# **844.** *The Structural Chemistry of Complex Fluorides of General Formula* $A^IB^VF_6$.

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The complex fluorides $A^IB^VF_6$ fall into five structural types, the structure adopted depending on the sizes of the ions A and B. This relation is here discussed. New preparations are also given for some complexes of this general type.

THE structures of complex fluorides of general formula $ABF_6$ have been discussed by Cox[1] who concluded that the distribution of structures cannot be accounted for solely on the basis of the radius ratio of the ions A and B. It is now possible to add considerably to the range of these complexes and it is found that with more data there is a very clearly defined relation between the size of the ions A and B and the structure which is adopted.

The results now available are presented in Table 1. The monopositive cations A form

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[1] Cox, *J.*, 1956, 876.

TABLE 1.

| | $A^+$ | Li | Na | Ag | K | Tl | Rb | Cs |
|---|---|---|---|---|---|---|---|---|
| | $r_{A+}$ | 0·60 | 0·95 | 1·26 | 1·33 | 1·40 | 1·48 | 1·69 |
| B(v) | $r_{A+}/r_{F-}$ | 0·45 | 0·71 | 0·95 | 1·0 | 1·05 | 1·10 | 1·25 |
| | $r_{B5+}$ | | | | | | | |
| P | 0·34 | $R_1{}^{a}\left\{\begin{array}{l} a = 5{\cdot}077 \\ \alpha = 57{\cdot}98^\circ \end{array}\right.$ | $C_1{}^{d}\ a = 7{\cdot}61$ | $C^{b}\ a = 7{\cdot}52$ | $C_2{}^{c}\ a = 7{\cdot}76$<br>$R_2{}^{c}\left\{\begin{array}{l} a = 4{\cdot}85 \\ \alpha = 94^\circ \end{array}\right.$ | $C_2{}^{e}\ a = 7{\cdot}94$ | $C_2{}^{b}\ a = 7{\cdot}92$ | $C_2{}^{c}\ a = 8{\cdot}19$ |
| As | 0·47 | $R_1{}^{a}\left\{\begin{array}{l} a = 5{\cdot}233 \\ \alpha = 57{\cdot}42^\circ \end{array}\right.$ | $R_1{}^{a}\left\{\begin{array}{l} a = 5{\cdot}586 \\ \alpha = 57{\cdot}06^\circ \end{array}\right.$ | $C^{b}\ a = 7{\cdot}74$ | $R_2{}^{bg}\left\{\begin{array}{l} a = 4{\cdot}92 \\ \alpha = 97{\cdot}2^\circ \end{array}\right.$ | $R_2{}^{a}\left\{\begin{array}{l} a = 5{\cdot}04 \\ \alpha = 97{\cdot}0^\circ \end{array}\right.$ | $R_2{}^{b}\left\{\begin{array}{l} a = 5{\cdot}00 \\ \alpha = 96{\cdot}1^\circ \end{array}\right.$ | $R_2{}^{b}\left\{\begin{array}{l} a = 5{\cdot}20 \\ \alpha = 96{\cdot}0^\circ \end{array}\right.$ |
| V | 0·59 | $R_1{}^{a}\left\{\begin{array}{l} a = 5{\cdot}30 \\ \alpha = 56{\cdot}3^\circ \end{array}\right.$ | $R_1{}^{a}\left\{\begin{array}{l} a = 5{\cdot}629 \\ \alpha = 56{\cdot}55^\circ \end{array}\right.$ | $T^{a}\left\{\begin{array}{l} a = 4{\cdot}90 \\ c = 9{\cdot}42 \end{array}\right.$ | $R_2{}^{h}\left\{\begin{array}{l} a = 4{\cdot}92 \\ \alpha = 97{\cdot}2^\circ \end{array}\right.$ | $R_2{}^{a}\left\{\begin{array}{l} a = 5{\cdot}10 \\ \alpha = 95{\cdot}2^\circ \end{array}\right.$ | $R_2{}^{b}\left\{\begin{array}{l} a = 5{\cdot}01 \\ \alpha = 97{\cdot}0^\circ \end{array}\right.$ | $R_2{}^{b}\left\{\begin{array}{l} a = 5{\cdot}24 \\ \alpha = 96{\cdot}2^\circ \end{array}\right.$ |
| Ru | 0·6 | $R_1{}^{i}\left\{\begin{array}{l} a = 5{\cdot}39 \\ \alpha = 56{\cdot}0^\circ \end{array}\right.$ | $R_1{}^{i}\left\{\begin{array}{l} a = 5{\cdot}80 \\ \alpha = 55{\cdot}2^\circ \end{array}\right.$ | $T^{a}\left\{\begin{array}{l} a = 4{\cdot}85 \\ c = 9{\cdot}54 \end{array}\right.$ | $R_2{}^{jk}\left\{\begin{array}{l} a = 4{\cdot}97 \\ \alpha = 97{\cdot}4^\circ \end{array}\right.$ | $R_2{}^{a}\left\{\begin{array}{l} a = 5{\cdot}09 \\ \alpha = 96{\cdot}6^\circ \end{array}\right.$ | $R_2{}^{jk}\left\{\begin{array}{l} a = 5{\cdot}07 \\ \alpha = 96{\cdot}9^\circ \end{array}\right.$ | $R_2{}^{jk}\left\{\begin{array}{l} a = 5{\cdot}25 \\ \alpha = 96{\cdot}3^\circ \end{array}\right.$ |
| Ir | 0·6 | $R_1{}^{i}\left\{\begin{array}{l} a = 5{\cdot}41 \\ \alpha = 56{\cdot}0^\circ \end{array}\right.$ | $R_1{}^{i}\left\{\begin{array}{l} a = 5{\cdot}80 \\ \alpha = 55{\cdot}2^\circ \end{array}\right.$ | $T^{a}\left\{\begin{array}{l} a = 4{\cdot}85 \\ c = 9{\cdot}70 \end{array}\right.$ | $R_2{}^{k}\left\{\begin{array}{l} a = 4{\cdot}98 \\ \alpha = 97{\cdot}4^\circ \end{array}\right.$ | | $R_2{}^{a}\left\{\begin{array}{l} a = 5{\cdot}105 \\ \alpha = 97{\cdot}0^\circ \end{array}\right.$ | $R_2{}^{k}\left\{\begin{array}{l} a = 5{\cdot}27 \\ \alpha = 96{\cdot}2^\circ \end{array}\right.$ |
| Os | 0·6 | $R_1{}^{i}\left\{\begin{array}{l} a = 5{\cdot}43 \\ \alpha = 55{\cdot}5^\circ \end{array}\right.$ | $R_1{}^{i}\left\{\begin{array}{l} a = 5{\cdot}80 \\ \alpha = 55{\cdot}2^\circ \end{array}\right.$ | $T^{a}\left\{\begin{array}{l} a = 4{\cdot}92 \\ c = 9{\cdot}58 \end{array}\right.$ | $R_2{}^{k}\left\{\begin{array}{l} a = 4{\cdot}991 \\ \alpha = 97{\cdot}18^\circ \end{array}\right.$ | | $R_2{}^{a}\left\{\begin{array}{l} a = 5{\cdot}106 \\ \alpha = 96{\cdot}74^\circ \end{array}\right.$ | $R_2{}^{k}\left\{\begin{array}{l} a = 5{\cdot}28 \\ \alpha = 96{\cdot}1^\circ \end{array}\right.$ |
| Re | 0·6 | $R_1{}^{a}\left\{\begin{array}{l} a = 5{\cdot}43 \\ \alpha = 55{\cdot}5^\circ \end{array}\right.$ | $C_1{}^{l}\ a = 8{\cdot}18$ | | $T^{a}\left\{\begin{array}{l} a = 5{\cdot}044 \\ c = 10{\cdot}09 \end{array}\right.$ | | $R_2{}^{l}\left\{\begin{array}{l} a = 5{\cdot}11 \\ \alpha = 96{\cdot}7^\circ \end{array}\right.$ | $R_2{}^{l}\left\{\begin{array}{l} a = 5{\cdot}28 \\ \alpha = 95{\cdot}9^\circ \end{array}\right.$ |
| Mo | 0·6 | $R_1{}^{a}\left\{\begin{array}{l} a = 5{\cdot}43 \\ \alpha = 57{\cdot}1^\circ \end{array}\right.$ | $C_1{}^{m}\ a = 8{\cdot}15$ | | $T^{am}\left\{\begin{array}{l} a = 5{\cdot}88 \\ c = 9{\cdot}98 \end{array}\right.$ | $R_2{}^{a}\left\{\begin{array}{l} a = 5{\cdot}135 \\ \alpha = 96{\cdot}13^\circ \end{array}\right.$ | $R_2{}^{m}\left\{\begin{array}{l} a = 5{\cdot}11 \\ \alpha = 96{\cdot}5^\circ \end{array}\right.$ | $R_2{}^{m}\left\{\begin{array}{l} a = 5{\cdot}29 \\ \alpha = 96{\cdot}0^\circ \end{array}\right.$ |
| W | 0·6 | $R_1{}^{a}\left\{\begin{array}{l} a = 5{\cdot}45 \\ \alpha = 57{\cdot}4^\circ \end{array}\right.$ | $C_1{}^{m}\ a = 8{\cdot}18$ | | $T^{am}\left\{\begin{array}{l} a = 5{\cdot}85 \\ c = 10{\cdot}08 \end{array}\right.$ | | $R_2{}^{m}\left\{\begin{array}{l} a = 5{\cdot}14 \\ \alpha = 97{\cdot}6^\circ \end{array}\right.$ | $R_2{}^{m}\left\{\begin{array}{l} a = 5{\cdot}31 \\ \alpha = 95{\cdot}5^\circ \end{array}\right.$ |
| Sb | 0·62 | $R_1{}^{an}\left\{\begin{array}{l} a = 5{\cdot}438 \\ \alpha = 57{\cdot}01^\circ \end{array}\right.$ | $C_1{}^{oq}\ a = 8{\cdot}18$ | $T^{a}\left\{\begin{array}{l} a = 4{\cdot}96 \\ c = 9{\cdot}61 \end{array}\right.$ | $T^{a}\left\{\begin{array}{l} a = 5{\cdot}151 \\ c = 10{\cdot}041 \end{array}\right.$ | $R_2{}^{p}\left\{\begin{array}{l} a = 5{\cdot}16 \\ \alpha = 96{\cdot}0^\circ \end{array}\right.$ | $R_2{}^{p}\left\{\begin{array}{l} a = 5{\cdot}11 \\ \alpha = 96{\cdot}5^\circ \end{array}\right.$ | $R_2{}^{p}\left\{\begin{array}{l} a = 5{\cdot}32 \\ \alpha = 96{\cdot}9^\circ \end{array}\right.$ |
| Nb | 0·70 | $R_1{}^{a}\left\{\begin{array}{l} a = 5{\cdot}473 \\ \alpha = 58{\cdot}09^\circ \end{array}\right.$ | $C_1{}^{ab}\ a = 8{\cdot}26$ | $T^{a}\left\{\begin{array}{l} a = 4{\cdot}968 \\ c = 9{\cdot}551 \end{array}\right.$ | $T^{f}\left\{\begin{array}{l} a = 5{\cdot}18 \\ c = 10{\cdot}05 \end{array}\right.$ | $R_2{}^{a}\left\{\begin{array}{l} a = 5{\cdot}142 \\ \alpha = 96{\cdot}37^\circ \end{array}\right.$ | $R_2{}^{b}\left\{\begin{array}{l} a = 5{\cdot}14 \\ \alpha = 96{\cdot}4^\circ \end{array}\right.$ | $R_2{}^{b}\left\{\begin{array}{l} a = 5{\cdot}32 \\ \alpha = 95{\cdot}8^\circ \end{array}\right.$ |
| Ta | 0·70 | $R_1{}^{a}\left\{\begin{array}{l} a = 5{\cdot}479 \\ \alpha = 58{\cdot}05^\circ \end{array}\right.$ | $C_1{}^{ab}\ a = 8{\cdot}28$ | $T^{a}\left\{\begin{array}{l} a = 4{\cdot}993 \\ c = 9{\cdot}634 \end{array}\right.$ | $T^{f}\left\{\begin{array}{l} a = 5{\cdot}20 \\ c = 10{\cdot}05 \end{array}\right.$ | $R_2{}^{a}\left\{\begin{array}{l} a = 5{\cdot}148 \\ \alpha = 96{\cdot}34^\circ \end{array}\right.$ | $R_2{}^{b}\left\{\begin{array}{l} a = 5{\cdot}14 \\ \alpha = 96{\cdot}4^\circ \end{array}\right.$ | $R_2{}^{b}\left\{\begin{array}{l} a = 5{\cdot}32 \\ \alpha = 95{\cdot}8^\circ \end{array}\right.$ |

The structures of $A^IB^VF_6$ compounds.

$C_1$, Cubic $NaSbF_6$ structure; $C_2$, cubic $CsPF_6$ structure; $R_1$, rhombohedral, $LiSbF_6$ structure; $R_2$ rhombohedral, $KOsF_6$ structure; $T$, tetragonal $KNbF_6$ structure.

References: *a*, Present work. *b*, Cox, *J.*, 1956, 876. *c*, Bode and Clausen, *Z. anorg. Chem.*, 1951, **265**, 229. *d*, Bode and Teufer, *ibid.*, 1952, **268**, 20. *e*, Bode and Teufer, *Z. anorg. Chem.*, 1952, **268**, 129. *f*, Bode and Döhren, *Acta Cryst.*, 1958, **11**, 80. *g*, Roof, *Acta Cryst.*, 1955, **8**, 739. *h*, Klemm, *Angew. Chem.*, 1954, **66**, 468. *i*, Boston and Sharp, *J.*, 1960, 907. *j*, Weise and Klemm, *Z. anorg. Chem.*, 1955, **279**, 74. *k*, Hepworth, Jack, and Westland, *J. Inorg. Nuclear Chem.*, 1956, **2**, 79. *l*, Peacock, *J.*, 1957, 467. *m*, Hargreaves and Peacock, *J.*, 1957, 4212. *n*, Burns, *Acta Cryst.*, 1962, **15**, 1098. *o*, Schrewelius, *Z. anorg. Chem.*, 1938, **238**, 241. *p*, Schrewelius, *Ark. Kemi, Mineral Geol.*, 1942, *B*,**16**, 1. *q*, Teufer, *Acta Cryst.*, 1956, **9**, 539.

the columns which are arranged from left to right in order of increasing ionic radius of A. The central pentapositive B atoms forming the rows are listed from top to bottom in order of increasing size. Where no finite differences in ionic radius are available from the literature the order is that which one might expect from a consideration of the position of the atom in the Periodic Table. It appears that these compounds contain discrete $BF_6^-$ anions and there is no real justification for using ionic radii as a measure of the size of B, but, in the absence of covalent radii, it is not unreasonable to assume that the actual size of the atoms in the complexes will follow the order of ionic radii. With the exception of seven missing compounds which would be extremely difficult to prepare, the 84 listed complexes have only five basic structure types. In some cases the structures found in the present work are different from those previously recorded. This could be due to the examination of other phases by previous investigators, but where there is good reason the result obtained in this work has been recorded. In such cases the discrepancy is discussed further. The five structural types adopted by $ABF_6$ structures are discussed below.

(*a*) $LiSbF_6$ *structure* ($R_1$).—This rhombohedral structure is found exclusively among the complex fluorides of the smaller cations ($Li^+$ and $Na^+$). The structural type was first recognised by Jack [2] in sodium hexafluoro-osmate(v), and a recent complete structure determination on lithium hexafluoroantimonate(v) by Burns [3] has shown that the structure may be considered as a slightly distorted sodium chloride lattice made up of $Li^+$ and $SbF_6^-$ ions. The hexafluoroantimonate(v) ion is a regular octahedron and each lithium ion is octahedrally co-ordinated by fluorines from six $SbF_6^-$ groups. The basic lattice is the same as that in vanadium trifluoride [4] (Table 2) with lithium and antimony ions occupying the positions of the vanadium atoms. The Li–F bonds are longer than the Sb–F bonds and discrete $SbF_6^-$ octahedra exist in the lattice. As expected from this relationship between the two lattices, the $R_1$-type lattice occurs only when the ions A and B are of comparable size and both are small.

(*b*) and (*c*) $NaSbF_6$ *structure* ($C_1$) *and* $CsPF_6$ *structure* ($C_2$).—Both structures are cubic and are related to the sodium chloride lattice but structure $C_1$ is based on a face-centred unit cell whilst structure $C_2$ is based on a primitive unit cell. The sodium hexafluoroantimonate structure [5] has a sodium chloride lattice of $Na^+$ and $SbF_6^-$ ions with a detailed arrangement of fluorine atoms which was considered by Schrewelius [5] to be similar to that now found in the $LiSbF_6$ structure, that is with octahedral co-ordination by fluorine atoms about the $A^+$ cations. The actual positions of the fluorine atoms have been questioned by Teufer,[6] but the overall structure remains the same. The $C_2$-structure appears to have a co-ordination number of 12 for each $A^+$ cation.[7] It is generally difficult to make a distinction between these two structures (see, for instance, the structure of thallous hexafluorophosphate [8]), but the otherwise anomalous fact that silver hexafluorophosphate has a unit cell smaller than that of sodium hexafluorophosphate [1] is explicable on the basis that the former (and $AgAsF_6$) have $C_2$-type structures whilst the latter has a $C_1$-type structure. There is much confusion in the literature as to the differences between the $C_1$- and the $C_2$-type structure and a full distinction between these must await accurate single-crystal structural determinations on the various compounds.

(*d*) $KNbF_6$ *structure* ($T$).—Most silver salts and some potassium salts have this tetragonal pseudo-cubic structure. A full structure determination on potassium hexafluoroniobate(v) by Bode and Döhren [9] shows that the arrangement is a cæsium chloride type

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[2] Jack, personal communication (1959) on structures of $NaOsF_6$ and $NaIrF_6$.
[3] Burns, *Acta Cryst.*, 1962, **15**, 1098.
[4] Gutmann and Jack, *Acta Cryst.*, 1951, **4**, 246.
[5] Schrewelius, *Z. anorg. Chem.*, 1938, **238**, 241.
[6] Teufer, *Acta Cryst.*, 1956, **9**, 539.
[7] Bode and Clausen, *Z. anorg. Chem.*, 1951, **265**, 229.
[8] Bode and Teufer, *Z. anorg. Chem.*, 1952, **268**, 129.
[9] Bode and Döhren, *Acta Cryst.*, 1958, **11**, 80.

TABLE 2.

Atom co-ordinates in the $VF_3$ and $LiSbF_6$ structures.

| Compound | Space group | B | A | F | A–F | B–F |
|---|---|---|---|---|---|---|
| $VF_3$ * ............ | $R\bar{3}c$ | (0,0,0) | $(\frac{1}{2},\frac{1}{2},\frac{1}{2})$ | (0·645, −0·145, 0·250) | 1·94 | 1·94 |
| $LiSbF_6$ † ...... | $R\bar{3}$ | (0,0,0) | $(\frac{1}{2},\frac{1}{2},\frac{1}{2})$ | (0·656, −0·134, 0·239) | 2·032 | 1·877 |

* Gutman and Jack, *Acta Cryst.*, 1951, **4**, 246. † Burns, *Acta Cryst.*, 1962, **15**, 1098.

lattice made up of $K^+$ and slightly distorted $NbF_6^-$ ions. Each potassium ion has eight fluorine atoms as nearest neighbours with four further fluorines as next nearest neighbours. Cox [1] and Sharp and Sharpe [10] considered that $KNbF_6$, $KTaF_6$, $AgVF_6$, $AgNbF_6$, and $AgTaF_6$ have cubic unit cells but the present work has given photographs of tetragonal phases only. Tetragonal phases were found for $KMoF_6$, $KWF_6$, and $KReF_6$ by Hargreaves and Peacock [11,12] but the *a* parameter was doubled. In the present work an *a* parameter similar to that found for $KNbF_6$ was recorded for these compounds. Bode and Voss [13,14] have concluded that $KSbF_6$ and $AgSbF_6$ have cubic cæsium chloride type structures and it may well be that different phases were studied by these authors. However, the *X*-ray powder photographs of samples prepared in the present work give $\sin^2\theta$ values which agree closely with many of the values published by Bode and Voss, and it is considered that the tetragonal unit cell of the $KNbF_6$ type describes the present values more accurately.

(*e*) $KOsF_6$ *structure* ($R_2$).—This rhombohedral structure is found amongst complex fluorides containing the largest cations ($Tl^+$, $Rb^+$, $Cs^+$) and amongst some potassium salts. The structure of $KOsF_6$ has been described by Hepworth, Jack, and Westland [15] and is closely related to the $BaSiF_6$ structure assigned by Hoard and Vincent.[16] $KOsF_6$ has a space group of slightly lower symmetry ($R\bar{3}$ compared with $R\bar{3}m$) than $BaSiF_6$, the lowering of symmetry being associated with a distortion of the $OsF_6^-$ octahedron by contraction along a three-fold axis. The present work would not distinguish between two such closely similar lattices and such a contraction is not ruled out in $BaSiF_6$ itself, the distortion increasing the regularity of the co-ordination about the barium ion. In both of these structures, which are related to the cæsium chloride lattice, the cation A is surrounded by twelve roughly close-packed fluorine atoms. Potassium hexafluoroplatinate(v) [17] has been shown to have this $R_2$ structure; other hexafluoroplatinates are not known but it would be expected that their structures would be closely similar to the hexafluoroiridates(v).

An examination of the distribution of the five structures over the range of compounds covered in Table 1 suggests that the major factor controlling the lattice type is the ionic radius of the cation A. As the size of the cation increases it will seek a higher co-ordination number and it is found that the co-ordination number of A does increase from 6 in $R_1$ and $C_1$ to 8 plus 4 in *T* and 12 in $R_2$ and $C_2$. Thus all lithium salts have the $R_1$, 6-co-ordinate, structure whereas all cæsium salts (except $CsPF_6$) have the $R_2$, 12-co-ordinate, structure and the $C_1$, $C_2$, and *T* structures are distributed between the two extremes. The prediction of Hoard and Vincent [16] that the barium hexafluorosilicate (essentially $R_2$-type) structure will occur among compounds $ABX_6$ when the radius ratio A : X is greater than one is vindicated in the case of the complex fluorides except for the hexafluorophosphates and a few potassium salts where the radius ratio is almost exactly unity. It is apparent that an increase in the co-ordination number of the $A^+$ cation can sometimes occur at the expense of a distortion of the $BF_6^-$ group. Such a possibility has already

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[10] Sharp and Sharpe, *J.*, 1956, 1855.
[11] Peacock, *J.*, 1957, 467.
[12] Hargreaves and Peacock, *J.*, 1957, 4212.
[13] Bode and Voss, *Z. anorg. Chem.*, 1951, **264**, 144.
[14] Bode, *Z. anorg. Chem.*, 1951, **267**, 62.
[15] Hepworth, Jack, and Westland, *J. Inorg. Nuclear Chem.*, 1956, **2**, 79.
[16] Hoard and Vincent, *J. Amer. Chem. Soc.*, 1940, **62**, 3126.
[17] Bartlett and Lohmann, *Proc. Chem. Soc.*, 1962, 115.

been mentioned in the $KOsF_6$ and $BaSiF_6$ structures, and Roof[18] has found that in $KAsF_6$ the octahedron is also distorted.

Since the central atom in the $BF_6^-$ groups is generally small, it is not unexpected that variation in B appears to have only a second-order effect on the actual structure adopted; thus all the cæsium salts studied, with the exception of $CsPF_6$, are isomorphous. The hexafluorophosphates appear to be anomalous on account of the very small size of the phosphorus(v) atom, but it must be added that, since potassium hexafluorophosphate exists in two phases, the $R_2$-type phase being completely in character with the position of $KPF_6$ in the Table of structures, $TlPF_6$, $RbPF_6$, and $CsPF_6$ should be capable of existing in the $R_2$-type phase. The presence of partially filled *d* orbitals in transition-metal derivatives should also produce some distortions in the octahedral $BF_6^-$ groupings. The examples considered in the present work which would come into this category are the Mo(v) and W(v) $d^1$, Re(v) $d^2$, and Ir(v) $d^4$ salts [Ru(v) and Os(v) are $d^3$ configurations and should have symmetrical octahedral environments]. As far as is detectable by *X*-ray powder photography, the structures of complex salts containing the above ions are completely regular and any distortions due to incompletely filled *d* shells are too small to be detected by this method and in any case are probably smaller than distortions produced by the size of the cation A.

Although the structures of seven compounds which should be included in Table 1 are unavailable owing to difficulties in preparation, it is not unreasonable to assume that they will fit in the existing sequences observed. Thus the thallium salts $TlIrF_6$, $TlOsF_6$, $TlReF_6$, and $TlWF_6$ are expected to have the rhombohedral $R_2$ structure and the silver salts $AgReF_6$, $AgMoF_6$, and $AgWF_6$ the tetragonal *T* structure.

## EXPERIMENTAL

Samples for *X*-ray examination were sealed in Lindemann glass capillaries with warm picein wax; all compounds were handled in a glove-box. *X*-Ray powder photographs were obtained by using Cu-$K_\alpha$ or Co-$K_\alpha$ radiation and were generally taken on a 9-cm. camera, although occasional use was made of a 19-cm. camera and also of a Guinier focussing camera. The calculations leading to the derivation of cell dimensions were made on the Ferranti Sirius computer of the Royal College of Science and Technology, Glasgow, with programmes written by one of us (D. R. R.). Final values of the cell constants were calculated by a least-squares method incorporating the Nelson–Riley function in an attempt to correct for systematic errors.[19] In general, the internal error of the values given in Table 1 was less than 0·2%.

*Preparations.—Phosphorus.* Lithium hexafluorophosphate(v) prepared by the action of bromine trifluoride on lithium fluoride and an excess of phosphorus pentoxide always contains lithium fluoride. A sample prepared by the action of phosphorus pentafluoride on lithium fluoride in anhydrous hydrogen fluoride for 12 hr. at 25° in a steel bomb contained only trace quantities of lithium fluoride. It was analysed for lithium as lithium sulphate (Found: Li, 4·7%. Calc. for $LiPF_6$: Li, 4·54%).

*Arsenic.* Alkali-metal hexafluoroarsenates were prepared by the action of bromine trifluoride on a mixture of alkali-metal halide and arsenic trioxide as described previously.[20] Thallium(I) hexafluoroarsenate was prepared by the action of arsenic pentafluoride on a solution of thallous fluoride in selenium tetrafluoride. The excess of selenium tetrafluoride was removed on heating but some decomposition occurred. Four *X*-ray powder lines out of the twenty observed could not be indexed and are attributed to decomposition products.

*Vanadium.* Lithium, sodium, and silver hexafluorovanadates have been prepared by the action of bromine trifluoride on a mixture of the alkali-metal halide or silver powder and vanadium trichloride.[21] The *X*-ray powder photographs of these products were found to vary from one sample to another and hexafluorovanadates were best prepared by the action of vanadium pentafluoride on a solution of the metal fluoride in anhydrous hydrogen fluoride

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[18] Roof, *Acta Cryst.*, 1955, **8**, 739.

[19] International Tables of Crystallography, Vol. II, Kynoch Press, Birmingham, 1959, p. 225.

[20] Emeléus and Woolf, *J.*, 1950, 165.

[21] Emeléus and Gutmann, *J.*, 1949, 2979.

at 50° in a steel bomb. Vanadium was estimated by titration with permanganate after hydrolysis and reduction with sulphur dioxide [Found (Li): V, 28·9. Calc. for $LiVF_6$: V, 29·6%. Found (Na): V, 26·6. Calc. for $NaVF_6$: V, 27·1%. Found (Ag): V, 19·0. Calc. for $AgVF_6$: V, 18·7%. Found (Tl): equiv., 124. Calc. for $TlVF_6$: equiv., 123].

*Ruthenium.* Silver hexafluororuthenate(v) was prepared by the action of bromine trifluoride on a 1 : 1 mixture of ruthenium metal and silver powder[22] (Found: Ag, 32·9. Calc. for $AgRuF_6$: Ag, 33·3%). Thallium(I) hexafluororuthenate was obtained by interaction of thallium(I) fluoride and ruthenium pentafluoride in anhydrous hydrogen fluoride (Found: Tl, 49·8. Calc. for $TlRuF_6$: Tl, 48·6%) (Tl determined as $Tl_2CrO_4$).

*Iridium.* Silver and rubidium hexafluoroiridates(v) were prepared as previously described[23] by fluorination of 1 : 1 mixtures of silver powder or rubidium chloride and $IrBr_3$ with bromine trifluoride.

*Osmium.* Silver and rubidium hexafluoro-osmates(v) were prepared as previously described,[23] by fluorination of 1 : 1 mixtures of silver powder or rubidium chloride and osmium tetrabromide with bromine trifluoride.

*Rhenium.* Lithium hexafluororhenate(v) was prepared by the action of lithium iodide on rhenium hexafluoride in liquid sulphur dioxide.[11] It is extremely unstable and did not give consistent analyses. Eight powder lines out of 23 could not be indexed. Potassium hexafluororhenate(v) was prepared by interaction of potassium iodide and rhenium hexafluoride in liquid sulphur dioxide.[11]

*Molybdenum. Lithium* and *thallium*(I) *hexafluoromolybdate*(v) were prepared by fluorination of 1 : 1 mixtures of the metal fluoride and molybdenum hexacarbonyl with sulphur tetrafluoride[24] (Found: Mo, 44·5. $LiMoF_6$ requires Mo, 44·2%. Found: Mo, 24·0. $TlMoF_6$ requires Mo, 23·2%).

*Tungsten.* Lithium hexafluorotungstate(v) was prepared by interaction between lithium iodide and tungsten hexafluoride in liquid sulphur dioxide.[12] The compound is extremely unstable, decomposing even at 50° *in vacuo*. Five powder lines out of 19 could not be indexed and are considered to be due to decomposition products. Potassium hexafluoromolybdate(v) and hexafluorotungstate(v) were indexed on photographs taken by Hargreaves and Peacock.

*Antimony.*—Hexafluoroantimonates(v) were prepared, as previously described, by fluorination of equivalent quantities of antimony trioxide and a metal halide with bromine trifluoride.[25]

*Niobium and tantalum.* Lithium, sodium, and thallium(I) hexafluoroniobates(v) and hexafluorotantalates(v) were prepared by fluorination of 2 : 1 mixtures of the metal fluoride and niobium pentoxide with sulphur tetrafluoride.[24] Silver hexafluoroniobate and hexafluorotantalate(v) were prepared, as previously described,[10] by fluorination of silver powder and niobium pentoxide with bromine trifluoride. Niobium and tantalum were estimated by weighing as $Nb_2O_5$ and $Ta_2O_5$, respectively [Found (Li): Nb, 43·6; $LiNbF_6$ requires Nb, 43·4%. Found (Tl): Nb, 23·1. $TlNbF_6$ requires Nb, 22·6%. Found (Na): Na, 39·8. $NaNbF_6$ requires Nb, 40·4%. Found (Li): Ta, 59·3. $LiTaF_6$ requires Ta, 59·9%. Found (Tl): Ta, 36·6. $TlTaF_6$ requires Ta, 36·2%. Found (Na): Ta, 56·1. $NaTaF_6$ requires Ta, 56·9%].

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