

SHORT STRUCTURAL PAPERS

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Hydrazinium(2+) Hexafluorosilicate(IV)

BY B. FRLEC, D. GANTAR, L. GOLIC AND I. LEBAN*

Chemistry Department and J. Stefan Institute, University E. Kardelj, Ljubljana, Yugoslavia

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Abstract. $N_2H_6[SiF_6]$, $M_r = 176.1$, orthorhombic, $Pbca$, $a = 7.603$ (2), $b = 7.594$ (3), $c = 8.543$ (4) Å, $V = 493.2$ Å³, $D_m = 2.39$ (by flotation), $D_x = 2.372$ Mg m⁻³, $\mu(Mo K\alpha) = 0.557$ mm⁻¹, $Z = 4$, at 293 K. Final $R = 0.032$ and $R_w = 0.044$ for 655 observed reflexions [$I > 3\sigma(I)$]. The structure consists of $N_2H_6^{2+}$ ions and SiF_6^{2-} octahedra [mean Si–F = 1.680 (1) Å], occupying centres of symmetry. There is a three-dimensional network of N–H...F hydrogen bonds, ranging from 2.714–2.945 (2) Å.

Introduction. Several hydrazinium(2+) fluorometalates(IV) of transition metals have been synthesized at the J. Stefan Institute, Ljubljana, and the crystal structures of $N_2H_6[TiF_6]$, $N_2H_6[ZrF_6]$ and $(N_2H_6)_2F_2[TiF_6]$ have been determined [see Golič, Kaučič & Kojić-Prodić (1980) for a concise list]. The present work is a continuation of the above study, with the main-group element Si as a central atom in the fluorometalate(IV) anion.

$N_2H_6[SiF_6]$ crystals were produced by adding $N_2H_6F_2$ to a solution of H_2SiF_6 (30 wt%). Well developed, colourless crystals were obtained by evaporation at room temperature. The systematically absent reflexions ($0kl: k = 2n + 1; h0l: l = 2n + 1; \text{and } hk0: h = 2n + 1$) on Weissenberg photographs and the mean value of $|E^2 - 1| = 1.025$ suggested the space group $Pbca$. Cell dimensions were obtained by least squares from 2θ values of 20 reflexions measured on a diffractometer [Mo $K\alpha_1$ radiation, $\lambda = 0.70926$ Å, $T = 293$ (1) K]. A prismatic crystal $0.3 \times 0.3 \times 0.6$ mm was used for data collection on the automatic computer-controlled Enraf–Nonius CAD-4 four-circle diffractometer with Mo $K\alpha$ radiation and a graphite monochromator. Reflexions were scanned in the ω - 2θ mode (moving crystal–moving counter) with a variable scan rate. Other details of the data collection and

Table 1. *Some data-collection details for $N_2H_6[SiF_6]$*

X-radiation	Mo $K\alpha$ ($\lambda = 0.71069$ Å)
2θ scan width (°)	$0.8 + 0.2 \tan \theta$
Scan rate (° min ⁻¹)	Minimum 2.0; maximum 20.1
Background	$\frac{1}{4}$ of the scan time at each of the scan limits
$2\theta_{\max}$ (°)	60
Maximum scan time (s)	40
Aperture (mm)	$2.5 + 0.9 \tan \theta$
Reference reflexions	141, 411, 233
Intensity decrease (%)	4
Measured reflexions	1689 (+h,+k,±l)
Averaged reflexions	714
Mean discrepancy on I (%)	1.3
Observed reflexions	655
Unobserved reflexions	59 [$I < 3\sigma(I)$]
$\sigma(I)$ base	Counting statistics

reduction are given in Table 1. The data were corrected for variation in reference reflexions and Lorentz–polarization effects, but not for absorption.

A Patterson function suggested the placing of Si at the 4(b) position, and the positions of N and F atoms were found in the subsequent electron density map. Isotropic full-matrix least-squares refinement proceeded to $R = 0.109$, and anisotropic refinement gave $R = 0.050$. A difference synthesis at this stage revealed the broad peaks of the H atoms of the $N_2H_6^{2+}$ group. Several attempts to refine H atom positional and isotropic thermal parameters were unsuccessful. Therefore, in the final course of the refinement, the N and H(1), H(2), H(3) were kept fixed and an anisotropic temperature factor for N and a common isotropic temperature factor for H(1), H(2) and H(3) were refined.

An empirical isotropic extinction parameter x was refined to 0.019 (Sheldrick, 1976) with the final $R = 0.032$, and $R_w = \sum w^{1/2} \Delta / \sum w^{1/2} |F_o| = 0.044$; the weighting scheme was $w = 9.1 / [\sigma^2(F_o) + 0.003 F_o^2]$. A final difference map showed no peaks $> 0.2 e \text{ \AA}^{-3}$. The average shift/error in the last cycle was 0.17 with a maximum of 0.60 for y of F(3). Final atomic

* To whom correspondence should be addressed.

Table 2. Final fractional coordinates ($\times 10^4$) and equivalent isotropic temperature factors [$U_{eq} = (U_{11} \cdot U_{22} \cdot U_{33})^{1/3}$] ($\times 10^4$)

	x	y	z	U_{eq} (\AA^2)
Si	5000	0	5000	138 (5)
N	4869 (3)	140 (3)	818 (2)	222 (11)
F(1)	6330 (2)	-1432 (2)	4067 (2)	317 (8)
F(2)	4390 (2)	-1557 (2)	6266 (2)	303 (8)
F(3)	6663 (2)	593 (2)	6194 (2)	297 (8)
H(1)	4494	1233	986	
H(2)	4091	-585	1200	
H(3)	5926	40	1327	

coordinates are given in Table 2.* Scattering factors were those included in *SHELX 76* (Sheldrick, 1976), which was used in all calculations on the CDC Cyber 172 computer at RRC Ljubljana.

Discussion. All complex fluorometallates(IV), $A[BF_6]$, crystallize with structures of the NaCl or CsCl types, depending mainly upon the sizes of the A^{II} and $B^{IV}F_6$ ions (Wells, 1975). A comparison of the crystal structures of $N_2H_6[TiF_6]$ (Kojić-Prodić, Matković & Šćavničar, 1971) and $N_2H_6[SiF_6]$ (present work) shows that $N_2H_6[TiF_6]$ has a CsCl-type structure with 8/8 coordination, whereas $N_2H_6[SiF_6]$ has a distorted NaCl-type structure, each $N_2H_6^{2+}$ ion being surrounded by six SiF_6^{2-} ions and *vice versa*, although, from the actual sizes of the separate ions, the opposite situation would be expected. The reason for this feature is probably the different distribution and strength of hydrogen bonds in the two structures.

The important interatomic distances and angles are listed in Table 3. A view of the structure along *a* is given in Fig. 1.

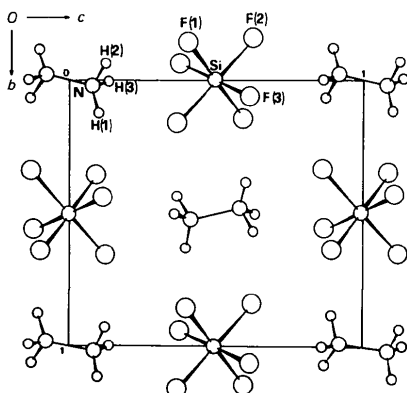


Fig. 1. Structure of $N_2H_6[SiF_6]$ viewed along *a*. For clarity only the ions at $x = 0.5$ are shown.

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35311 (6 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 3. Interatomic distances (\AA) and angles ($^\circ$)

SiF_6^{2-} octahedron			
Si—F(1), F(1 ^l)	1.685 (1)	F(1)—Si—F(2)	90.9 (1)
Si—F(2), F(2 ^l)	1.668 (1)	F(1)—Si—F(3)	90.5 (1)
Si—F(3), F(3 ^l)	1.686 (1)	F(2)—Si—F(3)	90.3 (1)
$N_2H_6^{2+}$ ion			
N—N ^{II}	1.428 (2)	N ^{II} —N—H(1)	110.0
N—H(1)	0.889	N ^{II} —N—H(2)	111.5
N—H(2)	0.872	N ^{II} —N—H(3)	109.2
N—H(3)	0.917	H(1)—N—H(2)	108.2
		H(1)—N—H(3)	106.4
		H(2)—N—H(3)	111.4

Hydrogen bonds for N—F < 3.000 \AA

N—H...F	H...F	N—F	$\angle N-H...F$
N—H(1)...F(1 ^{III})	1.881	2.760 (2)	169.3
N—H(3)...F(3 ^{VI})	1.899	2.714 (2)	147.0
N—H(2)...F(2 ^V)	2.183	2.772 (2)	124.5
N—H(2)...F(3 ^I)	2.299	2.861 (2)	122.2
N—H(2)...F(1 ^{VI})	2.207	2.945 (2)	142.3

Symmetry code

(i) $1 - x, -y, 1 - z$	(iv) $\frac{1}{2} - x, -y, -\frac{1}{2} + z$
(ii) $1 - x, -y, -z$	(v) $x, -\frac{1}{2} - y, -\frac{1}{2} + z$
(iii) $1 - x, \frac{1}{2} + y, \frac{1}{2} - z$	(vi) $-\frac{1}{2} + x, y, \frac{1}{2} - z$

The hydrazinium(2+) cations, lying across the centres of symmetry 4(*a*), have a *trans* (staggered) conformation with N—N = 1.428 (2) \AA . H(1), H(2) and H(3), located from a difference map at 0.889, 0.872 and 0.917 \AA from the N atom, form nearly tetrahedral angles (average values: N—N—H = 110.2 $^\circ$; H—N—H = 108.7 $^\circ$). The cations are oriented with the N—N bond nearly parallel to *c*; thus the unit cell is tetragonally distorted.

The Si atoms, occupying centres of symmetry at 4(*b*), are octahedrally coordinated by three pairs of symmetry-related F atoms at 1.685 (1), 1.668 (1) and 1.686 (1) \AA [average values: Si—F = 1.680 (1) \AA ; F—Si—F = 90.6 (1) $^\circ$].

The $N_2H_6^{2+}$ and SiF_6^{2-} units are held together by a three-dimensional network of four single hydrogen bonds and two trifurcated hydrogen bonds (Table 3) of the type N—H...F with N—F distances in the range 2.714–2.945 (2) \AA .

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