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## ELECTROCHEMICAL SYNTHESIS OF THALLIUM FLUORIDES AND STRUCTURE

OF  $Tl_3[SiF_6]F$

V. A. Shreider,\* I. M. Vol'pin,  
and Yu. E. Gorbunova

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Thallium forms stable complexes with the valence of the metal equal to both 1+ and 3+. The development of electrochemical methods of synthesis has made it possible to create a direct method for obtaining complex halides with the general formulas  $R_nNTlX_n$  and  $R_nNTlI_2$ , where  $R = Et$  and  $n-Bu$ , as a result of the anodic dissolution of Tl in the presence of a halogen  $X_2$  ( $X = Cl, Br, I$ ) [1]. However, this approach is not applicable to the electrochemical synthesis of complex fluorides of Tl due to the high reactivity of free fluorine. The traditional methods for the synthesis of complex fluorides of Tl include the titration of solutions of thallium fluoride by the corresponding fluorides [2] and the congruent melting of the fluorides of thallium and other metals [3, 4].

The possibility of the electrochemical synthesis of complex fluorides of Ti, Zr, and Hf as a result of the anodic dissolution of the metal in the presence of  $R_nNF \cdot HF$  ( $R = Et$ ) was previously demonstrated in [5]. In this communication we shall present the results of the electrochemical synthesis of complex fluorides of thallium and an investigation of the structure of  $Tl_3[SiF_6]F$ .

### EXPERIMENTAL

The original reagents, viz., tetralkylammonium fluoride polyhydrofluorides (I) and (II), were obtained according to the method in [6]. Table 1 presents the data from the elemental analysis and titrimetry of these compounds. The electrolysis was carried out in a glass or polyethylene electrochemical cell without a diaphragm. The anode was a metallic thallium rod with a surface area of 2-4 cm<sup>2</sup>, and the cathode was a platinum wire with  $d = 1$  mm and a length of 50 mm. The electrolysis was carried out under galvanostatic conditions with a current equal to 300 mA and a voltage from 10 to 70 V. The compounds obtained were recrystallized in glass or teflon vessels. The melting point was measured on a Kofler hot-stage apparatus, and in the case of melting above 300°C, it was measured in a capillary block furnace. The <sup>19</sup>F NMR spectra were recorded with CF<sub>3</sub>COOH as an external reference on Perkin-Elmer R-32 and Bruker 250 instruments. The x-ray diffraction patterns were obtained on a Dron diffractometer with CuK $\alpha$  radiation. A well-edged single crystal measuring 0.33 × 0.1 × 0.1 mm was used for the x-ray photographing. The experimental set of integrated intensities was obtained on a Syntex P2<sub>1</sub> automatic diffractometer: MoK $\alpha$  radiation (graphite monochromator),  $\theta/2\theta$  scan technique,  $2\theta_{max} = 62^\circ$ . The structure was interpreted and refined with the use of 305 independent reflections with  $I \geq 1.96 \sigma(I)$ . The absorption was not taken into account. The structure was solved by the heavy-atom method on the basis of the Patterson function and a series of ordinary and difference Fourier syntheses. The least-squares refinement of the positional and thermal parameters gave  $R = 0.052$ . The coordinates of the atoms are presented in Table 2, and the interatomic distances are presented in Table 3. The conditions of the electrosynthesis and the characteristics of the compounds obtained are presented in Table 4.

\*Deceased

A. N. Nesmeyanov Institute of Organometallic Compounds, Academy of Sciences of the USSR, Moscow. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 5, pp. 958-963, May, 1988. Original article submitted December 30, 1986.

TABLE 1. Composition of Tetraalkylammonium Fluoride Polyhydrofluorides

Reagent	Compound	Found/Calculated, %			Titer of NaOH (amount of HF/ mole) Found/ Calculated
		C	H	F	
(I)	Et <sub>4</sub> NF·3.2HF·0.3H <sub>2</sub> O	43,95	10,21	36,39	3,2/3,2
		43,96	10,16	36,54	
(II)	Bu <sub>4</sub> NF·14HF·7H <sub>2</sub> O	28,81	8,71	42,64	14,1/14,0
		28,79	8,55	42,73	

TABLE 2. Coordinates of Atoms in the Structure of Tl<sub>3</sub>[SiF<sub>6</sub>]F

Atom	X	Y	Z
Tl	0,16342	-0,16342	0,250
	0,333	0,666	0,750
F <sup>1</sup>	0,468(3)	0,234(4)	0,363(4)
F <sup>2</sup>	0	0	0
F <sup>3</sup>	0,872(3)	0,436(4)	0,094(4)

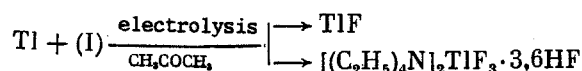
TABLE 3. Principal Interatomic Distances in the Structure of Tl<sub>3</sub>[SiF<sub>6</sub>]F

Bond	d, Å	Bond	d, Å	Bond	d, Å
Si-F <sup>1</sup>	1,57(3)×3	Tl-F <sup>2</sup>	2,830(1)×2	F <sup>1</sup> -F <sup>1</sup>	2,36(4)
Si-F <sup>3</sup>	1,78(2)×3	Tl-F <sup>3</sup>	3,03(3)	F <sup>3</sup> -F <sup>3</sup>	2,45(5)
Tl-F <sup>1</sup>	2,95(3)×2	Tl-F <sup>3</sup>	3,13(3)	F <sup>3</sup> -F <sup>3</sup>	2,33(4)
Tl-F <sup>1</sup>	2,85(3)×2				

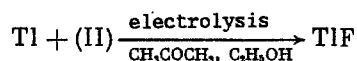
### RESULTS AND DISCUSSION

It was previously shown [5] that the anodic dissolution of group (IVa) elements in the presence of (I) results in the formation of complex fluorides of Ti, Zr, and Hf with the maximum oxidation number of the metal, which is equal to 4+. In the overwhelming majority of cases, the anodic dissolution of Tl in the presence of Cl, Br, and I also produces complex halides with the maximum valence of the metal [1].

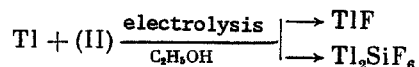
We discovered that the electrochemical dissolution of a thallium anode in the presence of (I) mainly produces the inorganic fluoride of Tl<sup>1+</sup>. However, along with the latter it is possible to recover a small quantity of a complex fluorothallate:



The use of tetrabutylammonium fluoride polyhydrofluoride (II) can result in the formation of several inorganic reaction products, depending on the electrolysis conditions. When the synthesis is carried out in a polyethylene electrochemical cell with subsequent crystallization of the compound obtained in teflon vessels, only the fluoride of univalent thallium was recovered regardless of the solvent used (acetone or ethanol):



However, the use of a glass cell drastically complicated the picture. For example, when ethanol was employed as the solvent, thallium hexafluorosilicate formed along with TlF:



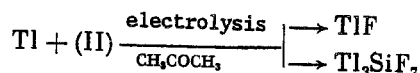
When an acetone solution of (II) was used, an undescribed thallium heptafluorosilicate formed along with TlF:

TABLE 4. Electrosynthesis Conditions and Characteristics of Compounds Obtained

Reagent	Q, A·h	Solvent	Compounds obtained	Mp, °C (solvent)	Yield, %		<sup>19</sup> F NMR, ppm	Found, %			Calculated, %		
					current efficiency	with respect to the metal		F	Tl	Si	F	Tl	Si
(I)	1.0	CH <sub>3</sub> COCH <sub>3</sub>	TlF (Et <sub>4</sub> N) <sub>2</sub> TlF <sub>3</sub> ·3.6HF*	<sup>315</sup> (CH <sub>3</sub> OH : H <sub>2</sub> O = 1 : 1) <sup>237</sup> (CH <sub>3</sub> COCH <sub>3</sub> : C <sub>2</sub> H <sub>5</sub> OC <sub>2</sub> H <sub>5</sub> = 3 : 1)	42	88	15	8.65	91.20	—	8.52	91.48	—
(I)	0.42	C <sub>2</sub> H <sub>5</sub> OH	TlF	<sup>315</sup> (CH <sub>3</sub> OH : H <sub>2</sub> O = 1 : 1)	1	4	23	21.44	34.31	—	21.13	34.45	—
(II) †	1.115	CH <sub>3</sub> COCH <sub>3</sub>	TlF	<sup>315-320</sup> (CH <sub>3</sub> COCH <sub>3</sub> : H <sub>2</sub> O = 1 : 1)	77	19	15	8.62	—	—	8.52	91.48	—
(II)	1.4	C <sub>2</sub> H <sub>5</sub> OH	Tl <sub>2</sub> SiF <sub>6</sub>	<sup>420</sup> (decomp.) (C <sub>2</sub> H <sub>5</sub> OH : H <sub>2</sub> O = 1 : 1)	65	73	15	8.75	—	—	8.52	91.48	—
(II)	1.0	CH <sub>3</sub> COCH <sub>3</sub>	TlF	<sup>315</sup> (C <sub>2</sub> H <sub>5</sub> OH : H <sub>2</sub> O = 1 : 1)	14	36	47	20.73	74.25	5.02	20.69	74.21	5.10
				<sup>420</sup> (sublim.) (CH <sub>3</sub> OH : H <sub>2</sub> O = 1 : 1)	30	57	15	8.59	91.35	—	8.52	91.48	—
				<sup>315</sup> (CH <sub>3</sub> OH : H <sub>2</sub> O = 1 : 1)	4	8	44	16.96	79.20	3.41	17.18	79.19	3.63
			TlF	<sup>315</sup> (CH <sub>3</sub> OH : H <sub>2</sub> O = 1 : 1)	67	80	15	8.58	91.30	—	8.52	91.48	—

\*Found: C, 32.69; H, 7.39; N, 4.83%. Calculated: C, 32.36; H, 7.35; N, 4.72%. Titration: 3.6 moles of HF.

†The synthesis was carried out in polyethylene, and the crystallization was carried out in teflon.



It is clear that the formation of the complex fluorosilicates of thallium is attributable to the reaction of the excess quantity of HF found in (II) with the glass to form fluorosilicic acid and that the anodic dissolution of thallium is accompanied by interactions not only with the F<sup>-</sup> ion, but also with the anion of fluorosilicic acid. In all likelihood, the weaker solvating ability of acetone in comparison to ethanol results in the formation in the acetone solution of the compound Tl<sub>3</sub>SiF<sub>7</sub>, which is unstable under other conditions.

In order to verify that Tl<sub>3</sub>SiF<sub>7</sub> is not a mechanical mixture of TlF and Tl<sub>2</sub>SiF<sub>6</sub>, we undertook an x-ray powder diffraction investigation. The x-ray phase composition (Table 5) of the TlF and Tl<sub>2</sub>SiF<sub>6</sub> obtained is in good agreement with the literature data [7]. At the same time, the values of the interplanar distances and the intensities for Tl<sub>3</sub>SiF<sub>7</sub> are not equal to the sums of the parameters for TlF and Tl<sub>2</sub>SiF<sub>6</sub>. Thallium heptafluorosilicate was previously assigned the formula Tl<sub>3</sub>SiF<sub>7</sub> on the basis of the x-ray diffraction pattern of a mixture of the substances formed upon the thermal decomposition of Tl<sub>2</sub>SiF<sub>6</sub> [8]. However, the substance was not isolated and characterized.

The compound Tl<sub>3</sub>SiF<sub>7</sub> crystallizes in the trigonal system with the parameters  $a = 7.908(2)$  and  $c = 6.927(1)$  Å, and the number of formula units  $Z = 2$ . The two possible space groups  $P\bar{3}_1c$  and  $P3_1c$  were determined from the systematic extinctions. A choice in favor of the centripetal  $P\bar{3}_1c$  group was made on the basis of an analysis of the statistical distribution of the intensities, as well as the Patterson function.

The structural motif of the compound Tl<sub>3</sub>SiF<sub>7</sub> = Tl<sub>3</sub>[SiF<sub>6</sub>]F is based on SiF<sub>6</sub><sup>2-</sup> anions, F<sup>-</sup> ions, and Tl<sup>+</sup> cations (Fig. 1). The hexafluorosilicate anion SiF<sub>6</sub><sup>2-</sup> has a distorted octahedral configuration, and there are two crystallographically inequivalent F atoms of the F<sup>1</sup> and F<sup>3</sup> types, which are realized randomly with a probability of 1/2, in the environment of the Si atoms.

The lengths of the Si-F bonds were differentiated into shorter Si-F<sup>1</sup> bonds measuring 1.57(3) Å and longer Si-F<sup>3</sup> bonds measuring 1.78(3) Å. Eight F atoms at Tl-F distances ranging from 2.830(1) to 3.13(3) Å are the closest neighbors of the Tl atoms. Four of them belong to two pairs of hexafluorosilicate groups which are translationally identical in the [010] direction, and the two F<sup>2</sup> atoms are free fluoride ions. For the other two F atoms there are two equally likely possibilities owing to their statistical positioning and the corresponding orientation of the SiF<sub>6</sub> groups: there are either two F<sup>1</sup> atoms from a pair of SiF<sub>6</sub> groups which are translationally identical in the [001] direction or two F<sup>3</sup> atoms belonging to a single SiF<sub>6</sub> group (in Fig. 1 they are indicated by the dashed lines).

It should be noted that the F<sup>2</sup> fluoride ions are located in octahedral spaces formed by the Tl atoms [the shortest Tl-Tl distance is 3.877(1) Å] and are strictly fixed on  $\bar{3}$  axes. They perform the role of bridges between the Tl atoms and additionally fasten them in the structure of the crystal.

TABLE 5. Comparative X-Ray Phase Composition of Thallium Compounds

Tl <sub>2</sub> SiF <sub>6</sub>				TlF				Tl <sub>3</sub> SiF <sub>7</sub>	
<i>d</i>	<i>I</i> , %	<i>d</i> *	<i>I</i> , %*	<i>d</i> **	<i>I</i> , %**	<i>d</i> *	<i>I</i> , %*	<i>d</i>	<i>I</i> , %
4.29	100	4.29	78	3.18	4	3.23	100	4.93	8
3.05	100	3.029	100	3.04	100	3.06	30	4.29	100
2.41	87	2.475	51	1.78	3	2.69	45	3.92	9
2.15	31	2.143	29	1.52	13	2.019	55	3.43	34
1.92	50	1.916	35			1.900	20	3.08	49
1.75	47	1.749	28			1.800	45	2.89	11
1.65	5	1.649	3			1.616	30	2.43	16
1.52	24	1.515	11			1.530	6	2.31	33
						1.342	8	1.98	93
						1.329	14	1.83	9
						1.304	25	1.73	31
								1.54	12
								1.53	13

\*[7]

\*\*FeKα radiation.

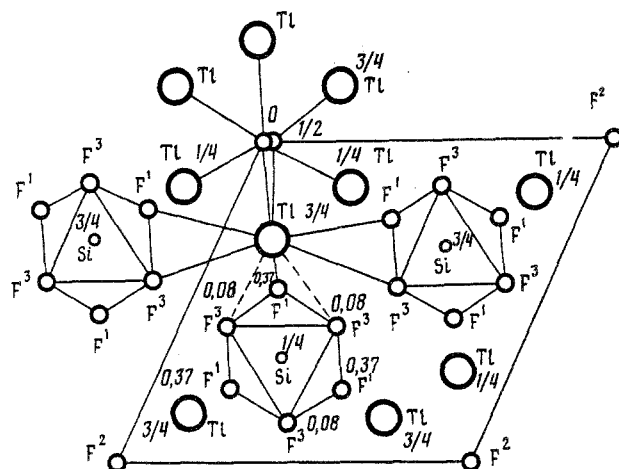


Fig. 1. Structure of  $Tl_3[SiF_6]F$

In the structure it is possible to clearly identify Tl-Si layers belonging to the [001] direction at heights equal to 1/4 and 3/4 of the period  $c$ . The layers are joined by means of the  $F^1$  and  $F^3$  atoms, which perform the role of bridges between the Tl and Si atoms, and a mixed three-dimensional framework is formed as a result. It should also be noted that the observed variability in the interatomic distances is apparently attributable to the errors due to the disregard of the absorption by the Tl atoms.

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#### CONCLUSIONS

1. The direct electrochemical synthesis of fluorides of Tl in nonaqueous solvents in the presence of tetraalkylammonium fluoride polyhydrofluorides has been carried out.
2. It has been shown that the anodic dissolution of thallium in a glass cell in the presence of a tetraalkylammonium fluoride polyhydrofluoride results in the formation of  $Tl_2SiF_6$  and the previously unknown compound  $Tl_3[SiF_6]F$ .
3. An x-ray structural investigation of the compound  $Tl_3[SiF_6]F$  has been carried out. It has been shown that the structure is built up from hexafluorosilicate anions ( $SiF_6^{2-}$ ), thallium cations ( $Tl^+$ ), and fluoride ions.

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