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Scientific paper

Non-spherical atom refinement applied in structure determination of $(N_2H_6)(H_3F_4)_2$ and crystal structure re-determination of $N_2H_6F_2$

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The author of this work was personally invited by Professor Boris Žemva to join his research team at the Jožef Stefan Institute in 2004. This invitation proved fateful and essentially determined the course of the author's entire future life. Boris Žemva will always be remembered as a renowned scientist, a good friend, and a man with a big heart.

Abstract

Hydrazinium trihydrogen tetrafluoride was synthesized and its structure investigated. Its crystal structure, determined by single-crystal X-ray diffraction, consists of $N_2H_6^{2+}$ dications and trigonal $H_3F_4^-$ anions interconnected via a complex system of N–H···F hydrogen bonds. The crystal structure of hydrazinium fluoride was redetermined. For more accurate determination of hydrogen atoms positions, non-spherical atom refinement was performed for both structures.

Keywords: hydrazinium, fluoride, non-spherical atom refinement

1. Introduction

Hydrazine has long been known and widely used in various fields.[1] Due to its basic properties, it forms a wide range of mono- and di-protonated salts. It should be noted that mono-protonated salts are more easily formed: the CCDC contains nearly 300 records with the $NH_2–NH_3^+$ cation,[2] but only 20 records concerning $(NH_3–NH_3)^{2+}$ dications. In the case of fluorine-containing anions, di-protonated hydrazinium salts can be readily obtained. A few fluoro- and hydrofluoro-derivatives have been structurally studied, including $(N_2H_5)F$,[3] $(N_2H_5)(HF_2)(HF)_2$,[4] $(N_2H_6)F_2$.[5] The family of hydrazinium fluoridometallates is much more extensively represented; a significant number were prepared and characterized by Slovenian researchers at the Jožef Stefan Institute and the University of Ljubljana: $(N_2H_6)_2F_2(TiF_6)$,[6] $(N_2H_6)_2F_2(GeF_6)$ and $(N_2H_6)(SbF_5)$,[7] $(N_2H_5)_2GeF_6$ and $(N_2H_6)_2(GeF_6)F_2$,[8] $(N_2H_6)_2(SnF_6)F_2$,[9] $(N_2H_5)_2(TiF_6)$,[10] $(N_2H_6)SbF_5$,[11] $(N_2H_6)(SbF_6)_2$ and $(N_2H_6)(Sb_2F_{11})_2$,[12] $(N_2H_6)_3(TaF_8)(TaF_7)HF_2$.[13] All of these compounds are distinguished by the presence of a diverse system of hydrogen bonds,[14,15] and the peculiarity of proton tunnelling has been studied in a series of compounds with the formula $(N_2H_5)_2HMF_6{\cdot}2H_2O$ (M = Ga, Fe).[16] Besides pure academic interest, practical applications have been reported for these compounds. The thermal decomposition of hydrazinium(1+) and hydrazinium(2+) fluoroaluminates is accompanied by the release of a large volume of gaseous products, resulting in inorganic fluorides with a high specific surface area.[17] The use of hydrazinium(1+) and hydrazinium(2+) coordination compounds in self-propagating high-temperature synthesis is a convenient method for producing nanomaterials.[18,19]

Major syntheses of the above salts were performed in hydrofluoric acid. It should be noted that the fluoride anion in HF media forms a range of anions such as HF_2^-, $H_2F_3^-$, $H_3F_4^-$, and others. Surprisingly, only one hydrazinium HF_2^- salt has been reported previously. To expand the family of fluorine-containing hydrazinium salts, hydrazinium trihydrogen tetrafluoride was synthesized and structurally characterized. This hydrogen-rich salt exhibits a variety of hydrogen bonds. To improve the quality of hydrogen bond characterization, the structure was refined using aspherical form factors (NoSpherA2 procedure).[20] The same approach was used to re-investigate the crystal structure of hydrazinium difluoride,

whose structure was published in 1942 and whose quality is clearly suboptimal.[5] The results are presented in this article.

1.1. Experimental section

All chemicals were of commercial origin: HF (Riedel-de Haen AG, 66%), Hydrazine hydrate 25% aqueous solution Fluka, ethanol (Carlo Erba, p.a) were used as supplied. Anhydrous HF (Linde AG, 99.995%) was treated with K_2NiF_6 (Advance Research Chemicals Inc., 99.9%) for several hours before use and was usually kept in FEP vessels above K_2NiF_6.

CAUTION! Anhydrous HF and some fluorides are highly toxic and must be handled in a well-ventilated fume hood, and protective clothing must be worn all the time!

1.2. Syntheses

70 mg (~1 mmol) of $N_2H_6F_2$ were loaded into reaction vessel [21] inside a drybox. Solvent (anhydrous HF, 3 mL) was condensed onto the reactant at 77 K, and the reaction mixture was warmed to ambient temperature. The resulting clear solution was decanted into the 6 mm o.d. side arm. Evaporation of the solvent from this side arm was carried out by maintaining a temperature gradient of ~10–20 °C between both tubes for one week. Slow distillation of aHF from the 6 mm o.d. tube into the 19 mm o.d. tube resulted in growth of $N_2H_6(H_3F_4)_2$ (**1**) salt crystals inside the 6 mm o.d. tube (yield ~90%). Crystals were immersed in perfluorodecalin (m.p. 263 K) inside a drybox, selected under a microscope, and mounted on the goniometer head of the diffractometer in a cold nitrogen stream.

Hydrazinium hydrate 25% aqueous solution (0.5 mL, 2.5 mmol) and 66% hydrofluoric acid aqueous solution (molar ratio 1:2.5 … 5) were dissolved in ethanol (~3 mL). After one day, crystals of the $(N_2H_6)F_2$ salt were obtained, yield ~70%.

1.3. X-ray structure determination

Single-crystal X-ray data for both compounds were collected on a Gemini A diffractometer with an Atlas CCD detector, using graphite monochromated Mo-Kα radiation. The data were processed using the *CrysAlisPro* program package.[22] An analytical absorption correction was applied to the data set. The structure was solved using the dual-space algorithm of the program *SHELXT* and the structure refinement was performed using the software *SHELXL*-2014,[23,24] both of which are implemented in the crystallographic software *Olex2*.[25] The positions of hydrogen atoms bound to nitrogen were found on difference Fourier maps and refined freely.

At the second stage, non-spherical atom refinement was performed using the NoSpherA2 procedure implemented in the *Olex2* software.[20] Theoretical wavefunctions were calculated using ORCA 6.1 software,[26] with the r^{2}SCAN method and the def2-SVP basis set. Integration accuracy was set to Normal. Water was chosen as the solvation medium. The high quality of diffraction data for compound **2** (resolution d = 0.5 Å, $I/\sigma(I)$ = 89) and the small number of refined parameters due to the highly symmetrical structure allow the thermal parameters of the hydrogen atoms to be refined anisotropically. A summary of the crystallographic data and structure refinement is given in Table 1, geometric parameters are listed in Table 2. CCDC-2500631 (**1**) and CCDC-2500630 (**2**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via https://www.ccdc.cam.ac.uk/structures/.

Table 1. Crystallographic data, details of data collection and structure refinement parameters

Compound	$(N_2H_6)(H_3F_4)_2$ (**1**)		$(N_2H_6)F_2$ (**2**)	
Formula	$F_8H_{12}N_2$		$F_2H_6N_2$	
M [g mol^{-1}]	192.096		72.07	
T [K]	150		100	
Crystal system	orthorhombic		trigonal	
Space group	$Pna2_1$		$R\bar{3}m$	
a [Å]	13.8306(4)		4.41778(15)	
b [Å]	14.3902(4)		4.41778(15)	
c [Å]	7.8458(2)		14.2871(5)	
V [Å^3]	1561.51(7)		241.481(18)	
Z	8		3	
F(000)	785		114	
ρ_{calcd} [g cm^{-3}]	1.634		1.487	
Radiation, λ [Å]	Mo $K\alpha$, 0.71073		Mo $K\alpha$, 0.71073	
μ [mm^{-1}]	0.235		0.181	
Refinement	**IAM**	**NoSpherA2**	**IAM**	**NoSpherA2**
Goodness-of-fit on F^2	1.087	1.067	1.202	1.275
Final R_1 *[I > 2σ(I)]*	0.029	0.028	0.026	0.018
Final R_1 *(all data)*	0.034	0.032	0.026	0.018
wR_2 *[I > 2σ(I)]*	0.068	0.060	0.076	0.052
wR_2 (all data)	0.070	0.062	0.076	0.052
Largest diff. peak and hole (e Å^{-3})	0.23, –0.20	0.22, –0.25	0.55, –0.22	0.37, –0.18

1.4. Raman spectroscopy

Raman spectra with a resolution of 0.5 cm^{-1} were recorded at room temperature on a Horiba Jobin Yvon LabRam-HR spectrometer equipped with an Olympus BXFM-ILHS microscope. Samples were excited by the 632.8 nm emission line of a He–Ne laser with a regulated power in the range 20–0.0020 mW, which gave 17–0.0017 mW focused on a 1 μm spot through a 50× microscope objective on the top surface of the sample. Raman spectrum of compounds **1** and **2** are shown in Figures 4 and 5, respectively.

2. Results and discussion

2.1. Non-spherical atom refinement comparatively to Independent-Atoms-Model

Standard refinement of the crystal structure, as implemented for example in *ShelXL* software,[23] is based on the spherical approximation of the electron density distribution around each atom (Independent-Atom-Model, IAM). This approach does not account for the participation of electrons in chemical bonding. This simplification of calculations most significantly affects the determination of hydrogen atoms positions, as their single electron is highly susceptible to influence due to involvement in chemical bonds. By using non-spherical atom refinement, hydrogen atom positions can be determined from X-ray data with the same accuracy as is possible with neutron diffraction experiments.[27] Because both investigated salts (especially **1**) are hydrogen-rich compounds, it was decided to perform non-spherical atom refinement of their crystal structures. As shown in Table 1, in both cases, non-spherical atom refinement yields lower R-values and, in the case of structure **2**, a smaller difference between the highest peak and deepest hole in the residual electron density values. Furthermore, the accuracy of bond lengths after non-spherical atom refinement is noticeably higher than after IAM refinement. Consequently, only the results of NoSpherA2 refinement will be used for further discussion.

2.2. Crystal structure of 1

The compound $(N_2H_6)(H_3F_4)_2$ (**1**) crystallizes in the orthorhombic space group $Pna2_1$. The asymmetric part of the unit cell contains two hydrazinium dications and four $H_3F_4^-$ anions (Figure 1). The N–N bond lengths differ noticeably from previously published values. The N1–N2 distance is 1.4035(13) Å, and the N3–N4 bond length is 1.393(2) Å. These values are much closer to those obtained by neutron diffraction study of hydrazinium sulphate,[28] whereas a search in the CCDC gives (X-ray diffraction and IAM refinement based) values around 1.44 Å. The N–H distances range from 0.90(3) to 1.05(2) Å, which again corresponds well to the results of neutron diffraction. It is worth noting, that standard IAM refinement results in N–H bond lengths shorter than 0.9 Å. Both dications exhibit staggered conformation with H–N–N–H torsion angles of 62.9 and 64.5°.

The $H_3F_4^-$ anions exhibit slightly deformed geometry, with $F_{terminal}$–$F_{central}$ distances ranging from 2.3119(11) to 2.3726(11) Å. These values are slightly shorter than those found in KH_3F_4 salt,[29] and are within the same range as the F…F distances in $(CH_3)_4N(H_3F_4)$.[30] The $F_{terminal}$–$F_{central}$–$F_{terminal}$ angles vary from 110.6° to 127.3°. This deviation from regular trigonal-planar geometry is much greater than in both of the above-mentioned salts. The H–$F_{terminal}$ distances are 0.92(3)–1.05(2) Å, which is similar to the values 0.965(7)–1.061(4) Å obtained by neutron diffraction study of hydrazinium sulphate.[28] Thermal ellipsoids of the central fluorine atom in each of the four $H_3F_4^-$ anions are markedly elongated in directions perpendicular to the plane of the entire anion. A similar shape of thermal ellipsoids was also observed in $Ba(H_3F_4)_2$ salt.[31]

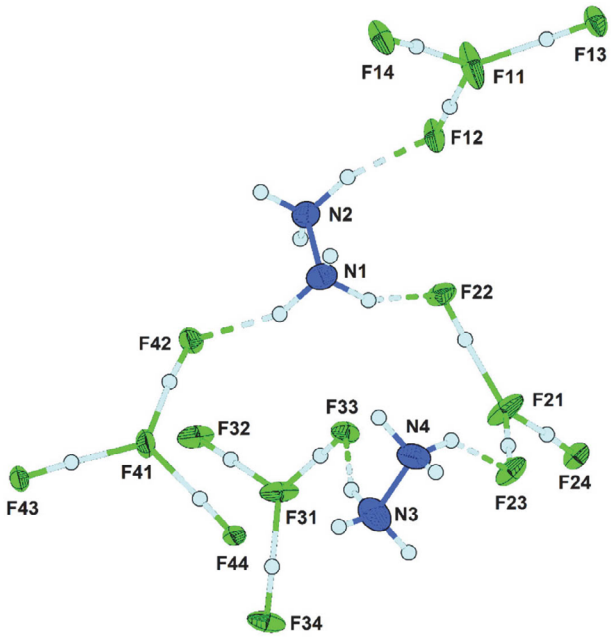

Figure 1. Crystallographically independent part of crystal structure **1**. Thermal ellipsoids are drawn at 50% probability.

The crystal structure of **1** contains an extensive system of hydrogen bonds involving all hydrogen atoms from the hydrazinium moieties. The N···F distances of 2.687–2.798 Å indicate rather strong hydrogen bonds. Each dication is linked to six anions, and each anion, in turn, is bound to three hydrazinium units, resulting in the formation of three-dimensional structure.

2.3. Re-determination of $N_2H_6F_2$ crystal structure

As was already reported, hydrazinium difluoride crystallizes in a trigonal $R\bar{3}m$ space group.[5] The asymmetric unit contains only one nitrogen, one hydrogen, and one fluorine atom. All atoms occupy special positions: F and N at the 6*c* Wyckoff positions (site symmetry 3*m*), and H at 18h (site symmetry *m*). The N–N distance is 1.4434(5) Å, and the N–H distance is 1.041(8) Å. It should be noted that the N–N distance is longer than that in compound **1**, probably due to the presence of fluoride anions instead of trihydrogen tetrafluorides in **1**, resulting in stronger polarization of the hydrazinium cation. The N···F distance of 2.61363(11) Å agrees well with the reported value of 2.61 Å in reference.[5] The N–N···F angle of 110° also corresponds well to the previously reported value.[5] The hydrazinium dication fully realizes its coordination properties,

Table 2. Selected bond lengths /Å and angles /° values in structures **1** and **2.** Results of NoSperA2 refinement are typed in bold.

Compound $(N_2H_6)(H_3F_4)_2$ (1)			
F24—H24	0.89(6)	N2—N1	1.414(2)
	1.04(4)		**1.4056(13)**
F33—H33	0.84(5)	N2—H2A	0.90(3)
	0.97(3)		**1.00(2)**
F12—H12	0.99(4)	N2—H2B	0.98(3)
	1.01(2)		**1.08(3)**
F43—H43	0.84(5)	N2—H2C	0.82(3)
	1.00(3)		**0.96(3)**
F42—H42	0.85(4)	N1—H1A	0.92(3)
	0.98(3)		**1.02(2)**
F13—H13	0.86(3)	N1—H1B	0.92(3)
	0.95(2)		**1.05(2)**
F44—H44	0.81(5)	N1—H1C	0.90(4)
	0.98(3)		**1.01(3)**
F23—H23	0.90(5)	N4—N3	1.402(2)
	1.08(3)		**1.3935(15)**
F14—H14	0.89(5)	N4—H4A	0.94(4)
	0.93(4)		**1.03(3)**
F22—H22	0.78(4)	N4—H4B	0.88(4)
	0.95(3)		**0.95(3)**
F34—H34	0.85(5)	N4—H4C	0.93(5)
	0.99(3)		**0.91(3)**
F32—H32	0.87(5)	N3—H3A	0.78(4)
	0.97(3)		**0.91(3)**
F21—H23	1.41(5)	N3—H3B	1.02(5)
	1.23(3)		**1.03(3)**
F11—H12	1.32(4)	N3—H3C	0.91(5)
	1.30(3)		**0.90(4)**
F11—H14	1.46(5)		
	1.42(4)		
Compound $(N_2H_6)F_2$ (2)			
N1—$N1^{i}$	1.4451(7)	N1—H1	0.875(13)
	1.4438(4)		**1.037(8)**
$N1^{i}$—N1—H1	107.9(7)	$H1^{ii}$—N1—$H1^{iii}$	111.0(7)
	110.7(3)		**110.69(15)**

Symmetry codes: (i) $-x + 2/3, -y + 4/3, -z + 4/3$; (ii) $-y + 1, x - y + 1, z$; (iii) $-x + y, -x + 1, z$.

forming strong hydrogen bonds with six F^- centers. In turn, each anion is connected to three H(N) centers. Interestingly, the geometry of the fluoride anion environment is slightly pyramidal, with a deviation of the fluoride anion by 0.26 Å from the plane of the three connected hydrogen atoms and H···F···H angles of 3 × 117.4°. Due to hydrogen bonding, the cations and anions in **2** are interconnected into a layered structure (Figure 3). Further association of these layers occurs through weak interactions only.

2.4. Raman spectra of salts 1 and 2

A strong peak observed at 1035 cm^{-1} (**1**, Fig. 4) and at 1039 cm^{-1} (**2**, Fig. 5) could be attributed to the N–N stretching vibration of the cation and it appears in the Raman spectra of all hydrazinium(2+) salts in the narrow region around 1030 cm^{-1}, this band is usually very intense.[16] Medium intensity peaks at 285 cm^{-1} could be as-

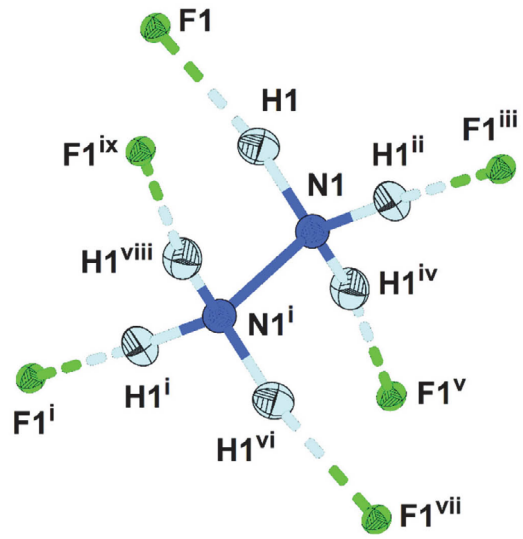

Figure 2. Hydrazinium(2+) cation surrounded by F^- anions in structure **2**. Thermal ellipsoids are drawn at 50% probability.

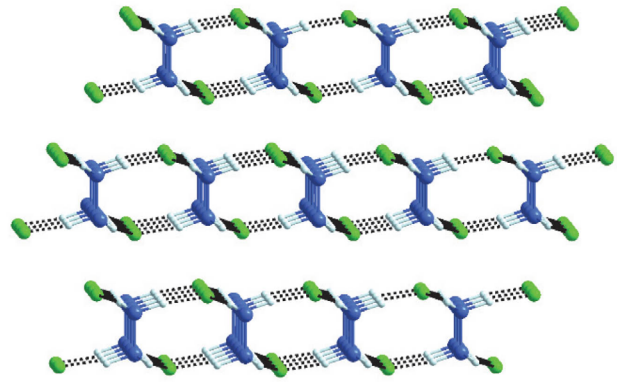

Figure 3. Packing diagram of compound **2**.

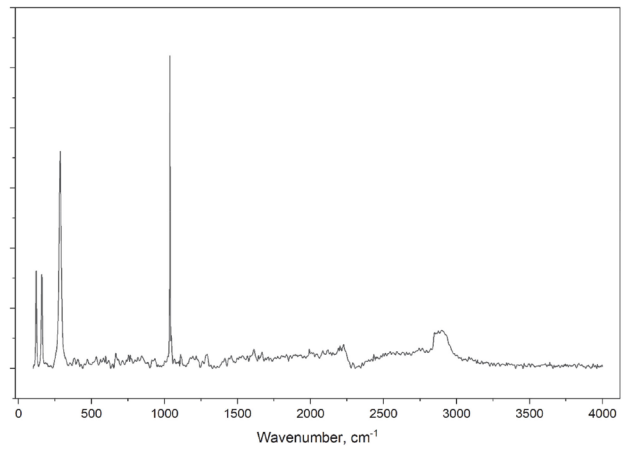

Figure 4. Raman spectrum of $N_2H_6(H_3F_4)_2$

signed to torsion modes of hydrazinium dications. Corresponding peaks were observed at 290–300 cm^{-1} in the Raman spectra of $(N_2H_6)TiF_6$ and $(N_2H_6)_2[TiF_6]F_2$.[32] Peaks observed at wavenumbers lower than 200 cm^{-1} can probably be attributed to lattice vibrations. The N–H bands appear in the range from 2800 to 3000 cm^{-1}. In both compounds **1** and **2**, these peaks are less visible. It should also be noted that the spectrum of $(N_2H_6)(H_3F_4)_2$ suffers from noticeable fluorescence, which makes the overall quality rather poor.

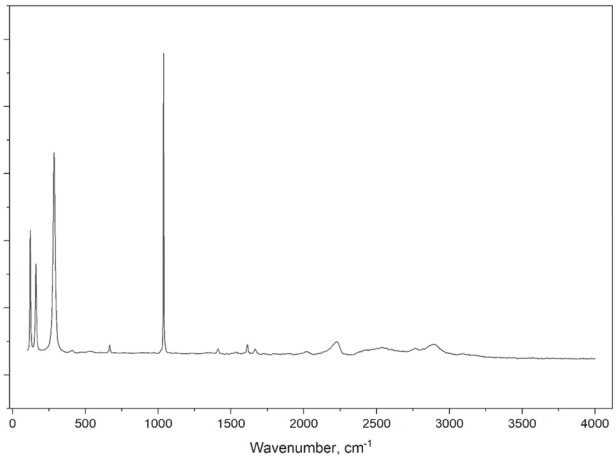

Figure 5. Raman spectrum of $N_2H_6F_2$

3. Conclusions

A new hydrazinium salt, trihydrogen tetrafluoride, was obtained and structurally investigated. The crystal structure of hydrazinium difluoride was redetermined. Non-spherical atom refinement performed for both structures has demonstrated significant advantages of this recently developed procedure, primarily the accurate determination of hydrogen atoms positions and, consequently, the correct description of hydrogen bonds.

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Povzetek

Hidrazinijev trihidrogen tetrafluorid je bil sintetiziran in strukturno raziskan. Njegova kristalna struktura, določena z rentgensko difrakcijo na monokristalu, je sestavljena iz dikationov $N_2H_6^{2+}$ in trigonalnih anionov $H_3F_4^-$, ki so povezani s kompleksnim sistemom vodikovih vezi N–H···F. Kristalna struktura hidrazinijevega difluorida je bila ponovno določena. Za obe strukturi je bilo izvedeno izboljšanje kristalne strukture z uporabo nesferičnih faktorjev sipanja.