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A Symmetric F–H–F Hydrogen Bond in Strontium Bifluoride, Sr[HF₂]₂


Dedicated to Prof. Dr. Caroline Röhrl on the Occasion of her 60th Birthday

Single crystal X-ray diffraction shows the hydrogen bond within the [F–H–F]⁻ anion of Sr[HF₂]₂ to be symmetric with H–F bond lengths of 1.143(5) Å and an intramolecular F–F distance of 2.2826(18) Å. The [HF₂]⁻ anion adopts crystallographic C₂ symmetry, however, it is essentially linear with a F–H–F angle of 174.8(6)°. Solid-state quantum chemical calculations agree with the experimental findings, showing a slightly bent F–H–F angle of 177.8°. The decomposition of Sr[HF₂]₂ to SrF₂ and HF is endothermic by +64 kJ/mol at room temperature. The bonding in the [F–H–F]⁻ anion is clearly ionic both in the solid state and gas phase.

Introduction

The alkali metal fluorides AF (A = Li–Cs) are able to form adducts with HF,[1] the simplest being the bifluorides containing the [HF₂]⁻ anion. Additionally, salts with higher HF contents contain more complex anions that exhibit strong hydrogen bonding, for example Na[HF₂]₂, Na[HF₃]⁺, and Na[H₂F₄]⁻.[1-3] Na[HF₂] is widely applied in pH adjustment, metal plating, surface pretreatment, and glass etching.[5] It has been characterized extensively using X-ray[8,9] and neutron diffraction[10] (including high pressure experiments[11]), IR,[12,13] Raman,[11] and NMR spectroscopy,[14] as well as quantum chemical calculations.[15,16]

HF molecules, as well as poly(hydrogenfluoride) anions, can also act as ligands to metal atoms and form heteroleptic complexes. Several such compounds, for example, La-HF₂[AsF₆]₃, Sr(HF)[TaF₆]₂, Sr(HF)₃[TaF₆]₂, Sr(HF)[BF₄]₂, have been reported.[17-21]

The [F–H–F]⁻ anions belonging to the alkali metal, thallium, and calcium bifluorides, as well as the bifluoride anions in Ag₂O₅[HF₂] were shown to be symmetric by NMR spectroscopy,[22,23] that is, the proton resides symmetrically between the F atoms. However, asymmetric [F–H–F]⁻ hydrogen bonds are also present in bifluorides, such as [CH₃C₆H₄NH₃][HF₂],[24] Sr[HF₂],[25] and Ba[HF₂],[25,26] as deduced from single-crystal X-ray diffraction and NMR spectroscopic investigations.[21,22,28] Currently, the only structurally characterized HF adduct of SrF₂ is the above mentioned Sr[HF₂],[25] however, Opalovskii and coworkers have also reported a compound having the composition “SrF₂·2.5HF”.[27]

Here we present the serendipitous synthesis of strontium bifluoride, Sr[HF₂]₂, and its crystal structure.

Results and discussion

WO₃ was reacted with SrF₂ in BrF₃ at room temperature in an attempt to synthesize Sr[WOF₅]₂. Initially, all starting materials had dissolved in the BrF₃ solution. After about a week, a couple of crystals were obtained and selected directly from the BrF₃ solution. Single crystal X-ray diffraction showed the composition of the compound to be Sr[HF₂]₂. A related compound containing one equivalent HF less per formula unit, Sr[HF₂], has previously been reported.[25]

In order to have synthesized strontium bifluoride from this reaction mixture, water must have been present as a source of hydrogen atoms. The synthesis may have taken place through the reduction of bromine trifluoride and oxidation of water. However, the reaction is complex, and brown vapors are always observed when BrF₃ reacts with water. It is likely that BrF₃ is reduced to Br₂ or forms a mixture of Br⁻, Br₂, and BrO⁻. Moreover, the formation of BrO₃⁻ is also possible because BrF₄⁻ reacts with water forming HF₂⁻, BrO₃⁻, Br₂, and O₂. Therefore, we can only report an idealized reaction, Equation 1.

Putative equation: \[
3 \text{SrF}_2 + 2\text{BrF}_3 + 4\text{H}_2\text{O} \rightarrow \text{Sr}[\text{HF}_2]_2 + 2\text{O}_2 + 2\text{HBr}
\]

(1)

To date, we have been unsuccessful in obtaining the title compound directly from SrF₂ and aHF, although others have succeeded using this synthetic route for the synthesis of
Ca[HF$_2$]$_2$.[26] Since the solubility of SrF$_2$ is much lower in water when compared to CaF$_2$, it might be expected that the solubilities of the salts in aHF are qualitatively similar to those in H$_2$O. This is however not the case for aHF where the solubilities at 12.2 °C have been given with 0.817 ± 0.015 g/100 g aHF for CaF$_2$, and 14.38 ± 0.09 g/100 g aHF for SrF$_2$.[29] Our investigations are ongoing.

Strontium bifluoride crystallizes in the orthorhombic space group Fddd (70) with the lattice parameters $a = 5.7203(8)$, $b = 10.6884(13)$, $c = 11.2690(13)$ Å, $V = 689.00(16)$ Å$^3$, $Z = 8$, $T = 100$ K, of56, 70hga. Selected crystallographic data and details of the single-crystal structure determination of Sr[HF$_2$]$_2$ are reported in Table 1. Atomic coordinates and equivalent isotropic displacement parameters for this compound are reported in Table 2.

The compound crystallizes isotypic to Ca[HF$_2$]$_2$,[28] both represent a new structure type. It contains a Sr atom on Wyckoff position 8a (222) and a F atom on site 32h (1). The H atom was clearly localizable from the Difference Fourier synthesis and was refined isotropic. It resides on Wyckoff position 16g (2). By site symmetry, a $C_2$-symmetric [F–H–F]$^–$ anion (Figure 1) is generated.

The H–F bond length is 1.143(5) Å and the intramolecular F–F distance is 2.2826(18) Å. The F–H–F angle is 174(4)° and the H atom is located circa 0.06(8) Å away from the virtual connection line between the two F atoms. However, as the standard uncertainties of the latter two values are quite large, the anion appears to be almost linear by X-ray diffraction. A respective angle of 177.12(8)° and a respective H atom deviation from the virtual connection line of circa 0.03 Å has been reported for Ca[HF$_2$]$_2$.[20] However, the z coordinate and the isotropic displacement parameter belonging to the H atom in Ca[HF$_2$]$_2$ were not freely refined, therefore, these values may be biased.[25] Intramolecular F–F distances of 2.269(6) and 2.2816(6) Å were reported for Sr[HF$_2$]$_2$ and Ba[HF$_2$]$_2$, respectively, and for Na[HF$_2$] and K[HF$_2$]$_2$ they are 2.277(1) and 2.277(6) Å, respectively.[9,22,30] The structurally related compound Ca[HF$_2$]$_2$ shows an essentially identical value compared to the title compound with a F–F distance of 2.283(2) Å.[20] The H–F distance in the symmetric [HF$_2$]$^–$ anion of Na[HF$_2$]$_2$ has been reported to be 1.1385(5) Å,[9] while the asymmetric H–F distance in SrF[HF$_2$] was reported to be 1.090(7) Å,[28] and the 19F NMR spectra taken on “SrF$_2$·2.5HF” were said to be essentially identical to Ca[HF$_2$]$_2$.[22] The H–F distance within the [HF$_2$]$^–$ anions of “SrF$_2$·2.5HF” was estimated by this method to be 1.17 Å with an asymmetric position of the H atom.[27] Only for Ca[HF$_2$]$_2$ was this later corrected to a symmetric hydrogen bond with a H–F distance of 1.143(20) Å and an F–F distance of 2.286(4) Å.[22,28] The crystal structure determination of Ca[HF$_2$]$_2$

![Figure 1](image-url) The [HF$_2$]$^–$ anion observed in Sr[HF$_2$]$_2$ shows symmetric hydrogen bonding with a H–F bond length of 1.143(5) Å, an intramolecular F–F distance of 2.2826(18) Å, and an F–H–F angle of 174(4)°. Displacement ellipsoids are shown at a 70% probability level at 100 K, the H atom is isotropic with an arbitrary radius.

---

**Table 1.** Selected crystallographic data and details of the single-crystal structure determination of Sr[HF$_2$]$_2$.

<table>
<thead>
<tr>
<th>Empirical formula</th>
<th>SrH$_2$F$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Color and appearance</td>
<td>colorless blocks</td>
</tr>
<tr>
<td>Molar mass / g·mol$^{-1}$</td>
<td>165.64</td>
</tr>
<tr>
<td>Crystal system</td>
<td>orthorhombic</td>
</tr>
<tr>
<td>Space group type (No.)</td>
<td>Fddd (70) 02</td>
</tr>
<tr>
<td>Pearson symbol</td>
<td>of56 incl. H atoms</td>
</tr>
<tr>
<td>$a$/Å</td>
<td>5.7203(8)</td>
</tr>
<tr>
<td>$b$/Å</td>
<td>10.6884(13)</td>
</tr>
<tr>
<td>$c$/Å</td>
<td>11.2690(13)</td>
</tr>
<tr>
<td>$V$/Å$^3$</td>
<td>689.00(16)</td>
</tr>
<tr>
<td>$Z$</td>
<td>8</td>
</tr>
<tr>
<td>$\mu$/cm$^{-1}$</td>
<td>3.194</td>
</tr>
<tr>
<td>$\lambda$/Å</td>
<td>0.71073 (Mo-K$_\alpha$)</td>
</tr>
<tr>
<td>$T$/K</td>
<td>100</td>
</tr>
<tr>
<td>$\mu$/mm$^{-1}$</td>
<td>15.57</td>
</tr>
<tr>
<td>$\theta$/°</td>
<td>4.4</td>
</tr>
<tr>
<td>$\theta$/°</td>
<td>33.0</td>
</tr>
<tr>
<td>$hkl$ range</td>
<td>$-8 \leq h \leq 8$, $-16 \leq k \leq 16$, $-17 \leq l \leq 17$</td>
</tr>
<tr>
<td>$R_{conv} $, $R_p$</td>
<td>0.065, 0.021</td>
</tr>
<tr>
<td>$R(F)$ (all data)</td>
<td>0.014, 0.016</td>
</tr>
<tr>
<td>$wR(F)$ (all data)</td>
<td>0.032, 0.033</td>
</tr>
<tr>
<td>S (all data)</td>
<td>1.10</td>
</tr>
<tr>
<td>Data, parameter, restraints</td>
<td>329, 16, 0</td>
</tr>
<tr>
<td>$\Delta \rho_{max}$, $\Delta \rho_{min}$/eÅ$^3$</td>
<td>0.53, −0.65</td>
</tr>
</tbody>
</table>

**Table 2.** Wyckoff positions, site symmetries, atomic coordinates, and equivalent isotropic displacement parameters $U_{iso}$ from the single-crystal X-ray diffraction of Sr[HF$_2$]$_2$ at 100 K.

<table>
<thead>
<tr>
<th>Atom</th>
<th>Position, symmetry</th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>$U_{iso}$/Å$^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sr</td>
<td>8a, 222</td>
<td>1/8</td>
<td>1/8</td>
<td>1/8</td>
<td>0.00629(10)</td>
</tr>
<tr>
<td>F</td>
<td>32h, 1</td>
<td>0.03165(15)</td>
<td>−0.05887(9)</td>
<td>0.25326(8)</td>
<td>0.01098(17)</td>
</tr>
<tr>
<td>H</td>
<td>16g, 2</td>
<td>1/8</td>
<td>1/8</td>
<td>0.509(7)</td>
<td>0.10(2)</td>
</tr>
</tbody>
</table>
also showed a symmetric hydrogen bond with a H–F distance of 1.1419(11) Å. Additionally, the HF content of “SrF₂·2.5HF” was determined by titration and it was concluded that the additional 0.5 equivalents of HF belonging to “SrF₂·2.5HF” were not detectable by NMR spectroscopy. In hindsight, it appears to us that Sr[HF₂]₂ may have already been obtained by these researchers. Through our X-ray diffraction study of Sr[HF₂]₂, we have determined the H–F and F–F distances to be 1.143(5) and 2.2826(18) Å, respectively. In comparison, the NMR spectroscopy study of “SrF₂·2.5HF” determined the H–F and F–F distances to be 1.143(20) and 2.286(4) Å, respectively. These previously-reported distances are in agreement with the distances reported here.

Panich concluded that asymmetric F–H–F hydrogen bonds show F–F distances between 2.28 and 2.55 Å, with a displacement of the proton from the center towards the donor atom ranging from 0.049 to 0.31 Å. On the other hand, symmetric F–H–F hydrogen bonds have a narrower range of F–F distances, ranging from 2.26 to 2.32 Å. Thus, F–F distances alone do not allow one to discriminate between symmetric and asymmetric hydrogen bonds. In our case, a symmetric hydrogen bond is present within the [HF₂]⁻ anion of Sr[HF₂]₂ due to site symmetry.

The [HF₂]⁻ anions are surrounded in a bisphenoid-like manner by Sr atoms, and each F⁻ anion of the [HF₂]⁻ molecule is bound to two Sr²⁺ cations. By these connections a three-dimensional infinite network is formed. The Sr²⁺ cation in Sr[HF₂]₂ is coordinated by eight fluorine atoms belonging to eight symmetry-equivalent [HF₂]⁻ anions. The Sr–F atomic distances are 2.4973(9) Å and a distorted square antiprismatic coordination polyhedron is formed around the Sr atom, see Figure 2. For comparison, the Sr–F distances within Sr[U₂F₁₂], also with a square antiprismic coordination sphere for the Sr²⁺ cations, are 2.479(4) Å, while those in SrF[HF₂] with C.N. = 9, are, as expected, a little larger, ranging from 2.574(4) to 2.662(3) Å.

The coordination sphere of the Sr atoms is quite different from that found in SrF[HF₂], where a tricapped trigonal prism was reported. However, a coordination number of eight is not uncommon for Sr²⁺ cations. The coordination polyhedra are connected via common edges on opposite sides so that the Sr atoms form a diamond-like topology and the [HF₂]⁻ anions reside within the voids. The nearest Sr–Sr distances are 4.1379(3) Å.

The [HF₂]⁻ anions are arranged in layers with their F atoms parallel to the ab plane at heights of z ≈ 0, 1/4, 1/2, and 3/4. These layers are interconnected by the Sr²⁺ cations residing in between which form hexagonally packed layers at heights of z = 1/8, 3/8, 5/8, and 7/8, forming a diamond-like topology.

We could not identify any other structure relationships and the crystal structure of Sr[HF₂]₂ is depicted in Figure 3.

To gain more insight into the thermodynamic and structural behavior of the title compound, we used quantum chemical calculations to investigate the crystal structures of Sr[HF₂]₂, SrF[HF₂], and SrF₂ as well as the bonding situation in the [HF₂]⁻ anion. All calculations were carried out with the PBE0 hybrid density functional method (DFT-PBE0).

The optimized lattice parameters of Sr[HF₂]₂ obtained with DFT-PBE0 are in good agreement with the observed ones. The lattice parameters a, b, and c differ from the experimentally

Figure 2. Coordination polyhedron observed for the Sr²⁺ cation in Sr[HF₂]₂. Displacement ellipsoids are shown at a 70% probability level at 100 K.
determined lattice parameters only by 0.1%, 0.1%, and 0.7%, respectively. The H–C0F bond length in the optimized structure of Sr[HF2]2 is 1.13 Å, in good agreement with the observed value of 1.143(5) Å. The F–H–F angle of 177.8° is also in agreement with the experimentally determined value of 174(4)°. For the known compound SrF[HF2] the position of the H atom could not be determined in the diffraction experiment but was assumed to be asymmetric based on crystal-chemical reasoning. Therefore, the H atom was arbitrarily placed in the middle of the two F atoms of the [HF2] unit at Wyckoff position 2e (m) for the calculations. After geometry optimization, the H–F distances were different, one being 1.07 Å and the other 1.19 Å, supporting the assumption of an asymmetric hydrogen bond. The Sr···F distances are equal for both F atoms of the [HF2] unit and were calculated to be 2.56 Å. The F–C0H–C0F angle was determined to be 179.5°, which is rather similar to the title compound. Selected distances and angles are compared in Table 3.

When looking at the atomic charges of Sr[HF2]2 with Mulliken population analysis, Sr shows an expected positive partial charge of +1.5 e−. The partial charges within the [HF2] unit are negative for the F atoms (−0.6 e−) and positive for the H atom (+0.6 e−). The solid-state partial charges are in good agreement with partial charges obtained from Intrinsic Bond Orbital (IBO) analysis of the gas-phase [HF2]− anion (−0.7 e− for the F atoms and +0.4 e− for the H atom).

We studied the thermodynamics of Sr[HF2]2 and SrF[HF2] by calculating the Gibbs Free energies for reactions 2 and 3:

\[
\begin{align*}
\text{Sr[HF}_2\text{]}_2 & \rightarrow \text{SrF}_2 + 2 \text{HF} \rightarrow \Delta G = +64 \text{ kJ/mol} \\
\text{SrF[HF}_2\text{]} & \rightarrow \text{SrF}_2 + \text{HF} \rightarrow \Delta G = +33 \text{ kJ/mol}
\end{align*}
\]

Both reactions are endothermic, suggesting that decomposition to SrF2 and HF is thermodynamically unfavorable at 298 K (the Gibbs Free energies of molecular HF are from gas phase calculations).

Finally, we studied the bonding situation of the [HF2]− anion with an IBO analysis. The analysis shows two equal H–C0F bonds with the F atoms contributing with 84% to the respective bond. This contribution consists of 67% 2p x orbital and 33% 2s orbital. The H atom contributes 16% with its 1s orbital. One of the two IBOs corresponding to the H–C0F bonds in [HF2]− is shown in Figure 4.

### Conclusion

We serendipitously synthesized strontium bifluoride, Sr[HF2]2. Its crystal structure shows symmetric hydrogen bonds within its [HF2]− anions with H–F bond lengths of 1.143(5) Å and an intramolecular F–F distance of 2.2826(18) Å. The [HF2]− anion is \( C_2 \)-symmetric by site symmetry. However, because of the magnitude and standard uncertainty of the F–H–F angle,
FEP tubes and was freshly distilled before use. For a gas-phase NaF molecule, in which the bond should be highly ionic, the contribution of the F atom is 96%. In the H2 molecule, pointing to a rather polarized bond, as expected. For comparison: H atom in white. The F atom contributes 84%, the H atom 16%, which has a purely covalent bond, the contribution of each atom is 50%.

It is essentially linear. This finding is supported by quantum chemical solid-state calculations. Both the decomposition of Sr[HF2]2, and the previously described SrF[HF2] to SrF2 and HF is endothermic at 298 K, indicating their thermodynamic stability at room temperature. Bonding analysis of the gas-phase [HF2]− anion shows the H–F bonds to be quite ionic. The bonding situation of the [HF2]− anion within the solid state seems to be same regarding atomic distances and charges.

Experimental Part

F2 and BrF3 are powerful oxidants and may pose a working hazard to those being unexperienced, untrained, and unskilled. HF and the bifluorides may lead to death as well. Suitable protective gear should be worn at all times and access to proper medical treatment is necessary.

Synthesis of BrF3

BrF3 was synthesized by passing fluorine (Solvay, > 99.0%) through bromine (Merck, p. A). The reaction was carried out in a FEP (perfluorinated ethylene-propylene) U-tube which was cooled with ice from the outside. After the synthesis, the remaining bromine was pumped-off and the BrF3 was stored in previously passivated FEP tubes and was freshly distilled before use.

Serendipitous Synthesis of Sr[HF2]2

A FEP vessel was charged with 0.1005 g of WO3 (0.43 mmol), 0.0552 g SrF2 (0.44 mmol), and 0.33 g BrF3 (2.5 mmol). After about one week of crystallization time, colorless crystals of Sr[HF2]2 were obtained of which a suitable specimen was selected for the diffraction experiment.

Single crystal structure determination

A suitable crystal of Sr[HF2]2 was selected from BrF3 solution and mounted using a MiTeGen loop. Intensity data of the crystal were recorded with an IPDS 2T diffractometer (Stoe & Cie). The diffractometer was operated with Mo-Kα radiation (0.71073 Å, graphite monochromator) and equipped with an image plate detector. Evaluation, integration and reduction of the diffraction data was carried out using the X-Area software suite.

A numerical absorption correction was applied with the modules X-Shape and X-Red32 of the X-Area software suite. The structure was solved with dual-space methods (SHELXT-2014/5) and refined against $\hat{F}^2$ (SHELXL-2018/3). All atoms were refined with anisotropic displacement parameters, the H atom was refined isotropic. The highest residual electron density after the final refinement was 1.1 Å distant from the Sr atom. Representations of the crystal structures were created with the Diamond software.

Computational Details

Sr[HF2]2, SrF[HF2], and SrF2 were investigated with PBE0 hybrid density functional method (DFT-PBE0) combined with triple-valence basis sets TZVP for F and H and a split-valence basis set (SVP) for Sr. All solid-state quantum chemical calculations were carried out with the CRYSTAL17 program suite. The geometries were fully optimized within the constraints of the respective space groups. Optimized geometries are listed in the Supporting Information. All optimized geometries were confirmed to be true local minima by means of harmonic frequency calculations. The reciprocal space was sampled with Monkhorst-Pack-type k-point grids (Sr[HF2]2: 4×4×4; SrF[HF2]: 4×7×6; SrF2: 8×8×8) for the evaluation of the Coulomb and exchange integrals (TOLINTEG), tighter thresholds of 8 8 8 16 were used. Default DFT integration grids were used. Molecular calculations for the [HF2]− anion were performed with the TURBOMOLE program package, using the DFT-PBE0 method and the Karlsruhe def2-TZVP basis set for all atoms. Multipole accelerated resolution-of-the-identity approximation (MA-RU) was used to speed up the DFT calculations and a m4 integration grid was used for the numerical integration of the exchange-correlation part. Intrinsic Bond Orbitals were obtained with the proper module of TURBOMOLE.

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Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Conflict of Interest

The authors declare no conflict of interest.
Keywords: bifluoride - strontium - crystal structure - symmetric hydrogen bond - hydrogen difluoride anion

[34] X-Area, STOE & Cie GmbH, Darmstadt, Germany, 2018.

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