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SYNTHESIS AND CHARACTERIZATION OF HYDRAZINIUM(2+) TETRAFLUOROBORATE(III)

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SUMMARY

The reaction between hydrazinium(2+) fluoride and boron trifluoride in anhydrous hydrogen fluoride yielded slightly soluble hydrazinium(2+) tetrafluoroborate. It was characterized by chemical analysis, vibrational spectra and thermal analysis. An X-ray diffraction study showed that crystals of $N_2H_6(BF_4)_2$ are triclinic, space group $P\bar{1}$ (No. 2). There are discrete $N_2H_6^{2+}$ and BF_4^- units in the crystals interlinked by hydrogen bonds of the type N-H...F..

INTRODUCTION

In recent years, a number of new hydrazinium(1+) and (2+) compounds have been isolated and characterized. These were prepared either from aqueous solution [1], or from anhydrous hydrogen fluoride [2,3].

Hydrazinium(1+) tetrafluoroborate has been isolated, by mixing a solution of hydrazinium hydrate with slightly more than the stoicheiometric quantity of fluoroboric acid solution, by Funk and Binder [4]. An attempt to prepare the analogous hydrazinium(2+) compound from aqueous solution failed, however, in anhydrous hydrogen fluoride, we found that hydrazinium(2+) fluoride reacted with boron trifluoride giving colourless needle-like crystals, slightly soluble in the solvent. Thermal analysis of the compound showed that its decomposition occured through the intermediate $N_2H_5BF_4$.

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RESULTS AND DISCUSSION

The tetrafluoroborate ion belongs to the point-group T_d and therefore the isolated anion has four normal modes of vibration: $\nu_1(A_1)$, $\nu_2(E)$, $\nu_3(T_2)$ and $\nu_4(T_2)$. All are active in the Raman, but only ν_3 and ν_4 are active in the infrared. The vibrational spectrum of $N_2H_6(BF_4)_2$ and its assignment are given in Table 1.

In the Raman spectrum of $N_2H_6(BF_4)_2$ the most intensive line observed at 776 cm^{-1} clearly corresponds to the ν_1 mode. Though this is a forbidden transition in the infrared region, it is also observed in the infrared spectrum of $N_2H_6(BF_4)_2$, suggesting distortion of the tetrahedron. The double degenerate ν_2 mode is observed as the weak Raman lines at 348 and 360 cm^{-1}, and the ν_3 mode occurs at 975 cm^{-1}. The structure of the bands of the ν_3 mode is more complex in the infrared region and appears to have five components. The band at 1310 cm^{-1} in the infrared spectrum is attributed to $(\nu_1 + \nu_4)$. The bands observed at 1575 and 1615 cm^{-1} in the infrared spectrum and at 1050 cm^{-1} in the Raman are assigned to the vibration of the $(N_2H_6^{2+})$ group. No bands other than those attributed to $N_2H_6^{2+}$ and BF_4^- ions appear in the vibrational spectrum of the compound.

TABLE 1

Vibrational spectrum (cm^{-1}) of $N_2H_6(BF_4)_2$

$N_2H_6(BF_4)_2$			KBF_4 [5]
IR	R	Assignment	IR
	348 (18) 360 (12)	$\nu_2 BF_4^-$	
515 sh	524 (7) sh		526
525 s	535 (26)	$\nu_4 BF_4^-$	536
775 m	776 (100)	$\nu_1 BF_4^-$	773
995 s,br	975 (9)	$\nu_3 BF_4^-$	1038
	1050 (44)	$\nu(N-N)_s$	1063
1050 s,br			1078
1080 s,br			1088
1135 s,br		$\nu_3 BF_4^-$	1107
1163 sh			1128
1310 m		$(\nu_1 + \nu_4)BF_4^-$	1312
			1330
1575 s		$\nu(NH_3^+)_d$	
1615 w			

Thermal analysis of $N_2H_6(BF_4)_2$ was also investigated (Figure 1),and confirmed the formation of the intermediate $N_2H_5BF_4$. Decomposition starts at 80°C in an argon atmosphere. In the first step, between 80°C and 253°C, the sample losses 42.0 % of its weight. The observed weight loss is equivalent to the loss of one mole of boron trifluoride and one mole of hydrogen fluoride (calculated weight loss is 42.25 %). This part of the decomposition is accompanied by an endothermic DTA peak at 200°C and a DTG minimum at the same temperature. Further decomposition occurs in the dynamic run (6°C/min) immediately and ends at 375°C with a weight loss of 57.5 %. An exothermic DTA peak at 265°C and two endothermic peaks at 363°C and 370°C accompany this step. DTG minima are observed at 265°, 350°, 360° and 370°C. The complex structure of this second decomposition suggests also simultaneous decomposition of hydrazine.

$N_2H_6(BF_4)_2$ decomposes according to the following equations (1)and(2)

$$N_2H_6(BF_4)_2 \longrightarrow N_2H_5BF_4 + BF_3 + HF \qquad (1)$$

$$N_2H_5BF_4 \longrightarrow BF_3 + N_2H_4 + HF \qquad (2)$$

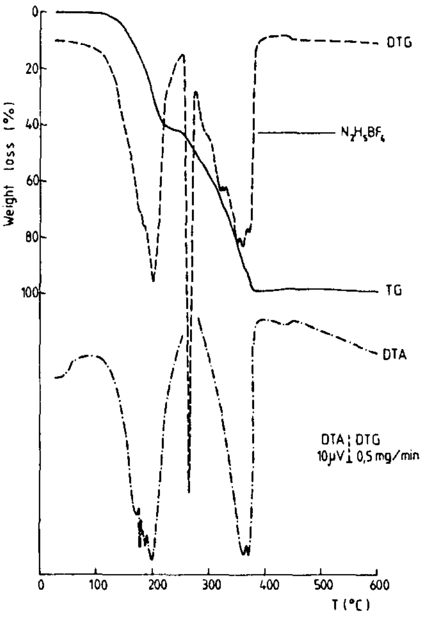

Fig. 1. TG, DTG and DTA curves for the decomposition of $N_2H_6(BF_4)_2$

Description of the structure

A view of the structure along the [100] direction is given in Figure 2. The crystal contains BF_4^- tetrahedra and $N_2H_6^{2+}$ units. Space-group constraints require the $N_2H_6^{2+}$ cation to be centrosymmetric and, therefore, in a trans (staggered) conformation. The N-N distance of 1.416(4) Å is shorter than the average value of 1.427(2) Å found in $N_2H_6SO_4$ [6], $N_2H_6SiF_6$ [7] and $N_2H_6GeF_6.H_2O$ [8], and very close to 1.417(6) Å found in $N_2H_6BeF_4$ [9]. The hydrogen atoms, H(1), H(2) and H(3) are found at 0.94(5), 1.04(8) and 0.98(8) Å from the N atom and form nearly tetrahedral angles (average values: N-N-H = 111(4)°; H-N-H = 108(6)°). The F atoms are tetrahedrally arranged around the B atom, forming a slightly distorted tetrahedron. The B-F lengths, in the range from 1.378(4) to 1.403(5) Å, are close to the reported values of 1.33 - 1.38 Å in $N_2H_5BF_4$ [10] and 1.362 - 1.389 Å in NH_4BF_4 [11]. The $N_2H_6^{2+}$ and BF_4^- ions are held together by a network of polyfurcated hydrogen bonds (Table 2) N-H...F, with the N-F distances in the range 2.683(4) - 3.026(5) Å.

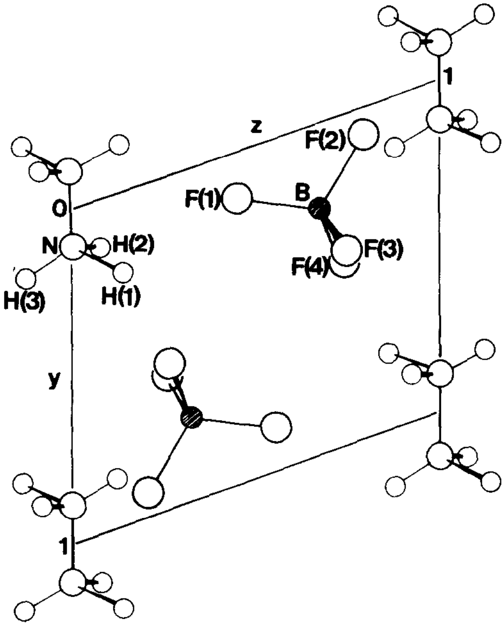

Fig. 2. A view of the unit cell of $N_2H_6(BF_4)_2$ along [100]

TABLE 2

Interatomic distances (Å) and angles (°)

BF_4^- tetrahedron

B-F(1)	1.378(4)	F(1)-B-F(2)	109.8(3)
B-F(2)	1.403(5)	F(1)-B-F(3)	110.5(3)
B-F(3)	1.382(5)	F(1)-B-F(4)	109.9(3)
B-F(4)	1.385(5)	F(2)-B-F(3)	107.6(3)
		F(2)-B-F(4)	107.3(3)
		F(3)-B-F(4)	111.7(3)

$N_2H_6^{2+}$ ion

N-N^i	1.416(5)	N^i-N-H(1)	116(5)
N-H(1)	0.94(5)	N^i-N-H(2)	113(5)
N-H(2)	1.04(8)	N^i-N-H(3)	107(5)
N-H(3)	0.98(8)	H(1)-N-H(2)	96(6)
		H(1)-N-H(3)	116(6)
		H(2)-N-H(3)	112(6)

Hydrogen-bond distances and angles

D-H...A	D-A	D-H	H...A	D-H...A
N-H(1)...F(1)	2.683(4)	0.94(5)	2.16(8)	114(6)
N-H(1)...F(3^v)	2.781(4)	0.94(5)	1.95(7)	147(8)
N-H(1)...F(4^{ii})	2.713(4)	0.94(5)	2.38(8)	101(6)
N-H(2)...F(2^{iii})	2.877(4)	1.04(8)	2.30(6)	114(5)
N-H(2)...F(2^{iv})	2.797(5)	1.04(8)	1.98(9)	134(7)
N-H(2)...F(4^{ii})	2.713(4)	1.04(8)	2.20(8)	108(5)
N-H(3)...F(1^i)	2.734(4)	0.98(8)	2.08(6)	123(6)
N-H(3)...F(2^{vi})	2.978(5)	0.98(8)	2.68(9)	98(5)
N-H(3)...F(2^{iii})	2.877(5)	0.98(8)	2.68(8)	92(6)
N-H(3)...F(3^{iii})	3.019(4)	0.98(8)	2.35(9)	125(6)
N-H(3)...F(3^{vi})	3.026(5)	0.98(8)	2.31(9)	130(5)

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

EXPERIMENTAL

Starting materials Hydrazinium(2+) fluoride was prepared by neutralization of hydrazine hydrate with hydrofluoric acid [12]. Boron trifluoride was prepared by fluorination of B_2O_3 or by reaction of elemental boron with uranium hexafluoride [13,14]. Commercial anhydrous hydrogen fluoride was purified by absorption-desorption using sodium fluoride in a nickel container [15].

Preparation of the sample Approximately 3 millimoles of hydrazinium(2+) fluoride were loaded into an all-KelF reaction vessel. About 4 grammes of anhydrous hydrogen fluoride was distilled onto the hydrazinium(2+) fluoride in an all-KelF vacuum line. Boron trifluoride was added stepwise and a slightly soluble compound appeared. After removal of volatiles at room temperature, the crystalline tetrafluoroborate was isolated.

Chemical analysis Hydrazine was determined potentiometrically by potassium iodate titration [16] and tetrafluoroborate ion was determined as nitron tetrafluoroborate[17]. Chemical analysis of $N_2H_6(BF_4)_2$: found, N_2H_4, 15.4; BF_4^-, 83.4; calc., N_2H_4, 15.41; BF_4^-, 83.62.

Infrared spectra of the powdered solid on silver chloride windows were obtained using a Zeiss UR-20 spectrophotometer. The solid was prepared in a dry box. The Raman spectrum of the solid contained in a glass tube was recorded with a homebuilt spectrometer using a Spex 1401 double monochromator with an Ar^+ laser.

Thermoanalytical data were obtained using a Mettler TA 1 Thermoanalyzer in an argon atmosphere and a flow rate of 5 litres per hour. The heating rate was 6°C per minute.

Single-crystal examination Because of twinning several crystals were examined by photographic methods before a suitable single crystal, sealed in a quartz capillary, with dimensions 0.4 x 0.4 x 0.3 mm, was selected for data collection. Exact cell dimensions were obtained by least-squares from 2θ values of 60 reflexions measured on an Enraf-Nonius CAD-4 diffractometer. Reflexions were scanned in the $\omega - 2\theta$ mode (moving crystal-moving counter) with a variable scan rate. Other details of the data collection and reduction are given in Table 3. The diffraction data were corrected for variation in reference reflexions and Lorentz-polarization effects, but not for absorption.

TABLE 3

Data-collection details for $N_2H_6(BF_4)_2$

Temperature (K)	293(1)
Diffractometer	CAD-4, automated, four-circle
X-radiation	MoK_α (λ = 0.71096 Å)
2θ scan width (°)	$0.8 \pm 0.2 \tan\theta$
Scan rate ($^\circ min^{-1}$)	min.: 2.9; max.: 20.1
Background	1/4 of the scan time at each of the scan limits
$2\theta_{max}$ (°)	54
Maximum scan time (s)	40
Aperture (mm)	$2.5 \pm 0.9 \tan\theta$
Reference reflexions	0 1 2, 2-1-1, 1 0 2
Measured reflexions	1432 ($\pm h$, $\pm k$, $\pm l$)
Observed reflexions	479
Unobserved reflexions	188 [$I < 2\sigma(I)$]
Discrepancy on I (%)	2.2 for 1400 refls.
(I) base	Counting statistics

Multisolution Σ_2 sign expansion [18] located all nonhydrogen atoms. Isotropic full-matrix least-squares refinement proceeded to R = 0.112, and subsequent anisotropic refinement gave R = 0.061. The hydrogen atoms were clearly visible in a difference Fourier map calculated at this stage. The refinement continued with constraint imposed on N-H bonds and a common isotropic temperature factor was used for hydrogen atoms. The final conventional R and R_w values were 0.047 and 0.049 for 479 observed reflexions. The least-squares weights were calculated from $w = 1.06/[\sigma^2(F_o) + 0.002 F_o^2]$. A final difference map showed no peaks greater than 0.19 $eÅ^{-3}$. The average shift/error in the last least-squares cycle was 0.22 with a maximum of 0.79 for z of H(2). Final atomic coordinates are given in Table 4, interatomic distances and bond angles are in Table 2. Lists of structure factors are available on request from the authors.

TABLE 4

Final fractional coordinates (x 10^4 for B, N, F; x 10^3 for H) and equivalent isotropic temperature factor U_{eq} (x 10^4) [20] for non-hydrogen and isotropic U_{iso} (x 10^3) for H atoms

	x	y	z	U_{eq} or U_{iso}
B	3499(8)	2743(8)	6847(6)	237(17)
F(1)	2375(4)	1453(4)	4495(3)	334(11)
F(2)	3815(4)	0845(4)	7986(4)	359(11)
F(3)	6070(5)	4283(5)	7481(4)	420(12)
F(4)	1745(5)	4273(5)	7542(4)	472(13)
N	-0371(6)	1270(6)	0163(5)	243(13)
H(1)	097(13)	260(13)	144(12)	127(15)
H(2)	-196(12)	144(16)	079(12)	127(15)
H(3)	-083(16)	160(16)	-131(11)	127(15)

Scattering factors were those included in SHELX-76 which was used in the calculations on the DEC-10 computer at RCU, 'E. Kardelj' University Ljubljana. The DATCOR program of X RAY-80 [19] was used for the data reduction procedure.

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