

367. *Complex Fluorides. Part I. The Structural Chemistry of Some Complex Fluorides of Potassium, Rubidium, Cæsium, Ammonium, and Thallium.*

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The occurrence of the K_2SiF_6 (cubic), K_2GeF_6 (trigonal), and K_2MnF_6 (hexagonal) structures among complex fluorides of formula A_2BF_6 (where A is a large univalent cation) is discussed. When prepared at room temperature, K_2TiF_6 , Rb_2TiF_6 , Cs_2TiF_6 , $(NH_4)_2TiF_6$, and Tl_2TiF_6 are isomorphous with K_2GeF_6 . Hexagonal forms of K_2TiF_6 and Rb_2TiF_6 , and cubic forms of K_2TiF_6 , Rb_2TiF_6 , Cs_2TiF_6 , and Tl_2TiF_6 have been obtained by heating samples at 300–350°. Except in $(NH_4)_3FeF_6$, there is at present no evidence for hydrogen bonding as an important factor in complex fluorides containing the ammonium ion.

It was suggested (Sharpe, *J.*, 1953, 197) that for complex fluorides of formula A_2BF_6 (where A = K, Rb, Cs, NH_4 , Tl) the two well-known structures of K_2SiF_6 and K_2GeF_6 are of nearly equal energy, and that their distribution is approximately a random one. We began a systematic search for further evidence in support of this hypothesis by examining the structures of the fluorotitanates; the recent publication of structural data for the complex fluorides K_2TiF_6 , K_2PdF_6 , Rb_2PdF_6 , K_2MnF_6 , Rb_2MnF_6 , and Cs_2MnF_6 , however, assists us considerably and prompts us to report our own work now and to summarise the present position in this field.

The K_2SiF_6 , K_2GeF_6 , and K_2MnF_6 structures may all be described (following Wells, "Structural Inorganic Chemistry," Oxford, 1945) as built up from close-packed layers of K and F atoms, with the Si, Ge, or Mn atoms in certain of the octahedral holes. In the cubic K_2SiF_6 structure, the layers are arranged in cubic close-packing (layer sequence ABC, ABC); in the ideal trigonal structure, from which K_2GeF_6 deviates slightly, the layers are arranged in hexagonal close-packing (sequence AB, AB); and in the hexagonal K_2MnF_6 structure (first described by Bode and Wendt, *Z. anorg. Chem.*, 1952, **269**, 165) the layers appear to be arranged in double hexagonal close-packing (sequence ABAC, ABAC). All available data for unit-cell dimensions of complex fluorides containing large univalent cations and silicon, germanium, titanium, manganese, nickel, palladium, or platinum are assembled in the Table; for details of the preparation of polymorphic forms by other authors, individual references should be consulted.

In the past, the deviations from ideal close-packing round the alkali-metal atoms in, e.g., K_2GeF_6 and Rb_2GeF_6 have probably attracted too much attention; but it should be pointed out that similar minor deviations also exist in K_2PtF_6 , K_2TiF_6 , and Cs_2PuCl_6 (Zachariasen, *Acta Cryst.*, 1948, **1**, 268). Furthermore, since most of the other complex fluorides (some of which are very unstable) have been subjected only to partial examination by powder methods, departures from ideal close-packing may be quite common. Nevertheless, the irregular distribution of the K_2SiF_6 , K_2GeF_6 , and K_2MnF_6 structures, and the existence of some of the complex fluorides in three modifications, suggest that the three structures are energetically equivalent and that their distribution is a random one.

The similarity in unit-cell dimensions between $(NH_4)_2TiF_6$ and Rb_2TiF_6 suggests that hydrogen bonding plays no significant part in determining the structure of the former compound [cf. Vincent and Hoard (*loc. cit.*), who made a similar observation on $(NH_4)_2GeF_6$ and Rb_2GeF_6]. Ammonium hexafluoroferrate (Pauling, *J. Amer. Chem. Soc.*, 1924, **46**, 2738; Minder, *Z. Krist.*, 1937, **96**, 15; Rice, Turner, and Brydon, *Nature*, 1952, **169**, 749) remains the only ammonium complex fluoride in which the unit cell is very much smaller than that of the analogous rubidium compound. Since FeF_6^{3-} is the only complex fluoride ion of known structure in which magnetic properties unambiguously indicate the presence of "ionic" or weak covalent bonds (see Nyholm and Sharpe, *J.*, 1952, 3579, for discussion) there may be a correlation between the weakness of the iron-fluorine bonds and the strength of the hydrogen bonding between fluorine and nitrogen. It is hoped to provide further

evidence concerning the existence of such a correlation by the preparation of ammonium fluorocobaltate, $(\text{NH}_4)_3\text{CoF}_6$, and the determination of its unit-cell size and magnetic moment.

Unit-cell dimensions (in Å).

	K_2	Rb_2	Cs_2	$(\text{NH}_4)_2$	Tl_2
SiF_6					
Trigonal...	—	—	—	$a=5.76, c=4.77$ ¹³	—
Cubic	$a=8.13, 8.17$ ¹⁰	$a=8.45$ ¹⁰	$a=8.87, 8.89$ ¹	$a=8.34, 8.38$ ¹²	$a=8.56, 8.60$ ¹¹
GeF_6					
Trigonal...	$a=5.62, c=4.65$ ⁷	$a=5.82, c=4.79$ ⁸	—	$a=5.85, c=4.77$ ⁷	—
Hexagonal	$a=5.71, c=9.27$ ⁶	$a=5.94, c=9.63$ ⁶	—	—	—
Cubic	—	—	$a=8.99$ ⁹	—	—
TiF_6					
Trigonal...	$a=5.71, c=4.65$ ^{1, 15}	$a=5.88, c=4.78$ ¹	$a=6.15, c=4.96$ ¹	$a=5.96, c=4.82$ ¹	$a=5.92, c=4.84$ ¹
Hexagonal	$a=5.75, c=9.46$ ¹	$a=5.91, c=9.81$ ¹	—	—	—
Cubic	$a=8.32$ ¹	$a=8.49$ ¹	$a=8.96$ ¹	—	$a=8.46$ ¹
MnF_6					
Trigonal...	$a=5.71, c=4.65$ ⁵	—	—	—	—
Hexagonal	$a=5.70, c=9.35$ ⁵	$a=5.85, c=9.50$ ⁵	—	—	—
Cubic	$a=8.28$ ⁵	$a=8.43$ ⁵	$a=8.92$ ⁵	—	—
NiF_6					
Cubic	$a=8.11$ ¹⁴	—	—	—	—
PdF_6					
Hexagonal	$a=5.75, c=9.51$ ⁴	$a=5.98, c=9.70$ ¹	—	—	—
Cubic	—	$a=8.57$ ⁴	$a=9.00, 9.01$ ²	—	—
PtF_6					
Trigonal...	$a=5.76, c=4.64$ ^{2, 3}	$a=5.96, c=4.83$ ²	$a=6.22, c=5.01$ ²	—	—

¹ Present work. ² Sharpe, *J.*, 1953, 197. ³ Mellor and Stephenson, *Austral. J. Sci. Res.*, 1951, 4, 406. ⁴ Hoppe and Klemm, *Z. anorg. Chem.*, 1952, 268, 364. ⁵ Bode and Wendt, *ibid.*, 269, 165. ⁶ Bode and Brockmann, *ibid.*, p. 173. ⁷ Hoard and Vincent, *J. Amer. Chem. Soc.*, 1939, 61, 2849. ⁸ Vincent and Hoard, *ibid.*, 1942, 64, 1233. ⁹ Wyckoff and Müller, *Amer. J. Sci.*, 1927, 13, 347. ¹⁰ Ketelaar, *Z. Krist.*, 1935, 92, 155. ¹¹ Tabet, *Gazzetta*, 1933, 63, 679. ¹² Bozorth, *J. Amer. Chem. Soc.*, 1922, 44, 1066. ¹³ Gossner and Kraus, *Z. Krist.*, 1934, 88, 223. ¹⁴ Klemm and Huss, *Z. anorg. Chem.*, 1949, 258, 221. ¹⁵ Siegel, *Acta Cryst.*, 1952, 5, 683.

Experimental.—Fluorotitanates were obtained from titanium dioxide, hydrofluoric acid, and metal fluorides. Titanium was determined as dioxide; thallium in *thallous fluorotitanate* was determined as chromate after precipitation of the titanium [Found, for the K salt: Ti, 20.0. Calc. for K_2TiF_6 : Ti, 20.0. Found, for the Rb salt: Ti, 14.5. Calc. for Rb_2TiF_6 : Ti, 14.4. Found, for the Cs salt: Ti, 11.3. Calc. for Cs_2TiF_6 : Ti, 11.2. Found, for the NH_4 salt: Ti, 24.1. Calc. for $(\text{NH}_4)_2\text{TiF}_6$: Ti, 24.2. Found, for the Tl salt: Tl, 70.7; Ti, 8.4. Tl_2TiF_6 requires Tl, 71.7; Ti, 8.4%].

The existence of polymorphic forms was investigated by heating small samples at temperatures between 275° and 350°; powder photographs of the residues were taken at room temperature. The potassium salt, after being heated at 350° for 24 hr., gave a powder pattern corresponding to a mixture of hexagonal and cubic forms. The structure of the rubidium salt was unchanged after 18 hr. at 275°; after 24 hr. at 300° the powder pattern was that of a mixture of hexagonal and cubic forms. At 300° the caesium salt remained trigonal, but heating it at 350° for 24 hr. resulted in a change to the cubic structure. The ammonium salt decomposed completely at 275°. Thallous fluorotitanate became cubic after 24 hr. at 350°, and was still cubic after six weeks at room temperature.

The sample of rubidium fluoropalladate used had been prepared at 150° (*J.*, 1953, 197).

X-Ray powder photographs were taken with Cu- $K\alpha$ radiation; samples were filled into Pyrex capillaries, the "dry box" technique being used for Rb_2PdF_6 , and the capillaries were sealed off with warm picein wax.

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