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Poly[perfluorotitanate(IV)] Salts of $[H_3O]^+$, Cs^+, $[Me_4N]^+$, and $[Ph_4P]^+$ and about the Existence of an Isolated $[Ti_2F_9]^-$ Anion in the Solid State

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The increase in the size of monocations (A^+) does not favor the formation of $[Ti_2F_9]^-$ against $[Ti_4F_{18}]^{2-}$ salts (with isolated $[Ti_2F_9]^-$ or $[Ti_4F_{18}]^{2-}$ anions, respectively) as previously proposed (Passmore, J.; et al. *Angew. Chem., Int. Ed.* **2005**, *44*, 7958−7961). The crystal structure determination of $[Me_4N]^+$ and $[Ph_4P]^+$ salts showed that both compounds are $[Ti_4F_{18}]^{2-}$ salts; i.e., $[Me_4N]_2[Ti_4F_{18}]$ and $[Ph_4P]_2[Ti_4F_{18}]$ were obtained instead of $[Me_4N][Ti_2F_9]$ and $[Ph_4P][Ti_2F_9]$. The product of the reaction of CsF with $2TiF_4$ could be formulated as $CsTi_2F_9$; however, instead of isolated $[Ti_2F_9]^-$ anions, infinite $([Ti_2F_9]^-)_n$ double chains are present. In the case of $H_3OTi_2F_9$, a similar result was obtained. On the basis of the similarities of vibrational spectra of $CsTi_2F_9$ and $NF_4Ti_2F_9$, it is also unlikely that the latter consists of isolated $[Ti_2F_9]^-$ ions.

Introduction

The reaction between TiF_4 and an excess of [15]crown-5 in CH_3CN yielded $[TiF_2([15]crown\text{-}5)][Ti_4F_{18}]\cdot 0.5CH_3CN$.[1] Its crystal structure consists of discrete $[TiF_2([15]crown\text{-}5)]^{2+}$ cations and $[Ti_4F_{18}]^{2-}$ anions. The estimation of how the sizes of mono- and dications promote the formation of $[Ti_2F_9]^-$ versus $[Ti_4F_{18}]^{2-}$ salts, and inversely, was also given in the same paper.[1] On the basis of the estimates of the corresponding energetics, applying the "volume-based" thermodynamic (VBT) approach, it was proposed that all monocations (A^+), with the exception of smaller ones [$V(A^+) < 0.019$ nm^3], favor the formation of $[Ti_2F_9]^-$ against $[Ti_4F_{18}]^{2-}$ salts. It was suggested that $NF_4Ti_2F_9$ [$V([NF_4]^+) = 0.06$ nm^3][2] probably contains isolated $[Ti_2F_9]^-$ anions;[3] however, for a slightly smaller Cs^+ ion [$V(Cs^+) = 0.01882$ nm^3],[2] it is still an open question of which salt is formed.[1] To verify those predictions (i.e., would the reaction between AF and $2TiF_4$ yield $[Ti_2F_9]^-$ or $[Ti_4F_{18}]^{2-}$ salt), selected single-charged cations (A^+) of various sizes were chosen and single crystals of their corresponding titanium(IV) salts were grown. Results of their crystal structure determination are given in the present paper.

Experimental Section

Caution! *Anhydrous HF and some fluorides are highly toxic and must be handled using appropriate apparatus and protective gear.*

Apparatus and Reagents. Volatile materials (anhydrous HF and F_2) were handled in an all-Teflon vacuum line equipped with Teflon valves. The manipulation of the nonvolatile materials was done in a drybox (M. Braun). The residual water in the atmosphere within the drybox never exceeded 2 ppm. The reactions were carried out in tetrafluoroethylene−hexafluoropropylene (FEP; Polytetra GmbH, Mönchengladbach, Germany) reaction vessels (length, 250−300 mm; i.d., 15.5 mm; o.d., 18.75 mm) equipped with Teflon valves and Teflon-coated stirring bars. Prior to use, all reaction vessels were passivated with elemental fluorine. Fluorine (Solvay Fluor und Derivate GmbH, Hannover, Germany), CsF (Aldrich, 99.9%), Me_4NF (Aldrich, 97%), and Ph_4PCl (Alfa Aesar, 98%) were used as supplied. Anhydrous HF (Fluka, Purum) was treated with K_2NiF_6 (Ozark Mahoning) for several hours prior to use. The compound TiF_4 was synthesized by the reaction between $TiCl_3$ (Aldrich, 99.999%) and elemental fluorine in aHF. The powder X-ray diffraction pattern and Raman spectrum of isolated TiF_4 were in agreement with the literature data.[4,5]

Raman Spectroscopy. Raman spectra with a resolution of 2 cm^{-1} were recorded (10−20 scans) on a Renishaw Raman Imaging Microscope System 1000, using the 632.8 nm excitation line of a He−Ne laser.

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(1) Decken, A.; Jenkins, H. D. B.; Knapp, C.; Nikiforov, G. B.; Passmore, J.; Rautiainen, J. M. *Angew. Chem., Int. Ed.* **2005**, *44*, 7958–7961.

(2) Jenkins, H. D. B.; Roobottom, H. K.; Passmore, J.; Glasser, L. *Inorg. Chem.* **1998**, *38*, 3609–3620.

(3) Here we have in mind the geometry where two Ti atoms are connected via three bridging F atoms and coordination of each Ti is completed by three terminal F atoms. In that way, the CN of each Ti in the $[Ti_2F_9]^-$ anion is equal to 6. Another possibility is the case where two Ti atoms are connected via one bridging F atom and coordination of each Ti is completed by four terminal F atoms. In that way, CN of each Ti is equal to 5. CN = 5 is clearly energetically less favorable than CN = 6.

(4) Christe, K. O.; Schack, C. J. *Inorg. Chem.* **1977**, *16*, 353–359.

(5) Bialowons, H.; Müller, M.; Müller, B. G. *Z. Anorg. Allg. Chem.* **1995**, *621*, 1227–1231.

Table 1. Crystal Data and Structure Refinement for $H_3OTi_2F_9$, $CsTi_2F_9$, $[Me_4N]_2[Ti_4F_{18}]$, and $[Ph_4P]_2[Ti_4F_{18}]$

chemical formula	$H_3OTi_2F_9$	$CsTi_2F_9$	$[Me_4N]_2[Ti_4F_{18}]$	$[Ph_4P]_2[Ti_4F_{18}]$
space group	*Pnma*	*C2/c*	*Pnma*	$P\bar{1}$
a (pm)	898.8(4)	1136.3(3)	1327.76(10)	1011.720(10)
b (pm)	545.1(2)	1471.1(3)	1049.35(6)	1300.11(3)
c (pm)	1474.8(6)	533.18(14)	1744.84(13)	2091.32(12)
α (deg)	90	90	90	83.880(9)
β (deg)	90	116.41(2)	90	80.335(8)
γ (deg)	90	90	90	69.988(6)
V (nm^3)	0.7226(5)	0.7982(4)	2.4311(3)	2.54444(19)
Z	4	4	4	2
fw (g mol^{-1})	285.76	399.71	681.77	1212.12
D_{calcd} (g cm^{-3})	2.627	3.325	1.863	1.582
T (K)	100	200	200	200
μ (mm^{-1})	2.335	6.596	1.401	0.767
R1[a]	0.0467	0.0617	0.0607	0.0753
wR2 [$I > 2.00\ \sigma(I)$][b]	0.1081	0.1391	0.1455	0.1871
GOF	1.257	1.149	1.167	1.094

[a] $R1=\sum||F_o| - |F_c||/\sum|F_o|$. [b] $wR2=[\sum(w(F_o^2-F_c^2)^2/\sum(w(F_o^2)^2]^{1/2}$, $GOF=[\sum w(F_o^2 - F_c^2)^2)/N_o-N_p)]^{1/2}$, where N_o=no. of reflections and N_p=no. of refined parameters.

Powder X-ray Diffraction Patterns. Powder X-ray diffraction patterns were obtained using the Debye−Scherrer technique with Ni-filtered Cu Kα radiation. Samples were loaded into quartz capillaries (0.3 mm) in a drybox. Intensities were estimated visually.

Crystal Growth of $A_2[Ti_4F_{18}]$ (A = $[Me_4N]^+$ and $[Ph_4P]^+$) and ATi_2F_9 (A = $[H_3O]^+$ and Cs^+). In a general procedure, single crystal growth was carried out in a double T-shaped apparatus consisting of two FEP tubes (19 and 6 mm. o.d.). Mixtures of AF/2TiF_4 (AF = 0.25 mmol of CsF and 0.28 mmol of MeN_4F) and Ph_4PCl/2TiF_4 (0.17 mmol of Ph_4PCl) were loaded into the wider arm of the crystallization vessel in a drybox. aHF (~4 mL for MeN_4 and Ph_4^+ and 10 mL for Cs^+ salt) was then condensed onto the starting material at 77 K. The crystallization mixtures were brought up to ambient temperature, and the clear solutions that developed were decanted into the narrower arm. The evaporation of the solvent from these solutions was carried out by first maintaining a temperature gradient corresponding to about 10 K between both tubes for 2 ($[Ph_4P]^+$ salt), 4 ($[Me_4N]^+$ salt), or 12 (Cs^+ salt) weeks, respectively. In the case of $[Me_4N]^+$ salt, the temperature gradient had been later increased to about 10 K for an additional 1 week. The effect of this treatment was to enable aHF to be slowly evaporated from a narrower tube into a wider tube, leaving the colorless crystals of $A_2[Ti_4F_{18}]$ (A = $[Me_4N]^+$ and $[Ph_4P]^+$) and $CsTi_2F_9$. Single crystals of $H_3OTi_2F_9$ were obtained unexpectedly as one of the phases obtained after crystallization of the products obtained by the reaction between TiO and AsF_5 in aHF. A detailed characterization of the products obtained in the TiO/AsF_5/aHF system is beyond the scope of this study and will be published elsewhere. Selected single crystals of $A_2[Ti_4F_{18}]$ (A = $[Me_4N]^+$ and $[Ph_4P]^+$) and ATi_2F_9 (A=Cs^+ and H_3O^+) were placed inside 0.3 mm quartz capillaries in a drybox and their Raman spectra recorded.

Crystal Structure Determination. Products of crystallization were immersed in a perfluorinated oil (ABCR, FO5960, melting point 263 K) in a drybox. Single crystals were then selected from the crystallization products under the microscope (at temperatures between 265 and 273 K) outside the drybox and then transferred into the cold nitrogen stream of the Oxford Instruments cooling system, installed on Rigaku AFC7 diffractometer (Mercury CCD area detector, with graphite-monochromated Mo Kα radiation). Data were collected at 100 or 200 K. The data were corrected for Lorentz and polarization effects. A multiscan absorption correction was applied to all data sets. Both structures were solved by direct methods using the *SIR-92*[6] program (program package TeXsan) and refined with *SHELXL-97*[7] software, implemented in the program package *WinGX*.[8] The figures were prepared using *DIAMOND 3.1*[9] and *Balls & Sticks*, freely available software.[10] The crystal data and details of the structure refinement are given in Table 1.

Results and Discussion

Previously, the estimations of the ΔH^{298}(s) ($\approx\Delta G^{298}$(s)) values of the reaction 2[cation]$^+[Ti_2F_9]^-$(s) → [cation]$_2^+[Ti_4F_{18}]^{2-}$(s) (eq 1) by using the equation of Jenkins et al. and applying the VBT approach were reported.[1] According to the results, the monocations with $V(A^+) > 0.019$ nm^3 (i.e., $[NF_4]^+$, $[Me_4N]^+$, $[Ph_4As]^+$, etc.) favor the formation of [cation]$[Ti_2F_9]$ with isolated $[Ti_2F_9]^-$ anions [because ΔH(s) ($\approx\Delta G$(s)) > 0]. The Cs^+ cation with $V(Cs^+) = 0.01882$ nm^3[2] and ΔG(eq 1) = −3 (±10) kJ mol^{-1} represents the borderline case where it was in question as to which anion is present. For those, we decided to prepare single crystals of poly[perfluorotitanate(IV)] salts of Cs^+ ($V(Cs^+) = 0.01882$ nm^3) as well as of larger cations such as $[Me_4N]^+$ ($V([Me_4N]^+) = 0.113$ nm^3)[2] and $[Ph_4P]^+$ ($V[Ph_4P]^+ \sim V[Ph_4As]^+ = 0.456$ nm^3).[1] Accidentally, single crystals of $[H_3O]^+$ poly[perfluorotitanate(IV)] salt were also obtained ($V([H_3O]^+) \sim V(K)^+ = 0.00986$ nm^3).[2] On the basis of previous estimations,[1] the following salts, with isolated $[Ti_2F_9]^-$ or $[Ti_4F_{18}]^{2-}$ anions, were expected: $[H_3O]_2[Ti_4F_{18}]$, $[Me_4N][Ti_2F_9]$, $[Ph_4P][Ti_2F_9]$, and $Cs_2[Ti_4F_{18}]$ or $CsTi_2F_9$. At first, larger cations such as $[Me_4N]^+$ and $[Ph_4P]^+$ were inspected. Single crystals of $[Me_4N]^+$ salt were grown from an aHF solution of Me_4NF and TiF_4 in a 1:2 molar ratio. Because Ph_4PF has not been commercially available, the corresponding chloride was used instead. In the presence of aHF, it was converted to fluoride salt, which further reacted with TiF_4. The crystal structure determination of grown crystals was not in accordance with the theoretically expected ones.[1] Isolated products were $[Ti_4F_{18}]^{2-}$ and not $[Ti_2F_9]^-$ salts (Figures 1 and 2). Important bond lengths and bond angles for $[Ti_4F_{18}]^{2-}$ units are listed in Table 2.

In all three compounds, the corresponding Ti−F bond lengths are in the same range and, as expected, Ti−F_t bond

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(6) Altomare, A.; Cascarano, M.; Giacovazzo, C.; Guagliardi, A. *J. Appl. Crystallogr.* **1993**, *26*, 343–350.

(7) Sheldrick, G. M. *Acta Crystallogr.* **2008**, *A64*, 112–122.

(8) Farrugia, L. J. *J. Appl. Crystallogr.* **1999**, *32*, 837–838.

(9) *DIAMOND v3.1*; Crystal Impact GbR: Bonn, Germany, **2004−2005**

(10) Ozawa, T. C.; Kang, S. J. *J. Appl. Crystallogr.* **2004**, *37*, 679; Balls & Sticks: Easy-to-Use Structure Visualization and Animation Creating Program (http://www.softbug.com/toycrate/bs/).

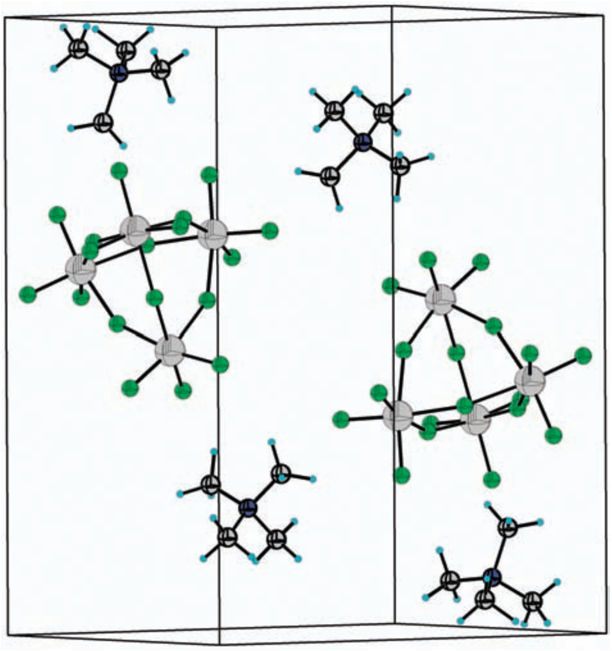

Figure 1. Part of the crystal structure of $[Me_4N]_2[Ti_4F_{18}]$.

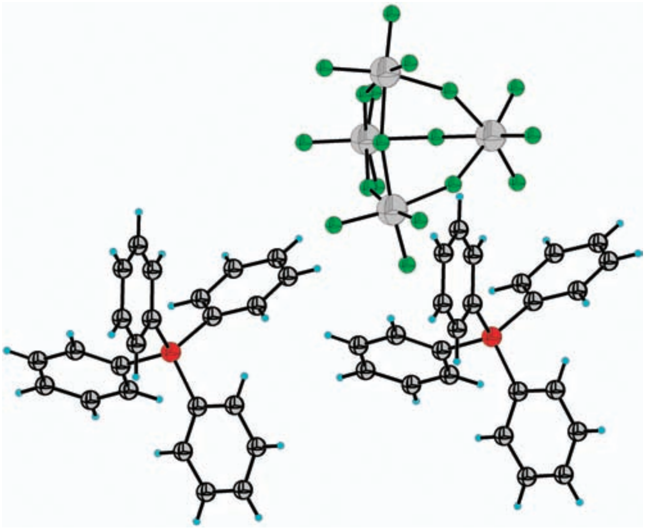

Figure 2. Part of the crystal structure of $[Ph_4P]_2[Ti_4F_{18}]$.

distances [175.2(4)−178.3(4) pm] are shorter than Ti−F_b ones [195.9(4)−201.9(4) pm]. Both sets of distances are in agreement with previously observed ones in various titanium-(IV) fluoride complexes.[11,12] In TiF_4, the corresponding distances are slightly shorter. The Ti−F_t bond distances are found in the 170.4−172.5 pm range and Ti−F_b in the 193.1−197.8 pm range.[5] The basic unit of the crystal structure of TiF_4 consists of three $[TiF_6]$ octahedra sharing joint apexes. So-formed $[Ti_3F_{15}]$ rings are further connected via trans-bridging F atoms into infinite columns.[5]

The corresponding Ti···Ti, F_t···F_t, and F_b···F_b nonbonding distances in $[Ti_4F_{18}]^{2-}$ of all three salts are also very similar (Table 2). It is valid also for corresponding F_t−Ti−F_t and F_b−Ti−F_b angles, where the latter is smaller than the former. As was already mentioned in ref 1, this is expected from VSPER[13] and a ligand−ligand repulsion model.[14,15] From the similarity of the corresponding bonding and corresponding nonbonding distances of $[Ti_4F_{18}]^{2-}$ anions in all three salts (Table 2), it is obvious that the geometry of the $[Ti_4F_{18}]^{2-}$ anion is not afected by the size of the cation.

Table 2. Selected Bond Lengths (pm), Nonbonding Contacts (pm), and Bond Angles (deg) in $[Ti_4F_{18}]^{2-}$ Salts of $[TiF_2([15]crown\text{-}5)]^{2+}$, $[Me_4N]^+$, and $[Ph_4P]^+$

	$[TiF_2([15]\text{-}crown\text{-}5)]^{2+\,a}$	$[Me_4N]^{+\,b)}$	$[Ph_4P]^{+\,b}$
Ti−F_t[c]	175.4(3)−177.7(3)	175.8(4)−176.8(4)	175.2(4)−178.3(4)
Ti−F_b	196.5(3)−201.0(3)	197.5(4)−200.3(4)	195.9(4)−201.9(4)
Ti···Ti	382.9−387.5	384.0−385.9	383.3−386.5
F_t···F_t	260.9−267.1	262.1−263.7	264.2−272.0
F_b···F_b	259.6−264.1	261.5−263.2	260.8−264.4
Ti···Ti···Ti	~60	~60	~60
F_t−Ti−F_t	94.9(1)−98.0(1)	95.9(3)−97.4(2)	97.0(2)−98.9(2)
F_b−Ti−F_b	81.9(1)−83.4(1)	81.6(2)−83.4(2)	82.1(2)−83.2(2)

[a] 198 K, ref 1. [b] 200 K, this work. [c] F_t = terminal F atom (Ti−F_t); F_b = bridging F atom (Ti−F_b−Ti).

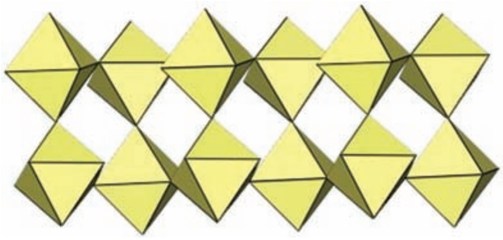

Figure 3. Infinite $([Ti_2F_9]^-)_n$ double chains in the crystal structure of $CsTi_2F_9$.

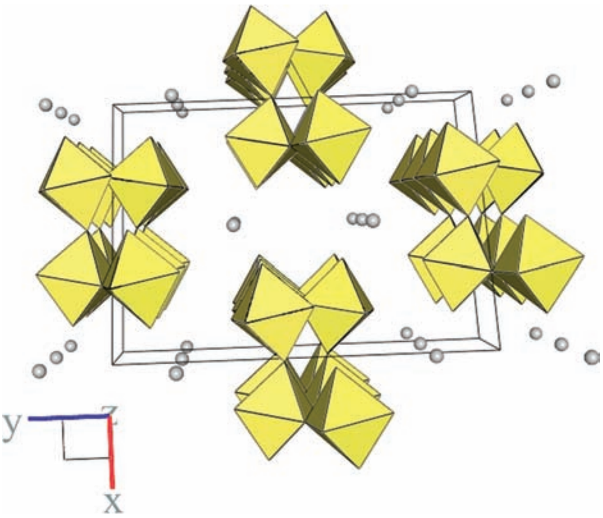

Figure 4. Packing of infinite $([Ti_2F_9]^-)_n$ double chains in the crystal structure of $CsTi_2F_9$.

The Cs^+ cation ($V(Cs^+) = 0.01882\ nm^3$)[2] is much smaller than $[Me_4N]^+$ ($V([Me_4N]^+) = 0.113\ nm^3$)[2] and $[Ph_4P]^+$

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(11) Roesky, H. W.; Haiduc, I. *J. Chem. Soc., Dalton Trans.* **1999**, 2249–2264.

(12) Murphy, E. F.; Murugavel, R.; Roesky, H. W. *Chem. Rev.* **1997**, *97*, 3425–3468.

(13) Gillespie, R. J.; Hargittai, I. *The VSPER Model of Molecular Geometry*; Allyn and Bacon: Boston, 1991.

(14) Robinson, E. A.; Gillespie, R. J. *Inorg. Chem.* **2003**, *42*, 3865–38752.

(15) Gillespie, R. J.; Robinson, E. A. *Chem. Soc. Rev.* **2005**, *34*, 396–407.

Table 3. Selected Bond Lengths (pm) and Bond Angles (deg) in H_3OTiF_5, $H_3OTi_2F_9$, $CsTi_2F_9$, and TiF_4

	$[H_3O][TiF_5]$[a]	$[H_3O][Ti_2F_9]$[b]	$CsTi_2F_9$[c]	TiF_4[a]
$Ti{-}F_t$[d]	176.4(4)−183.5(5)	175.4(2)−180.3(3)	175.8(7)−179.0(7)	170.4−172.5
$Ti{-}F_b$	196.1(3)−202.1(3)	196.6(3)−200.4(2)	195.5(3)−198.8(7)	193.1−197.8
$Ti{-}F_b{-}Ti$	146.6	143.7(2)/166.4(2)[e]	149.3(6)/156.3(4)[e]	159.2/169.9[f]

[a] References 5 and 16. [b] 100 K. [c] 200 K. [d] F_t = terminal F atom ($Ti{-}F_t$); F_b = bridging F atom ($Ti{-}F_b{-}Ti$). [e] See Figure 5. [f] Inside and between $[Ti_3F_{15}]$ rings.

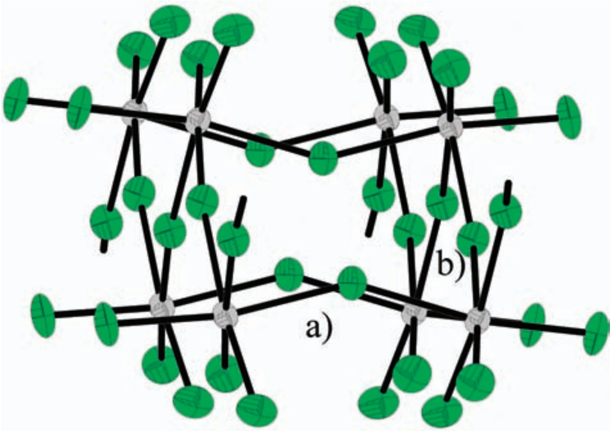

Figure 5. $Ti{-}F_b{-}Ti$ angles in the crystal structure of $[H_3O]Ti_2F_9$ [(a) 143.7(2)°; (b) 166.4(2)°] and $CsTi_2F_9$ [(a) 149.3(6)°; (b) 156.3(4)°].

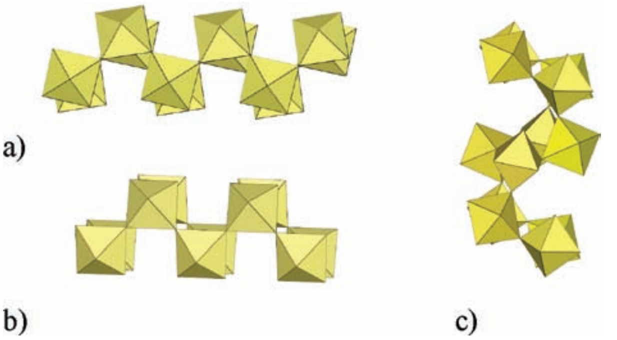

Figure 6. Formation of infinite $([Ti_2F_9]^-)_n$ double chains in the crystal structures of $CsTi_2F_9$ (a), $[H_3O]Ti_2F_9$ (b), and $O_2Mn_2F_9$ (c).[18]

$(V[Ph_4P]^+ \sim V[Ph_4As]^+ = 0.456\ nm^3)$.[1] According to the thermodynamic calculations, it was not clear if it would yield salt with isolated $[Ti_4F_{18}]^{2-}$ or $[Ti_2F_9]^-$ anions.[1] The crystal structure determination of the product between CsF and $2TiF_4$ showed that obtained product could be formulated as $CsTi_2F_9$; however, instead of isolated $[Ti_2F_9]^-$ anions, infinite $([Ti_2F_9]^-)_n$ double chains are present (Figures 3 and 4). Only vibrational spectra of $CsTi_2F_9$ have been previously reported.[4] In the case of $[H_3O]^+$, which is even smaller than the Cs^+ cation, a similar result was obtained; i.e., $H_3OTi_2F_9$ has been formed. Its crystal structure also consists of infinite $([Ti_2F_9]^-)_n$ double chains. Previously, only H_3OTiF_5 has been known.[16] The attempts to prepare $H_3OTi_2F_9$ by the same method as that of H_3OTiF_5 were unsuccessful.[16]

Important bond lengths and bond angles of $CsTi_2F_9$ and $H_3OTi_2F_9$ are listed in Table 3. For comparison, some bond lengths and bond angles of H_3OTiF_5[16] and TiF_4[5] have been added.

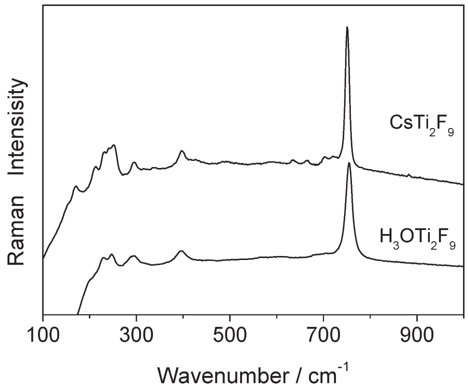

Figure 7. Raman spectra of $[H_3O][Ti_2F_9]$ and $CsTi_2F_9$.

Table 4. Raman Spectra of $[H_3O][Ti_2F_9]$ and $CsTi_2F_9$ together with the Previously Reported Data for $CsTi_2F_9$ and $NF_4Ti_2F_9$

$H_3OTi_2F_9$[a]	$CsTi_2F_9$[a]	$CsTi_2F_9$[b]	$NF_4Ti_2F_9$[b]
756(10)	751(10)	752(10)	752(10)
	721(0.7)		
	702(0.7)	701(0.1)	702(0.7)
	667(0.5)	670(0.4)	670(0.5)
	635(0.5)	645(+0)	645(+0)
397(1)	397(1.5)		
		388(0.9)	389(0.9)
		327(0.3)	326(0.3)
293(1)	294(0.9)	290(0.8)	290(0.9)
	253(2)	247(2.4)	247(2.4)
245(1.2)	241(1.9)	238(2.4)	237(2.4)
229(1)	229(1.6)	225(sh)	225(sh)
	211(0.7)		
198(sh)		192(0.5)	192(0.5)
	170(0.5)	162(0.4)	162(0.4)

[a] This work. [b] Reference 4.

In all four compounds, the Ti^{4+} ions are found in an octahedral coordination of six F atoms. The $[TiF_6]$ units are sharing joint apexes, forming in that way $([TiF_5]^-)_n$ single chains, i.e., $[H_3O][TiF_5]$, or $([Ti_2F_9]^-)_n$ double chains, i.e., $[H_3O][Ti_2F_9]$ and $CsTi_2F_9$, of cis-connected octahedra.

Some of the $Ti{-}F_t$ bond distances are slightly elongated because of hydrogen bonding. The shortest F···(H)···O distances in H_3OTiF_5 and $H_3OTi_2F_9$ are all in the limits of 250−320 pm. Hydrogen bonds falling in this range are classified as moderately strong hydrogen bonds, which could be described as mostly electrostatic.[17]

The $Ti{-}F_b{-}Ti$ angles within the individual single zigzag chains are kinked with an angle equal to 166.4(2)° for $[H_3O]^+$ salt and 156.3(4)° for Cs salt (Figure 6). The $Ti{-}F_b{-}Ti$ angles, where Ti atoms belong to two neighboring chains, are 143.7(2)° for $[H_3O]^+$ salt and 149.3(6)° for Cs salt (Figure 5).

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(16) Cohen, S.; Selig, H. *J. Fluorine Chem.* **1982**, *20*, 349–356.

(17) Steiner, T. *Angew. Chem., Int. Ed.* **2002**, *41*, 48–76.

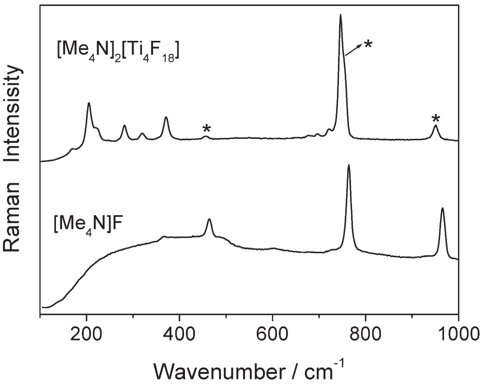

Figure 8. Raman spectra of $[Me_4N]_2[Ti_4F_{18}]$ and $[Me_4N]F$. The asterisk (*) denotes bands that could be assigned to $[Me_4N]^+$.

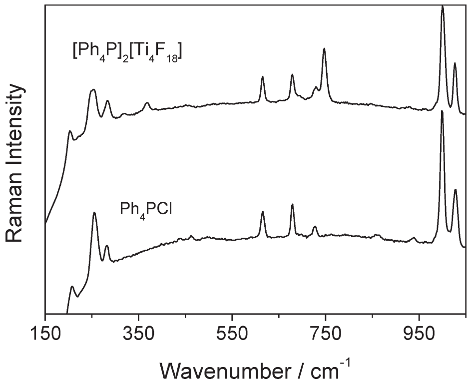

Figure 9. Raman spectra of $[Ph_4P]_2[Ti_4F_{18}]$ and $[Ph_4P]Cl$.

In the case of Cs^+ salt, the $[TiF_6]$ octahedra of the one individual zigzag chain are slightly rotated in view of the second chain, resulting in the lower symmetry of Cs^+ (Figure 6a) in comparison to $[H_3O]^+$ salt (Figure 6b). In the literature, only one additional example of the compound with the general formula AM_2F_9 ($A = A^+$ and $M = M^{4+}$) could be found. This is the unique dioxygenyl compound $O_2Mn_2F_9$.[18] In the latter, the linking of octahedra does not result in infinite straight chains but in crenellated strings (Figure 6c).

Vibrational Spectroscopy. Raman spectra of $([Ti_2F_9]^-)_n$ salts are shown in Figure 7, with additional details given in Table 4. The $([Ti_2F_9]^-)_n$ compounds have complex Raman spectra. The anion consists of infinite double chains $([Ti_2F_9]^-)_n$ of $[TiF_6]$ octahedra that share cis vertices. In the crystal structure of $CsTi_2F_9$, there is additional tilting of $[TiF_6]$ octahedra, resulting in lower symmetry and in larger numbers of vibrational bands than those in $[H_3O][Ti_2F_9]$. The Raman spectrum of $CsTi_2F_9$ reported in this work is in agreement with previously reported data.[4] The similarity of Raman data of Cs^+ with $[NF_4]^+$ salt (Table 4) and their comparison with calculated vibrational data for an isolated $[Ti_2F_9]^-$ anion[1] clearly indicate that it is unlikely that $NF_4Ti_2F_9$ consists of isolated $[Ti_2F_9]^-$ anions as previously proposed.[1]

Attempts to record the Raman spectrum of $[TiF_2([15]\text{-crown-5})][Ti_4F_{18}]\cdot 0.5CH_3CN$ were not successful.[1] Only the IR spectrum has been reported.[1] The Raman spectra of $[Me_4N]_2[Ti_4F_{18}]$ and $[Ph_4P]_2[Ti_4F_{18}]$ are shown in Figures 8 and 9. The observed frequencies are listed in Table 4.

Table 5. Raman Spectra of $[Me_4N]_2[Ti_4F_{18}]$ and $[Ph_4P]_2[Ti_4F_{18}]$ together with the Calculated Modes for the $[Ti_4F_{18}]^{2-}$ Anion

$[Me_4N]_2[Ti_4F_{18}]$ [a]	$[Ph_4P]_2[Ti_4F_{18}]$ [a]	calcd $[Ti_4F_{18}]^{2-}$ [b]
745(10)	747(10)	738(10)
720(0.7)	* [c]	712(0.7)
697(0.5)	695(0.5)	688(0.3)
681(0.3)	*	
372(2)	368(1)	364(0.9)
319(0.6)	318(0.5)	320(0.1)
280(1.2)	*	279(0.2)
219(sh)		215(0.1)
204(3)	*	197(0.5)
169(0.1)		162(0.1)

[a] This work. [b] Reference 1. [c] The asterisk (*) denotes $[Ti_4F_{18}]^{2-}$ vibrational bands that overlap with $[Ph_4P]^+$.

Table 6. List of Symmetric In-Phase Terminal Ti−F Stretching Modes for Various Complex Ti Anions

cation	anion	ν(Ti−F)	ref
Cs^+	$[TiF_6]^{2-}$	599	4
$[NF_4]^+$	$[TiF_6]^{2-}$	601	4
Cs^+	$[Ti_2F_{10}]^{2-}$	703	4
$[H_3O]^+$	$([TiF_5]^-)_n$	724	16
$[Me_4N]^+$	$[Ti_4F_{18}]^{2-}$	745	this work
$[Ph_4P]^+$	$[Ti_4F_{18}]^{2-}$	747	this work
Cs^+, $[NF_4]^+$	$([Ti_2F_9]^-)_n$	751/752	4 and this work
$[H_3O]^+$	$([Ti_2F_9]^-)_n$	756	this work
$[NF_4]^+$	$[Ti_3F_{13}]^-$	770	4
$[NF_4]^+$	$[Ti_6F_{25}]^-$	784	4
TiF_4	$[TiF_4]_n$	807	4

Although some of the vibrational bands of $[Ti_4F_{18}]^{2-}$ anions overlapped with those of the cations, the $[Ti_4F_{18}]^{2-}$ anion modes could be readily assigned with the help of Raman spectra of starting $[Me_4N]F$ or Ph_4PCl, respectively. Experimental data are in good agreement with calculated ones for the $[Ti_4F_{18}]^{2-}$ anion.

Because of their polymeric ($[H_3O][Ti_2F_9]$ and $CsTi_2F_9$) or oligomeric structures ($[Me_4N]_2[Ti_4F_{18}]$ and $[Ph_4P]_2[Ti_4F_{18}]$), all of the compounds reported in this work give very complex spectra. As reported, the most useful Raman band for identification of complex Ti anions is symmetric in-phase terminal Ti−F stretching mode, where the frequency of the band increases with an increase in the content of TiF_4 and a decrease in the charge of the anion.[4] The Raman data of $[H_3O][Ti_2F_9]$, $[Me_4N]_2[Ti_4F_{18}]$, and $[Ph_4P]_2[Ti_4F_{18}]$ fit well in that correlation (Table 6).

Conclusions

Unlike the expectation on the basis of the VBT approach,[1] it seems that cations larger than Cs^+ [$V(Cs^+) = 0.01882\ nm^3$] always favor the formation of $[Ti_4F_{18}]^{2-}$ salts, where the geometry of the anion is not affected by the different size of the cation. In the case of Cs^+ and smaller cations, chain-type $([Ti_2F_9]^-)_n$ salts were obtained. The assumption that only the size of the cation influenced the formation of $[Ti_2F_9]^-$ or $[Ti_4F_{18}]^{2-}$ salts (containing isolated anions) was too simplied, not considering possible aggregation of $[Ti_2F_9]$ units into polymeric $([Ti_2F_9]^-)_n$ chains. The presence of isolated $[Ti_2F_9]^-$ anions has been confirmed so far only by ^{19}F NMR spectroscopy in solutions of di-*n*-propylammonium hexafluorotitanate(IV) in liquid SO_2.[19] In aHF as the solvent, the rapid exchange between the solvent and the anion

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(18) Müller, B. G. *J. Fluorine Chem.* **1981**, *17*, 409–421.

(19) Dean, P. A. W. *Can. J. Chem.* **1973**, *51*, 4024–4030.

prevents the observation of well-resolved spectra. In liquid SO_2, besides $[Ti_2F_9]^-$, also $[Ti_2F_{10}]^{2-}$ and $[Ti_3F_{13}]^{3-}$ were observed. On the basis of the composition of isolated products from AF/2TiF_4/HF (A = $[H_3O]^+$ and Cs^+) mixtures, we can assume that the main species in aHF solutions are isolated $[Ti_2F_9]^-$ anions. When the solvent is removed, it is energetically more preferable that isolated $[Ti_2F_9]^-$ anions polymerize into $([Ti_2F_9]^-)_n$ chains than staying isolated. In the case of larger cations, the formation of dimeric $[Ti_4F_{18}]^{2-}$ anions is more preferable because it allows better packing with larger cations than if the interstices in the lattice of the infinite $([Ti_2F_9]^-)_n$ chains are filled by the large cations.

The search for the isolated triply fluorine-bridged $[Ti_2F_9]^-$ anion in the solid state remains open. The closest approximation could be found in $[(C_5Me_5)_2Ti_2F_7]$ units found in various titanium(IV) cyclopentadienyl compounds,[20] where two adjacent Ti atoms are connected via three bridging F atoms. The coordination of each Ti atom is completed by two terminal F atoms and one $[C_5Me_4]$ group.

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(20) Pevec, A.; Demšar, A.; Gramlich, V.; Petriček, S.; Roesky, H. W. *J. Chem. Soc., Dalton Trans.* **1997**, 2215–2216.