90	1.90	2.81	2.81										

B configuration

		bonds to X1	X2	X3	X4	X5	X6	bond valence sums	X-A-X bond angles X1-X2	X1-X3	X2-X3	X3-X4	X2-X5	X1-X6	Ref.
Sb-F															
typical	v.u.	0.72	0.72	0.66	0.42	0.24	0.24	3.00	89°	84°	84°	155°			
	Å	1.94	1.94	1.98	1.98	2.61	2.61								
$CsSb_2F_7$	v.u.	0.72	0.71	0.67	0.42	*	0.19	3.09(1)	90°	86°	81°	152°	-	158°	(28)
	Å	1.94	1.94	1.98	2.24		2.77								
$KSb_2F_7(1)$	v.u.	0.73	0.73	0.68	0.32	0.25	X	2.99(1)	08°	84°	84°	160°	160°	-	(29)
	Å	1.93	1.93	1.96	2.41	2.57									
Te-O (Arranged with those closest to A configuration at the top, those closest to C configuration at the bottom)															
typical	v.u.	1.16	1.16	0.98	0.40	0.15	0.15	4.00	97°	91°	91°	164°			
	Å	1.89	1.89	1.96	2.40	2.97	2.97								
δ-TeO_2	v.u.	1.18	1.04	0.77	0.60	0.26	0.13	3.98(9)	101°	90°	89°	168°	168°	165°	(50)
	Å	1.80	1.93	2.07	2.20	2.64	3.07								
$Fe_2Te_4O_{11}(4)$	v.u.	1.05	0.94	0.75	0.53	0.15	0.29	3.64(8)	98°	93°	81°	150°	160°	156°	(38)
	Å	1.93	1.98	2.08	2.25	2.99	2.61								
$Fe_2Te_4O_{11}(1)$	v.u.	1.05	1.15	0.94	0.48	0.17	0.15	3.94(9)	97°	81°	94°	155°	157°	152°	
	Å	1.89	1.93	1.98	2.30	2.89	2.96								
$Fe_2Te_4O_{11}(3)$	v.u.	1.40	1.24	0.72	0.37	0.14	0.11	3.99(10)	98°	86°	87°	149°	163°	151°	
	Å	1.81	1.86	2.10	2.43	3.00	3.18								
Denningite	v.u.	1.30	1.21	0.82	0.42	0.17	0.13	4.05(22)	98°	90°	85°	160°	135°	155°	(55)
	Å	1.84	1.86	2.04	2.36	2.90	3.05								
$UTeO_5$	v.u.	1.18	0.98	1.15	0.54	0.14	0.16	4.14(14)	102°	81°	74°	151°	140°	152°	(56)
	Å	1.88	1.96	1.89	2.24	3.05	2.94								
$CuTeO_3(2)$	v.u.	1.18	1.18	0.98	0.46	0.11	0.11	4.03(9)	106°	86°	86°	176°	156°	156°	(57)
	Å	1.88	1.88	1.96	2.32	3.16	3.16								
$CuTe_2O_5(2)$	v.u.	1.24	1.22	0.86	0.39	0.13	-	3.84(2)	99°	87°	89°	167°	150°	-	(24)
	Å	1.86	1.87	2.02	2.40	3.07									
Mackayite	v.u.	1.12	1.12	1.00	0.43	0.22	0.16	4.05(12)	96°	92°	92°	162°	167°	160°	(37)
	Å	1.90	1.90	1.95	2.37	2.75	2.94								
	(This structure gives very poor valence sums around oxygen)														
$Fe_2Te_4O_{11}(2)$	v.u.	1.47	1.27	0.82	0.33	0.18	0.15	4.22(10)	95°	92°	92°	170°	165°	134°	(36)
	Å	1.79	1.85	2.04	2.50	2.87	2.97								
$Zn_2Te_3O_8(2)$	v.u.	1.18	1.05	0.94	0.39	0.12	0.11	3.89(9)	98°	94°	80°	156°	135°	172°	(32)
	Å	1.88	1.93	1.98	2.41	2.72	3.17								
Poughite(2)	v.u.	1.21	1.10	1.15	0.41	0.14	0.12	4.13(8)	88°	105°	104°	170°	144°	161°	(58)
	Å	1.87	1.90	1.90	2.38	3.04	3.10								
Sonoraite(2)	v.u.	1.24	1.11	1.15	0.39	0.12	0.17	4.10(6)	96°	94°	92°	161°	152°	175°	(59)
	Å	1.86	1.91	1.89	2.57	3.12	2.88								
I-O (Arranged with those closest to A configuration at the top, those closest to C configuration at the bottom)															
typical	v.u.	1.54	1.54	1.10	0.36	0.23	0.23	5.00	98°	96°	96°				
	Å	1.79	1.79	1.81	2.47	2.73	2.73								
$I_2O_5(2)$	v.u.	1.64	1.39	1.04	0.56	0.31	X	5.05(15)	95°	98°	93°	171°	172°	-	(25)
	Å	1.79	1.83	1.95	2.23	2.54									
$HI_3O_8(2)$	v.u.	1.58	1.54	1.04	0.42	0.19	0.30	5.07(6)	96°	93°	93°	174°	169°	168°	(60)
	Å	1.78	1.79	1.95	2.38	2.83	2.56								
$KH(IO_3)_2(4)$	v.u.	1.70	1.58	1.04	0.36	0.26	0.24	5.18(12)	98°	99°	94°	176°	170°	173°	(61)
	Å	1.75	1.78	1.95	2.47	2.64	2.68								
$I_2O_5(1)$	v.u.	1.62	1.58	1.12	0.37	0.23	0.16	5.19(15)	99°	102°	96°	173°	176°	169°	(25)
	Å	1.77	1.78	1.92	2.45	2.72	2.94								
$KH(IO_3)_2(3)$	v.u.	1.58	1.54	1.14	0.34	0.23	0.19	5.01(13)	100°	94°	97°	172°	170°	171°	(61)
	Å	1.78	1.79	1.91	2.50	2.72	2.84								
α-HIO_3	v.u.	1.57	1.43	1.17	0.34	0.22	0.18	4.90(6)	101°	94°	98°	166°	174°	163°	(62)
	Å	1.78	1.82	1.90	2.50	2.77	2.88								
$HI_3O_8(1)$	v.u.	1.58	1.50	1.00	0.29	0.27	0.23	4.86(6)	98°	97°	88°	168°	161°	171°	(60)
	Å	1.78	1.80	1.97	2.58	2.62	2.71								
$HI_3O_8(3)$	v.u.	1.54	1.46	1.17	0.31	0.29	X	5.01(6)	99°	95°	94°	171°	178°	-	
	Å	1.79	1.81	1.90	2.54	2.59									
Mixed ligands		O	O	F	O	F	F								
M-SbOF(2)	v.u.	0.80	0.80	0.59	0.43	0.19	0.14	2.94(3)	98°	82°	83°	146°	170°	155°	(45)
	Å	2.01	2.01	2.04	2.30	2.82	3.08								

G configuration

		bonds to						bond valence sums	X-A-X bond angles						Ref.
		X1	X2	X3	X4	X5	X6		X1-X2	X1-X3	X2-X3	X3-X4	X2-X5	X1-X6	
Sn-F															
typical	v.u.	0.53	0.53	0.53	0.14	0.14	0.14	2.01	83°	83°	83°	155°			
	Å	2.08	2.08	2.08	3.05	3.05	3.05								
$Na_4Sn_3F_{10}$(1)	v.u.	0.64	0.52	0.48	0.29	-	0.10	2.02(3)	88°	81°	79°	140°	-	144	(30)
	Å	1.98	2.10	2.15	2.48		3.35								
$NaSn_2F_5$	v.u.	0.54	0.54	0.43	0.27	0.15	0.15	2.07(3)	89°	84°	81°	142°	127°	140°	(23)
	Å	2.07	2.08	2.22	2.53	3.01	2.98								
Sb-F															
typical	v.u.	0.72	0.72	0.72	0.28	0.28	0.28	3.00	88°	88°	88°				
	Å	1.94	1.94	1.94	2.50	2.50	2.50								
SbF_3	v.u.	0.77	0.72	0.72	0.24	0.24	0.23	2.92(5)	89°	89°	86°	156°	156°	163°	(39)
	Å	1.90	1.94	1.94	2.60	2.60	2.63								
	(There are 5 additional bonds between 3.0 and 4.0Å)														
Sn-O (All these crystals have additional weak (-0.10 v.u.) Sn-O bonds contributing to the bond valence sums)															
typical	v.u.	0.44	0.44	0.44	0.23	0.23	0.23	2.01	81°	81°	81°				
	Å	2.23	2.23	2.23	2.58	2.58	2.58								
$KSn(HCO_2)_3$	v.u.	0.53	0.49	0.50	0.12	0.14	0.12	2.00(2)	78°	83°	83°	148°	125°	123°	(5)
	Å	2.14	2.18	2.17	3.01	2.89	2.97								
β-$SnWO_4$	v.u.	0.46	0.46	0.46	0.16	0.16	0.16	2.09(1)	82°	82°	82°	154°	154°	154°	(63)
	Å	2.21	2.21	2.21	2.81	2.81	2.81								
$SnSO_4$	v.u.	0.43	0.41	0.41	0.10	0.10	0.13	1.96(1)	77°	77°	79°	118°	118°	143°	(64)
	Å	2.25	2.27	2.27	3.08	3.08	2.95								
$SnHPO_4$	v.u.	0.56	0.41	0.33	0.21	0.19	0.08	1.86(4)	78°	80°	83°	152°	142°	144°	(65)
	Å	2.12	2.27	2.38	2.63	2.68	3.24								
Te-O															
typical	v.u.	1.19	1.19	1.19	0.15	0.15	0.15	4.02	96°	96°	96°				
	Å	1.88	1.88	1.88	2.97	2.97	2.97								
Poughite(1)	v.u.	1.27	1.10	0.92	0.23	0.09	0.18	3.88(12)	97°	91°	88°	160°	153°	168°	(58)
	Å	1.85	1.91	1.99	2.70	3.30	2.87								
$CuTe_2O_5$(1)	v.u.	1.19	1.17	1.05	0.22	0.27	-	3.90(2)	95°	93°	91°	163°	168°	-	(24)
	Å	1.88	1.88	1.93	2.73	2.61									
Teinite	v.u.	1.36	1.18	1.18	0.15	0.14	0.13	4.14(24)	102°	98°	96°	150°	136°	175°	(66)
	Å	1.82	1.88	1.88	2.98	3.04	3.06								
Sonoraite(1)	v.u.	1.16	1.14	1.14	0.10	0.22	0.16	3.92(6)	100°	94°	96°	154°	166°	132°	(59)
	Å	1.89	1.89	1.90	3.23	2.74	2.95								
α-$TeVO_4$	v.u.	1.40	1.00	0.92	0.28	0.20	0.20	4.00(14)	92°	97°	94°	164°	169°	162°	(67)
	Å	1.81	1.94	1.98	2.58	2.78	2.79								
$BaTeO_3H_2O$	v.u.	1.28	1.24	1.24	0.09	X	0.14	4.06(3)	99°	103°	96°	160°	-	170°	(68)
	Å	1.85	1.86	1.86	3.35		3.04								
Rodalquilarite(1)	v.u.	1.24	1.10	1.10	Cℓ	0.16	0.13	3.73+(23)	97°	102°	90°	175°	146°	142°	(69)
	Å	1.86	1.91	1.91	3.06	2.93	3.09								
Rodalquilarite(2)	v.u.	1.10	1.18	1.18	0.30	0.27	Cℓ	4.03+(28)	88°	99°	97°	163°	168°	166°	
	Å	1.91	1.88	1.88	2.54	2.61	3.07								
	(Some of these bonds are not given by Dusausoy and Protas (69))														
$ZnTeO_3$	v.u.	1.24	1.18	1.15	0.10	0.14	0.23	4.05(9)	95°	95°	98°	169°	164°	166°	(70)
	Å	1.86	1.88	1.90	3.25	3.00	2.71								
Emmonsite(1)	v.u.	1.51	1.40	1.24	0.20	0.33	-	4.68(22)	94°	98°	90°	151°	160°	-	(71)
	Å	1.78	1.81	1.86	2.80	2.50									
Emmonsite(2)	v.u.	1.30	1.21	1.08	0.22	0.32	0.11	4.23(22)	92°	102°	94°	154°	164°	140°	
	Å	1.84	1.87	1.92	2.74	2.52	3.17								
Emmonsite(3)	v.u.	1.40	1.27	0.98	0.10	0.17	-	3.92(20)	96°	100°	93°	162°	150°	-	
	Å	1.81	1.85	1.96	3.28	2.88									
$CuTeO_3$(1)	v.u.	1.24	1.15	1.15	0.18	0.18	0.23	4.13(14)	96°	96°	93°	168°	168°	158°	(57)
	Å	1.86	1.89	1.89	2.86	2.86	2.71								

𝒞 configuration (cont'd)

		bonds to						bond valence sums	X-A-X bond angles						Ref.
		X1	X2	X3	X4	X5	X6		X1-X2	X1-X3	X2-X3	X3-X4	X2-X5	X1-X6	
1-O															
typical	v.u.	1.45	1.45	1.45	0.22	0.22	0.22	5.01	98°	98°	98				
	Å	1.81	1.81	1.81	2.75	2.75	2.75								
$Cu(IO_3)OH$	v.u.	1.57	1.42	1.42	0.24	0.24	0.34	5.23(43)	100°	100°	95	173°	173	173	(72)
	Å	1.78	1.82	1.82	2.69	2.69	2.50								
$Ca(IO_3)_2 6H_2O$	v.u.	1.45	1.45	1.42	0.20	0.18	0.17	4.88(12)	99°	97°	99°	171°	171	178	(6)
	Å	1.81	1.81	1.82	2.82	2.88	2.90								
$Ce(IO_3)_4H_2O(1)$	v.u.	1.45	1.38	1.35	0.15	0.15	0.17	4.66(12)	96°	100°	96°	164	160°	160	(73)
	Å	1.81	1.83	1.84	2.99	3.00	2.93								
$Ce(IO_3)_4H_2O(2)$	v.u.	1.42	1.42	1.38	0.15	0.31	0.21	4.89(12)	96°	97°	97°	152°	174°	170	
	Å	1.82	1.82	1.83	2.99	2.56	2.78								
$Ce(IO_3)_4H_2O(3)$	v.u.	1.42	1.38	1.29	0.33	0.12	0.23	4.77(12)	97°	98°	98°	175°	161°	170	
	Å	1.82	1.83	1.86	2.52	3.10	2.74								
$Ce(IO_3)_4H_2O(4)$	v.u.	1.61	1.42	1.42	0.31	0.26	0.15	5.16(12)	98°	101°	95	175	173	168	
	Å	1.76	1.82	1.82	2.54	2.66	3.06								
$LiIO_3$	v.u.	1.46	1.46	1.46	0.17	0.17	0.17	4.91(5)	96°	96°	96	166	166	166°	(74)
	Å	1.81	1.81	1.81	2.89	2.89	2.89								
NH_4IO_3	v.u.	1.64	1.48	1.34	0.20	0.21	0.19	5.08(5)	99°	101°	101°	174°	172	168	(2)
	Å	1.76	1.81	1.84	2.82	2.78	2.83								
$RbIO_3$	v.u.	1.46	1.46	1.46	0.22	0.22	0.22	5.06(2)	100°	100°	100	168°	168	168°	(3)
	Å	1.81	1.81	1.81	2.75	2.75	2.75								
$K_2H(IO_3)_2Cl(1)$	v.u.	1.62	1.46	1.33	Cl	0.15	0.17	4.73+(6)	99°	103	99	163°	173	158°	(75)
	Å	1.77	1.81	1.85	3.08	2.99	2.93								
$K_2H(IO_3)_2Cl(2)$	v.u.	1.60	1.49	1.10	0.32	Cl	0.16	4.67+(5)	104°	94°	93°	172	171°	162°	
	Å	1.77	1.80	1.93	2.54	3.05	2.95								
$KH(IO_3)_2(1)$	v.u.	1.66	1.52	1.47	0.08	0.13	0.14	5.01(10)	100°	101°	102°	173	167°	177°	(61)
	Å	1.76	1.79	1.81	3.43	3.08	3.04								
$KH(IO_3)_2(2)$	v.u.	1.54	1.50	1.42	0.10	0.16	0.18	4.89(13)	100°	98°	98°	-	172°	177°	
	Å	1.79	1.81	1.82	3.24	2.93	2.84								
Xe-O															
typical	v.u.	1.68	1.68	1.68	0.32	0.32	0.32	6.00	103°	103°	103°				
	Å	1.76	1.76	1.76	2.54	2.54	2.54								
XeO_3	v.u.	1.75	1.67	1.62	0.18	0.21	0.18	5.99(22)	100°	100°	101°	172°	163°	159°	(76)
	Å	1.74	1.76	1.77	2.89	2.80	2.89								
	(Bond valence sum includes 6 weaker bonds)														
Mixed ligands															
		O	F	O	O	F	F								
M-SbOF	v.u.	0.83	0.69	0.71	0.39	0.18	0.15	2.95(4)	90°	77°	88°	144°	166°	155°	(45)
	Å	1.99	1.95	2.06	2.36	2.84	3.02								

𝒟 configuration

		bonds to						bond valence sums	X-A-X bond angles											Re
		X1	X2	X3	X4	X5	X6		X1-X2	X1-X3	X1-X4	X1-X5	X2-X3	X2-X4	X3-X5	X4-X5	X3-X4	X2-X5	X1-X6	
Sb-F																				
typical	v.u.	0.74	0.63	0.63	0.37	0.37	0.26	3.00	84°	84°	79°	79°	83°	88°	88°	93°	163°	163°		
	Å	1.92	2.01	2.01	2.32	2.32	2.55													
$KSbF_4$ (1)	v.u.	0.72	0.61	0.61	0.48	0.48	-	2.90(35)												(34
	Å	1.98	2.06	2.06	2.18	2.18														
$KSbF_4$ (2)	v.u.	0.71	0.71	0.71	0.39	0.39	-	2.91(35)												
	Å	1.99	1.99	1.99	2.29	2.29														
	(Uncertainties in this structure determination are large)																			
$NaSbF_4$	v.u.	0.78	0.61	0.54	0.41	0.17	0.21	2.72(15)	85°	81°	71°	86°	76°	87°	98°	95°	149°	170°	153°	(33
	Å	1.93	2.03	2.08	2.19	2.84	2.51													
Te-F																				
typical	v.u.	0.85	0.80	0.80	0.54	0.54	(0.47)	4.00	87°	87°	77°	77°	85°	88°	88°	93°	164°	164°		
	Å	1.86	1.90	1.90	2.12	2.12														
TeF_4	v.u.	0.96	0.84	0.77	0.58	0.43	*	3.95(9)	88°	86°	77°	76°	85°	86°	90°	93°	161°	165°	142°	(31
	Å	1.80	1.87	1.92	2.08	2.26														
Mixed ligands																				
		O	O	O	F	F														
$KXeO_3F$	v.u.	1.71	1.66	1.54	0.44	0.37	X	5.91(7)	100°	86°	88°	98°	85°	77°	99°	172°	171°	-		(4
	Å	1.74	1.77	1.79	2.36	2.48														

figuration

		bonds to						bond valence sums	X-A-X bond angles										Ref.
		X1	X2	X3	X4	X5	X6		X1-X2	X1-X3	X1-X4	X1-X5	X2-X3	X2-X4	X3-X5	X4-X5	X3-X4	X2-X5	
cal	v.u.	0.68	0.56	0.56	0.56	0.56	0.08	3.00	81°	81°	81°	81°	88°	88°	88°	88°	158°	158°	
	Å	1.97	2.07	2.07	2.07	2.07	3.51												
F_5	v.u.	0.63	0.59	0.59	0.59	0.59	-	2.98(20)	83°	83°	83°	83°	(other angles not given)						(77)
	Å	2.00	2.04	2.04	2.04	2.04													
$)_2SbF_5$	v.u.	0.73	0.55	0.55	0.55	0.55	-	2.95(1)	79°	79°	79°	79°	86°	90°	90°	86°	159°	159°	(78)
	Å	1.92	2.08	2.08	2.08	2.08													
al	v.u.	0.85	0.72	0.72	0.72	0.72	(0.27)	4.00	79°	79°	79°	79°	88°	88°	88°	88°	158°	158°	
	Å	1.86	1.95	1.95	1.95	1.95													
	v.u.	0.85	0.72	0.72	0.72	0.72	*	3.97(1)	78°	78°	80°	80°	91°	85°	85°	90°	158°	158°	(77)
	Å	1.86	1.95	1.95	1.95	1.95													
al	v.u.	0.99	0.89	0.89	0.89	0.89	(0.55)	5.00	79°	79°	79°	79°	88°	88°	88°	88°	158°	158°	
	Å	1.82	1.87	1.87	1.87	1.87													
IF_5	v.u.	0.99	0.89	0.89	0.89	0.89	+	5.11(3)	81°	81°	81°	81°	89°	89°	89°	89°	162°	162°	(40)
	Å	1.82	1.87	1.87	1.87	1.87													
cal	v.u.	1.00	0.96	0.96	0.96	0.96	(1.16)	6.00	79°	79°	79°	79°	88°	88°	88°	88°	158°	158°	
	Å	1.84	1.86	1.86	1.86	1.86													
$_5)_2PdF_6$ (1)	v.u.	1.06	1.00	1.00	1.00	0.98	*	6.07(3)	81°	78°	78°	86°	85°	89°	87°	92°	156°	161°	(70)
	Å	1.81	1.84	1.84	1.84	1.85													
$_5)_2PdF_6$ (2)	v.u.	1.03	1.00	0.99	0.99	0.97	*	5.98(3)	78°	80°	80°	78°	88°	90°	85°	88°	160°	156°	
	Å	1.82	1.84	1.84	1.84	1.86													
RuF_6	v.u.	1.09	1.00	1.00	0.98	0.98	+	6.11(3)	79°	79°	79°	79°	88°	88°	87°	89°	160°	160°	(80)
	Å	1.79	1.84	1.84	1.85	1.85													
tF_6	v.u.	1.05	0.94	0.94	0.93	0.93	+	5.85(28)	79°	79°	80°	80°	87°	89°	89°	87°	160°	160°	(81)
	Å	1.81	1.81	1.81	1.88	1.88													
$_{11}AuF_6(1)$	v.u.	1.02	1.02	1.02	0.96	0.96	+	6.10(4)	80°	80°	79°	79°	87°	87°	87°	91°	159°	159°	(35)
	Å	1.83	1.83	1.83	1.86	1.86													
$_{11}AuF_6(2)$	v.u.	1.07	1.03	1.03	0.96	0.96	+	6.09(4)	79°	79°	81°	81°	89°	88°	88°	90°	160°	160°	
	Å	1.80	1.82	1.82	1.86	1.86													
(1)	v.u.	1.00		0.96	(average)		X	5.68(13)	77°	(average)			87°	(average)					(36)
	Å	1.84		1.86															
(2)	v.u.	1.16		0.86	(average)		*	5.59(9)	80°	(average)			88°	(average)					
	Å	1.76		1.92															

d ligands

		O	F	F	F	F													
F_4	v.u.	1.83	0.77	0.77	0.73	0.73	X	5.07(5)	90°	90°	88°	88°	89°	88°	88°	89°	179°	179°	(62)
	Å	1.72	1.95	1.95	1.98	1.98													