# CONTRIBUTIONS TO THE SYSTEMATICS OF FLUOROSILICATES AND FLUOROGERMANATES. III.*

## THALLIUM HEXAFLUOROGERMANATE

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Thallium hexafluorogermanate, $Tl_2GeF_6$, was prepared and by means of X-ray powder analysis it was found to crystallize in the trigonal system of the structural type $K_2GeF_6$ ($D^3_{3D}$ — P $\bar{3}$ ml). Parameters of its unit cell are $a_0 = 5{\cdot}86$ Å and $c_0 = 4{\cdot}87$ Å, which means that the compound belongs to the group IIA of Hoppe's structural systematics of ternary fluorides.

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Ternary fluorides of the type $A^I_2XF_6$, where $A^I = $ K, Rb, Cs and $NH_4$ and X = Ge and Si, crystallize in three structural types: $K_2PtCl_6$ (cubic type), $K_2MnF_6$ (hexagonal type) and $K_2GeF_6$ (trigonal type). In his structural chemical systematics of ternary fluorides, Hoppe[1] classifies them as belonging to the IIA group which also includes all the hitherto known alkali barium hexafluoro complexes of the type $MeMF_6$, as well as the compounds containing anions $[MF_7]^{n-}$, $[MF_5]^{n-}$ and $[MF_4]^{n-}$. All these compounds are ternary fluorides, having in their lattice besides cations Me only mononuclear complex anions $[MF_z]^{x-}$. One can expect a considerable similarity as to the structure and properties of fluorosilicates and fluorogermanates. However, it was found that hexafluorosilicates, $A^I_2SiF_6$ crystallize mostly in cubic system of the type $K_2PtCl_6$ (with ammonium hexafluorosilicate also the less stable trigonal modification is known[2]), whereas hexafluorogermanates $A^I_2GeF_6$ have usually structural lattice of the type $K_2GeF_6$ (except for $Cs_2GeF_6$ which is known only in cubic form[3]).

As a part of the investigation of some fluoro complexes and of their structural chemical systematics we have prepared a further compound of the type $A^I_2XF_6$, thallium hexafluorogermanate $Tl_2GeF_6$ and have identified its structure by means of X-ray powder method.

### EXPERIMENTAL

*Preparation of the compound.* Approximately 30% solution of fluorogermanic acid was prepared by solving germanium(IV) oxide (purity grade "for semiconductors", Lachema) in 40% hydrofluoric acid in an ice-cooled platinum vessel. This solution was treated under constant stirring by adding stepwise 20% aqueous solution of thallium acetate. After addition of the calculated amount (10% excess) 90% ethanol was added to the clear solution, so as to make the final concen-

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tration of ethanol 60%. After some minutes a white, crystallinic precipitate was formed. It was filtrated, washed with 90% ethanol, dissolved in a small amount of water and again precipitated with 90% ethanol. Then the filtrate was dried, first at room temperature in the air for 24 h, and afterwards at 60°C to constant weight.

*Analysis.* Total content of fluorine was determined by titration[4] with 0·04M-$Th(NO_3)_4$. Thallium was determined as chromate according to Mach and Lepper[5]. Germanium was determined as germanium(IV) fluoride according to Tananajev[6]. For thallium hexafluorogermanate, $Tl_2GeF_6$ (595·4) calculated: 68·65% Tl, 12·19% Ge, 19·14% F; found: 68·25% Tl, 12·21% Ge, 19·20% F.

*Roentgenographic measurements.* Diffraction recordings were taken on a X-ray diffractograph Rigaku-Denki (Japan), with radiation $CuK_\alpha = 0{\cdot}1542$ nm, Ni filter, 24 kV, 20 mA, time constant 2, sensitivity 800, region of exposures 2—45°. Relative intensities were evaluated planimetrically.

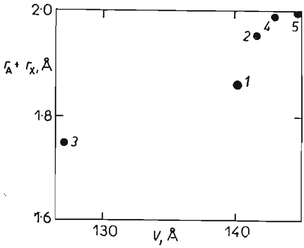

FIG. 1

Dependence of the Volume of Unit Cell, *V*, on the Sum of Ionic Radii $r_A + r_X$ for Hexafluorogermanates of the Type $A^I_2GeF_6$ and for Ammonium Hexafluorosilicate with Trigonal Lattice

*1* $(NH_4)_2SiF_6$, *2* $(NH_4)_2GeF_6$, *3* $K_2GeF_6$, *4* $Rb_2GeF_6$, *5* $Tl_2GeF_6$.

TABLE I

Debyegram of Thallium Hexafluorogermanate, $Tl_2GeF_6$

| $I/I_0$ | d, Å | hkl | $I/I_0$ | d, Å | hkl |
|---|---|---|---|---|---|
| 10 | 5·03 | 100 | 10 | 1·703 | 300 |
| 2 | 4·87 | 001 | 5 | 1·630 | 003 |
| 100 | 3·53 | 101 | 5 | 1·551 | 103 |
| 50 | 2·92 | 110 | 10 | 1·513 | 212 |
| 10 | 2·54 | 111 | 5 | 1·470 | 220 |
| 20 | 2·44 | 002 | 10 | 1·425 | 113 |
| 50 | 2·26 | 201 | 1 | 1·396 | 302 |
| 40 | 2·199 | 102 | 5 | 1·359 | 203 |
| 2 | 1·923 | 210 | 3 | 1·232 | 213 |
| 15 | 1·879 | 112 | 4 | 1·223 | 004 |
| 20 | 1·795 | 211 | 4 | 1·190 | 104 |
| 10 | 1·769 | 202 | 4 | 1·174 | 320 |

## RESULTS

By chemical analysis it was proved that the compound obtained by the above-described procedure is thallium hexafluorogermanate, $Tl_2GeF_6$. From the diffractogram it follows (Table I), upon assigning the *hkl* indexes to the respective diffraction lines, that the compound has a trigonal lattice of the structural type $K_2GeF_6$ (spatial group $D_{3D}^3 - P\,\bar{3}\,ml$) with the parameters of the unit cell $a_0 = 5{\cdot}86$ Å and $c_0 = 4{\cdot}87$ Å. Consequently, this type of hexafluorogermanate ranges with potassium, ammonium and rubidium hexafluorogermanates, also having this kind of crystal lattice, whereas analogous hexafluorosilicates have a cubic lattice. The validity of Gattow's rule[7], concerning the linear dependence (in the first approximation) of the volume of unit cell on the sum of ionic radii ($r_A + r_X = \text{const.}\ V + \text{const.}'$, where $r_A$, $r_X$ are the ionic radii of particles A and X and $V$ is the volume of unit cell) was also verified for hexafluorogermanates of the type $A_2^IGeF_6$ and for ammonium hexafluorosilicate (Fig. 1).

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