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# THERMAL DECOMPOSITION STUDY OF HYDRAZINIUM(2 + ) HEPTAFLUOROTANTALATE MONOHYDRATE AND IDENTIFICATION OF INTERMEDIATE COMPOUNDS

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## ABSTRACT

The thermal behaviour of hydrazinium(2+) heptafluorotantalate monohydrate, first isolated in 1971 [1], has not previously been reported, and therefore it was chosen as the subject of a study using TG, DTG and DTA measurements.

$N_2H_6TaF_7 \cdot H_2O$ decomposed in four steps through the intermediates, $N_2H_6TaF_7$, $N_2H_5TaF_6$ and $NH_4TaF_6$ which were isolated and characterized by chemical analysis and vibrational spectra.

The X-ray powder photographs were indexed for $N_2H_6TaF_7 \cdot H_2O$ on the basis of a monoclinic cell ($a = 5.94(5)$, $b = 12.42(3)$, $c = 8.41(0)$ Å, $\beta = 91.5°$, $V = 620.9$ Å$^3$); for $N_2H_6TaF_7$ as a monoclinic cell ($a = 5.93(4)$, $b = 12.44(6)$, $c = 8.28(6)$ Å, $\beta = 91.7°$, $V = 611.7$ Å$^3$); for $N_2H_5TaF_6$ as an orthorhombic cell ($a = 5.45(2)$, $b = 12.28(1)$, $c = 8.32(0)$ Å, $V = 557.1$ Å$^3$), and for $NH_4TaF_6$ as a tetragonal cell ($a = b = 10.52(5)$, $c = 9.97(3)$ Å, $V = 1104.8$ Å$^3$).

## INTRODUCTION

Ionic equilibria in solutions containing tantalum, hydrofluoric acid and hydrazine are very complex. From anhydrous hydrogen fluoride solutions, $N_2H_6(TaF_6)_2$ and $N_2H_6TaF_7$ were prepared depending on the molar ratio of hydrazinium(2 + ) fluoride and tantalum pentafluoride. From aqueous solutions of hydrofluoric acid, $N_2H_6TaF_7 \cdot H_2O$, $(N_2H_6)_3(TaF_8)_2 \cdot H_2O$, $(N_2H_5)_2TaF_7$ and $N_2H_5HTaF_7$ were obtained, depending on the concentration of HF [1]. The present paper is a part of our studies of the thermal behaviour of hydrazinium(1 + ) and (2 + ) fluorometalates.

We repeated the synthesis of $N_2H_6TaF_7 \cdot H_2O$ and examined its thermal decomposition in order to isolate and identify the possible intermediates. Among them a new complex, $N_2H_5TaF_6$, was isolated.

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## EXPERIMENTAL

$N_2H_6TaF_7 \cdot H_2O$ was prepared by dissolving $Ta_2O_5$ in 40% hydrofluoric acid. $N_2H_6F_2$ was added in the molar ratio $N_2H_6F_2$: $TaF_5 = 1:1$. The crystals formed were filtered off and dried in vacuo.

For thermal analysis a Mettler TA-1 thermoanalyser was employed. A 100 mg sample was heated in a platinum crucible in a dry argon atmosphere with a flow rate of 5 l $h^{-1}$. $\alpha$-$Al_2O_3$ was used as a reference material. The heating rate of the furnace was 1°C $min^{-1}$, the DTG range was 10 mg $min^{-1}$ and the DTA range was 100 $\mu$V. The starting weight of the sample was 200–300 mg when intermediates were isolated: $N_2H_6TaF_7$ was isolated at 95°C, $N_2H_5TaF_6$ at 148°C and $NH_4TaF_6$ at 243°C. $N_2H_5TaF_6$ is not stable in air. The product was also prepared in a vacuum system. Approximately 1 g of $N_2H_6TaF_7 \cdot H_2O$ was weighed in a nickel can, evacuated and warmed to 80°C and the water released pumped off. The temperature was increased to 140°C and the volatiles were collected in an infrared cell, cooled by liquid nitrogen. The gas was characterized by the infrared spectrum. Only absorption assignable to the HF molecule was observed. The infrared spectra of the powdered solids pressed between CsBr plates were recorded on a Perkin-Elmer 521 spectrometer; the gas released in the second step of the thermal decomposition in a vacuum system was recorded on a Zeiss UR-20 spectrometer. The Raman spectra were obtained using a Spex 1401 spectrometer with $Ar^+$ (514.5 nm) excitation from a Coherent Radiation model CR-3 laser.

X-ray powder diffraction patterns were obtained with a Debye–Scherrer type camera using Cu$K_\alpha$ radiation. The diffraction photographs were indexed using a Haendler program [5] on an IBM-1130 computer. Hydrazinium, ammonium and fluoride ions were determined by conventional analytical methods [2–4].

## RESULTS AND DISCUSSION

The thermal decomposition of $N_2H_6TaF_7 \cdot H_2O$ (Fig. 1) in the first two steps is very similar to that of $N_2H_6GeF_6 \cdot H_2O$, as was expected. The thermal behaviour is given in Table 1. The decomposition starts at 30°C and in the first step the sample loses 5.1% of its weight, corresponding to the formation of the anhydrous salt. The decomposition is endothermic with DTA peaks at 60 and 80°C, and the DTG minimum at 80°C. In the second step, which is also endothermic, the sample loses a further 5.3% of its weight and this is accompanied by a DTA peak and a DTG minimum at 120°C. The next step is exothermic with a DTA peak and a DTG minimum at 238°C. Up to 240°C the cumulative weight loss amounts to 15.5%. In the last step between 240 and 600°C, which is endothermic and accompanied

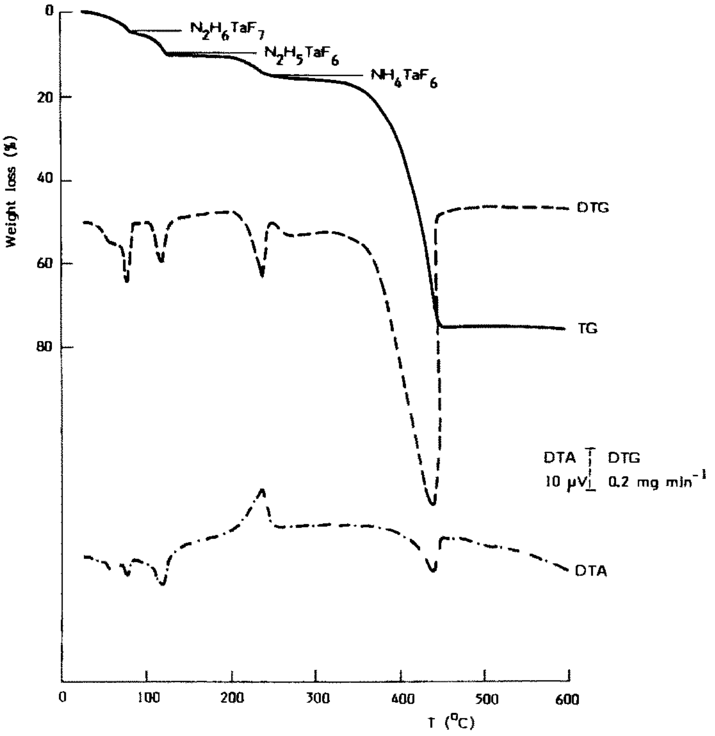

Fig. 1. TG, DTG and DTA curves of $N_2H_6TaF_7 \cdot H_2O$.

by a DTA peak at 442 °C and a DTG minimum at 440 °C, the decomposition products are all volatile; however, the weight loss of the sample is less than the theoretical value due to the tantalum pentafluoride which is deposited on the outer wall of the crucible and the cooler parts of the apparatus.

The thermal decomposition of $N_2H_6TaF_7 \cdot H_2O$ can be described with the

TABLE 1

Thermal behaviour of $N_2H_6TaF_7 \cdot H_2O$ (sample weight 100.0 mg)

| Temp. range ( °C) | Transformation | Weight loss (%) | |
|---|---|---|---|
| | | Calcd. | Found |
| 30– 84 | Removal of $H_2O$ and formation of $N_2H_6TaF_7$ | 4.92 | 5.1 |
| 84–130 | Removal of HF and formation of $N_2H_5TaF_6$ | 5.48 | 5.3 |
| 130–240 | Removal of gaseous components $N_2$ and $H_2$ and formation of $NH_4TaF_6$ | 4.09 | 5.1 |
| 240–600 | Removal of gaseous components. No residue | 85.51 | 60.8 |

TABLE 2

Chemical analysis of hydrazinium and ammonium fluorotantalates

| | Calcd. (%) | | | Found (%) | | |
|---|---|---|---|---|---|---|
| | $N_2H_4$ | $NH_4$ | F | $N_2H_4$ | $NH_4$ | F |
| $N_2H_6TaF_7 \cdot H_2O$ | 8.75 | | 36.33 | 8.8 | | 36.5 |
| $N_2H_6TaF_7$ | 9.21 | | 38.21 | 9.4 | | 38.7 |
| $N_2H_5TaF_6$ | 9.78 | | 34.75 | 9.5 | | 35.1 |
| $NH_4TaF_6$ | | 5.76 | 36.42 | | 5.5 | 36.1 |

equations:

$$N_2H_6TaF_7 \cdot H_2O \rightarrow N_2H_6TaF_7 + H_2O \qquad (1)$$

$$N_2H_6TaF_7 \rightarrow N_2H_5TaF_6 + HF \qquad (2)$$

$$2N_2H_5TaF_6 \rightarrow 2NH_4TaF_6 + N_2 + H_2 \qquad (3)$$

$$2NH_4TaF_6 \rightarrow N_2 + 3H_2 + 2HF + 2TaF_5 \qquad (4)$$

TABLE 3

Vibrational spectra ($cm^{-1}$) of heptafluorotantalates

| $N_2H_6TaF_7 \cdot H_2O$ | | $N_2H_6TaF_7$ | | $K_2TaF_7$ | | Assignment |
|---|---|---|---|---|---|---|
| Raman | IR | Raman | IR | Raman | IR | |
| 148(12) | | 176(2.5) | | | | (Ta–F) |
| 204(6) | | | | | | |
| | | 230(2.5) | | | | |
| 257(13.6) | | 263(3.8) | | 275w | 265msh | |
| | | | 288vs | | 285vs | |
| 316(9) | 309s | 300(3.8) | 313vs | | 315vs | |
| | 322sh | | | | | |
| 387(10.4) | 395w | 374(12.8) | 360m | 392m | | |
| 463(28) | 442sh | 438(2.5) | 442m | | | |
| | 520vs | 544(4.2) | 540vs | | 535vs | |
| 652(100) | 640sh | 656(100) | 650s | 640s | 641w | |
| | 878w | | | | | |
| | 922w | | 915w | | | $(N-N)_s$ |
| | 960w | | 960w | | | |
| 1030(35.6) | 1050vs | 1050(24.7) | | | | |
| | | 1068(29.4) | 1065vs | | | $(NH_3^+)_r$ |
| | 1102s | | 1092vs | | | |
| | | | 1147m | | | |
| | | | 1162sh | | | |
| 1305(25) | 1293w | | | | | |
| 1340(2.5) | | | 1455m | | | |
| | 1498vs | | 1518s | | | $(NH_3^+)_d$ |
| 1585(5) | 1578vs | | 1567m | | | |
| | | 1633(6.8) | | | | |
| | 1651m | | | | | |

TABLE 4

Vibrational spectra ($cm^{-1}$) of hexafluorotantalates

| $N_2H_5TaF_6$ | | $NH_4TaF_6$ | | $CsTaF_6$ | | Assignment |
|---|---|---|---|---|---|---|
| Raman | IR | Raman | IR | Raman | IR | |
| | | | | | 220vs | |
| | | | | | 232vs | $\nu_4(TaF_6^-)$ |
| | | | | | 245vssh | |
| 282(50) | 299m | 300(32) | 299sh | 272m | | $\nu_5(TaF_6^-)$ |
| | 310m | | | | | |
| | | | 398m | | | |
| | 408m | | 408m | | | |
| | | | | | 480msh | |
| | 560vs | | 570vs | | 582vs | $\nu_3(TaF_6^-)$ |
| 583(20) | | 580(18) | | 581s | | $\nu_2(TaF_6^-)$ |
| | | 652(18) | | | | |
| 702(100) | | 702(100) | | 692s | | $\nu_1(TaF_6^-)$ |
| | | | | | 720msh | |
| | | | 827w | | | |
| | | | 910w | | | |
| | | | 923w | | | |
| 978(30) | 958m | | 964w | | | $(N-N)_s$ |
| 1048(18) | | | | | | |
| | 1075m | | | | | $(NH_3^+)_r$ |
| 1120(8.5) | 1102m | | 1143m | | | |
| | 1222w | | 1162m | | | |
| | 1298w | | 1230w | | | |
| 1412(8) | | | | | | $(NH_2)_r$ |
| 1532(2) | 1528s | | | | | $(NH_3^+)_d$ |
| 1633(8.5) | 1592s | | | | | |
| 1655(2) | | | | | | |
| | | 3140(2.5) | 3104m | | | $\nu_3(NH_4^+)$ |
| | | | 3278vs | | | |

The starting material and the intermediates were characterized by chemical analysis (Table 2), vibrational spectra (Tables 3 and 4) and X-ray powder diffraction patterns (Tables 5–8).

The crystal structure of $K_2TaF_7$ [6] reveals that the tantalum is seven coordinated and exists as $TaF_7^{2-}$ units possessing distorted $C_{2v}$ symmetry (trigonal prism with the seventh $F^-$ ion centered above one square face). For undistorted $C_{2v}$ symmetry the 18 vibrations divide into symmetry species: $7A_1$ (IR, R) + $2A_2$ (R) + $4B_1$ (IR) + $5B_2$ (IR, R). The observed infrared spectrum of $K_2TaF_7$ consists of five vibrations [7], and in the Raman spectrum three bands are observed [8]. The very strong, sharp Raman line at 640 $cm^{-1}$ is probably due to a totally symmetric vibration and it coincides with the 641 $cm^{-1}$ infrared vibration. The stretching vibrations mentioned

TABLE 5

X-ray powder diffraction data for $N_2H_6TaF_7 \cdot H_2O$

| $h$ | $k$ | $l$ | $d_{calc}$ | $d_{obs.}$ | $I$ | $h$ | $k$ | $l$ | $d_{calc.}$ | $d_{obs.}$ | $I$ |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 0 | 0 | 1 | 8.40 | 7.70 | m | 2 | 3 | −2 | 2.113 | 2.123 | vw |
| 0 | 1 | 1 | 6.96 | 6.94 | s | 2 | 4 | −1 | 2.090 | 2.090 | vw |
| 0 | 2 | 1 | 5.00 | 5.06 | s | 2 | 1 | −3 | 2.038 | 2.043 | m |
| 1 | 1 | 1 | 4.47 | 4.52 | m | −1 | 0 | 4 | 1.997 | 1.995 | vw |
| 1 | 2 | 0 | 4.29 | 4.32 | s | 2 | 4 | −2 | 1.927 | 1.925 | w |
| 0 | 1 | 2 | 3.98 | 4.06 | w | 2 | 5 | −1 | 1.866 | 1.865 | m |
| 1 | 2 | −1 | 3.85 | 3.86 | w | 3 | 2 | 1 | 1.832 | 1.834 | m |
| 1 | −2 | 1 | 3.79 | 3.76 | s | 3 | 0 | 2 | 1.774 | 1.773 | m |
| 0 | 3 | 1 | 3.71 | 3.65 | s | −2 | 0 | 4 | 1.737 | 1.733 | m |
| 1 | 3 | 0 | 3.40 | 3.41 | m | 2 | 0 | 4 | 1.695 | 1.696 | w |
| 1 | 1 | 2 | 3.27 | 3.24 | m | 0 | 6 | 3 | 1.665 | 1.663 | vw |
| 1 | 3 | −1 | 3.17 | 3.16 | m | 2 | 2 | 4 | 1.635 | 1.634 | vw |
| 0 | 4 | 0 | 3.10 | 3.10 | m | 3 | 0 | 3 | 1.598 | 1.599 | vw |
| 2 | 1 | −1 | 2.755 | 2.744 | s | 2 | 3 | 4 | 1.568 | 1.570 | vw |
| 0 | 2 | 3 | 2.554 | 2.559 | m | 1 | 3 | 5 | 1.498 | 1.495 | vw |
| −2 | 0 | 2 | 2.457 | 2.441 | vw | 2 | 1 | 5 | 1.437 | 1.435 | vw |
|  |  |  |  | 2.257 | w | 3 | 2 | 4 | 1.387 | 1.386 | vw |

Indexed on the basis of a monoclinic cell with $a = 5.94(5)$, $b = 12.42(3)$, $c = 8.41(0)$ Å, $\beta = 91.5°$, $V = 620.9$ Å$^3$.

TABLE 6

X-ray powder diffraction data for $N_2H_6TaF_7$

| $h$ | $k$ | $l$ | $d_{calc.}$ | $d_{obs.}$ | $I$ | $h$ | $k$ | $l$ | $d_{calc.}$ | $d_{obs}$ | $I$ |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 1 | 0 | 5.35 | 5.20 | s | 3 | 2 | 1 | 1.826 | 1.818 | w |
| 0 | 2 | 1 | 4.98 | 4.98 | w | 2 | 5 | −2 | 1.744 | 1.741 | vw |
| 1 | 0 | 1 | 4.75 | 4.63 | m | 2 | 5 | 2 | 1.719 | 1.719 | w |
| 0 | 3 | 1 | 3.71 | 3.67 | s | 3 | 2 | 2 | 1.697 | 1.697 | vw |
| 0 | 2 | 2 | 3.45 | 3.46 | m | −3 | 0 | 2 | 1.631 | 1.634 | m |
| 1 | 2 | −2 | 3.01 | 3.01 | m | 2 | 2 | 4 | 1.617 | 1.613 | w |
| 2 | 1 | 0 | 2.885 | 2.882 | w | 3 | 4 | −2 | 1.561 | 1.560 | w |
| 0 | 0 | 3 | 2.760 | 2.744 | w | 1 | 5 | −4 | 1.546 | 1.544 | w |
| 1 | 3 | 2 | 2.606 | 2.610 | w | 1 | 3 | −5 | 1.499 | 1.495 | w |
| 2 | 2 | 1 | 2.528 | 2.528 | w | 1 | 3 | 5 | 1.479 | 1.479 | w |
| 2 | 1 | 2 | 2.336 | 2.334 | w | 2 | 6 | 3 | 1.437 | 1.437 | w |
| 2 | 2 | −2 | 2.276 | 2.276 | m | 2 | 2 | −5 | 1.426 | 1.424 | w |
| 0 | 5 | 2 | 2.133 | 2.132 | m | 1 | 1 | 6 | 1.328 | 1.330 | w |
| 2 | 4 | −1 | 2.089 | 2.091 | w | 2 | 4 | 5 | 1.298 | 1.300 | w |
| −2 | 0 | 3 | 2.051 | 2.050 | m | −3 | 0 | 5 | 1.289 | 1.289 | vw |
| 1 | 0 | 4 | 1.937 | 1.939 | m | −2 | 0 | 6 | 1.266 | 1.268 | vw |
| 2 | 5 | 0 | 1.907 | 1.907 | w | 3 | 1 | 5 | 1.245 | 1.254 | vw |

Indexed on the basis of a monoclinic cell with $a = 5.93(4)$, $b = 12.44(6)$, $c = 8.28(6)$ Å, $\beta = 91.7°$, $V = 611.7$ Å$^3$.

TABLE 7

X-ray powder diffraction data for $N_2H_5TaF_6$

| $h$ | $k$ | $l$ | $d_{calc.}$ | $d_{obs.}$ | $I$ | $h$ | $k$ | $l$ | $d_{calc.}$ | $d_{obs}$ | $I$ |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 0 | 0 | 1 | 8.32 | 7.40 | m | 1 | 3 | 2 | 2.573 | 2.579 | w |
| 0 | 1 | 1 | 6.89 | 6.80 | w | 0 | 2 | 3 | 2.527 | 2.527 | w |
| 0 | 2 | 0 | 6.14 | 6.10 | s | 1 | 1 | 3 | 2.423 | 2.435 | w |
| 1 | 0 | 0 | 5.45 | 5.34 | s | 0 | 5 | 1 | 2.355 | 2.355 | vw |
| 1 | 1 | 0 | 4.98 | 5.06 | s | 2 | 3 | 0 | 2.268 | 2.263 | m |
| 1 | 0 | 1 | 4.56 | 4.60 | vs | 2 | 3 | 1 | 2.189 | 2.203 | m |
| 0 | 0 | 2 | 4.16 | 4.17 | vw | 1 | 3 | 3 | 2.116 | 2.123 | w |
| 0 | 1 | 2 | 3.94 | 3.98 | vs | 0 | 0 | 4 | 2.080 | 2.079 | w |
| 0 | 3 | 1 | 3.67 | 3.68 | vs | 2 | 4 | 0 | 2.038 | 2.031 | w |
| 1 | 2 | 1 | 3.66 | 3.52 | w | 2 | 3 | 2 | 1.992 | 1.991 | m |
| 0 | 2 | 2 | 3.44 | 3.42 | w | 1 | 6 | 0 | 1.916 | 1.910 | w |
| 1 | 0 | 2 | 3.31 | 3.32 | m | 2 | 4 | 2 | 1.830 | 1.829 | w |
| 0 | 4 | 0 | 3.07 | 3.09 | m | 3 | 1 | 0 | 1.798 | 1.792 | w |
| 1 | 3 | 1 | 3.05 | 3.02 | m | 3 | 1 | 1 | 1.757 | 1.762 | w |
| 0 | 4 | 1 | 2.880 | 2.845 | w | 3 | 2 | 1 | 1.706 | 1.703 | w |
| 2 | 0 | 0 | 2.726 | 2.742 | vw | 2 | 5 | 2 | 1.671 | 1.670 | vw |
| 1 | 4 | 0 | 2.675 | 2.670 | w | | | | | | |

Indexed on the basis of an orthorhombic cell with $a = 5.45(2)$, $b = 12.28(1)$, $c = 8.32(0)$ Å, $V = 557.1$ Å$^3$.

are shifted to higher frequencies in the vibrational spectra of $N_2H_6TaF_7 \cdot H_2O$ and $N_2H_6TaF_7$ (Table 3). This shift can be explained by coordination of the $N_2H_6^{2+}$ ion to the metal [9]. Additional bands are also observed in the

TABLE 8

X-ray powder diffraction data for $NH_4TaF_6$

| $h$ | $k$ | $l$ | $d_{calc.}$ | $d_{obs.}$ | $I$ | $h$ | $k$ | $l$ | $d_{calc.}$ | $d_{obs.}$ | $I$ |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 1 | 0 | 7.44 | 7.41 | vw | 2 | 4 | 2 | 2.128 | 2.150 | s |
| 2 | 0 | 0 | 5.26 | 5.29 | vs | 3 | 4 | 1 | 2.059 | 2.056 | vw |
| 0 | 0 | 2 | 4.99 | 4.90 | w | 1 | 3 | 4 | 2.000 | 2.000 | vw |
| 1 | 2 | 0 | 4.71 | 4.70 | w | 4 | 4 | 0 | 1.861 | 1.859 | m |
| 1 | 0 | 2 | 4.50 | 4.45 | w | 6 | 0 | 0 | 1.754 | 1.755 | s |
| 1 | 2 | 1 | 4.26 | 4.26 | w | 2 | 6 | 0 | 1.664 | 1.666 | s |
| 1 | 1 | 2 | 4.14 | 4.10 | w | 4 | 0 | 5 | 1.589 | 1.588 | m |
| 2 | 2 | 0 | 3.72 | 3.72 | vs | 2 | 2 | 6 | 1.518 | 1.519 | m |
| 3 | 0 | 0 | 3.51 | 3.51 | m | 4 | 6 | 0 | 1.459 | 1.459 | m |
| 1 | 1 | 3 | 3.03 | 3.03 | s | 4 | 0 | 6 | 1.405 | 1.407 | s |
| 2 | 3 | 0 | 2.919 | 2.894 | w | 2 | 6 | 5 | 1.277 | 1.278 | m |
| 2 | 0 | 3 | 2.811 | 2.819 | w | 6 | 6 | 0 | 1.240 | 1.241 | m |
| 4 | 0 | 0 | 2.631 | 2.627 | m | 6 | 0 | 6 | 1.207 | 1.208 | w |
| 4 | 0 | 1 | 2.544 | 2.548 | vw | 4 | 6 | 5 | 1.178 | 1.178 | w |
| 2 | 4 | 0 | 2.353 | 2.353 | s | | | | | | |

Indexed on the basis of a tetragonal cell with $a = 10.52(5)$, $c = 9.97(3)$ Å, $V = 1104.8$ Å$^3$.

TABLE 9

Unit-cell parameters of fluorotantalates

| | $a$ (Å) | $b$ (Å) | $c$ (Å) | $\beta$ (°) | $V$ (Å$^3$) |
|---|---|---|---|---|---|
| $N_2H_6TaF_7 \cdot H_2O$ | 5.94(5) | 12.42(3) | 8.41(0) | 91.5 | 620.9 monoclinic |
| $N_2H_6TaF_7$ | 5.93(4) | 12.44(6) | 8.28(6) | 91.7 | 611.7 monoclinic |
| $N_2H_5TaF_6$ | 5.45(2) | 12.28(1) | 8.32(0) | | 557.1 orthorhombic |
| $NH_4TaF_6$ | 10.52(5) | 10.52(5) | 9.97(3) | | 1104.8 tetragonal |

Raman and infrared spectra, but fewer than would be expected for $C_{2v}$ symmetry. Therefore, assignment of the spectra cannot be made on the basis of the data available.

The $TaF_6^-$ ion has $O_h$ symmetry, for which $A_1$, $E_g$ and $E_{2g}$ symmetry species are Raman, $F_{2g}$ infrared active and $F_{2u}$ inactive. The Raman spectrum of crystalline $CsTaF_6$ [8] contains three bands and the infrared spectrum [7] two, each of which is split into three components indicating removal of the degeneracy. The vibrational spectra of $N_2H_5TaF_6$ and $NH_4TaF_6$ and their assignment are given in Table 4. The $\nu_4(TaF_6^-)$ mode was not observed as the spectrometer can be only used in the region 250 to 4000 cm$^{-1}$.

In the vibrational spectra of the compounds investigated, the bands in the region 1655 to 878 cm$^{-1}$ are attributed to the vibrations of the $N_2H_6^{2+}$ and $N_2H_5^+$ groups [10], and in the region from 3280 to 3100 cm$^{-1}$ to the $NH_4^+$ ion [11].

A comparison with the cell parameters of monoclinic $K_2NbF_7$ [12] ($a = 5.846$, $b = 12.693$, $c = 8.515$ Å, $\beta = 90.0°$, $V = 631.8$ Å$^3$, space group $P2_1/c$) shows that the structures of $N_2H_6TaF_7 \cdot H_2O$ and $N_2H_6TaF_7$ are closely related to the structure of $K_2NbF_7 \cdot N_2H_5TaF_6$ which crystallizes in the orthorhombic system. During thermal decomposition there is a gradual decrease of the cell volume.

$NH_4TaF_6$ crystallizes in the tetragonal system. The unit-cell parameters are similar to those of tetragonal $KTaF_6$ [13] ($a = 5.20$, $c = 10.05$ Å, $Z = 2$).

The results of indexed diffraction photographs are summarized in Table 9.

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