

The Crystal Structure of Hydrazinium(+2) Hexafluorotitanate(IV), $N_2H_6TiF_6$

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The crystal structure of hydrazinium(+2) hexafluorotitanate has been determined from three-dimensional X-ray data. The crystals are cubic, $a = 10.404 \text{ \AA}$, space group $Ia\bar{3}$ with eight formula weights in the unit cell. The structure is formed of discrete $[TiF_6]^{2-}$ octahedra, with $Ti-F = 1.855 \text{ \AA}$, connected by $N-H \cdots F$ bonds. The hydrazine(+2) group has a *trans* configuration and the N-N bond length is 1.474 \AA . The shortest $N \cdots F$ distances, three for each nitrogen atom, are 2.612 \AA .

Introduction

Some hydrazinium(+2) and (+1) fluoro complexes of transition metals have been prepared at the Institute 'Jožef Stefan', Ljubljana, Yugoslavia (Slivnik & Volavšek, 1968; Slivnik, Šmalc, Sedej & Vilhar, 1964). Crystals of $N_2H_6TiF_6$ were kindly supplied to us for a structure analysis. It was reasonable to expect an octahedral coordination for the titanium atom in a high symmetry, cubic structure of $N_2H_6TiF_6$ with a 1:6 ratio of Ti to F. This has been confirmed by the present structure analysis. Since there are only four known structures containing $N_2H_5^+$ ions (Kronberg & Harker, 1942; Donohue & Lipscomb, 1947; Nitta, Sakurai & Tomiie, 1951; Liminga, 1966) the investigation was also used to obtain more information about the configuration and structural function of $N_2H_5^+$.

Experimental

$N_2H_6TiF_6$ crystallizes in the diakisdodecahedral class $-m\bar{3}$. The crystals are colourless with well-developed (110) faces. When exposed to air the crystal surface becomes white. In order to prevent decomposition, the crystals were covered with silicone oil.

Crystal data

$N_2H_6TiF_6$ - cubic
 $a = 10.404 \pm 0.002 \text{ \AA}$

$V = 108.24 \text{ \AA}^3$

$D_m = 2.46$, $D_c = 2.37 \text{ g.cm}^{-3}$

$Z = 8$

Cu $K\alpha$ radiation, $\mu = 61.3 \text{ cm}^{-1}$

The systematic absences

$hkl: h+k+l = 2n+1$

$0kl: k, l = 2n+1$

indicate uniquely the space group $Ia\bar{3} (T_h^d)$, No. 206.

Equi-inclination Weissenberg photographs were obtained using the multiple-film technique (four films), and 250 independent reflexions were recorded on five layer-lines. The effect of fluorescent radiation was minimized by a thin Al foil placed in front of the film. Intensities were estimated with a microdensitometer. The crystal was ground into a cylinder of 0.014 cm radius in order to apply absorption corrections more easily. Corrections for absorption, polarization and Lorentz factors were made in the usual way. The observed structure amplitudes were placed on the same absolute scale through common reflexions. These scale factors were refined during the structure determination.

Structure determination

The symmetry of the space group and the formula of the compound suggested either positions $8(a)$ or $8(b)$ for the titanium atoms on an inversion triad axis and positions $16(c)$ for the nitrogen atoms on a rotation triad axis. A three-dimensional Patterson synthesis confirmed positions $8(a)$ for the titanium atoms and positions $16(c)$ for the nitrogen atoms. A three-dimensional Fourier synthesis was performed with the signs of structure factors based on the contribution of the titanium and nitrogen atoms only, and from it the location of the fluorine atoms in positions $48(e)$ was deduced (Table 1). The structure was refined by several cycles of full-matrix least-squares refinement with isotropic temperature factors and then with anisotropic temperature factors for all non-hydrogen atoms. In the course of refinement with isotropic temperature factors the R index decreased to 8.5%, and with anisotropic temperature factors to 8.0%. The weighting scheme adopted was $w = 1$ for all observed reflexions and $w = 0$ for unobserved and $w = 0.25$ for very weak reflexions. An attempt to locate hydrogen atoms by means of a difference synthesis was unsuccessful. Neutral atomic scat-

Table 1. *Final coordinates and anisotropic thermal parameters ($\times 10^4$) with e.s.d.'s in parentheses*

The thermal parameters refer to the expression: $\exp [-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$.

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
N	2091 (6)	2091 (6)	2091 (6)	52 (4)	52 (4)	52 (4)	1 (6)	1 (6)	1 (6)
F	3923 (5)	1303 (4)	566 (4)	73 (5)	51 (4)	73 (5)	14 (4)	23 (5)	0
Ti	0	0	0	24 (1)	24 (1)	24 (1)	0	0	0

Table 2. Observed and calculated structure factors

h k l		I _o		I _c		h k l		I _o		I _c		h k l		I _o		I _c			
1	0	0	1886	1911	2	1	11	201	-199	4	2	0	144	285	5	2	1	242	-182
4	0	0	189	-94	3	1	2	506	-547	8	2	0	1042	1040	5	2	1	85	-30
6	0	0	481	418	3	1	4	423	-434	10	2	0	191	167	5	2	7	306	309
8	0	0	1046	986	3	1	6	182	178	12	2	0	471	473	5	2	10	114	89
10	0	0	893	899	3	1	8	170	-155	2	2	2	806	794	7	2	1	561	-662
2	2	2	2140	2204	3	1	8	170	-155	2	2	2	806	794	7	2	1	561	-662
2	0	4	330	365	3	1	10	7	20	2	4	4	1244	1294	7	2	3	76	107
2	0	6	1014	1040	4	1	1	850	834	2	2	6	1019	1015	7	2	3	76	107
4	0	8	1117	1123	4	1	3	535	605	2	2	8	764	730	7	2	5	76	-97
2	0	10	542	567	4	1	5	184	-198	2	2	10	688	691	7	2	9	234	-181
2	0	12	457	473	4	1	7	191	-194	2	2	12	363	363	7	2	11	204	-150
4	0	2	230	111	4	1	9	202	113	4	2	2	1240	1294	9	2	1	212	211
4	0	4	1650	1625	4	1	11	57	54	4	2	4	132	1391	9	2	3	102	-110
4	0	6	1330	1418	5	1	2	598	-639	4	2	6	1057	1060	9	2	5	153	-189
4	0	8	769	777	5	1	4	131	-140	4	2	8	594	577	9	2	7	115	-118
4	0	10	898	838	5	1	6	506	-600	4	2	10	352	360	11	2	1	238	-199
4	0	12	904	868	5	1	8	158	174	4	2	12	450	394	11	2	3	25	18
6	0	2	948	811	5	1	10	14	-18	6	2	2	1011	1015	11	2	5	47	-33
6	0	4	1068	1068	5	1	12	421	-464	6	2	4	892	888	11	2	7	68	70
6	0	6	853	807	6	1	3	467	518	6	2	6	650	660	13	2	1	166	-174
6	0	8	589	660	6	1	5	549	-590	6	2	8	590	579	1	3	4	616	605
6	0	10	514	487	6	1	7	447	-511	6	2	10	539	550	1	3	6	540	518
8	0	2	1188	1202	6	1	9	145	117	8	2	2	756	736	1	3	8	253	-253
8	0	4	773	721	6	1	11	135	155	8	2	4	599	587	1	3	10	181	-174
8	0	6	570	393	7	1	2	450	516	8	2	6	488	503	2	3	1	536	-587
8	0	8	356	438	7	1	4	151	-188	8	2	8	539	565	2	3	3	1202	-1232
8	0	10	335	475	7	1	6	177	-137	8	2	10	582	575	2	3	5	224	-182
10	0	2	552	612	7	1	10	198	176	10	2	2	688	691	2	3	7	143	107
10	0	4	802	765	8	1	1	25	17	10	2	4	594	582	3	3	9	72	-110
10	0	6	514	463	8	1	3	312	-243	10	2	6	556	554	3	3	11	1202	-1232
10	0	8	311	186	8	1	5	216	-176	10	2	8	440	467	3	3	13	177	-173
12	0	2	547	541	8	1	7	25	-1	12	2	2	327	363	3	3	15	34	18
12	0	4	486	518	8	1	9	25	69	12	2	4	493	604	3	3	17	261	151
1	1	1	829	834	9	1	2	297	284	1	2	3	584	-587	3	3	19	207	188
1	1	3	499	464	9	1	4	285	-250	3	3	5	594	-639	3	3	21	173	-188
1	1	5	216	-220	9	1	6	156	-155	1	2	7	539	516	3	3	23	12	25
1	1	7	12	50	1	1	8	159	126	1	2	9	355	286	4	3	1	641	-634
1	1	9	120	-92	10	1	1	255	-230	3	3	1	140	137	4	3	3	184	-173
1	1	11	216	137	10	1	3	174	-174	3	3	3	1282	-1232	4	3	5	67	-69
2	1	1	242	308	10	1	5	145	140	3	3	5	382	-301	4	3	7	34	-7
2	1	3	549	492	10	1	7	218	211	3	3	7	565	539	4	3	9	11	51
2	1	5	262	211	2	2	0	1924	220*	3	2	9	561	508	5	3	11	321	-301

tering factors were taken from *International Tables for X-ray Crystallography* (1962).

The observed and calculated structure factors are listed in Table 2. Three-dimensional Fourier syntheses (Zelenko, 1968), the least-squares refinement (Polić, 1968) and the interatomic distances and bond angles (Trupčević, 1969) were computed on the Institute 'Rudjer Bošković' CAE 90/40 computer.

Description and discussion of the structure

The crystal structure of N₂H₆TiF₆ consists of discrete [TiF₆]²⁻ octahedral anions (Fig. 1) and N₂H₆²⁺ cations. Titanium atoms occupy the corners of the cubic cell, the middles of the edges, the centres of the faces, and the centre of the cube (Fig. 2).

The fluorine atoms are octahedrally disposed round the titanium atom. The Ti-F bond of length, 1.855 Å (Table 3), is considerably shorter than the sum of the ionic radii ($r_{\text{Ti}^{4+}}=0.68$, $r_{\text{F}^-}=1.36$ Å, Pauling, 1963). The shortening can be attributed to the high covalent character of the Ti-F bond. This value is smaller than some values reported earlier: 1.887 Å in CuTiF₆·4H₂O (Fischer, de Cian & Weiss, 1967); 1.882 Å in Na₃HTiF₈ (Weiss, Fischer & Chevrier, 1966) and NH₄CuTiF₇·4H₂O (de Cian, Fischer & Weiss, 1967).

Table 3. Interatomic distances, angles and their standard deviations (in parentheses)

Numbering of the atoms.			
Small letters indicate symmetry transformations or cell translations			
a	0.5-x,	0.5-y,	0.5-z
b	0.5+x,	0.5+y,	0.5+z
c	0.5+z,	x,	0.5-y
d	x,	0.5-y,	0.5+z
e	0.5+y,	0.5-z,	1-x
f	0.5-y,	0.5+z,	x
g	0.5-x,	y,	-z

Table 3 (cont.)

	Distance
N—N(a)	1.474 (7) Å
N—F	2.612 (6)
N—F(g)	3.070 (5)
Ti(b)—F(c)	1.855 (4)
F(c)—F(d)	2.600 (8)
F(c)—F(e)	2.646 (8)
F—F(g)	3.187 (9)
	Angle
N(a)—N—F	96.4 (0.5)
F(c)—Ti(b)—F(e)	91.0 (0.2)
F(c)—Ti(b)—F(f)	89.0 (0.2)

The octahedron (Fig. 1) is slightly extended along the threefold axis of the space group. It has therefore a trigonal distortion which reduces the symmetry of the octahedron to $\bar{3}$ and results in two values of the edge lengths (F...F distances), the six normal to $\bar{3}$ being

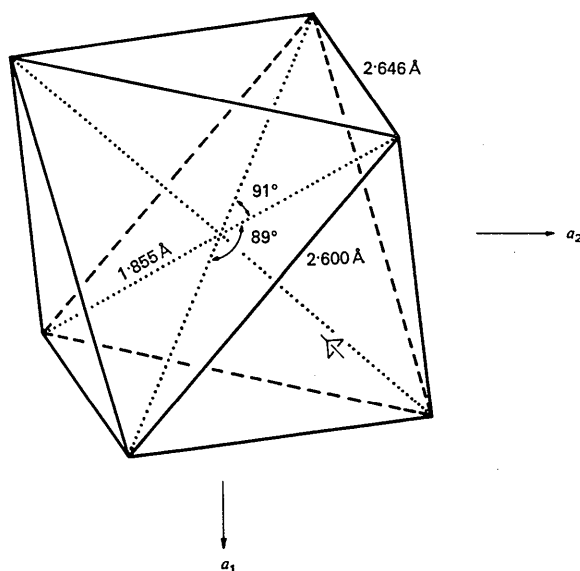


Fig. 1. The TiF₆ octahedron.

slightly shorter (2.600 Å) than the remaining six (2.646 Å). The eight hydrazinium ions in the unit cell are centred at the eight points (*b*) with symmetry $\bar{3}$. Six of these are on the six threefold axes that cross the unit cell from the centre of one cube edge to the centre of the face perpendicular to it. The remaining two are on the threefold axis (body diagonal). The position of the $\text{N}_2\text{H}_6^{2+}$ ion on the threefold axis with the centre of symmetry in the middle of the N–N bond requires a

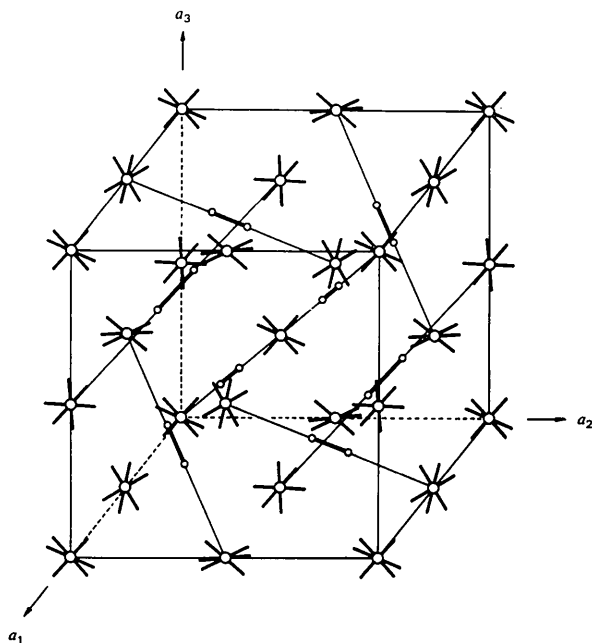


Fig. 2. Arrangement of $[\text{TiF}_6]^{2-}$ anions and N–N bonds in hydrazinium(+2) cations in the $\text{N}_2\text{H}_6\text{TiF}_6$ structure.

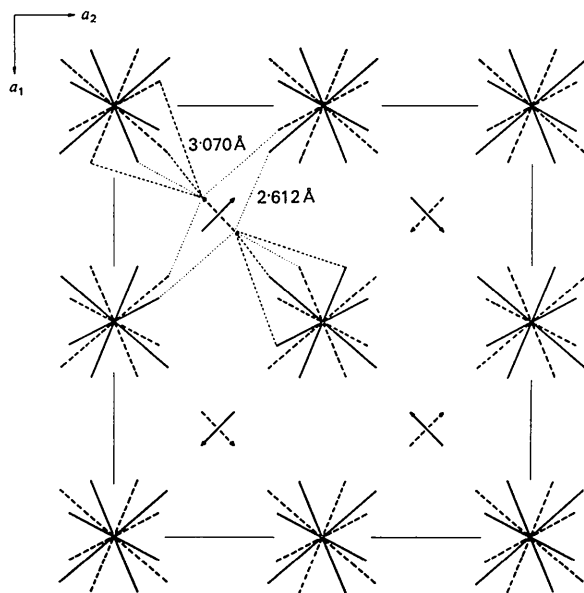


Fig. 3. Projection on (001); $[\text{TiF}_6]^{2-}$ ions at 0 and 1 are shown with dashed lines, those at $\frac{1}{2}$ with full lines. Dotted lines connect the hydrogen-bonded atoms, thin dashed lines the next nearest nitrogen and fluorine atoms.

trans configuration of the ion. The N–N bond length of 1.474 Å is considerably longer than the 1.43 Å found in $\text{N}_2\text{H}_6(\text{H}_2\text{PO}_4)_2$ (Liminga, 1966), 1.42 Å in $\text{N}_2\text{H}_6\text{F}_2$ (Kronberg & Harker, 1942) and $\text{N}_2\text{H}_6\text{Cl}_2$ (Donohue & Lipscomb, 1947) and 1.40 Å in $\text{N}_2\text{H}_6\text{SO}_4$ (Nitta, Sakurai & Tomiie, 1951). There is no evidence to suggest that the hydrazinium ions are disordered in this crystal. Around the $\text{N}_2\text{H}_6^{2+}$ ion there are six fluorine atoms with an $\text{N}\cdots\text{F}$ distance of 2.612 Å. These short distances indicate strong $\text{N}\cdots\text{F}$ interaction and suggest that $[\text{TiF}_6]^{2-}$ octahedra and $\text{N}_2\text{H}_6^{2+}$ ions are joined together by $\text{N}-\text{H}\cdots\text{F}$ hydrogen bonds. Six hydrogen-bonded fluorine atoms around one $\text{N}_2\text{H}_6^{2+}$ ion belong to six different $[\text{TiF}_6]^{2-}$ octahedra and so connect discrete groups into a three-dimensional framework (Fig. 3). No exact explanation has been found for the lengthening of the N–N bond to 1.474 Å; perhaps six strong $\text{N}-\text{H}\cdots\text{F}$ hydrogen bonds affect the length. Besides six fluorine atoms at an $\text{N}\cdots\text{F}$ distance of 2.612 Å around one $\text{N}_2\text{H}_6^{2+}$ ion there are also six fluorine atoms at $\text{N}\cdots\text{F}=3.070$ Å.

The Raman spectrum of $\text{N}_2\text{H}_6\text{TiF}_6$ was recorded by Dr Jacob Shamir (Inorganic and Analytical Chemistry Department, Hebrew University of Jerusalem, Jerusalem, Israel) and the N–N vibration frequency was assigned at 1040 cm^{-1} ; similar values for N–N vibrations in $\text{N}_2\text{H}_6\text{Cl}_2$ at 1024 cm^{-1} and in $\text{N}_2\text{H}_6\text{SO}_4$ at 1050 cm^{-1} have been found (Nitta, Sakurai & Tomiie, 1951).

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