

Received: August 17, 1981

THE STRUCTURE OF $\text{H}_3\text{O}^+\text{TiF}_5^-$

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SUMMARY

Oxonium pentafluorotitanate was prepared by the reaction of H_2O with TiF_4 in HF . Single crystal x-ray diffraction studies on $\text{H}_3\text{O}^+\text{TiF}_5^-$ show that the compound crystallizes in monoclinic form. The space group is C2/c and the unit cell dimensions are $a = 14.528(5)$, $b = 4.839(1)$, $c = 13.798(5)\text{Å}$, $\beta = 115.59(5)^\circ$ with 8 formula units per unit cell.

INTRODUCTION

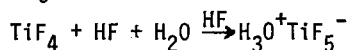
Although the oxonium ion, H_3O^+ , has been known for many years, in conjunction with fluoride counterions it is still a relative novelty. The first compounds of this type, $\text{H}_3\text{O}^+\text{AsF}_6^-$ and $\text{H}_3\text{O}^+\text{SbF}_6^-$, were reported by Christie, et al (1). Subsequently, transition metal fluorides with oxonium ions were reported as well (2-4). Only x-ray powder diffraction data have been obtained for these compounds, so that the role of the oxonium ion in the crystal structure is still obscure. In fact, no compounds with $\text{O-H}\cdots\text{F}$ hydrogen bonds appear to have been studied. Certain discrepancies between the calculated molecular volumes and those obtained from powder diffraction data of related compounds (2) make such a study particularly desirable. We have recently succeeded in growing single crystals of a new oxonium salt, $\text{H}_3\text{O}^+\text{TiF}_5^-$, for which a structural analysis thus became feasible.

PREPARATION

Titanium tetrafluoride was prepared by the reaction of TiCl_4 with anhydrous hydrogen fluoride (AHF) at 20° . The excess HF was distilled off

and the crude TiF_4 was resublimed twice (180° , 0.01 torr). Analysis = Ti : theor., 38.86% ; found 39.45% ; F , theor., 61.34% , found , 61.56%.

$\text{H}_3\text{O}^+\text{TiF}_5^-$ was prepared according to the reaction



1.26 gm H_2O (70.0 mmol) were added with a syringe to a cooled suspension of 8.68 gm TiF_4 (70.0 mmol) in 35 gm AHF contained in a Teflon bottle. A clear saturated solution resulted at 20° after gradual addition of AHF to a final weight of 76.5 gm (0.9 molal in $\text{H}_3\text{O}^+\text{TiF}_5^-$). A residue of 11.310 gm of colorless crystals remained after evaporation of the AHF at 25° (theor. 11.340 gm). The crystals were recrystallized from AHF . Analysis = Ti : theor. 29.59% , found 30.13% ; F , theor. 58.68% , found , 58.66%.

Attempts to prepare $\text{H}_3\text{O}^+\text{Ti}_2\text{F}_9^-$ ($\text{H}_2\text{O} : \text{TiF}_4 = 1:2$) or $\text{H}_5\text{O}_2^+\text{TiF}_5^-$ or $(\text{H}_3\text{O}^+)_2\text{TiF}_6^{2-}$ ($\text{H}_2\text{O} : \text{TiF}_4 = 2:1$) by this method were unsuccessful.

EXPERIMENTAL

X-ray crystallography

A clear crystal, measuring approximately 0.3 x 0.4 x 0.6 mm, was sealed in a thin-walled Pyrex capillary which was then mounted on a PW1100/20 Phillips four-circle computer controlled diffractometer. $\text{Mo K}\alpha$ ($\lambda = 0.71069 \text{ \AA}$) radiation with a graphite crystal monochromator was used. The cell constants obtained by the method of least-squares with 2θ values of 23 reflections are $a = 14.528(5)$, $b = 4.839(1)$, $c = 13.798(5) \text{ \AA}$, $\beta = 115.59(5)^\circ$ and $V = 875(1) \text{ \AA}^3$. Preliminary examination showed the existence of a c-centering and a c-glide plane. For space group C2/c with $Z = 8$ and formula weight 161.9 , the calculated density is 2.46 g-cm^{-3} .

The intensity data were collected with the ω - 2θ scan method. The scan range for each reflection was 1.2° with a constant scan time of 24 seconds. Background measurements were made for 12 seconds before and after each scan. There were 1249 unique data within the 1429 total data measured to a maximum 2θ of 60° . During data collection, the positions and intensities of three

standard reflections were reexamined at 60 minute intervals, indicating a minimal motion of the crystal in the capillary together with a linear (~50%) decay of intensity.

The data were corrected for decay, Lorenz and polarization effects. The linear absorption coefficient is 18.4 cm^{-1} ; no absorption correction was applied. Only 1098 reflections having structure factors greater than $65(F)$ were used to solve and refine the structure.

A statistical analysis made on 250 normalized structure amplitudes showed that the structure is centric. The direct method employing Multan was used to calculate phases for an electron density map which yielded the positions of the Ti and five F atoms. The oxygen atom was located from a subsequent difference map. Full matrix least-squares refinement in space group $C2/c$ converged to $R = 0.056$. ($R = \sum | |F_o| - |F_c| | / \sum |F_o|$) all atoms having anisotropic temperature factors. The final electron density difference map showed no peaks of structural significance. Final atomic parameters are given in Table I. Bond lengths and angles are summarized in Table II. A list of observed and calculated structure factors is available as supplementary material.

All crystallographic computing was done on a CYBER 74 computer using the SHELX77 structure determination package.

Vibrational spectra

Raman spectra were run on a Spex Raman spectrophotometer. Either 5145 \AA or 6471 \AA excitation was used. Infrared spectra were obtained on a Perkin-Elmer Model 597 Spectrophotometer. Powdered samples were dispersed between AgCl or polyethylene windows.

DISCUSSION

The structure of $\text{H}_3\text{O}^+\text{TiF}_5^-$ presents some unusual features. As might be expected, the anions form $(\text{TiF}_5^-)_n$ chains such that the titanium atoms are six-coordinated by fluorine atoms. Although cis- configurations are known for uncharged pentafluorides (5); only the trans-chain is known for

TABLE I

POSITIONAL AND THERMAL PARAMETERS AND THEIR STANDARD DEVIATIONS

	X	Y	Z	U11, Å ²	U22	U33	U12	U13	U23
Tl	.6398(1)	.5121(2)	.6785(1)	.0116(4)	.0141(4)	.0185(4)	0(3)	.0005(3)	-.0019(3)
F(1)	.7555(2)	.7492(7)	.7140(3)	.022(2)	.022(2)	.027(2)	-.009(1)	.005(1)	-.005(1)
F(2)	.6265(3)	.6742(6)	.7918(3)	.025(2)	.035(2)	.039(2)	-.003(2)	.013(2)	-.012(2)
F(3)	.6717(3)	.3351(8)	.5794(3)	.025(2)	.033(2)	.029(2)	-.003(2)	.005(1)	-.009(2)
F(4)	.5399(3)	.2698(8)	.6625(3)	.024(2)	.035(2)	.047(2)	-.015(2)	.011(2)	-.011(2)
F(5)	.5615(3)	.7526(9)	.5821(3)	.029(2)	.031(2)	.036(2)	.012(2)	-.003(2)	.008(2)
O	.8694(3)	.5161(9)	.5696(3)	.022(2)	.029(2)	.031(2)	-.005(2)	.010(2)	-.002(2)

ESTIMATED STANDARD DEVIATIONS IN THE LEAST SIGNIFICANT FIGURE ARE GIVEN IN PARENTHESES.
 THE FORM OF THE ANISOTROPIC THERMAL ELLIPSOID IS :

$$\exp [- 2\pi^2 (u_{11}^2 h^2 a^{*2} + u_{22}^2 k^2 b^{*2} + u_{33}^2 l^2 c^{*2} + 2u_{12} hka^*b^* + 2u_{13} hla^*c^* + 2u_{23} klb^*c^*)]$$

TABLE II

Bond Lengths and Angles

Ti...F1	1.961(3) Å	O...F2	2.511(6) Å
F1	2.021(3)		2.532(6)
F2	1.832(5)		2.558(5)
F3	1.835(5)		
F4	1.804(4)		
F5	1.764(4)		
F1 - Ti - F1	84.4(1)°	F2 - Ti - F3	171.7(2)°
F2	86.9(2)	F4	90.4(2)
F2	87.3(2)	F5	95.1(2)
F3	85.3(2)	F3 - Ti - F4	93.1(2)
F3	88.7(2)	F5	92.0(2)
F4	88.3(2)	F4 - Ti - F5	96.5(2)
F4	172.3(2)	F2 - O - F3	95.5(2)
F5	90.9(2)	F4	103.6(2)
F5	174.6(2)	F3 - O - F4	124.5(2)

structures of pentafluoride anions (6). The *cis*-linkages in $(\text{TiF}_5^-)_n$ are thus unusual. These chains are all essentially parallel to the *y*-axis (see Figure 1), their direction being defined by a line drawn through every second titanium atom of a given chain. The oxonium ions link three $(\text{TiF}_5^-)_n$ chains presumably via hydrogen bonds through groups of F2, F3 and F4 atoms, each fluorine atom taken from one of the three chains. The hydrogen atoms are not observable, but the shortest O...F distances ranging from 2.511 to

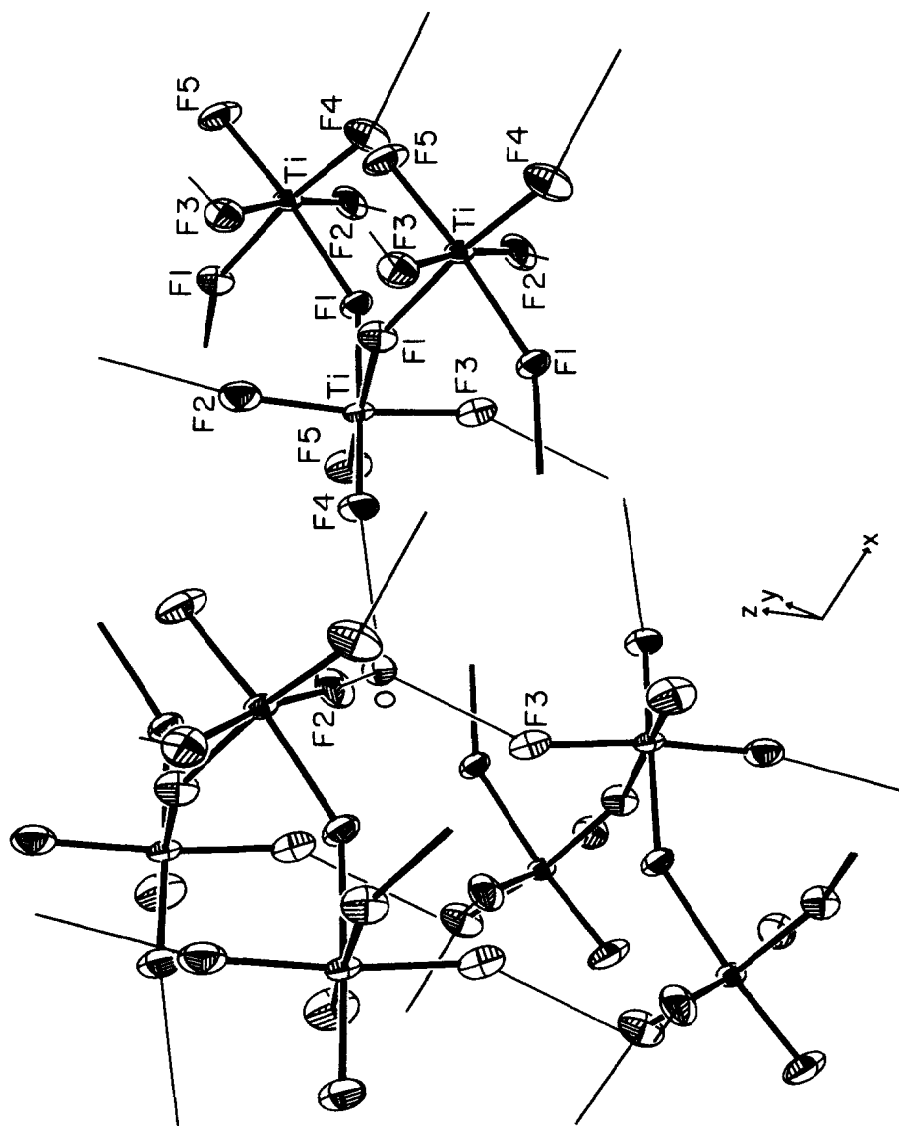


Fig. 1. Crystal structure of $\text{H}_3\text{O}^+\text{TiF}_5^-$. The thin lines are presumed linear hydrogen bonds.

2.558 Å fall in the hydrogen bonding range (7), and are considerably shorter than the shortest observed non-hydrogen bond O...F distance of 2.908 Å. Since the hydrogen bonds are not observable, one can only speculate on the linearity of the O-H...F bonds. If they are indeed linear, the three O-H...F bond angles of 103.3°, 95.5° and 124.5° deviate appreciably from the near tetrahedral angles observed in many known compounds containing the oxonium ion. In a neutron diffraction study (8) of $\text{H}_3\text{O}^+\text{CH}_3\text{C}_6\text{H}_4\text{SO}_3^-$, for example, near tetrahedral angles of 110.7°, 109.2° and 111.2° were measured. There are, however, exceptions (9); e.g., $\text{H}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ in which interbond angles in the pyramidal H_3O^+ are 101°, 106°, and 126°. Presumably, in $\text{H}_3\text{O}^+\text{TiF}_5^-$ the hydrogen bonds, if linear, are constrained by the parallel $(\text{TiF}_5^-)_n$ chains which are coordinated through the H_3O^+ . A distorted six-coordination sphere similar to that observed for $(\text{TiF}_5^-)_n$ has been previously observed (10) in the compound $[\text{U}_2]_2^{2+}[\text{Ti}_7\text{F}_{30}]^{2-}$. The latter structure has two types of titanium atoms - those with regular octahedrally coordinated fluorines, and those with irregularly octahedrally coordinated fluorines with Ti-F bond lengths varying from 1.73 Å to 2.09 Å.

Vibrational spectra

$\text{H}_3\text{O}^+\text{TiF}_5^-$ forms colorless crystals. No usable Raman spectra were obtained with powdered materials due to excess fluorescence even with red excitation. The Raman spectrum of a crystal (Figure 2) shows many similarities to those of structurally similar materials, such as VF_5 and TcF_5 (5). In the latter the MF_5 units also form cis-linked endless chains.

Infrared spectra showed very broad absorption bands at 3300 and 1620 cm^{-1} characteristic of H_3O^+ (1). In addition, broad Ti-F absorption bands were observed at 765, 640, 510, and 280 cm^{-1} . The 510 cm^{-1} band probably arises from the F-Ti-F asymmetric stretching vibration of the fluorine bridge.

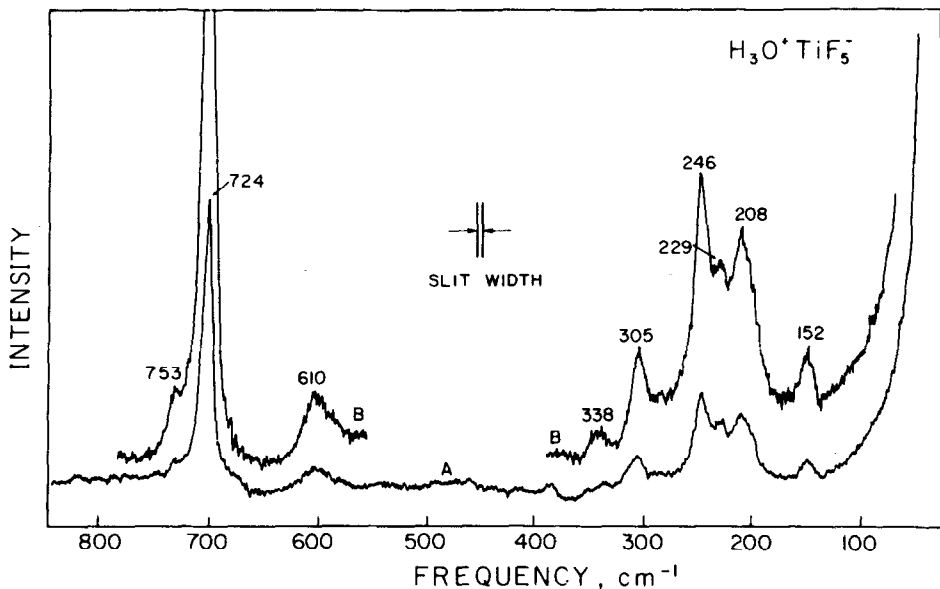


Fig. 2. Raman spectra of $\text{H}_3\text{O}^+\text{TiF}_5^-$.

A. 5145Å laser line, 120 mw. Slit width: 4cm^{-1} . F.S. 5K. T.C. 1 sec.

B. As above: F.S. 2K, T.C. 2 sec.

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