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Hydrazinium(1+) Hexafluorotitanate(IV), $2N_2H_5^+.TiF_6^{2-}$

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Abstract

The crystals exhibit racemic twinning. The structure consists of hydrazinium(1+), $N_2H_5^+$, cations and usual octahedral hexafluorotitanate(IV) anions. They are linked together *via* hydrogen bonds of the types N—H···F and N—H···N.

Comment

The current characterization of $2N_2H_5.TiF_6$ is one in a series of investigations of hydrazinium(1+) and hydrazinium(2+) fluorometallates. Examples of the crystal structures of $N_2H_5^+$ fluorometallates are few: $[N_2H_5][BF_4]$ and $[N_2H_5][ClO_4]$ (Conant & Roof, 1970), $[N_2H_5]_2[BeF_4]$ (Tedenac, Vilminot, Cot, Norbert & Maurin, 1971), $[N_2H_5]_3[CrF_6]$ (Kojić-Prodić, Šćavničar, Liminga & Šljukić, 1972), $Li[N_2H_5][BeF_4]$ (Anderson, Brown & Vilminot, 1973), $[N_2H_5][InF_4H_2O]$ (Bukovec & Golič, 1976), $[N_2H_5]_2[GeF_6]$ (Gantar, Golič, Leban & Rahten, 1985) and $[N_2H_5][Sn_3F_7]$ (Granier & Vilminot, 1988).

The crystal structure determination revealed two formula units in the asymmetric unit related by a pseudo-centre of symmetry. Subsequently, refinement was performed for racemic twinning and Flack's absolute structure parameter x was refined to 0.50 (3) (Flack, 1983). All H atoms were located in the difference map and included in the refinement. Restraints were imposed only on the lengths of the N—H bonds. A common isotropic displacement parameter U refined to 0.043 (3) Å². An extended network of hydrogen bonds of the types N—H···F and N—H···N exists. The distances and angles are generally as expected.

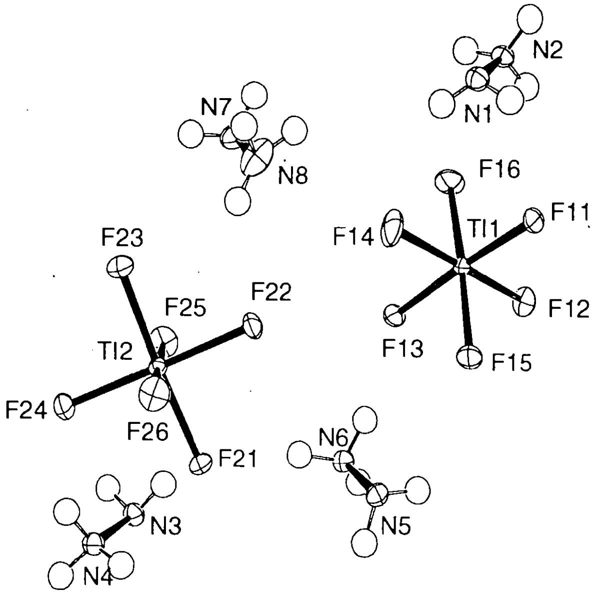

Fig. 1. *ORTEP* (Johnson, 1965) view of the asymmetric unit of the structure with atomic numbering.

Experimental

Crystals of the title compound were prepared in the Laboratory for Fluorine Chemistry at the Institute J. Stefan, Ljubljana.

Crystal data

$2(N_2H_5)[TiF_6]$
M_r = 228.02
Monoclinic
$P2_1$
a = 7.815 (1) Å
b = 10.019 (1) Å
c = 9.338 (1) Å
β = 93.58 (1)°
V = 729.72 (14) Å³
Z = 4
D_x = 2.076 Mg m^{-3}

Mo $K\alpha$ radiation
λ = 0.7107 Å
Cell parameters from 25 reflections
θ = 10–15°
μ = 1.235 mm^{-1}
T = 293 (2) K
Transparent prisms
0.42 × 0.26 × 0.18 mm
Colourless

Data collection

Enraf-Nonius CAD-4 diffractometer
Variable rate $\omega/2\theta$ scans
Absorption correction: none
4505 measured reflections
4228 independent reflections
3212 observed reflections [$I > 2\sigma(I)$]
$R_{\rm int}$ = 0.0188

$\theta_{\rm max}$ = 30.00°
h = 0 → 10
k = −14 → 14
l = −13 → 13
3 standard reflections monitored every 500 reflections
frequency: 40 min
intensity variation: 3.2%

Refinement

Refinement on F^2
$R(F) = 0.0355$
$wR(F^2) = 0.0923$
$S = 1.069$
4227 reflections
264 parameters
All H-atom parameters refined
Calculated weights $w = 1/[\sigma^2(F_o^2) + (0.0638P)^2 + 0.1007P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = -1.006$
$\Delta\rho_{\max} = 0.646$ e Å^{-3}
$\Delta\rho_{\min} = -0.460$ e Å^{-3}
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)
Absolute configuration: Flack (1983)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$U_{\rm eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j$.

	x	y	z	$U_{\rm eq}$
Ti1	0.77026 (8)	0.6742	0.99565 (6)	0.02001 (14)
F11	0.9198 (3)	0.5346 (3)	1.0259 (3)	0.0348 (6)
F12	0.8879 (3)	0.7684 (3)	1.1418 (2)	0.0376 (6)
F13	0.6248 (3)	0.8285 (3)	0.9698 (3)	0.0354 (6)
F14	0.6442 (4)	0.5843 (3)	0.8506 (3)	0.0552 (8)
F15	0.9082 (3)	0.7476 (3)	0.8626 (2)	0.0373 (6)
F16	0.6234 (4)	0.6081 (4)	1.1235 (4)	0.0608 (9)
Ti2	0.28182 (7)	0.86738 (7)	0.51720 (6)	0.01895 (14)
F21	0.4325 (3)	1.0136 (3)	0.5249 (2)	0.0328 (5)
F22	0.4346 (3)	0.7787 (3)	0.6493 (2)	0.0342 (5)
F23	0.1444 (3)	0.7139 (3)	0.5148 (3)	0.0391 (6)
F24	0.1288 (3)	0.9554 (3)	0.3923 (3)	0.0395 (6)
F25	0.1696 (3)	0.9339 (3)	0.6673 (3)	0.0423 (6)
F26	0.3989 (4)	0.7984 (3)	0.3691 (2)	0.0406 (7)
N1	0.7536 (5)	0.2808 (4)	0.9220 (4)	0.0299 (7)
N2	0.7286 (5)	0.2988 (4)	1.0706 (4)	0.0271 (7)
N3	0.2165 (5)	1.2605 (4)	0.5756 (4)	0.0301 (8)
N4	0.2289 (5)	1.2343 (4)	0.4247 (4)	0.0299 (8)
N5	0.8216 (5)	1.0004 (4)	0.7012 (4)	0.0285 (7)
N6	0.6706 (5)	1.0344 (4)	0.7726 (4)	0.0288 (7)
N7	0.2024 (5)	0.5430 (4)	0.7918 (5)	0.0377 (9)
N8	0.3376 (7)	0.5029 (6)	0.7101 (6)	0.0536 (13)

Table 2. *Selected geometric parameters* (Å, °)

Ti1—F16	1.831 (3)	Ti2—F24	1.842 (2)
Ti1—F11	1.833 (3)	Ti2—F23	1.875 (3)
Ti1—F15	1.848 (2)	Ti2—F21	1.879 (3)
Ti1—F12	1.855 (3)	Ti2—F22	1.885 (2)
Ti1—F14	1.857 (3)	N1—N2	1.425 (5)
Ti1—F13	1.925 (2)	N3—N4	1.442 (5)
Ti2—F25	1.825 (2)	N5—N6	1.432 (4)
Ti2—F26	1.839 (2)	N7—N8	1.400 (6)
F16—Ti1—F11	92.48 (14)	F25—Ti2—F26	178.57 (13)
F16—Ti1—F15	176.60 (14)	F25—Ti2—F24	89.27 (13)
F11—Ti1—F15	90.81 (12)	F26—Ti2—F24	92.15 (13)
F16—Ti1—F12	90.4 (2)	F25—Ti2—F23	90.36 (13)
F11—Ti1—F12	89.59 (12)	F26—Ti2—F23	89.67 (14)
F15—Ti1—F12	90.50 (13)	F24—Ti2—F23	92.07 (12)
F16—Ti1—F14	88.6 (2)	F25—Ti2—F21	90.92 (12)
F11—Ti1—F14	92.68 (13)	F26—Ti2—F21	88.96 (12)
F15—Ti1—F14	90.44 (14)	F24—Ti2—F21	91.81 (12)
F12—Ti1—F14	177.53 (14)	F23—Ti2—F21	175.93 (12)
F16—Ti1—F13	89.01 (13)	F25—Ti2—F22	89.13 (12)
F11—Ti1—F13	176.15 (12)	F26—Ti2—F22	89.44 (12)
F15—Ti1—F13	87.75 (12)	F24—Ti2—F22	178.39 (12)
F12—Ti1—F13	86.85 (12)	F23—Ti2—F22	87.73 (12)
F14—Ti1—F13	90.89 (12)	F21—Ti2—F22	88.43 (11)

The data crystal was sealed in a glass capillary. Crystals proved to be sensitive to air and humidity. Intensity data were collected using graphite-monochromated Mo $K\alpha$ radiation [maximum scan time 40 s, scan width (2θ) $(0.8 + 0.3\tan\theta)°$, aperture $(2.4 + 0.9\tan\theta)$ mm, background measured for $\frac{1}{4}$ of scan time at each scan limit]. Orientation was checked every 2 h. Data were corrected for intensity variation and Lp effects, but not for absorption because of the reasonable size of the crystals. Data collection and cell refinement were performed with *CAD*-4 *Software* (Enraf-Nonius, 1989). Data reduction employed *NRCVAX* (Gabe, Le Page, Charland, Lee & White, 1989). The structure was solved using *MULTAN*80 (Main *et al.*, 1980). The initial structural model was refined by full-matrix least squares on F_o^2 with *SHELXL* (Sheldrick, 1994). All e.s.d.'s were estimated using the full covariance matrix. The cell e.s.d.'s were taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters were only used when they were defined by crystal symmetry. Calculations were performed on the VAX8550 cluster at the University Computer Centre, Ljubljana, under VMS 5.2, and partially on a PC 486. Additionally, *NRCVAX* and the *GX* package (Mallinson & Muir, 1985) were used for data processing and the final interpretation of structural geometry. *ORTEP* was used for molecular graphics and *SHELXL* and *BONDLA* (*XRAY*76; Stewart *et al.*, 1976) were used to prepare material for publication.

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Lists of structure factors, anisotropic displacement parameters and H-atom coordinates have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71776 (14 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: NA1062]

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