

thermal parameters are given in Table 1* and bond lengths and angles in Table 2. The structure is shown in Fig. 2. Primed and double-primed symbols represent two split atoms for each O atom.

Discussion. A residual map of the electron density computed after the final refinement showed maximum anomalies of $0.2 e \text{ \AA}^{-3}$. Irregular maxima of $0.4 \sim 0.6 e \text{ \AA}^{-3}$ were located near O(1) and O(4). According to the significance test (Hamilton, 1965), the disordered model is rejected below the 0.005 level at every stage of the proposal that there are two disordered positions for an O atom, *i.e.* we are quite sure that the structure has disordered O atoms. It should be noted that a harmonic model for the vibrations describes well the contours of the S, N and Li atoms, but the values of the thermal parameters of these atoms are about twice those estimated from the room-temperature structure.

The sharing of the split atoms for the tetrahedral arrangements is determined from the condition that the centre of mass of the unit cell must be unchanged for polarization reversal. The two arrangements thus

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obtained are depicted in Fig. 2. The shapes of the SO_4 and LiO_4 tetrahedra are quite reasonable and one of the polar structures (drawn with thick lines in Fig. 2) can be superimposed on Dollase's structure, apart from the difference of about 0.1 \AA found in the atomic positions in the *ab* plane. Atomic shifts associated with polarization reversal are $0.22 (3) \text{ \AA}$ for O(1), $0.730 (5) \text{ \AA}$ for O(2), O(3) and $0.804 (6) \text{ \AA}$ for O(4).

It should be noted that the rotation of the SO_4 tetrahedron ($\sim 5^\circ$) about the *c* axis nearly carries Dollase's structure into one of the polar structures at 478 K. This suggests that the order parameter in the ferroelectric phase is not simply determined by the split ratio of the O atoms but is also connected with a gradual rotation of the SO_4 tetrahedron with temperature. Ferroelectric structures are now being investigated at several temperatures.

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Hydrazinium(2+) Hexafluorogermanate(IV) Monohydrate

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Abstract. $\text{N}_2\text{H}_6^{2+}[\text{GeF}_6]^{2-} \cdot \text{H}_2\text{O}$, $M_r = 238.66$, orthorhombic, *Pnma*, $a = 8.869 (1)$, $b = 9.292 (1)$, $c = 7.400 (1) \text{ \AA}$, $V = 609.8 \text{ \AA}^3$, $D_x = 2.599 \text{ Mg m}^{-3}$, $Z = 4$, $\mu(\text{Mo } K\alpha) = 5.395 \text{ mm}^{-1}$, $T = 293 (1) \text{ K}$. R and R_w were 0.018 and 0.024 for 794 contributing reflexions [$I > 4\sigma(I)$]. The structure consists of $\text{N}_2\text{H}_6^{2+}$ ions [staggered conformation, $\text{N}-\text{N} = 1.428 (2) \text{ \AA}$], GeF_6^{2-} octahedra [mean $\text{Ge}-\text{F} = 1.786 (2) \text{ \AA}$] and H_2O units interconnected by a network of three-dimensional $\text{N}-\text{H}\cdots\text{O}$ and $\text{N}-\text{H}\cdots\text{F}$ hydrogen bonds.

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Introduction. This investigation is part of a structural study of hydrazinium(2+) fluorometallates(IV) synthesized at the J. Stefan Institute, Ljubljana. The crystal structures of $\text{N}_2\text{H}_6[\text{TiF}_6]$, $\text{N}_2\text{H}_6[\text{ZrF}_6]$, $\text{N}_2\text{H}_6\text{F}_2[\text{TiF}_6]$ and $\text{N}_2\text{H}_6[\text{SiF}_6]$ have already been determined (Kojić-Prodić, Matković & Ščavničar, 1971; Kojić-Prodić, Ščavničar & Matković, 1971; Golič, Kaučič & Kojić-Prodić, 1980; Frlec, Gantar, Golič & Leban, 1980). Colourless single crystals were obtained by dissolving $\text{N}_2\text{H}_6\text{F}_2$ and GeO_2 in HF (40 wt %) and slowly evaporating the solution at room temperature. The systematically absent reflexions ($0kl$: $k+l = 2n+1$ and $hk0$: $h = 2n$) on Weissenberg films

Table 1. *Data-collection summary for*
 $N_2H_6[GeF_6] \cdot H_2O$

Temperature (K)	293 (1)
Diffractometer	CAD-4, automated, four-circle
X-radiation	Mo $K\alpha$ ($\lambda = 0.71069 \text{ \AA}$)
Monochromator	Graphite
Scan method	$\omega-2\theta$ (moving crystal-moving counter)
2θ scan width ($^\circ$)	$0.8 + 0.2 \tan \theta$
Scan rate ($^\circ \text{ min}^{-1}$)	min.: 1.8; max.: 20.1
Background	$\frac{1}{4}$ of the scan time at each of the scan limits
$2\theta_{\text{max}}$ ($^\circ$)	60
Maximum scan time (s)	40
Aperture (mm)	$2.5 + 0.9 \tan \theta$
Reference reflexions	432, 231, 222
Measured reflexions	877
Observed reflexions	794
Unobserved reflexions	83
$\sigma(I)$ base	Counting statistics
Linear absorption coefficient (mm^{-1})	5.395
Transmission	min.: 0.249; max.: 0.622

and the mean value of $|E^2 - 1| = 0.913$ indicated the space group $Pnma$. Cell dimensions were obtained by least-squares analysis from the 2θ values of 60 reflexions measured on a CAD-4 diffractometer [Mo $K\alpha_1$ radiation, $\lambda = 0.70926 \text{ \AA}$, $T = 293 (1) \text{ K}$]. A prismatic crystal $0.1 \times 0.33 \times 0.45 \text{ mm}$ was used to collect data on the diffractometer with monochromated Mo $K\alpha$ radiation. Reflexions were scanned in the $\omega-2\theta$ mode with a variable scan rate. Details of the data collection and reduction are given in Table 1. The data were corrected for variation in reference reflexions and Lp effects. An exact absorption correction based on the equations of the crystal faces was also applied.

Attempts to solve the structure by the Patterson method in space group $Pnma$ were unsuccessful. Application of direct methods in $P2_12_12_1$ with *MULTAN* 78 (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978) revealed the complete structure, which was transformed back to $Pnma$ for refinement, carried out with *SHELX* (Sheldrick, 1976) with anisotropic thermal parameters for the non-hydrogen atoms. The positions of the five H atoms were determined by a difference synthesis and were introduced in the refinement with isotropic thermal parameters. An empirical isotropic extinction parameter x was refined to 0.005 (Sheldrick, 1976). The final $R = 0.018$ and $R_w = \sum w^{1/2} \Delta / \sum w^{1/2} |F_o| = 0.024$ for 794 contributing reflexions.* The weighting scheme was $w = [\sigma^2(F_o) + 0.0015 F_o^2]^{-1}$. A final difference map

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Table 2. *Final fractional coordinates ($\times 10^4$ for Ge, F, O, N; $\times 10^3$ for H) and equivalent isotropic temperature factor U_{eq} ($\times 10^4$) (Hamilton, 1959) for non-hydrogen and isotropic U ($\times 10^3$) for H atoms*

	x	y	z	U_{eq} or U_{iso} (\AA^2)
Ge	6575 (1)	2500	5110 (1)	139 (2)
F(1)	8334 (2)	2500	3788 (2)	245 (8)
F(2)	4941 (2)	2500	6530 (2)	245 (8)
F(3)	5846 (1)	1158 (1)	3673 (2)	357 (6)
F(4)	7400 (1)	1138 (1)	6513 (1)	245 (5)
N	321 (2)	264 (2)	5820 (2)	215 (7)
O	2199 (2)	2500	4853 (2)	224 (9)
H(1)	-43 (3)	45 (3)	650 (4)	42 (7)
H(2)	97 (3)	89 (3)	559 (4)	42 (7)
H(3)	58 (3)	-44 (3)	643 (4)	39 (7)
H(4)	248 (4)	250	371 (6)	43 (11)
H(5)	289 (6)	250	566 (6)	65 (14)

showed no peaks $> 0.3 \text{ e \AA}^{-3}$. Table 2 gives the final atomic parameters. All calculations were performed on the CDC Cyber 172 computer at RRC Ljubljana.

Discussion. The structure contains $N_2H_6^{2+}$ ions, GeF_6^{2-} octahedra and water molecules held together by a three-dimensional network of $N-H \cdots F$ and $N-H \cdots O$ hydrogen bonds (Fig. 1). The important interatomic distances and angles are listed in Table 3. Each NH_3^+ group of $N_2H_6^{2+}$, lying across a centre of inversion, forms bifurcated and trifurcated $N-H \cdots F$ hydrogen bonds ranging from 2.698 (2) to 2.876 (2) \AA , and one $N-H \cdots O$ bond of 2.757 (2) \AA . The H atoms of the water molecule are engaged in two hydrogen bonds of the type $O-H \cdots F$ of 2.731 (3) and 2.877 (2) \AA ; thus the water molecule is tetrahedrally coordinated by H atoms (Table 3). The N-N distance of 1.428 (2) \AA in $N_2H_6^{2+}$ (staggered conformation) is in good agreement with the 1.426 (3) and 1.428 (2) \AA

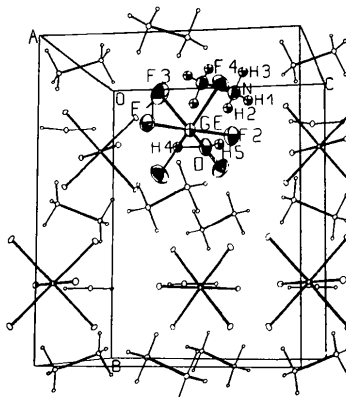


Fig. 1. A view of the unit cell along [100]. The atoms are represented by thermal ellipsoids drawn at the 50% probability level (Johnson, 1965).

Table 3. *Interatomic distances (Å) and angles (°)*

GeF ₆ octahedron				
Ge—F(1)	1.842 (2)	Ge—F(3),F(3')	1.762 (1)	
Ge—F(2)	1.789 (2)	Ge—F(4),F(4')	1.793 (1)	
F(1)—Ge—F(2)	176.1 (1)	F(3)—Ge—F(4)	90.0 (1)	
F(1)—Ge—F(3)	89.4 (1)	F(3)—Ge—F(3')	90.1 (1)	
F(1)—Ge—F(4)	87.8 (1)	F(3)—Ge—F(4')	177.2 (1)	
F(2)—Ge—F(3)	93.3 (1)	F(4)—Ge—F(4')	89.8 (1)	
F(2)—Ge—F(4)	89.5 (1)			
N ₂ H ₆ ²⁺ ion				
N—N ^{II}	1.428 (2)	N—H(1)	0.85 (3)	
		N—H(2)	0.83 (3)	
		N—H(3)	0.83 (3)	
N ^{II} —N—H(1)	105 (2)	H(1)—N—H(2)	121 (3)	
N ^{II} —N—H(2)	110 (2)	H(1)—N—H(3)	94 (3)	
N ^{II} —N—H(3)	108 (2)	H(2)—N—H(3)	118 (3)	
Water molecule				
O—H(4)	0.88 (4)	H(4)—O—H(5)	118 (4)	
O—H(5)	0.85 (5)	H(2)—O—H(4)	115 (2)	
O...H(2),H(2')	1.93 (3)	H(2)—O—H(5)	102 (2)	
		H(2)—O—H(2')	102 (2)	
Hydrogen-bond distances and angles				
<i>D</i> —H... <i>A</i>	<i>D</i> — <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> —H... <i>A</i>
N—H(1)...F(2 ^{III})	2.876 (2)	0.85 (3)	2.42 (3)	114 (2)
N—H(1)...F(3 ^{IV})	2.698 (3)	0.85 (3)	2.23 (3)	115 (2)
N—H(1)...F(4 ^V)	2.763 (2)	0.85 (3)	2.03 (3)	144 (3)
N—H(2)...O	2.757 (2)	0.83 (3)	1.94 (3)	170 (3)
N—H(3)...F(4 ^{VI})	2.847 (2)	0.83 (3)	2.15 (3)	142 (3)
N—H(3)...F(3 ^{IV})	2.698 (2)	0.83 (3)	2.19 (3)	120 (2)
O—H(4)...F(1 ^{VII})	2.877 (2)	0.88 (4)	2.00 (4)	174 (4)
O—H(5)...F(2)	2.731 (3)	0.85 (5)	1.93 (5)	155 (5)
Symmetry code				
(i)	$x, \frac{1}{2} - y, z$	(v)	$-1 + x, y, z$	
(ii)	$-x, -y, 1 - z$	(vi)	$1 - x, -y, 1 - z$	
(iii)	$-\frac{1}{2} + x, \frac{1}{2} - y, \frac{3}{2} - z$	(vii)	$-\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} - z$	
(iv)	$-\frac{1}{2} - x, -y, \frac{1}{2} + z$			

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Rhodium Scandium Disilicide with an Ordered YZn₃-Type Structure

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Abstract. ScRhSi₂, *Pnma*, *a* = 6.292 (4), *b* = 4.025 (4), *c* = 9.517 (5) Å, *Z* = 4, *D*_x = 5.62 (1) Mg m⁻³, *μ*(Mo *Kα*) = 10 mm⁻¹, *F*(000) = 376. This compound crystallizes with an ordered version of the

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in N₂H₆SO₄ (Jönsson & Hamilton, 1970) and N₂H₆[SiF₆] (Frlec, Gantar, Golič & Leban, 1980). The F atoms are octahedrally arranged around the Ge atom forming a slightly distorted octahedron. The Ge—F lengths, ranging from 1.762 (1) to 1.842 (2) Å, are close to the reported values of 1.71–1.80 (2) Å in, for example, Ge₅F₁₂ (Taylor & Wilson, 1973).

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YZn₃ structure type with the Rh and Si atoms occupying the corresponding Zn sites. The final weighted *R* = 0.052 for 536 reflections. It is shown that the structure types YZn₃, ScRhSi₂, CeZn₃, Re₃B and MgAl₂Cu are all geometrically related, the last three being higher-symmetry versions with space group *Cmcm*. Furthermore, some geometrical relationships