Ivlev, Sergei I.; Soltner, Theresa; Karttunen, Antti J.; Mühlbauer, Martin J.; Kornath, Andreas J.; Kraus, Florian

**Syntheses and Crystal Structures of Sodium Hydrogen Fluorides NaF·nHF (n = 2, 3, 4)**

*Published in:*  
Zeitschrift für Anorganische und Allgemeine Chemie

**DOI:**  
10.1002/zaac.201700228

Published: 17/11/2017

Please cite the original version:  
Syntheses and Crystal Structures of Sodium Hydrogen Fluorides

NaF·nHF (n = 2, 3, 4)

Dedicated to Professor Wolfgang Schnick on the Occasion of his 60th Birthday

Sergei I. Ivlev a, Theresa Soltner b, Antti J. Karttunen c, Martin J. Mühlbauer d, Andreas J. Kornath b, Florian Kraus* a

[a] Fachbereich Chemie, Philipps-Universität Marburg, Hans-Meerwein-Straße, 35032 Marburg, Germany
[b] Department Chemie, Ludwig-Maximilians-Universität München, 81377 München, Germany
[c] Department of Chemistry and Materials Science, Aalto University, 00076 Aalto, Finland
[d] Heinz Maier-Leibnitz Zentrum (MLZ), Technische Universität München, Lichtenbergstraße 1, 85747 Garching, Germany
[e] Institute for Applied Materials, Karlsruhe Institute of Technology, 76344 Eggenstein-Leopoldshafen, Germany

Abstract
A series of higher sodium hydrogen fluorides were synthesized and structurally characterized: Sodium tetrahydrogen pentafluoride, NaH₄F₅, crystallizes in space group type $I4_1/a$ with cell parameters $a = 6.0275(4)$ Å, $c = 11.6208(13)$ Å, $V = 422.19(7)$ Å³, $Z = 4$ at 100 K. Sodium trihydrogen tetrafluoride, NaH₃F₄, crystallizes in space group type $R\overline{3}$ with cell parameters $a = 6.5139(4)$ Å, $c = 13.4040(15)$ Å, $V = 492.55(8)$ Å³, $Z = 6$ at 100 K. Sodium dihydrogen trifluoride, NaH₂F₃, crystallizes in space group type $Pnma$ (No. 62) with cell parameters $a = 7.9276(9)$ Å, $b = 3.4514(3)$ Å, $c = 9.6937(10)$ Å, $V = 265.23(5)$ Å³, $Z = 4$ at 100 K. The investigations were complemented by IR spectroscopy and theoretical calculations. NaH₂F₃ was additionally characterized by means of powder neutron diffraction. All observed F–H···F hydrogen bonds are unsymmetric, close to linearity and can be considered as strong hydrogen bonds.

Keywords: sodium hydrogen fluorides, neutron diffraction, crystal structure, hydrogen bond, IR spectroscopy, DFT

Introduction
The NaF–HF system is known for a long time and has a remarkable impact in many industrial processes. As well as many other metal fluorides, NaF is able to form a whole series of sodium hydrogen fluorides with HF: NaHF\(_2\), NaH\(_2\)F\(_3\), NaH\(_3\)F\(_4\), and NaH\(_4\)F\(_5\). [1–5]

The first member of this series, NaHF\(_2\), is extensively used in processes such as metal plating, surface pretreatment, pH adjustment, and glass etching. [6] As a result of being widely applied, it has been characterized well using X-ray [7,8] and neutron diffraction [9] (including high pressure experiments [10]), IR [11,12], Raman [10], and NMR [13] spectroscopy, as well as quantum chemical calculations. [14,15] The HF\(_2^-\) anion in NaHF\(_2\) is believed to be a rare case of a symmetric hydrogen bond [16], which is also observed in KHF\(_2\) [16] but not, for example, in CH\(_3\)C\(_6\)H\(_4\)NH\(_3\)HF\(_2\) [17], SrF(HF\(_2\)) and BaF(HF\(_2\)). [18]

In contrast to NaHF\(_2\), the sodium hydrogen fluorides with higher HF content are significantly less studied. To the best of our knowledge, the first identification and visual description of NaF\(_n\)HF \((n = 2, 3, 4)\) has been carried out by Tananaev in 1941 by investigating the phase diagram of the triple system NaF–HF–H\(_2\)O. [1] Literature searches for more specific information on these compounds lead to a quite scarce number of publications describing their melting points [3,4], the thermochemistry [19,20], and the inelastic neutron scattering (for NaH\(_2\)F\(_3\) in HF only) [21]. Therefore, the fundamental structural characterization of these compounds is still missing. However, it is of interest in order to better understand the hydrogen bonds in the hydrogen fluoride anions. In this work we present our results on the determination of the crystal structures of NaF\(_n\)HF \((n = 2\) to \(4)\) by means of X-ray and neutron (for NaH\(_2\)F\(_3\)) diffraction assisted by IR spectroscopy and quantum chemical calculations.

**Synthesis of NaF\(_n\)HF \((n = 2, 3, 4)\)**

*Sodium tetrahydrogen pentafluoride NaH\(_4\)F\(_5\)*

The synthesis of NaH\(_4\)F\(_5\) (Compound 1) was carried out by direct interaction of NaF with anhydrous HF according to equation 1:

\[
\text{NaF} + 4 \text{HF} \rightarrow \text{NaH}_4\text{F}_5
\]  

(1)

Reaction 1 was carried out by condensing a high excess of anhydrous hydrogen fluoride into an FEP vessel with a pre-weighed amount of NaF at \(-196\) °C. After warming up the vessel, its contents appeared no longer as a powder, but, instead, as a hard solid under a layer of HF. The solid phase was identified as NaHF\(_2\) by means of powder X-ray diffraction (Figure S1, Supporting Information). We allowed the reaction vessel to remain at 50 °C while being intensively shaken on a vortex mixer for one hour. After the solid phase was completely dissolved in HF, the reaction vessel was cooled to room temperature, and the excess of HF was carefully removed by vacuum distillation until the contents of the vessel appeared as an almost dry crystalline solid with a mass
corresponding to the formation of NaH₄F₅. It should be noted that further evacuation of HF quickly leads to the formation of NaHF₂ even at room temperature which is in agreement with the known data. [1] The product was transferred into a glovebox with Ar atmosphere and stored in a tightly closed Teflon container in order to prevent its decomposition to NaHF₂.

Sodium trihydrogen tetrafluoride NaH₃F₄

NaH₄F₅ (Compound 2) was synthesized according to equation 2 by careful evacuation of HF from the molten NaH₄F₅ at 45 °C which is above its melting point of 39.8 °C [3,4]:

\[
\text{NaH}_4\text{F}_5 \rightarrow \text{NaH}_3\text{F}_4 + \text{HF}
\]  

The evacuation continued until the residue appeared as a slightly wet crystalline solid. Further evacuation as well as exposition of the product to an open atmosphere lead to its decomposition to NaHF₂.

Sodium dihydrogen trifluoride NaH₂F₃

NaH₃F₄ (Compound 3) was synthesized similar to NaH₃F₄ according to equation 3 by careful evacuation of HF from the molten NaH₃F₄ at 70 °C which is above its melting point of 60.5 °C [3]:

\[
\text{NaH}_3\text{F}_4 \rightarrow \text{NaH}_2\text{F}_3 + \text{HF}
\]  

The evacuation continued until the residue appeared as a slightly wet crystalline solid. Further evacuation as well as exposition of the product to the open atmosphere lead to its decomposition to NaHF₂. Evacuation at temperatures above 80 °C also leads to the formation of NaHF₂ instead of the desired compound.

Crystal Structure Determinations

The described syntheses directly lead to the formation of crystalline material suitable for single crystal X-ray diffraction. The crystals of each compound were selected and mounted in perfluorinated oil under a stream of cold nitrogen gas in order to prevent their decomposition. The crystallographic details are collected in Table 1.

### Table 1. Crystallographic details of the compounds NaFₙHF (n = 2, 3, 4)

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Compound 1</th>
<th>Compound 2</th>
<th>Compound 3 (SC XRD)</th>
<th>Compound 3 (neutron powder diffraction)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Empirical formula</td>
<td>F₃H₂Na</td>
<td>F₄H₃Na</td>
<td>F₃H₂Na</td>
<td>F₂H₂Na</td>
</tr>
<tr>
<td>Color and appearance</td>
<td>Colorless blocks</td>
<td>Colorless blocks</td>
<td>Colorless blocks</td>
<td>White powder</td>
</tr>
<tr>
<td>M / g·mol⁻¹</td>
<td>122.02</td>
<td>102.01</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Crystal system</td>
<td>Tetragonal</td>
<td>Trigonal</td>
<td></td>
<td>Orthorhombic</td>
</tr>
<tr>
<td>Space group</td>
<td>I₄/a (No. 88)</td>
<td>R₃ (No. 148)</td>
<td></td>
<td>Pna (No. 62)</td>
</tr>
<tr>
<td>a / Å</td>
<td>6.0275(4)</td>
<td>6.5139(4)</td>
<td>7.9276(9)</td>
<td>7.9741(4)</td>
</tr>
</tbody>
</table>
\[ b / \text{Å} = a = a = 3.4514(3) = 3.4913(2) \]
\[ c / \text{Å} = 11.6208(13) = 13.4040(15) = 9.6937(10) = 9.7579(5) \]
\[ V / \text{Å}^3 = 422.19(7) = 492.55(8) = 265.23(5) = 271.66(3) \]
\[ Z = 4 \]
\[ \rho_{\text{calc}} / \text{g cm}^{-3} = 1.920 = 2.064 = 2.054 = 2.005 \]
\[ \lambda / \text{Å} = 0.71073 (\text{Mo-K\textalpha}) = 0.71073 (\text{Mo-K\textalpha}) = 0.71073 (\text{Mo-K\textalpha}) = 1.548385 (\text{neutrons}) \]
\[ T / \text{K} = 100 = 100 = 100 \]
\[ R_{\text{int}}, R_{\sigma} = 0.0439, 0.0254 = 0.0651, 0.0265 = 0.0564, 0.0212 \]
\[ R(F^2) / wR(F^2) (\text{all data}) = 0.0258, 0.0378 = 0.0228, 0.0450 = 0.0385, 0.0579 = 0.0628, 0.0442 \]
\[ S (\text{all data}) = 1.168 = 1.100 = 1.044 \]
\[ \text{No. of data points, parameters, constraints, restraints} = 332, 18, 0, 0 = 364, 20, 0, 0 = 521, 31, 0, 0 = 3020, 57, 0, 0 \]
\[ 20^\circ \text{ range measured (min; max; increment)} = 7.02, 63.96, - = 7.84, 63.88, - = 6.64, 63.79, - = 0.95, 151.90, 0.05 \]
\[ 20^\circ \text{ range refined (min; max)} = 7.02, 63.96 = 7.84, 63.88 = 6.64, 63.79 = 11.05, 151.85 \]
\[ \Delta \rho_{\text{max}}, \Delta \rho_{\text{min}} / \text{e Å}^{-3} = 0.117, -0.121 = 0.140, -0.138 = 0.216, -0.205 \]

**NaH\textsubscript{4}F\textsubscript{5}**

Compound 1, NaH\textsubscript{4}F\textsubscript{5}, crystallizes in the tetragonal body-centered space group \textit{I}4\textsubscript{1}/\textit{a} (No. 88) with the cell parameters \( a = 6.0275(4), \ c = 11.6208(13) \ \text{Å}, \ V = 422.19(7) \ \text{Å}^3, \ Z = 4 \) at 100 K. It is isotypic to KH\textsubscript{4}F\textsubscript{5} [22–24]. The crystal packing of NaH\textsubscript{4}F\textsubscript{5} is shown in Figure 1; a section of the crystal structure showing one formula unit is presented in Figure 2.

![Figure 1. The crystal structure of NaH\textsubscript{4}F\textsubscript{5} (projection along \textit{a}-axis). Displacement ellipsoids are shown at 70% probability level at 100 K. Non-hydrogen atoms are shown anisotropic, H-atoms are shown with arbitrary radii.](image-url)
The sodium cations occupy the special \(4a\) (\(\bar{4}..\)) Wyckoff position, and the central \(\mu_4\)-F atom of the \(\text{H}_4\text{F}_5^-\) anions, which are more precisely formulated as \([\text{FH}_4\text{F}]^-\) anions, resides on the special \(4b\) (\(\bar{4}..\)) position. The other fluorine and hydrogen atoms of the HF molecules occupy the common \(16f\) (1) position. The resulting coordination polyhedron of the \(\text{Na}^+\) cation is a distorted quadratic prism (C.N. = 8). The shortest \(\text{Na}^+\cdots\text{F}\) distances are 2.4337(5) and 2.5104(4) Å, which are – due to the smaller ionic radius of \(\text{Na}^+\) – shorter than the \(\text{K}^+\cdots\text{F}\) distances of 2.770(2) and 2.774(2) Å in the isotypic compound \(\text{KH}_4\text{F}_5^-\) [23].

The shape of the \(\text{H}_4\text{F}_5^-\) anion is tetrahedron like with four HF molecules bound by hydrogen bonds to its central \(\mu_4\)-F ion. The tetrahedral shape seems to be typical for \(\text{H}_4\text{F}_5^-\) and has been observed also in \(\text{KH}_4\text{F}_5\) [22,23], NOF-4HF [25] and \(\text{NH}_4\text{F}-4\text{HF}\) [26]. However, two more isomers are possible [27] (the branched \([\text{FH(FHF)(HF)}_2]^-\) was found in \(\text{Me}_3\text{N}\cdot5\text{HF}\) [28]; the chain-like isomer is, to the best of our knowledge, yet to be discovered).

The actual point group of the \(\text{H}_4\text{F}_5^-\) anion in \(\text{NaH}_4\text{F}_5\) is \(C_2\), however, its symmetry is close to \(C_{2v}\) (or even \(T_d\)). The \(\text{F}^+\cdots\text{H}^\cdots\text{F}^+\) angle is 178(1)° resulting in almost linear (within the 3\(\sigma\) criterion) hydrogen bonds. The \(\text{H}^\cdots\text{F}\) and \(\text{H}^\cdots\text{F}^+\) distances are equal to 0.739(13) and 1.698(12) Å, of which the former is likely to be underestimated and the latter is likely to be overestimated. In general, the molecular structure of the \(\text{H}_4\text{F}_5^-\) anion of \(\text{NaH}_4\text{F}_5\) is very similar to that of \(\text{KH}_4\text{F}_5\) [29], NOF-4HF [25] and \(\text{NH}_4\text{F}-4\text{HF}\) [26]. These anions exhibit the same features, such as the shortening of the \(\text{H}^\cdots\text{F}\) distances (0.70(8), 0.81(3), 0.74(2) Å, respectively) and the close-to-linear hydrogen bonds with the \(\text{F}^+\cdots\text{H}^\cdots\text{F}\) angles equal to 176(8), 178(4), and 177(2)°, respectively. \(\text{Me}_3\text{N}\cdot5\text{HF}\), which contains a branched isomer of \(\text{H}_4\text{F}_5^-\) with one \(\mu_2\) and one \(\mu_3\) fluorine atom instead of a \(\mu_4\)-F atom,
demonstrates average elongations of these bonds: H–F from 0.88(7) to 1.13(9) Å and F···H–F from 168(8) to 174(4)° [28].

**NaH$_3$F$_4$**

Compound 2, NaH$_3$F$_4$, crystallizes in the trigonal space group $R\overline{3}$ (No. 148) with the cell parameters $a = 6.5139(4)$, $c = 13.4040(15)$ Å, $V = 492.55(8)$ Å$^3$, $Z = 6$ at 100 K. The crystal packing of NaH$_3$F$_4$ is shown in Figure 3; a section of the crystal structure showing one formula unit is presented in Figure 4.

Figure 3. The crystal structure of NaH$_3$F$_4$ (projection along $b$-axis). Displacement ellipsoids are shown at 70% probability level at 100 K. Non-hydrogen atoms are shown anisotropic, H-atoms are shown with arbitrary radii.
The sodium cations of compound 2 occupy the special 6c (3 . .) Wyckoff position, and the central $\mu_3$-F atoms of the $\text{H}_3\text{F}^-$ (or $[[\text{FH}]_3\text{F}]^-$) anions reside on the special 6c (3 . .) position. The other fluorine and hydrogen atoms occupy the common 18(1) position. The resulting coordination sphere of the Na$^+$ cation is mono-capped distorted octahedral (C.N. = 7). The vertices of the octahedron are formed by the peripheral F(2) atoms, whereas the capped face is based on the $\mu_3$-F(1) atom. The shortest Na···F distances are 2.3363(5), 2.3730(5) Å, and 2.4724(9) Å. The similar compound KH$_3$F$_4$, which is however not isotypic, shows the shortest K···F distances to be 2.7045(9) and 2.9545(1) Å. [30] Thus, the resulting coordination polyhedron of the potassium ion in KH$_3$F$_4$ is also different and may be considered as only slightly distorted tetragonal prismatic (C.N. = 8). Thus it seems that the size of the cation plays a decisive role in this case and allows to coordinate more counter-ions leading to a different crystal structure.

The $\text{H}_3\text{F}^-$ anion of compound 2 is of trigonal pyramidal shape and possesses $C_3$ point group symmetry. In general, the star-like $\text{H}_3\text{F}^-$ anion can have point group symmetry $D_{3h}$ or $C_3v$ (or close to them) in the solid state. Isomers with this structure can be found in many other compounds [28], such as KF·3HF [30], NOF·3HF [25], Me$_4$NF·3HF [31], 3IF$_5$·CsF·3HF [32], K$_3$BiCl$_6$·2KCl·KF·3HF [33], NH$_3$·4HF [26], Me$_3$N·4HF [28], Et$_3$N·4HF [28], Py·4HF [34]. The other $\text{H}_3\text{F}^-$ isomer has a chain-like structure and has been observed in KF·2.5HF [30] and H$_2$O·4HF [35].

The F···H–F angle in NaH$_3$F$_4$ equals 170(1)$^\circ$, which may indicate weaker hydrogen bonds in comparison to NaH$_4$F$_5$. The H–F bond length equals 0.685(14) Å, which seems to be underestimated, whereas the donor-acceptor distance between the hydrogen-bonded fluorine atoms is 2.3970(6) Å. The three F–($\mu_3$-F)–F angles equal 111.15(2), 111.16(2), and 111.17(1)$^\circ$ and are essentially equivalent within the 3σ criterion. The central $\mu_3$-F atom is located at 0.7297(8) Å above a virtual least-squares plane formed by the three other symmetry-equivalent fluorine atoms. Interestingly, KH$_3$F$_4$, which is not isotypic and crystallizes in the trigonal space group $R\bar{3}c$ (No. 167), contains a trigonal planar H$_3$F$_4^-$ anion ($D_{3h}$ point group) with the central fluorine atom lying exactly in the plane of the anion [30]. Based on X-ray diffraction, the H–F bond lengths in KH$_3$F$_4$ are longer and equal 0.775(8) Å, while the F–$\mu_3$–F distances are 2.401(1) Å and are essentially equal to those in NaH$_3$F$_4$.

$NaH_2F_3$
Compound 3, NaH₂F₃, crystallizes in the orthorhombic space group *Pnma* (No. 62) with cell parameters \(a = 7.9276(9)\), \(b = 3.4514(3)\), \(c = 9.6937(10)\) Å, \(V = 265.23(5)\) Å³, \(Z = 4\) at 100 K. The crystal structure of NaH₂F₃ is shown in Figure 5; a section of the crystal structure showing one formula unit is presented in Figure 6.

![Figure 5. The crystal structure of NaH₂F₃ (projection along b-axis). Displacement ellipsoids are shown at 70% probability level at 100 K. Non-hydrogen atoms are shown anisotropic, H-atoms are shown with arbitrary radii.](image)

![Figure 6. Formula unit of NaH₂F₃. Displacement ellipsoids are shown at 70% probability at 100 K, non-hydrogen atoms are shown anisotropic, H-atoms are shown with arbitrary radii.](image)

All atoms of compound 3 occupy the special 4c \((. m .)\) Wyckoff position. The H₂F₃⁻ anion (or \([(HF)₂F]⁻\) lies therefore exactly in the mirror plane and exhibits the \(C_s\) point group symmetry which is however close to \(C_{2v}\). The resulting coordination sphere of the Na⁺ cation is distorted octahedral (C.N. = 6). The shortest Na⁺–F distances are 2.2824(11), 2.2973(7), 2.3042(12), and
2.3074(7) Å. The corresponding potassium compound, KH$_2$F$_3$, is not isotypic (orthorhombic space group type $P2_12_12_1$, No. 19) and incorporates two crystallographically different potassium ions with K–F distances from 2.67(2) to 3.05(2) Å. [36]

The H$_2$F$_3^-$ anion of compound 3 is not linear with its F(2)–F(1)–F(3) angle equal to 115.59(5)°. Rather strong intramolecular hydrogen bonds seem to be present: The H–F bond lengths are equal to 0.86(2) and 0.87(2) Å. The H···μ-F distances are observed with 1.47(3) and 1.51(3) Å, and the F–H–μ-F angles are equal to 176(3) and 178(3)°. Taking into account the 3σ criterion, one may suppose that both F–H···μ-F moieties are equivalent leading to an exact $C_{2v}$ point group symmetry of the anion. Other examples of this anion were reported for KF·2HF [36], KF·2.5HF [30], Me$_4$NF·2HF [31], [(C$_{10}$H$_{12}$Se$_4$)$_2$]F·2HF [37], Me$_3$N·3HF [28], Et$_3$N·3HF [28], Py·3HF [34].

Neutron Diffraction Study on NaH$_2$F$_3$

For an additional structural investigation using powder neutron diffraction we chose compound 3 as it exhibits the strongest (after NaHF$_2$) hydrogen bonding among the sodium hydrogen fluorides. The crystallographic details are given in Table 1, the powder neutron diffraction pattern is shown in Figure 7 and a section of the crystal structure of compound 3 obtained using neutron diffraction showing the displacement ellipsoids of the H-atoms is depicted in Figures S2 and S3, respectively.

NaH$_2$F$_3$ crystallizes at room temperature in the same orthorhombic space group type $Pnma$ (No. 62) with cell parameters $a = 7.9741(4)$, $b = 3.4913(2)$, $c = 9.7579(10)$ Å, $V = 271.66(3)$ Å$^3$, $Z = 4$ at 293 K. In general more realistic distances to H atoms can be obtained by neutron diffraction data. Here, both H–F bond lengths are equal to 1.00(2) Å at 293 K and thus approximately 0.14 Å longer compared to the low-temperature X-ray data. Therefore, the H···μ-F distances are expected to be shorter by circa 0.14 Å and are observed to be 1.33(2) and 1.35(1) Å which is in agreement with this expectation. The F–H–μ-F angles are 174(1) and 179(1)°. Again, the point symmetry of the anion is $C_5$. Since all values are essentially equivalent within the 3σ criterion, the H$_2$F$_3^-$ anion is again close to $C_{2v}$ symmetry.
Further experimental characterization

We attempted to characterize the synthesized compounds using powder X-ray diffraction and IR spectroscopy. Experimental challenges, such as the fast decomposition of the compounds and their almost immediate reaction with the glass X-ray capillaries, could however not be overcome yet, so no representative powder patterns (besides the results of the powder neutron diffraction as vanadium sample holders are used) have been obtained so far.

As far as IR spectra are concerned, we observed mixtures of the title compounds with NaHF$_2$ instead of the pure compounds due to their fast decomposition (HF-loss). In order to facilitate the assignment of the vibrational bands we additionally employed quantum chemical calculations (for representative spectra and computational details see the Supporting Information).

Computational Study

For a better understanding of the structure of the anions we carried out full structural optimizations of the elucidated crystal structures at the DFT-PBE0/TZVP level of theory (see Experimental Section for the computational details). The cell parameters and the selected bond lengths and angles are given in Table 2. The experimental and calculated atomic positions are given in Tables S1–S3 (see Supporting Information).
Table 2. Experimental and calculated cell parameters and selected atomic distances and angles for NaF\(_n\)HF (\(n = 2\) to 4).

<table>
<thead>
<tr>
<th>Parameter</th>
<th>(\text{NaH}_2\text{F}_3)</th>
<th>(\text{NaH}_3\text{F}_4)</th>
<th>(\text{NaH}_4\text{F}_5)</th>
</tr>
</thead>
<tbody>
<tr>
<td>exp. (X-ray) T = 100 K</td>
<td>exp. (neutron) T = 293 K</td>
<td>calc. T = 0 K</td>
<td>exp. T = 100 K</td>
</tr>
<tr>
<td>(a / \text{Å})</td>
<td>7.9276(9)</td>
<td>7.9741(4)</td>
<td>7.97</td>
</tr>
<tr>
<td>(b / \text{Å})</td>
<td>3.4514(3)</td>
<td>3.4913(2)</td>
<td>3.52</td>
</tr>
<tr>
<td>(c / \text{Å})</td>
<td>9.6937(10)</td>
<td>9.7579(5)</td>
<td>9.75</td>
</tr>
<tr>
<td>(V / \text{Å}^3)</td>
<td>265.23(5)</td>
<td>271.66(3)</td>
<td>273.8</td>
</tr>
<tr>
<td>H–F / (\text{Å})</td>
<td>0.86(2)</td>
<td>1.00(2)</td>
<td>1.02</td>
</tr>
<tr>
<td>H···F / (\text{Å})</td>
<td>1.46(3)</td>
<td>1.33(2)</td>
<td>1.30</td>
</tr>
<tr>
<td>F–H···F / °</td>
<td>177(3)</td>
<td>174(1)</td>
<td>176.5</td>
</tr>
<tr>
<td>Distance of the H atom from the line connecting two F atoms / (\text{Å})</td>
<td>0.002</td>
<td>0.035</td>
<td></td>
</tr>
</tbody>
</table>

According to the obtained results the calculated cell parameters, bond lengths and angles are in good correspondence with the experimentally observed values. The largest deviation of the cell parameters is observed in the case of \(\text{NaH}_3\text{F}_4\) (1.7% for the \(c\) parameter). The calculated H–F distances lie within an interval from 0.86 to 1.03 \(\text{Å}\) for all the compounds, and are in better correspondence with typically observed values [38] than with data obtained using single crystal X-ray diffraction.

The characterizing values for the \(\text{H}_2\text{F}_3^-\) anion are collected in Table 3. Since no imaginary frequencies are obtained during the harmonic frequency calculation (see Supporting Information), we can conclude that at 0 K the true point group of \(\text{H}_2\text{F}_3^-\) in \(\text{NaH}_3\text{F}_3\) is \(C_s\) and also that no lowering of the space group symmetry is necessary – all this is true under the assumption that there is no low temperature modification of different crystal structure.

Table 3. Selected distances and angles for the \(\text{H}_2\text{F}_3^-\) anion obtained from the DFT calculations.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>F(3)–H(1)···F(1)</th>
<th>F(2)–H(2)···F(1)</th>
</tr>
</thead>
<tbody>
<tr>
<td>F–H bond / (\text{Å})</td>
<td>1.033</td>
<td>1.025</td>
</tr>
<tr>
<td>H···F distance / (\text{Å})</td>
<td>1.304</td>
<td>1.323</td>
</tr>
<tr>
<td>F–H···F angle / °</td>
<td>179.8</td>
<td>176.5</td>
</tr>
<tr>
<td>Distance of the H atom from the line connecting two F atoms / (\text{Å})</td>
<td>0.002</td>
<td>0.035</td>
</tr>
</tbody>
</table>
Besides the structure optimizations we carried out harmonic frequency calculations of the relaxed structures to verify whether the compounds are thermodynamically stable in order to justify their decomposition when exposed to open atmosphere, that is, the lack of HF counter pressure. For understanding the thermodynamics, not only the electronic energies at 0 K, but also the thermal contributions at 298 K were calculated. The results are shown in Table 4. Table S5 gives total and Gibbs free energies.

Table 4. The calculated energy changes of NaF\(\cdot\)\(n\)HF (\(n = 0\) to \(4\)) and HF in gas phase at 298 K (negative energy change corresponds to an exothermic reaction)

<table>
<thead>
<tr>
<th>Reaction</th>
<th>(\Delta E) (kJ mol(^{-1}))</th>
<th>(\Delta G) (kJ mol(^{-1})) *</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaHF(_2) (\rightarrow) NaF + HF</td>
<td>96.9</td>
<td>+28.2</td>
</tr>
<tr>
<td>NaH(_2)F(_3) (\rightarrow) NaHF(_2) + HF</td>
<td>65.7</td>
<td>–1.5</td>
</tr>
<tr>
<td>NaH(_3)F(_4) (\rightarrow) NaHF(_2) + 2HF</td>
<td>128.6</td>
<td>–10.7</td>
</tr>
<tr>
<td>NaH(_4)F(_5) (\rightarrow) NaHF(_2) + 3HF</td>
<td>186.8</td>
<td>–22.9</td>
</tr>
</tbody>
</table>

* Gibbs free energies calculated at STP.

Since both enthalpy and entropy are available, it is possible to consider the change of Gibbs free energy in the course of decomposition reactions. As it follows from Table 4, the only stable sodium hydrogen fluoride at standard temperature and pressure conditions is NaHF\(_2\). In the three other cases an excess of HF is required to shift the reaction equilibrium to the formation of higher sodium hydrogen fluorides. Therefore, the experimental observations described in the previous sections are in full correspondence with the theoretical predictions.

**Comparison of the structures**

As it follows from Table 2 and the crystallographic data in the previous sections, all the anions in the compounds NaF\(\cdot\)\(n\)HF (\(n = 2\) to \(4\)) have rather similar bond lengths and angles. According to the H–F and H···F distances as well as the corresponding vibrational frequencies (see Supporting Information), the strength of the hydrogen bonds increases from \([\text{H}_{2}\text{F}_5]^-\) to \([\text{H}_2\text{F}_3]^-\) which is expected and observed in the other known compounds containing these anions, in particular, in KF\(\cdot\)\(n\)HF (\(n = 3, 4\); for \(n = 2\) no hydrogen positions available). [22,30]

Another difference in the crystal structures of NaF\(\cdot\)\(n\)HF (\(n = 2\) to \(4\)) is the coordination sphere of the sodium cations. The lowest coordination number of Na\(^+\) is observed in NaH\(_2\)F\(_3\) (C.N. = 6), and then it increases with the increase of the size of the anion through C.N. = 7 in NaH\(_3\)F\(_4\), to C.N. = 8 in NaH\(_4\)F\(_5\). For the potassium compounds, which contain structurally similar anions, only C.N. = 8 is reported [22,30,36], which may be explained by the larger ionic radius of K\(^+\) and, therefore, the smaller influence of the size of the anion.
Conclusions

In this work, we have synthesized sodium tetrahydrogen pentafluoride NaH₄F₅ directly from sodium fluoride and anhydrous HF. By careful decomposition of the latter we have obtained sodium trihydrogen tetrafluoride NaH₃F₄ and sodium dihydrogen trifluoride NaH₂F₃.

All synthesized compounds feature [H₃F₄⁺]⁻ anions, which are held together by rather strong hydrogen bonds. The [H₄F₅⁻] anion has a tetrahedron-like structure ion with the μ₄-F atom in the center. The shape of the [H₃F₄⁻] anion is trigonal pyramidal instead of trigonal planar as previously observed for KH₃F₄. A reason for this difference may be the radii difference of the cations and therefore the different crystal structures that result. The [H₂F₃⁻] anion is bent. X-ray and neutron data show a point group symmetry of C₃ which is however quite close to C₂ᵥ. Quantum chemical calculations support the assignment to the C₃ point group.

All sodium hydrogen fluorides (except for NaHF₂) are unstable to the loss of HF when exposed to an open atmosphere (even inside a glove box with dry argon) and readily decompose to NaHF₂ with the release of hydrogen fluoride.

Experimental Section

General: All operations with sodium hydrogen fluorides were carried out in an atmosphere of dry and purified argon (Westfalen AG, Germany), so that a possible contact of the substances with moisture or air was minimized (O₂ < 1 ppm, H₂O < 1 ppm). NaF was used without further purification. Anhydrous HF was additionally dried by mixing with K₂NiF₆ which efficiently reacts with traces of moisture, and then separated by vacuum distillation in a Monel Schlenk line. Then, NaF and HF were used for the preparation of NaFₙHF (n = 2, 3, 4).

Preparation of NaH₄F₅: NaF (5.00 g, 119 mmol, 1.00 equiv.) was loaded into an FEP tube. Approximately 30 mL of anhydrous HF (30 g, 1500 mmol, 3.15 equiv.) were condensed at −196 °C. Then the reaction vessel was heated up to 50 °C and allowed to stay for one hour under intensive shaking on a vortex mixer until the solid phase was completely dissolved. After that the excess of HF was carefully removed in vacuo yielding slightly wet crystal agglomerates with the mass highly dependent on the evacuation time. The product used for further characterization weighed 13.9 g (113.9 mmol, 95.7% of theory).

Preparation of NaH₃F₄: NaH₁F₅ (12.5 g, 102 mmol) was loaded into an FEP tube and heated up to 45 °C until all amount was melted. After that the reaction vessel was carefully evacuated until the formation of slightly wet crystal agglomerates with the mass highly dependent on the evacuation time. The product used for further characterization weighed 10.1 g (7.6 mmol, 96.7% of theory).

Preparation of NaH₂F₃: NaH₂F₅ (9 g, 88.2 mmol) was loaded into an FEP tube and heated up to 70 °C until all amount was melted. After that the reaction vessel was carefully evacuated until the formation of slightly wet crystal agglomerates with the mass highly dependent on the evacuation time. The product used for further characterization weighed 6.9 g (84.1 mmol, 95.4% of theory).
**Single Crystal X-ray Diffraction:** Diffraction experiments on NaFₙHF (n = 2, 3, 4) were carried out using a Stoe IPDS 2T diffractometer with monochromated molybdenum radiation (Mo-Kα, λ = 0.71073 Å, plane graphite monochromator) and an image plate detector. Evaluation and integration of the diffraction data was carried out using the Stoe X-Area software suite [39], and an empirical absorption correction was applied. The structures were solved using Direct Methods (SHELXT) [40] and refined against $F^2$ (SHELXL) [41]. All non-hydrogen atoms were located by Difference Fourier synthesis and refined with anisotropic displacement parameters. The hydrogen atoms were initially located by the investigation of the difference Fourier map, and then refined with isotropic displacement parameters using additional constraints on the latter. Further details of the crystal structure investigation may be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (Fax: +49-7247-808-666; E-Mail: crysdata@fiz-karlsruhe.de, http://www.fiz-karlsruhe.de/request for deposited data.html) on quoting the depository numbers CSD-433034 (NaH₅F₃), CSD-433033 (NaH₆F₄), CSD-433031 (NaH₇F₅, X-ray), CSD-433032 (NaH₈F₆, neutron).

**Powder Neutron Diffraction:** The powder pattern of NaH₅F₃ was recorded in an indium sealed vanadium ampoule of 12 mm diameter and approximately 60 mm height at 293 K using the SPODI neutron powder diffractometer ($\lambda = 1.548385$ Å) at the neutron source FRM II / Heinz Maier-Leibnitz Zentrum [42].

**IR Spectroscopy:** The IR spectra of NaFₙHF (n = 2, 3, 4) were recorded on a Bruker Alpha FTIR spectrometer under Ar atmosphere, and the data were handled using the OPUS software package [43].

**Computational Details:** The structural and spectroscopic properties of NaFₙHF (n = 2, 3, 4) were investigated using the CRYSTAL14 program package [44,45]. Both the atomic positions and the lattice parameters were fully optimized using the PBE0 hybrid density functional method [46,47]. Triple-zeta valence + polarization (TZVP) level basis sets were applied for all atoms (see Supporting information for additional basis set details). The reciprocal space was sampled using a compound-dependent Monkhorst-Pack-type k-point grid [48]. For the evaluation of the Coulomb and exchange integrals (TOLINTEG), tight tolerance factors of 8, 8, 8, 8, and 16 were used (in case of NaF: 10, 10, 10, 20, 50). Default optimization convergence thresholds and DFT integration grids were applied in all calculations. The harmonic vibrational frequencies [49,50] and IR intensities [51] were obtained by using the computational schemes implemented in CRYSTAL.

**Acknowledgement**

We thank the Deutsche Forschungsgemeinschaft and the Deutscher Akademischer Austauschdienst for funding. We gratefully acknowledge the Forschungs-Neutronenquelle Heinz Maier-Leibnitz for granting beam time. F.Kraus thanks the DFG for a Heisenberg professorship. A.J.Karttunen thanks the Academy of Finland for funding (grant 294799) and CSC, the Finnish IT Center for Science, for computational resources.

**References**