

Sulfur Tetrafluoride

The Solid-State Structure of SF₄: The Final Piece of the Puzzle**

James T. Goettel, Nathan Kostiuk, and Michael Gerken*

Sulfur tetrafluoride is one of the fundamental binary main-group fluorides, and since its discovery in 1929,^[1] its structure and chemistry, particularly as a fluorinating agent in organic chemistry, has been the subject of many studies.^[2] The structure of SF₄ has been determined in the gas phase by microwave spectroscopy^[3] and electron diffraction,^[4] revealing its molecular seesaw geometry (*C*_{2v}), which is in accord with the VSEPR model. Vibrational spectra of liquid SF₄ have also been assigned in terms of molecular *C*_{2v} point symmetry.^[5] Sulfur tetrafluoride is one of the typical examples for a fluxional trigonal bipyramidal geometry, with rapidly exchanging axial and equatorial fluorine environments on the NMR timescale at room temperature.^[6] At low temperature, the exchange can be slowed down, allowing the observation of two triplets in the ¹⁹F NMR spectrum. The exchange of axial and equatorial fluorine environments of pure SF₄ has been shown to proceed by Berry pseudorotation with activation energies of 11.9 (gas phase) and 11.2 (liquid, solution) kcal mol⁻¹.^[6] An NMR study of the temperature dependence of the ¹⁹F NMR chemical shifts and ²*J* coupling constants suggested the presence of labile fluorine bridging, with the possibility of dimer or chain formation being discussed.^[7] Solid-state Raman spectroscopic data have been interpreted in terms of three different polymorphs, suggesting fluorine-bridged chains for the solid-state structure of SF₄.^[8] Using miniature zone-melting techniques, the crystal structure of SF₄ has been reported to be severely disordered, and no discernible structure could be determined.^[9] Despite the broad interest in the structure of SF₄, its solid-state structure has remained elusive as a consequence of its low melting point and highly reactive nature. The crystal structures of SeF₄ and TeF₄, on the other hand, have previously been obtained.^[10] Tellurium tetrafluoride exists as TeF₃⁺ units bridged by two fluoride ions, whereas SeF₄ contains distinct disphenoidal SeF₄ units, having Se...F contacts to two adjacent SeF₄ molecules.

Herein, we were able to obtain crystals of SF₄, which has a melting point of -121 °C, using two different methods: a) by slow cooling of neat liquid SF₄; and b) by crystallization from CF₂Cl₂ solvent. Both types of crystals were mounted at -145 °C and were shown to have the same unit cell. The initial data suggested a tetragonal unit cell. The correct structural

solution, however, showed that SF₄ is twinned and crystallized in the orthorhombic system with two crystallographically unique ordered SF₄ molecules in the asymmetric unit (Figure 1). In our study, we did not find any evidence for a polymorph of SF₄.

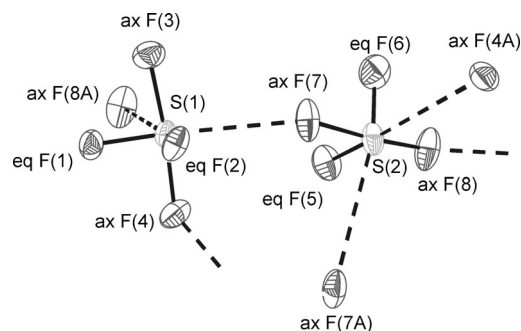


Figure 1. Thermal ellipsoid plot of SF₄. Ellipsoids are set at 50% probability. Selected bond lengths [Å], contacts [Å], and angles [°]: S1–F1 1.527(4), S1–F2 1.535(4), S1–F3 1.647(5), S1–F4 1.676(5); F1–S1–F2 101.0(2), F3–S1–F4 172.6(3), S1...F7 2.954(5), S1...F8A 3.031(5), F7...S1...F8A 121.2(2); S2–F5 1.553(4), S2–F6 1.474(6), S2–F7 1.671(5), S2–F8 1.635(4); F5–S2–F6 99.6(3), F7–S2–F8 171.6(3); S2...F4A 2.975(4), S2...F7A 3.261(6), F4A...S2...F7A 116.2(1).

The geometry of the SF₄ molecules agrees well with the seesaw geometry found for the gas phase.^[3,4] The axial S–F bonds are longer (1.635(4)–1.671(5) Å) and more ionic in nature than the shorter equatorial S–F bonds (1.474(6)–1.553(4) Å). The axial and equatorial F–S–F angles found in the solid-state structure are indistinguishable from those of the gas-phase structure. The extended structure can be described as a three-dimensional network of SF₄ molecules linked by two weak intermolecular S...F contacts per SF₄ molecule. The shortest S...F contact found in the structure is 2.954(5) Å, which is shorter than the sum of the van-der-Waals radii (3.27 Å).^[11] These contacts are exclusively formed by the more ionic axial fluorine atoms to the sulfur atoms of adjacent SF₄ molecules. None of the equatorial fluorine atoms form significant intermolecular contacts. This agrees very well with the more covalent nature of the S–F_{eq} bonds and the lower fluorobasicity of the equatorial fluorine atoms compared to the axial fluorine atoms. Because of the location of the lone pair in the F_{eq}–S–F_{eq} plane, the F...S...F angles (121.2(2)° and 116.2(1)°) are significantly larger than the F_{eq}–S–F_{eq} angles (101.0(2)° and 99.6(3)°). The weakness of the contacts is reflected in the low freezing point of SF₄ and the fact that the gas-phase and solid-phase metric parameters of the SF₄ molecule are the same within the experimental errors. The structures of SF₄ and SeF₄ are related in respect that both contain contacts between the axial fluorine atoms and the

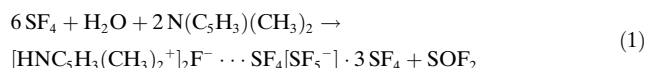
[*] J. T. Goettel, N. Kostiuk, Prof. Dr. M. Gerken
Department of Chemistry and Biochemistry
University of Lethbridge
4401 University Drive, Lethbridge, AB T1K 3M4 (Canada)
E-mail: michael.gerken@uleth.ca

[**] This work was funded by the Natural Sciences and Engineering Research Council of Canada (NSERC).

Supporting information for this article is available on the WWW under <http://dx.doi.org/10.1002/anie.201302917>.

chalcogen atoms resulting in a fluorine-bridged network. In SF₄, however, only three of the four crystallographically different axial fluorine atoms form contacts, while in SeF₄ all axial fluorine atoms form Se–F···Se bridges.

A solid-state structural motif similar to that of neat SF₄ is observed in the crystal structure of the novel [HNC₅H₃(CH₃)₂]₂F[−]···SF₄[SF₅][−]·3SF₄ salt. Excess SF₄ reacts with a mixture of water and 2,6-dimethylpyridine, yielding a white crystalline solid according to Equation (1). The [HNC₅H₃(CH₃)₂]₂F[−]···SF₄[SF₅][−]·3SF₄ salt is stable up to −90 °C, above which temperature the crystals decompose.



The asymmetric unit of [HNC₅H₃(CH₃)₂]₂F[−]···SF₄[SF₅][−]·3SF₄ contains two 2,6-dimethylpyridinium cations that are hydrogen-bonded to a fluoride anion, an SF₅[−] anion (Figure 2), and four crystallographically different SF₄ molecules. Two different interaction modalities between F[−] and

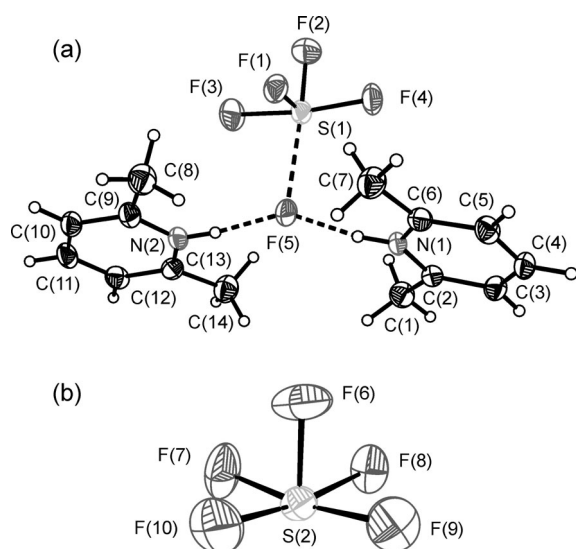


Figure 2. Thermal ellipsoid plot of a) the [HNC₅H₃(CH₃)₂]₂F[−]···SF₄ moiety and b) the SF₅[−] anion in [HNC₅H₃(CH₃)₂]₂F[−]···SF₄[SF₅][−]·3SF₄. Ellipsoids are set at 50% probability. Selected bond lengths [Å], contacts [Å], and angles [°]: S1–F1 1.545(2), S1–F2 1.549(2), S1–F3 1.650(2), S1–F4 1.706(2); S1···F5 2.487(2), F5···N1 2.554(3), F5···N2 2.553(3); S2–F6 1.564(2), S2–F7 1.730(2), S2–F8 1.763(2), S2–F9 1.719(2), S2–F10 1.664(2); F7–S2–F9 171.08(13), F8–S2–F10 170.70(13).

SF₄ are present in this structure. The fluoride-ion acceptor properties of SF₄ towards F[−] has been established by the formation of salts containing the SF₅[−] anion^[12] and recently, the Lewis-acidity of SF₄ towards organic bases has conclusively been shown for the base N(C₂H₅)₃.^[13]

In the present structure, the fluoride which is hydrogen-bonded to two 2,6-dimethylpyridinium cations forms F···S1 contacts (2.487(2) Å) with one SF₄ molecule. These contacts are significantly stronger than the F···S contacts found in solid SF₄, resulting in an increase of the average S–F bond lengths in the F[−]···SF₄ moiety. The effect of coordination of fluoride

on the structure of SF₄ in this salt is however less pronounced than that of N(C₂H₅)₃ coordination observed in the structure of SF₄·N(C₂H₅)₃,^[13] reflecting the weaker interaction between SF₄ and a fluoride that is hydrogen-bonded to two cations. A second significantly weaker interaction between sulfur and a fluorine atom from the SF₅[−] anion expands the coordination environment about S1 to six. The second fluoride ion in the structure is sufficiently naked to form the SF₅[−] anion, which adopts the expected square pyramidal structure. Apart from Rb[SF₅], Cs₆[SF₅]₄[HF₂]₂,^[12d] and [Cs([18]crown-6)₂][SF₅],^[12e] this is the fourth structurally characterized salt containing the SF₅[−] anion. Because three of the four equatorial fluorine atoms of this anion form F···S contacts, the anion is locked into one position without being disordered. As a consequence of the contacts, the anion geometry deviates from an idealized square pyramid. As expected, the axial S–F bond (1.564(2) Å) is much shorter than the equatorial S–F bonds (1.664(2) to 1.763(2) Å). The three equatorial fluorine atoms that have contacts to adjacent SF₄ molecules have significantly longer S–F bonds (1.719(2)–1.763(2) Å) than the bond to the other equatorial fluorine, which does not form contacts. The average of the equatorial S–F bond lengths is 1.719 Å, which is in excellent agreement with the average equatorial bond length reported for Rb[SF₅] (1.718 Å). Moreover, the average of each pair of equatorial S–F bond lengths that are *trans* to each other gives this value within the experimental error. The fluorine in SF₅[−] that forms the strongest contact, that is, F8, has the longest and most ionic S–F bond and is *trans* to the shortest most covalent equatorial bond, that is, S2–F10. As mentioned for the anion in Rb[SF₅],^[12d] the presence of the lone pair on sulfur results in sulfur being 0.136 Å below the plane formed by the four equatorial fluorine atoms.

The packing of [HNC₅H₃(CH₃)₂]₂F[−]···SF₄[SF₅][−]·3SF₄ shows two distinct layers along the *ab* plane. The SF₄ molecule that exhibits S···F contacts to the fluoride is located within a layer of the [HNC₅H₃(CH₃)₂]₂F[−] and SF₅[−] anions. The other three SF₄ molecules form a layer separating two ionic layers (Figure 3). The two types of SF₄ molecules show significant differences in the size of their fluorine atom ellipsoids, that is, the SF₄ coordinated to F[−] exhibits smaller thermal parameters than the fluorine atoms of the free SF₄, reflecting significantly more thermal motion. This is paralleled by the relatively large thermal ellipsoids found in solid SF₄ at −173 °C. The coordination environments about sulfur in all SF₄ molecules include two S···F contacts (Supporting Information, Figure S3), which is similar to the coordination environment found in solid neat SF₄. The contacts involving fluorine atoms from the SF₅[−] anion (2.755(2) to 2.937(2) Å) are in general shorter than those from fluorine atoms of adjacent SF₄ molecules (2.867(2) to 3.164(3) Å), reflecting the larger fluorobasicity of the anions. The F₄S···FSF₃ contacts are similar to those found in the structure of neat SF₄. As shown in Figure 3, the SF₄ molecules in the layer form contacts to molecules within the layer, as well as to the adjacent ionic layers, holding the layers together.

The Raman spectrum of solid SF₄ exhibits significant splitting as previously observed.^[8] These splittings can be

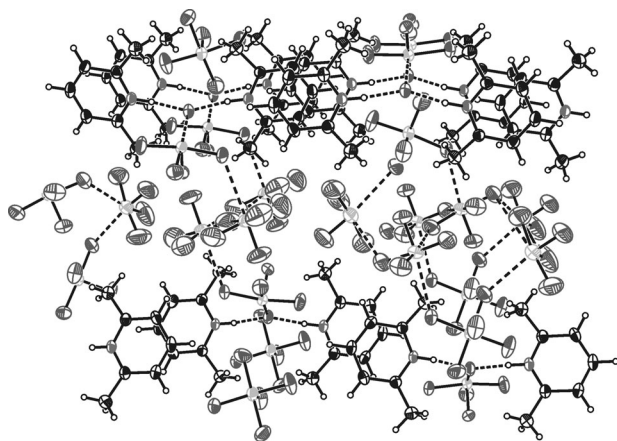


Figure 3. Thermal ellipsoid view along the *a* axis of the packing of $[\text{HNC}_5\text{H}_3(\text{CH}_3)_2]^+_2\text{F}^-\cdots\text{SF}_4[\text{SF}_5^-]\cdot 3\text{SF}_4$. Ellipsoids are set at 50% probability.

explained by the presence of two crystallographically different SF_4 molecules and/or by vibrational coupling between SF_4 molecules in one unit cell. The Raman spectrum of $[\text{HNC}_5\text{H}_3(\text{CH}_3)_2]^+_2\text{F}^-\cdots\text{SF}_4[\text{SF}_5^-]\cdot 3\text{SF}_4$ at -100°C is depicted in Figure 4 and contains the characteristic signals associated

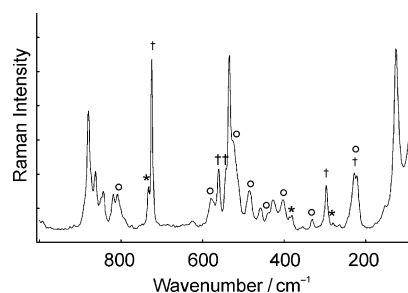


Figure 4. Raman spectrum of $[\text{HNC}_5\text{H}_3(\text{CH}_3)_2]^+_2\text{F}^-\cdots\text{SF}_4[\text{SF}_5^-]\cdot 3\text{SF}_4$ at -100°C . Asterisks (*) denote bands arising from the FEP sample tube. Bands attributed to the 2,6-dimethylpyridinium cation and to the SF_5^- anion are denoted by (†) and (○), respectively.

with the $\text{HNC}_5\text{H}_3(\text{CH}_3)_2^+$ cation and the SF_5^- anion. The latter were assigned based on the vibrational assignments previously reported for the Cs^+ and $[\text{Cs}(\text{18crown-6})_2]^+$ salts.^[12] The Raman spectrum also shows several bands attributable to SF_4 . Interestingly, two sets of bands in the equatorial SF_2 stretching region can be distinguished and tentatively assigned to $\nu_s(\text{SF}_{2,\text{eq}})$ of SF_4 in the layer (880 cm^{-1}), which is close to that of neat solid SF_4 ($888, 879\text{ cm}^{-1}$), and that of SF_4 coordinated by F^- (863 cm^{-1} ; Supporting Information, Table S1). A Raman spectrum of solid $[\text{HNC}_5\text{H}_3(\text{CH}_3)_2]^+_2\text{F}^-\cdots\text{SF}_4[\text{SF}_5^-]\cdot 3\text{SF}_4$ recorded at -85°C contains a broadened signal at 884 cm^{-1} , which resembles the broad signal observed in liquid SF_4 . This observation corroborates the observation of significant thermal motion within the SF_4 layer and suggests the onset of decomposition via release of SF_4 .

In conclusion, the structure of SF_4 in the solid state has been elucidated for the first time. The structure can best be

described as a network with weak intermolecular $\text{S}\cdots\text{F}$ contacts formed exclusively with the axial fluorine atoms that exhibit more ionic character. The structure is different from previous predictions of chain-type or dimeric structures.^[7] A similar structural motif is found in the novel $[\text{HNC}_5\text{H}_3(\text{CH}_3)_2]^+_2\text{F}^-\cdots\text{SF}_4[\text{SF}_5^-]\cdot 3\text{SF}_4$ salt which contain SF_4 layers. As in neat SF_4 , the SF_4 molecules within the layer of the salt have two $\text{S}\cdots\text{F}$ contacts of similar distances and do not form distinct dimers or chains. Because of the weakness of interactions, the overall structure, that is, network versus layer, greatly depends on the nature of composition of the compound. The $[\text{HNC}_5\text{H}_3(\text{CH}_3)_2]^+_2\text{F}^-\cdots\text{SF}_4[\text{SF}_5^-]\cdot 3\text{SF}_4$ salt is the first compound that contains a range of interaction motifs between SF_4 and F^- , that is, $\text{F}_4\text{S}-\text{F}^-$ ($1.564(2)$ to $1.763(2)\text{ \AA}$), $\text{F}_4\text{S}\cdots\text{F}^-$ ($2.587(2)\text{ \AA}$), $\text{F}_4\text{S}\cdots\text{FSF}_4^-$ ($1.755(2)$ to $2.937(2)\text{ \AA}$), and $\text{F}_4\text{S}\cdots\text{FSF}_3$ ($2.867(2)$ to $3.164(2)\text{ \AA}$).

Experimental Section

All volatile materials were handled on a vacuum line constructed of nickel, stainless steel, and FEP. Reaction vessels were fabricated from FEP tubing ($1/4$ -in (0.635 cm) o.d.) and outfitted with Kel-F valves. All reaction vessels were rigorously dried under dynamic vacuum followed by treatment with more than 1 atm of F_2 gas.

Sulfur tetrafluoride (Ozark-Mahoning Co.) was purified by passing the gas through a column of activated charcoal. Traces of thionyl fluoride and sulfur hexafluoride were present in the sulfur tetrafluoride, but did not interfere with the chemistry. Difluorodichloromethane (Synquest Labs Inc.), 2,6-dimethylpyridine (Sigma-Aldrich) were used as received.

$[\text{HNC}_5\text{H}_3(\text{CH}_3)_2]^+_2\text{F}^-\cdots\text{SF}_4[\text{SF}_5^-]\cdot 3\text{SF}_4$: Water (0.016 g , 0.89 mmol) was injected into a $1/4$ -in. FEP reactor equipped with a Kel-F valve using a micro syringe. 2,6-dimethylpyridine (0.176 g , 1.64 mmol) was then injected into the $1/4$ -in. FEP reactor in a dry nitrogen filled glove bag. A large excess of SF_4 was vacuum-distilled onto the frozen mixture at -196°C . Upon melting of SF_4 at -120°C , a vigorous reaction occurred, causing a white insoluble precipitate to form. Warming the reaction mixture to 0°C formed a clear colorless solution. Upon cooling of this solution to -85°C large needles formed. Excess SF_4 was partially removed under dynamic vacuum at -95°C , yielding 0.691 g of a white solid, namely $[\text{HNC}_5\text{H}_3(\text{CH}_3)_2]^+_2\text{F}^-\cdots\text{SF}_4[\text{SF}_5^-]\cdot 3\text{SF}_4$ with small amounts of residual SF_4 .

Raman spectra were recorded on a Bruker RFS 100 FT Raman spectrometer with a quartz beam splitter, a liquid-nitrogen cooled Ge detector, and R-496 temperature accessory. The actual usable Stokes range was 50 to 3500 cm^{-1} . The 1064-nm line of an Nd:YAG laser was used for excitation of the sample. The Raman spectra were recorded at -110°C with a spectral resolution of 2 cm^{-1} using laser powers of 300 mW .

X-ray crystallography: SF_4 , formula weight $M_r = 108.06\text{ g cm}^{-3}$, clear colorless plate ($0.17 \times 0.15 \times 0.14\text{ mm}^3$), orthorhombic, $P2_12_12_1$, $Z = 8$, $a = 6.773(4)$, $b = 6.812(4)$, $c = 13.122(8)\text{ \AA}$, $V = 605.5(6)\text{ \AA}^3$, $\rho_{\text{calcd}} = 2.371\text{ g cm}^{-3}$, $2\theta_{\text{max}} = 54.4^\circ$, $\lambda(\text{MoK}\alpha) = 0.71073\text{ \AA}$, $100(2)\text{ K}$, 6874 reflections, 1387 unique reflections ($R_{\text{int}} = 0.052$), absorption coefficient ($\mu = 0.98\text{ mm}^{-1}$), $R_1 = 0.050$, $wR_2 = 0.112$.

$\text{C}_{14}\text{H}_{20}\text{F}_{22}\text{N}_2\text{S}_5$: formula weight $M_r = 794.61\text{ g cm}^{-3}$, clear colorless block ($0.16 \times 0.19 \times 0.57\text{ mm}^3$), orthorhombic, $P2_12_12_1$, $Z = 4$, $a = 7.4597(10)$, $b = 18.150(2)$, $c = 21.863(3)\text{ \AA}$, $V = 2960.2(7)\text{ \AA}^3$, $\rho_{\text{calcd}} = 1.783\text{ g cm}^{-3}$, $2\theta_{\text{max}} = 55.2^\circ$, $\lambda(\text{MoK}\alpha) = 0.71073\text{ \AA}$, $133(2)\text{ K}$, 33934 reflections, 6819 unique reflections ($R_{\text{int}} = 0.033$), absorption coefficient ($\mu = 0.54\text{ mm}^{-1}$), $R_1 = 0.042$, $wR_2 = 0.117$.

The crystals were mounted at low temperature under a stream of cold dry nitrogen as previously described.^[14] The crystals were centered on a Bruker SMART APEX II diffractometer, controlled

by the APEX2 Graphical User Interface software.^[15] The program SADABS^[16] was used for scaling of diffraction data, the application of a decay correction, and a multi-scan absorption correction. The program SHELXS-97^[17] was used for both solution and refinement. A structure solution was obtained by direct methods. Further details on the crystal structure investigations may be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: (+49)7247-808-666; e-mail: crysdata@fiz-karlsruhe.de), on quoting the depository number CSD-425996 (SF₄). CCDC 932409 (C₁₄H₂₀F₂₂N₂S₅) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Received: April 8, 2013

Revised: May 2, 2013

Published online: June 19, 2013

Keywords: crystallography · fluorine · Raman spectroscopy · structure elucidation · sulfur tetrafluoride

- [1] J. Fischer, W. Jaenckner, *Angew. Chem.* **1929**, 42, 810–811.
- [2] a) W. C. Smith, *Angew. Chem.* **1962**, 74, 742–751; *Angew. Chem. Int. Ed. Engl.* **1962**, 1, 467–475; b) W. Dmowski in *Houben-Weyl, Organo-Fluorine Compounds, Vol. E10a* (Eds.: B. Baasner, H. Hagemann, J. C. Tatlow), Thieme, Stuttgart, **2000**, chap. 8.
- [3] W. M. Tolles, W. D. Gwinn, *J. Chem. Phys.* **1962**, 36, 1119–1121.
- [4] a) K. Kimura, S. H. Bauer, *J. Chem. Phys.* **1963**, 39, 3172–3178; b) V. C. Ewing, L. E. Sutton, *Trans. Faraday Soc.* **1963**, 59, 1241–1247.
- [5] K. O. Christe, X. Zhang, J. A. Sheehy, R. Bau, *J. Am. Chem. Soc.* **2001**, 123, 6338–6348, and references therein.
- [6] a) A. N. Taha, N. S. True, C. B. LeMaster, C. L. LeMaster, S. M. Neugebauer-Crawford, *J. Chem. Phys. A* **2000**, 104, 3341–3348; b) F. Seel, W. Gombler, *J. Fluorine Chem.* **1974**, 4, 327–331.
- [7] W. Gombler, F. Seel, *J. Fluorine Chem.* **1974**, 4, 333–339.
- [8] a) C. V. Berney, *J. Mol. Struct.* **1972**, 12, 87–97; b) K. O. Christe, E. C. Curtis, C. J. Schack, S. J. Cyvin, J. Brunvoll, W. Sawodny, *Spectrochim. Acta Part A* **1976**, 32, 1141–1147.
- [9] D. Mootz, L. Korte, *Z. Naturforsch. B* **1984**, 39, 1295–1299.
- [10] R. Kniep, L. Korte, R. Kryschi, W. Poll, *Angew. Chem.* **1984**, 96, 351–352; *Angew. Chem. Int. Ed. Engl.* **1984**, 23, 388–389.
- [11] A. Bondi, *J. Phys. Chem.* **1964**, 68, 441–451.
- [12] a) R. Tunder, B. Siegel, *J. Inorg. Nucl. Chem.* **1963**, 25, 1097–1098; b) K. O. Christe, E. C. Curtis, C. J. Schack, D. Pilipovich, *Inorg. Chem.* **1972**, 11, 1679–1682; c) L. F. Drullinger, J. E. Griffiths, *Spectrochim. Acta Part A* **1971**, 27, 1793–1799; d) J. Bittner, J. Fuchs, K. Seppelt, *Z. Anorg. Allg. Chem.* **1988**, 557, 182–190; e) M. Clark, C. J. Kellen-Yuen, K. D. Robinson, H. Zhang, Z. Y. Yang, K. V. Madappat, J. W. Fuller, J. L. Atwood, J. S. Thrasher, *Eur. J. Solid State Inorg. Chem.* **1992**, 29, 809–833.
- [13] J. T. Goettel, P. Chaudhary, P. Hazendonk, H. P. A. Mercier, M. Gerken, *Chem. Commun.* **2012**, 48, 9120–9122.
- [14] M. Gerken, D. A. Dixon, G. J. Schrobilgen, *Inorg. Chem.* **2000**, 39, 4244–4255.
- [15] APEX 2, Version 2.2-0; Bruker AXS Inc.: Madison, WI, **2007**.
- [16] G. M. Sheldrick, *SADABS*, Version 2007/4, Bruker AXS Inc., Madison, WI, **2007**.
- [17] G. M. Sheldrick, *SHELXTL97*, University of Göttingen, Germany, **2007**.