

Crystal Structures and Raman Spectra of Imidazolium Poly[perfluorotitanate(IV)] Salts Containing the $[\text{TiF}_6]^{2-}$, $([\text{Ti}_2\text{F}_9]^-)_\infty$, and $[\text{Ti}_2\text{F}_{11}]^{3-}$ and the New $[\text{Ti}_4\text{F}_{20}]^{4-}$ and $[\text{Ti}_5\text{F}_{23}]^{3-}$ Anions

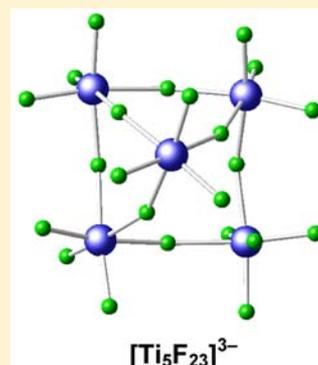
Igor M. Shlyapnikov,[†] H  l  ne P. A. Mercier,[‡] Evgeny A. Goreshnik,[†] Gary J. Schrobilgen,^{*,‡} and Zoran Mazej^{*,†}

[†]Department of Inorganic Chemistry and Technology, Jo  zef Stefan Institute, Jamova 39, SI-1000 Ljubljana, Slovenia

[‡]Department of Chemistry, McMaster University, Hamilton, Ontario L8S 4M1, Canada

Supporting Information

ABSTRACT: Reactions between imidazole (Im, $\text{C}_3\text{H}_4\text{N}_2$) and TiF_4 in anhydrous hydrogen fluoride (aHF) in different molar ratios have yielded $[\text{ImH}]_2[\text{TiF}_6] \cdot 2\text{HF}$, $[\text{ImH}]_3[\text{Ti}_2\text{F}_{11}]$, $[\text{ImH}]_4[\text{Ti}_4\text{F}_{20}]$, $[\text{ImH}]_3[\text{Ti}_5\text{F}_{23}]$, and $[\text{ImH}][\text{Ti}_2\text{F}_9]$ upon crystallization. All five structures were characterized by low-temperature single-crystal X-ray diffraction. The single-crystal Raman spectra of $[\text{ImH}]_4[\text{Ti}_4\text{F}_{20}]$, $[\text{ImH}]_3[\text{Ti}_5\text{F}_{23}]$, and $[\text{ImH}][\text{Ti}_2\text{F}_9]$ were also recorded and assigned. In the crystal structure of $[\text{ImH}]_2[\text{TiF}_6] \cdot 2\text{HF}$, two HF molecules are coordinated to each $[\text{TiF}_6]^{2-}$ anion by means of strong F–H...F hydrogen bonds. The $[\text{Ti}_2\text{F}_{11}]^{3-}$ anion of $[\text{ImH}]_3[\text{Ti}_2\text{F}_{11}]$ results from association of two TiF_6 octahedra through a common fluorine vertex. Three crystallographically independent $[\text{Ti}_2\text{F}_{11}]^{3-}$ anions, which have distinct geometries and orientations, are hydrogen-bonded to the $[\text{ImH}]^+$ cations. The $[\text{ImH}]_4[\text{Ti}_4\text{F}_{20}]$ salt crystallized in two crystal modifications at low (α -phase, 200 K) and ambient (β -phase, 298 K) temperatures. The tetrameric $[\text{Ti}_4\text{F}_{20}]^{4-}$ anion of $[\text{ImH}]_4[\text{Ti}_4\text{F}_{20}]$ consists of rings of four TiF_6 octahedra, which each share two *cis*-fluorine vertices, whereas the pentameric $[\text{Ti}_5\text{F}_{23}]^{3-}$ anion of $[\text{ImH}]_3[\text{Ti}_5\text{F}_{23}]$ results from association of five TiF_6 units, where four of the TiF_6 octahedra share two *cis*-vertices, forming a tetrameric ring as in $[\text{Ti}_4\text{F}_{20}]^{4-}$, and the fifth TiF_6 unit shares three fluorine vertices with three TiF_6 units of the tetrameric ring. The $[\text{ImH}][\text{Ti}_2\text{F}_9]$ salt also crystallizes in two crystal modifications at low (α -phase, 200 K) and high (β -phase, 298 K) temperatures and contains polymeric $([\text{Ti}_2\text{F}_9]^-)_\infty$ anions, which appear as two parallel infinite zigzag chains comprised of TiF_6 units, where each TiF_6 unit of one chain is connected to a TiF_6 unit of the second chain through a shared fluorine vertex. Quantum-chemical calculations at the B3LYP/SDDALL level of theory were used to arrive at the gas-phase geometries and vibrational frequencies of the $[\text{Ti}_4\text{F}_{20}]^{4-}$ and $[\text{Ti}_5\text{F}_{23}]^{3-}$ anions, which aided in the assignment of the experimental vibrational frequencies of the anion series.



1. INTRODUCTION

Complex poly[perfluorotitanate(IV)] compounds are of interest because they are used as stereoselective catalysts in organic synthesis¹ and in reactions leading to olefin polymerization.² Two types of main-group titanium fluoride complexes exist: organometallic complexes with chemical bonds between titanium and organic molecules³ and coordination complexes in which the fluorotitanate anions are coordinated to their cations through fluorine atoms.⁴

Among the many possible poly[perfluorotitanate(IV)] anions, $[\text{Ti}_x\text{F}_{4x+y}]^{y-}$ ($x, y \geq 1$), several have been synthesized, namely, $[\text{TiF}_6]^{2-}$,^{5,6} $[\text{Ti}_2\text{F}_{10}]^{2-}$,^{7,8} $[\text{Ti}_2\text{F}_{11}]^{3-}$,⁹ $[\text{Ti}_4\text{F}_{18}]^{2-}$,^{4,10} $([\text{TiF}_5]^-)_\infty$ (single chains),¹¹ $([\text{Ti}_2\text{F}_9]^-)_\infty$ (double chains),⁴ $([\text{Ti}_3\text{F}_{13}]^-)_\infty$ (columns),¹² $([\text{Ti}_7\text{F}_{30}]^{2-})_\infty$ (columns),¹³ and $([\text{Ti}_8\text{F}_{33}]^-)_\infty$ (layers).¹⁴ Salts of the $[\text{TiF}_7]^{3-}$ anion are presently unknown. Salts that have been formulated as $\text{Cs}_3[\text{TiF}_7]$ ¹⁵ and $[\text{NH}_4][\text{Cu}][\text{TiF}_7] \cdot 4\text{H}_2\text{O}$ ¹⁶ are actually comprised of isolated $[\text{TiF}_6]^{2-}$ anions and a fluoride ion and are correctly formulated as $\text{Cs}_2[\text{TiF}_6] \cdot \text{Cs}[\text{F}]$ ^{15,17} and $[\text{Cu}]$ -

$[[\text{H}_2\text{O}]_4[\text{TiF}_6]] \cdot [\text{NH}_4][\text{F}]$.¹⁸ The $[\text{Ti}_4\text{F}_{19}]^{3-}$ anion was recently isolated for the first time as the $[\text{XeF}_5]_3[\text{Ti}_4\text{F}_{19}]$ salt.¹⁹

In the present paper, crystallizations of imidazole (Im, $\text{C}_3\text{H}_4\text{N}_2$) and TiF_4 have been carried out in anhydrous hydrogen fluoride (aHF) and have yielded five imidazolium salts containing the $[\text{TiF}_6]^{2-}$, $[\text{Ti}_2\text{F}_{11}]^{3-}$, $[\text{Ti}_4\text{F}_{20}]^{4-}$, $[\text{Ti}_5\text{F}_{23}]^{3-}$, and $([\text{Ti}_2\text{F}_9]^-)_\infty$ anions. The salts have been isolated, and their crystal structures were determined and are described in the present paper. Although $[\text{TiF}_6]^{2-}$ salts are well-known, salts containing $([\text{Ti}_2\text{F}_9]^-)_\infty$ and $[\text{Ti}_2\text{F}_{11}]^{3-}$ are rare.^{4,9} The $[\text{Ti}_4\text{F}_{20}]^{4-}$ anion represents a new example of a tetrameric anion comprised of four vertex-sharing octahedral TiF_6 units, whereas the $[\text{Ti}_5\text{F}_{23}]^{3-}$ anion is comprised of five vertex-sharing TiF_6 octahedra, providing a novel example of a pentameric poly[perfluorotitanate] anion. Quantum-chemical calculations have been used to compare the experimental geometries of $[\text{Ti}_4\text{F}_{20}]^{4-}$ and $[\text{Ti}_5\text{F}_{23}]^{3-}$ with their calculated gas-phase

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Table 1. Crystal Data and Refinement Results for Imidazolium Poly[perfluorotitanate(IV)] Salts Arising from Im–TiF₆–aHF Systems

	[ImH] ₂ [TiF ₆]·2HF	[ImH] ₃ [Ti ₂ F ₁₁]	β-[ImH] ₄ [Ti ₄ F ₂₀] ^a	α-[ImH] ₄ [Ti ₄ F ₂₀] ^a	[ImH] ₃ [Ti ₅ F ₂₃]	β-[ImH][Ti ₂ F ₉] ^a	α-[ImH][Ti ₂ F ₉] ^a
fw (g/mol)	340.07	512.07	847.96	847.96	883.78	335.89	335.89
space group	C2/c	C2/m	C2/m	P $\bar{1}$	Pna2 ₁	Pnma	P2 ₁ /a
a (Å)	14.437(8)	13.5371(2)	13.2139(4)	8.791(3)	22.0259(4)	5.3978(2)	5.3914(3)
b (Å)	7.436(4)	25.7451(4)	15.2096(7)	9.971(4)	10.2622(2)	12.2169(6)	15.4836(10)
c (Å)	13.261(8)	10.4139(2)	8.9514(3)	10.126(4)	12.3180(2)	15.2345(7)	11.9543(8)
α (deg)	90.00	90.00	90.00	118.808(8)	90.00	90.00	90.00
β (deg)	115.77(2)	100.980(1)	129.690(1)	92.366(3)	90.00	90.00	90.977(4)
γ (deg)	90.00	90.00	90.00	113.595(8)	90.00	90.00	90.00
V (Å ³)	1282.1(13)	3562.95(10)	1384.35(10)	681.8(5)	2784.29(9)	1004.63(8)	997.78(11)
Z	4	8	2	1	4	4	4
D _{calc} (g/cm ³)	1.762	1.909	2.034	2.065	2.108	2.221	2.236
T (K)	200	200	298	200	200	298	200
R ₁ ^b	0.0882	0.0481	0.0518	0.0466	0.0317	0.0490	0.0655
wR ₂ ^c	0.2181	0.1416	0.1561	0.1181	0.0898	0.1523	0.1576

^aThe symbols α and β correspond to the low- and high-temperature modifications, respectively, of [ImH]₄[Ti₄F₂₀] and [ImH][Ti₂F₉]. ^bR₁ is defined as $\sum ||F_o| - |F_c|| / \sum |F_o|$ for $I > 2\sigma(I)$. ^cwR₂ is defined as $[\sum (w(F_o^2 - F_c^2)^2) / \sum w(F_o^2)^2]^{1/2}$ for $I > 2\sigma(I)$.

geometries. Their Raman spectra were assigned with the aid of the calculated frequencies and vibrational-mode descriptions.

2. RESULTS AND DISCUSSION

Crystal Structures of [ImH]₂[TiF₆]·2HF, [ImH]₃[Ti₂F₁₁], [ImH]₄[Ti₄F₂₀], [ImH]₃[Ti₅F₂₃], and [ImH][Ti₂F₉]. The title salts were crystallized from aHF, providing single crystals from which their X-ray crystal structures were determined. The corresponding crystal data and refinement results are summarized in Table 1, geometrical parameters are summarized in Tables 2–4 and S1–S3 (Supporting Information), and packing diagrams are shown in Figures S1–S7 (Supporting Information) for [ImH]₂[TiF₆]·2HF, [ImH]₃[Ti₂F₁₁], [ImH]₄[Ti₄F₂₀], [ImH]₃[Ti₅F₂₃], and [ImH][Ti₂F₉].

(a) [ImH]₂[TiF₆]·2HF. The crystal structure of [ImH]₂[TiF₆]·2HF consists of [TiF₆]²⁻ anions and two HF solvent molecules that are coordinated to the F2 ligands of [TiF₆]²⁻ by means of F–H···F hydrogen bonds, whereas the F3 and F1 ligands of [TiF₆]²⁻ are more weakly hydrogen-bonded to [ImH]⁺ cations (Figure 1). The [ImH]⁺ cations are 2-fold-disordered. The Ti–F2 bonds are longer [1.908(4) Å] than the Ti–F3 [1.811(4) Å] and Ti–F1 [1.837(3) Å] bonds. The F4(H)···F2(–Ti) distance [2.374(6) Å] is shorter, i.e., the HF molecules are more strongly hydrogen-bonded than in K₂CrF₆·2HF [F(–H)···F(–Cr), 2.455 Å].²⁰ Each [TiF₆]²⁻ anion is coordinated to six [ImH]⁺ cations, and the [ImH]⁺ cations are each coordinated to three TiF₆ units through N–H···F and C–H···F hydrogen bonds.

(b) [ImH]₃[Ti₂F₁₁]. The crystal structure of [ImH]₃[Ti₂F₁₁] consists of discrete [Ti₂F₁₁]³⁻ anions in which two TiF₆ octahedra of [Ti₂F₁₁]³⁻ share a common vertex (Figure 2). The Ti–F_i bond lengths range from 1.768(3) to 1.908(2) Å and from 1.9683(5) to 1.9805(6) Å for the Ti–F_b bond lengths (Table 2 and Figure 3) and are comparable to the corresponding bond lengths in [C₅H₆N]₂[H₃O][Ti₂F₁₁] [Ti–F_i, 1.776(2)–1.880(2) Å; Ti–F_b, 1.9732(10) Å].⁹

In contrast with [C₅H₆N]₂[H₃O][Ti₂F₁₁], where only one Ti₂F₁₁ unit is defined,⁹ there are three crystallographically independent Ti₂F₁₁ units in [ImH]₃[Ti₂F₁₁] which have different conformations and coordination spheres (Figures 2 and 3). The Ti₂F₁₁ unit containing Ti1 is comprised of two symmetry-related octahedra with Ti1–F_b and Ti1–F_i bonds

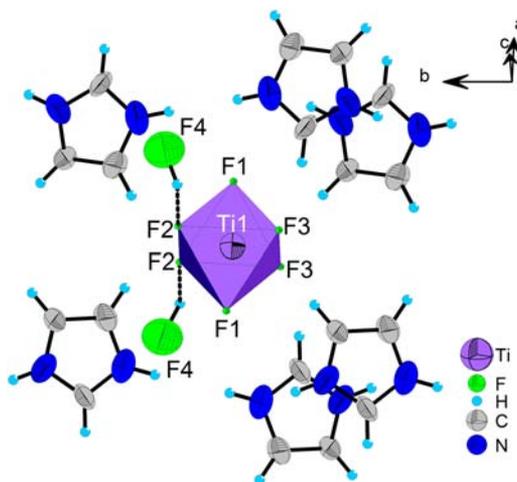


Figure 1. Crystal structure of [ImH]₂[TiF₆]·2HF showing coordination of the hydrogen atoms of the HF molecules to the fluorine atoms of the [TiF₆]²⁻ anion. Thermal ellipsoids are drawn at the 50% probability level. Only one of the two orientations of the disordered [ImH]⁺ cations is depicted.

equal to 1.9805(6) and 1.796(4)–1.857(2) Å, respectively, and a Ti1–F_b–Ti1 angle of 180°. The equatorial TiF₄ planes of the TiF₆ octahedra of [Ti₂F₁₁]³⁻ are eclipsed. The Ti₂F₁₁ unit containing Ti2 is likewise comprised of two symmetry-related octahedra, but their TiF₄ planes have a gauche conformation with a dihedral angle of 8.50(6)° (Figure S8 in the Supporting Information). The Ti2–F_b bond [1.9683(5) Å] is longer than the Ti2–F_i bonds [1.792(2)–1.862(2) Å] and shorter than the corresponding Ti1–F_b bond, with a Ti2–F_b–Ti2 angle that is slightly bent [174.28(18)°]. The Ti₂F₁₁ unit containing Ti3 has a Ti3–F_b bond length [1.9778(8) Å] that is very similar to the Ti1–F_b bond length [1.9805(6) Å] with a linear Ti3–F_b–Ti3 angle and eclipsed TiF₄ planes.

The coordination spheres formed by the [ImH]⁺ cations of the three crystallographically independent [Ti₂F₁₁]³⁻ anions differ with respect to their hydrogen-bonded contacts (Table S4 in the Supporting Information). The [Ti₂F₁₁]³⁻ anions are hydrogen-bonded to eight [ImH]⁺ cations containing the non-disordered N3 and N4 atoms and the disordered N5/NSA and

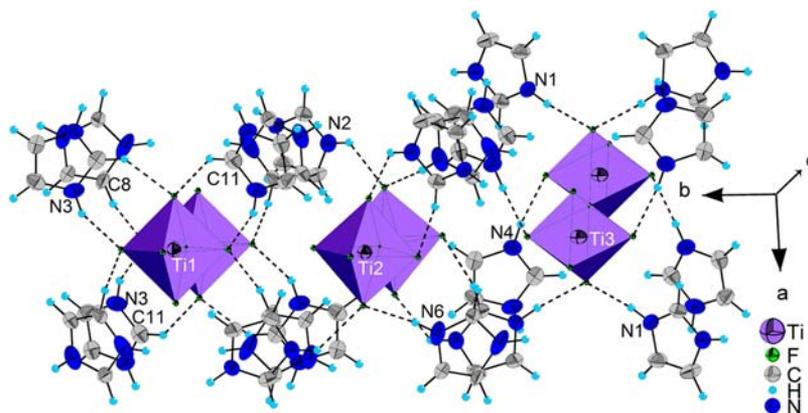


Figure 2. Crystal structure of $[\text{ImH}]_3[\text{Ti}_2\text{F}_{11}]$ showing coordination between the hydrogen atoms of the $[\text{ImH}]^+$ cations and the fluorine atoms of the $[\text{Ti}_2\text{F}_{11}]^{3-}$ anion. Thermal ellipsoids are drawn at the 50% probability level. Only one of the two orientations of the disordered $[\text{ImH}]^+$ cations is depicted.

Table 2. Experimental Geometrical Parameters of the Three Crystallographically Independent $[\text{Ti}_2\text{F}_{11}]^{3-}$ Anions in the Crystal Structure of $[\text{ImH}]_3[\text{Ti}_2\text{F}_{11}]^a$

Bond Lengths (Å)					
Ti1–F3	1.796(3)	Ti2–F9	1.792(2)	Ti3–F14	1.768(3)
Ti1–F2	1.849(3)	Ti2–F8	1.862(2)	Ti3–F13	1.908(2)
Ti1–F4	1.824(2)	Ti2–F11	1.841(2)	Ti3–F15	1.798(3)
Ti1–F5	1.857(2)	Ti2–F10	1.834(2)	Ti3–F16	1.847(2)
Ti1–F5A	1.857(2)	Ti2–F7	1.837(2)	Ti3–F16B	1.847(2)
Ti1–F1	1.9805(6)	Ti2–F6	1.9683(5)	Ti3–F12	1.9770(8)
Bond Angles (deg)					
F3–Ti1–F2	93.55(15)	F9–Ti2–F8	93.73(9)	F14–Ti3–F13	89.55(13)
F3–Ti1–F4	93.63(14)	F9–Ti2–F11	93.36(9)	F14–Ti3–F15	96.56(16)
F3–Ti1–F5	93.00(6)	F9–Ti2–F10	94.11(10)	F14–Ti3–F16	94.90(7)
F3–Ti1–F5A	93.00(6)	F9–Ti2–F7	92.35(9)	F14–Ti3–F16B	94.90(7)
F3–Ti1–F1	179.38(11)	F9–Ti2–F6	179.01(11)	F14–Ti3–F12	176.17(12)
F2–Ti1–F4	172.82(12)	F8–Ti2–F11	172.92(8)	F13–Ti3–F15	173.89(14)
F2–Ti1–F5	89.52(5)	F8–Ti2–F10	88.62(7)	F13–Ti3–F16	86.92(6)
F2–Ti1–F5A	89.52(5)	F8–Ti2–F7	89.26(7)	F13–Ti3–F16B	86.92(6)
F2–Ti1–F1	85.83(10)	F8–Ti2–F6	86.78(6)	F13–Ti3–F12	86.61(8)
F4–Ti1–F5	90.10(5)	F11–Ti2–F10	90.95(7)	F15–Ti3–F16	92.54(5)
F4–Ti1–F5A	90.10(5)	F11–Ti2–F7	90.37(7)	F15–Ti3–F16B	92.54(5)
F4–Ti1–F1	86.99(9)	F11–Ti2–F6	86.13(6)	F15–Ti3–F12	87.28(12)
F5–Ti1–F5A	173.97(12)	F10–Ti2–F7	173.32(9)	F16–Ti3–F16B	168.37(14)
F5–Ti1–F1	87.00(6)	F10–Ti2–F6	86.75(11)	F16–Ti3–F12	84.90(7)
F5A–Ti1–F1	87.00(6)	F7–Ti2–F6	86.81(11)	F16B–Ti3–F12	84.90(7)
Ti1–F1–Ti1A	180.0	Ti2–F6–Ti2A	174.28(18)	Ti3–F12–Ti3A	180.0

^aThe atom-labeling schemes correspond to those used in Figure 3.

N6/N6A atoms [N3...F5, 2.813(3) Å; N5A...F2, 2.925(9) Å; C8...F5, 2.957(10) Å; C11...F4, 3.017(3) Å]. The $[\text{Ti}_2\text{F}_{11}]^{3-}$ anions are hydrogen-bonded to six $[\text{ImH}]^+$ cations containing the N1 and N2 atoms and the disordered N5/N5A and N6/N6A atoms [N2...F11, 2.793(3) Å; N6...F8, 2.866(3) Å; C8A...F10, 2.868(4) Å]. Each $[\text{Ti}_3\text{F}_{11}]^{3-}$ anion is hydrogen-bonded to eight non-disordered $[\text{ImH}]^+$ cations containing the N1 and N2 atoms and the N3 and N4 atoms [N4...F16, 2.743(3) Å; N1...F13, 2.749(2) Å; C1...F16, 2.996(4) Å]. The three Ti_2F_{11} units are pairwise coordinated so that $[\text{Ti}_1\text{F}_{11}]^{3-}$ is bridged to $[\text{Ti}_2\text{F}_{11}]^{3-}$ through $[\text{ImH}]^+$ cations containing N5/N5A and N6/N6A and to $[\text{Ti}_3\text{F}_{11}]^{3-}$ through cations containing N3 and N4, whereas $[\text{Ti}_2\text{F}_{11}]^{3-}$ is bridged to $[\text{Ti}_3\text{F}_{11}]^{3-}$ through cations containing N1 and N2.

(c) $[\text{ImH}]_4[\text{Ti}_4\text{F}_{20}]$. The crystalline phase corresponding to an Im:TiF₄ molar ratio of 1:1 is formulated as $[\text{ImH}]_4[\text{Ti}_4\text{F}_{20}]$,

where the $[\text{Ti}_4\text{F}_{20}]^{4-}$ anion has been structurally characterized for the first time. Examples of tetrameric metal fluoride species are rare. The first evidence for a tetramer comprised of four MF₆ octahedra sharing four vertices was provided by the ¹¹⁹Sn and ¹⁹F NMR spectra of “N₅SnF₅” in a HF solution, which yielded the gross geometry of the $[\text{Sn}_4\text{F}_{20}]^{4-}$ anion.²¹ Two tetrameric perfluorotitanate salts, $[\text{Ti}_4\text{F}_{18}]^{2-}$,^{4,10} and $[\text{Ti}_4\text{F}_{19}]^{3-}$,¹⁹ and two tetrameric non-titanium compounds, $[\text{C}_6\text{N}_4\text{H}_{21}]_2[\text{V}_4\text{O}_4\text{F}_{14}] \cdot 3\text{H}_2\text{O}$ ²² and $[\text{CN}_4\text{H}_8]_4[\text{Zr}_4\text{F}_{24}] \cdot 4\text{H}_2\text{O}$,²³ have been described in the literature. The $[\text{V}_4\text{O}_4\text{F}_{14}]^{6-}$ anion is comprised of four VOF₅ octahedra sharing two vertices and two edges, whereas the $[\text{Zr}_4\text{F}_{24}]^{8-}$ anion is comprised of four ZrF₈ square antiprisms sharing four edges.

The α - and β -phases of $[\text{ImH}]_4[\text{Ti}_4\text{F}_{20}]$ (the crystal structures were determined at 200 and 298 K, respectively) consist of tetrameric $[\text{Ti}_4\text{F}_{20}]^{4-}$ anions and $[\text{ImH}]^+$ cations that

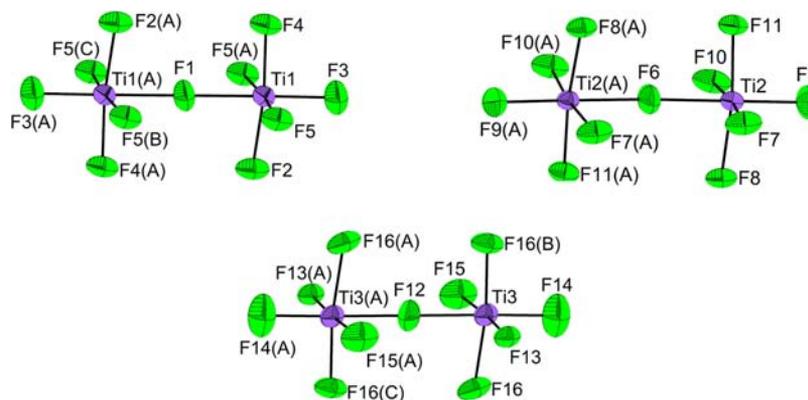


Figure 3. Experimental geometries of the $[\text{Ti}_2\text{F}_{11}]^{3-}$ anions in the crystal structure of $[\text{ImH}]_3[\text{Ti}_2\text{F}_{11}]$. Thermal ellipsoids are drawn at the 50% probability level.

interact through hydrogen bonds. The two $[\text{ImH}]^+$ cations defined in the β -phase are 2-fold disordered. The $[\text{Ti}_4\text{F}_{20}]^{4-}$ anion is comprised of four TiF_6 octahedra sharing two cis vertices (Figures 4 and 5). All titanium atoms in β -

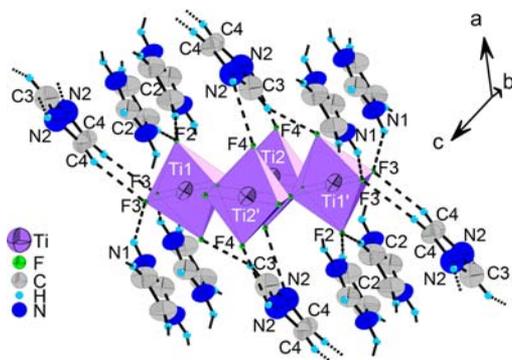


Figure 4. Crystal structure of β - $[\text{ImH}]_4[\text{Ti}_4\text{F}_{20}]$, determined at 298 K, showing coordination between the hydrogen atoms of the $[\text{ImH}]^+$ cations and the fluorine atoms of the $[\text{Ti}_4\text{F}_{20}]^{4-}$ anion. Thermal ellipsoids are drawn at the 50% probability level. Only one of the two orientations of the disordered $[\text{ImH}]^+$ cations is depicted.

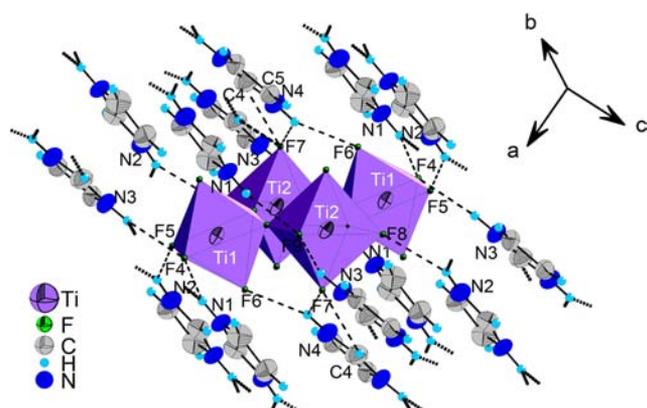


Figure 5. Crystal structure of α - $[\text{ImH}]_4[\text{Ti}_4\text{F}_{20}]$ determined at 200 K showing coordination between the hydrogen atoms of the $[\text{ImH}]^+$ cations and the fluorine atoms of the $[\text{Ti}_4\text{F}_{20}]^{4-}$ anion. Thermal ellipsoids are drawn at the 50% probability level.

$[\text{ImH}]_4[\text{Ti}_4\text{F}_{20}]$ are situated in the same plane with four equal $\text{Ti}\cdots\text{Ti}$ distances [3.897(1) Å] and $\text{Ti}\cdots\text{Ti}\cdots\text{Ti}$ angles close to 90° [$\text{Ti}2\cdots\text{Ti}1\cdots\text{Ti}2$, $94.2(2)^\circ$; $\text{Ti}2\cdots\text{Ti}1\cdots\text{Ti}2$,

$85.8(2)^\circ$]. Each titanium atom is coordinated to two bridging and four terminal fluorine atoms. The $\text{Ti}-\text{F}_t$ bond lengths range from 1.776(3) to 1.824(4) Å and are significantly shorter than the $\text{Ti}-\text{F}_b$ bonds, i.e., $\text{Ti}1-\text{F}_b$, 1.956(2) Å; $\text{Ti}2-\text{F}_b$, 1.978(2) Å (Table 3).

Each $[\text{Ti}_4\text{F}_{20}]^{4-}$ anion is hydrogen-bonded to 12 $[\text{ImH}]^+$ cations, with $\text{N}-\text{H}\cdots\text{F}$ and $\text{C}-\text{H}\cdots\text{F}$ distances of 2.872(7)–3.093(22) and 2.836(13)–3.153(12) Å, respectively (Table S4 in the Supporting Information).

The $\text{Ti}\cdots\text{Ti}$ distances and $\text{Ti}-\text{F}_t$ and $\text{Ti}-\text{F}_b$ bond lengths in α - $[\text{ImH}]_4[\text{Ti}_4\text{F}_{20}]$ (Figure 5) are comparable to those in the β -modification [$\text{Ti}\cdots\text{Ti}$, 3.854(1)–3.902(1) Å; $\text{Ti}-\text{F}_t$, 1.790(2)–1.840(2) Å; $\text{Ti}-\text{F}_b$, 1.965(2)–1.989(2) Å]. Each $[\text{Ti}_4\text{F}_{20}]^{4-}$ anion is hydrogen-bonded to 14 $[\text{ImH}]^+$ cations. Eight $[\text{ImH}]^+$ cations containing N1 and N2 atoms are hydrogen-bonded to different anions through one $\text{C}-\text{H}\cdots\text{F}$ [$\text{C}1\cdots\text{F}10$, 2.990(4) Å] and four $\text{N}-\text{H}\cdots\text{F}$ [$\text{N}2\cdots\text{F}5$, 2.847(4) Å; $\text{N}2\cdots\text{F}8$, 2.936(4) Å; $\text{N}1\cdots\text{F}4$, 2.839(3) Å; $\text{N}1\cdots\text{F}9$, 2.977(4) Å] hydrogen bonds. The remaining six $[\text{ImH}]^+$ cations containing N3, N4, and C4 are coordinated to two $[\text{Ti}_4\text{F}_{20}]^{4-}$ anions through two $\text{N}-\text{H}\cdots\text{F}$ [$\text{N}4\cdots\text{F}6$, 2.811(4) Å; $\text{N}3\cdots\text{F}9$, 3.003(4) Å] hydrogen bonds and to two other anions through two $\text{N}-\text{H}\cdots\text{F}$ [$\text{N}3\cdots\text{F}4$, 2.906(4) Å; $\text{N}4\cdots\text{F}7$, 2.961(5) Å] and through one $\text{C}-\text{H}\cdots\text{F}$ [$\text{C}4\cdots\text{F}7$, 2.935(5) Å] hydrogen bonds (Table S4 in the Supporting Information).

(d) $[\text{ImH}]_3[\text{Ti}_5\text{F}_{23}]$. The $[\text{ImH}]_3[\text{Ti}_5\text{F}_{23}]$ salt was obtained from a starting molar ratio of $\text{Im}:\text{TiF}_4 = 1:1.67$ (3:5). To the authors' knowledge, no pentameric units consisting of MX_n ($X = \text{F}$ or F/O , $n = 4-8$) polyhedra have been reported thus far for organically templated metal fluorides.²⁴ The $[\text{Ti}_5\text{F}_{23}]^{3-}$ anion, which is comprised of five TiF_6 octahedra, represents a unique geometry among known pentameric polyanions comprised of octahedra. Each of four TiF_6 octahedra share two cis vertices with adjacent TiF_6 units, forming a tetrameric ring (Figure 6 and Table 4). The fifth TiF_6 unit shares three vertices with three octahedra of the tetrameric ring. All titanium atoms are crystallographically independent. Four of them ($\text{Ti}2$, $\text{Ti}3$, $\text{Ti}4$, and $\text{Ti}5$) are coordinated to three bridging and three terminal fluorine atoms. The unique $\text{Ti}1$ atom is coordinated to two cis-bridged and to four terminal fluorine atoms. The $\text{Ti}-\text{F}_t$ and $\text{Ti}-\text{F}_b$ bond length ranges are 1.757(3)–1.848(3) and 1.942(2)–2.014(2) Å, respectively. The $[\text{Ti}_5\text{F}_{23}]^{3-}$ anion is coordinated to six $[\text{ImH}]^+$ cations (three are crystallographically unique) through eight $\text{N}-\text{H}\cdots\text{F}$ [$\text{N}\cdots\text{F}$, 2.805(4)–2.999(4) Å] and two $\text{C}-\text{H}\cdots\text{F}$ [$\text{C}\cdots\text{F}$, 2.989(4)–2.995(4) Å]

Table 3. Experimental and Calculated Geometrical Parameters for the $[\text{Ti}_4\text{F}_{20}]^{4-}$ Anion

		exptl ^{a,b}		calcd (D_{2d}) ^{b,c}	
		β - $[\text{Ti}_4\text{F}_{20}]^{4-}$	α - $[\text{Ti}_4\text{F}_{20}]^{4-}$		
Bond Lengths (Å)					
Ti1–F1	1.956(2)	Ti1–F1	1.965(2)	Ti1–F1	2.007
Ti1–F1A	1.956(2)	Ti1–F2	1.970(2)	Ti1–F2	2.007
Ti1–F2	1.807(4)	Ti1–F3	1.807(2)	Ti1–F3	1.839
Ti1–F3	1.793(3)	Ti1–F4	1.817(2)	Ti1–F4	1.842
Ti1–F3A	1.793(3)	Ti1–F5	1.793(2)	Ti1–F5	1.842
Ti1–F7	1.824(4)	Ti1–F6	1.840(2)	Ti1–F6	1.839
Ti2–F1	1.978(2)	Ti2–F1	1.989(2)	Ti2–F1	2.007
Ti2–F1B	1.978(2)	Ti2–F7	1.826(2)	Ti2–F7	1.839
Ti2–F4	1.803(3)	Ti2–F8	1.790(2)	Ti2–F8	1.842
Ti2–F4B	1.803(3)	Ti2–F9	1.800(2)	Ti2–F9	1.842
Ti2–F6	1.776(3)	Ti2–F10	1.800(2)	Ti2–F10	1.839
Ti2–F6B	1.776(3)	Ti2–F2A	1.989(2)	Ti2–F11	2.007
Bond Angles (deg)					
F1–Ti1–F1A	89.18(18)	F1–Ti1–F2	89.46(9)	F1–Ti1–F2	86.9
F1–Ti1–F2	86.35(14)	F1–Ti1–F3	86.47(10)	F1–Ti1–F3	88.9
F1–Ti1–F3A	178.06(15)	F1–Ti1–F4	177.75(10)	F1–Ti1–F4	177.5
F1–Ti1–F3	89.20(13)	F1–Ti1–F5	89.71(10)	F1–Ti1–F5	90.6
F1–Ti1–F7	86.92(13)	F1–Ti1–F6	87.09(9)	F1–Ti1–F6	88.9
F1A–Ti1–F2	86.35(14)	F2–Ti1–F3	86.22(9)	F2–Ti1–F3	88.9
F1A–Ti1–F3A	89.20(13)	F2–Ti1–F4	88.43(10)	F2–Ti1–F4	90.6
F1A–Ti1–F3	178.06(15)	F2–Ti1–F5	179.14(9)	F2–Ti1–F5	177.5
F1A–Ti1–F7	86.92(13)	F2–Ti1–F6	86.07(9)	F2–Ti1–F6	88.9
F2–Ti1–F3A	92.49(13)	F3–Ti1–F4	92.37(10)	F3–Ti1–F4	91.1
F2–Ti1–F3	92.49(13)	F3–Ti1–F5	93.95(10)	F3–Ti1–F5	91.1
F2–Ti1–F7	170.54(19)	F3–Ti1–F6	170.14(10)	F3–Ti1–F6	176.9
F3A–Ti1–F3	92.41(20)	F4–Ti1–F5	92.40(10)	F4–Ti1–F5	91.9
F3A–Ti1–F7	94.05(13)	F4–Ti1–F6	93.55(9)	F4–Ti1–F6	91.1
F3–Ti1–F7	94.05(13)	F5–Ti1–F6	93.67(10)	F5–Ti1–F6	91.1
F1–Ti2–F1B	82.93(17)	F1–Ti2–F2A	82.51(9)	F1–Ti2–F11	86.9
F1–Ti2–F4	86.23(14)	F1–Ti2–F7	86.15(10)	F1–Ti2–F7	88.9
F1–Ti2–F6	90.60(14)	F1–Ti2–F8	90.58(10)	F1–Ti2–F8	90.6
F1–Ti2–F6B	173.46(16)	F1–Ti2–F9	172.74(10)	F1–Ti2–F9	177.5
F1–Ti2–F4B	87.78(14)	F1–Ti2–F10	88.11(10)	F1–Ti2–F10	88.9
F1B–Ti2–F4	87.78(14)	F2A–Ti2–F7	86.74(10)	F11–Ti2–F7	88.9
F1B–Ti2–F6	173.46(16)	F2A–Ti2–F8	173.08(10)	F11–Ti2–F8	88.9
F1B–Ti2–F6B	90.60(14)	F2A–Ti2–F9	90.41(10)	F11–Ti2–F9	90.6
F1B–Ti2–F4B	87.78(14)	F2A–Ti2–F10	86.17(10)	F11–Ti2–F10	88.9
F4–Ti2–F6	92.74(16)	F7–Ti2–F8	92.43(11)	F7–Ti2–F8	91.1
F4–Ti2–F6B	92.62(15)	F7–Ti2–F9	91.85(10)	F7–Ti2–F9	91.1
F4–Ti2–F4B	172.00(20)	F7–Ti2–F10	171.41(10)	F7–Ti2–F16	176.9
F6–Ti2–F6B	95.88(24)	F8–Ti2–F9	96.48(11)	F8–Ti2–F9	91.9
F6–Ti2–F4B	92.62(15)	F8–Ti2–F10	94.02(11)	F8–Ti2–F10	91.1
F6B–Ti2–F4B	92.74(16)	F9–Ti1–F10	93.06(11)	F9–Ti2–F10	91.1
Ti1–F1–Ti2	164.40(19)	Ti1–F1–Ti2	154.16(13)	Ti1–F1–Ti2	176.9
Ti1–F1A–Ti2A	164.40(19)	Ti1–F2–Ti2A	160.53(12)	Ti1–F2–Ti1A	176.9

^aExperimental geometrical parameters correspond to α - and β - $[\text{ImH}]_4[\text{Ti}_4\text{F}_{20}]$. ^bThe atom-labeling schemes correspond to those used in Figure 10. ^cThe SDDALL basis set was used.

hydrogen bonds (Table S4 in the Supporting Information). Each of the six cations is coordinated to two anions.

(e) $[\text{ImH}][\text{Ti}_2\text{F}_9]$. The smallest proportion of $[\text{ImH}]^+$ cations ($\text{Im}:\text{TiF}_4 = 1:2$) is observed in $[\text{ImH}][\text{Ti}_2\text{F}_9]$, which crystallized in two modifications (Figures 7 and 8). A high-temperature β -phase (structure determined at 298 K) crystallized in an orthorhombic unit cell, and a low-temperature α -phase (structure determined at 200 K) crystallized in a monoclinic unit cell. The crystallographically unique $[\text{ImH}]^+$ cation of the β -phase is 2-fold-disordered.

There is only one crystallographically independent titanium atom in the β -phase. The $[\text{Ti}_2\text{F}_9]^-$ anion is an infinite dimeric zigzag chain comprised of TiF_6 octahedra sharing vertices (Figure 7). Each TiF_6 octahedron shares three of its vertices with three other TiF_6 units so that each titanium atom is coordinated to three bridging $[\text{Ti}-\text{F}_b]$, two within a chain, 1.9669(8) and 1.973(2) Å, and one between two polymeric chains, 1.979(2) Å and three terminal $[\text{Ti}-\text{F}_t]$, 1.763(2)–1.772(3) Å fluorine atoms. Nearest-neighbor pairs of TiF_6 octahedra, belonging to different chains, coordinate to a single

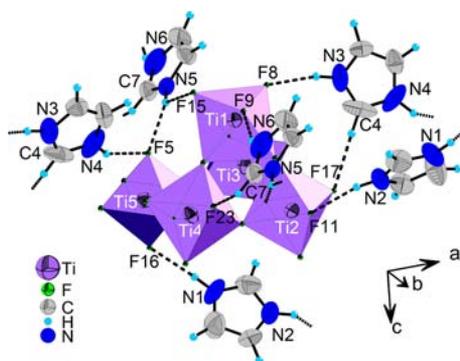


Figure 6. Crystal structure of $[\text{ImH}]_3[\text{Ti}_5\text{F}_{23}]$ showing coordination between the hydrogen atoms of the $[\text{ImH}]^+$ cations and the fluorine atoms of the $[\text{Ti}_5\text{F}_{23}]^{3-}$ anion. Thermal ellipsoids are drawn at the 50% probability level.

bridging $[\text{ImH}]^+$ cation through two crystallographically equivalent $\text{N}-\text{H}\cdots\text{F}$ (or $\text{C}-\text{H}\cdots\text{F}$) hydrogen bonds [$\text{N1A}\cdots\text{F2}$, 2.907(7) Å (or $\text{C2}\cdots\text{F2}$, 2.992(7) Å); Table S4 in the Supporting Information].

The α -phase (Figure 8) is comprised of infinite dimeric chains consisting of crystallographically independent TiF_6 octahedra that coordinate to nearest-neighbor TiF_6 units in a manner similar to that observed in the β -phase. The $\text{Ti}-\text{F}_t$ [1.768(2)–1.787(2) Å] and $\text{Ti}-\text{F}_b$ [1.963(1)–1.991(1) Å] bond lengths are similar to the corresponding $\text{Ti}-\text{F}$ bond lengths in $\text{Cs}[\text{Ti}_2\text{F}_9]$ at 200 K [$\text{Ti}-\text{F}_t$, 1.758(7)–1.790(7) Å; $\text{Ti}-\text{F}_b$, 1.955(3)–1.988(7) Å] and $[\text{H}_3\text{O}][\text{Ti}_2\text{F}_9]$ at 100 K [$\text{Ti}-\text{F}_t$, 1.754(2)–1.803(3) Å; $\text{Ti}-\text{F}_b$, 1.966(3)–2.004(2) Å].⁴ Nearest-neighbor pairs of TiF_6 octahedra, belonging to different chains, coordinate to two different $[\text{ImH}]^+$ cations through two crystallographically inequivalent $\text{N1}-\text{H}\cdots\text{F6}$ [$\text{N}\cdots\text{F}$, 2.810(3) Å] and $\text{N2}-\text{H}\cdots\text{F8}$ [$\text{N}\cdots\text{F}$, 2.929(3) Å] hydrogen bonds (Table S4 in the Supporting Information); no $[\text{ImH}]^+$ bridging occurs between the octahedra of neighboring chains.

The $\text{Ti}-\text{F}_b-\text{Ti}$ angles within the individual zigzag chains of the dimers are crystallographically equivalent in β - $[\text{ImH}][\text{Ti}_2\text{F}_9]$ [152.1(1)°], whereas these angles are comparable in α - $[\text{ImH}][\text{Ti}_2\text{F}_9]$ [149.54(8)° and 151.21(9)°]. The corresponding angles in $[\text{H}_3\text{O}][\text{Ti}_2\text{F}_9]$ and $\text{Cs}[\text{Ti}_2\text{F}_9]$ are more open [$[\text{H}_3\text{O}]^+$, 166.4(2)°; Cs^+ , 156.3(4)°].⁴ The $\text{Ti}-\text{F}_b-\text{Ti}$ angles in $[\text{ImH}][\text{Ti}_2\text{F}_9]$, where the titanium atoms belong to two neighboring chains, are the same, within $\pm 3\sigma$ for the α -phase [162.27(8)°] and β -phase [163.1(2)°]. These angles are 143.7(2)° and 149.3(6)°, respectively, in the H_3O^+ and Cs^+ salts.⁴

In the case of $\text{Cs}[\text{Ti}_2\text{F}_9]$, the TiF_6 octahedra within one chain of the dimer are slightly rotated relative to those in the other chain (Figure 9a), with a dihedral angle of 22°. The corresponding dihedral angle (17°) of α - $[\text{ImH}][\text{Ti}_2\text{F}_9]$ (Figure 9c) results in $([\text{Ti}_2\text{F}_9]^-)_\infty$ chains of lower symmetry. In contrast, the TiF_6 octahedra of one chain eclipse those of the second chain in β - $[\text{ImH}][\text{Ti}_2\text{F}_9]$ (Figure 9d) and in $[\text{H}_3\text{O}][\text{Ti}_2\text{F}_9]$ (Figure 9b).

Computational Results. The gas-phase geometries of $[\text{Ti}_4\text{F}_{20}]^{4-}$ and $[\text{Ti}_5\text{F}_{23}]^{3-}$ were energy-minimized starting from the crystallographic coordinates and resulted in stationary points with all frequencies real. The B3LYP/SDDALL results are reported in Tables 3 and 4 and Figure 10. The energy-minimized geometry and vibrational frequencies (Table S5 in

the Supporting Information) of $[\text{TiF}_6]^{2-}$ were also calculated ($\text{Ti}-\text{F}$, 1.893 Å) and served as a benchmark; the calculated $\text{Ti}-\text{F}$ bond lengths are shown to be overestimated by 0.03 Å, whereas the $\text{Ti}-\text{F}$ stretching frequencies are underestimated by ca. 40 cm^{-1} .

The calculated geometries of $[\text{Ti}_4\text{F}_{20}]^{4-}$ and $[\text{Ti}_5\text{F}_{23}]^{3-}$ are in good agreement with the experimental geometries, although all bond lengths are slightly overestimated, as observed for the $[\text{TiF}_6]^{2-}$ anion.

(a) $[\text{Ti}_4\text{F}_{20}]^{4-}$. All calculated terminal $\text{Ti}-\text{F}$ bonds trans to terminal ($\text{Ti}-\text{F}_{tt}$) and bridging ($\text{Ti}-\text{F}_{tb}$) bonds are similar (1.839 and 1.842 Å, respectively), as observed experimentally [β , 1.803(3)–1.824(4) and 1.776(3)–1.793(3) Å; α , 1.800(2)–1.840(2) and 1.790(2)–1.817(2) Å, respectively; Table 3]. The $\text{Ti}-\text{F}_b$ bonds are significantly longer (2.007 Å), in accordance with the experimental structure [β , 1.956(2)–1.978(2) Å; α , 1.965(2)–1.989(2) Å].

(b) $[\text{Ti}_5\text{F}_{23}]^{3-}$. The major features of the experimental $[\text{Ti}_5\text{F}_{23}]^{3-}$ anion structure are well reproduced, i.e., five TiF_6 units form a four-membered ring, with three of the TiF_6 units connected to a fifth TiF_6 unit through three F_b atoms. The terminal $\text{Ti}-\text{F}_{tt}$ bond lengths that are trans to another terminal $\text{Ti}-\text{F}_{tt}$ bond are longer than the terminal $\text{Ti}-\text{F}_{tb}$ bond lengths that are trans to $\text{Ti}-\text{F}_b$ bridge bonds, in accordance with the experimental bond lengths (Table 4). The bridging $\text{Ti}-\text{F}_b$ bonds range from 1.930 to 2.054 Å [exptl, 1.946(2)–2.014(2) Å]. The $\text{Ti}-\text{F}_{tt}$ and $\text{Ti}-\text{F}_{tb}$ bonds are shorter than the analogous bonds in $[\text{Ti}_4\text{F}_{20}]^{4-}$. Experimentally, this trend is only apparent for the $\text{Ti}-\text{F}_{tb}$ bonds. Among the $\text{F}_b-\text{Ti}-\text{F}_b$ angles of the four-membered ring, the $\text{F2}-\text{Ti5}-\text{F18}$ angle (81.6°) is the smallest and is unique because F2 and F18 are not F -bridged to the triply F -bridged TiF_6 unit. The other $\text{F}_b-\text{Ti}-\text{F}_b$ angles within the four-membered ring (av. 85.9°) are comparable to the $\text{F}_b-\text{Ti}-\text{F}_b$ angles of the $[\text{Ti}_4\text{F}_{20}]^{4-}$ anion (av. 86.9°). The $\text{F}_{tt}-\text{Ti}-\text{F}_{tt}$ angle is smaller (168.3°) in $[\text{Ti}_5\text{F}_{23}]^{3-}$ than that in $[\text{Ti}_4\text{F}_{20}]^{4-}$ (176.9°). The calculated angles are in good agreement with the experiment.

Raman Spectroscopy of β - $[\text{ImH}][\text{Ti}_2\text{F}_9]$, β - $[\text{ImH}][\text{Ti}_4\text{F}_{20}]$, and $[\text{ImH}]_3[\text{Ti}_5\text{F}_{23}]$. The Raman spectra of β - $[\text{ImH}][\text{Ti}_2\text{F}_9]$ (Figure 11), β - $[\text{ImH}]_4[\text{Ti}_4\text{F}_{20}]$, and $[\text{ImH}]_3[\text{Ti}_5\text{F}_{23}]$ (Figures 12 and S9 and S10 in the Supporting Information) were acquired on randomly oriented single crystals. It was not possible to acquire usable spectra for the $[\text{Ti}_2\text{F}_{11}]^{3-}$ and $[\text{TiF}_6]^{2-}$ salts. As previously reported,²⁵ the frequency of the most intense Raman band can be used to identify complex titanium fluoride anions. This band corresponds to the symmetric in-phase terminal $\text{Ti}-\text{F}$ stretching mode and has been shown to increase in frequency with increasing TiF_4 content and decreasing anion charge. The experimental Raman frequencies and intensities for the $[\text{ImH}]^+$ cation (Table S6 in the Supporting Information) compare well with previously published values²⁶ and are not discussed.

(a) $[\text{Ti}_2\text{F}_9]^-$. In contrast to the well-known $[\text{TiF}_6]^{2-}$ anion, and as previously observed for $[\text{H}_3\text{O}][\text{Ti}_2\text{F}_9]^4$ and $\text{Cs}[\text{Ti}_2\text{F}_9]^4$, the Raman spectra of polymeric $[\text{Ti}_2\text{F}_9]^-$ anions are more complex (Figure 11) because the $([\text{Ti}_2\text{F}_9]^-)_n$ anions consist of infinite double chains of TiF_6 octahedra that share *cis*-vertices within each chain and because the component chains are joined by means of neighboring octahedra sharing a common vertex (Figure 7). The Raman spectrum of $\text{Cs}[\text{Ti}_2\text{F}_9]$ is the most complex, presumably because of the twisted orientation of the TiF_6 octahedra in one chain relative to those of the other chain. The twist results in symmetry lowering (i.e., the center of

Table 4. Experimental and Calculated Geometrical Parameters for the $[\text{Ti}_5\text{F}_{23}]^{3-}$ Anion

	exptl ^{a,b}	calcd (C_1) ^{b,c}		exptl ^c	calcd (C_1) ^c
Bond Lengths (Å)					
Ti1–F4	1.985(2)	1.974	Ti3–F3	1.983(2)	2.010
Ti1–F15	1.770(2)	1.793	Ti3–F19	1.770(2)	1.803
Ti1–F14	1.942(2)	1.975	Ti3–F10	1.771(2)	1.795
Ti1–F9	1.769(2)	1.799	Ti4–F18	1.956(2)	1.932
Ti1–F8	1.785(2)	1.799	Ti4–F20	1.757(3)	1.796
Ti1–F1	1.971(2)	1.997	Ti4–F13	1.758(3)	1.795
Ti2–F3	1.982(2)	1.974	Ti4–F23	1.776(3)	1.803
Ti2–F1	2.007(2)	1.995	Ti4–F7	1.999(2)	2.007
Ti2–F7	1.946(2)	1.977	Ti4–F14	1.991(2)	2.011
Ti2–F11	1.784(2)	1.799	Ti5–F12	1.783(2)	1.812
Ti2–F22	1.761(2)	1.792	Ti5–F16	1.814(3)	1.826
Ti2–F17	1.772(2)	1.799	Ti5–F6	1.782(2)	1.812
Ti3–F21	1.769(4)	1.795	Ti5–F18	1.995(2)	2.054
Ti3–F2	1.961(2)	1.930	Ti5–F5	1.848(3)	1.826
Ti3–F4	1.980(2)	2.010	Ti5–F2	2.014(2)	2.051
Bond Angles (deg)					
F15–Ti1–F4	89.01(11)	90.7	F10–Ti3–F2	89.45(11)	91.2
F14–Ti1–F4	86.84(11)	85.5	F3–Ti3–F4	83.35(9)	81.4
F9–Ti1–F4	172.05(12)	172.4	F19–Ti3–F4	90.10(12)	88.5
F1–Ti1–F4	82.09(9)	83.2	F10–Ti3–F4	168.89(11)	171.8
F8–Ti1–F4	87.69(11)	90.1	F19–Ti3–F3	88.53(11)	88.3
F15–Ti1–F14	89.33(10)	91.0	F10–Ti3–F3	88.45(11)	90.7
F9–Ti1–F15	98.20(11)	95.5	F19–Ti3–F10	97.21(12)	93.6
F15–Ti1–F1	168.75(11)	171.6	F20–Ti4–F18	90.17(12)	91.9
F15–Ti1–F8	95.50(11)	95.7	F13–Ti4–F18	90.11(12)	91.2
F9–Ti1–F14	89.87(11)	90.0	F23–Ti4–F18	169.52(12)	172.8
F14–Ti1–F1	83.36(9)	82.9	F18–Ti4–F7	84.27(10)	86.3
F8–Ti1–F14	172.64(11)	172.1	F18–Ti4–F14	82.47(10)	85.8
F9–Ti1–F1	90.35(10)	90.2	F20–Ti4–F13	98.40(13)	97.0
F9–Ti1–F8	94.92(12)	93.7	F20–Ti4–F23	95.99(14)	93.5
F8–Ti1–F1	91.01(10)	90.0	F20–Ti4–F7	171.01(12)	172.0
F3–Ti2–F1	82.23(9)	83.2	F20–Ti4–F14	91.22(12)	90.7
F7–Ti2–F3	83.49(10)	85.6	F13–Ti4–F23	97.33(13)	93.7
F11–Ti2–F3	169.75(12)	172.3	F13–Ti4–F7	88.70(12)	90.6
F22–Ti2–F3	89.71(11)	90.8	F13–Ti4–F14	167.89(12)	171.8
F17–Ti2–F3	89.52(11)	90.1	F23–Ti4–F7	88.52(12)	93.7
F7–Ti2–F1	83.94(10)	82.9	F23–Ti4–F14	88.92(12)	88.5
F11–Ti2–F1	88.64(11)	90.0	F14–Ti4–F7	81.07(10)	81.6
F22–Ti2–F1	170.90(11)	171.7	F12–Ti5–F16	96.13(12)	93.9
F17–Ti2–F1	87.38(10)	90.1	F6–Ti5–F12	96.43(12)	96.1
F22–Ti2–F7	90.99(12)	90.0	F12–Ti5–F18	172.33(11)	172.7
F11–Ti2–F7	90.95(11)	90.8	F6–Ti5–F5	90.76(11)	93.9
F17–Ti2–F7	169.51(11)	172.2	F12–Ti5–F2	89.60(10)	91.2
F22–Ti2–F11	99.02(13)	95.6	F6–Ti5–F16	96.43(12)	93.9
F17–Ti2–F11	94.72(11)	93.5	F16–Ti5–F18	86.25(11)	85.6
F22–Ti2–F17	96.81(12)	95.7	F16–Ti5–F5	169.57(11)	168.3
F21–Ti3–F2	90.26(11)	91.2	F16–Ti5–F2	85.68(11)	85.6
F21–Ti3–F4	91.90(11)	90.7	F12–Ti5–F5	90.55(12)	91.2
F21–Ti3–F3	173.84(11)	171.8	F6–Ti5–F18	90.53(11)	93.9
F19–Ti3–F21	95.41(13)	93.8	F6–Ti5–F2	173.35(11)	172.7
F10–Ti3–F21	95.73(12)	97.1	F5–Ti5–F18	86.13(11)	85.6
F2–Ti3–F4	82.42(10)	85.9	F18–Ti5–F2	83.30(10)	81.5
F2–Ti3–F3	85.26(10)	86.0	F5–Ti5–F2	86.37(10)	85.5
F19–Ti3–F2	170.77(11)	172.6			

^aExperimental geometrical parameters correspond to $[\text{ImH}]_3[\text{Ti}_5\text{F}_{23}]$. ^bThe atom-labeling schemes correspond to those used in Figure 10. ^cThe SDDALL basis set was used.

symmetry of Ti_2F_9 is removed), and as a consequence, a larger number of vibrational bands is observed (Table 5).

(b) $[\text{Ti}_4\text{F}_{20}]^{4-}$ and $[\text{Ti}_5\text{F}_{23}]^{3-}$. The observed and calculated frequencies and detailed mode descriptions for $[\text{Ti}_4\text{F}_{20}]^{4-}$ and

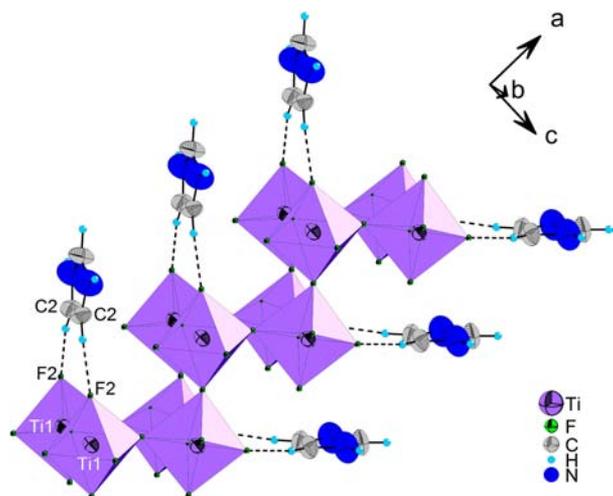


Figure 7. Crystal structure of β -[ImH][Ti₂F₉] showing coordination between the hydrogen atoms of the [ImH]⁺ cations and the fluorine atoms of the [Ti₂F₉]⁻ anion chains. Thermal ellipsoids are drawn at the 50% probability level. Only one of the two orientations of the disordered [ImH]⁺ cations is depicted.

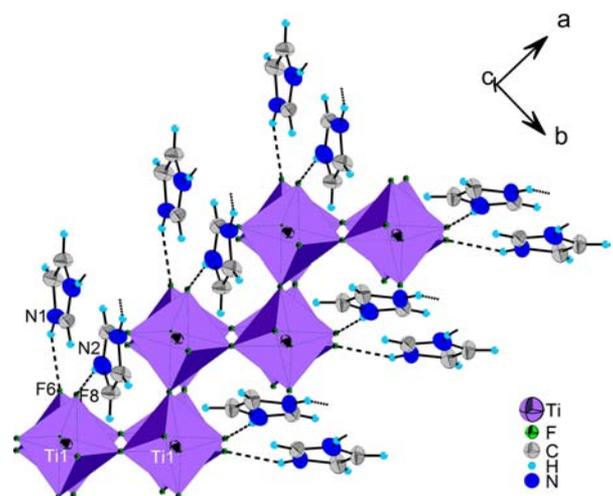


Figure 8. Crystal structure of α -[ImH][Ti₂F₉] showing coordination between the hydrogen atoms of the [ImH]⁺ cations and the fluorine atoms of the [Ti₂F₉]⁻ anion chains. Thermal ellipsoids are drawn at the 50% probability level. The Ti2 octahedra are eclipsed by the Ti1 octahedra and therefore are not labeled.

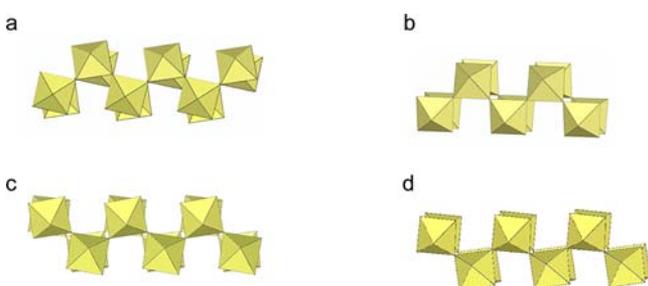


Figure 9. Infinite ([Ti₂F₉]⁻)_∞ dimeric chains in the crystal structures of (a) Cs[Ti₂F₉], (b) [H₃O][Ti₂F₉], (c) α -[ImH][Ti₂F₉], and (d) β -[ImH][Ti₂F₉].

[Ti₅F₂₃]³⁻ are provided in Tables 6 and 7 and S6 and S7 in the Supporting Information, respectively, where the atom number-

ing schemes correspond to those given in Figure 10. Spectral assignments for [Ti₄F₂₀]⁴⁻ and [Ti₅F₂₃]³⁻ were made by comparison with the calculated frequencies and Raman intensities of the energy-minimized gas-phase geometries, which are in good agreement with the experimental values at the B3LYP level of theory.

(i) [Ti₄F₂₀]⁴⁻. The vibrational spectrum of [Ti₄F₂₀]⁴⁻ was assigned under *D*_{2d} symmetry. A total of 66 fundamental vibrational modes belonging to the irreducible representations 10A₁ + 7B₁ + 16E + 7A₂ + 10B₂ are expected, where the E and B₂ modes are both Raman- and IR-active, the A₁ and B₁ modes are Raman-active, and the A₂ modes are both Raman- and IR-inactive. The most intense band at 695 cm⁻¹ is assigned to the totally symmetric Ti–F_{tb} stretch (F_{tb}, fluorine atom trans to a bridging fluorine atom), in good agreement with the calculated value (659 cm⁻¹), which is also predicted to be the most intense band in the Raman spectrum (Table 6). The bands at 560 and 624 cm⁻¹ are assigned to the Ti–F_{tt} and Ti–F_{tb} (F_{tt}, fluorine atom trans to a terminal fluorine atom) symmetric and asymmetric stretching modes, respectively, and also compare well with the calculated values (547 and 604 cm⁻¹). The Ti–F_b stretches are predicted at ca. 450 cm⁻¹ and are expected to be very weak in the Raman spectrum and are therefore unlikely to be observed. The remaining experimental bands at 189, 241, 271, 295, and 350 cm⁻¹ are assigned to deformations that occur in the calculated frequency ranges.

(ii) [Ti₅F₂₃]³⁻. The vibrational spectrum of [Ti₅F₂₃]³⁻ was assigned under *C*₁ symmetry. A total of 78 fundamental Raman (IR) vibrational modes and bands are predicted. All bands that were calculated to be intense, were observed in the Raman spectrum. The most intense band at 741 cm⁻¹ is assigned to the totally symmetric in-phase Ti–F_{tb} stretches, which is in very good agreement with the calculated frequency (732 cm⁻¹) and is also predicted to be the most intense band in the Raman spectrum (Table 7). The band at 717 cm⁻¹ is assigned to the out-of-phase coupled Ti–F_{tb} and Ti–F_{tt} stretches, in good agreement with the predicted values at 700 and 710 cm⁻¹. The bands at 678 and 694 cm⁻¹ are assigned to out-of-phase coupled Ti–F_{tt} stretches that are predicted to occur at 648, 678, and 681 cm⁻¹. The broad bands appearing at 476 and 562 cm⁻¹ also involve Ti–F_b and Ti–F_{tb} out-of-phase and in-phase stretches, respectively. The medium-intensity band at 373 cm⁻¹ is assigned to the δ (F_b–Ti–F_b) deformation, which is well reproduced by the calculation (366 cm⁻¹).

3. CONCLUSIONS

Although [TiF₆]²⁻ salts are well-known, structural reports of poly[perfluorotitanate(IV)] anions were limited to ([TiF₅]⁻)_∞,¹¹ ([Ti₂F₉]⁻)_∞,⁴ [Ti₂F₁₀]²⁻,^{7,8} [Ti₂F₁₁]³⁻,⁹ ([Ti₃F₁₃]⁻)_∞,¹² [Ti₄F₁₈]²⁻,^{4,10} [Ti₄F₁₉]³⁻,¹⁹ ([Ti₇F₃₀]²⁻)_∞,¹³ and ([Ti₈F₃₃]⁻)_∞.¹⁴ Investigations of the Im–TiF₄ system in aHF solvent have afforded five new salts, [ImH]₂[TiF₆]·2HF, [ImH]₃[Ti₂F₁₁], [ImH]₄[Ti₄F₂₀], [ImH]₃[Ti₅F₂₃], and [ImH][Ti₂F₉], where two of them have provided examples of new poly[perfluorotitanate] anions, namely, [Ti₄F₂₀]⁴⁻ and [Ti₅F₂₃]³⁻.

Quantum-chemical calculations using the B3LYP method have been used to obtain energy-minimized gas-phase geometries for the [TiF₆]²⁻, [Ti₄F₂₀]⁴⁻, and [Ti₅F₂₃]³⁻ anions. The Raman spectra of the [Ti₄F₂₀]⁴⁻ and [Ti₅F₂₃]³⁻ anions have been assigned based on the calculated vibrational frequencies and vibrational displacements of their respective modes.

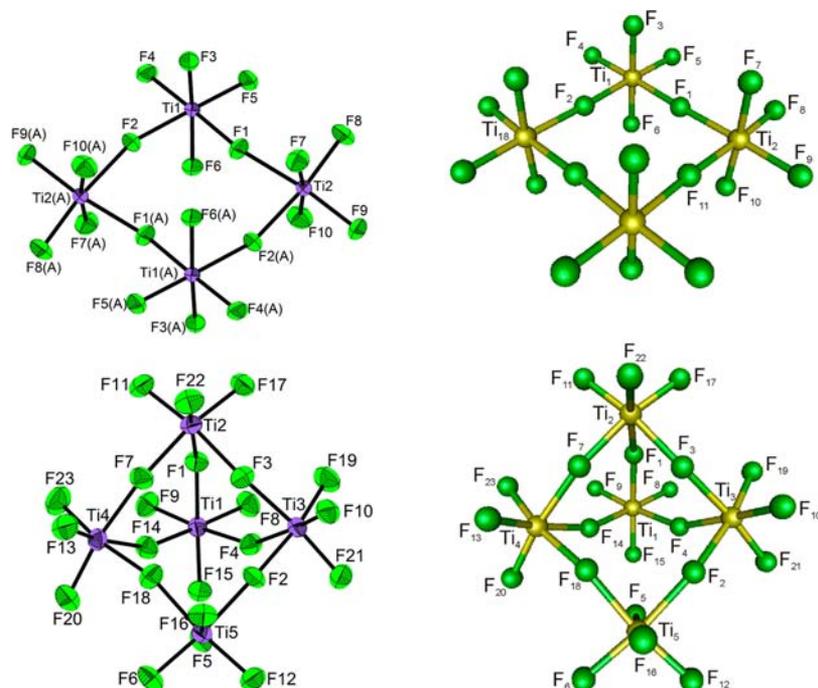


Figure 10. Experimental (left column) and calculated (right column; B3LYP/SDDALL) geometries of the $[\text{Ti}_4\text{F}_{20}]^{4-}$ and $[\text{Ti}_5\text{F}_{23}]^{3-}$ anions. The geometrical parameters are provided in Tables 3 and 4. Thermal ellipsoids are drawn at the 50% probability level.

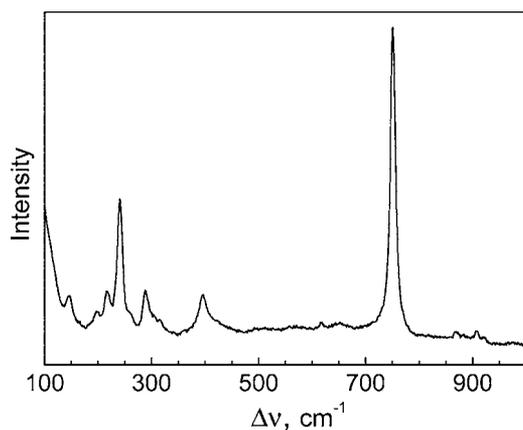


Figure 11. Raman spectrum of β - $[\text{ImH}][\text{Ti}_2\text{F}_9]$ recorded at room temperature on a randomly oriented single crystal sealed in a quartz capillary using 632.8-nm excitation.

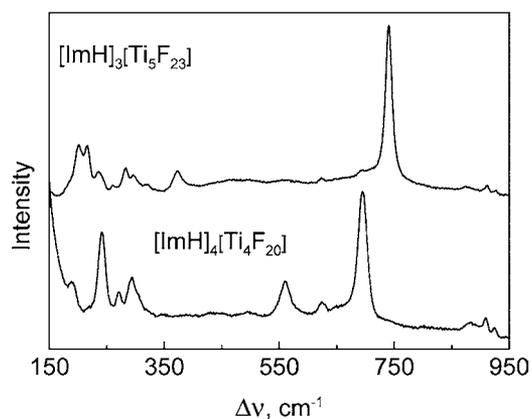


Figure 12. Raman spectra of $[\text{ImH}]_3[\text{Ti}_5\text{F}_{23}]$ and β - $[\text{ImH}]_4[\text{Ti}_4\text{F}_{20}]$ recorded at room temperature on randomly oriented single crystals sealed in quartz capillaries using 632.8-nm excitation.

4. EXPERIMENTAL SECTION

Reagents. Fluorine (Solvay Fluor and Derivate GmbH, Hannover, Germany), aHF (Linde AG, Puliach, Germany), and imidazole (Aldrich, 99%) were used. Titanium tetrafluoride was synthesized by the reaction of TiCl_3 (Sigma-Aldrich, 99.999%) with elemental fluorine F_2 in aHF. The purity of TiF_4 was confirmed by Raman spectroscopy and chemical analysis.

Synthetic Apparatus. All manipulations were carried out under anhydrous conditions. Volatile compounds, such as aHF and F_2 , were handled on a vacuum line constructed from nickel/Teflon, and nonvolatile materials were handled in a drybox (M. Braun) in an argon atmosphere (<0.5 pmm H_2O). Single crystals of imidazolium poly[perfluorotitanates(IV)] were grown in T-shaped crystallization vessels comprised of two tetrafluoroethylene-hexafluoropropylene block copolymer (FEP; Polytetra GmbH, Germany) tubes (one 16-mm i.d. \times 19-mm. o.d. and the other 4-mm i.d. \times 6-mm. o.d.); each tube was heat-sealed on one end and joined at 90° through a Teflon T-connector. A Teflon valve was connected at 180° to the 19-mm-o.d.

tube. Before use, the above-mentioned reaction/crystallization vessel assemblies were dried under dynamic vacuum and passivated with elemental fluorine at 1.1 bar for 2 h. Anhydrous HF (Linde, 99.995%) was treated with K_2NiF_6 (Advance Research Chemicals, Inc.) for several hours prior to use.

Crystal Growth of Imidazolium Poly[perfluorotitanates(IV)]. Stoichiometric amounts of imidazole and TiF_4 (totaling ca. 200 mg) were loaded into the 19-mm o.d. arm of the crystallization vessel inside a drybox (Table 8). The reagent mixture was then transferred to a metal/Teflon manifold, where aHF (5–7 mL) was condensed onto the starting material at -196°C . The crystallization mixture was warmed to ambient temperature, and the resulting clear, colorless solution was decanted into the 6-mm o.d. side arm. Evaporation of the solvent from this solution was carried out by maintaining a temperature gradient of ca. 10 – 20°C between the 6-mm o.d. (22 – 32°C) and 19-mm o.d. (ca. 12°C) tubes for several weeks. When the HF level in the smaller-diameter vessel ceased to further decrease, it was necessary to increase the temperature gradient. This was accomplished by slowly cooling the larger vessel in a cryostat from

Table 5. Experimental Raman Frequencies and Intensities for β -[ImH][Ti₂F₉] Compared with Those of Cs[Ti₂F₉] and [H₃O][Ti₂F₉]^a

β -[ImH][Ti ₂ F ₉] ^b	[H ₃ O][Ti ₂ F ₉] ^c	Cs[Ti ₂ F ₉] ^c
751(10)	756(10)	751(10)
		721(0.7)
		702(0.7)
		667(0.5)
		635(0.5)
396(1)	397(1)	397(1.5)
291(1)	293(1)	294(0.9)
		253(2)
241(3)	245(1.2)	241(1.9)
217(0.5)	229(1)	229(1.6)
		211(0.7)
198(0.1)	198 (sh)	
		170(0.5)
147(0.2)		

^aFrequencies are given in cm⁻¹. ^bThis work. ^cFrom ref. 4.

+12 to -20 °C and then to -55 °C for [ImH]₂[TiF₆]-2HF. Several days to several weeks were required to induce crystallization. Slow distillation of aHF from the 6-mm o.d. tube into the 19-mm o.d. tube resulted in crystal growth inside the 6-mm o.d. tube. Selected single crystals were transferred to 0.3-mm quartz capillaries inside the drybox, and their Raman spectra were recorded at several random positions.

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 μm spot through a 50× microscope objective on the top surface of the sample.

Single crystals were mounted in the drybox in previously vacuum-dried quartz capillaries, which were initially sealed with Halocarbon 25-SS grease (Halocarbon Corp.) inside the drybox and later heat-sealed in an oxygen–hydrogen flame outside the drybox. Raman spectra of [ImH][Ti₂F₉], [ImH]₃[Ti₅F₂₃], and [ImH]₄[Ti₄F₂₀] were recorded at 17 mW with a 5 s exposure time for each scan. For [ImH]₃[Ti₅F₂₃] and [ImH]₄[Ti₄F₂₀], five scans, and for [ImH][Ti₂F₉], three scans were accumulated.

X-ray Crystal Structure Determinations. Crystals were immersed in perfluorodecalin (ABCR, 98%) inside a drybox, selected

Table 7. Experimental and Calculated Vibrational Frequencies^a and Intensities^b for the [Ti₅F₂₃]³⁻ Anion in [ImH]₃[Ti₅F₂₃]

exptl ^c	calcd ^d	assgnts (C ₁) ^e
741(100)	732(85)[9]	$\nu(\text{Ti-F}_{\text{tb}})_{\text{ip}}$
717 ^f	{ 710(4)[860] 710(5)[532] 700(3)[97]	$\nu(\text{Ti-F}_{\text{tt}})_{\text{oop}} / \nu(\text{Ti-F}_{\text{tb}})_{\text{oop}}$ $\nu(\text{Ti-F}_{\text{tb}})_{\text{oop}}$
694(20)	{ 681(5)[63] 681(5)[383] 678(2)[3]	$\nu(\text{Ti-F}_{\text{tb}})_{\text{oop}}$ $\nu(\text{Ti-F}_{\text{tb}})_{\text{oop}} / \nu(\text{Ti-F}_{\text{b}})_{\text{ip}}$
623(2)	{ 658(2)[1052] 648(2)[554]	$\nu(\text{Ti-F}_{\text{tb}})_{\text{oop}}$
562(1) br	{ 592(4)[121] 562(4)[165]	$\nu(\text{Ti-F}_{\text{tt}})_{\text{ip}} / \nu(\text{Ti-F}_{\text{tb}})_{\text{ip}} / \nu(\text{Ti-F}_{\text{b}})_{\text{ip}}$ $\nu(\text{Ti-F}_{\text{b}})_{\text{ip}} / \nu(\text{Ti-F}_{\text{tt}})_{\text{ip}}$
472 ^f	501(12)[479]	$\nu(\text{Ti-F}_{\text{tt}})_{\text{ip}} / \nu(\text{Ti-F}_{\text{b}})_{\text{oop}}$
373(16)	366(8)[5]	$\delta(\text{F}_{\text{b}}-\text{Ti-F}_{\text{b}}) / \delta(\text{F}_{\text{tb}}-\text{Ti-F}_{\text{tb}})$
321(5)	324(<1)[<1]	$\delta(\text{F}_{\text{b}}-\text{Ti-F}_{\text{b}})$
297(10)	288(1)[118]	$\delta(\text{F}_{\text{b}}-\text{Ti-F}_{\text{b}})$
282(15)	{ 282(2)[<1] 279(5)[23]	$\rho_{\text{t}}(\text{F}_{\text{tt}}-\text{Ti-F}_{\text{tt}}) / \rho_{\text{t}}(\text{F}_{\text{tb}}-\text{Ti-F}_{\text{tb}})$ $\delta(\text{F}_{\text{b}}-\text{Ti-F}_{\text{b}})$
261(1)	256(<0.1)[12]	
236(14)	{ 225(1)[<0.1] 221(1)[<0.1]	$\rho_{\text{t}}(\text{F}_{\text{tb}}-\text{Ti-F}_{\text{b}}) / \rho_{\text{t}}(\text{F}_{\text{tb}}-\text{Ti-F}_{\text{tb}})$
216(30)	212(2)[<1]	$\rho_{\text{t}}(\text{F}_{\text{b}}-\text{Ti-F}_{\text{b}})$
202(30)	{ 207(3)[<0.1] 199(3)[<1]	$\rho_{\text{t}}(\text{F}_{\text{tb}}-\text{Ti-F}_{\text{tb}})$

^aFrequencies are given in cm⁻¹. The full set of calculated frequencies is reported in Table S8 (Supporting Information). ^bValues in parentheses denote relative Raman intensities. The abbreviation sh denotes a shoulder. Modes associated with the cation were also observed at 928(2), 912(5), and 876(2) cm⁻¹. ^cThe Raman spectrum was recorded at ambient temperature on a randomly oriented single crystal sealed in a quartz capillary using 632.81-nm excitation. ^dThe B3LYP/SDDALL method was used. Values in parentheses denote Raman intensities (Å⁴ u⁻¹). Values in square brackets denote IR intensities (km mol⁻¹). ^eVibrational assignments were based on modes calculated at the B3LYP level of theory. The abbreviations denote in-phase (ip), out-of-phase (oop), stretch (ν), bend (δ), rock (ρ_{rock}), torsion (ρ_{t}), a fluorine atom that is trans to a terminal fluorine atom (F_{tt}), a fluorine atom that is trans to a bridging fluorine atom (F_{tb}), and a bridging fluorine atom (F_b). ^fThis band was visible for some crystals at specific orientations (Figure S10, Supporting Information).

under a microscope, and mounted on the goniometer head of the diffractometer in a cold nitrogen stream. Although up to 15 crystals of consistent crystal habit were screened for each phase (Table 8), the

Table 6. Experimental and Calculated Vibrational Frequencies^a and Intensities^b for the [Ti₄F₂₀]⁴⁻ Anion in β -[ImH]₄[Ti₄F₂₀]

exptl ^c	calcd ^d		assgmnt (D _{2d}) ^e
695(100)	659(70)[0]	A ₁	$\nu_{\text{s}}(\text{Ti-F}_{\text{tb}})$
624(12)	604(7)[0]	B ₁	$\nu_{\text{as}}(\text{Ti-F}_{\text{tb}})$
560(30)	547(22)[0]	A ₁	$\nu_{\text{s}}(\text{Ti-F}_{\text{tt}})$
350sh ^f	341(6)[0]	A ₁	$\delta(\text{F}_{\text{tt}}-\text{Ti-F}_{\text{tt}}) / \delta(\text{F}_{\text{tb}}-\text{Ti-F}_{\text{tb}}) / \delta(\text{F}_{\text{b}}-\text{Ti-F}_{\text{b}})$
295(30)	299(2)[<0.1]	E	$\delta(\text{TiF}_{2\text{tb}}\text{F}_{2\text{b}})_{\text{umb}}$
271(15)	277(4)[<0.1]	B ₂	$\delta(\text{F}_{\text{tt}}-\text{Ti-F}_{\text{tt}}) / \delta(\text{F}_{\text{tb}}-\text{Ti-F}_{\text{tb}})$
241(65)	233(5)[<1]	E	$\delta(\text{F}_{\text{tt}}-\text{Ti-F}_{\text{tb}}) / \delta(\text{F}_{\text{tt}}-\text{Ti-F}_{\text{b}}) / \rho_{\text{t}}(\text{F}_{\text{tb}}-\text{Ti-F}_{\text{b}})$
189(25)	170(3)[<0.1]	B ₂	$\rho_{\text{w}}(\text{F}_{\text{tt}}-\text{Ti-F}_{\text{tt}}) / \delta(\text{F}_{\text{tb}}-\text{Ti-F}_{\text{tb}})$

^aFrequencies are given in cm⁻¹. The full set of calculated frequencies is reported in Table S7 (Supporting Information). ^bValues in parentheses denote Raman intensities (Å⁴ u⁻¹). Values in square brackets denote IR intensities (km mol⁻¹). ^cThe Raman spectrum was recorded at ambient temperature on a randomly oriented single crystal sealed in a quartz capillary using 632.81-nm excitation. Values in parentheses denote relative Raman intensities. The abbreviation sh denotes a shoulder. Bands associated with the cation were also observed at 926(5), 908(10), and 882(5) cm⁻¹. ^dThe B3LYP/SDDALL method was used. ^eVibrational assignments were based on modes calculated at the B3LYP level of theory. The abbreviations denote symmetric (s), asymmetric (as), stretch (ν), bend (δ), wag (ρ_{w}), a fluorine atom that is trans to a terminal fluorine atom (F_{tt}), a fluorine atom that is trans to a bridging fluorine atom (F_{tb}), and a bridging fluorine atom (F_b). ^fThis band was visible for some crystals at specific orientations (Figure S9 in the Supporting Information).

Table 8. Stoichiometries Used To Crystallize Imidazolium Poly[perfluorotitanates(IV)] and Phases Observed after Crystallization of Imidazole (Im) and TiF₄ in aHF

starting $n(\text{Im}):n(\text{TiF}_4)$ molar ratios	phases observed after crystallization
2:1	[ImH] ₂ [TiF ₆]·2HF, [ImH] ₃ [Ti ₂ F ₁₁]
1.5:1	<i>a</i>
1:1	[ImH] ₄ [Ti ₄ F ₂₀], [ImH] ₃ [Ti ₅ F ₂₃]
1:1.5	[ImH] ₄ [Ti ₄ F ₂₀], [ImH] ₃ [Ti ₅ F ₂₃], [ImH][Ti ₂ F ₉]
1:1.67	[ImH] ₃ [Ti ₅ F ₂₃], [ImH][Ti ₂ F ₉]
1:2	[ImH][Ti ₂ F ₉]

^aThe nature of this phase is unknown because the single crystals that were grown were too small for an X-ray structure determination. In addition, Raman spectra could not be obtained because of an intense fluorescence background.

presence of other crystal phase(s) cannot be definitively ruled out. Data were collected at 200 or 298 K on a Rigaku AFC7 diffractometer equipped with a Mercury CCD area detector using graphite-monochromated Mo K α radiation ($\lambda = 0.71069 \text{ \AA}$).

Processing of the raw data sets of [ImH]₂[TiF₆]·2HF, α -[ImH]₄[Ti₄F₂₀], and α -[ImH][Ti₂F₉] were completed using the TEXSAN package.²⁷ Processing of the raw data sets of [ImH]₃[Ti₂F₁₁], β -[ImH]₄[Ti₄F₂₀], [ImH]₃[Ti₅F₂₃], and β -[ImH][Ti₂F₉] were completed by using APEX2 GUI software,²⁸ which applied Lorentz and polarization corrections to three-dimensionally integrated diffraction spots. This was done after converting the data format from the Rigaku AFC7 to the Bruker APEX2 format. The program SADABS²⁹ was used for the scaling of diffraction data, the application of decay corrections, and empirical absorption corrections on the basis of the intensity ratios of redundant reflections. Although the data for [ImH]₂[TiF₆]·2HF are not of good quality (see the CIF files in the Supporting Information), the authors are convinced that the structure solution is correct and have therefore integrated this result into the manuscript to provide a more comprehensive account.

In the case of [ImH]₂[TiF₆]·2HF, α -[ImH]₄[Ti₄F₂₀], and α -[ImH][Ti₂F₉], the TEXSAN²⁷ program was used to confirm the unit cell dimensions and the crystal lattices. In the case of [ImH]₃[Ti₂F₁₁], β -[ImH]₄[Ti₄F₂₀], [ImH]₃[Ti₅F₂₃], and β -[ImH][Ti₂F₉], the XPREP³⁰ program was used to confirm the unit cell dimensions and crystal lattices. The solutions were obtained by direct methods using the SIR-92 (as implemented in the program package WinGX)³¹ or the SHELXTL-plus^{30,32} programs, which located the positions of the titanium and fluorine atoms. All further solution refinements were performed using the SHELXTL-plus program.³⁰ The positions of the remaining carbon and nitrogen atoms were revealed in successive difference Fourier syntheses. In the case of [ImH]₂[TiF₆]·2HF, [ImH]₃[Ti₂F₁₁], β -[ImH]₄[Ti₄F₂₀], and β -[ImH][Ti₂F₉], 2-fold disorders had to be taken into account when refining some or all of the [ImH]⁺ cations. Hydrogen atoms were included on idealized positions and allowed to ride on the atoms they were bonded to. The final refinements were obtained by introducing anisotropic thermal parameters and the recommended weightings for all atoms except the hydrogen atoms. The maximum electron densities in the final difference Fourier maps were located near the heavy atoms. The choices of space group were confirmed by PLATON from the WinGX software package.³¹ Figures were prepared using the program DIAMOND 3.1.³³

CCDC 907014 ([ImH]₂[TiF₆]·2HF), 907015 ([ImH]₃[Ti₂F₁₁]), 907016 (β -[ImH]₄[Ti₄F₂₀]), 907017 (α -[ImH]₄[Ti₄F₂₀]), 907018 ([ImH]₃[Ti₅F₂₃]), 907019 (β -[ImH][Ti₂F₉]), and 907020 (α -[ImH]-[Ti₂F₉]) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre at www.ccdc.cam.ac.uk/data_request/cif.

Computational Methods. The optimized geometries and frequencies of the [Ti₄F₂₀]⁴⁻ and [Ti₅F₂₃]³⁻ anions were calculated at the B3LYP³⁴ level of theory. The Stuttgart semirelativistic large-core

and effective-core pseudopotential basis sets (SDDall) augmented for fluorine, oxygen, and titanium atoms with two d-type polarization functions by Huzinaga et al.³⁵ were used.

Quantum-chemical calculations were carried out using the program Gaussian 03.³⁴ The levels and basis sets were benchmarked by calculating [TiF₆]²⁻ (Table S5 in the Supporting Information). The geometries were fully optimized using analytical gradient methods. The vibrational frequencies were calculated at the B3LYP level using the appropriate minimized structure, and the vibrational mode descriptions were arrived at with the aid of GaussView.³⁶

■ ASSOCIATED CONTENT

■ Supporting Information

List of geometrical parameters for [ImH]₂[TiF₆]·2HF (Table S1) and α - and β -[ImH][Ti₂F₉] (Tables S2 and S3), unit cells of [ImH]₂[TiF₆]·2HF (Figure S1), [ImH]₃[Ti₂F₁₁] (Figure S2), β -[ImH]₄[Ti₄F₂₀] (Figure S3), α -[ImH]₄[Ti₄F₂₀] (Figure S4), [ImH]₃[Ti₅F₂₃] (Figure S5), β -[ImH][Ti₂F₉] (Figure S6), and α -[ImH][Ti₂F₉] (Figure S7), hydrogen-bonding geometries in α - and β -[ImH][Ti₂F₉], [ImH]₃[Ti₂F₁₁], α - and β -[ImH]₄[Ti₄F₂₀], and [ImH]₃[Ti₅F₂₃] (Table S4), geometries of [Ti₂F₁₁]³⁻ anions (Figure S8), vibrational data for [TiF₆]²⁻ (Table S5), Raman spectra of β -[ImH]₄[Ti₄F₂₀] and [ImH]₃[Ti₅F₂₃] (Figures S9 and S10), experimental vibrational frequencies for imidazolium cations in β -[ImH][Ti₂F₉], β -[ImH]₄[Ti₄F₂₀], and [ImH]₃[Ti₅F₂₃] (Table S6); complete list of experimental and calculated vibrational frequencies for the [Ti₄F₂₀]⁴⁻ and [Ti₅F₂₃]³⁻ anions (Tables S7 and S8), complete ref 34, and X-ray crystallographic files in CIF format for the structure determinations of [ImH]₂[TiF₆]·2HF, α - and β -[ImH][Ti₂F₉], [ImH]₃[Ti₂F₁₁], α - and β -[ImH]₄[Ti₄F₂₀], and [ImH]₃[Ti₅F₂₃]. This material is available free of charge via the Internet at <http://pubs.acs.org>.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: schrobil@mcmaster.ca (G.J.S.), zoran.mazej@ijs.si (Z.M.).

Notes

The authors declare no competing financial interest.

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