186. *Complex Fluorides. Part IV.* The Structural Chemistry of Complex Fluorides of the General Formula* ABF_6.

By B. Cox.

Lattice constants for a large number of complex fluorides of the formula ABF_6 have been determined. The distribution of the $NaSbF_6$, $KSbF_6$, and $BaSiF_6$ structures in this series cannot be accounted for solely by radius-ratio effects.

In Part I[1] a discussion of the occurrence of the dipotassium hexafluoro-silicate (cubic), germanate (trigonal), and -manganate (hexagonal) structures among complex fluorides of the formula A_2BF_6 (where A is a large cation) led to the conclusion that the distribution is, to a first approximation, random. In this paper the distribution of the common structures in the complex fluorides of general formula ABF_6 is considered; here A may be a univalent or bivalent cation with B a quinquevalent or quadrivalent element respectively. The results of many new partial structure determinations, together with data by earlier workers, are summarised in Table 1.

We conclude that, as with members of the A_2BF_6 series, the distribution of structures cannot be satisfactorily interpreted solely on the basis of radius-ratio effects. Although most salts of the larger cations crystallise with the trigonal barium hexafluorosilicate structure (co-ordination number round the cation 8), described by Wells[2] as a distorted cæsium chloride-type of structure, and many salts of smaller cations crystallise with the sodium chloride structure (co-ordination number 6), the hexafluorophosphates examined all crystallise with the latter structure. Potassium, rubidium, and cæsium hexafluorophosphates are thus the only members of the series in which potassium, rubidium, and cæsium possess the lower co-ordination number.

It should be noted that the cell side reported for sodium hexafluorophosphate[3] is larger than that found for the silver salt. Comparison of the cell dimensions of the hexafluorophosphates and the corresponding fluorides (Table 2), which have the same structure, suggests that, of these two, the lattice constant of the silver salt is very close to the value which would be expected for it, whereas that of the sodium salt is not. However, Bode's value for the cell constant of sodium hexafluorophosphate has been confirmed and the anomaly in the length of the cell sides of the sodium and silver salts remains unexplained.

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* Part III, *J.*, 1954, 3251.

[1] Part I, Cox and Sharpe, *J.*, 1953, 1783.
[2] Wells, "Structural Inorganic Chemistry," 2nd Edition, Oxford, 1950, p. 294.
[3] Table 1, ref. *c*.

TABLE 1. *Structures of* ABF_6 *type.*

Structural type is indicated by: C (CsCl), N (NaCl), or T (trigonal). Values of *a* are followed by α (in parentheses). Anions are in order of increasing size as determined from the cell sides of their trigonal salts.

	Na^+	Ag^+	K^+		
Anion	Ca^{2+}	Sr^{2+}	Ba^{2+}	Rb^+	Cs^+
SiF_6^{2-}	—	—	T [a] 4·75 (98°)	—	—
GeF_6^{2-}	—	—	T [a] 4·83 (98)	—	—
PF_6^-	N 7·61 [b,c]	N 7·52 [b]	N 7·76 [d] T [d] 4·85 (94)	N 7·92 [b]	N 8·19 [b,d]
TiF_6^{2-}	—	—	T [b,e] 4·87 (98·2)	—	—
RuF_6^{2-}	—	—	T [f,g] 4·87 (98)	—	—
PtF_6^{2-}	—	T [h] 4·74 (97·8°)	T [g,h] 4·88 (98)	—	—
PdF_6^{2-}	—	T [h] 4·72 (98·2)	T [h] 4·88 (98·4)	—	—
AsF_6^-	—	N 7·74 [b]	T [b] 4·92 (97·2)	T [b] 5·00 (97·1°)	T [b] 5·20 (96°)
VF_6^-	—	C 9·52 [b]	T [b,g] 4·92 (97·2)	T [b] 5·01 (97)	T [b] 5·24 (96·2
RuF_6^-	—	—	T [f,g] 4·96 (97·5)	T [f,g] 5·08 (97)	T [f,g] 5·25 (96·2)
SnF_6^{2-}	—	—	T [b,g] 4·97 (96·4)	—	—
SbF_6^-	N 8·18 [i]	C 9·85 [i,j]	C 10·15 [k]	T [l] 5·11 (96·5)	T [l] 5·32 (96·9)
TaF_6^-	N 8·27 [b]	—	C 10·29 [b]	T 5·14 (96·4) [b]	T 5·32 (95·8) [b]
NbF_6^-	N 8·27 [b]	—	C 10·29 [b]	T 5·14 (96·4) [b]	T 5·32 (95·8) [b]

[a] Hoard and Vincent, *J. Amer. Chem. Soc.*, 1940, **62**, 3126. [b] Present work. [c] Bode and Teufer, *Z. anorg. Chem.*, 1952, **268**, 20. [d] Bode and Clausen, *ibid.*, 1951, **265**, 229. [e] Hanawalt, Rinne, and Frevel, *Ind. Eng. Chem. Anal.*, 1938, **10**, 457. [f] Weise and Klemm, *Z. anorg. Chem.*, 1955, **279**, 74. [g] Klemm, *Angew. Chem.*, 1954, **66**, 468. [h] D. W. A. Sharp, personal communication. [i] Schrewelius, *Z. anorg. Chem.*, 1938, **238**, 241. [j] Bode, *ibid.*, 1951, **267**, 62. [k] Bode and Voss, *ibid.*, 1951, **264**, 144. [l] Schrewelius, *Arkiv Kemi*, 1942, *B*, **16**, No. 7.

TABLE 2.

	NaF [m]	AgF [m]	KF [m]	RbF [m]	CsF [m]	$NaPF_6$ [c]	$AgPF_6$ [b]	KPF_6 [b,d]	$RbPF_6$ [b]	$CsPF_6$ [b,d]
a (Å) ...	4·62	4·92	5·34	5·64	6·01	7·61	7·52	7·76	7·92	8·19
Increase	—	0·30	0·42	0·30	0·37	—	Negative	0·24	0·16	0·27

[m] Wyckoff, "Crystal Structures," Interscience, New York, 1951. For other refs. see Table 1.

In view of the interest in the structure of the iodohexafluoride ion,[4] attempts were made to determine the structures of potassium, rubidium, and cæsium iodohexafluorides. A powder photograph which could be indexed on a cubic cell ($a = 11{\cdot}90$ Å) was obtained for the potassium salt; this could not be repeated, however, and similar photographs could not be obtained for the rubidium or cæsium salts.

EXPERIMENTAL

Phosphorus.—Hexafluorophosphates of silver, rubidium, and cæsium were prepared by fluorination of a mixture of the metal, or metal chloride, and excess of phosphoric oxide with bromine trifluoride. Sodium fluorophosphate was prepared by fluorination of sodium metaphosphate (prepared by heating sodium dihydrogen phosphate to 600°) with bromine trifluoride[5] (Found: Ag, 42·1. Calc. for $AgPF_6$: Ag, 42·7. Found: PF_6, 63·0. Calc. for $RbPF_6$: PF_6, 62·9. Found: PF_6, 50·6. Calc. for $CsPF_6$: PF_6, 52·1%).

Arsenic.—Lithium, sodium, potassium, rubidium, cæsium, and silver fluoroarsenates were prepared by fluorination of mixtures of the metal halide, or silver, and arsenic trioxide in 1 : 1 molecular proportions with bromine trifluoride.[6] The powder photograph of sodium fluoroarsenate could not be indexed on a cubic unit cell of the sodium chloride type although it was very similar to those of the other sodium salts. The lithium salt is isomorphous with the sodium salt, but again the photograph could not be indexed (Found: As, 36·1. Calc. for $LiAsF_6$: As, 38·2. Found: As, 34·6. Calc. for $NaAsF_6$: As, 35·3. Found: As, 32·4. Calc. for $KAsF_6$: As, 32·9. Found: As, 26·9. Calc. for $RbAsF_6$: As, 27·3. Found: As, 23·05. Calc. for $CsAsF_6$: As, 23·25. Found: Ag, 35·9. Calc. for $AgAsF_6$: Ag, 36·4%).

Vanadium.—Sodium, potassium, rubidium, cæsium, and silver hexafluorovanadates(v) were prepared by fluorination of mixtures of the metal halide, or silver, and vanadium trichloride in

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[4] Sharpe, *Quart. Rev.*, 1950, **4**, 115.

[5] Emeléus and Woolf, *J.*, 1950, 164.

[6] Woolf and Emeléus, *J.*, 1949, 2865.

1 : 1 molecular proportions with bromine trifluoride.[7] The vanadium trichloride was prepared essentially by Emeléus and Gutmann's modification [7] of Ruff and Lickfett's method.[8] Sodium hexafluorovanadate was not isomorphous with sodium hexafluoroantimonate, but was isomorphous with lithium and sodium fluoroarsenates (Found : V, 26·8. Calc. for $NaVF_6$: V, 27·1. Found : V, 25·4. Calc. for KVF_6 : V, 25·0. Found : V, 21·4. Calc. for $RbVF_6$: V, 20·4. Found : V, 16·9. Calc. for $CsVF_6$: V, 17·1%).

Antimony.—The powder photograph of a sample of lithium fluoroantimonate prepared by Woolf [6] showed this compound to be isomorphous with lithium and sodium fluoroarsenates.

Tantalum.—Fluorotantalates of lithium, sodium, potassium, rubidium, and cæsium were prepared by Gutmann and Emeléus's method.[9] The powder photograph of lithium fluorotantalate showed it to be isomorphous and isodimensional with lithium fluoroniobate; the lines could not be indexed, however, and the photograph was not similar to those of the other series of isomorphous lithium and sodium salts whose photographs could not be indexed (Found : Ta, 60·5. Calc. for $LiTaF_6$: Ta, 59·5. Found : Ta, 58·1. Calc. for $NaTaF_6$: Ta, 57·0. Found : Ta, 54·9. Calc. for $KTaF_6$: Ta, 54·4. Found : Ta, 48·7. Calc. for $RbTaF_6$: Ta, 47·6. Found : Ta, 42·5. Calc. for $CsTaF_6$: Ta, 42·3%).

Niobium.—Lithium, sodium, potassium, rubidium, and cæsium fluoroniobates were prepared by Gutmann and Emeléus's method.[9] The powder photograph of lithium fluoroniobate showed it to be isomorphous and isodimensional with lithium fluorotantalate, but no further interpretation was possible (Found : Nb, 43·0. Calc. for $LiNbF_6$: Nb, 43·4. Found : Nb, 39·9. Calc. for $NaNbF_6$: Nb, 40·4. Found : Nb, 38·0. Calc. for $KNbF_6$: Nb, 37·8. Found : Nb, 31·7. Calc. for $RbNbF_6$: Nb, 31·8. Found : Nb, 27·2. Calc. for $CsNbF_6$: Nb, 27·3%).

Titanium.—Barium fluorotitanate was prepared by fluorination of a 1 : 1 mixture of barium chloride and titanium dioxide with bromine trifluoride. Attempts to prepare the calcium and the strontium salt by a similar method resulted in products whose powder photographs bore no resemblance to those of any of the known ABF_6 type structures.

Tin.—Barium fluorostannate was prepared from stannic chloride and barium chloride in 1 : 1 molecular proportions by fluorination with bromine trifluoride. Attempts to prepare the calcium and the strontium salt and to determine their structures were unsuccessful.

Iodine.—Iodohexafluorides were prepared by Aynsley, Nichols, and Robinson's method.[10]

X-Ray powder photographs were taken and interpreted as described in Part II.[11]

Grateful acknowledgment is made to the Department of Scientific and Industrial Research for a Maintenance Grant.

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[7] Emeléus and Gutmann, *J.*, 1949, 2979.
[8] Ruff and Lickfett, *Ber.*, 1911, **44**, 506.
[9] Gutmann and Emeléus, *J.*, 1950, 1046.
[10] Aynsley, Nichols, and Robinson, *J.*, 1953, 623.
[11] Part II, Cox and Sharpe, *J.*, 1954, 1798.