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Syntheses and the crystal chemistry of the perfluoridotitanate(IV) compounds templated with ethylenediamine and melamine

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Abstract

Chemical reactions between ethane-1,2-diamine $[C_2H_4(NH_2)_2;$ ethylenediamine, abbr. *en*] and 1,3,5-triazine-2,4,6-triamine $[C_3H_6N_6;$ melamine, abbr. *mel*], with titanium tetrafluoride (TiF₄) were carried out in liquid anhydrous hydrogen fluoride (aHF). The latter acted in a dual role: as a reagent and as a solvent. The *n(en)* : *n*(TiF₄) = 2:1, 1:1, 1:3, 1:4, and *n(mel)* : *n*(TiF₄) = 2:1, 1:1, 1:2, 1:3, 1:4 molar ratios were studied. Crystallizations of the products from the saturated HF solutions yielded single crystals of $[enH_2]F_2\cdot 2HF$, previously known $[enH_2][TiF_6]$ and three new perfluoridotitanate(IV) salts, i.e., $[enH_2][TiF_6]\cdot HF$, $[enH_2]_{0.5}[TiF_5]$ and $[melH_2][TiF_6]\cdot HF$. Their crystal structures were determined including the crystal structure of the low-temperature modification of $[enH_2][TiF_6]$. The $[enH_2]_{0.5}[TiF_5]$ phase represents the first example of a structurally characterized perfluoridotitanate(IV) compound with a double charged cation, where instead of the usual octahedral $[TiF_6]^{2-}$ monomer, another kind of anion is present, i.e., polymeric chain-like ($[TiF_5]^{-})_{\infty}$ anion. The reactions in *en*/TiF₄/HF and *mel*/TiF₄/aHF systems are not selective enough to enable syntheses of individual $[enH_2]^{2+}$ and $[melH_2]^{2+}$ perfluoridotitanate(IV) in large quantities.

Keywords: ethylenediamine, melamine, titanium, fluorides, structure elucidation, hybrid compounds

1. Introduction

Perfluoridotitanates(IV) form an extensive class of the inorganic and hybrid compounds with a great structural diversity of the anions in the solid state.^{1,2,3} Majority of them are the $[TiF_6]^{2^-}$ salts where the anionic parts consist of the isolated TiF₆ octahedra.² Besides being isolated, the TiF₆ octahedra could be linked together yielding larger oligomeric (0-D geometry) or polymeric (1-D: chains, columns; 2-D: layers, slabs; 3-D: three-dimensional framework) poly[perfluoridotitanate(IV)] anions. In principle two octahedral TiF₆ units can share one, two or three fluorine atoms resulting in vertex-, edge- or face-sharing geometries of the linked octahedra. The latter example would represent the isolated $[Ti_2F_9]^-$ anion, predicted just theoretically.⁴ All the experimental attempts to prepare such salts failed so far.⁵ Instead of the isolated $[Ti_2F_9]^-$ anions, the compounds formulated as ATi_2F_9 (A = single charged cation) consist of the polymeric ($[Ti_2F_9]^-$)_∞ double chain-like anions. In the case of larger cations the formula is doubled (i.e., $A_2Ti_4F_{18}$) and the compounds contain isolated $[Ti_4F_{18}]^{2^-}$ oligomers.⁵

In the last decade we have successfully prepared a whole range of new perfluoridotitanates(IV) compounds. Many of them consist of previously unknown poly[perfluoridotitanate(IV)] anions as for example oligomeric $[Ti_4F_{19}]^{3-}$, ⁶ $[Ti_4F_{20}]^{4-}$, ^{7,8} $[Ti_{5}F_{23}]^{3-,7}$ $[Ti_{6}F_{27}]^{3-,8}$ $[Ti_{8}F_{36}]^{4-,8,9}$ $[Ti_{10}F_{45}]^{5-,10}$ and polymeric $([Ti_{2}F_{9}]^{-})_{\infty}$,^{2,5,7,8} $([Ti_3F_{13}])_{\infty}^{10}$ $([Ti_4F_{19}]^3)_{\infty}^2$ and $([Ti_6F_{27}]^3)_{\infty}^2$ In all cases, single charged cations (organic or inorganic) of various size and geometry were used as counter cations. The examples of the hybrid perfluoridotitanates(IV) containing dications are scarce and mostly limited to $[TiF_6]^{2-}$ salts. One of the structurally characterized hybrid phase of diprotonated cation is hexafluoridotitanate(IV), $[enH_2]$ [TiF₆]. 11 ethylenediammonium Besides it. the $[enH_2]$ [TiF_{4.3}(OH)_{1.7}], where part of the fluorine atoms is replaced by OH⁻ groups, is also known.¹²

As previously evidenced, the $[enH_2][TiF_6]$ undergoes a first-order phase transition at around 130 K.¹¹ In order to determine the crystal structure of the low-temperature phase (T < 130 K) and to check the possibility of the existence of other possible perfluoridotitanate(IV) salts of ethylenediammonium (abbr. *en*), crystallizations between various ratios of *en* and TiF₄ in an anhydrous hydrogen fluoride (aHF) were carried out. Additionally, reactions between 1,3,5-triazine-2,4,6-triamine (melamine; abbr. *mel*) and TiF₄ in aHF were investigated. The melamine was chosen because its corresponding protonated cation can occur in three forms: singly, doubly or triply protonated.¹³ Syntheses in *en*/TiF₄/aHF and *mel*/TiF₄/aHF systems resulted in the detection of seven perfluoridotitanate(IV) compounds. Four of them were

structurally characterized. These are low temperature form of $[enH_2][TiF_6]$ (β -modification), $[enH_2]_{0.5}[TiF_5]$ and HF containing compounds $[enH_2][TiF_6]$ ·HF and $[melH_2][TiF_6]$ ·HF. The latter two are new examples of compounds containing HF species.¹⁴ Previously known examples with first row transition metals (3*d*) are A₂CrF₆·2HF (A = Na, K),¹⁵ A₂CrF₆·4HF (A = Rb, Cs),¹⁵ K₃Cr₂F₁₁·2HF,¹⁵ K₂MF₆·HF (M = Ti, Cr),¹⁶ ATiF₅·HF (A = Na, K, Rb),² (*im*H)₂TiF₆·2HF (*im* = imidazolium),⁷ NaTi₂F₉·HF,² K₄Ti₈F₃₆·8HF,⁹ Rb₄Ti₈F₃₆·6HF,⁹ (H₃O)₃[Cr(SbF₆)₆](Sb₂F₁₁)·HF¹⁷ and CoSr₅(AsF₆)₁₂·8HF.¹⁴ Additionally, crystal structure of [*en*H₂]F₂·2HF has been determined within this study. Besides of cationic part and HF molecules its crystal structure consists also of so called »independent« or »lone« fluoride ions as previously reported in many anhydrous and hydrated metal fluorides.¹⁸ Results of both studies (*en*/TiF₄/aHF and *mel*/TiF₄/aHF) are reported in this paper.

2. Experimental section

CAUTION: Anhydrous HF and some fluorides are highly toxic and must be handled in a well-ventilated hood and protective clothing must be worn all the time!

2.1. Materials and Methods

2.1.1. Reagents.

Ethane-1,2-diamine (Sigma-Aldrich, 99 %) was kept above the molecular sieves. 1,3,5triazine-2,4,6-triamine (Sigma-Aldrich, 99 %) was used as supplied. Anhydrous HF (Linde AG, 99.995 %) was kept above K_2NiF_6 (Advance Research Chemicals Inc, 99.9 %) and was used after at least four hours of treatment. Titanium tetrafluoride was synthesized by two different methods: 1) by a reaction between TiCl₃ (Sigma-Aldrich, 99.999 %) and aHF and subsequent fluorination with elemental F_2 in aHF; 2) by a reaction between TiCl₄ (Acros Organics, 99.9%) and liquid aHF at ambient temperature. The purity of TiF₄ was confirmed using Raman spectroscopy and elemental chemical analysis.

2.1.2. Synthetic and crystallization apparatus.

Because of the high hygroscopicity of TiF_4 and fluoridotitanate(IV) compounds all manipulations with them were carried out under anhydrous conditions. Non-volatile materials were handled in a M. Braun glove box in an argon atmosphere, where quantity of water has not exceeded 0.5 ppm. Volatile compounds, such as aHF and F₂, were handled on a vacuum line constructed of nickel and PTFE (polytetrafluoroethylene).

Vessels, used for syntheses and single crystal growth, were manufactured from tetrafluoroethylene-hexafluoropropylene block-copolymer (FEP; Polytetra GmbH, Germany) tubes. Detailed information about reaction and crystallization vessels is given in ESI in **Figures S1** and **S2**.

Prior to use all reaction and crystallization vessels were dried under dynamic vacuum and passivated with elemental fluorine F_2 (Solvay Fluor and Derivate GmbH, 99.98 %) at 1 bar for 2 hours.

2.1.3. Synthesis and crystal growth.

Syntheses between ethylenediamine and melamine with TiF_4 were carried out by two ways. The first approach was used for reactions with starting $n(en) : n(TiF_4) = 2:1$ and 1:1 molar ratio. The approximate amount of ethylenediamine was condensed into the preliminarily dried reaction vessel and its mass was further accurately determined. After that the required amount of TiF_4 was loaded into another reaction vessel. Around 4–8 ml of aHF was condensed to the ethylenediamine at 77 K and after the solution was warmed up to ambient temperature, it was poured to the reaction vessel filled with TiF_4 . Reactions were usually left to proceed 1–3 days at ambient temperature with constant mixing. At the end the liquid phase was decanted from the insoluble residue to another reaction vessel, all volatiles were pumped out and isolated solids characterized.

In aHF soluble phases were loaded into crystallization vessels, the aHF was condensed to the samples at 77 K and the vessel was warmed up to an ambient temperature. When the samples were completely dissolved, clear solutions were decanted into the narrower arm of the vessel. In order to achieve evaporation of the aHF from the narrower arm, a temperature gradient between two arms of the crystallization vessel was maintained. In the beginning of the process, it was 10 degrees and later slowly increased to 50 K. The obtained crystals were isolated by pumping away the volatiles and then transferred to a glovebox.

The second synthetic approach was used for the reactions with higher starting rate of TiF₄, i.e., with starting $n(en) : n(TiF_4) = 1:3$ and 1:4 molar ratios. The approximate amount of ethylenediamine (~20 µL) was added by automatic pipette into a few centimeters long FEP tube (4 mm i.d. × 6 mm) in a glove box. The tube was equipped with PTFE valve. After the mass of reactant was accurately determined, the PTFE valve was removed and the whole tube inserted inside the wider arm (16 mm i.d. × 19 mm o.d) of crystallization vessel containing requested amount of TiF₄. Whole procedure was done in glove box. On the vacuum system, approximately 10–13 mL of aHF was condensed to the reagents and the content of the vessel mixed well. After several days the liquid phase was decanted into the narrower arm of double-

arm crystallization vessel and the crystallization process began. Both, the products recovered from decanted solutions and in aHF insoluble remains were characterized.

In attempts to synthesize melaminium perfluoridotitanate(IV) compounds, calculated amounts of the solid reactants (melamine and TiF₄) were loaded to the reaction vessels in the glove box. Approximately 10-13 ml of aHF was condensed onto the reagents, the reactions were left to proceed for several days and finally the liquid phase was decanted to the narrower arm of the crystallization vessel. Both, the products recovered from decanted solutions and in aHF insoluble remains were characterized. Additional experiments were done to dissolve in aHF insoluble melamine/TiF₄ phases in SO₂ and CH₃CN in an attempt to prepare saturated solutions for single-crystal growths.

The masses of the reactants for all ethylenediamine/TiF₄/aHF and melamine/TiF₄ /aHF reactions are given in **Tables S1** and **S2**.

2.2. Characterization Methods

2.2.1. Raman spectroscopy.

Raman spectra with a resolution of 0.5 cm⁻¹ were recorded at room temperature on a Horiba Jobin Yvon LabRam-HR spectrometer equipped with an Olympus BXFM-ILHS microscope. Samples were excited by the 632.8 nm emission line of a He–Ne laser with regulated power in the range 20–0.0020 mW, which gives 17–0.0017 mW focused on a 1 μ m spot through a 50× microscope objective on the top surface of the sample.

Powdered materials were mounted in the glove box in previously vacuum-dried and fluorinated quartz capillaries, which were initially sealed with Halocarbon 25-5S grease (Halocarbon Corp.) inside the glove box and later heat-sealed in an oxygen-hydrogen flame outside the glove box.

2.2.2. Single crystal X-ray diffraction analysis.

Single crystal X-ray diffraction data were collected on a Rigaku AFC7 diffractometer equipped with a Mercury CCD area detector for $[enH_2][TiF_6]$ ·HF and $[melH_2][TiF_6]$ ·HF compounds and on "Agilent Gemini A" diffractometer equipped with Atlas CCD detector for β - $[enH_2][TiF_6]$, $[enH_2]_{0.5}[TiF_5]$ and $[enH_2]F_2$ ·2HF compounds. In all cases graphite-monochromated Mo K_a radiation ($\lambda = 0.7107$ Å) was used. Diffraction data were collected at 100 K for β - $[enH_2][TiF_6]$ and at 200 K for the other four compounds.

Crystals were immersed in perfluorodecalin (Fluorochem, Cat. Code: 003283, melting point 263 K) inside a glove box, selected under a microscope, and mounted on the goniometer head of the diffractometer in a cold nitrogen stream, created by Oxford Cryojet cooling

system. Although up to 15 crystals from the same batch were screened, the presence of other crystal phases cannot be definitively excluded.

The diffraction data, collected on the Rigaku AFC7 diffractometer, were processed using Rigaku CrystalClear software.¹⁹ Data, collected on the "Agilent Gemini A" diffractometer were processed with the CrysAlis PRO program.²⁰ The crystal structures of $[enH_2][TiF_6]$ ·HF and $[melH_2][TiF_6]$ ·HF were solved by direct methods using SIR-92²¹, implemented in teXan software.²² Structures of β - $[enH_2][TiF_6]$, $[enH_2]_{0.5}[TiF_5]$ and $[enH_2]F_2$ ·2HF were solved by charge flipping method using the Superflip program²³ (Olex crystallographic software²⁴). The electron density map, obtained with the Superflip software, was analyzed with the EDMA program,²⁵ which gave initial models of the structures. Final refinement was done with SHELXL-2013,²⁶ implemented in Olex crystallographic software.²⁴ Figures were prepared using the program DIAMOND 4.4.²⁷ The thermal ellipsoids in figures are drawn at the 50 % probability level. Hydrogen atoms are presented by circles of arbitrary size.

All hydrogen atoms in the structure of $[enH_2]F_2 \cdot 2HF$ were found on a difference Fourier map, their positional and isotropic thermal parameters were refined. Hydrogen atoms belonging to melaminium or ethylenediaminium cations in all other structures were placed on ideal positions and refined as the riding atoms with relative isotropic displacement parameters. Positions of hydrogen atoms belonging to HF molecules in structures of $[enH_2]TiF_6 \cdot HF$ and $[melH_2][TiF_6] \cdot HF$ were found on difference Fourier maps, their positional and isotropic thermal parameters were refined.

Carbon atoms of $[enH_2]^{2+}$ cation in the structure of β - $[enH_2]$ [TiF₆] are moderately disordered, resulting in strong elongation of respective thermal ellipsoids. All attempts to split the positions of carbon atoms in $[enH_2]^{2+}$ cation resulted in unstable refinement and unrealistic bonds lengths.

3. Results and discussion

3.1. Syntheses and crystallizations of ethylenediammonium perfluoridotitanate(IV) compounds

Ethylenediammonium poly[perfluoridotitanate(IV)] compounds were synthesized by the chemical reactions between liquid ethylenediamine $C_2H_4(NH_2)_2$ (*en*) and titanium tetrafluoride TiF₄ in an excess of an anhydrous hydrogen fluoride (aHF). The latter acted in a dual role: as a reagent and as a solvent. Starting $n(en) : n(TiF_4)$ molar ratios of reagents were

equal to 2:1, 1:1, 1:3 and 1:4. In all *en*/TiF₄/aHF reactions two phases – liquid and insoluble solid material – were always observed (**Scheme 1**). In the 2:1 and 1:1 reaction systems the liquid phases were firstly separated from insoluble residues. After that, volatiles were pumped away, solid products recovered and finally characterized. Part of the sample, isolated from solution, was re-dissolved in aHF in attempt to grow single crystals. In the case of reactions with larger amounts of TiF₄ (1:3 and 1:4) the liquid phase was decanted from one arm of the crystallization vessel into another one without prior isolation in an attempt to grow single crystals.



Scheme 1. Products of reactions between ethylenediamine and TiF_4 in an anhydrous aHF (serving as a reagent and also as a solvent) with different starting molar ratios of reactants, i.e., $n(en) : n(\text{TiF}_4) = 2:1, 1:1, 1:3, \text{ and } 1:4.$

Raman spectra of the solids, recovered from the HF solutions prepared by reactions between *en* and TiF₄ (molar ratios: 2:1 and 1:1) in aHF, were almost identical (**Figure 1**). They show vibrational bands, that can be assigned to $[\text{TiF}_6]^{2^-}$ anions (609 cm⁻¹, 284 cm⁻¹ and weak at 487 cm⁻¹)^{7,8} and $[enH_2]^{2+}$ cations.²⁸ Subsequent crystallization of the soluble phase of 2:1 system yielded single crystals of $[enH_2]\text{F}_2 \cdot 2\text{HF}$, $[enH_2][\text{TiF}_6]^{11}$ as well as traces of $[\text{H}_3\text{O}][\text{TiF}_5]$ phase,²⁹ as a by-product. The formation of $[\text{H}_3\text{O}]^+$ compounds was a result of a contamination of reactants with traces of water, which is protonated in the superacid aHF with the formation of $[\text{H}_3\text{O}]^+$ cations. The second system, with the starting $n(en) : n(\text{TiF}_4) = 1:1$ molar ratio, revealed single crystals of three phases: prevailing $[enH_2][\text{TiF}_6]$ and its solvated

form $[enH_2][TiF_6]$ ·HF and only a few crystals of $[enH_2]_{0.5}[TiF_5]$, containing polymeric zigzag chain-like $([TiF_5]^-)_{\infty}$ anion.



Figure 1. Raman spectra of in HF soluble materials, isolated after reactions between ethylenediamine and TiF₄ in 2:1 and 1:1 molar ratios. The vibrational bands at 609 cm⁻¹, 487 cm⁻¹ and 284 cm⁻¹ belong to $[\text{TiF}_6]^{2-}$ anion.

Chemical reactions between ethylenediamine and larger amounts of titanium tetrafluoride $[n(en) : n(\text{TiF}_4) = 1:3$ and 1:4 molar ratios] yielded products which were insoluble in aHF. Their Raman spectra (**Figure 2**) do not show the presence of TiF₄ (**Figure S14**). Raman spectrum of insoluble solid obtained in a reaction with $n(en):n(\text{TiF}_4) = 1:3$ molar ratio is similar to the Raman spectra of insoluble residues after reactions between *en* and TiF₄ with 2:1 and 1:1 molar ratios (**Figure 2**). There are two vibrational bands at 706 cm⁻¹ and 750 cm⁻¹, that can be assigned to a symmetric Ti–F stretching modes of perfluoridotitanate(IV) anions.^{2,5,7,8,9,10} On the basis of previous results those bands can be assigned as belonging to $[enH_2]^{2+}$ compound which consists of polymeric ($[\text{TiF}_5]^-$)_∞ and ($[\text{Ti}_2\text{F}_9]^-$)_∞ anions. Raman spectrum of the solid residue after a reaction of *en* with TiF₄ (molar

ratio 1:4) in aHF, shows strong vibrational band at 759 cm⁻¹, that can be assigned to $([Ti_2F_9]^{-})_{\infty}$ anion, e.g., the formation of $[enH_2]_{0.5}[Ti_2F_9]$ or its HF-solvated form (**Figure 2**). This indicates that the compound obtained in 1:3 system (vibrational bands at 706 cm⁻¹ and 750 cm⁻¹) is most probably not a mixture of $[enH_2]_{0.5}[TiF_5]$ and $[enH_2]_{0.5}[Ti_2F_9]$ phases but more likely a mixed-anion $[enH_2][TiF_5][Ti_2F_9]$ compound. In the former case, the band assigned to $([Ti_2F_9]^{-})_{\infty}$ anion (at 750 cm⁻¹) should be observed at the same position as in 1:4 product $[enH_2]_{0.5}[Ti_2F_9]$ (759 cm⁻¹; **Figure 2**). Since the products obtained in $en/TiF_4/aHF$ systems with larger contents of TiF₄ are insoluble in aHF it will be necessary to find another way of single crystal growth to get the final answer about their composition.



Figure 2. Raman spectra of in aHF insoluble residues after reactions between ethylenediamine and TiF₄ in 2:1, 1:1, 1:3 and 1:4 molar ratios. The marked intense bands correspond to a symmetric Ti–F stretching $[v_s(Ti-F)]$ of perfluoridotitanate(IV) anions $([TiF_5]^-)_{\infty}$ and $([Ti_2F_9]^-)_{\infty}$.

3.2. Syntheses and crystallizations of 1,3,5-triazine-1,3-diium-2,4,6-triamine poly[perfluoridotitanate(IV)] compounds

Possible formation of the previously unknown perfluoridotitanate(IV) salts of 1,3,5triazine-2,4,6-triamine (mel; melamine) was screened by carrying out chemical reaction between melamine and TiF₄ in an anhydrous HF (serving as a reagent and also as a solvent) with different starting n(mel) : $n(TiF_4)$ molar ratios (2:1, 1:1, 1:2, 1:3, 1:4 and 1:5; Table S2 and Scheme 2). The product of the reaction with the highest rate of melamine, n(mel): $n(TiF_4)$ equal to 2:1, was completely soluble in HF. The Raman spectrum of the isolated solid, after pumping away HF, revealed the formation of the hexafluoridotitanate(IV) and hydrogen difluoride salts of melamine. The vibrational band at $\sim 560 \text{ cm}^{-1}$ (Figure 3) confirms the presence of [HF₂]⁻ anion.³⁰ This vibrational band is not present in pure melamine but it appears after its treatment with aHF (Figure 3). In the superacidic aHF melamine is protonated leading to $[melH_x]^{x+}([HF_2])_x$ (x = 1, 2 or 3). Without the single crystal structure determination the degree of protonation (i.e., single-, double- or triple-protonated) cannot be exactly known. Subsequent crystallization of the product from the saturated HF solution (obtained by n(mel) : $n(TiF_4) = 2:1$ molar ratio) led to the single crystals of the solvated $[melH_2]$ [TiF₆]·HF phase. The product of the second reaction, with starting $n(mel) : n(TiF_4)$ molar ratio equal to 1:1, was mostly composed from the $[TiF_6]^{2-}$ phase as proved by Raman spectroscopy. A small amount of the insoluble phase precipitated from the HF solution after one day of mixing. The crystallization of the product from the saturated HF solution [n(mel)]: $n(\text{TiF}_4) = 1:1$ yielded small single crystals of the $[melH_2][\text{TiF}_6] \cdot \text{HF}$ phase.

In the course of the reactions with higher ratios of TiF₄ [n(melamine) : n(TiF₄) = 1:2, 1:3, 1:4 and 1:5] there was always a lot of insoluble solid visible. The HF solutions above the solid residues were decanted to the narrower arms of the crystallization vessels. Only the crystals of the solvated phase [$melH_2$][TiF₆]·HF grew from the decanted solutions obtained in the melamine/TiF₄ systems with starting $n(mel) : n(TiF_4) = 1:3$ and 1:4 molar ratios (**Scheme 2**). The quality of single crystals grown during crystallization of the soluble product in the system with 1:2 molar ratio of reactants, was too poor for a crystal structure determination. The crystallization from the decanted solution obtained by reaction with reactant ratio $n(mel) : n(TiF_4) = 1:5$ resulted in the precipitation of the fine powder only.



Scheme 2. Products of reactions between 1,3,5-triazine-2,4,6-triamine and TiF4 in an anhydrous aHF (serving as a reagent and also as a solvent) with different starting molar ratios of reactants, i.e., $n(mel) : n(\text{TiF}_4) = 2:1, 1:1, 1:2, 1:3, 1:4$ and 1:5.

The insoluble products formed after the reactions $[n(mel) : n(TiF_4) = 1:2, 1:3, 1:4 \text{ and}$ 1:5] were isolated separately and studied by means of Raman spectroscopy (Figure 3). The most intensive vibrational band at 690 cm^{-1} corresponds to the protonated melamine vibrations.¹³ The other two intensive bands, found in the range typical for the symmetric inphase Ti-F_t stretching vibrations of perfluoridotitanate(IV) anions, 2,5,7,8,9,10 are determined at 713 and 755 cm^{-1} . These vibrational bands can be assigned to the polymeric anions $([TiF_5])_{\infty}^{2,8,10,29,31}$ and $([Ti_2F_9])_{\infty}^{2,5,7,8,32}$ respectively. The phase with the single-chain like $([TiF_5])_{\infty}$ anion predominates in the products with lower rate of TiF₄ (Figure 3; reactions with 1 : 2 and 1 : 3 molar ratios). The compound containing the double-chain like $([Ti_2F_9])_{\infty}$ anion appears in larger amounts in the products of the reactions with greater amounts of TiF₄ (Figure 3; reactions with 1:4 and 1:5 molar ratios). On the basis that the intensities of vibrational bands (Figure 3; ratios 1:2, 1:3, 1:4 and 1:5) vary and are found at the same positions (713 and 755 cm⁻¹) we can assume that we have a mixture of $([TiF_5])_{\infty}$ and $([Ti_2F_9])_{\infty}$ salts and not a $([TiF_5])_{\infty}/([Ti_2F_9])_{\infty}$ mixed-anion compound. The vibrational band at around 555 cm⁻¹ in the Raman spectra of the 1:2 to 1:5 products (Figure 3) is not necessary connected with the presence of $[HF_2]^-$ anion. It more likely belongs to the vibrations of $([TiF_5])_{\infty}$ chain as previously observed in ATiF₅ (A = K, Rb, Cs).²

Attempts to grow single crystals of in aHF insoluble phases from aprotic solvents, as SO₂ and CH₃CN, failed. Either powdered (using SO₂) or either low crystalline or powdered and sticky material was recovered (using CH₃CN).



Figure 3. Raman spectra of in aHF insoluble residues recorded after reactions between melamine and TiF₄ (1:2, 1:3, 1:4 and 1:5 molar ratios) in aHF. Raman spectra of melamine, melamine treated with aHF, melaminium $[\text{TiF}_6]^{2^-}$ salt (1:1 molar ratio), and Raman spectrum of the product of the reaction between 2:1 molar ratio of melamine and TiF₄ in aHF, are also given. The marked intense bands correspond to a symmetric Ti–F stretching $[v_s(\text{Ti}-F)]$ of perfluoridotitanate(IV) anions $[\text{TiF}_6]^{2^-}$, $([\text{TiF}_5]^{-})_{\infty}$ and $([\text{Ti}_2\text{F}_9]^{-})_{\infty}$.

3.3. Single crystal structures of ethylenediammonium perfluoridotitanates β -[C₂H₄(NH₃)₂][TiF₆], [C₂H₄(NH₃)₂][TiF₆]·HF, and [C₂H₄(NH₃)₂]_{0.5}[TiF₅].

The corresponding single crystal structure data of ethylenediammonium, i.e., $[enH_2]^{2+}$, compounds, isolated from the C₂H₄(NH₂)₂/TiF₄/aHF systems are summarized in **Table 1**.

Chem. formula	β -[<i>en</i> H ₂][TiF ₆]	$[enH_2]$ [TiF ₆]·HF	$[enH_2]_{0.5}[TiF_5]$	[<i>en</i> H ₂]F ₂ · 2HF
CCDC #	1885310	1885309	1885308	1885312
$F_w(g/mol)$	223.97	244.03	347.84	140.14
Crys. system	Triclinic	Triclinic	Monoclinic	Monoclinic
Space group	$P \overline{1}$	$P \overline{1}$	$P2_{1}/c$	<i>I2/m</i>
<i>a</i> (Å)	5.8601(4)	5.8821(8)	5.7801(3)	5.2645(4)
<i>b</i> (Å)	5.9228(4)	5.9338(8)	15.447(1)	4.6185(4)
<i>c</i> (Å)	10.6118(7)	11.958(2)	5.4825(3)	12.787(1)
α (°)	94.706(5)	91.353(6)	90	90
β (°)	92.210(5)	96.867(6)	92.433(5)	97.141(7)
γ (°)	93.383(5)	98.318(7)	90	90
$V(\text{\AA}^3)$	366.09(4)	409.67(9)	489.06(5)	308.48(4)
Ζ	2	2	2	2
$T(\mathbf{K})$	100	200	200	200
R_1^{a}	0.043	0.046	0.033	0.031
wR_2^{b}	0.116	0.130	0.086	0.088
<i>a</i> b · 1 ° 1				

Table 1. Crystal data and refinement results of β -[*en*H₂][TiF₆], [*en*H₂][TiF₆]·HF, [*en*H₂]_{0.5}[TiF₅] and [*en*H₂]F₂·2HF

^{*a*} R_1 is defined as $\Sigma ||F_0| - |F_c|| / \Sigma |F_0|$ for $I > 2\sigma(I)$. ^{*b*} wR_2 is defined as $[\Sigma[w(F_0^2 - F_c^2)^2] / \Sigma w(F_0^2)^2]^{\frac{1}{2}}$.

3.3.1. Crystal structure of β -[*en*H₂][TiF₆].

One of the products of the chemical reaction between ethylenediamine (en) and TiF₄ n(en) : $n(TiF_4)$ with starting 2:1 molar ratio was ethylenediaminium hexafluoridotitanate(IV). The α -[enH₂][TiF₆] crystallizes in the monoclinic A2/a space group $(a = 10.655 \text{ Å}, b = 8.7081 \text{ Å}, c = 7.9704 \text{ Å}, \beta = 95.032^{\circ} \text{ at ambient temperature}).^{11} \text{ As}$ previously evidenced by thermal investigations by differential scanning microcalorimetry and dielectric measurements a first order phase transition in [enH₂][TiF₆] is present at around 130 K¹¹, but the crystal structure of the low-temperature phase has not been reported until now. To fill this gap the single crystal of [enH₂][TiF₆] was cooled down from 200 K to 100 K in two hours on the goniometer of the diffractometer. The phase transition led to a symmetry decrease. Its low-temperature modification, β -[enH₂][TiF₆], crystalizes in the triclinic P $\overline{1}$ space group. Detailed crystallographic data are given in Table S3.

The crystal structure of the low-temperature phase consists of two crystallographically independent octahedral $[\text{TiF}_6]^{2^-}$ anions (one of them is disordered) and one crystallographically independent ethylenediammonium cation, $[enH_2]^{2^+}$ (**Figure 4**). The geometry of the $[\text{TiF}_6]^{2^-}$ anion in the crystal structure of β - $[enH_2][\text{TiF}_6]$ is the same as for previously reported $[\text{TiF}_6]^{2^-}$ anions. Titanium atoms are in octahedral coordination of six

fluorine atoms with the Ti–F bond lengths ranging from 1.846(2) to 1.873(4) Å. The F–Ti–F angles differ from 90 ° by up to 0.8 ° (**Table S4**). The geometry of the ethylenediammonium cation in the β -phase slightly differs from that in the α -phase: one C–N and the C–C bonds are slightly elongated, and another C–N bond is shortened in the low-temperature modification comparatively to the high-temperature modification. The C–C–N angles and N–C–C–N torsion angles are practically identical in both modifications.

The packing of the $[\text{TiF}_6]^{2^-}$ anions and the $[enH_2]^{2^+}$ cations in the unit cells of α - and β -[enH_2][TiF₆] compounds is presented in **Figure 4**. The packing observed in the hightemperature modification is very similar (**Figure 4**) with the only one clearly visible difference – disordering of one anion in the low-temperature modification.

The hydrogen atoms, bonded to nitrogen atoms are involved in hydrogen bonding with the $[\text{TiF}_6]^{2-}$ anions. The hydrogen bonding pattern in both structures is very similar: each $[enH_2]^{2+}$ cation forms hydrogen-bonds with six anions, while the shortest H…F distance in the high-temperature modification is 1.971 Å, whereas in the low-temperature modification the shortest H…F distance is 1.818 Å.



Figure 4. The unit cells of α -[*en*H₂][TiF₆] (upper) and β -[*en*H₂][TiF₆] (lower) compounds. Two disordered positions of the [TiF₆]²⁻ anions are shown.

3.3.2. Crystal structure of [*en*H₂][TiF₆]·HF.

Among single crystals, grown during the crystallization of the products of the chemical reaction between ethylenediamine (*en*) and TiF₄ in aHF with the $n(en) : n(TiF_4) = 1:1$ molar ratio from aHF, several single crystals of monosolvated hexafluoridotitanate(IV) phase $[enH_2][TiF_6]$ ·HF were observed. It crystallizes in the triclinic $P \ \overline{l}$ space group (**Table S5**).

The crystal structures of solvated and non-solvated α - and β -[*en*H₂][TiF₆] phases consist of octahedral [TiF₆]²⁻ anions. In the case of α -[*en*H₂][TiF₆] the hexafluoridotitanate anion is more symmetrical with three independent Ti–F bonds with very similar lengths (1.848 Å, 1.849 Å and 1.859 Å). The F…Ti…F angles in the octahedra differ from 90 ° by up to 0.5 °.¹¹ In the crystal structure of [*en*H₂][TiF₆]·HF, where HF molecules are incorporated in the crystal structure, hydrogen bonds between HF and the anion appear, leading to the distortion of the [TiF₆]²⁻ anion. In TiF₆ unit all seven atoms (one Ti and six F) are crystallographically independent with the Ti–F bond lengths ranging from 1.834(2) to 1.913(2) Å (**Figure S4**). The longest Ti–F bond is between Ti and F3 atom, where the latter is involved in hydrogen bonding with HF. The shortest bond is between Ti atom and F5 atom, which is situated in *trans*- position to the F3 atom involved in hydrogen bonding. Other geometric parameters of the [TiF₆]²⁻ anion are given in **Table S6**.

In the crystal structure of $[enH_2]$ [TiF₆]·HF, all fluorine atoms of the [TiF₆]^{2–} anion and all hydrogen atoms (bonded to nitrogen atoms) of $[enH_2]^{2+}$ cations are involved in hydrogen bonding. The F3····F7 distance, between the F3 atom of [TiF₆]^{2–} anion and F7 atom of HF molecule involved in hydrogen bonding, equals to 2.384(4) Å (**Figure 5**). Such hydrogen bonding between HF molecules and [TiF₆]^{2–} anions in hybrid compounds was previously observed in imidazolium salt $[imH]_2$ [TiF₆]·2HF.⁷ Corresponding F···F distances between fluorine atoms involved in hydrogen bonding are comparable (2.374(6) Å)⁷ to those observed in the crystal structure of $[enH_2]$ [TiF₆]·HF. Such strong hydrogen bonding prevents release of HF under dynamic vacuum and makes single crystals of $[enH_2]$ [TiF₆]·HF stable in inert atmosphere at ambient temperature. The remaining five fluorine atoms of the [TiF₆]^{2–} anion form hydrogen bonds with five $[enH_2]^{2+}$ cations on the way that each F atom is coordinated to one H atom of each $[enH_2]^{2+}$ cation. Additionally, one of the $[enH_2]^{2+}$ cations is hydrogen bonded (N2–H···F7) to F7 atom of the HF molecule (**Figure S5**).

Two crystallographically independent $[enH_2]^{2+}$ cations are determined in the crystal structure of $[enH_2][\text{TiF}_6]\cdot\text{HF}$. Each $[enH_2]^{2+}$ cation, constructed of N1 and C1 atoms, forms six hydrogen bonds with the six $[\text{TiF}_6]^{2-}$ anions with the N…F distances ranging from 2.712(4) to 2.796(4) Å (**Figure S6**). Each $[enH_2]^{2+}$ cation, consisting of N2 and C2 atoms, is

hydrogen bonded with the four $[\text{TiF}_6]^{2^-}$ anions with the N…F distances 2.788(4) and 2.846(2) Å and weakly hydrogen bonded with two HF molecules with the N…F distance equal to 3.051(4) Å. Detailed parameters of hydrogen bonding are depicted in **Table S7**.

The packing of the structural units in the unit cell of the $[enH_2][TiF_6]$ ·HF compound is presented in **Figure 5**. As in the crystal structures of all hybrid poly[perfluoridotitanate(IV)] compounds, inorganic anions and organic cations are interconnected in 3-D structure by hydrogen bonding. The HF molecules are located inside the voids.



Figure 5. The unit cell of $[enH_2]$ [TiF₆]·HF compound viewed along the *b*-axis. The atoms of the asymmetric unit are labeled.

3.3.3. Crystal structure of [*en*H₂]_{0.5}[TiF₅].

Single crystals of another ethylenediammonium poly[perfluoridotitanate(IV)] compound were observed as a minor product after the crystallization of the reaction mixture of ethylenediamine and TiF₄ in aHF with the $n(en) : n(TiF_4) = 1:1$ molar ratio. New phase corresponds to $[enH_2]_{0.5}[TiF_5]$ compound. It crystallizes in the $P2_1/c$ space group with four formula units per unit cell. Detailed crystallographic data are given in **Table S8**.

The crystal structure of ethylenediammonium bis[pentafluoridotitanate(IV)] consists of one crystallographically independent ethylenediammonium $[enH_2]^{2+}$ cation and polymeric $([TiF_5]^-)_{\infty}$ anions in the form of monomeric zig-zag chain of slightly distorted TiF₆ octahedra, linked by *cis*-vertices (**Figure 6**). Bond distances between titanium and terminal fluorine

atoms, ranging from 1.780(1) to 1.850(2) Å, are considerably shorter than the bond lengths between titanium and bridging fluorine atoms (2.023(1) - 2.028(1) Å). Other geometric parameters of the $([\text{TiF}_5]^-)_{\infty}$ are given in **Table S9**. The observed bond lengths are in good agreement with the Ti–F bond lengths in previously reported $([\text{TiF}_5]^-)_{\infty}$ salts (**Table S11**), i.e., $[\text{H}_3\text{O}][\text{TiF}_5]$,²⁹ $[\text{NH}_4][\text{TiF}_5]$,³¹ A[TiF₅]·HF (A = Na, K, Rb, Cs),² $[\text{XeF}_5][\text{TiF}_5]^{10}$ and $[C(\text{NH}_2)_3]_4[\text{H}_3\text{O}]_4[\text{Ti}_4\text{F}_{20}][\text{TiF}_5]_4$.⁸ All Ti–F_b–Ti angles in the crystal structure of $[en\text{H}_2]_{0.5}[\text{TiF}_5]$ are equivalent and equal to 138.31(7) °.

All terminal fluorine atoms of the $([\text{TiF}_5]^-)_{\infty}$ anion are involved in hydrogen bonding with the $[enH_2]^{2+}$ cations (**Table S10**). Three nearest neighbouring TiF₆ octahedra are hydrogen bonded with F1, F2 and F3 atoms to the same hydrogen atom of the $[enH_2]^{2+}$ cation with the N…F distances ranging from 2.783(3) to 2.897(3) Å (**Figures 6** and **S7**). Two TiF₆ units, separated by the third one, are connected *via* Ti–F4…H–N hydrogen bonds with the same $[enH_2]^{2+}$ cation, where one hydrogen bond is stronger and one weaker (the N…F distances equal to 2.839(3) and 3.047(3) Å, respectively).



Figure 6. The unit cell of $[enH_2]_{0.5}$ [TiF₅] compound and coordination of the $([TiF_5]^-)_{\infty}$ anions by $[enH_2]^{2+}$ cations. Symmetry codes: (i) *x*, 1.5–*y*, -0.5+*z*; (ii) *x*, *y*, -1+*z*; (iii) –1+*x*, *y*, *z*.

Each $[enH_2]^{2+}$ cation forms hydrogen bonds with four TiF₅ chains (**Figures 6 and S8**). The polymeric $([TiF_5]^-)_{\infty}$ anions are closely packed and connected together by hydrogen bonding with the $[enH_2]^{2+}$ cations (**Figure S9**).

3.4. Single crystal structure of melaminium perfluoridotitanate [C₃H₈N₆][TiF₆]·HF

The crystallizations of the melaminium poly[perfluoridotitanate(IV)] compounds from the saturated aHF solutions led to small single crystals. Among the crystallized products of the reactions between melamine and TiF₄ in aHF with the $n(mel) : n(TiF_4) = 2:1, 1:1, 1:2, 1:3$ and 1:4 molar ratios, only the single crystals of [*mel*H₂][TiF₆]·HF phase were of sufficient quality for X-ray diffraction analysis. The corresponding single crystal structure data of [*mel*H₂][TiF₆]·HF are given in **Table 2**.

	Chem. formula	[C ₃ H ₈ N ₆][TiF ₆]·HF	
	CCDC #	1885311	
	$F_w(g/mol)$	310.06	
	Crystal system	Triclinic	
	Space group	$P \overline{1}$	
	a (Å)	6.694(1)	
	<i>b</i> (Å)	7.4705(8)	
	<i>c</i> (Å)	9.865(2)	
	α (°)	86.65(3)	
	β (°)	87.27(3)	
	γ (°)	74.47(2)	
	$V(\text{\AA}^3)$	474.2(1)	
	Ζ	2	
	$T(\mathbf{K})$	200	
	R_1^{a}	0.063	
	wR_2^{b}	0.178	
aR_1	is defined as $\Sigma F_{o} $	$- F_{\rm c} /\Sigma F_{\rm o}$ for $I > 2\sigma(I)$	
b.	wR_2 is defined as $[\Sigma]$	$w(F_o^2 - F_c^2)^2] / \Sigma w(F_o^2)^2]^{1/2}$.	

Table 2. Crystal data and refinement results of [melH₂][TiF₆]·HF.

The hexafluoridotitanate(IV) salt of melaminium crystallizes from the saturated aHF solution as a monosolvate in a triclinic $P \ \overline{I}$ space group with two formula units per unit cell. The detailed crystallographic data are given in **Table S14**. In the superacidic aHF medium, two nitrogen atoms of melamine, belonging to the aromatic ring, are protonated yielding $[C_3H_8N_6]^{2+}$ cations. The charge balance is maintained by well-known octahedral $[TiF_6]^{2-}$ anions. The crystal structure also includes HF molecules coordinated to anions. The $[TiF_6]^{2-}$ anion is slightly distorted (**Figure 7**). The Ti–F bond lengths range from 1.824(2) to

1.923(2) Å. The longest Ti–F bond includes F7 atom involved in hydrogen bonding with HF molecule. This bond is longer than the corresponding Ti–F bond in the crystal structure of the $[enH_2][TiF_6]$ ·HF compound (1.912(2) Å). Other geometric parameters are given in **Table S15**.



Figure 7. Part of the crystal structure of $[melH_2]$ [TiF₆]·HF. The atoms of the asymmetric unit are labeled.

Hydrogen bonding in the crystal structure of $[melH_2]$ [TiF₆]·HF involves all terminal fluorine atoms of the anion and all hydrogen atoms of the cation (**Figures 7, S12, S13**, and **Table S16**). Each of the three fluorine atoms of TiF₆ unit (F2, F3 and F4) forms one hydrogen bond with one $[melH_2]^{2+}$ cation. The hydrogen bond between N3 and F3 atoms with the shortest N…F distance causes significant elongation of the Ti–F3 bond (1.854(2) Å) in comparison to the Ti–F4 and Ti–F2 bonds, where hydrogen bond between N2 and F4 atoms is weaker and that between N1 and F2 is the weakest. Other two fluorine atoms, F5 and F6, are coordinated each to the one $[melH_2]^{2+}$ cation *via* two hydrogen bonds. One of hydrogen bonds includes the hydrogen atom of $-NH_2$ group (N1 and N2) and another – the hydrogen atom bonded to the N4 or N5 nitrogen atoms in the aromatic ring (**Figure S12**). Those hydrogen

bonds cause equivalent elongations of the Ti–F5 and Ti–F6 bonds. The remaining F7 fluorine atom of the $[TiF_6]^{2-}$ anion also forms two hydrogen bonds: one with the $[melH_2]^{2+}$ cation and one with HF molecule (**Figure 7**). The (Ti–)F7…F1(–H) distance between the F7 fluorine atom belonging to the $[TiF_6]^{2-}$ anion and the F1 fluorine atom of HF molecule is 2.490(3) Å. It is longer than corresponding distances in ethylenediaminium $[enH_2][TiF_6]$ ·HF and imidazolium $[imH]_2[TiF_6]$ ·2HF salts (2.384(4) and 2.374(6) Å, respectively). Nevertheless, the hydrogen bond between the anion and HF molecule is strong enough to make crystals of $[melH_2][TiF_6]$ ·HF compound stable under dynamic vacuum and in inert atmosphere at ambient temperature.

All $[melH_2]^{2+}$ cations are coordinated with six $[TiF_6]^{2-}$ anions *via* hydrogen bonds, involving all hydrogen atoms of $-NH_2$ groups (**Figure S13**). On such way the $[melH_2]^{2+}$ cations, $[TiF_6]^{2-}$ anions and HF molecules of the $[melH_2][TiF_6]$ ·HF are connected through multiple hydrogen bonds into 3-D network. Anions and cations are packed so that the alternation of cationic and anionic layers along the *b*-axis can be observed (**Figure 8**).



Figure 8. Alternating layers of $[melH_2]^{2+}$ cations, HF molecules and $[TiF_6]^{2-}$ anions in $[melH_2][TiF_6]$ ·HF.

3.5. Single crystal structure of fluoride [C₂H₄(NH₃)₂]F₂·2HF

Single crystals of ethylenediammonium fluoride disolvate $[enH_2]F_2 \cdot 2HF$ were grown from saturated solution prepared by dissolution of the products of the reaction between TiF₄ and excess of ethylenediamine $[n(en): n(TiF_4) = 2:1 \text{ molar ratio}]$. The $[enH_2]F_2 \cdot 2HF$ crystallizes in the I2/m space group with the two formula units per unit cell. Detailed crystallographic data are given in **Table S12**.

In $[enH_2]F_2 \cdot 2HF$, the F···F distances between (H–)F1 and lone F2 atom (**Figure S10**) are slightly elongated [2.322(1) Å] in comparison to the usual F···F distances in the $[HF_2]^-$ anion [2.213(4) – 2.277(6) Å].³³ The H atom is much closer to the F1 atom than to the F2 atom [H1c···F1 and H1c···F2 bond lengths are 0.95(4) and 1.38(4) Å, respectively, **Figure S10**]. Additionally, the hydrogen bond pattern reveals formation of strong hydrogen bonds between cations and the lone fluorine atom F2 and only weak between cations and the F1 atom. There are no strict borders between [HF₂]⁻ and [F⁻·HF] formulations. In some works, the FHF moiety with similar geometry as in $[enH_2]F_2 \cdot 2HF$, is rather described as [HF₂]⁻ anion.³⁴ Nevertheless in the $[enH_2]F_2 \cdot 2HF$ compound the FHF moieties are better described as HF molecules hydrogen-bonded to lone fluoride ligands, following previous researches based on both crystallographic and NMR spectroscopic studies of the similar systems.³³

Each F⁻ anion (F2 atom) forms four strong hydrogen bonds with three $[enH_2]^{2+}$ cations and one HF molecule (**Figure S10**). The N···F2 distances are 2.709(1) and 2.871(2) Å. The F1 atoms of the HF molecule are involved in very weak hydrogen bonding³⁵ with the $[enH_2]^{2+}$ cations with N···F1 distances 2.927(1) and 3.013(2) Å and more acute N–H–F angles between 92 and 106 °. All six hydrogen atoms of each $[enH_2]^{2+}$ cation, bonded to nitrogen atoms, form hydrogen bonds with six different F⁻ anions (**Figure S11**). The distances and angles, associated with the hydrogen bonding in $[enH_2]F_2$ ·2HF are depicted in **Table S13**.

Because of the described hydrogen bonding in the crystal structure of $[enH_2]F_2 \cdot 2HF$, the ethylenediammonium cations, fluoride anions and HF molecules are interconnected into an infinite 2-D layers by strong hydrogen bonds, that are connected between themselves by weak hydrogen bonds with HF molecules (**Figure 9**).



Figure 9. Part of the crystal structure of $[enH_2]F_2 \cdot 2HF$. Strong hydrogen bonds are shown by black dashed lines; weak hydrogen bonds are shown by grey dashed lines.

4. Conclusions

The chemical reactions between ethane-1,2-diamine (*en*) and 1,3,5-triazine-2,4,6-triamine (*mel*) with TiF₄ in anhydrous hydrogen fluoride (aHF) are not selective enough to synthesize individual phases of ethylenediammonium or melaminium perfluoridotitanates(IV) in larger quantities. In aHF insoluble phases are, besides of corresponding cations, probably composed of polymeric perfluoridotitanate(IV) $([TiF_5]^-)_{\infty}$ and/or $([Ti_2F_9]^-)_{\infty}$ anions. With increasing amount of ethylenediammine or melamine $[n(en/mel) : n(TiF_4) = 2:1 \text{ and } 1:1]$, the formation of $[TiF_6]^{2^-}$ anions is favored, resulting in aHF soluble products. The $[enH_2][TiF_6]$ (and most likely $[melH_2][TiF_6]$) salt and their solvated forms $[enH_2][TiF_6] \cdot HF$ and $[melH_2][TiF_6] \cdot HF$ can be recovered from such solutions.

On the basis of Raman spectra and crystallographic data we can assume that at least five different phases ($[enH_2][TiF_6]$, $[enH_2][TiF_6] \cdot HF$, $[enH_2]_{0.5}[TiF_5]$, $[enH_2][TiF_5][Ti_2F_9]$, $[enH_2]_{0.5}[Ti_2F_9]$) exist in the $en/TiF_4/aHF$ system and at least three ($[melH_2][TiF_6] \cdot HF$, $[melH_2]_{0.5}[TiF_5]$, $[melH_2]_{0.5}[Ti_2F_9]$) in the $mel/TiF_4/aHF$ system.

The $[enH_2]_{0.5}$ [TiF₅] compound represents the first example of structurally characterized perfluoridotitanate(IV) phase with a double charged cation, where instead of the usual octahedral $[TiF_6]^{2-}$ monomer, another kind of anion is present, i.e., polymeric chain-like $([TiF_5]^{-})_{\infty}$.

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Conflicts of interest

The authors declare no competing financial interest.

Appendix A. Supplementary data

Supplementary data associated with this article are available including crystal data, refinement results, geometric parameters of perfluoridotitanate(IV) anions, and distances and angles, associated with the hydrogen bonding.

CCDC 1885308 – 1885312 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, U.K.; fax: +44 1223 336033.

1. Doble charged organic cations template perfluoridotitanate(IV) compounds

2. Polymeric ([TiF5]-)∞ anions as a counterions for a double charged cation

3. Low-temperature modification of ethylenediaminium hexafluoridotitanate is determined

4. HF molecules form strong hydrogen bonds with F^{-} and $[TiF_{6}]^{2^{-}}$ anions

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