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HYDRAZINIUM(1+) HEXAFLUOROGERMANATE(IV) AND HYDRAZINIUM(2+) HEXAFLUOROGERMANATE(IV) DIFLUORIDE

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SUMMARY

$(N_2H_5)_2GeF_6$ and $(N_2H_6)_2(GeF_6)F_2$ have been prepared by reactions of $N_2H_4.H_2O$ and $N_2H_6F_2$ with fluorogermanic acid. The solids have been characterized by chemical analysis and vibrational spectra. X-ray diffraction study has shown that crystals of $(N_2H_5)_2GeF_6$ are monoclinic, space group P $2_1/n$, with unit-cell dimensions a = 6.015 (2), b = 5.249 (1), c = 11.181 (2) Å, β = 100.15 (2)°, and Z = 2. There are $N_2H_5^+$ cations and GeF_6^{2-} anions in the crystals interconnected by hydrogen bonds of the type N-H····F and N-H····N.

INTRODUCTION

The hexafluorogermanates of the alkali metals, silver, thallium and barium have been known for many years [1]. In 1933 salts with nitrogen bases were prepared and their chemical analyses and optical properties were reported [2]. Fluorogermanates of some divalent metals have since been studied by Russian authors [3]. A vibrational analysis of the active fundamental modes of GeF_6^{2-} showed that interpretation of the spectra of its salts should take account of space group and site group selection rules [4].

Since 1964 research on hydrazinium(1+) and (2+) fluorometalates has been intense at the 'Jožef Stefan' Institute [5]. Among others, $N_2H_6GeF_6.H_2O$ was isolated by reaction of $N_2H_6F_2$ with fluorogermanic acid and its crystal structure was resolved [6]. Later on we found that a 2:1 molar ratio of $N_2H_6F_2$ and H_2GeF_6 solution yielded a new compound with a composition $2N_2H_6F_2.GeF_4$. This suggested the formulas $(N_2H_5)_2(GeF_6)$ .2HF or

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$(N_2H_6)_2(GeF_6)F_2$. A vibrational spectrum of the solid has now confirmed the latter formulation. This type of hydrazinium(2+) compound has been observed previously in $(N_2H_6)_2(TiF_6)F_2$ for which a crystal structure has been determined [7]. Its vibrational spectrum has also been analysed and the decomposition of $(N_2H_6)_2(TiF_6)F_2$ has been elucidated by Raman spectroscopy [8].

$(N_2H_5)_2GeF_6$ has been characterized by means of its vibrational spectrum and a single-crystal X-ray study.

RESULTS AND DISCUSSION

Vibrational spectra of $(N_2H_6)_2(GeF_6)F_2$ and $(N_2H_5)_2GeF_6$ are given in Table 1. Their assignment has been made according to the literature [4,9]. In the anionic part of the spectra the additional bands and the splitting of the bands can be attributed to the distortion of the octahedral GeF_6^{2-} ion. The infrared active antisymmetric F-Ge-F stretching mode ν_3 (f_{1u}) is observed at 570 cm^{-1} in $(N_2H_6)_2(GeF_6)F_2$ and at 545 cm^{-1} in $(N_2H_5)_2GeF_6$, which is at much lower frequencies than that observed (602 cm^{-1}) in $BaGeF_6$ [4] in which the lowering of the symmetry of the anion is attributed to the position of the cation in the lattice.

The cationic part of the spectrum of $(N_2H_6)_2(GeF_6)F_2$ differs distinctly in the region of the N-N stretching vibration from that of $(N_2H_5)_2GeF_6$. In the Raman spectrum of $(N_2H_6)_2(GeF_6)F_2$ the strongest band assigned to the N-N vibration in $N_2H_6^{2+}$ is observed at 1062 cm^{-1}; the weak band at 980 in the Raman and the absorption at 965 cm^{-1} in the infrared are a consequence of the decomposition of the sample in the laser beam. In the spectrum of $(N_2H_5)_2GeF_6$ the bands observed from 968 to 982 cm^{-1} clearly confirm the presence of the $N_2H_5^+$ ion. Another important difference between the infrared spectra of $(N_2H_6)_2(GeF_6)F_2$ and $(N_2H_5)_2GeF_6$ can be seen in the region from 2000 to 3000 cm^{-1}. Weak broad absorptions at 2016, 2400 and 2640 cm^{-1} appear only in the spectrum of $(N_2H_6)_2(GeF_6)F_2$, at similar frequencies to those observed for $(N_2H_6)_2(TiF_6)F_2$. Therefore we assigned these bands to the strong hydrogen bond between $N_2H_6^{2+}$ and F^- ions. We assume that decomposition of $(N_2H_6)_2(GeF_6)F_2$ in the laser beam occurred with the same mechanism as that suggested by Milićev et al for $(N_2H_6)_2(TiF_6)F_2$, that is, by proton transfer between $N_2H_6^{2+}$ and F^- producing $N_2H_5^+$ and liberating HF [8].

TABLE I

Vibrational spectra (cm^{-1}) of $(N_2H_6)_2(GeF_6)F_2$ and $(N_2H_5)_2GeF_6$

$(N_2H_6)_2(GeF_6)F_2$		$(N_2H_5)_2GeF_6$		Assignment
R	IR	R	IR	
		122 (6)		
131 (9)				
158 (10)		162 (7)		
235 (4)		202 (5)		
		248 (7)		
291 (7)	302 m			
	327 m		325 m	ν_4
	371 m		350 m,sh	
342 (35)		332 (25)		ν_5
458 (7)		452 (7)	455 w	ν_2
		497 (10)		
	570 vs		545 vs	
			578 vs,sh	ν_3
	601 vs		600 vs	
625 (100)		629 (100)		ν_1
980 (7)	965 vw	969 (22)	968 vs	
1051 (15)		982 (41)	978 vs,sh	$(NN)_s$
1062 (67)	1052 vw			
	1078 vw		1079 s	
1121 (7)	1106 vw	1122 (21)	1108 vs	
	1149 w			
			1245 w	$(NH_3^+)_r$
1268 (7)	1295 w		1298 w	
1313 (7)	1338 vw		1337 w	
	1378 vw		1370 w	
1421 (2)		1411 (15)	1407 vw	$(NH_2)_r$
			1545 vs	
1592 (7)	1585 vs	1576 (10)		$(NH_3^+)_d$
1633 (11)	1627 m	1626 (14)	1602 vs	
1650 (9)		1659 (21)	1656 s	$(NH_2)_d$

A thermal decomposition study of $(N_2H_6)_2(GeF_6)F_2$ on a Mettler Thermoanalyzer confirmed that $(N_2H_5)_2GeF_6$ was formed in the first step of decomposition.

Description of the structure

Crystal data and a data-collection summary are given in Table 2.

TABLE 2

Crystal data and data-collection summary for $(N_2H_5)_2GeF_6$

M_r	252.69
Crystal system	monoclinic
Space group	$P2_1/n$
a, (Å)	6.015 (2)
b	5.249 (1)
c	11.181 (2)
β (°)	100.15 (2)
Volume (Å^3)	347.49
Z	2
Density calc. (gcm^{-3})	2.415
Temperature (K)	293 (1)
Diffractometer	CAD-4, 4-circle, automated
X-rays (Å)	MoKα, $\lambda = 0.71069$
2Θ scan width (°)	$1.0 + 0.3 \tan\Theta$
$2\Theta_{max}$ (°)	70
Maximum scan time (s)	40
Aperture (mm)	$2.5 + 0.9 \tan\Theta$
Reference reflexions	0 2-6, -3 2-3, 2 3-3
Measured reflexions	1376 (+h, +k, ±l)
Observed reflexions	1152
Unobserved reflexions	224 $[I < 3\sigma(I)]$
σ (I) base	counting statistics

The structure of the $(N_2H_5)_2GeF_6$ contains discrete $N_2H_5^+$ ions and GeF_6^{2-} *octahedra linked together by a network of N-H ····· F and N-H ···· N* hydrogen bonds.

Space group constraints require the octahedron GeF_6^{2-} to be centrosymmetric. The arrangement of fluorine atoms around germanium is octahedral. The octahedron is slightly elongated in one direction. The Ge-F lengths, Ge-F(1) 1.782(2) Å, Ge-F(2) 1.783(2) Å and Ge-F(3) 1.811(2) Å, are close to the reported values in e.g. $N_2H_6GeF_6.H_2O$ [6] which range from 1.762(1) to 1.842(2) Å.

Each part of the $N_2H_5^+$ ion, NH_3^+ and NH_2, is involved in hydrogen bonding. Hydrogens of NH_3^+ form three nearly linear bonds with two fluorine atoms of two different GeF_6 octahedra and with the nitrogen atom of another $N_2H_5^+$ ion, whereas the hydrogens of the NH_2 group form two trifurcated hydrogen bonds (see Table 3 for details). The hydrogen bond length of the type N-H·····N is 2.903(4) Å, the bonds N-H·····F range from 2.920(4) to 3.203(4) Å.

The N(1)-N(2) bond distance of the $N_2H_5^+$ ion of 1.448(4) Å is similar to reported values e.g. 1.451(4) Å found in $N_2H_5[InF_4(H_2O)]$ [10] and 1.438(7) and 1.446(7) Å in N_2H_5HS [11].

A projection of the unit cell along [010] is shown in Figure 1.

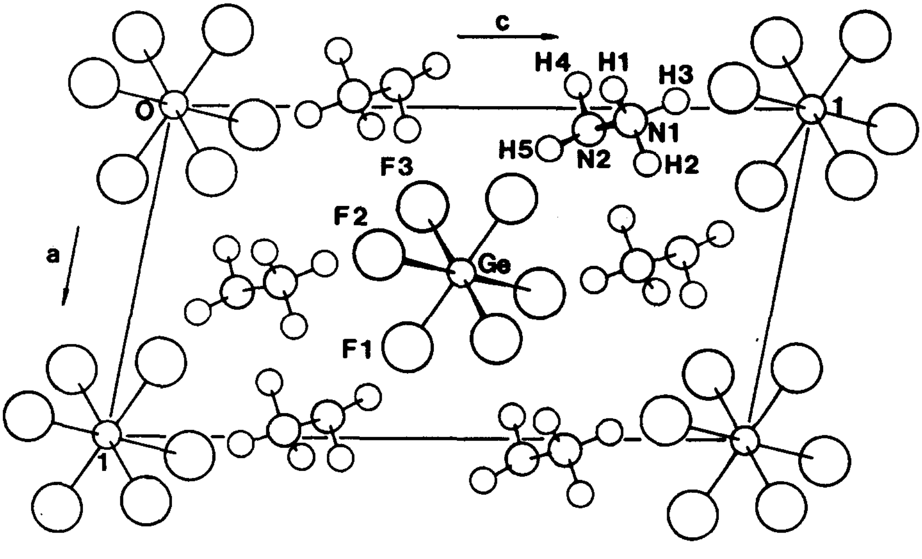

Fig. 1. A view of the unit cell of $(N_2H_5)_2GeF_6$ along [010] direction

TABLE 3

Interatomic distances (Å) and angles (^{o})

GeF_6 octahedron

Ge-F(1), F(1^{i})	1.782(2)	F(1)-Ge-F(2)	90.0(1)
Ge-F(2), F(2^{i})	1.783(2)	F(1)-Ge-F(3)	90.7(1)
Ge-F(3), F(3^{i})	1.811(2)	F(2)-Ge-F(3)	88.5(1)

$N_2H_5^+$ ion

N (1)-N(2)	1.448(4)	N(2)-N(1)-H(1)	111(3)
N(1)-H(1)	0.91(4)	N(2)-N(1)-H(2)	110(3)
N(1)-H(2)	0.91(4)	N(2)-N(1)-H(3)	104(3)
N(1)-H(3)	0.91(4)	H(1)-N(1)-H(2)	114(4)
N(2)-H(4)	0.91(3)	H(1)-N(1)-H(3)	111(4)
N(2)-H(5)	0.90(4)	H(2)-N(1)-H(3)	107(4)
		N(1)-N(2)-H(4)	103(3)
		N(1)-N(2)-H(5)	105(3)
		H(4)-N(2)-H(5)	100(4)

Torsion angles*

H(1)-N(1)-N(2)-H(4)	-55(4)
H(1)-N(1)-N(2)-H(5)	49(4)
H(5)-N(1)-N(2)-H(2)	78(4)
H(2)-N(1)-N(2)-H(3)	114(4)
H(3)-N(1)-N(2)-H(4)	63(4)

Hydrogen-bond distances and angles

D-H ······· A	D-A	D-H	H ····· A	D-H-A
N(1)-H(1)·····F(3^{ii})	2.920(4)	0.91(4)	2.02(4)	169(5)
N(1)-H(2)·····N(2^{iii})	2.903(4)	0.91(4)	2.00(4)	170(4)
N(1)-H(3)·····F(3^{iv})	2.933(4)	0.91(4)	2.02(4)	180(4)
N(2)-H(4)·····F(1^{v})	3.036(4)	0.91(3)	2.55(4)	114(4)
N(2)-H(4)·····F(2^{ii})	3.123(4)	0.91(3)	2.43(3)	133(4)
N(2)-H(4)·····F(3^{vi})	3.203(4)	0.91(3)	2.43(4)	142(4)
N(2)-H(5)·····F(1^{v})	3.036(4)	0.90(4)	2.66(4)	106(3)
N(2)-H(5)·····F(1^{i})	3.120(4)	0.90(4)	2.52(5)	124(3)
N(2)-H(5)·····F(2^{i})	3.092(4)	0.90(4)	2.69(5)	108(3)

Symmetry code: (i)	1-x, 1-y, 1-z
(ii)	-x, 1-y, 1-z
(iii)	1/2-x, 1/2+y, 3/2-z
(iv)	-1/2+x, 1/2-y, 1/2+z
(v)	-1+x, y, z
(vi)	-x, -y, 1-z

*The torsion angles are taken as positive if the bond in front has to be turned clockwise in order to eclipse the rear bond.

EXPERIMENTAL

Preparation of the sample

$(N_2H_6)_2(GeF_6)F_2$ was prepared by reaction of $N_2H_6F_2$ with fluorogermanic acid in a 2:1 molar ratio. The crystals were obtained by slow evaporation of a solution at higher temperature. Reaction of a 50% solution of hydrazine hydrate and fluorogermanic acid yielded a solution from which $(N_2H_5)_2GeF_6$ was isolated as colourless crystals after addition of 95% ethylalcohol.

Chemical analysis

Hydrazine was determined potentiometrically by potassium iodate titration [12], fluorine by a modified Wilhard-Winter distillation [13] and germanium by atomic absorption spectroscopy [14].

$(N_2H_6)_2(GeF_6)F_2$: Found, N_2H_4, 22.3; Ge, 25.1; F, 51.2; Calc., N_2H_4, 21.89; Ge, 24.80; F, 51.93

$(N_2H_5)_2GeF_6$: Found, N_2H_4, 25.7; Ge, 28.5; F, 45.0; Calc., N_2H_4, 25.36; Ge, 28.73; F, 45.11

The infrared spectra of Nujol mulls pressed between CsBr plates were obtained using a Perkin-Elmer 521 spectrometer. The Raman spectra of the solids in a Pyrex tube were recorded on a Spex 1401 spectrometer with Ar^+ (5145 Å) excitation from a Coherent Radiation mode CR-3 laser.

X-ray diffraction on monocrystals

Several transparent single crystals were sealed in glass capillaries. Preliminary examinations on Weissenberg and precession cameras suggested the space group $P\,2_1/n$ (No. 14). Precise cell dimensions were obtained by least-squares from the 2Θ values of 60 moderately high-order reflexions measured on a CAD-4 diffractometer. Reflexions were scanned in the ω- 2Θ mode (moving crystal-moving counter) with a variable scan rate. Crystal data and a data collection summary are given in Table 2. The diffraction data were corrected for variations in reference reflexions and Lorentz-polarization effects. An exact absorption correction ($\mu = 44.09\ \mathrm{cm}^{-1}$), based on known crystal faces, was also performed.

The value $Z = 2$ for the space group $P\,2_1/n$ suggested the initial position of 0.5, 0.5, 0.5 for the germanium atom. A subsequent electron-density map revealed the remaining non-hydrogen atoms. The structure was refined by full-matrix least-squares, minimizing $\Sigma w(|F_o| - k|F_c|)^2$, where w was chosen to keep $\Sigma w(\Delta F)^2$ uniform over the ranges of $(\sin\Theta)/\lambda$ and $|F_o|$. At this stage, with the anisotropic temperature factors, the conventional R-value was 0.052. The positions of the five hydrogen atoms were determined by a difference synthesis and were introduced in the refinement with a common isotropic temperature factor. A constraint was also imposed on nitrogen-hydrogen bonds. An empirical isotropic extinction parameter x was refined to 0.008 (3). The final R and R_w values were 0.043 and 0.046 for 1152 contributing reflexions. The weighting scheme was $w = 2.1\,[\sigma^2(F_o)+0.001\,F_o^2]$. The final difference synthesis revealed no peak higher than 0.3 $e.\text{Å}^{-3}$. In the final refinement cycle, the average and maximum shift/error for the refined parameters were 0.17 and 1.48, respectively, for the x coordinate of H (3). Scattering factors for Ge, F and N were those given in reference 15 and for H were obtained from reference 16. Final atomic coordinates are given in Table 4; interatomic distances, bond angles and torsion angles are collected in Table 3. Lists of structure factors and anisotropic temperature factors are available on request from the authors. All calculations were performed on the DEC-10 computer at RCU Ljubljana with the SHELX-76 [18] system of crystallographic programmes.

TABLE 4

Fractional atomic coordinates (x 10^4 for Ge, F, N; x 10^3 for H) and equivalent isotropic temperature factor U_{eq} (x 10^4) [17] for non-hydrogen and isotropic U_{iso} (x 10^3) for H atoms

	x	y	z	U_{eq}	or	U_{iso}
Ge	5000	5000	5000	166(2)		
F(1)	7279(3)	3535(4)	4435(2)	278(9)		
F(2)	4454(4)	6975(4)	3684(2)	277(9)		
F(3)	3038(4)	2695(4)	4203(2)	276(9)		
N(1)	315(4)	3985(6)	7227(3)	249(12)		
N(2)	664(5)	1653(5)	6594(3)	255(11)		
H(1)	-58(9)	508(7)	673(4)			37(6)
H(2)	167(6)	465(8)	757(6)			37(6)
H(3)	-39(7)	345(8)	784(3)			37(6)
H(4)	-78(5)	112(9)	631(5)			37(6)
H(5)	108(8)	216(9)	589(3)			37(6)

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