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REVIEW ARTICLE

Structural depolymerization of titanium(IV) fluoride: basis for the formation of titanium(IV) fluoride complexes

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Abstract

The applicability of the concept of structural depolymerization is demonstrated by the example of titanium(IV) fluoride and its complex salts obtained in the systems CsF/TiF_4/aHF, $(Gua)_2CO_3$/TiF_4/aHF, (Gua)Cl/TiF_4/aHF, and Im/TiF_4/aHF (aHF, anhydrous hydrogen fluoride; (Gua^+), guanidinium cation, $[C(NH_2)_3]^+$; Im, imidazole). The compositions of the fluoridotitanates(IV) formed in these systems and their crystal structures are considered in terms of the degree of polymerization (ε). The latter is defined as the ratio between the number of bridging fluorine atoms ($M-F_b-M$) and the number of terminal fluorine atoms ($M-F_t$) in the $[M_nF_{4n+x}]^{x-}$ ($M=Ti$; $n \geq 1$) structural fragments. With increasing initial amount of fluoride ion donors (AX = CsF or in situ formed (Gua)F and ImHF) in AF/TiF_4 reactions, the degree of polymerization of the crystal structures of the obtained salts decreases.

Keywords Titanium · Fluoride · Cesium · Guanidinium · Imidazolium · Crystal structure · Depolymerization

Introduction

In [1], the concept of structural depolymerization of metal fluoride compounds is formulated, which is the basis for the formation of complex metal fluorides and the formation of their crystal structures. The experimental basis for the concept of structural depolymerization of metal fluoride compounds is the depolymerizing effect of fluoride ions ($F^{-)}$ (provided by fluoride ion donors AF) on metal fluoride compounds (MF_n) whose structures contain $M-F_b-M$ bridges.

Transition metal fluorides (MF_n) have a polymeric structure with $M-F_b-M$ fluoride bridges in the crystalline state. When a metal fluoride compound MF_n containing $M-F_b-M$ bridging bonds is exposed to fluoride ions (F^-) that have a greater affinity for the metal (M) than the bridging fluorine atoms (F_b), the $M-F_b-M$ bonds in these compounds are broken, and the originally polymeric structures are sequentially depolymerized. Thus, the formation of complex metal fluorides during the interaction of F^- ions with binary (MF_n) or more complex fluorides ($A_xM_yF_n$) can be represented as a process of sequential depolymerization of a metal fluoride compound under the action of fluoride ions. The degree of depolymerization of MF_n depends on the molar ratio of the reacting components. The proposed concept of structural depolymerization of metal fluoride compounds is justified on the basis of an analysis of crystal structures of complete series of zirconium and hafnium fluoride complexes [2, 3] with the same cations and on the basis of experimental data of synthesis fluoride complexes of zirconium and hafnium.

To assess the degree of polymerization of the crystal structure of a compound, the ratio between the number of bridging fluorine atoms (F_b) and the number of terminal fluorine (F_t) atoms in the structural fragment of the compound, denoted by the letter ε, is usually used. For example, for the compound TiF_4, in which each Ti atom is surrounded by four bridging and two terminal F atoms (structural fragment $TiF_{2/1}F_{4/2}$), the degree of polymerization of the structure is

Highlights
- Depolarizing effect of F ions on transition metal fluorides with M-F-M bonds.
- Structural depolymerization—the basis for the formation of fluoride complexes and its structures.
- With increasing molar ratio in AF/TiF_4 reactions, the degree of the polymerization of the obtained salts decreases.

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$\varepsilon = F_b:F_t = 4:2 = 2$. For $Cs_2[TiF_6]$ with the structural fragment $TiF_{6/1}F_{0/2}$, in whose structure there are no bridging F atoms, $\varepsilon = 0$.

One of the most important provisions of the concept of structural depolymerization of metal fluoride compounds is the decrease in the degree of polymerization of the crystal structure of the compound with increasing amount of the reacting component providing fluoride ions (F^-) in a series of complex fluorides with the same cation. The application of the concept of structural depolymerization [1] of metal fluoride compounds has already been shown in the case of fluoride complexes of zirconium structural depolymerization [4, 5]. Structural depolymerization of uranyl fluoride complexes is discussed in [6].

In 2001, the study was published [7], containing provisions similar to the concept of structural depolymerization of metal fluoride compounds [1]. The authors proposed a practical formalism for the manipulation of solid structures, called “dimensional reduction” [7]. Similar to the concept of structural depolymerization of metal fluoride compounds [1], the proposed dimensional reduction is a general formalism that describes how the framework of a parent compound MX_x is degraded upon reaction with an ionic reagent A_aX to form a child compound $A_{na}MX_{x+n}$ [7]. The added X^- anions disrupt the $M-X-M$ bridges in an MX_x parent compound, resulting in a less tightly bound framework. The possibilities of transforming the crystal structures of different types of compounds are formally considered, but the mechanism causing these transformations is not considered or discussed [4].

Recently, a series of papers have been published dealing with the synthesis and study of the crystal structure of new fluoridotitanates(IV) with alkali metal [8], guanidinium [9], and imidazolium [10] cations.

In [8], a systematic study of the reaction between alkali metal fluorides (AF, A = Li, Na, K, Rb, Cs) and titanium(IV) fluoride (TiF_4) in anhydrous hydrogen fluoride (aHF) at ambient temperature and a molar ratio $n(AF):n(TiF_4)$ of 3:1 to 1:3 was carried out. The formation of the following types of compounds was observed: $A_2[TiF_6]$, $A_2[TiF_6]\cdot HF$, $A[TiF_5]$, $A[TiF_5]\cdot HF$, $A_3[Ti_4F_{19}]$, $A[Ti_2F_9]$, $A[Ti_2F_9]\cdot HF$, and $A_3[Ti_6F_{27}]$. Investigation of their crystal structure showed that they consisted of monomeric $[TiF_6]^{2-}$ anions (0-D), polymeric $([TiF_5]^-)_\infty$ chains (1-D), $([Ti_4F_{19}]^{3-})_\infty$ columns (1-D), $([Ti_2F_9]^-)_\infty$ double chains (1-D), and $([Ti_6F_{27}]^{3-})_\infty$ three-dimensional frameworks (3-D).

In [9], the reaction between guanidinium carbonate (and/or chloride) and TiF_4 in aHF was carried out in the molar ratios $n([C(NH_2)_3]^+):n(TiF_4)$ from 2:1 to 1:4. Five guanidinium fluoridotitanate(IV) salts were isolated and structurally studied: the already known $[C(NH_2)_3]_2[TiF_6]$ and the new complexes $[C(NH_2)_3][Ti_2F_9]$, $[C(NH_2)_3]_4[Ti_4F_{20}]$, $[C(NH_2)_3]_3[Ti_6F_{27}]\cdot SO_2$, and $[C(NH_2)_3]_4[H_3O]_4[Ti_4F_{20}][TiF_5]_4$. The crystal structures of the synthesized new guanidinium fluoridotitanates(IV) contain oligomeric $[Ti_4F_{20}]^{4-}$ and $[Ti_6F_{27}]^{3-}$, and polymeric $([TiF_5]^-)_\infty$ and $([Ti_2F_9]^-)_\infty$ anions.

The reactions between imidazole (Im) and TiF_4 in aHF in the molar ratios $n(Im):n(TiF_4)$ ranging from 2:1 to 1:2 resulted in the formation of five fluoridotitanates(IV): $[ImH]_2[TiF_6]\cdot 2HF$, $[ImH]_3[Ti_2F_{11}]$, $[ImH]_4[Ti_4F_{20}]$, $[ImH]_3[Ti_5F_{23}]$, and $[ImH][Ti_2F_9]$ [10]. Their crystal structures were determined by a single-crystal X-ray diffraction method.

In [8], the authors state that, with the exception of compound $A_2[TiF_6]$, whose structure consists of cations A^+ and octahedral monomeric complex anions $[TiF_6]^{2-}$, all other synthesized alkali metal fluoridotitanates(IV) are formed by condensation of TiF_6 groups. The same is true for the guanidinium and imidazolium fluoridotitanates(IV) [9, 10].

The study of the initial conditions, the formed fluoridotitanate(IV) salts, and the corresponding crystal structures [8–10] allows us to consider the formation of the synthesized fluoride complexes of titanium from the point of view of the concept of structural depolymerization of fluoride metal compounds.

Results and discussion

Structural depolymerization of titanium(IV) fluoride in the system CsF/TiF$_4$/aHF

The structural depolymerization of titanium(IV) fluoride under the action of F^- ions of alkali metal fluorides is considered by the example of the study the structural depolymerization of TiF_4 in the $CsF/TiF_4/aHF$ system. The synthesis of cesium fluoridotitanates(IV) was carried out by the reaction between CsF and TiF_4, which has a polymeric crystal structure [11]. When CsF is added to TiF_4 in aHF or in another aprotic solvent, structural depolymerization of TiF_4 occurs under the action of F^- ions, which is illustrated by the breaking of the $M-F_b-M$ bridges in TiF_4. The degree of depolymerization of the TiF_4 structure depends on the initial $n(CsF):n(TiF_4)$ molar ratio of the reacting components.

The crystal structure of TiF_4 contains three crystallographically distinct Ti atoms, each of which is octahedrally surrounded by six F atoms [11]. Each TiF_6 octahedron in the structure is connected to each of the other two TiF_6 octahedra by two *cis*-located equatorial F atoms to form a $[Ti_3F_{15}]$ ring of three vertex-linked octahedra. In addition, each octahedron is connected to two octahedra of the same type by trans-positioned F atoms to form isolated columns. In each TiF_6 octahedron of the TiF_4 structure, two terminal F atoms occur for four bridging F atoms, and the structural fragment is $TiF_{2/1}F_{4/2}$. The degree of polymerization of the TiF_4 structure is $\varepsilon = 2$ (Table 1).

Table 1 Structural depolymerization of TiF_4 in the system $CsF/TiF_4/aHF$

Initial molar ratio $n(CsF):n(TiF_4)$	Obtained product[a] and cryst. unique TiF_6 units	Structural fragment	ε	Geometry of the anion	Association[b]	Ref.
	TiF_4 $Ti(1)F_6$—$Ti(3)F_6$	$TiF_{2/1}F_{4/2}$	2	$[TiF_4]_\infty$, columns built of $[Ti_3F_{15}]$ trimers	4	[11]
1:3 to 1:2	$Cs[Ti_2F_9]$ $Ti(1)F_6$	$TiF_{3/1}F_{3/2}$	1	$([Ti_2F_9]^-)_\infty$, double zigzag chain	3	[8, 12]
3:4	$Cs_3[Ti_4F_{19}]$ $Ti(1)F_6$ $Ti(2)F_6$	$Ti(1)F_{4/1}F_{2/2}$ $Ti(2)F_{3/1}F_{3/2}$	(0.75)[c] 0.5 1	$([Ti_4F_{19}]^{3-})_\infty$, column	2 3	[8]
1:1	$Cs[TiF_5]$ $Ti(1)F_6$	$TiF_{4/1}F_{2/2}$	0.5	$([TiF_5]^-)_\infty$, zigzag chain	2	[8]
2:1	$Cs_2[TiF_6]$ $Ti(1)F_6$	$TiF_{6/1}F_{0/2}$	0	$[TiF_6]^{2-}$, octahedra	0	[8, 13]

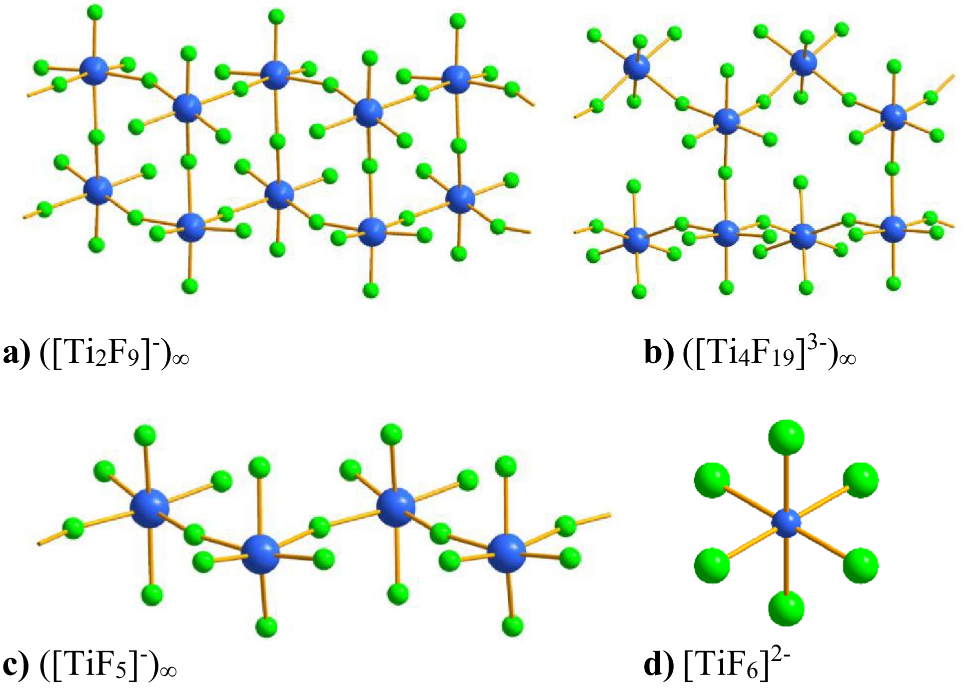
[a] $CsTi_2F_9$, $CsTiF_5$, and Cs_2TiF_6 were prepared as pure phases in bulk. Crystallizations with appropriate initial molar ratios of CsF:TiF_4 also yielded only one phase. An exception is $Cs_3[Ti_4F_{19}]$, where attempts to prepare pure phase (by synthesis or crystallization) always resulted in a mixture of three phases, namely, $Cs_3[Ti_4F_{19}]$, $Cs[TiF_5]$ and $Cs[Ti_2F_9]$. [8, 12]

[b] Number of $Ti-F_b$ bonds in each TiF_6 unit, where F_b bridges two Ti atoms

[c] An average value

When CsF is added to TiF_4 in aHF at a CsF:TiF_4 molar ratio 1:3 or 1:2, titanium fluoride is partially depolymerized, and the $CsTi_2F_9$ compound crystallizes from solution (Table 1). The structure of $CsTi_2F_9$ consists of Cs^+ cations and complex anions $([Ti_2F_9]^-)_\infty$. In the $CsTi_2F_9$ structure, the octahedral TiF_6 groups connected by *cis*-vertices form polymeric double chain-like anions $([Ti_2F_9]^-)_\infty$, with each octahedron sharing its three vertices with three other TiF_6 octahedra (Fig. 1a). Three bridging F atoms and three terminal fluorine atoms coordinate each Ti atom in the $CsTi_2F_9$ structure. The structural fragment of the crystal structure of $CsTi_2F_9$ is $TiF_{3/1}F_{3/2}$, and the degree of polymerization is $\varepsilon = 1$ (Table 1).

Changing the CsF:TiF_4 ratio in the $CsF/TiF_4/aHF$ system to 3:4 is accompanied by an increase in the degree depolymerization of TiF_4 and leads to the formation of the compound $Cs_3[Ti_4F_{19}]$. The crystal structure of $Cs_3[Ti_4F_{19}]$ consists of Cs^+ cations and polymeric double chain anions $([Ti_4F_{19}]^{3-})_\infty$ (Fig. 1b) [8]. The structure of $Cs_3[Ti_4F_{19}]$ contains two crystallographically independent Ti atoms


a) $([Ti_2F_9]^-)_\infty$

b) $([Ti_4F_{19}]^{3-})_\infty$

c) $([TiF_5]^-)_\infty$

d) $[TiF_6]^{2-}$

Fig. 1 Fragments of crystal structures of cesium fluoridotitanates(IV): $Cs[Ti_2F_9]$ **a**, $Cs_3[Ti_4F_{19}]$ **b**, $Cs[TiF_5]$ **c**, $Cs_2[TiF_6]$ **d**

[Ti(1) and Ti(2)], each coordinated by six F atoms. In each of the chains, the Ti(1)F_6 octahedra are connected by common vertices to two adjacent Ti(2)F_6. The Ti(2)F_6 octahedra, in turn, are connected via three common vertices to three octahedra — two Ti(1)F_6 octahedra in the same chain and one Ti(2)F_6 octahedron of the adjacent chain. Thus, in the Ti(1)F_6 octahedra, there are two bridging atoms per four terminal F atoms, the structural fragment is $TiF_{4/1}F_{2/2}$ and $\varepsilon = 0.5$, and in the Ti(2)F_6 octahedra, there are three bridging atoms per three terminal F atoms, structural fragment $TiF_{3/1}F_{3/2}$ ($\varepsilon = 1$). The average degree of polymerization of the $Cs_3[Ti_4F_{19}]$ structure is 0.75 (Table 1).

$CsTiF_5$, is obtained using an initial molar ratio of $CsF{:}TiF_4 = 1{:}1$ (Table 1). The crystal structure of $CsTiF_5$ consists of one-dimensional polymeric zigzag chains $([TiF_5]^-)_\infty$ (Fig. 1c) formed by vertex-linked TiF_6 octahedra and Cs^+ cations [8]. Of the six F atoms coordinated to the Ti atom, four are terminal, and two are bridging, and the structural fragment is $TiF_{4/1}F_{2/2}$. Consequently, the degree of polymerization of the $CsTiF_5$ structure is $\varepsilon = 0.5$ (Table 1).

The final product of structural depolymerization of TiF_4 under the action of F^- ions in the CsF/TiF_4/aHF system is Cs_2TiF_6, which is formed at a molar ratio of $CsF{:}TiF_4$ of 2:1 (Table 1). The crystal structure of Cs_2TiF_6 consists of Cs^+ cations and isolated monomeric octahedral $[TiF_6]^{2-}$ anions (Fig. 1d) in which all fluorine atoms are terminal [8, 13]. The structural fragment of the Cs_2TiF_6 crystal structure is $TiF_{6/1}F_{0/2}$, and the degree of polymerization of the Cs_2TiF_6 structure is $\varepsilon = 0$ (Table 1).

In the CsF/TiF_4/aHF system, structural depolymerization of TiF_4 under the action of F^- ions converts the TiF_4 framework structure with the $TiF_{2/1}F_{4/2}$ ($\varepsilon = 2$) structural fragment into the $CsTi_2F_9$ polymer structure with double chains and the $TiF_{3/1}F_{3/2}$ ($\varepsilon = 1$) structural fragment and then to the $Cs_3[Ti_4F_{19}]$ structure with zigzag double chains in which every second bridge bond between the TiF_6 groups of one polymer chain and the TiF_6 groups of the second chain is missing, with Ti(1)$F_{4/1}F_{2/2}$ ($\varepsilon = 0.5$) and Ti(2) $F_{3/1}F_{3/2}$, ($\varepsilon = 1$) (an average degree of polymerization of the $Cs_3[Ti_4F_{19}]$ structure $\varepsilon = 0.75$). The next product of structural depolymerization of TiF_4 is the $CsTiF_5$ compound, the structure of which contains one-dimensional polymeric zigzag $([TiF_5]^-)_\infty$ chains formed by vertex-linked TiF_6 octahedra with the $TiF_{4/1}F_{2/2}$ structural fragment ($\varepsilon = 0.5$). The final product of the structural depolymerization of TiF_4 in the CsF/TiF_4/aHF system is the Cs_2TiF_6 compound with the structural fragment $TiF_{6/1}F_{0/2}$ and the degree of polymerization $\varepsilon = 0$ (Table 1).

In the series of titanium fluoride compounds TiF_4-$CsTi_2F_9$-$Cs_3[Ti_4F_{19}]$-$CsTiF_5$-Cs_2TiF_6, the degree of polymerization of the crystal structure of the obtained compounds decreases from $\varepsilon = 2$ (TiF_4) to $\varepsilon = 0$ (Cs_2TiF_6) when the molar ratio of the reacting components in the CsF/TiF_4/aHF system changes from 1:3 to 2:1.

Structural depolymerization of titanium(IV) fluoride in the systems $[C(NH_2)_3]_2CO_3$ (and/or $[C(NH_2)_3]Cl$)/TiF_4/aHF

The reaction between guanidinium carbonate (and/or chloride) with TiF_4 in aHF was carried out by two methods [9]. In the first method, aHF was added to a mixture of the guanidinium salt and TiF_4 in various molar ratios. In the second method, the required amount of guanidinium salt was preliminarily converted into guanidinium polyhydrogen fluoride $[C(NH_2)_3]F{\cdot}n$HF by interaction with aHF. The latter was then used for the reaction with TiF_4 in aHF. $[C(NH_2)_3]F$ had a depolymerizing effect on TiF_4, the degree of depolymerization of TiF_4 depending on the initial molar ratio of the reacting components, i.e., $n[C(NH_2)_3]^+{:}n(TiF_4)$.

In the system $[C(NH_2)_3]_2CO_3/TiF_4$/aHF at a molar ratio of $[C(NH_2)_3]^+{:}TiF_4$ 1:3 and 1:2, the TiF_4 compound undergoes partial depolymerization under the action of F^- ions to form $[C(NH_2)_3][Ti_2F_9]$. The crystal structure of $[C(NH_2)_3][Ti_2F_9]$ consists of guanidinium cations $[C(NH_2)_3]^+$ and polymeric anion $([Ti_2F_9]^-)_\infty$ structure similar to polymer chains in the $Cs[Ti_2F_9]$ structure (Fig. 1a) [8]. Each titanium atom in the $([Ti_2F_9]^-)_\infty$ anion is coordinated by three bridging and three terminal fluorine atoms, forming a $TiF_{3/1}F_{3/2}$ structural fragment. The degree of polymerization of the $[C(NH_2)_3][Ti_2F_9]$ structure is $\varepsilon = 1$ (Table 2).

$[C(NH_2)_3]_4[Ti_4F_{20}]$ crystallizes from HF solution when less $[C(NH_2)_3]F$ was present in the $[C(NH_2)_3]_2CO_3/TiF_4$/aHF system. The structure $[C(NH_2)_3]_4[Ti_4F_{20}]$ consists of oligomeric tetrameric $[Ti_4F_{20}]^{4-}$ anions and guanidinium cations [9]. In the tetrameric anion $[Ti_4F_{20}]^4$ (Fig. 2a), two bridging and four terminal F atoms form a structural fragment $TiF_{4/1}F_{2/2}$. The degree of polymerization of $[C(NH_2)_3]_4[Ti_4F_{20}]$ is $\varepsilon = 0.5$.

As in the CsF/TiF_4/aHF system, the final product of TiF_4 structural depolymerization in the $[C(NH_2)_3]_2CO_3/TiF_4$/aHF system is guanidinium hexafluoridotitanate(IV), $[C(NH_2)_3]_2[TiF_6]$ (Table 2). [9, 14]. The Ti atoms in the $[TiF_6]^{2-}$ anion are coordinated by six F ligands and form distorted octahedra (structural fragment $TiF_{6/1}F_{0/2}$). The degree of polymerization of the structure $[C(NH_2)_3]_2TiF_6$ is $\varepsilon = 0$ (Table 2).

In the system $[C(NH_2)_3]_2CO_3/TiF_4$/aHF, structural depolymerization of TiF_4 under the action of F^- ions converts the framework structure of TiF_4 with the structural fragment $TiF_{2/1}F_{4/2}$ ($\varepsilon = 2$) into the $[C(NH_2)_3][Ti_2F_9]$ with a polymeric structure of double chains and the structural fragment $TiF_{3/1}F_{3/2}$ ($\varepsilon = 1$). The next step is the formation of $[C(NH_2)_3]_4[Ti_4F_{20}]$, whose crystal structure contains oligomeric tetrameric anions $[Ti_4F_{20}]^{4-}$, with the structural

Table 2 Structural depolymerization of TiF_4 in the systems $(Gua)_2CO_3$ (and/or (Gua)Cl)/TiF_4/aHF

Initial molar ratio $n(Gua)_2CO_3$ (and/or (Gua) Cl):$n(TiF_4)$ [a]	Obtained product[b] and cryst. unique TiF_6 units	Structural fragment	ε	Geometry of the anion	Association[c]	Ref.
	TiF_4 $Ti(1)F_6$–$Ti(3)F_6$	$TiF_{2/1}F_{4/2}$	2	$[TiF_4]_\infty$, columns built of $[Ti_3F_{15}]$ trimers	4	[11]
$(Gua)_2CO_3$:TiF_4 1:3, 1:2	$[C(NH_2)_3][Ti_2F_9]$ $Ti(1)F_6$	$TiF_{3/1}F_{3/2}$	1	$([Ti_2F_9]^-)_\infty$, double zigzag chain	3	[9]
$(Gua)_2CO_3$:TiF_4 1:2, 1:1, 3:2	$[C(NH_2)_3]_4[Ti_4F_{20}]$ $Ti(1)F_6$–$Ti(2)F_6$	$TiF_{4/1}F_{2/2}$	0.5	$[Ti_4F_{20}]^{4-}$, tetramer	2	[9]
$(Gua)_2CO_3$:TiF_4 1:2 to 2:1	$[C(NH_2)_3]_2[TiF_6]$ $Ti(1)F_6$	$TiF_{6/1}F_{0/2}$	0	$[TiF_6]^{2-}$, octahedra	0	[9, 14]
(Gua)Cl:TiF_4 1:4	$[C(NH_2)_3]_3[Ti_6F_{27}]\cdot SO_2$ $Ti(1)F_6$–$Ti(12)F_6$	$TiF_{3/1}F_{3/2}$	1	$[Ti_6F_{27}]^{3-}$, trigonal prism	3	[9]
(Gua)Cl:TiF_4 1:4	$[C(NH_2)_3]_4[H_3O]_4[Ti_4F_{20}]$-$[TiF_5]_4$ $Ti(3)F_6$–$Ti(4)F_6$ $Ti(1)F_6$–$Ti(2)F_6$	$TiF_{4/1}F_{2/2}$ $TiF_{4/1}F_{2/2}$	$(1)^d$ 0.5 0.5	$[Ti_4F_{20}]^{4-}$, tetramer $([TiF_5]^-)_\infty$, chain	2 2	[9]

[a] (Gua^+) = guanidinium

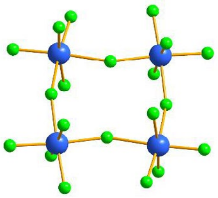
[b] $[C(NH_2)_3][Ti_2F_9]$ (bulk and single crystals) and $[C(NH_2)_3]_3[Ti_6F_{27}]\cdot SO_2$ (single crystals) were prepared as pure phases. Attempts to prepare pure $[C(NH_2)_3][Ti_2F_9]$ and $[C(NH_2)_3]_4[Ti_4F_{20}]$ resulted in mixture of $[C(NH_2)_3]_2[TiF_6]$, $[C(NH_2)_3][Ti_2F_9]$, and $[C(NH_2)_3]_4[Ti_4F_{20}]$ [9]

[c] Number of $Ti-F_b$ bonds in each TiF_6 unit, where F_b bridges two Ti atoms

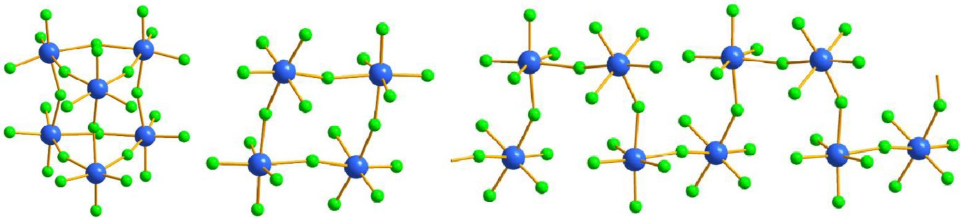
[d] Total value

fragment $TiF_{4/1}F_{2/2}$ and the degree of polymerization $\varepsilon = 0.5$. The final product of structural depolymerization of TiF_4 is guanidinium hexafluoridotitanate(IV) $[C(NH_2)_3]_2[TiF_6]$ with the structural fragment $TiF_{6/1}F_{0/2}$ and degree of polymerization $\varepsilon = 0$ (Table 2).

In the system $[C(NH_2)_3]Cl/TiF_4$/aHF, virtually, the same compounds are formed as in the system $[C(NH_2)_3]_2CO_3/TiF_4$/aHF (Table 2) [9]. In the case of large amounts of TiF_4 ($[C(NH_2)_3]Cl:TiF_4$ = is 1:4), the product(s) formed are insoluble in aHF. Crystallization of this insoluble product(s) from SO_2 solution led to the formation of the solvated phase $[C(NH_2)_3]_3[Ti_6F_{27}]\cdot SO_2$. Its Raman spectrum is very similar to the Raman spectrum of the product insoluble in aHF obtained from a mixture of guanidinium salt and TiF_4 at the initial molar ratios of the reagents 1:3 and 1:4. On this basis, the authors of [9] concluded that the insoluble phase in aHF is mainly $[C(NH_2)_3]_3[Ti_6F_{27}]$ or its HF-solvate form. The crystal structure of $[C(NH_2)_3]_3[Ti_6F_{27}]\cdot SO_2$ contains two crystallographically independent anions $[Ti_6F_{27}]^{3-}$, reminiscent of the column-like structure of TiF_4. The oligomeric



a) $[Ti_4F_{20}]^{4-}$



b $[Ti_6F_{27}]^{3-}$ **c**, 1 $[Ti_4F_{20}]^{4-}$ and **c**, 2 $([TiF_5]^-)_\infty$

Fig. 2 Fragments of crystal structures of guanidinium fluoridotitanates(IV): $[C(NH_2)_3]_4[Ti_4F_{20}]$ **a**, $[C(NH_2)_3]_3[Ti_6F_{27}]\cdot SO_2$ **b**, $[C(NH_2)_3]_4[H_3O]_4[Ti_4F_{20}][TiF_5]_4$ **c**, **1**; **c**, **2**

$[Ti_6F_{27}]^{3-}$ anions are formed by six TiF_6 octahedra: three TiF_6 octahedra, sharing *cis*-corners form a trimeric ring, and the other three octahedra form the same trimeric ring, connected to the first ring by three bridging fluorine atoms, forming a trigonal prismatic geometry (Fig. 2b) [9]. All Ti atoms in the $[Ti_6F_{27}]^{3-}$ anion are bonded to three terminal and three bridging F atoms, and the structural fragment of the $[C(NH_2)_3]_3[Ti_6F_{27}]\cdot SO_2$ is $TiF_{3/1}F_{3/2}$ ($\varepsilon = 1$).

Long-term crystallization from a CH_3CN solution of a phase insoluble in aHF, formed in the system $[C(NH_2)_3]Cl/TiF_4$/aHF at a molar ratio of $[C(NH_2)_3]Cl:TiF_4 = 1:4$, resulted in few crystals of $[C(NH_2)_3]_4[H_3O]_4[Ti_4F_{20}][TiF_5]_4$ [9].The crystal structure of $[C(NH_2)_3]_4[H_3O]_4[Ti_4F_{20}][TiF_5]_4$ consists of $[C(NH_2)_3]^+$ and H_3O^+ cations as well as tetrameric $[Ti_4F_{20}]^{4-}$ and polymeric chain-like $([TiF_5]^-)_\infty$ anions (Fig. 2, c, 1) [9]. The structure of the tetrameric anion is similar to that in the structure of $[C(NH_2)_3]_4[Ti_4F_{20}]$ described above. The second anion in the structure of $[C(NH_2)_3]_4[H_3O]_4[Ti_4F_{20}][TiF_5]_4$ is a polymeric chain-like $([TiF_5]^-)_\infty$, consisting of *cis*-linked TiF_6 octahedra (Fig. 2, c, 2).

Structural depolymerization of titanium(IV) fluoride in the Im/TiF_4/aHF system

The reaction between imidazole (Im) and TiF_4 in aHF in the molar ratios of 2:1 to 1:2 resulted in the formation of five fluoridotitanates(IV): $[ImH]_2[TiF_6]\cdot 2HF$, $[ImH]_3[Ti_2F_{11}]$, $[ImH]_4[Ti_4F_{20}]$, $[ImH]_3[Ti_5F_{23}]$, and $[ImH\ [Ti_2F_9]$ [10].

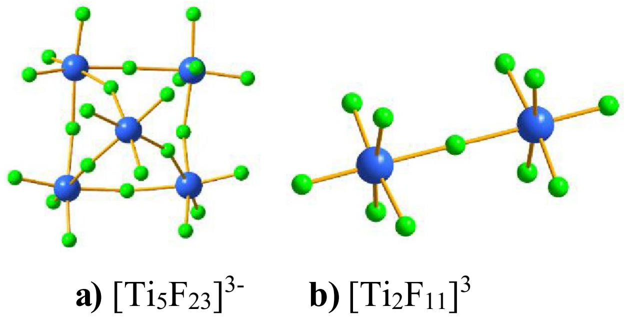


Fig. 3 Fragments of crystal structures of imidazolium fluoridotitanates(IV): $(ImH)_3[Ti_5F_{23}]$ **a**, $(ImH)_3[Ti_2F_{11}]$ **b**

In the system Im/TiF_4/aHF, in the molar ratios Im:TiF_4 1:2 and 2:3, structural depolymerization of TiF_4 takes place under the action of F^- ions of ImHF, and the $[ImH][Ti_2F_9]$ salt crystallizes from solution. Its structure consists of ImH^+ cations and $([Ti_2F_9]^-)_\infty$ anions with a double-chain geometry structure similar to polymer chains in the $Cs[Ti_2F_9]$ and $C(NH_2)_3][Ti_2F_9]$ structure (Fig. 1a) [8]. The structural fragment is $TiF_{3/1}F_{3/2}$, and the degree of polymerization is $\varepsilon = 1$ (Table 3).

With larger amount of imidazole, the depolymerization of TiF_4 increases yielding $[ImH]_3[Ti_5F_{23}]$, $[ImH]_4[Ti_4F_{20}]$, $(ImH)_3[Ti_2F_{11}]$, and $(ImH)_2[TiF_6]\cdot 2HF$. The former contains pentameric $[Ti_5F_{23}]^{3-}$ anion with a unique geometry consisting of five octahedral TiF_6 groups (Fig. 3a) [10].

Table 3 Structural depolymerization of TiF_4 in the system Im/TiF_4/aHF

Initial molar ratio $n(Im)^a:n(TiF_4)$	Obtained product^b and cryst. unique TiF_6 units	Structural fragment	ε	Geometry of the anion	Association^c	Ref.
	TiF_4 $Ti(1)F_6$–$Ti(3)F_6$	$TiF_{2/1}F_{4/2}$	2	$[TiF_4]_\infty$, columns built of $[Ti_3F_{15}]$ trimers	4	[11]
1:2, 2:3	$(ImH)[Ti_2F_9]$ $Ti(1)F_6$	$TiF_{3/1}F_{3/2}$	1	$([Ti_2F_9]^-)_\infty$, double zigzag chain	3	[10]
3:5, 2:3, 1:1	$(ImH)_3[Ti_5F_{23}]$ $Ti(2)F_6$–$Ti(5)F_6$ $Ti(1)F_6$	$TiF_{3/1}F_{3/2}$ $TiF_{4/1}F_{2/2}$	$(0.9)^d$ 1 0.5	$[Ti_5F_{23}]^{3-}$, pentamer	3 2	[10]
2:3, 1:1	$[ImH]_4[Ti_4F_{20}]$ $Ti(1)F_6$–$Ti(2)F_6$	$TiF_{4/1}F_{2/2}$	0.5	$[Ti_4F_{20}]^{4-}$, tetramer	2	[10]
2:1	$(ImH)_3[Ti_2F_{11}]$ $Ti(1)F_6$–$Ti(3)F_6$	$TiF_{5/1}F_{1/2}$	0.2	$[Ti_2F_{11}]^{3-}$, dimer	1	[10]
2:1	$(ImH)_2[TiF_6]\cdot 2HF$ $Ti(1)F_6$	$TiF_{6/1}F_{0/2}$	0	$[TiF_6]^{2-}$, octahedra	0	[10]

[a] (Im) = imidazole

[b] $(ImH)_3[Ti_2F_{11}]$ was prepared as a pure phase. Attempts to prepare pure $[ImH]_4[Ti4F_{20}]$ and $[ImH]_3[Ti_5F_{23}]$ salts failed. The former was contaminated with small amounts of $[ImH]_3[Ti_5F_{23}]$ and the latter with small amounts of $(ImH)[Ti_2F_9]$. At isolation at room temperature, $(ImH)_2[TiF_6]\cdot 2HF$ released HF, and it was converted to $(ImH)_2[TiF_6]$. [10]

[c] Number of Ti – F_b bonds in each TiF_6 unit, where F_b bridges two Ti atoms

[d] An average value

In $[Ti_5F_{23}]^{3-}$, each of the four octahedra shares two *cis*-vertices with the neighboring octahedron, forming a tetrameric ring. The fifth octahedron TiF_6 shares three vertices with three octahedra of the tetrameric ring, forming the Ti_5F_{23} pentamer (Fig. 3a). The structural fragments of Ti(2)-Ti(5) atoms are $TiF_{3/1}F_{3/2}$ ($\varepsilon = 1$), and the structural fragment of Ti(1) atom is $TiF_{4/1}F_{2/2}$, ($\varepsilon = 0.5$) (numbering of Ti atoms according to [10]). The average degree of polymerization of the structure $[ImH]_3[Ti_5F_{23}]$ is $\varepsilon = 0.9$.

The crystal structures of $(ImH)_4[Ti_4F_{20}]$ salt (Table 3) consist of $[Ti_4F_{20}]^{4-}$ anions (Fig. 2a) and ImH^+ cations interacting via hydrogen bonds [10]; the structural fragment is $TiF_{4/1}F_{2/2}$. The degree of polymerization of the $(ImH)_4[Ti_4F_{20}]$ structure is $\varepsilon = 0.5$ (Table 3). The $(ImH)_4[Ti_4F_{20}]$ compound can also be considered as a product of structural depolymerization of $[ImH]_3[Ti_5F_{23}]$. Under the action of F^- ions, the $Ti-F_b-Ti$ bridges in the pentameric $[Ti_5F_{23}]^{3-}$ anion are broken, giving rise to the tetrameric anion $[Ti_4F_{20}]^{4-}$, which forms the basis of the crystal structure $(ImH)_4[Ti_4F_{20}]$.

Dimeric anions $[Ti_2F_{11}]^{3-}$ (Fig. 3b), consisting of two octahedral TiF_6 groups sharing a common vertex, are present in the crystal structure of $[ImH]_3[Ti_2F_{11}]$, which crystallizes in the Im/TiF_4/aHF system at a molar ratio Im:TiF_4 = 2:1 [10]. In contrast to $(C_5H_5NH)_2(H_3O)[Ti_2F_{11}]\cdot H_2O$ [12], whose structure contains only a crystallographically unique $[Ti_2F_{11}]^{3-}$ anion, the $[ImH]_3[Ti_2F_{11}]$ structure contains three crystallographically independent Ti_2F_{11} groups with different conformations and coordination domains. The structural fragment of the $[ImH]_3[Ti_2F_{11}]$ crystal structure is $TiF_{5/1}F_{1/2}$, and the degree of polymerization of the structure is $\varepsilon = 0.2$. The $[ImH]_3[Ti_2F_{11}]$ compound can also be obtained by depolymerization of $(ImH)_4[Ti_4F_{20}]$ under the action of F^- ions, which leads to the rupture of some of the trans-located bridging bonds between TiF_6 groups in the Ti_4F_{20} tetramer.

In the Im/TiF_4/aHF system with a molar ratio of Im:TiF_4 = 2:1, the compound $[ImH]_2[TiF_6]\cdot 2HF$ crystallizes. The structure of $[ImH]_2[TiF_6]\cdot 2HF$ is formed from imidazolium cations $[ImH]^+$, octahedral $[TiF_6]^{2-}$ anions, and two HF molecules [10]. The structural fragment of the compound $[ImH]_2[TiF_6]\cdot 2HF$ is $TiF_{6/1}F_{0/2}$, and the degree of polymerization is $\varepsilon = 0$. The $[ImH]_2[TiF_6]$ salt can also be obtained as a result of the structural depolymerization of $[ImH]_3[Ti_2F_{11}]$ in HF solution under the action of F^- ions by breaking the $Ti–F_b–Ti$ bridge in the Ti_2F_{11} group.

Conclusions

The structural depolymerization of TiF_4, which is the basis for the formation of the crystal structure of fluoride complexes of titanium(IV), was studied in the systems CsF/TiF_4/aHF, $[C(NH_2)_3]_2CO_3$ (and/or $[C(NH_2)_3]Cl$)/TiF_4/aHF, and Im/TiF_4/aHF. The compositions of fluoridotitanates(IV) formed in these systems and their crystal structures are considered in terms of the degree of polymerization (ε). With increasing initial amount of fluoride ion donors (AF = CsF or in (Gua)F and ImHF formed in situ) in AF/TiF_4 reactions, the degree of polymerization of the crystal structures of the obtained salts decreases. In all systems studied, the final products of TiF_4 structural depolymerization are $A_2[TiF_6]$ salts. The Ti atoms in the $[TiF_6]^{2-}$ anion are coordinated by six F ligands and form octahedra. The corresponding structural fragment is $TiF_{6/1}F_{0/2}$, and the degree of polymerization is $\varepsilon = 0$. The highest degree of polymerization ($\varepsilon = 2$) is present in the crystal structure of TiF_4 with structure fragments $TiF_{2/1}F_{4/2}$.

In conclusion, it should be noted that the proposed concept of structural depolymerization of metal fluoride compounds [1, 4] was considered in [15] as applied to the formation of fluoride glasses. In [16], the structure of fluorindate glasses is discussed on the position of structural depolymerization of “octahedral structures.” In particular, it is indicated that the sequential addition of mono- and divalent metal fluorides to InF_3, the structure of which is formed from InF_6 octahedral groups linked by vertices, takes place, as in the concept of structural depolymerization of metal fluoride compounds, sequential structural depolymerization: framework (InF_3) – layer $(InF_4^-)_\infty$ – $(InF_5^{2-})_\infty$ chain – isolated $[InF_6]^{3-}$ octahedra.

Author contribution Zoran Mazej syntheses, Evgeny Goreshnik structure determination, and Ruven Davidovich conclusions and writing.

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Code availability Not applicable.

Declarations

Conflict of interest The authors declare no competing interests.

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