PROPERTIES OF [SF₃][MF₆] (M = Sb, As), WOF₄ DERIVATIVES, 1-ETHYL-3-METHYLIMIDAZOLIUM BIFLUORIDE, PERFLUOROCARBOXYLIC ACIDS AND PERFLUOROCARBOXYLATES

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Master of Science, University of Lethbridge, 2011

A Thesis
Submitted to the School of Graduate Studies
of the University of Lethbridge
in Partial Fulfillment of the
Requirements for the Degree

DOCTOR OF PHILOSOPHY

Department of Chemistry and Biochemistry
University of Lethbridge
LETHBRIDGE, ALBERTA, CANADA

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PROPERTIES OF [SF$_3$][MF$_6$] $(M = \text{Sb, As})$, WOF$_4$ DERIVATIVES, 1-ETHYL-3-METHYLIMIDAZOLIUM BIFLUORIDE, PERFLUOROCARBOXYLIC ACIDS AND PERFLUOROCARBOXYLATES

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ABSTRACT

The Lewis acid chemistry of [SF$_3$][MF$_6$] (M = Sb, As) salts with the nitrogen bases pyridine, acetonitrile, 1,10-phenanthroline and 4-dimethylaminopyridine (DAMP) is being explored, yielding 1:2 adducts for the mono-dentate bases and 1:1 adduct with the bidentate 1,10-phenanthroline. The crystal structures of α- and γ-[SF$_3$][SbF$_6$] are characterized for the first time along with that of [SF$_3$][AsF$_6$]. Preliminary results for the deoxofluorination of two ketones, carboxylic acids and an alcohol are being presented using [SF$_3$][MF$_6$] (M = Sb, As).

Chemistry of WOF$_4$ has been explored using SO$_2$, [(CH$_3$)$_4$N][F] and a fluorinated aliphatic alcohol, CF$_3$CH$_2$OH. The products, i.e. WOF$_4$·SO$_2$, [(CH$_3$)$_4$N][WOF$_5$] and CH$_3$CN·WOF$_3$(OCH$_2$CF$_3$) have been fully characterized by X-ray crystallography and Raman spectroscopy.

Crystal structures of perfluorinated carboxylic acids and carboxylates of environmental concern are reported for the first time.

The 1-ethyl-3-methylimidazolium bifluoride (EMIMHF$_2$) ionic liquid has been studied with solid-state MAS NMR spectroscopy at low temperature to explore its structural features.
ACKNOWLEDGEMENTS

I would like to thank my supervisor(s) Prof. Michael Gerken and Prof. Paul Hazendonk for providing me an opportunity to work in their laboratories. With their guidance and support, I handled both specialized areas of research, i.e., fluorine chemistry and NMR spectroscopy.

I would like to thank my committee members Profs. Peter Dibble, Paul Hayes, Adriana Predoi-Cross and the members of examination committee for their interest and investment of time.

I am thankful to Prof. Carsten Jenne for being my external examiner and investing his valuable time.

I would like to thank Tony Montina, NMR manager, as well as Michael Opyr for their support in running solid-state NMR experiments. Many thanks to Heinz Fischer for fixing the Raman low-temperature assembly unit time to time.

I would like to thank Alberta Ministry of Education and the University of Lethbridge for financial support. Again, many thanks to Alberta Innovates – Technology Futures for a Graduate Scholarship and the Len Bolger Scholarship. I would like to thank the Department of Chemistry and Biochemistry for the support in research.

Finally, I am thankful to my wife, my parents, my brother and my son for their support as I finished my studies.
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General

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<tr>
<td>ax</td>
<td>axial</td>
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<tr>
<td>eq</td>
<td>equatorial</td>
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<tr>
<td>Kel-F</td>
<td>chlorotrifluoroethylene</td>
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<td>Nuclear Magnetic Resonance</td>
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<td>TEA</td>
<td>triethylamine</td>
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<td>br</td>
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<td>EMIMHF₂</td>
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Nuclear Magnetic Resonance

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<td>δ</td>
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<tr>
<td>J</td>
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<td>ppm</td>
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<td>HFB</td>
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<td>MAS</td>
<td>magic angle spinning</td>
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X-ray Crystallography

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Chapter-1

1. Introduction

1.1 Fluorine chemistry

Fluorine is a unique element because of its properties, such as the highest electronegativity of all elements in the periodic table and its relatively small size (van der Waal radius of 1.47 Å).\(^1\)\(^2\) As a consequence, fluorine can impart special properties onto inorganic and organic compounds.

Fluorine forms ionic as well as covalent compounds depending on the electronegativity difference between the atoms involved in the bonding. If the electronegativity difference is large, an ionic fluoride is formed, e.g., NaF, CaF\(_2\), etc. If the difference is small, the covalent character of the element–fluorine bond increases. Many covalent, molecular inorganic fluorine compounds are very reactive and unstable towards hydrolysis, e.g., XeF\(_2\), SF\(_4\), PF\(_5\).\(^1\)

Inorganic fluorine compounds have various applications. For example, low concentration of F\(^-\) (0.5 to 0.7 ppm in Lethbridge in the form of hydrofluorosilisic acid)\(^3\) are added to the drinking water (fluoridation) and F\(^-\) is present in toothpaste (between 1000 and 1500 ppm in the form of NaF, SnF\(_2\) or Na\(_2\)PO\(_3\)F) to improve dental health to strengthen the enamel.\(^4\) In the semiconductor industry SF\(_6\) has been used as an insulator and to create intricate circuitry patterns upon silicon wafers,\(^5\) and Na\(_3\)AlF\(_6\) is essential in the production of aluminium.\(^1\) Inorganic fluorine compounds have also been used as reagents to introduce F into organic molecules, e.g., SF\(_4\) and some of its derivatives have been used to convert –COOH to –C(O)F, –OH to –F and >C=O to >CF\(_2\).\(^6\) Inorganic fluorine compounds have also been instrumental to validate the VSEPR model introduced by Gillespie. For example,
the VSEPR model is correct in predicting the see-saw geometry of SF$_4$ and the linear geometry of XeF$_2$.\textsuperscript{7}

In contrast to the reactivity of many inorganic molecular fluorine compounds, organic fluorine compounds generally exhibit great stability, since they contain very strong C–F bonds. The bond energy of a C–F bond is 485.7 kJ/mol which is significantly larger than that of a C–H bond, (around 337 kJ/mol).\textsuperscript{9} Organofluorine compounds have a variety of applications because the fluoro substituent or fluorinated group, e.g., (–CF$_3$) increase the lipophilicity and metabolic stability.\textsuperscript{10} The introduction of fluorine into organic substrates can result in more potent pharmaceutical compounds, and the use of fluorinated drugs is increasing rapidly. A good practical example of this type of application is the antibiotic drug, ciprofloxacin from Pfizer Inc. (scheme-I) in which the fluorine atom is introduced to have the polar as well as the directional effects. Another good example is Lipitor from NOVARTIS (scheme-I), a cholesterol lowering drug.\textsuperscript{11}

![Scheme-I (a) Ciprofloxacin (b) Lipitor](image)

Fluorinated pesticides are also extensively being used in agriculture. For example, Fluopicolide is used as a fungicide to control disease in potatoes by oomycetes, and Flamprop is used as an herbicide to control broadleaf weeds.\textsuperscript{12}
The use of organofluorine compounds extends to the polymer field. Fluoropolymers are high-performance materials with many specific applications. Most widely known in the general public, Teflon (DuPont) coating is used on utensils for even heat distribution and for oil-free cooking. But at the same time, the compounds used as the polymerization aid in the generation of PTFE (polytetrafluoroethylene) can also cause environmental problems. Perfluorooctanoic acid (PFOA) is used to stabilize emulsion in the production of PTFE and is widely found in the environment due to its persistent nature.13,14

1.1.1 Nucleophilic fluorinating reagents

Approximately 30% of all agrochemicals and 20% of all pharmaceuticals contain fluorine.15,16 Introduction of fluorine into the targeted organic compounds has found several applications in modern medicine, including diagnostic imaging, eye surgery, oxygen delivering systems, cancer therapy and respiratory medicine.10 The Antibiotic 1-cyclopropyl-6-fluoro-4-oxo-7-(piperazin-1-yl)-quinoline-3-carboxylic acid (ciprofloxacin) (scheme-I), antibiotic fluoroquinolone (levofloxacin), and antitumor fluoronucleoside (tegafur) (scheme-II) are examples of the successful introduction of fluorine into organic molecules to obtain a pharmaceutically active compound.

(a) [Chemical structure of ciprofloxacin]
(b) [Chemical structure of levofloxacin]

Scheme-II (a) Levofloxacin (b) Tegafur
Fluorine creates changes in the lipophilicity, acidity/basicity, dipole moment, overall reactivity, stability and the conformation of a compound. When substituting hydrogen, fluorine does not change the overall volume too dramatically (van der Waals radii for fluorine and hydrogen are 1.47 and 1.20 Å, respectively). The higher amount of C–F bond energy (485.7 kJ/mol) gives relative stability to C–F bonds against metabolic transformations. The replacement of hydrogen by fluorine can increase the lipid solubility of bioactive molecules. This results in easier drug transport and good absorption rates in biological systems. As a consequence, the development of fluorination processes is essential for the synthesis of pharmaceutical and agricultural compounds and, hence, there is an ongoing demand for safe and efficient fluorinating reagents.

Among the different available techniques for fluorination (electrophilic fluorination, electrochemical fluorination and nucleophilic fluorination), nucleophilic fluorination is the most popular process because of the ease of handling of most of the reagents involved. The nucleophilic displacement of oxygen by fluorine, commonly known as deoxofluorination, is one of the most effective and routinely used approaches in medicinal chemistry. Sometimes, the –OH group on these organic molecules can also be replaced by an –F group as required. Hydrogen fluoride (HF), some metal fluorides (e.g. CoF$_3$, KF), [Bu$_4$N][F] and many sulfur fluorides make up the series of nucleophilic fluorinating reagents. Hydrogen fluoride has limited usage because of its toxic, corrosive properties and low reactivity. Its low reactivity is a result of strong H–F bond. Many ionic metal fluorides are hygroscopic in nature and water molecules can be strongly hydrogen bonded to these fluorides resulting in lower reactivity. Trimethyltin fluoride, Me$_3$SnF is also a representative of the nucleophilic fluorinating reagent series. Alternatively, there
are many fluoro-sulfur compounds available on commercial scales (SF₄, DAST, Dexo-
Fluor®, Fluolead™, XtalFluor-E®, XtalFluor-M®).

1.1.2 Fluoro-sulfur compounds as deoxofluorinating reagents

Sulfur tetrafluoride, SF₄, is one of the well-known binary sulfur fluorides and has been used
as a fluorinating agent in the preparation of inorganic fluorine-containing compounds, such
as IF₅, SeF₄, SnF₄, MoF₆ and UF₆ in high yields by fluorination of I₂O₅, SeO₂, SnS₂, MoO₃
and UO₃, respectively²⁴ and in synthesizing oxyfluorides.²⁵ More importantly, SF₄ has
extensively been used as a deoxofluorinating reagent in organic chemistry for the
conversion of R₂C=O to R₂CF₂, –OH to –F and –COOH to –CF₃.²⁶ Since the gaseous,
corrosive and toxic nature of SF₄ requires special equipment and techniques, a number of
other sulfur-containing fluorinating reagents capable of selectively introducing fluorine in
the target compounds have been developed. These fluorinating reagents are relatively easy
to handle and do not require any special protocol for the fluorination process. Diethylamino
sulfurtrifluoride, DAST (Et₂N-SF₃), Deoxo-Fluor® ((CH₃O)₂(CH₂)₄N–SF₃), Fluolead™
((4-tert-butyl)(2,6-dimethyl)C₆H₃SF₃), XtalFluor-E® ([Et₂N=SF₂][BF₄]), and XtalFluor-
M® (morpholinodifluorosulfinium tetrafluoroborate) as shown in scheme–III are some
common commercially available fluoro-sulfur nucleophilic fluorinating reagents.
DAST was originally developed as an alternative to SF$_4$. Its main advantage was its liquid form which is easier to handle and did not require special technique as is required in case of SF$_4$. DAST had a main disadvantage as well. At temperatures exceeding 90 °C, DAST decomposes in two stages. First, it decomposes to SF$_4$ and (Et$_2$N)$_2$SF$_2$ at 90 °C. After heating above 90 °C, (Et$_2$N)$_2$SF$_2$ can detonate. In the search for a safer alternative for DAST, Deoxo-Fluor$^\circledR$ was synthesized. Deoxo-Fluor$^\circledR$ (CH$_3$O)$_2$(CH$_2$)$_4$N-SF$_3$ decomposes slowly with less heat evolution but the problem regarding its decomposition temperature (90 °C) remained the same. Upon use, both DAST and Deoxo-Fluor$^\circledR$ generates HF, which is highly volatile and toxic. With the invention of Fluolead$^{TM}$ ((4-tert-buty1)(2,6-dimethyl)C$_6$H$_3$SF$_3$) (Ishikawa’s reagent) in 2008, some improvement in the stability was achieved owing to the higher stability of C–S bonds but there is always the possibility of obtaining amides and esters side products. In 2010, two very useful and more selective fluorinating reagents namely XtalFluor-E$^\circledR$ and XtalFluor-M$^\circledR$, were developed by Omegachem.$^{27}$ These two solid reagents are more stable than DAST as shown by differential scanning calorimetry and have shown the capability to selectively convert R$_2$C=O to R$_2$CF$_2$, –COOH to –COF and –OH to –F.$^{27}$ The following mechanisms (scheme–IV) for the deoxofluorination reactions of carbonyl and hydroxyl groups by SF$_4$ in the presence of HF have been proposed in which SF$_3^+$ is the active species responsible for the deoxofluorination reaction.$^{70}$. The presence of SF$_3^+$ and HF$_2^-$ in the SF$_4$-HF system was
demonstrated by conductivity measurements.\textsuperscript{28}

\begin{align*}
\text{(a) } & R\overset{\cdot}{O} + \text{SF}_3 & \rightarrow & R\overset{\cdot}{O}\cdot\text{SF}_2 + \text{F}^- \\
\text{(b) } & R\overset{\cdot}{O} + \text{H} + \text{SF}_3^+ & \rightarrow & R\overset{\cdot}{O}\cdot\text{SF}_3 + \text{F}^- \\
& & & \text{RO-SF}_3 + \text{H-F}
\end{align*}

Scheme-IV Proposed mechanism for deoxofluorination process of (a) carbonyl group and (b) hydroxyl group by SF\textsubscript{4} in the presence of HF\textsuperscript{28}

1.2 Sulfur tetrafluoride and [SF\textsubscript{3}][MF\textsubscript{6}] (M = Sb, As) salts

1.2.1 Fluoride-ion donor properties of SF\textsubscript{4}

Sulfur tetrafluoride, SF\textsubscript{4}, is a corrosive and toxic gas at ambient temperature with a melting point of \(-121\) °C and a boiling point of \(-38\) °C. It readily forms HF upon contact with water. On one hand, SF\textsubscript{4} acts as a weak Lewis acid and can form Lewis acid-base adducts with F\textsuperscript{-} and nitrogen bases.\textsuperscript{29} on the other hand, SF\textsubscript{4} can donate a fluoride ion towards strong Lewis acids such as BF\textsubscript{3}, AsF\textsubscript{5}, SbF\textsubscript{5} to form the corresponding SF\textsubscript{3}\textsuperscript{+} salts, e.g., [SF\textsubscript{3}][BF\textsubscript{4}], [SF\textsubscript{3}][AsF\textsubscript{6}] and [SF\textsubscript{3}][SbF\textsubscript{6}] as shown in equation 1.1 and 1.2.\textsuperscript{8}

\begin{align*}
\text{SF}_4 + \text{BF}_3 & \rightarrow [\text{SF}_3]\text{[BF}_4]\text{ .................................................................(1.1)} \\
\text{SF}_4 + \text{MF}_5 & \rightarrow [\text{SF}_3]\text{[MF}_6] \text{ (M = Sb, As) .................................................................(1.2)}
\end{align*}
In 1956, Bartlett and Robinson first reported that SF₄ can form solid complexes with a number of highly Lewis acidic inorganic fluorides, i.e., BF₃, AsF₅, and SbF₅, and noted the melting points of the resultant solids.³⁰ They suggested the possibility of [F₃B ↔ :SF₄] Lewis acid-base interactions. Bartlett, Robinson found that the SF₄ adduct with BF₃ can be used to obtain pure SF₄ because of the reversibility of the formation reaction.³⁰ In 1958, Cotton and George carried out IR spectroscopic measurements on the [F₃B ↔ :SF₄] adduct and presented arguments in favour of the ionic nature of the solid adduct based on the observation of BF₄⁻ bands. Since they were limited in carrying out their work in an air-free environment, they could not, however, conclusively prove their claim because of the highly hydrolytic nature of the BF₃–SF₄ reaction product, because it could form BF₄⁻ in the presence of moisture.³¹ In 1961, Muetterties and coworkers filed a patent on the formation and use of a number of SF₄ adducts, i.e., SF₄·BF₃, SF₄·SbF₅, SF₄·PF₅ and SF₄·AsF₃. In the ¹⁹F NMR spectrum of the SF₄–AsF₃ system at temperatures as low as −60 °C, only one type of fluorine resonance was observed, which was interpreted in terms of fluorine bridging between sulfur and arsenic.³² An ¹⁹F NMR study by Barr and Dunell on the SF₄ adduct with AsF₅, which is a much stronger Lewis acid than AsF₃, showed two distinct resonances in a 1:2 ratio confirming the ionic nature of the reaction product between SF₄ and AsF₅, i.e. [SF₃][AsF₆].³³ Seel and Detmer studied the reaction between SF₄ and BF₃, AsF₅ and SbF₅ and looked at the thermal stability of the products. The sublimation temperature of [SF₃][AsF₆] and [SF₃][SbF₆] was reported as 90 °C and 253 °C, respectively. In addition, they studied the BF₃–SF₄ adduct by IR spectroscopy. The infrared band at 1050 cm⁻¹ was attributed to the BF₄⁻ ion and the S–F stretching bands at 908 and 940 cm⁻¹ were assigned to the SF₅⁺ cation since they were significantly shifted to higher frequencies as compared to the S–F stretching bands of SF₄ (896 and 857 cm⁻¹). They also compared the BF₄⁻ band
of [SF₃][BF₄] to the BF₄⁻ bands present in [NH₄][BF₄] and [Na][BF₄] salts to conclude the presence of BF₄⁻ ion. The [SF₃][BF₄] adduct has a significant vapor pressure (approximately 100 mm Hg) at room temperature and dissociates into the original reactant components as determined by gas-phase IR spectroscopy. This dissociation can be utilized to get pure SF₄. Gillespie and coworkers extended the vibrational characterization to Raman spectroscopy of [SF₃][BF₄], [SF₃][PF₆], [SF₃][AsF₆] and [SF₃][SbF₆] and interpreted the spectra in terms of SF₃⁺ cation, BF₄⁻ and MF₆⁻ (where M = P, As, Sb) anions. Deviations of the observed spectra from those predicted for idealized ion symmetry were attributed to fluorine bridging between anions and cations. For example, the Raman spectrum of [SF₃][SbF₆] showed a band at 680 cm⁻¹, which can be assigned to the υ₃ mode of SbF₆⁻ anion with O₆h symmetry although this mode is formally Raman inactive. They also observed splitting for υ₂ and υ₅ bands of SbF₆⁻ around 568 and 291 cm⁻¹. They attributed the splitting and the observation of formally inactive Raman bands as the consequence of lowering in symmetry due to the fluorine bridging between SbF₆⁻ and SF₃⁺.

Conductivity measurements on [SF₃][BF₄] and [SF₃][SbF₆] adducts in anhydrous HF yielded conductivities that are very similar to those of [K][BF₄] and [K][SbF₆] showing their dissociation in HF solution. Brownstein and Shamir carried out the Raman spectroscopic measurements of solutions of [SF₃][BF₄], [SF₃][PF₆] and [SF₃][AsF₆] salts in anhydrous HF confirming the ionic formulations of these salts. The Raman spectrum of the molten [SF₃][SbF₆] salt at 250 °C also indicated the ionic form [SF₃][SbF₆].

In 1983, O’Brien and Desmarteau synthesized room-temperature unstable salts of SF₃⁺ with SO₃F⁻ and CF₃SO₃⁻ counter anions according to the reactions (1.3) to (1.5).

\[
2\text{SF}_4 + \text{ClO}_2\text{SO}_2\text{F} \rightarrow [\text{SF}_3][\text{FSO}_3] + \text{SF}_5\text{Cl} \quad (–90 \text{ to } –40 °C \text{ for 4h}) \quad (1.3)
\]

\[
2\text{SF}_4 + \text{ClO}_2\text{SO}_2\text{CF}_3 \rightarrow [\text{SF}_3][\text{CF}_3\text{SO}_3] + \text{SF}_5\text{Cl} \quad (–78 \text{ to } –40 °C \text{ for 1 h}) \quad (1.4)
\]
2SF₄ + BrOSO₂CF₃ → [SF₃][CF₃SO₃] + SF₅Br (−70 to −10 °C for 3–6 h)……..(1.5)

These salts were characterized by Raman spectroscopy which provided the characteristic S–F stretching frequencies of the SF₃⁺ cation.⁹

Neil Bartlett and coworkers grew crystals of [SF₃][BF₄] salt by sublimation and presented the first conclusive X-ray structural data of an SF₃⁺ salt. In the crystal structure of [SF₃][BF₄], the SF₃⁺ cation forms three S···F contacts of 2 × 2.624(2) Å and 2.593(3) Å with fluorine atoms of three adjacent BF₄⁻ anions, increasing the coordination number of sulfur to six.³⁷ Bartlett et al. tried to grow [SF₃][AsF₆] crystals by sublimation and obtained unit cell parameters for [SF₃][AsF₆] (Orthorhombic Cmc2₁ with the dimensions a = 20.375(3) Å, b = 8.508(3) Å, c = 11.224 (3) Å, and V = 1945.7 Å³). The quality of the X-ray crystallographic data for [SF₃][AsF₆] were poor³⁷ and did not allow for the localization of the fluorine atoms. Crystals of [SF₃][SbF₆] could not be obtained. As a consequence, no conclusive structural information was obtained for [SF₃][AsF₆] and [SF₃][SbF₆] salts. Subsequently, Bartlett and coworkers also prepared the SF₃⁺ salts with GeF₅⁻ and GeF₆²⁻ anions. The [SF₃][GeF₅] salt was prepared by displacing BF₃ with GeF₄ in [SF₃][BF₄] salt at −126 °C. The [SF₃][GeF₅] salt is thermally unstable and dissociate to [SF₃]₂[GeF₆] and GeF₄ at room temperature, except under liquid GeF₄. The formation of the [SF₃][GeF₅] salt was verified by characteristic bands for SF₃⁺ salts (945, 932, 914 cm⁻¹ for υ(A₁) and 904, 887, 874 cm⁻¹ for υ(E)) in the Raman spectrum.³⁸ The [SF₃]₂[GeF₆] salt was also prepared by reaction of SF₄ and GeF₄ in 2:1 molar ratio according to equation 1.7.

Dissociation

SF₄ + GeF₄ → [SF₃][GeF₅] ← [SF₃]₂[GeF₆] + GeF₄…………………..(1.6)

2SF₄ + GeF₄ → [SF₃]₂[GeF₆] …………………………………………………………..(1.7)
The $[\text{SF}_3]_2[\text{GeF}_6]$ salt readily sublimes at room temperature and the crystals of this material were obtained by the sublimation at 30–35 °C. $[\text{SF}_3]_2[\text{GeF}_6]$ crystallizes in the orthorhombic $Pmn$ space group. The $\text{SF}_3^+$ has $C_{3v}$ symmetry with all S–F bonds of equal length (1.519(1) and 1.515(2) Å) within 3σ and all F–S–F angles equal (96.12(8)–96.23(10)°). The bridging contacts of fluorine bonded to germanium to sulfur (2.367(2) and 2.420(1) Å) are shorter than those found in the crystal structure of $[\text{SF}_3][\text{BF}_4]$ (2.593(3) and 2.624(2) Å).\(^{39}\) Holloway and Rook synthesized $[\text{SF}_3][\text{OsF}_6]$ and $[\text{SF}_3][\text{IrF}_6]$ by a different approach.\(^{40}\) They attempted the synthesis of $\text{MF}_4\text{S}$ ($\text{M} = \text{Os}$ or Ir) by the reaction of appropriate hexafluoride with ZnS or $\text{B}_2\text{S}_3$ at elevated temperatures (200 – 300 °C). However, by comparing the IR spectra of the reactants and the products, they concluded that instead of $\text{MF}_4\text{S}$, the reaction product was $[\text{SF}_3][\text{MF}_6]$ ($\text{M} = \text{Os}$ or Ir) in addition to several by-products including a range of sulfur fluorides. In this reaction, OsF$_6$ and IrF$_6$ readily oxidatively fluorinates ZnS and $\text{B}_2\text{S}_3$. In solution $^{19}\text{F}$ NMR spectra of these compounds using anhydrous HF as solvent, a broad singlet characteristic to $\text{SF}_3^+$ cation at +31.0 ppm was observed.

The order of melting points of several $\text{SF}_3^+$ salts in decreasing order can be given as $[\text{SF}_3][\text{SbF}_6]$ (m.p. 253 °C) > $[\text{SF}_3][\text{AsF}_6]$ > $[\text{SF}_3][\text{IrF}_6]$ > $[\text{SF}_3][\text{BF}_4]$ > $[\text{SF}_3][\text{PF}_6]$ > $[(\text{SF}_3)_2][\text{GeF}_6]$ > $[\text{SF}_3][\text{AsF}_4]$ (m.p. –20 °C).\(^{40}\) Recently, the crystal structures of $[\text{SF}_3][\text{SbF}_6]$ and $[\text{SF}_3][\text{AsF}_6]$ have been predicted to be $P2_1/c$ and the unit cell parameters have been predicted based on molecular mechanics calculations,\(^{41}\) but it is in contrast to the experimentally obtained unit cell data for $[\text{SF}_3][\text{AsF}_6]$.\(^{37}\)
1.3 SF$_3^+$–nitrogen bases adducts

1.3.1 Introduction

Trifluorosulfonium salts such as [SF$_3$][BF$_4$], [SF$_3$][AsF$_6$] and [SF$_3$][SbF$_6$] have been synthesized and analyzed using different techniques for a long time.$^{5,6,7,8}$ [SF$_3$][AsF$_6$] and [SF$_3$][SbF$_6$] salts with melting points of 90 and 253 °C, are of higher interest. In these SF$_3^+$ salts, sulfur is highly Lewis acidic.$^{37,42}$

It had been postulated by Mews and coworkers that [SF$_3$][BF$_4$] should react with NSF$_3$ to give [F$_3$S–NSF$_3$][BF$_4$] which then converts to the observed product F$_5$SN–SF$_2$ after releasing BF$_3$ according to the equation 1.8.$^{43}$

\[
-\text{BF}_3
\]

\[
[\text{SF}_3][\text{BF}_4] + \text{NSF}_3 \rightarrow [\text{F}_3\text{S–NSF}_3][\text{BF}_4] \rightarrow [\text{F}_2\text{SN–SF}_4][\text{BF}_4] \rightarrow \text{F}_5\text{SN–SF}_2 
\]

… (1.8)

In the literature, the X-ray crystal structure of the [SF$_3$(NSF$_3$)$_2$][AsF$_6$] salt was reported as the accidental decomposition product of [F$_4$S=N–Xe---NSF$_3$][AsF$_6$] in an effort to grow crystals of [F$_4$S=N–Xe---NSF$_3$][AsF$_6$] from NSF$_3$ at 0 °C.$^{44}$ This crystal structure shows the 1:2 adduct cation in contrast to the intermediate proposed by Mews.$^{43}$

Mews and coworkers performed $^{19}$F solution NMR spectroscopy of [SF$_3$][AsF$_6$] with CH$_3$CN in 1:1 molar ratio using SO$_2$ as solvent at −30 °C. Based on the change of $^{19}$F chemical shift from SF$_3^+$ in SO$_2$ (30.5 ppm) to 17.4 ppm when CH$_3$CN was added, the formation of the [SF$_3$NCCH$_3$]$^+$ adduct was proposed according to equation 1.9.$^{43}$

\[
-30 \degree\text{C}
\]

\[
[\text{SF}_3][\text{AsF}_6] + \text{CH}_3\text{CN} \rightarrow [\text{SF}_3\text{NCCH}_3][\text{AsF}_6] 
\]

… (1.9)

It was also stated that the proposed adduct decomposes according to the equation-
\[-30 \, ^\circ C\]
\[
\text{[SF}_3\text{NCCH}_3\text{][AsF}_6] \rightleftharpoons \text{[AsF}_5\text{NCCH}_3\text{]}\text{[AsF}_6\text{]} + \text{SF}_4 \, (g) \]

Mews and coworkers also carried out the reactions of mono and di substituted SF$_3^+$ salts, i.e. [(CF$_3$)SF][AsF$_6$] and [(CF$_3$)$_2$SF][AsF$_6$] with CH$_3$CN in the presence of SO$_2$ according to equations 1.11 and 1.12 and proposed the formation of [(CF$_3$)SF$_2$\cdot$\text{NCCH}_3$][AsF$_6$] and [(CF$_3$)$_2$SF\cdot$\text{NCCH}_3$][AsF$_6$].

\[
\text{[(CF}_3\text{)SF}_2\text{][AsF}_6] + \text{CH}_3\text{CN} \rightleftharpoons \text{[(CF}_3\text{)SF}_2\cdot\text{NCCH}_3\text{]}\text{[AsF}_6\text{]} \, (1.11)
\]

\[
\text{[(CF}_3\text{)}_2\text{SF}[\text{AsF}_6] + \text{CH}_3\text{CN} \rightleftharpoons \text{[(CF}_3\text{)}_2\text{SF\cdotNCCH}_3\text{]}\text{[AsF}_6\text{]} \, (1.12)
\]

They observed a change of $^{19}$F chemical shift for [(CF$_3$)SF$_2$]$^+$ in SO$_2$ from –54.7 ppm to –50.5 ppm when CH$_3$CN was added and a chemical shift change of –159.0 ppm to –78.5 ppm for [(CF$_3$)$_2$SF$_2$]$^+$ salt.$^{43}$ There are hardly any examples of trifluorosulfur cationic species in the pentacoordinate and difluorosulfur cationic species in the tetracoordinate state.$^{43,45}$

Several reports have been published on the existence of the [SF$_3$(C$_5$H$_5$N)$_2$]$^+$ and [SF$_3$(CH$_3$CN)$_2$]$^+$ cationic species on the basis of results from mass spectrometry and molecular orbital calculations.$^{46,47,48,49}$ It was suggested that the formation of [SF$_3$(C$_5$H$_5$N)$_2$]$^+$ and [SF$_3$(CH$_3$CN)$_2$]$^+$ species should be possible by direct reaction of SF$_3^+$ species with pyridine and acetonitrile.
1.4 Tungsten oxide tetrafluoride, WOF$_4$

1.4.1 Introduction

Tungsten oxide tetrafluoride, WOF$_4$, was first synthesized by O. Ruff et al. in 1907. They synthesized tungsten oxide tetrafluoride by the following two procedure as shown by reaction 1.13 and 1.14.

\[
\text{WOCl}_4 + 4\text{HF (anhydrous)} \rightarrow \text{WO}_4^4 + 4\text{HCl} \tag{1.13}
\]

\[
\text{WOCl}_4 + 2\text{PbF}_2 \xrightarrow{\Delta} \text{WO}_4^4 + 2\text{PbCl}_2 \tag{1.14}
\]

Tungsten oxide tetrafluoride is a tetrameric compound represented by the formula WOF$_4$. It is a white crystalline solid, which melts at 104.7 °C. WOF$_4$ can be synthesized by many ways. It can be synthesized by the fluorination of WO$_3$ at 300 °C, direct fluorination of W in the presence of O$_2$ at 300 °C, slow hydrolysis of WF$_6$, or by the reaction of WOCl$_4$ with HF. Wilson and Christe synthesized WOF$_4$ by the reaction of silica with excess WF$_6$ in the presence of anhydrous HF (aHF) according to equation 1.15.

\[
\text{aHF} \quad 2\text{WF}_6 + \text{SiO}_2 \rightarrow 2\text{WO}_4^4 + \text{SiF}_4 \tag{1.15}
\]

Excess amount of WF$_6$ avoids the formation of [H$_3$O][WOF$_5$] and [H$_3$O][W$_2$O$_2$F$_9$] salts. Pure WOF$_4$ can be obtained by the sublimation of this mixture under dynamic vacuum.

Initial X-ray crystallographic work by Edwards and Jones suggested an oxygen bridged cyclic tetrameric structure of WOF$_4$. The W–O–W angle was given as 183°. Infrared spectroscopy of WOF$_4$ was carried out showing a band at 1055 cm$^{-1}$, which was assigned to the W–O stretch and a band at 650 cm$^{-1}$, which was assigned to a W–O–W stretch. In 1974, Alexander et al. showed the tetrameric WOF$_4$ structure does not contain oxygen bridges. In fact, it has fluorine bridges and they assigned W–F–W stretching mode at 550 cm$^{-1}$. Another study was based on infrared and $^{19}$F NMR spectroscopy of
In the infrared spectrum, two W–O stretching bands were observed. One very sharp signal at 997 and a second weak signal at 1053 cm\(^{-1}\). These wavenumbers correspond to W–\(^{18}\)O and W–\(^{16}\)O stretches. In the \(^{19}\)F NMR spectrum two signals were observed at low temperatures. \(T_1\) relaxation times for the two signals were 3-4 min and 0.1 s, indicating two very different fluorine environments on WOF\(_4\): a terminal fluorine and a bridging fluorine environment. At higher temperatures only one narrow line dominated the spectrum.

Tungsten oxide tetrafluoride is Lewis acidic. The tungsten center in WOF\(_4\) can easily accept an electron pair from Lewis base. WOF\(_4\) forms two different types of addducts with pyridine (WOF\(_4\)·C\(_5\)H\(_5\)N and WOF\(_4\)·2C\(_5\)H\(_5\)N).\(^{59}\) The acidic character of WOF\(_4\) has also been demonstrated by its reaction with CsF\(^{58}\) or ClOF\(_3\).\(^{60}\)

Tungsten oxide fluorides form an important class of compounds being used in getting high purity metals, in organic synthesis as active halogenating agents and in catalysts.\(^{61}\) Some enzymatic processes are also completed with the help of tungsten complexes in the living organism.\(^{61}\) For example, tungsten-containing enzymes typically reduce carboxylic acids to aldehydes.\(^{62}\) Tungsten is among one of the heavy metals known to be participating in the biological activities.\(^{62}\)

Many derivatives of WF\(_6\) have been prepared by replacement of a single fluorine atom with an RO\(^-\) ligand, such as CH\(_3\)O\(^-\), C\(_2\)H\(_5\)O\(^-\), C\(_6\)H\(_5\)O\(^-\), CF\(_3\)CH\(_2\)O\(^-\).\(^{63,64,65,66,67}\) CH\(_3\)OWF\(_5\) was prepared by the reaction of WF\(_6\) and CH\(_3\)OSi(CH\(_3\))\(_3\) and was characterized by solution \(^{19}\)F NMR spectroscopy.\(^{68,69}\)
1.5 Solid-state NMR spectroscopy

(The following discussion is based on the NMR text books, Spin Dynamics (Levitt, M. H. 2001) and Understanding NMR Spectroscopy (Keeler, J. 2010), and articles about Hamiltonians of NMR by Smith et al. in Concept of Magnetic Resonance, 1992)

1.5.1 Solid-state NMR interaction tensors

The interaction associated with two magnetic field components ($\mathbf{I}$ and $\mathbf{J}$), either generated by two spins or by one spin and the externally applied magnetic field is written in the form of equation 1.16.

$$\hat{H} = C \hat{\mathbf{M}} \cdot \mathbf{I} \cdot \mathbf{J} \quad \text{.................................................................(1.16)}$$

where, $\hat{\mathbf{M}}$ represents the spatial tensor in the form of a 3×3 matrix and ‘C’ is a constant.

(Suppose $\hat{\mathbf{I}}$ is a 1 × n matrix, $\hat{\mathbf{M}}$ is an n × n matrix and $\hat{\mathbf{J}}$ is an n × 1 matrix. Thus the traces for the combination of A, B and C matrices can be given as,

$$\text{Tr}(\hat{\mathbf{I}} \cdot \hat{\mathbf{M}} \cdot \hat{\mathbf{J}}) = \text{Tr}(\hat{\mathbf{M}} \cdot \hat{\mathbf{J}} \cdot \hat{\mathbf{I}}) = \text{Tr}(\hat{\mathbf{J}} \cdot \hat{\mathbf{M}} \cdot \hat{\mathbf{I}})) \quad \text{.................................................................(1.17)}$$

This Hamiltonian can be rewritten as,

$$\hat{H} = C \hat{\mathbf{M}} \cdot \hat{\mathbf{I}} \otimes \hat{\mathbf{J}} \quad \text{(‘$\otimes$’ is the outer product of $\hat{\mathbf{I}}$ with $\hat{\mathbf{J}}$).................................................................(1.17)}$$

$$\hat{H} = C \hat{\mathbf{M}} \cdot \hat{\mathbf{X}} \quad \text{\quad (‘$\hat{\mathbf{X}}$’ is spin tensor representing the outer product of $\hat{\mathbf{I}}$ with $\hat{\mathbf{J}}$) .............(1.18)}$$

$\hat{\mathbf{M}}$ and $\hat{\mathbf{X}}$ tensors are rank 2 tensors and can be written in the form of following three irreducible Cartesian tensors $\hat{\mathbf{I}}^0_0$ (isotropic), $\hat{\mathbf{I}}^0_2$ (anisotropy), $\hat{\mathbf{I}}^{\pm 2}_2$ (asymmetry),

$$\hat{\mathbf{M}} = \begin{bmatrix} m_{xx} & m_{xy} & m_{xz} \\ m_{yx} & m_{yy} & m_{yz} \\ m_{zx} & m_{zy} & m_{zz} \end{bmatrix} = \begin{bmatrix} 0 & 0 & 0 \\ 0 & \alpha_{xy} & \alpha_{xz} \\ 0 & \alpha_{yz} & 0 \end{bmatrix} + \begin{bmatrix} \delta_{xx} & \delta_{xy} & \delta_{xz} \\ \delta_{yx} & \delta_{yy} & \delta_{yz} \\ \delta_{zx} & \delta_{zy} & \delta_{zz} \end{bmatrix}$$

$$\hat{\mathbf{I}}^0_0, \quad \hat{\mathbf{I}}^0_2, \quad \hat{\mathbf{I}}^{\pm 2}_2 \quad \text{.................................................................(1.19)}$$
The components of this simplification can be described as,

\[ M_{\text{iso}} = \frac{1}{2} (m_{xx} + m_{yy} + m_{zz}) \]  \hspace{1cm} \text{(1.20)}

\[ \alpha_{uv} = \frac{1}{2} (m_{uv} - m_{vu}) \]  \hspace{1cm} \text{(1.21)}

\[ \delta_{\text{iso}} = \frac{1}{2} (m_{uv} + m_{vu} - 2m_{\text{iso}}) \]  \hspace{1cm} \text{(1.22)}

\[ \hat{M}, \text{ the spatial part, is always in the principal axis system (PAS) frame and } \hat{X}, \text{ the spin part, is always in the lab frame at the starting point.} \]

In the principal axis system (PAS), the tensor \( \hat{M} \) can be written as,

\[ \hat{M} \text{ (PAS)} = \begin{bmatrix} m_{xx} & 0 & 0 \\ 0 & m_{yy} & 0 \\ 0 & 0 & m_{zz} \end{bmatrix} = M_{\text{iso}} \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix} + \begin{bmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix} + \begin{bmatrix} \delta_{xx} & 0 & 0 \\ 0 & \delta_{yy} & 0 \\ 0 & 0 & \delta_{zz} \end{bmatrix} \]

\hspace{1cm} \text{……………………………………………………(1.23)}

\[ M_{\text{iso}} \text{ (PAS)} = \frac{1}{3} (m_{xx} + m_{yy} + m_{zz}) \text{ or } \frac{1}{3} \text{ Tr}\{\hat{M}\} \]  \hspace{1cm} \text{(1.24)}

\[ \delta_{uu} \text{ (PAS)} = (m_{uu} - m_{\text{iso}}) \]  \hspace{1cm} \text{(1.25)}

To go from the principal axis system (PAS) frame to the Lab frame, first the components of the principal axis system are converted to the rotor frame components by using angle \( \alpha, \beta, \gamma \). The rotor frame components are then converted to the lab frame components using angles \( 0, \theta_m, \omega_r t \).

\[ \text{PAS} \xrightarrow{(\alpha, \beta, \gamma)} \text{Rotor Frame} \xrightarrow{(0, \theta_m, \omega_r t)} \text{Lab Frame} \]  \hspace{1cm} \text{…………………..(1.26)}

\( \hat{X} \) is the Cartesian form of the spin tensor and is in the lab frame.

The different components for tensor \( \hat{M} \) in the Cartesian system and in the principal axis system (PAS) can be written as mentioned in the following Table 1.1.
Table 1.1 Different components for tensor $\hat{\mathbf{M}}$ in the Cartesian system and in the principal axis system (PAS)

<table>
<thead>
<tr>
<th>Components in the Cartesian system</th>
<th>Components in the PAS system</th>
</tr>
</thead>
<tbody>
<tr>
<td>$M^0_0 = -1/\sqrt{3} (M_{xx} + M_{yy} + M_{zz})$</td>
<td>$M^0_0 (\text{PAS}) = -1/\sqrt{3} (\text{Tr}{\hat{\mathbf{M}}})$</td>
</tr>
<tr>
<td>$M^1_0 = -i/\sqrt{2} (M_{xy} - M_{yx})$</td>
<td>$M^1_0 (\text{PAS}) = 0$</td>
</tr>
<tr>
<td>$M^\pm_1 = -1/2 [M_{zx} - M_{xz} \pm i(M_{zy} - M_{yz})]$</td>
<td>$M^\pm_1 (\text{PAS}) = 0$</td>
</tr>
<tr>
<td>$M^0_2 = -1/\sqrt{6} [3M_{zz} - (M_{xx} + M_{yy} + M_{zz})]$</td>
<td>$M^0_2 (\text{PAS}) = \sqrt{3/2} (M_{zz} - 1/3 \text{Tr}{\hat{\mathbf{M}}})$</td>
</tr>
<tr>
<td>$M^\pm_2 = \mp 1/2 [M_{xz} + M_{zx} \pm i(M_{yz} + M_{zy})]$</td>
<td>$M^\pm_2 (\text{PAS}) = 0$</td>
</tr>
<tr>
<td>$M^\pm_2 = -1/2 [M_{xx} - M_{yy} \pm i(M_{xy} - M_{yx})]$</td>
<td>$M^\pm_2 (\text{PAS}) = 1/2 (M_{xx} - M_{yy})$</td>
</tr>
</tbody>
</table>

This principal axis system (PAS) notation is converted to the rotor frame spherical tensor system using the Wigner Eckart theorem in the following way,

$$\hat{\mathbf{M}}^m_l (\text{RF}) = \sum_{m'} D^l_{m m'}(\alpha, \beta, \gamma) \hat{\mathbf{M}}^m_l (\text{PAS})$$

.................................(1.27)

where, $D^l_{m m'}(\alpha, \beta, \gamma) = e^{-i(m\alpha + m'\gamma)} d^l_{m m'}(\beta)$

.................................(1.28)

These rotor frame (RF) components is converted to the lab frame (LF) tensor components using the Wigner Eckart theorem by taking $\alpha = 0, \beta = \theta_m, \gamma = \omega_r t$ in equation 1.29.

$$\hat{\mathbf{M}}^m_l (\text{LF}) = \sum_{m'} D^l_{m m'}(0, \theta_m, \omega_r t) \hat{\mathbf{M}}^m_l (\text{RF})$$

.................................(1.29)

The components $X^m_l$ in the form of Cartesian components in Lab frame can be given according to the following Table 1.2.
Table 1.2 Components $X^m_l$ in the form of Cartesian components in lab frame

<table>
<thead>
<tr>
<th>Components in the Cartesian System</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>$X^0_0$ (LF) = $-1/\sqrt{3} (X_{xx} + X_{yy} + X_{zz})$</td>
<td></td>
</tr>
<tr>
<td>$X^0_0$ (LF) = $i/\sqrt{2} (X_{xy} + X_{yx})$</td>
<td></td>
</tr>
<tr>
<td>$X^\pm_1$ (LF) = $1/2 [X_{xx} - X_{xz}] \pm i(X_{zy} - X_{yz})$</td>
<td></td>
</tr>
<tr>
<td>$X^0_0$ (LF) = $-1/\sqrt{6} [3X_{zz} - (X_{xx} + X_{yy} + X_{zz})]$</td>
<td></td>
</tr>
<tr>
<td>$X^\pm_1$ (LF) = $\mp 1/2 [X_{xz} - X_{xx} \pm i(X_{zy} + X_{yz})]$</td>
<td></td>
</tr>
<tr>
<td>$X^\pm_2$ (LF) = $1/2 [X_{xx} - X_{yy} \pm i(X_{xy} - X_{yx})]$</td>
<td></td>
</tr>
</tbody>
</table>

The resultant Hamiltonian is obtained by,

$$\hat{H} = C \hat{\mathbf{M}} \cdot \hat{\mathbf{X}} = C \sum_{l=0}^{2} \sum_{m=-l}^{l} (-1)^m M^m_l (LF) X^m_l (LF)$$  \hspace{1cm} (1.30)

1.5.2 Chemical shift ($\delta$)

Suppose $\hat{I}$ is the spin vector, $\hat{\sigma}$ is the chemical shielding tensor and $\hat{B}$ is the static magnetic field. Thus the chemical shift Hamiltonian, $\hat{H}^{cs}$ can be written as,

$$\hat{H}^{cs} = \hbar \gamma \cdot \hat{I} \cdot \hat{\sigma} \cdot \hat{B}$$  \hspace{1cm} (1.31)

For $\hat{I} = \begin{bmatrix} \hat{I}_x & \hat{I}_y & \hat{I}_z \end{bmatrix}$ and $\hat{B} = \begin{bmatrix} 0 \\ 0 \\ B_0 \end{bmatrix}$, chemical shift Hamiltonian can be given as,

$$\hat{H}^{cs} = \hbar \gamma \cdot \hat{\sigma} \cdot \begin{bmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ \hat{I}_x B_0 & \hat{I}_y B_0 & \hat{I}_z B_0 \end{bmatrix}$$  \hspace{1cm} (1.32)

Thus, following the procedure mentioned in section 1.5.1, the complete chemical shift Hamiltonian can be given as,

$$\hat{H}^{cs} = C [\hat{X}_0^0 (LF) \hat{\sigma}_0^0 (LF) + \hat{X}_2^0 (LF) \hat{\sigma}_2^0 (LF)]$$  \hspace{1cm} (1.33)

iso-term \hspace{1cm} aniso-term
\[ \hat{H}^{cs} = h\nu(I_xB_0)[\sigma_{iso} + (1/4)\delta_{zz}[(3\cos^2\theta_m - 1)(3\cos^2(\beta) - 1) + \eta\sin^2(\beta)\cos2\gamma] + (\sin2\theta_m)[3\cos(a + \omega_r t)\sin2\beta - 2\eta\sin\beta\cos2\gamma\cos(a + \omega_r t) - \sin(a + \omega_r t)\sin2\gamma]] + (\sin^2\theta_m)[3\cos(a + \omega_r t)\sin^2\beta + \eta\cos2\gamma(1 + \cos^2\beta)\cos2(a + \omega_r t) + \sin2\gamma\cos\beta\sin(a + \omega_r t))] \]  

After a complete rotor cycle, the sinusoidal function \( \sin2\theta_m \) and \( \sin^2\theta_m \) in equation 34 becomes zero and the chemical shift expression becomes,

\[ \hat{H}^{cs} = h\nu(I_xB_0)[\sigma_{iso} + 1/4\delta_{zz}[(3\cos^2\theta_m - 1)(3\cos^2(\beta) - 1) + \eta\sin^2(\beta)\cos2\gamma] \]  

After a complete rotor cycle, the sinusoidal function \( \sin2\theta_m \) and \( \sin^2\theta_m \) in equation 34 becomes zero and the chemical shift expression becomes,

\[ \hat{H}^{cs} = h\nu(I_xB_0)[\sigma_{iso} + 1/4\delta_{zz}[(3\cos^2\theta_m - 1)(3\cos^2(\beta) - 1) + \eta\sin^2(\beta)\cos2\gamma] \]  

The effect of the asymmetry parameter (\( \eta \)) on the shape of the solid-state NMR spectrum is shown in Figure 1.1.
1.5.3 Dipolar coupling

Dipolar coupling is the interaction of two nuclear spins through space. Because each nuclear spin is magnetic, it generates a magnetic field. Another nuclear spin in its proximity experiences this magnetic field and is affected by it. The same thing happens for the first
spin. This phenomenon may happen in the case of nuclear spins of the same type of nuclei (homonuclear dipolar coupling) or nuclear spins of different nuclei (heteronuclear dipolar coupling). Dipole-dipole interaction is directly proportional to the gyromagnetic ratios of the two interacting nuclei and inversely proportional to the cube root of the distance between them.

The energy between two dipoles ($\mathbf{I}_i$ and $\mathbf{I}_j$) with a separation $r_{ij}$ is given by,

$$E_{\text{DIP}}(ij) = \sum_i \sum_{j>i} \left[ \frac{I_i \cdot I_j}{r_{ij}^3} - 3 \left( \frac{\mathbf{I}_i \cdot \mathbf{e}_{ij}}{r_{ij}} \right) \left( \frac{\mathbf{I}_j \cdot \mathbf{e}_{ij}}{r_{ij}} \right) \right]$$  

\[\text{(36)}\]

The dipolar Hamiltonian ($H_{\text{DIP}}$) can be written in the form of above expression as,

$$\hat{H}(ij) = \sum_i \sum_{j>i} \frac{\mu_0 \gamma_i \gamma_j h^2}{4\pi r_{ij}^3} \left[ \mathbf{I}_i \cdot \mathbf{I}_j - 3 \left( \frac{\mathbf{I}_i \cdot \mathbf{e}_{ij}}{r_{ij}} \right) \left( \frac{\mathbf{I}_j \cdot \mathbf{e}_{ij}}{r_{ij}} \right) \right]$$  

\[\text{(1.37)}\]

$$\hat{H}(ij) = \sum_i \sum_{j>i} \frac{\mu_0 \gamma_i \gamma_j h^2}{4\pi r_{ij}^3} \left[ \mathbf{I}_i \cdot \mathbf{I}_j - 3 (\mathbf{I}_i \cdot \mathbf{e}_{ij})(\mathbf{I}_j \cdot \mathbf{e}_{ij}) \right], \text{ where unit vector } \mathbf{e}_{ij} = \frac{r_{ij}}{r_{ij}}$$  

\[\text{(1.38)}\]
\[ \hat{H}_{ij} = \sum_{i}^{\text{spins}} \sum_{j>i}^{\text{spins}} \frac{\mu_0}{4\pi} \frac{\gamma_i \gamma_j h^2}{r_{ij}^3} [\hat{I}_i \cdot \hat{\mathbf{e}} \cdot \hat{I}_j - 3 (\hat{I}_i \cdot \hat{\mathbf{e}} \cdot \hat{I}_j)], \] where \( \hat{\mathbf{e}} = e_{ij} \otimes e_{ij} \)

\[ \hat{H}_{ij} = \sum_{i}^{\text{spins}} \sum_{j>i}^{\text{spins}} \frac{\mu_0}{4\pi} \frac{\gamma_i \gamma_j h^2}{r_{ij}^3} [\hat{I}_i (\hat{\mathbf{e}} - 3 \hat{\mathbf{e}}) \hat{I}_j] \] .................................(1.39)

\[ \hat{H}_{ij} = \sum_{i}^{\text{spins}} \sum_{j>i}^{\text{spins}} \frac{\mu_0}{4\pi} \frac{\gamma_i \gamma_j h^2}{r_{ij}^3} [\hat{I}_i \cdot \hat{\mathbf{A}} \cdot \hat{I}_j], \] .................................(1.41)

where, \( \hat{\mathbf{A}} = (\hat{\mathbf{I}} - 3 \hat{\mathbf{e}}) \) is called the dipolar coupling tensor.

For a single spin pair, the dipolar Hamiltonian can be given as,

\[ \hat{H}_{ij} = \frac{\mu_0}{4\pi} \frac{\gamma_i \gamma_j h^2}{r_{ij}^3} [\hat{I}_i \cdot \hat{\mathbf{A}} \cdot \hat{I}_j] \] .................................(1.42)

where the elements of 3 × 3 matrix \( \hat{\mathbf{A}} \) are given by,

\[ \left\langle u | \hat{\mathbf{A}}_{ij} | v \right\rangle = \delta_{uv} - 3 e_u(j) e_v(i) \] .................................(1.43)

\[ \hat{H}_{ij} = \frac{\mu_0}{4\pi} \frac{\gamma_i \gamma_j h^2}{r_{ij}^3} [\hat{\mathbf{A}} \cdot \hat{\mathbf{X}}], \] where \( \hat{\mathbf{X}} = \hat{I}_i \otimes \hat{I}_j \) .................................(1.44)

\[ \hat{H} = C[\hat{\mathbf{A}} \cdot \hat{\mathbf{X}}] \] .................................(1.45)

\( C \) is the dipolar coupling constant.

\[ \hat{\mathbf{A}}_{ij} = \begin{bmatrix} 1 - 3e_{xx} & -3e_{xy} & -3e_{xz} \\ -3e_{yx} & 1 - 3e_{yy} & -3e_{yz} \\ -3e_{zx} & -3e_{zy} & 1 - 3e_{zz} \end{bmatrix} \] or \( \hat{\mathbf{A}}^{(\text{PAS}, ij)} = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -2 \end{bmatrix} \) .................................(1.46)

The dipolar tensor is traceless. Hence, there will be no rank 0 component, and no off-diagonal elements, thus, there will be no rank 1 components. The spatial tensor in the principal axis system, \( \hat{\mathbf{A}}^{(\text{PAS})} \) can be given as,

\[ \hat{\mathbf{A}}^{(\text{PAS})} = 0 + 0 + \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -2 \end{bmatrix} \] .................................(1.47)

The spin components in the Cartesian form can be given as,
Following the procedure mentioned in section 1.5.1, the dipolar coupling Hamiltonian can be written as,

\[
\hat{H} = C(-1/4)[[(3\cos^2\theta_m - 1)][(3\cos^2\beta - 1) + 3\sin2\theta_m \sin2\beta \cos(\omega_r t + \gamma) + 3\sin^2\theta_m \sin^2\beta \cos(2\omega_r t + 2\gamma)]\{3\hat{I}_z \hat{I}_z - (\hat{\mathbf{I}} \cdot \hat{\mathbf{I}})\}]
\]

\[\text{(1.49)}\]

1.5.4 Magic angle spinning (MAS) technique

In solid-state NMR spectroscopy, all anisotropic interaction (CSA and dipolar coupling) terms depend on the orientation dependent trigonometric term \(\frac{1}{2}(3\cos^2 \theta - 1)\). It means that wherever this orientation term is involved, that part can be made zero by equating \(\frac{1}{2}(3\cos^2 \theta - 1)\) term zero. Equating \(\frac{1}{2}(3\cos^2 \theta - 1)\) to zero, yields the value of \(\theta\) to 54.7°,
which is called the magic angle. If the sample is spun at 54.7° (with respect to the applied magnetic field) faster than the dipolar coupling strength, the homonuclear dipolar coupling can be reduced significantly and the isotropic value of the chemical shifts and possibly scalar couplings can be obtained. The dipolar coupling value, however, cannot be suppressed completely because of the presence of \((3\hat{I}_{1z}\hat{I}_{1z} - \hat{I}_1 \cdot \hat{I}_2)\) term, which leads to the flip-flop \(\frac{\hat{I}_1\hat{I}_2 + \hat{I}_2\hat{I}_1}{2}\) term. This term cannot be averaged out completely.

1.5.5 Relaxation

Relaxation is the process in which the nuclear magnetization returns to its equilibrium state after the removal of an applied radiofrequency pulse. After a 90° pulse, the magnitude of \(z\)-magnetization (longitudinal magnetization), \(M_z\) increases gradually while the magnetization in the XY-plane (transverse magnetization) decreases. The longitudinal relaxation process of the net magnetization is called the spin-lattice relaxation and the time constant taken for this exponential decay is called spin lattice relaxation time \((T_1)\) and the exponential decay of the net magnetization in the transverse plane is called the spin-spin relaxation and the time constant taken for this process is called transverse relaxation time \((T_2)\). \(T_1\) is a growing exponential of magnetization and \(T_2\) is a decaying exponential of magnetization. These two processes can be written by the following formulas;

\[
M_z = M_0(1 - e^{-t/T_1}) \quad \text{for } T_1 \text{ relaxation} \quad \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots
correlated with itself at different time points. The value for this autocorrelation function is zero for a long period of time and non-zero for a short period of time. The distribution of the magnetic field can be found by knowing its standard deviation $\frac{1}{\tau_c} < B_x^2(t) > i.e. by$ $< B_x^2(t) >= 0$. The distribution of the magnetic field can be narrow or broad and it gives information about the amplitude of the field. Suppose at any time $t$, the auto correlation function is $B_x(t)$ and at time $t+\tau$, the function is $B_x(t+\tau)$. Thus, fluctuations between these time intervals can be defined as,

$$G(\tau) = < B_x(t)B_x(t+\tau) > \neq 0 \text{ for short period of time}$$

$$= 0 \text{ for long period of time.} \hspace{1cm} (1.52)$$

The function $G(t)$ is an exponential function and can be written by,

$$G(t) = < B_x^2(t) > e^{\frac{-t}{\tau_c}} \text{ where, } \tau_c \text{ is the correlation time or correlation time constant of decay. If there are fast fluctuations, the decay of this function is fast giving short correlation time and if the fluctuations are slow, the function decays slowly giving a long correlation time.}$$

![Figure 1.4. Variation of auto correlation function $G(t)$ with time ($t$)](image-url)
A fast rotating molecule experiences fast random fluctuations and thus has a short correlation time, relaxing at a fast rate, resulting in a broad spectrum (short $\tau_c$). A slow rotating molecule experiences a larger correlation time, relaxing at a slow rate and thus giving narrow spectrum (long $\tau_c$).

1.5.6 Spectral density function

The transitions between the energy states are given by the fluctuating transverse field. The probability of transition from one energy state to the other is given by the spectral density function $J(\omega)$, which is defined as,

$$J(\omega) = 2 \int_{0}^{\infty} \langle B_x^2(t) \rangle e^{-t/\tau_c} dt \quad \text{.................................(1.53)}$$

$$J(\omega) = 2\langle B_x^2(t) \rangle \frac{\tau_c}{1+\omega^2\tau_c^2} \quad \text{.................................(1.54)}$$

$J(\omega)$ is a relaxation driver in terms of frequency. $\langle B_x^2(t) \rangle$ is the strength of interactions. The term $\frac{\tau_c}{1+\omega^2\tau_c^2}$ is the frequency dependent term and is called the normalized spectral density function.

1.5.7 Spin-lattice relaxation ($T_1$)

This process is related to the rate of change of populations of the spins in the lower energy state ($\alpha$) and higher energy state ($\beta$). When a radiofrequency radiation is applied, the equilibrium of spins is disturbed raising the number of spins in the higher energy state, and the magnetization vector of the spins is placed in the XY-plane. This magnetization vector returns back to the equilibrium state after the applied pulse is turned off; the number of spins are transferred back from the higher energy state to the lower energy state by the
dissipation of energy to the lattice. That is why the process is termed as spin-lattice relaxation process. In the $T_1$ process exchange of energy (loss of energy to the surroundings) takes place, thus it is analogous to a cooling process. The spin lattice relaxation time ($T_1$) is written in the form of following expression,

$$M_z(t) = M_0(1 - e^{-\frac{t}{T_1}})$$

In terms of the correlation time ($\tau_c$), the spin lattice relaxation ($T_1$) is written by the following expression,

$$T_1 = \frac{1}{\gamma^2 \langle B_x^2 \rangle} \left( \frac{1}{\tau_c} + \frac{1}{\tau_c \omega^2} \right)$$

Spin lattice relaxation time ($T_1$) gives information about the reorientation of the molecule in the lattice thus providing information about the rotational and translational motion. A relation between relaxation time and correlation time (figure 1.5) shows that the $T_1$ first decreases with the correlation time and increases again after a minimum. The first correlation follows when the correlation time is short i.e. the fast motional regime while the latter is true for the long correlation time i.e. slow motional regime (figure 1.6).

![Figure 1.5. Variation of relaxation times with correlation time](image-url)
Figure 1.6. Dependence of relaxation time ($T_1$) on frequency ($\omega_0$)

From the above equation 1.56, it follows that,

$$\frac{1}{\tau_c} \propto (\omega_0)$$

(1.57)

($\omega_0$) is the static field strength for a particular nucleus. It means that if a control on the magnetic field strength is achieved, the different motional timescale regimes can be detected. In a $T_{1\rho}$ experiment, the power of the applied pulse field strength ($\omega_1$ instead of $\omega_0$) can be controlled and the change of $\tau_c$ can be observed by varying the temperature to observe whether the motion is on the scale of ms and $\mu$s. In the solution state, the magnetic field is fixed in terms of a static instrument magnet field (MHz) and thus the motion on the nanosecond time scale can be observed by $T_1$ experiment. However, for the millisecond and microsecond timescale motion, a $T_{1\rho}$ experiment is performed.
The correlation time $\tau_c$ depends on temperature and the type of motional regime. For example, in the fast motional regime, if the given sample is warmed up, the fluctuations become faster, reducing the correlation time, increasing $T_1$. Cooling down the sample reduces fluctuations, increasing the correlation time and thus reducing $T_1$. The correlation time $\tau_c$ is also defined as the correlation time for fluctuations. In the solution state, $\tau_c$ is in the range of tens of picoseconds to several nanoseconds (Figure 1.7).

### 1.5.8 Spin-spin relaxation ($T_2$)

The decay rate of the net magnetization in the transverse plane is given by the equation $T_2$. The overall transverse relaxation rate is equal to the sum of the dephasing rate due to field inhomogeneity and natural rate relaxation decay rate.

\[
\frac{1}{T_2} = \frac{1}{T_2'} + \frac{1}{T_2} \tag{1.58}
\]

During the $T_2$ process, the total energy of the system remains constant. Mathematically, $T_2$ relaxation can be written as
This decaying process of magnetization in the transverse plane is usually governed mainly by the following four types of interaction,

1. Quadrupolar coupling interaction between nuclei and the electric field gradient
   (about 1–300 MHz)
2. Dipolar interactions such as among $^1$H nuclei. (about 10–100 kHz)
3. CSA interactions such as for $^{13}$C nuclei. (about 0.01–10 kHz)
4. Spin rotations which results in a local field such as in the case of heavy metals
   (mercury, lead etc.)
5. Relaxation due to the presence of paramagnetic species

1.5.9 $T_1$ relaxation in the rotating frame ($T_{1\rho}$)

If the tilted net magnetization spin vector is held in the XY-plane with the help of an applied radiofrequency pulse, the net magnetization spin vector decays slowly under the spin lock magnetic field ($B_1$). Under the spin lock, a transverse relaxation is happening since it has an analogy to $T_1$ relaxation being relaxed under the parallel applied magnetic field (in this case radio-frequency magnetic field, $B_1$ instead of static magnetic field, $B_0$). The mathematical expression for the $T_{1\rho}$ is given by the following equation.

$$M_x(t) = M_0 e^{\left(\frac{-t}{T_{1\rho}}\right)}$$

The pulse sequence for the $T_{1\rho}$ experiment is shown in the following figure 1.8.
In terms of the spectral density function, $T_{1\rho}$ can be written in the form of the following formula,

$$T_{1\rho}^{-1} = (\frac{3}{20})b^2\{J(0) + 10J(\omega^0) + 2J(2\omega^0)\}$$

……………………………………(1.61)

### 1.5.10 Fluorine ($^{19}$F) solid-state NMR spectroscopy of solids containing both proton ($^{1}$H) and fluorine ($^{19}$F)

Fluorine-19 NMR spectroscopy is an ideal characterization technique to obtain structural information for fluorinated compounds. The reason is the high natural abundance (100%) of $^{19}$F and its high gyromagnetic ratio, $25.181 \times 10^7 \text{ rad s}^{-1}\text{T}^{-1}$ corresponding to a frequency of 470.322 MHz on a 500 MHz NMR spectrometer. The high chemical shift range (about 350 ppm) present the opportunity to obtain higher resolution in $^{19}$F NMR spectra. The close resonance frequencies of $^{19}$F and $^{1}$H present a challenge in their separation (470.322 MHz for $^{19}$F and 500 MHz for $^{1}$H on a 500 MHz NMR instrument). To record high-resolution spectra high powers of the radio frequency field are required. There is a need of a highly sensitive filtering circuit, which can cleanly separate the frequency powers of $^{1}$H and $^{19}$F. The presence of strong heteronuclear coupling (between $^{1}$H and $^{19}$F) and strong homonuclear coupling (between two $^{19}$F nuclei and between two $^{1}$H nuclei) make the task
more difficult. Therefore, higher magic angle spinning speeds (>20 kHz) and special decoupling sequences are required such as XY-16 to remove strong heteronuclear coupling between $^1$H and $^{19}$F. Very efficient homonuclear decoupling can be achieved with sequences such as Lee-Goldburg. Moreover, the spinning of the fluorinated sample is a very difficult task except in case of stable fluorinated materials which have high melting points. In the case of unstable and sensitive fluorinated materials, very high rotor spinning speed cannot be applied without sufficiently cooling off the sample. If the material is air sensitive, special inserts of perfluorinated polymers are required to pack the materials and these inserts are then inserted in the rotor.72

1.5.11 Dipolar dephasing experiment

The basic principle behind the dipolar dephasing experiment is that an NMR signal should completely diphase or disappear in a certain definite dephasing delay depending on the distance between the observed nucleus and a dipolar coupled nucleus.

If the signal does not dephase in that certain time period, it indicates some kind of dynamical feature of the compound. For example, if the motion is too fast as in the case of
methyl groups, the $^{13}$C signal originating from it will be hardly suppressed by a dipolar-dephasing experiment. In this experiment, first the cross polarization is done from $^1$H to $^{13}$C. Then the signal is allowed to evolve under $^1$H-$^{13}$C dipolar coupling for a fixed period of time as depicted in Figure 1.9. After this time period, the decoupling on the $^1$H channel is turned on while the chemical shift evolution on $^{13}$C channel is refocused with the application of a $\pi$-pulse. The FID is now acquired on the $^{13}$C channel. If an appreciable amount of dipolar coupling is present between $^{13}$C and $^1$H atoms, the signal intensity will be appreciably suppressed depending on the amount of dipolar coupling while if dipolar coupling value is small, there will be a minute suppression in the signal intensity. If the value of dephasing time exceeds the value of expected dephasing time (calculated from distances obtained from X-ray crystallography), some kind of dynamics is expected in the compound.
References


Chapter-2

2. Experimental section

2.1 Standard techniques

The compounds used in the course of this work, except perfluorocarboxylic acids and carboxylates, are moisture- and air-sensitive; consequently all manipulations were carried out under rigorously anhydrous inert-atmosphere conditions. Glass and metal vacuum line systems, a dry-nitrogen-filled glove bag, and the oxygen- and moisture-free atmosphere of a Vacuum Atmospheres (Omni Lab) drybox were used.

Volatile materials that were non-corrosive towards glass in the absence of water were manipulated on a Pyrex-glass vacuum line equipped with grease-free 6-mm J. Young glass stopcocks equipped with PTFE barrels (Figure 2.1). Pressures inside the manifold were monitored using a Heise gauge (model CC, 0–1000 mmHg, beryllium/copper Bourdon tube, Dresser Instruments). The final vacuum was monitored by a Varian thermocouple gauge connected to the vacuum line between the liquid-nitrogen trap and the vacuum pump.

Volatile materials, which attacked glass, were handled on a metal vacuum line constructed from nickel and 316 stainless steel, and equipped with 316 stainless steel valves and fittings (Autoclave Engineers Inc.), PTFE, and FEP (Figure 2.2). Pressures were measured at ambient temperature using Baratron capacitance manometers (MKS, Type 626A, effective range 0 – 1000 mmHg) having inert wetted surfaces constructed of inconel, in conjunction with a digital readout.
Figure 2.1 Glass vacuum line system equipped with J.Young PTFE / glass stop cocks and a Heise gauge (M.Sc. thesis from Jared Nieboer).¹
Vacuum on the glass (ca. $10^{-5}$ Torr) and metal lines (ca. $10^{-4}$ Torr) was attained by the use of Edwards two-stage direct-drive RV8 Edward vacuum pumps. Three vacuum pumps were used on a metal vacuum line, one for the rough vacuum and two for the fine vacuum on the two sides of the vacuum line. The rough pump was connected to a fluoride/fluorine trap consisting of a stainless-steel cylinder (75 cm length, 17 cm outer diameter) packed with soda lime absorbent (EMD, 4-mesh). Removal and disposal of volatile reactive fluorinated compounds was accomplished by pumping through and entrapment on a bed of soda lime followed by trapping of the volatile reaction products,
CO₂ and H₂O, in a glass liquid-nitrogen trap. The second vacuum pump provided the high
vacuum source for the manifold and was cold trapped with a glass liquid-nitrogen trap.

All the preparative work involving SF₄, AsF₅, SbF₅, WOF₄ and anhydrous HF was
carried out in ¼-in, ¾-in or 4-mm outer diameter FEP tubes which were heat-sealed at one
end and connected through 45° flares to Kel-F or 37° flares to stainless steel valves. The
FEP sample tubes were dried under dynamic vacuum overnight on a glass vacuum line
prior to transfer on the metal line where they were checked for leaks, passivated with
fluorine at 1 atm for 12 hours, re-evacuated and then back filled with dry N₂ before
transferring to the dry box. Pyrex-glass reaction vessels were dried under dynamic vacuum
overnight periodically flamed out by use of a Bunsen burner.

Nuclear magnetic resonance (NMR) spectra were recorded on samples prepared in
4-mm o.d. FEP tubes. The NMR tubing had one end heat sealed by pushing the end of the
FEP tube into the hot end of a thin-walled 5-mm o.d. NMR tube and the other end was
fused to a ¼-in. o.d. thick-walled FEP tubing which was heat-flared for direct attachment
to a Kel-F valve (Figure 2.3(a)). The 4-mm sample tubes used for NMR spectroscopy were
heat sealed under dynamic vacuum with a heat gun while the sample was frozen at –196
°C. All heat-sealed samples were stored submerged in liquid nitrogen (−196 °C) until they
could be spectroscopically characterized. For NMR measurements, the 4-mm FEP tubes
were inserted into standard 5-mm precision NMR tubes before insertion into the NMR
probe.
Figure 2.3 Common FEP reactors used to conduct experiments: (a) 4-mm o.d. reaction vessel equipped with a Kel-F valve. (b) ¼-in. o.d. FEP T-reactor equipped with Kel-F valve (M.Sc. thesis from Jared Nieboer).¹

Raman spectra of solids that are stable at room temperature and which do not attack glass were recorded on samples in Pyrex-glass melting point capillaries. Before use, the melting point capillaries were heated under dynamic vacuum for 24 h at 200 °C and then stored in the drybox where they were loaded with the appropriate materials. The end of the loaded melting point capillary was temporarily sealed with Kel-F grease before removal from the drybox. The capillaries were then immediately heat-sealed with an oxygen-natural gas torch.
Vessels were attached to vacuum lines through thick-walled FEP tubing and ¼-in. PTFE Swagelok connectors or ¼-in. stainless-steel Ultra-Torr connectors fitted with viton rubber O-rings.

2.2 Preparation of inserts for solid-state NMR spectroscopy

Solid-state NMR spectra of imidazolium ionic liquids were recorded with the use of an FEP insert, which was prepared by using a 3.2-mm o.d. FEP tube through heat-sealing it at one end and then loading the required material in it inside the glove box. The filled inserts were plugged using an FEP plug and the plug was fused to the insert-walls outside of the dry box, permanently sealing the insert. This FEP insert was inserted in the 4-mm zirconia rotor before recording spectra at low temperature.

2.3 Purification of different materials

2.3.1 Purification of HF, SF₄, C₅H₅N, CH₃CN, AsF₅, SbF₅, WF₆ and 2,2,2-CF₃CH₂OH, 1,10-phenanthroline, 4-dimethylaminopyridine, 4-tert-butylcyclohexanone, 1,4-dioxaspiro[4.5]decan-8-one, cyclooctanol and pentafluorobenzoic acid

Anhydrous hydrogen fluoride (Air Products) was stored at room temperature in a nickel storage vessel equipped with a monel (Autoclave Engineers) valve. Hydrogen fluoride was dried over potassium hexafluoronickeolate(VI) in a ¾-in o.d. FEP vessel (Figure 2.4), equipped with a stainless steel valve, prior to transfer to reaction vessels by vacuum distillation on the metal vacuum line through connections constructed of FEP.

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.
Pyridine (Sigma-Aldrich, 99.8%) was added to CaH$_2$ in a glass storage bulb equipped with a PTFE J. Young stopcock inside a glove bag. Then, the liquid was vacuum distilled from the original storage bulb onto fresh CaH$_2$ in a glass bulb equipped with a PTFE J. Young stopcock.

Antimony pentafluoride, SbF$_5$ (Ozark-Mahoning Co.) was purified by vacuum distillation in a PTFE and glass apparatus connected with PTFE Swagelok unions and stored in a glass U-tube equipped with PTFE J. Young stopcocks, which was kept in a desiccator. Subsequent transfers of SbF$_5$ were performed through a glass Y-piece with PTFE Swagelok connections.

Acetonitrile (Sigma-Aldrich) was purified according to the literature procedure.\textsuperscript{2} CH$_3$CN was added to molecular sieves (4Å) in glass bulbs inside the glove bag, followed by vacuum distillation onto fresh molecular sieves in glass storage bulbs equipped with a PTFE J. Young stopcock.

WF$_6$ (Elf Atochem) was used as provided. 2,2,2-Trifluoroethanol (CF$_3$CH$_2$OH) was purchased from Sigma-Aldrich (≥99%) and dried over molecular sieves (4Å).

1,10-phenanthroline (Sigma-Aldrich) and 4-dimethylaminopyridine (Sigma-Aldrich) were used as received without any further purification.

Also, 4-\textit{tert}-butylecyclohexanone (TCI Chemicals), 1,4-dioxaspiro[4,5]decan-8-one (TCI Chemicals), cyclooctanol (TCI Chemicals) and pentafluorobenzoic acid (Sigma-Aldrich) were used without any further purification.
2.3.2 Purification of perfluorooctanoic acid (PFOA), sodium perfluorooctanoate (SPFO), perfluorodecanoic acid (PFDA) and sodium perfluorobutyrate (SPFB)

Perfluorooctanoic acid, 96% and perfluorodecanoic acid, 98% were purchased from Sigma Aldrich SPFO, 98% and SPFB was purchased from SynQuest Laboratories Ltd. (USA). All of these chemicals were used without any further purification.

2.4 Synthesis of different fluorine containing compounds

2.4.1 Synthesis of AsF$_5$. Arsenic pentafluoride (AsF$_5$) was synthesized according to the given literature by reacting AsF$_3$ with F$_2$.\textsuperscript{3}
2.4.2 Synthesis of WOF₄. The synthesis of WOF₄ was done according to the procedure described in the literature.⁴ Quartz wool (0.2256 g; 3.735 mmol) was transferred to a ¾” FEP reactor having a Teflon coated magnetic stirring bar. WF₆ (15.958 mmol) and about 250 mL of anhydrous HF was distilled over quartz wool. The reactants were warmed up to room temperature and mixed with magnetic stirrer for 48 hrs. until all the quartz wool was dissolved. The excess anhydrous HF was pumped off from –90 °C to –10 °C. The resulted solid was sublimed between 55–60 °C under dynamic vacuum to collect the pure sublimed WOF₄ (0.9747 g).

2.4.3 Synthesis of [SF₃][SbF₆] and [SF₃][AsF₆] and scoping reactions for the use of [SF₃][MF₆] (M = Sb, As) as deoxofluorinating reagents for 4-tert-butylcyclohexanone, 1,4-dioxaspiro[4.5]decan-8-one, benzoic acid, pentafluorobenzoic acid, and cyclooctanol.

The [SF₃][SbF₆] and [SF₃][AsF₆] salts were prepared according to literature reports.⁵,⁶,⁷

2.4.3.1 Synthesis of [SF₃][SbF₆]. On a glass vacuum line, 0.362 g (1.67 mmol) of SbF₅ was transferred to a ¼-in o.d. vacuum-dried FEP reactor. Approximately 3.70 mmol SF₄ was vacuum distilled into the reactor at –196 °C. The reactor was slowly warmed up to –78 °C, and then to ambient temperature (20 °C) and properly agitated. The reactor was then agitated in warm water (32 °C) for the completion of reaction. The reactor was again transferred to an ethanol bath maintained at –78 °C. The excess SF₄ was removed on the vacuum line by slowly warming the reactor up to ambient temperature where a white [SF₃][SbF₆] (0.447 g or 1.37 mmol) salt was obtained.

2.4.3.1.1 Crystal growth of [SF₃][SbF₆]. An amount of 0.012 g (0.037 mmol) of [SF₃][SbF₆] was transferred to a ¼” FEP reactor. About ~2.0 mL of SO₂ was transferred to the reactor at –40 °C. After dissolving [SF₃][SbF₆] in SO₂, the reactor was transferred to
cryobath at –70 °C. After the crystal growth the SO₂ was pumped off at about –50 °C. The crystals were mounted immediately after pumping off excess SO₂.

**2.4.3.2 Synthesis of [SF₃][AsF₆].** On a steel vacuum line, approximately 2.11 mmol of SF₄ was vacuum distilled into a 4-mm o.d. FEP reactor. Approximately 1.90 mmol AsF₅ was vacuum distilled into the reactor. The reactor was slowly warmed to –78 °C and then to –40 °C by proper agitation for the completion of reaction. [SF₃][AsF₆] was resulted as product in the form of a white salt. The excess SF₄ was removed by warming the reactor to ambient temperature (20 °C). The weight of white [SF₃][AsF₆] salt was 0.445 g (1.60 mmol).

**2.4.3.2.1 Crystal growth of [SF₃][AsF₆].** An amount of 0.021 g (0.76 mmol) of [SF₃][AsF₆] was transferred to a ¼” FEP reactor. Then about ~ 2.5 mL of SO₂ was transferred to the reactor at –40 °C. After dissolving [SF₃][AsF₆] in SO₂, the reactor was transferred to cryobath at –70 °C. After the crystal growth the SO₂ was pumped off at about –50 °C. The crystals were mounted immediately after pumping off excess SO₂.

**2.4.3.3 Deoxofluorination of 4-tert-butylicyclohexanone at –20 °C.** Inside the dry-box, 0.15 mmol (0.049 g) of [SF₃][SbF₆] and 0.097 mmol (0.015 g) of 4-tert-butylicyclohexanone were taken into a 4-mm FEP reactor and approximately 0.006 g (0.04 mmol) of CsF was added to it. The reactor was hooked to the SO₂ line and excess SO₂ (~1.5 mL) was distilled to the reactor on a glass vacuum line. The reaction was allowed to take place at ambient temperature. The resultant product was monitored with the help of solution ¹⁹F and ¹H NMR spectroscopy at –20 °C (for safe handling of SO₂).

**2.4.3.4 Deoxofluorination of 1,4-dioxaspiro[4.5]decan-8-one.** Inside the dry-box, 0.10 mmol (0.032 g) of [SF₃][SbF₆] and 0.10 mmol (0.016 g) of 1,4-dioxaspiro[4.5]decan-8-one were taken into a 4-mm FEP reactor and 0.006 g (0.04 mmol) of CsF was added to it.
The reactor was attached to the CH$_3$CN line and excess CH$_3$CN (~ 2.0 mL) was distilled to the reactor on a glass vacuum line. The reaction was allowed to take place at $-20^\circ$C. The resultant product was monitored with the help of $^{19}$F NMR spectroscopy at $-20^\circ$C.

2.4.3.5 Deoxofluorination of pentafluorobenzoic acid. Inside the dry-box, 0.063 mmol (0.020 g) of [SF$_3$][SbF$_6$] and 0.059 mmol (0.012 g) of pentafluorobenzoic acid were taken into a 4-mm FEP reactor and 0.006 g (0.04 mmol) of CsF was added to it. The reactor was hooked to the SO$_2$ line and excess SO$_2$ (~ 1.9 mL) was distilled to the reactor on a glass vacuum line. The reaction was allowed to take place at ambient temperature. The resultant product was monitored with the help of $^{19}$F NMR spectroscopy at $-20^\circ$C.

2.4.3.6 Deoxofluorination of benzoic acid. Inside the dry-box, 0.06 mmol (0.019 g) of [SF$_3$][SbF$_6$] and 0.06 mmol (0.006 g) of benzoic acid were taken into a 4-mm FEP reactor and 0.006 g (0.04 mmol) of CsF was added to it. The reactor was hooked to the SO$_2$ line and excess SO$_2$ (~ 1.6 mL) was distilled to the reactor on a glass vacuum line. The reaction was allowed to take place at ambient temperature. The resultant product was monitored with the help of $^{19}$F NMR spectroscopy at $-20^\circ$C.

2.4.3.7 Deoxofluorination of cyclooctanol. Inside the dry-box, 0.75 mmol (0.021 g) of [SF$_3$][AsF$_6$] and 0.07 mmol (0.008 g) of cyclooctanol were taken into a 4-mm FEP reactor and 0.006 g (0.04 mmol) of CsF was added to it. The reactor was hooked to the SO$_2$ line and excess SO$_2$ (~ 1.9 mL) was distilled to the reactor on a glass vacuum line. The reaction was allowed to take place at ambient temperature. The resultant product was monitored with the help of $^{19}$F NMR spectroscopy at $-20^\circ$C.
2.4.4 Synthesis of \([\text{SF}_3(\text{N-base})_2][\text{MF}_6]\) solvate (where M = Sb, As and N-base = C_5H_5N, CH_3CN), \([\text{SF}_3(\text{Phen})][\text{SbF}_6]\cdot2\text{CH}_2\text{Cl}_2\) and \([\text{SF}_2(\text{DMAP})_2][\text{SbF}_6]\)·\text{CH}_3\text{CN}

2.4.4.1 Synthesis of \([\text{SF}_3(\text{C}_5\text{H}_5\text{N})_2][\text{SbF}_6]\)·\(n\)C_5H_5N. The low-temperature stable yellow \([\text{SF}_3(C_5H_5N)_2][\text{SbF}_6]\)·\(n\)C_5H_5N (where \(n = 0.15\)) salt was prepared by the reaction of 0.25 mmol (0.080 g) of \([\text{SF}_3][\text{SbF}_6]\) and 1.00 mL (16.7 mmol) neat C_5H_5N at –40 °C. Excess pyridine was removed up to –30 °C to get 0.149 g of the salt.

2.4.4.1.1 Crystal growth for \([\text{SF}_3(C_5\text{H}_5\text{N})_2][\text{SbF}_6]\)·C_5H_5N. 0.149 g of \([\text{SF}_3(C_5\text{H}_5\text{N})_2][\text{SbF}_6]\) was dissolved in 2.5 mL of CH_2Cl_2 and 0.5 mL of C_5H_5N inside a \(\frac{1}{4}\) in. o.d. FEP tube equipped with a Kel-F valve and the solution was cooled to –70 °C for 12 h. The crystals were formed after 1 h. The solvent was slowly removed under dynamic vacuum at this temperature over a period of 12 h and yellow crystals of \([\text{SF}_3(C_5\text{H}_5\text{N})_2][\text{SbF}_6]\)·C_5H_5N in the form of needles were obtained.

2.4.4.1.2 Crystal growth for \([\text{SF}_3(C_5\text{H}_5\text{N})_2][\text{SbF}_6]\)·\text{CH}_3\text{CN}. The product was synthesized by using 0.020 g of \([\text{SF}_3][\text{SbF}_6]\) using about 1.00 mL pyridine as solvent. After pumping off excess pyridine, the product was dissolved in 1.5 mL of CH_2Cl_2 and 0.5 mL of CH_3CN inside a \(\frac{1}{4}\) in. o.d. FEP tube equipped with a Kel-F valve and the solution was cooled to –70 °C for 12 h. The crystals appeared after 1 h. The solvent was slowly removed under dynamic vacuum at this temperature over a period of 12 h and yellow crystals in the form of needle of \([\text{SF}_3(C_5\text{H}_5\text{N})_2][\text{SbF}_6]\)·\text{CH}_3\text{CN} were obtained.

2.4.4.1.3 Crystal growth for \([\text{SF}_3(C_5\text{H}_5\text{N})_2][\text{SbF}_6]\)·\text{CH}_2\text{Cl}_2. The product was synthesized using about 0.030 g of \([\text{SF}_3][\text{SbF}_6]\) using 1.00 mL pyridine as solvent. After pumping off excess pyridine, the product was dissolved in 3.0 mL of CH_2Cl_2 inside a \(\frac{1}{4}\) in. outer diameter (o.d.) FEP tube equipped with a Kel-F valve was cooled to –70 °C for 12 h. The crystal formation takes place after 2 h. All the solvent was slowly removed under dynamic
vacuum up to –30 °C over a period of approximately 9 h and yellow needle crystals were isolated.

2.4.4.2 Synthesis of [SF$_3$(C$_5$H$_5$N)$_2$][AsF$_6$]-nC$_5$H$_5$N. The low temperature stable [SF$_3$(C$_5$H$_5$N)$_2$][AsF$_6$]-nC$_5$H$_5$N salt was prepared by the reaction of 0.11 mmol (0.030 g) of [SF$_3$][AsF$_6$] and 0.45 mL (5.7 mmol) neat C$_5$H$_5$N at –40 °C. Excess pyridine was removed up to –30 °C to synthesize [SF$_3$(C$_5$H$_5$N)$_2$][AsF$_6$]-nC$_5$H$_5$N.

2.4.4.2.1 Crystal growth for [SF$_3$(C$_5$H$_5$N)$_2$][AsF$_6$]-C$_5$H$_5$N. The product was synthesized from about 0.020 g of [SF$_3$][AsF$_6$] in ca. 1.0 mL pyridine as solvent. After pumping off excess pyridine, the product was dissolved in 2.0 mL of CH$_2$Cl$_2$ and 0.5 mL of CH$_3$CN inside a ¼ in. o.d. FEP tube equipped with a Kel-F valve and the solution was cooled to –70 °C for 12 h. The crystals appeared after 45 minutes. The solvent was slowly removed under dynamic vacuum at this temperature over a period of 12 h and yellow crystals of [SF$_3$(C$_5$H$_5$N)$_2$][AsF$_6$]-C$_5$H$_5$N were obtained.

2.4.4.2.2 Crystal growth for [SF$_3$(C$_5$H$_5$N)$_2$][AsF$_6$]-CH$_2$Cl$_2$. The [SF$_3$(C$_5$H$_5$N)$_2$][AsF$_6$]-CH$_2$Cl$_2$ crystals were grown by the following procedure. First the reaction of SF$_4$:C$_5$H$_5$N (1:1 adduct) was carried out with excess AsF$_5$ at –56 °C. After pumping off excess AsF$_5$, the product was dissolved in 4.0 mL of CH$_2$Cl$_2$ inside a ¼ in. o.d. FEP tube equipped with a Kel-F valve and was placed in the cryo-bath at –72 °C for crystal growth. After 14 h excess CH$_2$Cl$_2$ was pumped off from the reaction mixture to obtain the crystals of [SF$_3$(C$_5$H$_5$N)$_2$][AsF$_6$]-CH$_2$Cl$_2$.

2.4.4.3 Synthesis of [SF$_3$(CH$_3$CN)$_2$][SbF$_6$]. The low temperature stable yellow [SF$_3$(CH$_3$CN)$_2$][SbF$_6$] salt was prepared by the reaction of 0.19 mmol (0.062 g) of [SF$_3$][SbF$_6$] and 0.60 mL (1.2 mmol) neat CH$_3$CN at –40 °C. Excess acetonitrile was pumped off to –30 °C to get 0.078 g of [SF$_3$(CH$_3$CN)$_2$][SbF$_6$].
2.4.4.3.1 Crystals growth for \([\text{SF}_3(\text{CH}_3\text{CN})_2][\text{SbF}_6]\). A solid sample of 0.078 g of \([\text{SF}_3(\text{CH}_3\text{CN})_2][\text{SbF}_6]\) in 3.0 mL of CH\(_2\)Cl\(_2\) inside a \(\frac{1}{4}\) in. o.d. FEP tube equipped with a Kel-F valve was cooled to –70 °C for 12 h. Crystals appeared after 2 h. The solvent was slowly removed under dynamic vacuum up to –30 °C over a period of approximately 9 h and yellow needle crystals were isolated.

2.4.4.4 Synthesis of \([\text{SF}_3(\text{CH}_3\text{CN})_2][\text{AsF}_6]\). The low-temperature stable \([\text{SF}_3(\text{CH}_3\text{CN})_2][\text{AsF}_6]\) salt was prepared by the reaction of 0.13 mmol (0.036 g) of \([\text{SF}_3][\text{AsF}_6]\) with 0.45 mL (8.61 mmol) neat CH\(_3\)CN at –40 °C. Excess acetonitrile was pumped off to –30 °C.

2.4.4.5 Synthesis of \([\text{SF}_3(\text{Phen})][\text{SbF}_6]\cdot 2\text{CH}_2\text{Cl}_2\). The low-temperature stable \([\text{SF}_3(\text{Phen})]\text{SbF}_6\) salt was prepared by the reaction 0.089 mmol (0.029 g) of \([\text{SF}_3][\text{SbF}_6]\) and 0.083 mmol (0.015 g) of phenanthroline in the presence of 2.0 mL CH\(_3\)CN at –40 °C. Excess acetonitrile was pumped off up to –20 °C.

\[
\text{where, Phen} = 1,10 \text{ Phenanthroline}
\]

2.4.4.5.1 Crystal growth for \([\text{SF}_3(\text{Phen})][\text{SbF}_6]\cdot 2\text{CH}_2\text{Cl}_2\). The synthesized material in section 2.4.4.5 was dissolved in 3.5 mL of CH\(_2\)Cl\(_2\). The crystals appeared after 2 h. The solvent was slowly removed under dynamic vacuum up to –25 °C over a period of approximately 9 h and yellow needle crystals were isolated.

2.4.4.6 Synthesis of \([\text{SF}_2(\text{DMAP})_2][\text{SbF}_6]\cdot 2\text{CH}_3\text{CN}\). The low temperature stable \([\text{SF}_2(\text{DMAP})_2][\text{SbF}_6]\) salt was prepared by the reaction of 3.69 × 10\(^{-5}\) mol (0.012 g) of \([\text{SF}_3][\text{SbF}_6]\) with 0.046 g (0.038 mmol) of DMAP in 3.0 mL CH\(_3\)CN at –40 °C.
2.4.4.6.1 Crystal growth of \([\text{SF}_2(\text{DMAP})_2][\text{SbF}_6]_2\cdot\text{CH}_3\text{CN}\). The \([\text{SF}_2(\text{DMAP})_2][\text{SbF}_6]_2\cdot\text{CH}_3\text{CN}\) crystals were obtained by pumping off excess \(\text{CH}_3\text{CN}\) from the product as obtained in section 2.4.4.6 in the reactor to \(-35^\circ\text{C}\). The resultant material was redissolved in 4.0 mL \(\text{CH}_2\text{Cl}_2\) at \(-30^\circ\text{C}\) and kept in the cryo-bath at \(-72^\circ\text{C}\) for 14 h. The crystal growth took place after 1.5 h. The excess solvent was slowly pumped off under dynamic vacuum up to \(-35^\circ\text{C}\) over a period of approximately 8 h and yellow needle crystals were isolated.

2.4.4.6.2 Crystal growth of \([\text{SF}(\text{DMAP})_4][\text{SbF}_6]_3\cdot2\text{CH}_3\text{CN}\). The low temperature stable \([\text{SF}(\text{DMAP})_4][\text{SbF}_6]_3\) crystal was obtained by the reaction of 0.080 mmol (0.026 g) of \([\text{SF}_3][\text{SbF}_6]\) with 0.010 g (0.082 mmol) of DMAP in 3.9 mL \(\text{CH}_3\text{CN}\) at \(-40^\circ\text{C}\) inside a \(\frac{1}{4}\) in. o.d. FEP tube equipped with a Kel-F valve. Excess acetonitrile was slowly pumped off to \(-28^\circ\text{C}\). Dark yellow material having needle crystals was isolated.

2.4.5 Synthesis of \(\text{WO}_4\text{SO}_2\), \([(\text{CH}_3)_4\text{N}][\text{WO}_5]\) and \((\text{CH}_3\text{CN})\text{WO}_3(\text{OCH}_2\text{CF}_3)\)

2.4.5.1 Synthesis of \(\text{WO}_4\text{SO}_2\). To a \(\frac{1}{4}\)” FEP reactor, 0.783 mmol (0.216 g) of \(\text{WO}_4\) were transferred and excess \(\text{SO}_2\) was transferred on top of it so that the solid, completely dissolves the \(\text{WO}_4\) at room temperature. The mixture was kept below \(-30^\circ\text{C}\) and all of excess \(\text{SO}_2\) was pumped off up to \(-30^\circ\text{C}\). The resultant \(\text{WO}_4\text{SO}_2\) off-white solid was always kept below \(-30^\circ\text{C}\) to avoid the dissociation of \(\text{WO}_4\text{SO}_2\) to \(\text{WO}_4\) and \(\text{SO}_2\).
2.4.5.1.1 Crystal growth for WOF₄SO₂. Approximately 0.054 mmol (0.015 g) of WOF₄ were transferred into a ¼” FEP reactor and 2.0 mL of SO₂ were transferred on top of it so that all of WOF₄ gets dissolved. The mixture was kept below –70 °C for 12 h and excess SO₂ was pumped off up to –30 °C. The resultant crystals were stored at –70 °C to avoid the dissociation of WOF₄·SO₂.

2.4.5.2 Synthesis of [(CH₃)₄N][WOF₅]. To the ¼” FEP reactor, 1.11 mmol (0.316 g) of WOF₄ were transferred and subsequently 1.15 mmol (0.107 g) of [(CH₃)₄N][F] was added to the same reactor inside the dry box. Excess CH₃CN was transferred to the reactor and the temperature was kept cold (approximately –30 °C). The reaction mixture was mixed properly and excess CH₃CN was pumped off by warming up the reactor to –10 °C. The resultant [(CH₃)₄N][WOF₅] (0.407 g) was obtained in the form of a white solid in a 99.0% yield.

2.4.5.2.1 Crystal growth for [(CH₃)₄N][WOF₅]. Approximately 0.041 mmol (0.015 g) of [(CH₃)₄N][F] were transferred to the ¼” FEP reactor and excess anhydrous HF was transferred to the same reactor. The reactor was transferred to the cryo-bath to keep it cold (approx. –70 °C). After 12 h crystals grew and excess HF was pumped off at –30 °C. The resultant crystals were stored in the cryo-bath at –70 °C.

2.4.5.3 Synthesis of (CH₃CN)W(O)F₃(OCH₂CF₃). A definite amount of WOF₄ (0.050 g or 0.18 mmol) was transferred in a ¼” FEP reactor and excess anhydrous CH₃CH₂OH (0.180 g or 1.79 mmol) was distilled over this WOF₄. The reaction mixture was warmed up to 20 °C. After pumping off excess CH₃CH₂OH up to ambient temperature for 12 h, a highly viscous liquid, W(O)F₃(OCH₂CF₃) (0.097 g) results. Excess CH₃CN (~ 2.0 mL) was distilled over WOF₃(OCH₂CF₃) and a solid product, (CH₃CN)W(O)F₃(OCH₂CF₃) was obtained after puming off excess CH₃CN.
2.4.5.3.1 Crystal growth for (CH₃CN)WO₅(OCH₂CF₃). 0.015 g (or 0.054 mmol) of WOF₄ was transferred in a ¼” FEP reactor and then excess anhydrous CF₃CH₂OH (~ 1.0 mL, 14 mmol) was distilled on top of WOF₄. The reaction mixture was warmed up to 30 °C. After pumping off excess solvent up to ambient temperature for 12 h, excess CH₃CN (~ 1.0 mL) was distilled over WO₅(OCH₂CF₃) and excess CH₃CN was pumped off. The resultant solid was dissolved in about 2.0 ml of CH₂Cl₂ at ambient temperature and the reactor was transferred to cryo-bath maintained at –70 °C. Next day (after 12 h) after the crystal growth excess CH₂Cl₂ was pumped off up to –30 °C. The resultant crystals were stored at –70 °C.

2.5 Crystal growth for PFOA·H₂O, SPFO, PFDA·H₂O, and SPFB.

2.5.1 Crystal growth of PFOA·H₂O. 24 mmol (~ 1.0 g) of PFOA was dissolved in ~ 5.0 mL of 2,2,2-trifluoroethanol as solvent. The solvent was allowed to evaporate very slowly for five days. The resultant crystals were stored in the glass vial at ambient temperature.

2.5.2 Crystal growth for sodium perfluorooctanoate (SPFO). 28 mmol (~ 1.2 g) of SPFO was dissolved in ~ 4.5 mL of anhydrous ethanol (99.5%). The ethanol was allowed to evaporate very slowly for three days. The resulted crystals were stored in the glass vial at ambient temperature.

2.5.3 Crystal growth for perfluorodecanoic acid as PFDA·H₂O. 2.9 mmol (~ 1.5 g) of PFDA was dissolved in ~ 6.0 mL of n-butanol as solvent. The solvent was allowed to evaporate very slowly for five days. The resulted crystals were stored in the glass vial at ambient temperature.

2.5.4 Crystal growth for sodium perfluorobutyrate (SPFB). 5.5 mmol (~ 1.5 g) of SPFB was dissolved in ~ 5.0 mL of ethanol as solvent. The ethanol was allowed to evaporate very
slowly for four days. The resulted crystals were stored in the glass vial at ambient temperature.

### 2.6 Low-temperature crystal mounting

A low-temperature crystal mounting technique was utilized for the thermally unstable and moisture-sensitive crystals. The FEP reactor containing crystals was cut open below the Kel-F valve under a flow of dry nitrogen while the lower part of the FEP reactor, which contained the crystals, was immersed in dry ice at –78 °C. The crystals were then quickly transferred from the chilled tube into an aluminum trough that was cooled by a flow of dry-nitrogen, which was passed through a 5-L Dewar of liquid nitrogen (Figure 2.5). The temperature of the trough had been adjusted to approximately –85 °C (except in case of α-[SF$_3$][SbF$_6$] crystals) and had been measured with a copper-constantan thermocouple inserted midway into the stream ca. 2-mm above the trough. A crystal was selected under a microscope and mounted on a glass fibre using an inert perfluorinated polyether, Fomblin Z-25 (Ausimont Inc.) while being kept in the cold nitrogen stream. The polyether selected for crystal mounting was sufficiently viscous to adhere to the crystal, engulf it, and freeze quickly thereafter. The glass fibre had previously been attached using an epoxy to a metallic pin that was, in turn, mounted on a magnetic base, which was attached to a magnetic wand, while picking the crystal. The pin with the crystal was quickly (<30 s) transferred from the wand to the goniometer head of the X-ray instrument using cryotongs, which had been chilled with liquid nitrogen prior to use, and attached to the magnetic base on the goniometer head.
2.6.1 Collection of X-ray data

X-ray data was collected at –120 °C on a Bruker SMART APEX-II X-ray diffractometer, which was equipped with an Apex II 4K charge-coupled device (CCD) area detector, a Kryo-Flex low-temperature device, and a Mo Kα radiation (λ = 0.71073 Å) source with a graphite monochromator. The crystal-to-detector distance was 6.120 cm. A hemisphere of data was collected with 30 s exposure time.

2.6.2 Solution and refinement of structures

Calculations were performed using the SHELXTL-plus v.6.14 package\textsuperscript{8,9} for structure determination, refinement and molecular graphics. The Xprep program was used to confirm the unit cell dimensions and the crystal lattice. The crystal structure was solved using direct method. Successive difference Fourier syntheses revealed all lighter atoms. The structures
were minimized by least squares refinement based on the square of the structure factors, $F^2$ (equivalent to intensity). Atom positions were refined anisotropically and the extinction coefficient was calculated for the crystal structure. Both residual values, $R_1$ based on $F$ and the weighted residual values $wR_2$ based on $F^2$, are available in the structure refinement tables along with the goodness of fit $GooF$. They represent the following equations:

$$R_1 = \frac{\sum |Fo| - |Fc|}{\sum |Fo|}$$  The conventional R-factor based upon the structure factor.

$$wR_2 = \sqrt{\frac{\sum [w(Fo^2 - Fc^2)^2]}{\sum [w(Fo^2)^2]}}$$  The weighted R-factor based on the square of the structure factors (observed and calculated, $F^2$ (based upon intensity).

$$GooF = \sqrt{\frac{\sum [w(Fo^2 - Fc^2)]}{(n - p)}}$$  The $GooF$ is based upon intensity where $n$ is the number of reflections, $p$ is the number of parameters refined.

The X-ray crystallography data was collected for the following crystals listed in Table 2.1.
Table 2.1 List of the crystal materials with code number and data collection temperature

<table>
<thead>
<tr>
<th>Code No.</th>
<th>Material</th>
<th>Temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MG11039</td>
<td>[SF$_3$(C$_5$H$_5$N)$_2$][SbF$_6$]·CH$_2$Cl$_2$</td>
<td>−120</td>
</tr>
<tr>
<td>MG11042</td>
<td>[SF$_3$(C$_5$H$_5$N)$_2$][SbF$_6$]·CH$_3$CN</td>
<td>−120</td>
</tr>
<tr>
<td>MG11047</td>
<td>[SF$_3$(CH$_3$CN)$_2$][SbF$_6$]</td>
<td>−120</td>
</tr>
<tr>
<td>MG11065</td>
<td>[SF$_3$(C$_5$H$_5$N)$_2$][SbF$_6$]·C$_3$H$_5$N</td>
<td>−120</td>
</tr>
<tr>
<td>MG12041</td>
<td>(CH$_3$CN)WOF$_3$(OCH$_2$CF$_3$)</td>
<td>−120</td>
</tr>
<tr>
<td>MG12046</td>
<td>[(CH$_3$)$_4$N][WOF$_5$]</td>
<td>−120</td>
</tr>
<tr>
<td>MG12058</td>
<td>[SF$_3$(C$_5$H$_5$N)$_2$][AsF$_6$]·C$_3$H$_5$N</td>
<td>−120</td>
</tr>
<tr>
<td>MG12082</td>
<td>[SF$_3$(C$_5$H$_5$N)$_2$][AsF$_6$]·CH$_2$Cl$_2$</td>
<td>−120</td>
</tr>
<tr>
<td>MG12093</td>
<td>[SF$_2$(DMAP)$_2$][SbF$_6$]·CH$_3$CN</td>
<td>−120</td>
</tr>
<tr>
<td>MG12109</td>
<td>PFOA·H$_2$O</td>
<td>−120</td>
</tr>
<tr>
<td>MG13003</td>
<td>[SF$_3$(Phen)][SbF$_6$]·2CH$_2$Cl$_2$</td>
<td>−120</td>
</tr>
<tr>
<td>MG13021</td>
<td>[SF(DMAP)$_4$][SbF$_6$]·2CH$_3$CN</td>
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<tr>
<td>MG13025</td>
<td>SPFO</td>
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<tr>
<td>MG13043</td>
<td>SPFB</td>
<td>−120</td>
</tr>
<tr>
<td>MG13061</td>
<td>PFDA·H$_2$O</td>
<td>−120</td>
</tr>
<tr>
<td>MG13066</td>
<td>γ-[SF$_3$][SbF$_6$]</td>
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</tr>
<tr>
<td>MG14001</td>
<td>[SF$_3$][AsF$_6$]</td>
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<tr>
<td>MG14016</td>
<td>WOF$_4$·SO$_2$</td>
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<td>MG14022</td>
<td>α-[SF$_3$][SbF$_6$]</td>
<td>−40</td>
</tr>
<tr>
<td>MG14028</td>
<td>EMIMHF$_2$ (1-ethyl 3-methyl imidazolium hydrogenbifluoride)</td>
<td>−120</td>
</tr>
</tbody>
</table>

2.7 Raman spectroscopy:

All Raman spectra were recorded on a Bruker RFS 100 FT Raman spectrometer equipped with a quartz beam splitter, a liquid-nitrogen cooled Ge detector, and low-temperature accessory. The backscattered (180°) radiation was sampled. The useable Stokes range was 50-3500 cm$^{-1}$ with a spectral resolution of 2 cm$^{-1}$. A Nd:Yag laser with a 1064-nm line was used for excitation of the sample. Spectra were recorded on solution samples in either 4-mm or ¼-in. FEP reactors using Laser powers of 150–200 mW. The spectra were collected between the temperature ranges 20 °C to −110 °C.
2.8 NMR spectroscopy

2.8.1 Solution-state NMR spectroscopy

All the solution-state NMR spectra were recorded on a 300 MHz Bruker Avance II NMR spectrometer. All the samples were contained in 4-mm FEP inliners and the NMR spectra were collected unlocked and were referenced externally. Fluorine-19 NMR spectra were referenced externally relative to neat CFCl₃ (δ(¹⁹F) = 0 ppm), while ¹H and ¹³C NMR spectra were referenced relative to neat TMS (δ(¹³C) = 0 ppm; δ(¹H) = 0 ppm) at room temperature.

2.8.2 Solid-state NMR spectroscopy

All the solid-state NMR spectra were recorded on a 500 MHz Varian-Inova NMR spectrometer. The imidazolium ionic liquid salt samples were contained in 3.2-mm o.d. FEP inserts and all NMR spectra were collected unlocked at low temperature and were referenced externally. Fluorine-19 NMR spectra were referenced externally relative to neat hexafluorobenzene (δ(¹⁹F) = –166.4 ppm), while ¹H and ¹³C NMR spectra were referenced relative to adamantane, (δ(¹³C) = –38.5 ppm; δ(¹H) = 1.63 ppm) at room temperature. A 4.0 µs excitation pulse was applied in acquiring ¹H direct polarization spectrum while for the ¹H-to-¹⁹F, ¹⁹F-to-¹H and ¹H-to-¹³C cross polarizations, 5.0 µs pulse was used in chapter-7.
References:


Chapter-3

3. Structural characterization of [SF₃][MF₆] (M = Sb, As) and their use in deoxofluorination reactions

3.1 Introduction

Sulfur tetrafluoride, SF₄, is known as a weak Lewis acid and for its fluoride-ion donor properties towards strong Lewis acids.¹ ² It forms a variety of different SF₃⁺ salts, i.e., [SF₃][SbF₆],² ³ [SF₃][AsF₆],² ³ [SF₃][IrF₆],⁴ [SF₃][BF₄],² ³ [SF₃][PF₆],³ [SF₃]₂[GeF₆],⁵ [SF₃][OsF₆],⁴ and [SF₃][AsF₄],³ with the Lewis acids SbF₅, AsF₅, IrF₅, BF₃, PF₅, GeF₄, OsF₅, AsF₃, respectively. Among these, [SF₃][AsF₆] and [SF₃][SbF₆] are stable at ambient temperature under exclusion of moisture with melting points of 90 °C and 253 °C, respectively. The limitation of appropriate inert solvents for these salts makes it difficult to grow single crystals suitable for X-ray crystallography. Earlier attempts to grow single crystals of [SF₃][SbF₆] through sublimation failed.⁵(i) Crystals of poor quality were obtained for [SF₃][AsF₆] by the sublimation process, yielding only unit cell parameters.⁵(i) Previously, crystal structures for SF₃⁺ salts were only reported for [SF₃][BF₄],² ³ ⁵ and for [SF₃]₂[GeF₆].⁴

Sulfur tetrafluoride has been found to exist in an equilibrium with SF₃⁺ in anhydrous HF (equation 3.1) based on conductivity experiments.¹ This equilibrium is thought to be also operative in the presence of traces of HF. Since the presence of at least traces of HF are important in deoxofluorinating reactions using SF₄, SF₃⁺ has been considered the reactive intermediate in the deoxofluorination reaction of SF₄, which can convert –COOH to –CF₃, >C=O to >CF₂ and –OH to –F functional groups.

SF₄ + HF → SF₃⁺ + HF₂⁻ ................................................................. (3.1)
The structures of [SF₃][MF₆] (M = Sb, As) salts were studied in the present work because they are the only previously known SF₃⁺ salts that are stable at room-temperature and, hence, could be used as storable reagents for deoxofluorination reactions.

3.2 Single-crystal X-ray structure determination of [SF₃][SbF₆] and [SF₃][AsF₆]

Previously, three phases of [SF₃][SbF₆] were identified by variable temperature solid-state $^{19}$F MAS NMR and Raman spectroscopy between –25 and –125 °C, while only one phase was found for [SF₃][AsF₆] in the same temperature range. Attempts were made to grow crystals of [SF₃][SbF₆] via sublimation, anhydrous HF, N-basic donor solvents such as CH₃CN and pyridine (Chapter-4) and SO₂(l). As previously reported, the sublimation process did not provide crystalline material. With anhydrous HF, crystals of [SF₃](HF)[SbF₆] were obtained. The use of nitrogen bases solvents resulted in adduct formation between SF₃⁺ and nitrogen bases (See Chapter-4). Liquid SO₂ was found to be an excellent solvent for SF₃⁺ salts as demonstrated by Mews et al. for [SF₃][AsF₆]. Their report that no fluorine-oxygen exchange between SF₃⁺ and SO₂ occurs at room temperature was confirmed in the present study by $^{19}$F NMR and Raman spectroscopy. Crystals of [SF₃][SbF₆] and [SF₃][AsF₆] suitable for X-ray crystallography were obtained using this solvent.

3.2.1 X-ray crystallography of [SF₃][SbF₆]

In order to structurally characterize the three phases of [SF₃][SbF₆], crystals were grown from liquid SO₂. Crystallization from liquid SO₂ at low temperatures furnished transparent crystals of [SF₃][SbF₆] in the form of transparent needles. The crystals were manipulated at different temperatures depending on the phase of [SF₃][SbF₆] salt. Good quality crystals
for γ-[SF₃][SbF₆] and α-[SF₃][SbF₆] were obtained by this method while material obtained for the β- modification was a single crystal.

<table>
<thead>
<tr>
<th></th>
<th>γ-[SF₃][SbF₆]</th>
<th>α-[SF₃][SbF₆]</th>
<th>[SF₃][AsF₆]</th>
</tr>
</thead>
<tbody>
<tr>
<td>chem formula</td>
<td>SF₉Sb</td>
<td>SF₉Sb</td>
<td>SF₉As</td>
</tr>
<tr>
<td>crystal system</td>
<td>Monoclinic</td>
<td>Monoclinic</td>
<td>Orthorhombic</td>
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<tr>
<td>space group</td>
<td>P2₁/n</td>
<td>P2₁/c</td>
<td>Cmc2₁</td>
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<tr>
<td>a (Å)</td>
<td>7.6922(9)</td>
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<tr>
<td>b (Å)</td>
<td>10.5446(13)</td>
<td>11.698(16)</td>
<td>8.369(6)</td>
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<tr>
<td>c (Å)</td>
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<td>11.026(15)</td>
<td>11.091(8)</td>
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<td>98.063(16)</td>
<td>90</td>
</tr>
<tr>
<td>V (Å³)</td>
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<td>709.5(17)</td>
<td>1885(2)</td>
</tr>
<tr>
<td>Z</td>
<td>4</td>
<td>4</td>
<td>8</td>
</tr>
<tr>
<td>mol wt (g mol⁻¹)</td>
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<td>324.81</td>
<td>277.98</td>
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<tr>
<td>ρcalcd (g cm⁻³)</td>
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<td>3.041</td>
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<td>–40</td>
<td>–130</td>
</tr>
<tr>
<td>μ (mm⁻¹)</td>
<td>4.67</td>
<td>4.29</td>
<td>5.87</td>
</tr>
<tr>
<td>R₁ᵃ</td>
<td>0.0133</td>
<td>0.0721</td>
<td>0.0193</td>
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<tr>
<td>wR₂ᵇ</td>
<td>0.0296</td>
<td>0.1973</td>
<td>0.0427</td>
</tr>
</tbody>
</table>

ᵃR₁ is defined as Σ|F₀| – |Fₑ|/Σ|F₀| for I > 2σ(I). ᵃwR₂ is defined as [Σ[w(F₀² – Fₑ²)]²/Σ[w(F₀²)]²]¹/₂ for I > 2σ(I).

### 3.2.1.1 γ-[SF₃][SbF₆]

The γ-[SF₃][SbF₆] crystallizes in the monoclinic P2₁/n space group with four formula units in the unit cell. Selected crystallographic data is mentioned in Table 3.1, while the bond lengths and bond angles are given in Table 3.2. A comparison with the known SF₃⁺...
structures is summarized in Table 3.3. The thermal ellipsoid plot of the crystallographic unit of $\gamma$-[SF$_3$][SbF$_6$] is shown in Figure 3.1.

![Image](image_url)

Figure 3.1 (a) X-ray crystallographic structure of $\gamma$-[SF$_3$][SbF$_6$] (b) Extended view. Thermal ellipsoids are drawn at the 50% probability level.

<table>
<thead>
<tr>
<th>Bond lengths (Å)</th>
<th>Bond angles (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>S1-F1 1.5092(12)</td>
<td>F1-S1-F2 97.23(7)</td>
</tr>
<tr>
<td>S1-F2 1.5037(11)</td>
<td>F1-S1-F3 97.05(8)</td>
</tr>
<tr>
<td>S1-F3 1.5009(13)</td>
<td>F2-S1-F3 97.94(7)</td>
</tr>
<tr>
<td>S1···F6 2.502(1)</td>
<td>F4-Sb1-F5 90.25(5)</td>
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<tr>
<td>S1···F7 2.660(1)</td>
<td>F5-Sb1-F6 90.53(6)</td>
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<tr>
<td>S1···F8 2.517(1)</td>
<td>F4-Sb1-F6 90.63(5)</td>
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<tr>
<td>Sb1-F4 1.8645(11)</td>
<td>F7-Sb2-F8 90.04(5)</td>
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<tr>
<td>Sb1-F5 1.8609(11)</td>
<td>F8-Sb2-F9 90.34(5)</td>
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<td>Sb1-F6 1.8921(11)</td>
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<td>Sb2-F7 1.8815(10)</td>
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<td>Sb2-F8 1.8880(10)</td>
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<tr>
<td>Sb2-F9 1.8567(10)</td>
<td></td>
</tr>
</tbody>
</table>
The asymmetric unit contains one SF$_3^+$ cation located on a general position and two half SbF$_6^-$ anions, which lie on crystallographic inversion centres. The SF$_3^+$ cation adopts a trigonal pyramidal geometry with approximate $C_3v$ symmetry having S–F bond lengths of 1.5009(13), 1.5037(11) and 1.5092(12) Å which are in excellent agreement with the known SF$_3^+$ structures (Table 3.3). The coordination sphere about S is expanded to hexacoordination by two short (2.502(1) and 2.517(1) Å) and one somewhat longer (2.660(1) Å) S···F contacts to adjacent SbF$_6^-$ anions. The contacts avoid the location of the lone pair on sulfur. All of these long contacts are shorter than the sum of van der Waal’s radii of sulfur and fluorine atoms (3.27 Å).

Table 3.3 Bond lengths, contacts and bond angles for SF$_3^+$ in different compounds

<table>
<thead>
<tr>
<th>Reference</th>
<th>S–F bond length (Å)</th>
<th>S···F contacts (Å)</th>
<th>F–S···F bond angle (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[SF$_3$][BF$_4$]</td>
<td>1.499(2)</td>
<td>2.593(3)</td>
<td>97.62(7)</td>
</tr>
<tr>
<td></td>
<td>1.495(2)</td>
<td>2.624(2)</td>
<td>97.39(12)</td>
</tr>
<tr>
<td>[SF$_3$]$_2$[GeF$_6$]</td>
<td>1.515(2)</td>
<td>2.420(1)</td>
<td>96.23(10)</td>
</tr>
<tr>
<td></td>
<td>1.519(1)</td>
<td>2.367(2)</td>
<td>96.12(8)</td>
</tr>
<tr>
<td>[SF$_3$][AsF$_6$]</td>
<td>1.503(3)</td>
<td>2.595(3)</td>
<td>97.16(18)</td>
</tr>
<tr>
<td></td>
<td>1.501(3)</td>
<td>2.566(3)</td>
<td>97.91(17)</td>
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<tr>
<td></td>
<td>1.511(3)</td>
<td>2.558(3)</td>
<td>98.36(18)</td>
</tr>
<tr>
<td></td>
<td>1.502(3)</td>
<td>2.494(3)</td>
<td>97.56(17)</td>
</tr>
<tr>
<td></td>
<td>1.496(4)</td>
<td>2.983(3)</td>
<td>97.56(17)</td>
</tr>
<tr>
<td>γ-[SF$_3$][SbF$_6$]</td>
<td>1.504(1)</td>
<td>2.660(1)</td>
<td>97.23(7)</td>
</tr>
<tr>
<td></td>
<td>1.501(1)</td>
<td>2.517(1)</td>
<td>97.05(8)</td>
</tr>
<tr>
<td></td>
<td>1.509(1)</td>
<td>2.502(1)</td>
<td>97.94(7)</td>
</tr>
<tr>
<td>α-[SF$_3$][SbF$_6$]</td>
<td>1.523(10)</td>
<td>2.519</td>
<td>98.3(6)</td>
</tr>
<tr>
<td></td>
<td>1.524(11)</td>
<td>2.587</td>
<td>95.8(6)</td>
</tr>
<tr>
<td></td>
<td>1.533(10)</td>
<td>2.608</td>
<td>98.7(6)</td>
</tr>
</tbody>
</table>
The F–S–F angles in the SF$_3^+$ cation are between 97.05(8) and 97.9(7)$^\circ$. The F–S–F angle of the isoelectronic neutral PF$_3$ in the gas phase is essentially the same with 97.8(2)$^\circ$, evidencing that the anion-cation contacts in [SF$_3$][SbF$_6$] do not significantly contribute to the size of F–S–F angle in the solid state. The F···S···F angles, on the other hand, vary significantly (80.13(4) to 108.67(4)$^\circ$), because the weakness of the contacts makes these angles more susceptible to packing effects compared to the F–S–F angles. The fluorine contacts between SF$_3^+$ and SbF$_6^-$ in this structure are similar to those found in [SF$_3$][BF$_4$] (2.593(3) and 2.624(2) Å), but significantly longer than those in [SF$_3$]:[GeF$_6$] (2.367(2) and 2.420(1) Å). The short contacts in the latter salt is a result of the larger anionic charge and, therefore, the more ionic nature of the fluorine atoms in the GeF$_6^2^-$ anion. The Sb–F bond lengths in the SbF$_6^-$ anion are within the expected range. The fluorine atoms which form S···F contacts have longer Sb–F bonds (1.8921(11), 1.8815(10), 1.8880(10) Å) than those of the other Sb–F bonds (1.8609(11), 1.8645(11), 1.8567(10) Å). The difference in bond lengths and small deviations of the F–Sb–F angles from 90$^\circ$, yield a distorted octahedral anion structure.

3.2.1.2 Factor group analysis of the Raman spectrum of $\gamma$-[SF$_3$][SbF$_6$]

Raman spectra of the three different phases of [SF$_3$][SbF$_6$] had been recorded. The X-ray crystal structures of the $\gamma$- phase of [SF$_3$][SbF$_6$] enable the factor group analysis for this modification. Vibrational frequencies of [SF$_3$][SbF$_6$] at –25 °C and –125 °C for the $\alpha$- and $\gamma$- phases, respectively, are listed in Table 3.4. The free SF$_3^+$ cation and SbF$_6^-$ anion are expected to adopt C$_{3v}$ and O$_h$ point symmetries, respectively, on the basis of the VSEPR model. Hence, the symmetry labels of the C$_{3v}$ and O$_h$ point groups are used in the discussion of the Raman spectra. In the Raman spectrum of $\gamma$-[SF$_3$][SbF$_6$], all the four bands for $\nu_1$, $\nu_2$, $\nu_3$ and $\nu_4$ of SF$_3^+$ should be observed. Based on the factor group analysis (Table 3.5), $\nu_1$(A$_1$)
and $\nu_2(A_1)$ should split into two Raman-active components whereas $\nu_3(E)$ and $\nu_4(E)$ should show four splittings in the Raman spectrum of $\gamma$-[SF$_3$][SbF$_6$]. Experimentally, two components are observed for $\nu_1(A_1)$ (955 and 939 cm$^{-1}$), while no splitting was observed for $\nu_2(A_1)$ (527 cm$^{-1}$). For the $\nu_3(E)$ and $\nu_4(E)$ modes two bands were observed (929 and 923 cm$^{-1}$), and (406 and 410 cm$^{-1}$), respectively as a consequence of the removal of degeneracy.

Table 3.4. Raman frequencies and their assignments for [SF$_3$][SbF$_6$]$^6$

<table>
<thead>
<tr>
<th>Frequency (cm$^{-1}$)</th>
<th>Assignments</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\alpha$-[SF$_3$][SbF$_6$]</td>
<td>$\gamma$-[SF$_3$][SbF$_6$]</td>
</tr>
<tr>
<td>$\alpha$-[SF$_3$][SbF$_6$]</td>
<td>$\gamma$-[SF$_3$][SbF$_6$]</td>
</tr>
<tr>
<td>$\alpha$-[SF$_3$][SbF$_6$]</td>
<td>$\gamma$-[SF$_3$][SbF$_6$]</td>
</tr>
</tbody>
</table>

$-25^\circ\text{C}$  
955(20)  
946(79)  
928sh  
669sh  
652(100)  
643sh  

- 25°C  
939(95)  
929(15)  
923(23)  

$\nu_1(A_1)$, $\nu_s$(SF$_3$)  
$\nu_3(E)$, $\nu_{as}$(SF$_3$)  
$\nu_3(T_{1u})$, $\nu_{as}$(SbF$_6$)  
$\nu_1(A_{1g})$, $\nu_s$(SbF$_6$)  

658(100)  
581sh  
598(6)  
593(6)  

585(15)  
581sh  
575(3)  
557(8)  

552(46)  
550(23)  

532(21)  
527(14)  
411(12)  
406(12)  

410(9)  
406(6)  
406(6)  

288(25)  

283(57)  
281(15)  
276sh  

$\nu_2(E_g)$, $\nu_{as}$(SbF$_6$)  
$\nu_2(A_1)$, $\delta$(SF$_3$)  
$\nu_4(E)$, $\delta$(SF$_3$)  
$\nu_5(T_{2g})$, $\delta$(SbF$_6$)
Table 3.5. Correlation table for SF₃⁺ cation for γ-[SF₃][SbF₆]

<table>
<thead>
<tr>
<th>SF₃⁺ free ion Site symmetry</th>
<th>Factor group symmetry</th>
</tr>
</thead>
<tbody>
<tr>
<td>C₃v</td>
<td>C₁</td>
</tr>
<tr>
<td>4T, 4v₁, 4v₂</td>
<td>A₁</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td>4R</td>
<td>A₂</td>
</tr>
<tr>
<td>4T, 4R, 4v₃, 4v₄</td>
<td>E</td>
</tr>
</tbody>
</table>

Γₜₐₚ = 2A₁ + 2E

Table 3.6 Correlation table for SbF₆⁻ anion for γ-[SF₃][SbF₆]

<table>
<thead>
<tr>
<th>SbF₆⁻ free ion Site symmetry</th>
<th>Factor group symmetry</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oₐ</td>
<td>C₁</td>
</tr>
<tr>
<td>4v₁</td>
<td>A₁g</td>
</tr>
<tr>
<td>4v₂</td>
<td>Eg</td>
</tr>
<tr>
<td>4R</td>
<td>T₁g</td>
</tr>
<tr>
<td>4v₅</td>
<td>T₂g</td>
</tr>
<tr>
<td>4T, 4v₃, 4v₄, 4v₆</td>
<td>T₁u, T₂u</td>
</tr>
</tbody>
</table>

Γₜₐₚ = A₁g + Eg + T₂g + 2T₁u + T₂u

Three bands, ν₁(A₁g), ν₂(Eg), and ν₅(T₂g) for SbF₆⁻ are expected in the Raman spectrum of γ-[SF₃][SbF₆]. The factor group analysis (Table 3.6) predicts four Raman-active components for ν₁(A₁g), eight for ν₂(Eg) and twelve for ν₅(T₂g). Two bands for the A₁ mode (658 and 655 cm⁻¹) are observed. The E₉ band is split into six components (551, 558, 598, 593, 585 and 575 cm⁻¹).

3.2.1.3 α-SF₃SbF₆

The α-phase of [SF₃][SbF₆] crystallizes in the monoclinic space group P2₁/c with four formula units per unit cell. Selected crystallographic data are given in Table 3.1. The bond lengths and bond angles are given in Table 3.7. The thermal ellipsoid plot of the crystallographic unit of α-[SF₃][SbF₆] is shown in Figure 3.2.
The deterioration of the crystal at −40 °C resulted in an incomplete data set and low accuracy of the metric parameters. The $\text{SF}_3^+$ cation adopts a trigonal pyramidal geometry with approximate $C_{3v}$ symmetry having S–F bond lengths of 1.523(10), 1.524(11) and 1.533(10) Å. Three long contacts (2.519, 2.587 and 2.608 Å) from sulfur to the fluorine atoms bound to antimony make the coordination number of sulfur six. A comparison for the known $[\text{SF}_3]^+$ structures, i.e., $[\text{SF}_3][\text{BF}_4]^{2,3}$ and $[(\text{SF}_3)_2][\text{GeF}_6]$, is summarized in the Table 3.3. The F–S–F angles in the $\text{SF}_3^+$ cation are 98.30(6), 95.80(6) and 98.70(6)° in agreement with the PF$_3$ angles as discussed in 3.2.1.1. The Sb–F bond lengths in the SbF$_6^-$ anion are within the expected range. As in the γ- phase, three S···F contacts are present between sulfur and fluorine of the adjacent SbF$_6^-$ anion. The fluorine atoms which form S···F contacts exhibit longer Sb–F bonds (1.921(10) Å) compared to the Sb–F bonds (1.871(10) Å) without contacts to the cation. The difference in bond lengths and small deviations of the F–Sb–F angles from 90°, yield a distorted octahedral anion structure. The anion-cation packing in the α- and γ- modifications is similar to a distorted CsCl structure, with the SbF$_6^-$ anions packed in a simple cubic fashion and the $\text{SF}_3^+$ cations in the cubic...
holes. The anion-cation contacts result in displacing the cation from the center of the cubic hole.

Table 3.7. Bond lengths (Å) and bond angles (°) for α-[SF₃][SbF₆]

<table>
<thead>
<tr>
<th>Bond lengths (Å)</th>
<th>Bond angles (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>S1-F1 1.523(10)</td>
<td>F1-S1-F2 98.3(6)</td>
</tr>
<tr>
<td>S1-F2 1.524(11)</td>
<td>F1-S1-F3 95.8(6)</td>
</tr>
<tr>
<td>S1-F3 1.533(10)</td>
<td>F2-S1-F3 98.7(6)</td>
</tr>
<tr>
<td>Sb1-F4 1.865(11)</td>
<td>F4-Sb1-F5 90.5(5)</td>
</tr>
<tr>
<td>Sb1-F5 1.870(9)</td>
<td>F5-Sb1-F6 88.6(4)</td>
</tr>
<tr>
<td>Sb1-F6 1.921(10)</td>
<td>F6-Sb1-F7 89.3(5)</td>
</tr>
<tr>
<td>Sb1-F7 1.871(10)</td>
<td>F7-Sb1-F8 91.4(5)</td>
</tr>
<tr>
<td>Sb1-F8 1.891(10)</td>
<td>F8-Sb1-F9 90.9(6)</td>
</tr>
<tr>
<td>Sb1-F9 1.881(10)</td>
<td>F9-Sb1-F4 91.1(6)</td>
</tr>
</tbody>
</table>

3.2.1.4 Factor group analysis of α-[SF₃][SbF₆]

As for γ-[SF₃][SbF₆], the crystal structure of α-phase enabled a factor group analysis of the modification. In the Raman spectrum of SF₃⁺ cation of α-[SF₃][SbF₆], the ν₁(A₁) is expected to split into two components based on the factor group analysis (Table 3.8) but no splitting was resolved for this band at 946 cm⁻¹. The ν₃(E) mode should show four splittings, however, the ν₃(E) band has only been observed as a shoulder at 928 cm⁻¹. The ν₂(A₁) mode comes at 532 cm⁻¹ without splitting and ν₄(E) mode appears at 283 cm⁻¹ although ν₂(A₁) and ν₄(E) should give two and four splittings, respectively.
### Table 3.8. Correlation Table for $\text{SF}_3^+$ Cation for $\alpha$-[SF$_3$][SbF$_6$]

<table>
<thead>
<tr>
<th>$\text{SF}_3^+$ Free Ion</th>
<th>Site Symmetry</th>
<th>Factor Group Symmetry</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C_3v$</td>
<td></td>
<td>$A_g$ v$_1$, v$_2$, 2v$_3$, 2v$_4$, 3R, 3T RAMAN</td>
</tr>
<tr>
<td>$C_1$</td>
<td></td>
<td>$B_g$ v$_1$, v$_2$, 2v$_3$, 2v$_4$, 3R, 3T RAMAN</td>
</tr>
<tr>
<td>$C_{2h}$</td>
<td></td>
<td>$A_u$ v$_1$, v$_2$, 2v$_3$, 2v$_4$, 3R, 3T IR</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$B_u$ v$_1$, v$_2$, 2v$_3$, 2v$_4$, 3R, 3T IR</td>
</tr>
</tbody>
</table>

$\Gamma_{\text{vib}} = 2A_1 + 2E$

### Table 3.9. Correlation Table for $\text{SbF}_6^-$ Anion for $\alpha$-[SF$_3$][SbF$_6$]

<table>
<thead>
<tr>
<th>$\text{SbF}_6^-$ Free Ion</th>
<th>Site Symmetry</th>
<th>Factor Group Symmetry</th>
</tr>
</thead>
<tbody>
<tr>
<td>$O_h$</td>
<td></td>
<td>$A_g$ v$_1$, v$_2$, 2v$_3$, 3v$_4$, 3v$_5$, v$_6$, 3R, 3T RAMAN</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$B_g$ v$_1$, v$_2$, 2v$_3$, 3v$_4$, 3v$_5$, v$_6$, 3R, 3T RAMAN</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$A_u$ v$_1$, v$_2$, 2v$_3$, 3v$_4$, 3v$_5$, v$_6$, 3R, 3T IR</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$B_u$ v$_1$, v$_2$, 2v$_3$, 3v$_4$, 3v$_5$, v$_6$, 3R, 3T IR</td>
</tr>
<tr>
<td>$A_1g$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$E_g$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$T_{1g}$</td>
<td></td>
<td></td>
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<tr>
<td>$T_{2g}$</td>
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<td></td>
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<tr>
<td>$T_{1u}$</td>
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<td></td>
</tr>
<tr>
<td>$T_{2u}$</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$\Gamma_{\text{vib}} = A_{1g} + E_g + T_{2g} + 2T_{1u} + T_{2u}$

The factor group analysis for $\text{SbF}_6^-$ anion predicts the $T_{1u}$ mode to be Raman active (Table 3.9) although the $T_{1u}$ mode is Raman inactive for isolated octahedral species and the band is predicted to have twelve Raman-active components. The $T_{1u}$ mode has been observed at 669 cm$^{-1}$ as shoulder without splitting. The $v_1(A_{1g})$ mode should give two splitting. The $v_1(A_{1g})$ band of $\text{SbF}_6^-$ anion comes at 652 cm$^{-1}$ and the splitting appear in the form of shoulder at 643 cm$^{-1}$ for this band. The $v_2(E_g)$ band should give four splitting, however, it gives two very broad contributions at 581 and 552 cm$^{-1}$ due to lift in degeneracy. For the $T_{2g}$ band at 283 cm$^{-1}$, no splitting shows up because of the broadness of the band although twelve splitting are expected for this band.
3.2.1.5 $\beta$-[SF$_3$][SbF$_6$]

Due to the poor quality of the crystal, a set of diffraction spots among the large number of observed reflections could be indexed with monoclinic cells. Refinement of the structures in the monoclinic space groups $P2_1/m$ and $P2/m$ resulted $R_1$ values below 2%. It was not possible to index all reflections, which might be the consequence of shattering of the crystal at $-70^\circ C$. In both crystal structure solutions, the sulfur in SF$_3^+$ is disordered while the SbF$_6^-$ acquires the octahedral geometry. The unit cell parameters for the monoclinic $P2_1/m$ solution were: $a = 5.3060(12)$ Å, $b = 10.608(2)$ Å, $c = 5.8862(14)$ Å and $\beta = 92.787(2)^\circ$ while for monoclinic $P2/m$, the unit cell parameters were: $a = 5.309(7)$ Å, $b = 5.309(7)$ Å, $c = 5.287(8)$ Å and $\beta = 92.80(1)^\circ$. Because of the multiple crystal nature of the material and some chemically strange bond lengths obtained from the refinement, doubts about the correct unit cell and structure remains.

3.2.2 X-ray crystallography of [SF$_3$][AsF$_6$]

In order to structurally characterize [SF$_3$][AsF$_6$], crystals were grown by dissolving [SF$_3$][AsF$_6$] in liquid SO$_2$. Crystallization from liquid SO$_2$ at $-60^\circ C$ furnished transparent crystals of [SF$_3$][AsF$_6$] in the form of needles. These crystals were manipulated at low temperature, i.e., below $-60^\circ C$. The unit cell parameters of [SF$_3$][AsF$_6$] are in excellent agreement with those reported previously.$^{15}$ The [SF$_3$][AsF$_6$] salt crystallizes in the orthorhombic $Cmc2_1$ space group with two crystallographically unique cation-anion pairs (one full and one half) (Figure 3.3) having eight formula units in the unit cell. Selected crystallographic data has been given in Table 3.1. Bond lengths and bond angles are given in Table 3.10. The comparison of S–F bond length, S····F long distances and F–S–F bond angles among SF$_3^+$ salts is summarized in the Table 3.3.
Figure 3.3 Thermal ellipsoid plots of the two independent \([\text{SF}_3][\text{AsF}_6]\) formula units in the X-ray crystal structure of \([\text{SF}_3][\text{AsF}_6]\). Thermal ellipsoids are drawn at 50% probability level.

The \(\text{SF}_3^+\) cations adopt the expected trigonal pyramidal geometry with approximate \(C_3v\) symmetry having \(\text{S}--\text{F}\) bond lengths ranging from 1.496(4) to 1.511(3) Å, which are in good agreement with the \(\text{S}--\text{F}\) bond lengths found in \([\text{SF}_3][\text{BF}_4]\) (2.593(3) and 2.624(2) Å),\(^2,3\) and in \([\text{SF}_3]_2[\text{GeF}_6]\) (2.367(2) and 2.420(1) Å).\(^5\) The \(\text{S}(2)\) atom has two close \(\text{S}--\text{F}\) contacts (2 × 2.494(3) Å) and one long \(\text{S}--\text{F}\) contact (2.983(3) Å) with adjacent anions. The coordination sphere of \(\text{S}(1)\) is also extended by three \(\text{S}--\text{F}\) contacts (2.558(3), 2.567(3) and 2.595(3) Å) with fluorine atoms of three \(\text{AsF}_6^-\) anions. These long distances increases the total coordination number of \(\text{S}(1)\) and \(\text{S}(2)\) to six. All of these contacts are shorter than the sum of van der Waal’s radii (3.27 Å).\(^12\) The fluorine contacts between \(\text{SF}_3^+\) and \(\text{AsF}_6^-\) in this structure are similar to those found in \([\text{SF}_3][\text{BF}_4]\) (2.593(3) and 2.624(2) Å),\(^2,3\) but significantly longer than those in \([\text{SF}_3]_2[\text{GeF}_6]\) (2.367(2) and 2.420(1) Å).\(^5\) The environment about \(\text{S}(2)\) in \([\text{SF}_3][\text{AsF}_6]\) is rather unusual as the three \(\text{S}--\text{F}\) contacts are of similar length in all other known \(\text{SF}_3^+\) salts (Table 3.3). The \(\text{As}--\text{F}\) bond lengths ranges from 1.690(3) to 1.732(2) Å. The \(\text{S}--\text{F}\) distance between \(\text{F}15\) of \(\text{As}2\) to \(\text{S}1\) is 2.567(3) Å increasing the \(\text{As}2--\text{F}15\) bond length to 1.709(3) Å while shortening the opposite \(\text{As}2--\text{F}13\)
bond length to 1.690(3) Å. F11 of As1 has a long contact with S1 (2.557(3) Å), thus the As1–F11 bond length becomes 1.732(2) Å while As1–F7 bond length becomes 1.729(3) Å. Similarly, F10 on As1 establishes a long contact with S1 (2.598 Å) making As1–F10 1.726(3) Å and shortening As1–F8 to 1.691(3) Å at the same time in a slightly distorted octahedral geometry of AsF$_6^-$ anion in [SF$_3$][AsF$_6$]. The As–F bond lengths are of about the same size as were found for [K][AsF$_6$] (1.712(1) Å).

Table 3.10 Bond lengths (Å), contacts (Å) and bond angles (°) for [SF$_3$][AsF$_6$]

<table>
<thead>
<tr>
<th>Bond lengths (Å)</th>
<th>Bond angles (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>S1-F1</td>
<td>1.503(3)</td>
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<tr>
<td>S1-F2</td>
<td>1.511(3)</td>
</tr>
<tr>
<td>S1-F3</td>
<td>1.501(3)</td>
</tr>
<tr>
<td>S2-F4</td>
<td>1.502(3)</td>
</tr>
<tr>
<td>S2-F5</td>
<td>1.496(4)</td>
</tr>
<tr>
<td>S1···F11</td>
<td>2.557(3)</td>
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<tr>
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<td>1.711(3)</td>
</tr>
<tr>
<td>As2-F15</td>
<td>1.709(3)</td>
</tr>
<tr>
<td></td>
<td></td>
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<td></td>
</tr>
</tbody>
</table>
3.2.2.1 Factor group analysis of [SF₃][AsF₆]

The crystal structure of [SF₃][AsF₆] allows for a factor group analysis. The observed vibrational Raman frequencies of [SF₃][AsF₆] at ambient temperature are given in Table 3.11. The recorded Raman frequencies are in agreement with those recorded by Azeem et al.¹

<table>
<thead>
<tr>
<th>Frequency (cm⁻¹)</th>
<th>Assignment</th>
<th>SF₃⁺ (C₃ᵥ)</th>
<th>AsF₆⁻ (O₅)</th>
</tr>
</thead>
<tbody>
<tr>
<td>960 (sh)</td>
<td>v₁(A₁), v₄(SF₃)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>945(81)</td>
<td>v₃(E), v₆(SF₃)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>715(20)</td>
<td></td>
<td>v₃(T₁u), v₆(AsF₆)</td>
<td></td>
</tr>
<tr>
<td>686(100)</td>
<td></td>
<td>v₁(A₁g), v₆(AsF₆)</td>
<td></td>
</tr>
<tr>
<td>587(23)</td>
<td></td>
<td>v₂(E₂), v₆(AsF₆)</td>
<td></td>
</tr>
<tr>
<td>563(32)</td>
<td>v₂(A₁), δ(SF₃)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>530(20)</td>
<td>v₄(E), δ(SF₃)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>411(22)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>379(44)</td>
<td>v₅(T₂g), δ(AsF₆)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

In the X-ray crystal structure of [SF₃][AsF₆], two different SF₃⁺ cations and two AsF₆⁻ anions are present. One SF₃⁺ and AsF₆⁻ are on the general position (C₁ site symmetry) and the other SF₃⁺ and AsF₆⁻ are on the mirror planes (C₅ symmetry). Thus, the factor group analysis is different for both pairs of SF₃⁺ and AsF₆⁻. The isolated SF₃⁺ cation and AsF₆⁻ anion have molecular C₃ᵥ and O₅ symmetries, respectively.
Table 3.12 Correlation table for the general position $\text{SF}_3^+$ cation in $[\text{SF}_3][\text{AsF}_6]$  

<table>
<thead>
<tr>
<th>$\text{SF}_3^+$ free ion</th>
<th>Site symmetry</th>
<th>Factor group symmetry</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C_{3v}$</td>
<td>$C_1$</td>
<td>$C_{2v}$</td>
</tr>
<tr>
<td>4T, 4v₁, 4v₂</td>
<td>A₁</td>
<td>A₁ v₁, v₂, 2v₃, 2v₄, 3R, 3T RAMAN IR</td>
</tr>
<tr>
<td>A</td>
<td></td>
<td>A₂ v₁, v₂, 2v₃, 2v₄, 3R, 3T RAMAN</td>
</tr>
<tr>
<td>4R</td>
<td>A₂</td>
<td>B₁ v₁, v₂, 2v₃, 2v₄, 3R, 3T RAMAN IR</td>
</tr>
<tr>
<td>E</td>
<td></td>
<td>B₂ v₁, v₂, 2v₃, 2v₄, 3R, 3T RAMAN IR</td>
</tr>
</tbody>
</table>

$\Gamma_{\text{vib}} = 2A₁ + 2E$

Table 3.13 Correlation table for the $\text{SF}_3^+$ cation on the mirror plane in $[\text{SF}_3][\text{AsF}_6]$  

<table>
<thead>
<tr>
<th>$\text{SF}_3^+$ free ion</th>
<th>Site symmetry</th>
<th>Factor group symmetry</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C_{3v}$</td>
<td>$C_s$</td>
<td>$C_{2v}$</td>
</tr>
<tr>
<td>4T, 4v₁, 4v₂</td>
<td>A₁</td>
<td>A₁ 2v₁, 2v₂, 2v₃, 2v₄, 2R, 4T RAMAN IR</td>
</tr>
<tr>
<td>A</td>
<td></td>
<td>A₂ 2v₃, 2v₄, 4R, 2T RAMAN</td>
</tr>
<tr>
<td>4R</td>
<td>A₂</td>
<td>B₁ 2v₃, 2v₄, 4R, 2T RAMAN IR</td>
</tr>
<tr>
<td>E</td>
<td></td>
<td>B₂ 2v₁, 2v₂, 2v₃, 2v₄ 2R, 4T RAMAN IR</td>
</tr>
</tbody>
</table>

$\Gamma_{\text{vib}} = 2A₁ + 2E$

Table 3.14 Correlation table for the general position $\text{AsF}_6^-$ anion in $[\text{SF}_3][\text{AsF}_6]$  

<table>
<thead>
<tr>
<th>$\text{AsF}_6^-$ free ion</th>
<th>Site symmetry</th>
<th>Factor group symmetry</th>
</tr>
</thead>
<tbody>
<tr>
<td>$O_h$</td>
<td>$C_1$</td>
<td>$C_{2v}$</td>
</tr>
<tr>
<td>4v₁</td>
<td>A₁g</td>
<td>A₁ v₁, 2v₂, 2v₃, 2v₄, 3v₅, 3v₆, 3R, 3T RAMAN IR</td>
</tr>
<tr>
<td>4v₂</td>
<td>E₁g</td>
<td>A₂ v₁, 2v₂, 2v₃, 2v₄, 3v₅, 3v₆, 3R, 3T RAMAN</td>
</tr>
<tr>
<td>4R</td>
<td>T₁g</td>
<td>B₁ v₁, 2v₂, 2v₃, 2v₄, 3v₅, 3v₆, 3R, 3T RAMAN IR</td>
</tr>
<tr>
<td>4v₅</td>
<td>T₂g</td>
<td>B₂ v₁, 2v₂, 2v₃, 2v₄, 3v₅, 3v₆, 3R, 3T RAMAN IR</td>
</tr>
<tr>
<td>4v₆</td>
<td>T₁u</td>
<td></td>
</tr>
</tbody>
</table>

$\Gamma_{\text{vib}} = A₁g + E₁g + T₂g + 2T₁u + T₂u$

Table 3.15 Correlation table for the $\text{AsF}_6^-$ anion on the mirror plane in $[\text{SF}_3][\text{AsF}_6]$  

<table>
<thead>
<tr>
<th>$\text{AsF}_6^-$ free ion</th>
<th>Site symmetry</th>
<th>Factor group symmetry</th>
</tr>
</thead>
<tbody>
<tr>
<td>$O_h$</td>
<td>$C_s$</td>
<td>$C_{2v}$</td>
</tr>
<tr>
<td>4v₁</td>
<td>A₁g</td>
<td>A₁ 2v₁, 4v₂, 6v₅, 18R, RAMAN IR</td>
</tr>
<tr>
<td>4v₂</td>
<td>E₁g</td>
<td>A₂ 6v₃, 6v₄, 6v₆ 18T RAMAN</td>
</tr>
<tr>
<td>4R</td>
<td>T₁g</td>
<td>B₁ 6v₃, 6v₄, 6v₆, 18T RAMAN IR</td>
</tr>
<tr>
<td>4v₅</td>
<td>T₂g</td>
<td>B₂ 2v₁, 4v₂, 6v₅, 18R RAMAN IR</td>
</tr>
<tr>
<td>4v₆</td>
<td>T₁u</td>
<td></td>
</tr>
</tbody>
</table>

$\Gamma_{\text{vib}} = A₁g + E₁g + T₂g + 2T₁u + T₂u$
The SF$_3^+$ cation has two $A_1$ normal modes of vibration (one stretching and one bending) as well as two doubly degenerate $E$ modes (one stretching, one bending). All of these modes are Raman active. According to the factor group analysis for the SF$_3^+$ cation (Table 3.12) on the general position, each of $\nu_1(A_1)$ and $\nu_2(A_1)$ bands should split into four Raman-active components while $\nu_3(E)$ and $\nu_4(E)$ should split into eight. For the SF$_3^+$ cation situated on the mirror plane, the factor group analysis (Table 3.13) predicts the splitting of $\nu_1(A_1)$ and $\nu_2(A_1)$ into four while $\nu_3(E)$ and $\nu_4(E)$ should show eight splitting.

For the AsF$_6^-$ anion, on the general position, six vibrational frequencies should be observed in the Raman spectrum $\nu_1(A_{1g})$. According to the factor group analysis (Table 3.14), $\nu_1(A_{1g})$ mode should split into four, $\nu_2(E_g)$ into eight while $\nu_3(T_{1u})$, $\nu_4(T_{1u})$, $\nu_5(T_{2g})$ and $\nu_6(T_{2u})$ is predicted to split into twelve splitting. The $T_{1u}$ and $T_{2u}$ modes should also be observable by Raman spectroscopy according to the factor group analysis Table 3.7 and 3.8. For the AsF$_6^-$ anion on the mirror plane, $\nu_1(A_{1g})$ should show four and $\nu_2(E_g)$ frequency should show eight splitting while $\nu_3(T_{1u})$, $\nu_4(T_{1u})$ and $\nu_5(T_{2g})$ frequencies should show twelve splitting (Table 3.15).

In the experimental Raman spectrum of [SF$_3$][AsF$_6$] (Table 3.11), all the observed vibrational bands are relatively broad and do not narrow appreciably upon cooling the sample. None of the predicted splittings for the SF$_3^+$ bands are resolved. This is likely the consequence of overlap, which contributes to the broadness of the Raman bands. In the case of AsF$_6^-$ anion, the asymmetric $T_{1u}$ mode is being assigned at 715 cm$^{-1}$ as it is predicted to have a Raman active component (Table 3.6 and 3.8). The only observed splitting is that of the asymmetric anion stretching $E_g$ mode into two components (587 and 563 cm$^{-1}$). As for the cation bands, almost all of the predicted splittings of the anion bands are not resolved, contributing to broadness.
3.3 Solution $^{19}$F NMR spectroscopy and Raman spectroscopy of [SF$_3$][MF$_6$] (M = Sb, As) salts using liquid SO$_2$ solvent

3.3.1 Solution $^{19}$F NMR spectroscopy of [SF$_3$][MF$_6$] (where M = Sb, As) salts using liquid SO$_2$ solvent

The chemical shifts from $^{19}$F MAS NMR as well as solution NMR spectroscopy of [SF$_3$][SbF$_6$] and [SF$_3$][AsF$_6$] in liquid SO$_2$ and anhydrous HF solvent are summarized in Table 3.16. The chemical shift values for the SF$_3^+$ cation of [SF$_3$][AsF$_6$] and [SF$_3$][SbF$_6$] salts in liquid SO$_2$ solvent is close to the values obtained with solid-state $^{19}$F MAS NMR spectroscopy. In the solution $^{19}$F NMR spectrum of [SF$_3$][AsF$_6$], a singlet is observed at +32.9 ppm for the SF$_3^+$ cation. The observation of one signal for the SF$_3^+$ cation shows the equivalency of fluorine atoms. For AsF$_6^-$ anion a broad peak is observed at $-58.5$ ppm in liquid SO$_2$ solvent. The chemical shift for AsF$_6^-$ anion in [SF$_3$][AsF$_6$] is in good agreement with the literature where $^{19}$F NMR spectrum was recorded in liquid SO$_2$ for C$_{60}$(AsF$_6$)$_x$ ($-64.5$ ppm). The broadness of the AsF$_6^-$ anion signal is due to the fast relaxing $^{75}$As quadrupolar nucleus. The fast relaxation of $^{75}$As nucleus removes the $^1J(^{75}$As–$^{19}$F) scalar coupling information. Similarly, in $^{19}$F solution NMR spectroscopy of [SF$_3$][SbF$_6$] salt, only one signal is observed for the SF$_3^+$ cation. Because of the fast quadrupolar relaxation due to unsymmetrical fluorine environment about Sb, $^1J$–coupling between $^{19}$F and $^{121}$Sb as well as $^{123}$Sb were not observed in $^{19}$F NMR spectra. Instead a broad peak resulted due to fast quadrupolar relaxation effect.
3.3.2 Raman spectrum of [SF₃][MF₆] (M = Sb, As) salts in SO₂(l)

No change in the frequency position and band pattern of the SF₃⁺ and MF₆⁻ signals was observed in the Raman spectrum of [SF₃][MF₆] (M = Sb, As) in SO₂(l). The example of [SF₃][SbF₆] in SO₂(l) is being demonstrated in Figure 3.5. For the confirmation of inertness of SO₂(l) towards [SF₃][MF₆] (M = Sb, As) salts, the reaction between [SF₃][MF₆] (M = Sb, As) salts and SO₂(l) was done at room temperature and then the Raman spectrum was recorded at −110 °C.
Figure 3.4 Solution $^{19}$F NMR spectra of (a) [SF$_3$][SbF$_6$] and (b) [SF$_3$][AsF$_6$] salts in liquid SO$_2$.

Figure 3.5 Raman spectrum of [SF$_3$][SbF$_6$] in liquid SO$_2$ at $-110$ °C after getting them reacted at ambient temperature.
3.4 Scoping reactions for the use of [SF$_3$][MF$_6$] (M=Sb, As) salts as deoxofluorinating reagents

A number of nucleophilic fluorinating reagents is available for deoxofluorination reactions in organic chemistry, ranging from SF$_4$ as the first fluorosulfur reagent (1958) to XtalFluor-E$^\circledR$ and XtalFluor-M$^\circledR$, which are among the latest fluorosulfur nucleophilic reagents (2010). The ionic XtalFluor reagents have been shown to be stable in reactions at temperatures up to 205 °C.$^{12}$ The [SF$_3$][MF$_6$] (M=Sb, As) salts have been known since 1956 and have a high melting point of 230 °C in the case of [SF$_3$][SbF$_6$]. Furthermore, the SF$_3^+$ cation is more electrophilic compared to SF$_4$ based on the positive charge situated on sulfur and the three highly electronegative substituents. Thus the reactions should proceed at lower temperature as compared to SF$_4$ or the [Et$_2$NSF$_2$]$^+$ cation which is part of XtalFluor-E$^\circledR$. Some of the results for the scoping reactions using [SF$_3$][MF$_6$] (M=Sb, As) salts are presented in the following sections.

3.4.1 Reaction procedure for the nucleophilic fluorination reaction using [SF$_3$][MF$_6$] (M=Sb, As) salts

Stoichiometric amounts or a slight excess of one of the [SF$_3$][MF$_6$] (M=Sb, As) salts was combined with the organic compound and a substoichiometric amount of a F$^-$ ion source such as anhydrous CsF or TMAF was added. This fluoride source presumably acts as a catalyst for the reaction. (The use of anhydrous HF in place of an ionic fluoride gave the product in low yield.) The fluorination reaction were carried out in solvents such as SO$_2$, CH$_3$CN or CH$_2$Cl$_2$. In the case of CH$_3$CN a low temperature of ca. –20 °C was maintained whereas with CH$_2$Cl$_2$ and SO$_2$, the reaction was carried out at ambient temperature. With CH$_3$CN, low temperature should be maintained all the time to avoid reaction involving CH$_3$CN. Deoxofluorination reactions using SF$_3^+$ salts were investigated for examples of
ketones (4-tert-butylcyclohexanone, 1,4-dioxaspiro[4.5]decan-8-one), carboxylic acids (pentafluorobenzoic acid, benzoic acid) and alcohol (cyclooctanol). These substrates have been used to evaluate the efficiency of XtalFluor-E®.12

3.4.2 Deoxofluorination of ketones

3.4.2.1 Deoxofluorination of 4-tert-butylcyclohexanone

The deoxofluorination of a ketone to the respective difluoro compound (equation 3.2) was tested for 4-tert-butylcyclohexanone. For the reaction, [SF₃][SbF₆] and 4-tert-butylcyclohexanone was taken in an approximately 1.5:1 ratio and CsF was added to the reaction mixture (ketone : CsF molar ratio; 1 : 0.4). The reaction was carried out either in excess liquid SO₂ or dry CH₂Cl₂ at ambient temperature in a thick wall ¼” FEP reactor which can handle the vapor pressure of the SO₂ and the pressure generated from SOF₂ and SF₄ gases. The production of 4-tert-butyl-1,1-difluorcyclohexane was monitored by ¹⁹F NMR spectroscopy (Figure 3.6) and ¹H NMR spectroscopy (Figure 3.7).

In the ¹⁹F{¹H} NMR spectrum, two doublets were observed for the reaction mixture consistent with the generation of 4-tert-butyl-1,1-difluorcyclohexane (−87.1 and −98.9 ppm with a ²J(¹⁹F–¹⁹F) coupling constant of 237 Hz).12 In the coupled ¹⁹F NMR spectrum the ³J(¹H–¹⁹F) coupling value is 36 Hz was observed for the axial fluorine signal at −98.9 ppm, which shows closeness to the protons of the cyclohexane ring. These NMR parameters are in excellent agreement with those observed for 4-tert-butyl-1,1-
difluorocyclohexane.\(^{12}\) Other signals at 73.6, 59.9 and \(-120.8\) ppm were assigned to SOF\(_2\), SF\(_4\) and SbF\(_6^-\), respectively. No \(^1J\)(\(^{121}\)Sb–\(^{19}\)F) and \(^1J\)(\(^{123}\)Sb–\(^{19}\)F) couplings were observed in case of SbF\(_6^-\). The integration value for the two doublets of 4-\textit{tert}-butyl-1,1-difluorocyclohexane is 1:1 while the integration value for SOF\(_2\) with respect to one \(^{19}\)F doublet of 4-\textit{tert}-butyl-1,1-difluorocyclohexane signal was (26 : 1). This ratio is much larger than the expected ratio of 2:1. This may be due to the production of extra SOF\(_2\) because of the reaction of SF\(_3^+\) salt with moisture (Figure 3.4).

![Figure 3.6 Solution-state \(^{19}\)F NMR spectrum (a) \(^{19}\)F{\(^1\)H} (b) \(^{19}\)F with no decoupling of 4-\textit{tert}-butylcyclohexanone in [SF\(_3\)][SbF\(_6\)], CsF using liquid SO\(_2\) (or CH\(_2\)Cl\(_2\)) as solvent at ambient temperature.](image)

In the \(^1\)H NMR spectrum, the signals of the 2\(^{\text{nd}}\), 3\(^{\text{rd}}\) and 4\(^{\text{th}}\) proton positions have been shifted at higher frequency due to the replacement of oxygen of the carbonyl group to the more electronegative fluorine. The protons at position 2 are shifted from 1.48 to 1.89
ppm, proton at position 4 is shifted from 1.36 to 1.48, protons at position 3 are shifted from 0.73 to 0.86 ppm. The protons of t-butyl group are shifted slightly from 0.21 to 0.23 ppm. These shifts also support the formation of 4-\textit{tert}-butyl-1,1-difluorocyclohexane.

![Diagram](image)

Figure 3.7 Overlap of solution-state $^1\text{H}$ DP NMR spectrum (a)grey color for 4-\textit{tert}-butylcyclohexanone in CH$_2$Cl$_2$ and (b) brown color for 4-\textit{tert}-butylcyclohexanone in [SF$_3$][SbF$_6$], CsF using liquid CH$_2$Cl$_2$ as solvent at ambient temperature.

### 3.4.2.2 Deoxofluorination of 1,4-dioxaspiro[4.5]decan-8-one

![Diagram](image)

1,4-dioxaspiro[4.5]decan-8-one and [SF$_3$][SbF$_6$] were allowed to react in 1:1 ratio using liquid CH$_3$CN solvent and CsF (ketone to CsF molar ratio of 1 : 0.4) at –20 °C. Doublets at –68.1 and –114.5 ppm ($^2J(^{19}\text{F}–^{19}\text{F}) = 9.1$ Hz) in the $^{19}\text{F}$ NMR spectrum (Figure 3.8) indicate the production of 8,8-difluoro-1,4-dioxaspiro[4.5]decan as the product. The $^2J(^{19}\text{F}–^{19}\text{F})$ coupling value is 9.1 Hz, which seems to be unexpectedly low. The yield of 8,8-difluoro-1,4-dioxaspiro[4.5]decan is low and significant amounts of HF (–180.4 ppm)
were produced as a side product. The singlet at 71.4 ppm represents SOF$_2$ and the triplets at 31.6 and 80.6 ppm represents SF$_4$ production. The multiplet signal at -122.6 ppm for SbF$_6^-$ is a combination of sextet and octet resulted from $^1J(^{121}\text{Sb}^-\text{F})$ and $^1J(^{123}\text{Sb}^-\text{F})$. These coupling values are 1952 and 1046 Hz, respectively. The production of large amounts of HF suggests that the reactant 1,4-dioxaspiro[4.5]decan-8-one was wet and the residual moisture resulted in the production of HF. Presumably because of the moisture present in the reaction mixture and the small scale of this reaction, excess SOF$_2$ was also present and the integration value of one fluorine from 8,8-difluoro-1,4-dioxaspiro[4.5]decane to SOF$_2$ was 1 : 60.

![Figure 3.8 Solution-state $^{19}$F NMR spectrum of 1,4-dioxaspiro[4.5]decan-8-one in [SF$_3$][SbF$_6$], CsF using liquid CH$_3$CN as solvent at $-30$ °C.](image)
3.4.3 Deoxofluorination of carboxylic acids (–COOH group) to acyl fluorides (–C(O)F group)

3.4.3.1 Deoxofluorination of pentafluorobenzoic acid

\[
\begin{align*}
\text{[SF}_3\text{][SbF}_6]^{\text{−}}\text{SO}_2/\text{CsF} & \quad \text{Pentafluorobenzoic acid and [SF}_3\text{][SbF}_6] \text{ were taken in a 1:1:1 ratio and CsF (carboxylic acid to CsF molar ratio of 1 : 0.7) using SO}_2 \text{ solvent at ambient temperature. The production of pentafluorobenzoyl fluoride was confirmed by }^{\text{19}}\text{F NMR spectroscopy (Figure 3.9). The triplet obtained at } 35.1 \text{ ppm confirms the presence of } \text{–C(O)F group due to the coupling of fluorine of } \text{–C(O)F group to the two fluorine atoms in the ortho positions on the pentafluorobenzyl ring } (^{\text{3}}J(^{\text{19}}\text{F−H}) = 42.9 \text{ Hz). The multiplet at } −133.7 \text{ ppm indicate two magnetically inequivalent ortho fluorines in pentafluorobenzoyl fluoride. The multiplets at } −141.8 \text{ and } −159.5 \text{ ppm represent the para and meta fluorines of pentafluorobenzoyl fluoride. The single peak at } 74.6 \text{ ppm with isotopic shift for } ^{34}\text{S (}^{\text{1}}\Delta^{34}/^{32}\text{S} = −0.054 \text{ ppm) shows the presence of SOF}_2 \text{ as a reaction product in agreement with the literature}^{16} \text{ while the broad signal at } 35.1 \text{ ppm is indicative of excess SF}_3^{+} \text{ salt in the reaction mixture. The very broad signal at } −121.1 \text{ ppm was observed for SbF}_6^{−} \text{ anion. The integration values for the ortho, para and meta fluorine of pentafluorobenzoyl fluoride is } 1.0 : 0.5 : 0.9 \text{ while for }
\end{align*}
\]

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SOF$_2$ is 3.4. The production of excess SOF$_2$ may be due to the reaction of excess [SF$_3$][SbF$_6$] salt with traces of moisture present in the solvent.

![Diagram](image.png)

Figure 3.9 Solution-state $^{19}$F NMR spectrum for production of pentafluorobenzoyl fluoride using [SF$_3$][SbF$_6$], CsF in liquid SO$_2$ as solvent at ambient temperature.

### 3.4.3.2 Deoxofluorination of benzoic acid

Benzoic acid was combined with [SF$_3$][SbF$_6$] in 1:1 ratio with CsF (carboxylic acid to CsF molar ratio of 1 : 0.7) using CH$_3$CN solvent at –20 °C. The singlet at 17.1 ppm in the $^{19}$F NMR spectrum (Figure 3.10) can be assigned to the –C(O)F group of C$_6$H$_5$C(O)F, which is in agreement with the literature. The singlet at 72.5 ppm represents the SOF$_2$ and the sextet and octet at –122.6 ppm represents the $^{1}J$(121$^{19}$Sb–$^{19}$F) and $^{1}J$(123$^{19}$Sb–$^{19}$F) coupling of the SbF$_6^{-}$ anion signal. The coupling values for them were found to be 1935 Hz and 1049 Hz, respectively. These couplings have been observed in the HF solution of NaSbF$_6$ where the values for $^{1}J$(121$^{19}$Sb–$^{19}$F) and $^{1}J$(123$^{19}$Sb–$^{19}$F) were found to be 1945 ± 5 Hz and 1055 ± 5 Hz, respectively. The integration value of –C(O)F signal with respect to SOF$_2$ (1.0 : 3.1) does not correlate well with the expected ratio of 1:2 and may be due to production of SOF$_2$ by the reaction of some SF$_3^{+}$ salt with the moisture in SO$_2$. 

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3.4.4 Deoxofluorination of alcohol

3.4.4.1 Deoxofluorination of cyclooctanol. Cyclooctanol was combined with $[\text{SF}_3][\text{AsF}_6]$ in a 1.1 : 1 ratio with CSF (alcohol to CsF molar ratio of 1 : 0.6) using liquid SO$_2$ as the solvent at ambient temperature. $^{19}$F NMR spectroscopy (Figure 3.11) demonstrated the production of 1-fluoroctane as the product in the form of broad signal due to the viscous nature of the product in the form of oil at $-158.5$ ppm in agreement with the literature value ($-159.0$ ppm). The $^3J$(H–$^{19}$F) coupling was not observed because of the broadness of the resonance. The singlet at 74.9 ppm represents SOF$_2$ with characteristic sulfur isotopic peak and a broad signal at 63.3 ppm demonstrate the formation of SF$_4$. No $^1J$(75 As–$^{19}$F) coupling was not observed because of the broad peak for $\text{AsF}_6^-$ signal due to fast relaxation of the
quadrupolar\textsuperscript{75} As nucleus. The integration value of 1-fluoroctane to SOF\textsubscript{2} was 5.1:1.0 and cannot be correlated. The reason may be the low solubility of SOF\textsubscript{2} in viscous solution.

\begin{equation}
\text{[SF\textsubscript{3}][AsF\textsubscript{6}] SO\textsubscript{2}/CsF}
\end{equation}

(3.6)

Figure 3.11 Solution-state \textsuperscript{19}F NMR spectrum of 1-fluorocyclooctane in [SF\textsubscript{3}][AsF\textsubscript{6}], CsF using liquid SO\textsubscript{2} as solvent at ambient temperature.

3.5 Conclusion and future directions

The crystal structures of two modifications of [SF\textsubscript{3}][SbF\textsubscript{6}] (γ- and α-phases) and of [SF\textsubscript{3}][AsF\textsubscript{6}] are being reported for the first time because of the difficulty present in the crystallization procedure. The scoping reactions for deoxofluorination of two ketones, two carboxylic acids and an alcohol have been carried out with [SF\textsubscript{3}][SbF\textsubscript{6}] and [SF\textsubscript{3}][AsF\textsubscript{6}] using SO\textsubscript{2}, CH\textsubscript{3}CN, and CH\textsubscript{2}Cl\textsubscript{2} solvents. These reactions need to be further optimized and scaled up. Furthermore, the isolation of the products need to be done.
References


Chapter-4

4. Synthesis and characterization of Lewis acid-base interactions between SF$_3^+$ and nitrogen bases

4.1 Introduction

Sulfur tetrafluoride is highly reactive in contrast to SF$_6$, which is inert because of its perfectly octahedral molecular geometry. Fluoride can be abstracted from SF$_4$ using strong Lewis acids such as BF$_3$, AsF$_5$, and SbF$_5$, yielding [SF$_3$]$^+$ salts. In the solid state, [SF$_3$][SbF$_6$] and [SF$_3$][AsF$_6$] were found to have contacts between sulfur and fluorine atoms of MF$_6^-$ anion (M = Sb, As) that are significantly shorter than the sum of van der Waal’s radii of sulfur and fluorine (See Chapter 3). In the case of γ-[SF$_3$][SbF$_6$] and [SF$_3$][AsF$_6$], the S---F contacts are as short as 2.502(1) and 2.494(3) Å, respectively. Such contacts have also been observed in solid [SF$_3$][BF$_4$]$^1$ and [SF$_3$]$_2$[GeF$_6$].$^2$ These short contacts despite the relatively weakly coordinating nature of the MF$_6^-$ anions (M = Sb, As) show the highly Lewis acidic nature of SF$_3^+$ cation. Recently, the weakly Lewis acidic SF$_4$ has conclusively been shown to form 1:1 Lewis acid-bases adducts with Lewis bases such as pyridine, 4-dimethylaminopyridine, 4-methylpyridine using low-temperature X-ray crystallography.$^3$

Because of the electron-poor nature of the SF$_3^+$ cation, Lewis acid-base adducts of the [SF$_3$]$^+$ cation with nitrogen bases are expected to be formed. Mews and coworker proposed the formation of [SF$_3$(CH$_3$CN)][AsF$_6$] by the reaction of [SF$_3$][AsF$_6$] with CH$_3$CN in SO$_2$ solvent at low-temperature (−30 °C) based on $^{19}$F NMR chemical shifts which change from 30.5 ppm ([SF$_3$][AsF$_6$] in SO$_2$) to 17.4 ppm up on addition of CH$_3$CN to the solution of [SF$_3$][AsF$_6$] in SO$_2$.$^4$ Schrobilgen et al. have structurally characterized the 1:2 adduct of SF$_3^+$ and the N-base, N≡SF$_3$, by X-ray crystallography as the [SF$_3$(NSF$_3$)$_2$][AsF$_6$] salt, which formed upon decomposition of [F$_4$S=N–Xe---NSF$_3$][AsF$_6$] in an effort to grow
crystals of [F₄S=N–Xe---NSF₃][AsF₆] from NSF₃ at 0 °C. In addition, the [SF₃(C₅H₅N)₂]⁺
and [SF₃(CH₃CN)₂]⁺ cations have been detected by pentaquadrupole mass spectrometer
(comprising of three Q1, Q3, Q5 mass analyzer quadrupoles and two Q2, Q4 reaction
quadrupoles). These cationic adducts were generated by the reaction of the SF₃⁺ cation,
which was formed by electron ionization of SF₆ at 70 eV, with the nitrogen base in Q2.⁶,⁷,⁸,⁹
These findings sparked the interest in synthesizing adducts of SF₃⁺ in bulk and fully
characterizing salts containing SF₃⁺–nitrogen base adducts.

4.2 Results and discussion

4.2.1 Synthesis and properties of [SF₃(C₅H₅N)₂][MF₆]·solvent (M = Sb, As; solvent =
CH₂Cl₂, C₅H₅N, CH₃CN), [SF₃(CH₃CN)₂][MF₆] (M = Sb, As), and
[SF₃(phen)][SbF₆]·2CH₂Cl₂

The [SF₃(C₅H₅N)₂][MF₆]·nC₅H₅N (M = Sb, As) salts were prepared by the reaction of
[SF₃][MF₆] salts with excess C₅H₅N at −40 °C according to equation 4.1. Excess pyridine was
removed up to −30 °C under dynamic vacuum. The [SF₃(C₅H₅N)₂][MF₆]·nC₅H₅N salts were
characterized by Raman in the solid state and NMR spectroscopy in solution. In the mass
balance study, the molar ratio of [SF₃][SbF₆] to pyridine was found to be 1 : 2,15, indicating
the presence of additional, non-adducted pyridine in the solid, as observed by Raman
spectroscopy and X-ray crystallography. This excess pyridine proved difficult to remove
under dynamic vacuum even at 3 °C. These salts are of yellow color and are readily soluble
in CH₂Cl₂, CH₃CN and SO₂, slightly soluble in THF and insoluble in toluene and CFCl₃.
The [SF₃(C₅H₅N)₂][SbF₆]·nC₅H₅N salt is stable to 3 °C as shown by variable temperature
Raman spectroscopy. Above 3 °C, the salt decomposes and turns to a brown-coloured
unidentified solid. The \([\text{SF}_3(\text{C}_5\text{H}_5\text{N})_2][\text{AsF}_6] \cdot n\text{C}_5\text{H}_5\text{N}\) salt is stable only to \(-20 \, ^\circ\text{C}\) after which it turns to a brown color.

\[
\text{[SF}_3[\text{MF}_6] + (2+n) \text{C}_5\text{H}_5\text{N} \xrightarrow{-40 \, ^\circ\text{C}} \text{[SF}_3(\text{C}_5\text{H}_5\text{N})_2][\text{MF}_6] \cdot n\text{C}_5\text{H}_5\text{N} \quad (M = \text{Sb, As}) \quad \text{(4.1)}
\]

Crystallization of \([\text{SF}_3(\text{C}_5\text{H}_5\text{N})_2][\text{MF}_6] \quad (M = \text{Sb, As})\) salts from \(\text{CH}_2\text{Cl}_2\), and a \(\text{C}_5\text{H}_5\text{N}/\text{CH}_2\text{Cl}_2\) solvent mixture at low-temperature furnished transparent crystals of \([\text{SF}_3(\text{C}_5\text{H}_5\text{N})_2][\text{MF}_6] \cdot \text{CH}_2\text{Cl}_2\) and \([\text{SF}_3(\text{C}_5\text{H}_5\text{N})_2][\text{MF}_6] \cdot \text{C}_5\text{H}_5\text{N} \quad (M = \text{Sb, As})\), respectively, in the form of needles. Crystal growth of \([\text{SF}_3(\text{C}_5\text{H}_5\text{N})_2][\text{SbF}_6]\) from a mixture of \(\text{CH}_3\text{CN}\) and \(\text{CH}_2\text{Cl}_2\) yielded crystals of \([\text{SF}_3(\text{C}_5\text{H}_5\text{N})_2][\text{SbF}_6] \cdot \text{CH}_3\text{CN}\). It was observed that one solvent molecule is required for the crystallization of \([\text{SF}_3(\text{C}_5\text{H}_5\text{N})_2][\text{MF}_6]\) salts. The solvent molecule is apparently required for efficient packing of the anions and cations in the solid state.

The \([\text{SF}_3(\text{CH}_3\text{CN})_2][\text{MF}_6]\) salts are prepared by the reaction of \([\text{SF}_3][\text{MF}_6] \quad (M = \text{Sb, As})\) with excess \(\text{CH}_3\text{CN}\) at \(-40 \, ^\circ\text{C}\) according to equation 4.2. Excess acetonitrile was pumped off at \(-30 \, ^\circ\text{C}\). These salts are of yellow colour and were characterized by Raman spectroscopy and X-ray crystallography in the solid state and \(^{19}\text{F}\) NMR spectroscopy in solution. These salts are readily soluble in \(\text{CH}_2\text{Cl}_2\) and \(\text{SO}_2\), slightly soluble in \(\text{THF}\) and insoluble in toluene and \(\text{CFCl}_3\). The \([\text{SF}_3(\text{CH}_3\text{CN})_2][\text{SbF}_6]\) salt is stable to \(-20 \, ^\circ\text{C}\) based on Raman spectroscopy above which it turns into an unidentified brown solid.

\[
[\text{SF}_3][\text{MF}_6] + 2\text{CH}_3\text{CN} \xrightarrow{-40 \, ^\circ\text{C}} [\text{SF}_3(\text{CH}_3\text{CN})_2][\text{MF}_6] \quad (M = \text{Sb, As}) \quad \text{..................(4.2)}
\]
The $[\text{SF}_3(\text{phen})][\text{SbF}_6] \cdot 2\text{CH}_2\text{Cl}_2$ salt was prepared by the reaction of $[\text{SF}_3][\text{SbF}_6]$ salt and 1,10-phenanthroline in 1:1 ratio in $\text{CH}_2\text{Cl}_2$ solvent at $-40 \degree \text{C}$ according to reaction equation 4.3. Excess $\text{CH}_2\text{Cl}_2$ was pumped off at $-20 \degree \text{C}$. This salt was characterized by Raman and solution NMR spectroscopy as well as by X-ray crystallography. This salt also is of yellow color and is readily soluble in $\text{CH}_2\text{Cl}_2$, $\text{CH}_3\text{CN}$ and $\text{SO}_2$, slightly soluble in THF and insoluble in toluene and CFCl$_3$. Variable-temperature Raman spectroscopy shows that $[\text{SF}_3(\text{phen})][\text{SbF}_6] \cdot 2\text{CH}_2\text{Cl}_2$ is stable to $+15 \degree \text{C}$. The chelating effect of bidentate 1,10-phenanthroline contributes to its stability at higher temperature compared to $[\text{SF}_3(\text{C}_5\text{H}_5\text{N})_2][\text{MF}_6]$ and $[\text{SF}_3(\text{CH}_3\text{CN})_2][\text{MF}_6]$ ($\text{M} = \text{Sb}, \text{As}$).

$$[\text{SF}_3][\text{SbF}_6] + \text{phen} + 2\text{CH}_2\text{Cl}_2 \xrightarrow{-40 \degree \text{C}} [\text{SF}_3(\text{phen})][\text{SbF}_6] \cdot 2\text{CH}_2\text{Cl}_2 \quad \text{..................(4.3)}$$

where, phen = 1,10-Phenanthroline

4.2.2 Synthesis and properties of $[\text{SF}_2(\text{DMAP})_2][\text{SbF}_6] \cdot \text{CH}_3\text{CN}$ and crystal Growth of $[\text{SF}(\text{DMAP})_4][\text{SbF}_6] \cdot 2\text{CH}_3\text{CN}$

The $[\text{SF}_2(\text{DMAP})_2][\text{SbF}_6] \cdot \text{CH}_3\text{CN}$ salt was prepared by the reaction of $[\text{SF}_3][\text{SbF}_6]$ with DMAP in 1:1 ratio in excess $\text{CH}_3\text{CN}$ at $-40 \degree \text{C}$ according to reaction equation 4.4, followed by the removal of volatiles at $-35 \degree \text{C}$. This salt was characterized by X-ray crystallography and Raman spectroscopy in the solid state and by NMR spectroscopy in $\text{CH}_3\text{CN}$ solvent. It is of intense yellow color and is readily soluble in $\text{CH}_2\text{Cl}_2$, $\text{CH}_3\text{CN}$ and $\text{SO}_2$ and insoluble in toluene and CFCl$_3$. Surprisingly, no evidence for the $[\text{SF}_3(\text{DMAP})_2]^+$ cation was observed by Raman and solution NMR spectroscopy at temperatures as low as $-40 \degree \text{C}$, even when using a
1:2 molar ratio of [SF$_3$][SbF$_6$] to DMAP. The [SF$_3$(DMAP)$_2$]$^+$ cation is supposedly unstable and decomposes rapidly into [SF$_2$(DMAP)$_2$]$^{2+}$ and SF$_4$ (Eq 4.5). The stoichiometry of the products of the reaction equation 4.5 has been confirmed by $^{19}$F NMR spectroscopy (vide infra).

\[
2[SF_3][SbF_6] + 2\text{DMAP} \xrightarrow{\text{CH}_3\text{CN} - 40 \, ^\circ\text{C}} [SF_2(\text{DMAP})_2][SbF_6]_2\cdot\text{CH}_3\text{CN} + \text{SF}_4 \quad \text{..................(4.4)}
\]

where, DMAP = 4-dimethylaminopyridine

\[
2[SF_3(\text{DMAP})_2]^+ \rightarrow [SF_2(\text{DMAP})_2]^{2+} + \text{SF}_4 \quad \text{..........................(4.5)}
\]

Crystals of [SF(DMAP)$_4$][SbF$_6$]$_3$·2CH$_3$CN were obtained by the reaction of [SF$_3$][SbF$_6$] salt with DMAP in 1:2 ratio in excess CH$_3$CN at $-40 \, ^\circ\text{C}$, in an attempt to grow crystals of [SF$_2$(DMAP)$_2$][SbF$_6$]$_2$ from CH$_3$CN solvent. Excess acetonitrile was pumped off to $-28 \, ^\circ\text{C}$. The [SF(DMAP)$_4$]$^{3+}$ cation presumably forms in a ligand transfer reaction from [SF$_2$(DMAP)$_2$]$^{2+}$ according to equation 4.6.

\[
3[SF_2(\text{DMAP})_2]^{2+} \rightarrow [SF(\text{DMAP})_4]^{3+} + 2\text{SF}_4 + 2\text{DMAP} \quad \text{..........................(4.6)}
\]
4.2.3 X-ray Crystallography

4.2.3.1 X-ray crystallography of $[\text{SF}_3(\text{C}_5\text{H}_5\text{N})_2][\text{MF}_6]\cdot\text{solute (M = Sb, As; solute = CH}_2\text{Cl}_2, \text{C}_5\text{H}_5\text{N, CH}_3\text{CN})$.

The $[\text{SF}_3(\text{C}_5\text{H}_5\text{N})_2][\text{MF}_6]\cdot\text{CH}_2\text{Cl}_2$, $[\text{SF}_3(\text{C}_5\text{H}_5\text{N})_2][\text{MF}_6]\cdot\text{C}_5\text{H}_5\text{N}$ (M = Sb, As) and $[\text{SF}_3(\text{C}_5\text{H}_5\text{N})_2][\text{SbF}_6]\cdot\text{CH}_3\text{CN}$ salts were characterized by single-crystal X-ray diffraction. It was observed that $[\text{SF}_3(\text{C}_5\text{H}_5\text{N})_2][\text{MF}_6]$ (M = Sb, As) salts crystallized with a solvent of crystallization such as C$_5$H$_5$N, CH$_3$CN and CH$_2$Cl$_2$. The two $[\text{SF}_3(\text{C}_5\text{H}_5\text{N})_2][\text{MF}_6]\cdot\text{CH}_2\text{Cl}_2$ salts with M = Sb, As were found to be isostructural, crystallizing in the monoclinic $C2/c$ space group with four formula units in the unit cell. The two $[\text{SF}_3(\text{C}_5\text{H}_5\text{N})_2][\text{MF}_6]\cdot\text{C}_5\text{H}_5\text{N}$ (M = Sb, As) salts were also isostructural, crystallizing in the monoclinic $C2/c$ space group with eight formula units of in the unit cell. The $[\text{SF}_3(\text{C}_5\text{H}_5\text{N})_2][\text{SbF}_6]\cdot\text{CH}_3\text{CN}$ salt crystallizes in triclinic $P\overline{1}$ space group with two formula units of $[\text{SF}_3(\text{C}_5\text{H}_5\text{N})_2][\text{SbF}_6]\cdot\text{CH}_3\text{CN}$ in the unit cell. The structural units in the X-ray crystal structures of $[\text{SF}_3(\text{C}_5\text{H}_5\text{N})_2][\text{SbF}_6]\cdot\text{CH}_2\text{Cl}_2$, $[\text{SF}_3(\text{C}_5\text{H}_5\text{N})_2][\text{SbF}_6]\cdot\text{C}_5\text{H}_5\text{N}$ and $[\text{SF}_3(\text{C}_5\text{H}_5\text{N})_2][\text{SbF}_6]\cdot\text{CH}_3\text{CN}$ salts are shown in Figures 4.1, 4.2 and 4.3, respectively. A summary of the refinement results and other crystallographic data has been given in Table 4.1. Selected bond lengths, contact distances, and bond angles are given in Tables 4.2, 4.3 and 4.4.
Table 4.1. Crystallographic data for [SF$_3$(C$_5$H$_5$N)$_2$][MF$_6$]·CH$_2$Cl$_2$ (M = Sb, As), [SF$_3$(C$_5$H$_5$N)$_2$][MF$_6$]·C$_5$H$_5$N (M = Sb, As), [SF$_3$(C$_5$H$_5$N)$_2$][SbF$_6$]·CH$_3$CN, and [SF$_3$(CH$_3$CN)$_2$][SbF$_6$].

<table>
<thead>
<tr>
<th>Chemical formula</th>
<th>Crystal system</th>
<th>Space group</th>
<th>a (Å)</th>
<th>b (Å)</th>
<th>c (Å)</th>
<th>α (°)</th>
<th>β (°)</th>
<th>γ (°)</th>
<th>Z</th>
<th>Formula weight (g mol$^{-1}$)</th>
<th>Calcd density (g cm$^{-3}$)</th>
<th>T (°C)</th>
<th>μ (mm$^{-1}$)</th>
<th>R$_1^a$</th>
<th>wR$_2^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>[SF$_3$(C$_5$H$_5$N)$_2$][SbF$_6$]·CH$_2$Cl$_2$</td>
<td>Monoclinic</td>
<td>C2/c</td>
<td>10.9125(14)</td>
<td>12.6405(16)</td>
<td>14.3435(19)</td>
<td>90</td>
<td>108.040(10)</td>
<td>90</td>
<td>4</td>
<td>567.94</td>
<td>1.5826</td>
<td>–120</td>
<td>3.855</td>
<td>0.0240</td>
<td>0.0548</td>
</tr>
<tr>
<td>[SF$_3$(C$_5$H$_5$N)$_2$][AsF$_6$]·CH$_2$Cl$_2$</td>
<td>Monoclinic</td>
<td>C2/c</td>
<td>10.836(3)</td>
<td>12.472(3)</td>
<td>14.118(3)</td>
<td>90</td>
<td>107.463(3)</td>
<td>90</td>
<td>4</td>
<td>392.53</td>
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<td>–120</td>
<td>4.384</td>
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<td>[SF$_3$(C$_5$H$_5$N)$_2$][SbF$_6$]·CH$_3$CN</td>
<td>Monoclinic</td>
<td>P –I</td>
<td>7.6726(19)</td>
<td>9.059(2)</td>
<td>14.157(4)</td>
<td>71.383(3)</td>
<td>78.418(3)</td>
<td>79.548(3)</td>
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<tr>
<td>[SF$_3$(C$_5$H$_5$N)$_2$][SbF$_6$]·C$_5$H$_5$N</td>
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<td>C2/c</td>
<td>26.913(4)</td>
<td>8.5679(11)</td>
<td>18.443(2)</td>
<td>90</td>
<td>125.151(10)</td>
<td>90</td>
<td>8</td>
<td>562.12</td>
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</tr>
<tr>
<td>[SF$_3$(C$_5$H$_5$N)$_2$][AsF$_6$]·C$_5$H$_5$N</td>
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<td>26.694(11)</td>
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<td>17.978(7)</td>
<td>90</td>
<td>124.422(5)</td>
<td>90</td>
<td>8</td>
<td>515.28</td>
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<td>2.244</td>
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<td>0.0655</td>
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</table>

$^a$ $R_1$ is defined as $\sum||F_o| - |F_c||/\sum|F_o|$ for $I > 2\sigma(I)$. $^b$ wR$_2$ is defined as $[\sum w(F_o^2 - F_c^2)^2]/[\sum w(F_o^2)^2]^{1/2}$ for $I > 2\sigma(I)$. 

| 98 |
Figure 4.1 The thermal ellipsoid plots of (a) structural unit in the X-ray crystal structure of [SF₃(C₅H₅N)₂][SbF₆]-CH₂Cl₂ in the crystal of [SF₃(C₅H₅N)₂][SbF₆]-CH₂Cl₂ and (b) one component of the disordered [SF₃(C₅H₅N)₂]⁺ cation. Thermal ellipsoids are drawn at the 50% probability level.

Table 4.2 Bond lengths (Å) and bond angles (°) for [SF₃(C₅H₅N)₂][MF₆]-CH₂Cl₂ (M = Sb, As)

<table>
<thead>
<tr>
<th>Bond lengths (Å) and bond angles (°)</th>
<th>[SF₃(C₅H₅N)₂][SbF₆]-CH₂Cl₂</th>
<th>[SF₃(C₅H₅N)₂][AsF₆]-CH₂Cl₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>S1-F1</td>
<td>1.614(4)</td>
<td>S1-F1</td>
</tr>
<tr>
<td>S1-F2</td>
<td>1.573(4)</td>
<td>S1-F2</td>
</tr>
<tr>
<td>S1-F1A</td>
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<td>S1-F1A</td>
</tr>
<tr>
<td>S1-N1</td>
<td>2.106(2)</td>
<td>S1-N1</td>
</tr>
<tr>
<td>S1-N1A</td>
<td>2.124(2)</td>
<td>S1-N1A</td>
</tr>
<tr>
<td>Sb1-F3</td>
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<td>1.8651(13)</td>
<td>As1-F4</td>
</tr>
<tr>
<td>Sb1-F5</td>
<td>1.8633(16)</td>
<td>As1-F5</td>
</tr>
<tr>
<td>F1-S1-F2</td>
<td>89.47(18)</td>
<td>F1-S1-F2</td>
</tr>
<tr>
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<td>90.10(17)</td>
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<td>90.86(13)</td>
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<td>N1-S1-N1A</td>
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<tr>
<td>F3-Sb1-F4</td>
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<td>90.11(8)</td>
<td>F4-As1-F5</td>
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<td>F4-Sb1-F5</td>
<td>90.17(8)</td>
<td>F3-As1-F4</td>
</tr>
</tbody>
</table>
Figure 4.2 Thermal ellipsoid plot of the $[\text{SF}_3(\text{C}_5\text{H}_5\text{N})_2][\text{SbF}_6] \cdot \text{C}_5\text{H}_5\text{N}$ structural unit in the crystal of $[\text{SF}_3(\text{C}_5\text{H}_5\text{N})_2][\text{SbF}_6] \cdot \text{C}_5\text{H}_5\text{N}$. Thermal ellipsoids are drawn at the 50% probability level.

Table 4.3 Bond lengths (Å) and bond angles (°) for $[\text{SF}_3(\text{C}_5\text{H}_5\text{N})_2][\text{MF}_6] \cdot \text{C}_5\text{H}_5\text{N}$ (M = Sb, As)

<table>
<thead>
<tr>
<th>Bond lengths (Å) and bond angles (°)</th>
<th>$[\text{SF}_3(\text{C}_5\text{H}_5\text{N})_2][\text{SbF}_6] \cdot \text{C}_5\text{H}_5\text{N}$</th>
<th>$[\text{SF}_3(\text{C}_5\text{H}_5\text{N})_2][\text{AsF}_6] \cdot \text{C}_5\text{H}_5\text{N}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>S1-F1</td>
<td>1.6000(12)</td>
<td>S1-F1</td>
</tr>
<tr>
<td>S1-F2</td>
<td>1.5609(12)</td>
<td>S1-F2</td>
</tr>
<tr>
<td>S1-F3</td>
<td>1.6288(13)</td>
<td>S1-F3</td>
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Figure 4.3 Thermal ellipsoid plot of the \([\text{SF}_3(\text{C}_5\text{H}_5\text{N})_2][\text{SbF}_6]\)-\text{CH}_3\text{CN} structural unit in the crystal of \([\text{SF}_3(\text{C}_5\text{H}_5\text{N})_2][\text{SbF}_6]\)-\text{CH}_3\text{CN}. Thermal ellipsoids are drawn at the 50% probability level.

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In [SF$_3$(C$_5$H$_5$N)$_2$][MF$_6$]·CH$_2$Cl$_2$ (M = Sb, As), the [SF$_3$(C$_5$H$_5$N)$_2$]$^+$ cation and the CH$_2$Cl$_2$ molecule are positionally disordered along a C$_2$ axis (50:50% disorder). The disorder in the [SF$_3$(C$_5$H$_5$N)$_2$]$^+$ cation was modeled by defining two orientations of the SF$_3$ moieties in which the axial fluorine atom points to opposite sides. A disorder in the two pyridine moieties of the [SF$_3$(C$_5$H$_5$N)$_2$]$^+$ cation could not be resolved. The disorder in the CH$_2$Cl$_2$ molecule was modeled by defining two positions for carbon (and as a consequence two positions for the hydrogen atoms). The two chlorine atoms in CH$_2$Cl$_2$ were not split in the disorder model and were taken as the pivot points. In [SF$_3$(C$_5$H$_5$N)$_2$][MF$_6$]·C$_5$H$_5$N (M = Sb, As), the cation was ordered, while the solvent C$_5$H$_5$N molecule, which is situated on a crystallographic inversion centre, exhibits a six-fold rotational disorder along the axis perpendicular to the molecular plane. The crystal structure of [SF$_3$(C$_5$H$_5$N)$_2$][SbF$_6$]·CH$_3$CN is the only structure in this series that does not exhibit any disorder.

The [SF$_3$(C$_5$H$_5$N)$_2$]$^+$ cation adopts a square pyramidal molecular geometry in all of the above mentioned salts in accord with an AX$_3$Y$_2$E VSEPR geometry having six electron pairs about sulfur. Two fluorine atoms and the two pyridine molecules are located in the equatorial position while one fluorine occupies the axial position, trans to the lone pair. In Table 4.5, selected metric parameters of the [SF$_3$(C$_5$H$_5$N)$_2$]$^+$ cation are compared with those of other square pyramidal sulfur species, the SF$_5^-$ anion and the [SF$_3$(NSF)$_2$]$^+$ cation. The F–S–F angles about sulfur in the [SF$_3$(C$_5$H$_5$N)$_2$]$^+$ cation are quite close to 90°. Such angles reflect a substantial geometry change of the SF$_3$ moiety upon adduct formation with pyridine (γ-[SF$_3$][SbF$_6$] 97.23(7), 97.05(8), 97.94(7)°, [SF$_3$][AsF$_6$] 97.16(18), 97.91(17), 98.36(18), 97.56(17)°), and [SF$_3$][BF$_4$] (97.62(7), 97.39(12)°). In the [SF$_3$(C$_5$H$_5$N)$_2$]$^+$ cation, the axial S–F bond length is significantly shorter than the equatorial S–F bond lengths ([(SF$_3$(C$_5$H$_5$N)$_2$)][SbF$_6$]·CH$_2$Cl$_2$: F$_{ax}$ 1.573(4), F$_{eq}$ 1.608(4)/1.614(4) Å;
[SF₃(C₅H₅N)₂][AsF₆]∙CH₂Cl₂: Fₐₓ 1.566(4), Fₑₒₜ 1.617(4)/1.620(4) Å;
[SF₃(C₅H₅N)₂][SbF₆]∙C₅H₅N: Fₐₓ 1.5609(12), Fₑₒₜ 1.6000(12)/1.6288(13) Å;
[SF₃(C₅H₅N)₂][AsF₆]∙C₅H₅N: Fₐₓ 1.584(4), Fₑₒₜ 1.628(4)/1.564(4) Å;
[SF₃(C₅H₅N)₂][SbF₆]∙CH₃CN: Fₐₓ 1.559(3), Fₑₒₜ 1.600(3)/1.627(3) Å). The same has been observed for the SF₅⁻ anion in [Rb][SF₅] salt with the axial and equatorial bond lengths being 1.559(15) Å and 1.707(14)/1.729(13) Å, respectively. Upon complexation of the SF₅⁺ cation by pyridine, all S–F bond lengths are elongated, reflecting more ionic S–F bonds upon donation of electron density to sulfur (γ-[SF₅][SbF₆]: 1.501(1) to 1.509(1) Å;
[SF₅][AsF₆]: 1.501(3) to 1.510(3) Å; [SF₅(C₅H₅N)₂]⁺: 1.559(3) to 1.729(13) Å). When compared to the adduct with a much weaker Lewis base, NSF₃, the axial and equatorial bond lengths are longer in the [SF₅(C₅H₅N)₂]⁺ than the corresponding axial and equatorial bond lengths found in [SF₅(NSF₃)₂][AsF₆] salt (1.511(1), 1.520(1) and 1.519(1) Å) (Table 4.5), also reflecting the larger electron donating power of pyridine than NSF₃.
Table 4.5 Comparison of distances and angles in different fluorosulfur(IV) compounds

| Compound | Distance (Å) | Distance (Å) | Distance (Å) | Angle(s) (°) | Angle(s) (°) | Ref
|----------|--------------|--------------|--------------|--------------|--------------|---
|          | S–F<sub>ax</sub> | S–F<sub>eq</sub> | S···N | S···F | F<sub>ax</sub>–S–F<sub>eq</sub> | F<sub>eq</sub>–S–F<sub>eq</sub> | N<sub>1</sub>–S–N<sub>2</sub> |
| [Rb][SF<sub>5</sub>] | 1.559(15) | 1.707(14) | 1.729(13) | 2.511(2) | 2.558(2) | 96.2(1) | 96.8(1) | 96.3(1) | PW | 33
| [SF<sub>5</sub>(NSF<sub>3</sub>)<sub>2</sub>][AsF<sub>6</sub>] | 1.511(1) | 1.519(1) | 1.520(1) | 1.5104(16) | 2.458(3) | 2.458(3) | 96.38(7) | 96.38(7) | 94.90(14) | 101.3(4) | PW | 31
| [SF<sub>5</sub>(CH<sub>3</sub>CN)<sub>2</sub>][SbF<sub>6</sub>] | 1.505(2) | 1.5104(16) | 1.5104(16) | 1.5104(16) | 2.458(3) | 2.458(3) | 96.38(7) | 96.38(7) | 94.90(14) | 101.3(4) | PW | 31
| [SF(AsF<sub>3</sub>)<sub>2</sub>][AsF<sub>6</sub>] | 1.559(3) | 1.568(3) | 1.568(3) | 1.584(4) | 1.601(3) | 2.106(2) | 2.124(2) | 3.324(9) | 89.5(2) | 90.9(2) | PW | 31
| [SF(AsF<sub>3</sub>)<sub>2</sub>][AsF<sub>6</sub>] | 1.550(2) | 1.5104(16) | 1.5104(16) | 1.5104(16) | 2.458(3) | 2.458(3) | 96.38(7) | 96.38(7) | 94.90(14) | 101.3(4) | PW | 31
| [SF(AsF<sub>3</sub>)<sub>2</sub>][AsF<sub>6</sub>] | 1.559(3) | 1.672(3) | 1.672(3) | 1.600(3) | 2.106(2) | 2.124(2) | 3.324(9) | 89.5(2) | 90.9(2) | PW | 31
| [SF(AsF<sub>3</sub>)<sub>2</sub>][AsF<sub>6</sub>] | 1.5609(12) | 1.6000(12) | 1.6288(13) | 1.6000(12) | 1.6288(13) | 2.1421(16) | 2.0613(16) | 3.304(9) | 88.65(7) | 90.76(8) | PW | 31
| [SF(AsF<sub>3</sub>)<sub>2</sub>][AsF<sub>6</sub>] | 1.554(2) | 1.613(3) | 1.613(3) | 1.601(3) | 2.140(3) | 2.111(3) | 3.015(3) | 89.7(1) | 93.7(1) | PW | 31
| [SF(AsF<sub>3</sub>)<sub>2</sub>][AsF<sub>6</sub>] | 1.701(4) | 1.701(4) | 1.701(4) | 2×1.878(7) | 2×1.924(7) | 4.297 | 100.4(3) | PW | 31
| [SF(AsF<sub>3</sub>)<sub>2</sub>][AsF<sub>6</sub>] | 1.594(8) | 2×1.924(7) | 3.500 | 90.0(3) | PW | 31
| [SF(DMAP)<sub>4</sub>][SbF<sub>6</sub>] | 1.701(4) | 1.701(4) | 1.701(4) | 2×1.878(7) | 2×1.924(7) | 4.297 | 100.4(3) | PW | 31
| [SF(DMAP)<sub>4</sub>][SbF<sub>6</sub>] | 1.701(4) | 1.701(4) | 1.701(4) | 2×1.878(7) | 2×1.924(7) | 4.297 | 100.4(3) | PW | 31

<sup>a</sup>PW-Present Work
The coordination of the two pyridine ligands to sulfur is slightly unsymmetrical (the S---N distances for [SF₅(C₅H₅N)₂][SbF₆]·CH₂Cl₂ and [SF₅(C₅H₅N)₂][AsF₆]·CH₂Cl₂ are 2.106(2)/2.124(2) Å and 2.098(2)/2.106(2) Å, respectively). For the structures that incorporate a pyridine and acetonitrile of crystallization, the asymmetry is somewhat more pronounced: 2.1421(16)/2.0613(16) Å ([SF₅(C₅H₅N)₂][SbF₆]·C₅H₅N), 2.154(5)/2.052(5) Å ([SF₅(C₅H₅N)₂][AsF₆]·C₅H₅N), and 2.062(4)/2.143(4) Å ([SF₅(C₅H₅N)₂][SbF₆]·CH₃CN).

A significant asymmetry of S---N distances has been predicted by computational means for the isolated cation in the gas phase with distances of 2.28 and 2.44 Å. All of these S---N distances are shorter than the sum of van der Waal’s radii of sulfur and nitrogen (3.35 Å) and considerably shorter than what has been found in SF₄·NC₅H₅ adduct (2.5138(18) Å) indicating a strong coordination of C₅H₅N with SF₅⁺ cation in [SF₅(C₅H₅N)₂][MF₆]·Solvent. This is expected due to SF₅⁺ being more Lewis acidic than SF₄. The shortest S···F cation-anion distances in the [SF₅(C₅H₅N)₂][MF₆] (M = Sb, As) salts are longer or close to the limit of the sum of the van der Waal’s radii, i.e., 3.27 Å, (3.324(9) Å, in [SF₅(C₅H₅N)₂][SbF₆]·CH₂Cl₂ and 3.417(5) Å in [SF₅(C₅H₅N)₂][AsF₆]·CH₂Cl₂), indicating well separated anions and cations in these structures. With two dative bonds from the nitrogen of C₅H₅N, the coordination sphere about sulfur in [SF₅(C₅H₅N)₂][MF₆]·CH₂Cl₂ (M = Sb, As) and [SF₅(C₅H₅N)₂][MF₆]·C₅H₅N (M = Sb, As) salts is expanded increasing the total coordination number of sulfur to five and sufficiently saturated that no further donation of electron density is needed. The MF₆− (M = Sb, As) anion in these salts have approximate octahedral geometries.
4.2.3.2 X-ray crystallography of [SF$_3$(CH$_3$CN)$_2$][SbF$_6$]

The [SF$_3$(CH$_3$CN)$_2$][SbF$_6$] salt crystallizes in the orthorhombic space group $Pnma$ with four formula units of [SF$_3$(CH$_3$CN)$_2$][SbF$_6$] in the unit cell. A summary of the refinement results and other crystallographic data has been given in Table 4.6. Selected bond lengths, contact distances, and angles are given in Table 4.7. Unlike the [SF$_3$(C$_5$H$_5$N)$_2$]$^+$ salts, the [SF$_3$(CH$_3$CN)$_2$]$^+$ salt crystallizes without any solvent of crystallization. In the crystal structure of [SF$_3$(CH$_3$CN)$_2$][SbF$_6$] (Figure 4.4), the [SF$_3$(CH$_3$CN)$_2$]$^+$ cation lies on a crystallographic mirror plane and has a distorted square pyramidal geometry. Two fluorine atoms of [SF$_3$(CH$_3$CN)$_2$]$^+$ cation are in the equatorial position (S–F distance, 2 $\times$ 1.5104(16) Å) along with two CH$_3$CN molecules (S---N distance, 2 $\times$ 2.458(3) Å), which are shorter than the sum of van der Waal’s radii of sulfur and nitrogen (3.35 Å)\textsuperscript{12}, while one of the fluorine is in the axial position with the S–F bond length of 1.505(2) Å. These S–F bond lengths are of the same size as those present in $\gamma$-[SF$_3$][SbF$_6$] (1.501(1) to 1.509(1) Å) showing the small effect of the CH$_3$CN coordination. The F–S–F angles in [SF$_3$(CH$_3$CN)$_2$]$^+$ cation (94.90(14), 2 $\times$ 96.38(7)°) are somewhat smaller than those in $\gamma$-[SF$_3$][SbF$_6$] salt (97.05(8), 97.23(7) and 97.94(7)°) as a result of the coordination of two CH$_3$CN molecules.

In addition to two dative bonds with the nitrogen of CH$_3$CN, the coordination sphere about S in [SF$_3$(CH$_3$CN)$_2$]$^+$ is expanded by a S···F contact to one fluorine atom of an adjacent SbF$_6^-$ anion (2.616(3) Å), which is significantly shorter than the sum of van der Waal’s radii (3.27 Å).\textsuperscript{12} As a result, the total coordination number about sulfur becomes six. The long sulfur-fluorine contact between [SF$_3$(CH$_3$CN)$_2$]$^+$ and SbF$_6^-$, i.e., 2.616(3) Å, in this structure is about the same length as those found in $\gamma$-[SF$_3$][SbF$_6$] (2.660(1), 2.517(1) and 2.502(1) Å). In the SbF$_6^-$ anion, one of the Sb–F distance (1.891(2) Å) is significantly
longer than the other Sb–F distances (1.8280(18) to 1.861(2) Å) because of the stronger interaction of this fluorine atom towards sulfur.

The S–F bond lengths and the S–N interactions are different in [SF$_3$(CH$_3$CN)$_2$][SbF$_6$] compared to those in the [SF$_3$(C$_5$H$_5$N)$_2$][SbF$_6$]-Solvent structures. The S–F bond lengths in the [SF$_3$(C$_5$H$_5$N)$_2$][SbF$_6$]-C$_5$H$_5$N crystal structures (1.5609(12), 1.6000(12) and 1.6288(13) Å) are longer as compared to the S–F bond lengths in the [SF$_3$(CH$_3$CN)$_2$][SbF$_6$] (2×1.5104(16) and 1.505(2) Å) and the S···N bond lengths are shorter ([SF$_3$(C$_5$H$_5$N)$_2$][SbF$_6$]-C$_5$H$_5$N: 2.1421(16) to 2.0613(16) Å) as a result of the stronger Lewis basicity of C$_5$H$_5$N compared to that of CH$_3$CN. As a consequence of the weaker electron donating effect of CH$_3$CN, the sulfur has one additional S···F contact in the CH$_3$CN adduct, which has also been observed in the crystal structure of [SF$_3$(NSF)$_2$][AsF$_6$].

Figure 4.4 Thermal ellipsoid of the cation anion pair in the X-ray crystal structure of [SF$_3$(CH$_3$CN)$_2$][SbF$_6$]. Thermal ellipsoids are drawn at the 50% probability level.
Table 4.6. Crystallographic data for \([\text{SF}_3(\text{CH}_3\text{CN})_2][\text{SbF}_6]\) and \([\text{SF}_3(\text{Phen})][\text{SbF}_6] \cdot 2\text{CH}_2\text{Cl}_2\), \([\text{SF}_2(\text{DMAP})_2][\text{SbF}_6]_2 \cdot \text{CH}_3\text{CN}\) and \([\text{SF}(\text{DMAP})_4][\text{SbF}_6]_3 \cdot 2\text{CH}_3\text{CN}\) salts

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\(^a\) \(R_1\) is defined as \(\Sigma ||F_o| - |F_c||/\Sigma |F_o|\) for \(I > 2\sigma(I)\). \(^b\) \(wR_2\) is defined as \(\Sigma [w(F_o^2 - F_c^2)^2]/\Sigma w(F_o^2)^{1/2}\) for \(I > 2\sigma(I)\).
Table 4.7 Bond lengths (Å) and bond angles (°) for [SF₃(CH₂CN)₂][SbF₆]

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4.2.3.3 X-ray crystallography of [SF₃(phen)][SbF₆]·2CH₂Cl₂

The [SF₃(phen)][SbF₆]·2CH₂Cl₂ crystallizes in the monoclinic space group P2₁/c with four formula units in the unit cell. A summary of the refinement results and other crystallographic data has been given in Table 4.6. Selected bond lengths and bond angles are given in Table 4.8. The structural unit in the X-ray crystal structure of [SF₃(phen)][SbF₆]·2CH₂Cl₂ is shown in Figure 4.5. In the crystal structure of [SF₃(phen)][SbF₆]·2CH₂Cl₂, the [SF₃(phen)]⁺ cation is square pyramidal with two equatorial S–F bonds (1.601(3) and 1.613(3) Å), two S⋯N coordinate bonds (2.140(3) and 2.111(3) Å), and one axial S–F bond length of 1.554(2) Å. The S–F bond lengths in the [SF₃(phen)]⁺ cation are longer than those present in γ-[SF₃][SbF₆] (1.501(1) to 1.509(1) Å). The angles about sulfur are close to 90°, as found for the [SF₃(C₅H₅N)₂]⁺ cation, although the bidentate nature of 1,10-phenanthroline constrains the N–S–N angle in the equatorial plane (Table 4.5). The closest S⋯F cation anion distance is 3.015(3) Å, which is close to the sum of van der Waal’s radii of sulfur and fluorine (3.27 Å). This very weak contact
does not have any significant influence on the cation geometry, as indicated by the bond angles in the \([\text{SF}_3(\text{phen})]^+\) cation.

Table 4.8 Bond lengths (Å) and bond angles (°) for \([\text{SF}_3(\text{phen})][\text{SbF}_6]\cdot2\text{CH}_2\text{Cl}_2\)

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Figure 4.5 The thermal ellipsoid of the structural unit in the X-ray crystal structure of \([\text{SF}_3(\text{phen})][\text{SbF}_6]\cdot2\text{CH}_2\text{Cl}_2\) in the crystal of \([\text{SF}_3(\text{phen})][\text{SbF}_6]\cdot2\text{CH}_2\text{Cl}_2\). Thermal ellipsoids are drawn at the 50% probability level.

110
4.2.3.4 X-ray crystallography of \([\text{SF}_2(\text{DMAP})_2][\text{SbF}_6]_2\cdot\text{CH}_3\text{CN}\) and \([\text{SF}(\text{DMAP})_2][\text{SbF}_6]_3\cdot2\text{CH}_3\text{CN}\)

4.2.3.4.1 X-ray crystallography of \([\text{SF}_2(\text{DMAP})_2][\text{SbF}_6]_2\cdot\text{CH}_3\text{CN}\). The \([\text{SF}_2(\text{DMAP})_2][\text{SbF}_6]_2\) salt co-crystallizes with a CH$_3$CN solvent molecule, in the form of \([\text{SF}_2(\text{DMAP})_2][\text{SbF}_6]_2\cdot\text{CH}_3\text{CN}\), which crystallizes in the monoclinic C2/c space group with four formula units in the unit cell. The structural unit in the X-ray crystal structure of \([\text{SF}_2(\text{DMAP})_2][\text{SbF}_6]_2\cdot\text{CH}_3\text{CN}\) is shown in Figure 4.6. The crystallographic data are given in Table 4.6. Selected bond lengths and angles are given in Table 4.9. In the crystal structure of \([\text{SF}_2(\text{DMAP})_2][\text{SbF}_6]_2\cdot\text{CH}_3\text{CN}\), the \([\text{SF}_2(\text{DMAP})_2]^{2+}\) cation crystallizes in a see-saw geometry with two symmetry–related fluorine atoms in the axial positions with S–F bond lengths of 1.701(4) Å, which are much longer than those present in \(\gamma\)-[S$_3$F$_3$][SbF$_6$] (1.504(1), 1.501(1) and 1.509(1) Å) despite of the additional positive charge of the \([\text{SF}_2(\text{DMAP})_2]^{2+}\) cation. These axial S–F bond lengths is similar what was found for bis(imidazole)sulfur difluoride, \([(\text{C}_3\text{H}_3\text{N}_2)_2\text{SF}_2]\), (1.709(2) and 1.693(2) Å)$^{13}$ whereas longer than those present in solid SF$_4$ (1.647(5) and 1.675(5) Å). Two DMAP molecules occupy the equatorial position with the S–N bond lengths of 1.724(5) Å. The S–N bonds represent strong covalent bonding between sulfur and nitrogen, unlike the weaker bonds in the cationic adducts of SF$_3^+$ and nitrogen bases. In bis(imidazole)sulfur difluoride, the S–N bonds are shorter (1.700(2) and 1.690(3) Å) than those present in the \([\text{SF}_2(\text{DMAP})_2]^{2+}\) cation. The lone pair is in the equatorial plane of the distorted trigonal bipyramidal geometry in accord with the VSEPR model. The axial F7–S1–F7A bond angle of 175.4(3)$^\circ$ deviates somewhat from the linearity due to the lone pair – bond pair repulsion. The F–S–F bond angle is 173.86(12)$^\circ$ in case of bis(imidazole)sulfur difluoride. The closest S···F distance in \([\text{SF}_2(\text{DMAP})_2][\text{SbF}_6]_2\cdot\text{CH}_3\text{CN}\) is 4.297 Å which is much longer than the sum of van der
Waal’s radii of sulfur and fluorine (3.27 Å),\(^1\) indicating well separated \([\text{SF}_2(\text{DMAP})_2]^+\) cation and \(\text{SbF}_6^-\) anion.

![Figure 4.6 The thermal ellipsoid of the structural unit in the X-ray crystal structure of \([\text{SF}_2(\text{DMAP})_2][\text{SbF}_6]_2\cdot\text{CH}_3\text{CN}\) in the crystal of \([\text{SF}_2(\text{DMAP})_2][\text{SbF}_6]_2\cdot\text{CH}_3\text{CN}\). Thermal ellipsoids are drawn at the 50% probability level.](image)

<table>
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<th>Bond lengths (Å)</th>
<th>Bond angles (°)</th>
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4.2.3.4.2 X-ray crystallography of \([\text{SF}(\text{DMAP})_4][\text{SbF}_6]_3\cdot2\text{CH}_3\text{CN}\). The \([\text{SF}(\text{DMAP})_4]_2[\text{SbF}_6]_3\cdot2\text{CH}_3\text{CN}\) crystallizes in the monoclinic space group \(C2/c\) with four
formula units in the unit cell. The crystallographic data is given in Table 4.6. The structural unit in the X-ray crystal structure of [SF(DMAP)$_4$][SbF$_6$]$_3$·2CH$_3$CN is shown in Figure 4.7 and the bond lengths and angles are given in Table 4.10. In the crystal structure of [SF(DMAP)$_4$][SbF$_6$]$_3$·2CH$_3$CN, the [SF(DMAP)$_4$]$^{3+}$ cation adopts a square pyramidal VSEPR geometry. The fluorine on sulfur is disordered with respect to a crystallographic C$_2$ axis and was refined by taking into account a 50% occupancy. The fluorine atom is in the axial position with S–F bond length of 1.594(8) Å, which is longer than the S–F bond length present in γ-[SF$_3$][SbF$_6$] (1.504(1), 1.501(1) and 1.509(1) Å). Four DMAP molecules are in the equatorial position. The S–N bond lengths of 2×1.878(7) Å and 2×1.924(7) Å are strong covalent bonds, but longer than the S–N bonds in the [SF$_2$(DMAP)$_2$]$^{2+}$ cation. The N–S–N bond angles are 90.0(3)° giving the structure a square shape in the equatorial plane. The shortest S···F distance (3.500 Å) between [SF(DMAP)$_4$]$^{3+}$ cation and SbF$_6^-$ anion in [SF(DMAP)$_4$][SbF$_6$]$_3$·2CH$_3$CN is longer than the sum of the van der Waal’s radii of sulfur and fluorine i.e. 3.27 Å, separating the [SF(DMAP)$_4$]$^{3+}$ cation and SbF$_6^-$ anion completely. In the crystal structure, the lone pair on sulfur is situated trans to the axial fluorine to avoid any repulsion between lone pair and bond pair.
Figure 4.7 The thermal ellipsoid of the structural unit of [SF(DMAP)₄]³⁺ cation in the X-ray crystal structure of [SF(DMAP)₄][SbF₆]₃·2CH₃CN. Thermal ellipsoids are drawn at the 50% probability level.

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<th>Bond lengths (Å)</th>
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<td>1.924(7)</td>
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</table>
4.2.4 Raman spectroscopy

4.2.4.1 Raman spectroscopy of [SF₃(C₅H₅N)₂][MF₆]·solvent (M = Sb, As; solvent = CH₂Cl₂, C₅H₅N and [SF₃(C₅H₅N)₂][SbF₆]·CH₂CN

The Raman spectra of [SF₃(C₅H₅N)₂][MF₆]·nC₅H₅N (M = Sb, As) salts at −110 °C (with n = 0.15 determined by mass balance in case of [SF₃(C₅H₅N)₂][SbF₆]·nC₅H₅N salt) are depicted in Figure 4.8 along with the spectrum of neat C₅H₅N and the vibrational frequencies for [SF₃(C₅H₅N)₂][SbF₆]·nC₅H₅N, [SF₃(C₅H₅N)₂][AsF₆]·nC₅H₅N, [SF₃(C₅H₅N)₂][SbF₆]·CH₂CN, [SF₃(C₅H₅N)₂][SbF₆]·CH₂Cl₂, and [SF₃(C₅H₅N)₂][AsF₆]·CH₂Cl₂ are listed in Table 4.11, 4.12, 4.13, 4.14 and 4.15, respectively.

After the formation of the adducts between [SF₃][MF₆] (where M = Sb, As) salts and C₅H₅N, shifts in the Raman frequencies for the SF₃⁺ moiety, and C₅H₅N are expected to be observed. In the case of [SF₃(C₅H₅N)₂][SbF₆]·C₅H₅N, the symmetric SF₃ stretching band (νₛ) is shifted to 816 cm⁻¹ for [SF₃(C₅H₅N)₂]⁺ cation as compared to 939 cm⁻¹ for [SF₃]⁺ cation in [SF₃][SbF₆], while in the case of [SF₃(C₅H₅N)₂][AsF₆]·C₅H₅N salt, the νₛ(SF₃) appears at 812 cm⁻¹ for [SF₃(C₅H₅N)₂]⁺ cation in comparison to 945 cm⁻¹ for [SF₃]⁺ cation in [SF₃][AsF₆]. Similar νₔ(SF₃) frequencies are observed for [SF₃(C₅H₅N)₂][SbF₆]·CH₂Cl₂ (815 cm⁻¹), [SF₃(C₅H₅N)₂][AsF₆]·CH₂Cl₂ (818 cm⁻¹) and [SF₃(C₅H₅N)₂][SbF₆]·CH₂CN (808 and 828 cm⁻¹). Upon complexation of [SF₃][MF₆] (M = Sb, As) salts with C₅H₅N, the S–F bond lengths in the [SF₃(C₅H₅N)₂]⁺ cations become longer as observed in the crystal structures, which is paralleled by a decrease of the S–F bond strength. Several Raman signals associated with the C₅H₅N part of the adduct are significantly shifted compared to those of the free pyridine. One set of signals, however, is unshifted indicating the presence of some unadducted pyridine in the resultant salt. For
example, the most intense band in the Raman spectrum of free pyridine comes at 990 cm$^{-1}$, which corresponds to the symmetric C$_5$N ring breathing mode. This band shifts to higher frequency upon complexation of C$_5$H$_5$N with [SF$_3$][MF$_6$] (M = Sb, As) salts, i.e., to 1018 cm$^{-1}$ in case of [SF$_3$(C$_5$H$_5$N)$_2$][SbF$_6$]·C$_5$H$_5$N and 1022 cm$^{-1}$ in case of [SF$_3$(C$_5$H$_5$N)$_2$][AsF$_6$]·C$_5$H$_5$N. Similar frequencies were observed for the C$_5$N breathing mode (1020 cm$^{-1}$) in [SF$_3$(C$_5$H$_5$N)$_2$][SbF$_6$]·CH$_2$Cl$_2$, [SF$_3$(C$_5$H$_5$N)$_2$][AsF$_6$]·CH$_2$Cl$_2$ (1019 cm$^{-1}$) and [SF$_3$(C$_5$H$_5$N)$_2$][SbF$_6$]·CH$_3$CN (1018 cm$^{-1}$). A strong shift in the ν$_s$(C$_5$N) mode of C$_5$H$_5$N in [SF$_3$(C$_5$H$_5$N)$_2$][MF$_6$]·C$_5$H$_5$N (M = Sb, As) salts shows that C$_5$H$_5$N is strongly bonded with [SF$_3$][MF$_6$] (M = Sb, As). The C$_5$N ring breathing mode for C$_5$H$_5$N in case of the strong BF$_3$·NC$_5$H$_5$ adduct was shifted to 1026 cm$^{-1}$ in comparison to the free pyridine C$_5$N mode at 990 cm$^{-1}$, whereas it was shifted to 1003 cm$^{-1}$ in case of weak SF$_4$·C$_5$H$_5$N adduct and to 1016 cm$^{-1}$ for the WSF$_4$·C$_5$H$_5$N adduct. The signals from the C$_5$N ring breathing mode shows splitting likely from vibrational coupling of the C$_5$H$_5$N molecules in the adduct at 1010, 1032 and 1038 cm$^{-1}$ for [SF$_3$(C$_5$H$_5$N)$_2$][SbF$_6$]·nC$_5$H$_5$N, 1022 and 1031 cm$^{-1}$ for [SF$_3$(C$_5$H$_5$N)$_2$][AsF$_6$]·nC$_5$H$_5$N salt, 1032 and 1041 cm$^{-1}$ for [SF$_3$(C$_5$H$_5$N)$_2$][SbF$_6$]·CH$_3$CN, 1012, 1032 and 1038 cm$^{-1}$ for [SF$_3$(C$_5$H$_5$N)$_2$][SbF$_6$]·CH$_2$Cl$_2$ and at 1006, 1034 and 1041 cm$^{-1}$ for [SF$_3$(C$_5$H$_5$N)$_2$][AsF$_6$]·CH$_2$Cl$_2$. Upon complexation of pyridine with BF$_3$, a shift of the C–C stretching mode from 1581 to 1631 cm$^{-1}$ has been observed. A similar shift from 1581 to 1607 cm$^{-1}$ was observed for [SF$_3$(C$_5$H$_5$N)$_2$][SbF$_6$]·nC$_5$H$_5$N, to 1604 cm$^{-1}$ in case of [SF$_3$(C$_5$H$_5$N)$_2$][AsF$_6$]·nC$_5$H$_5$N, to 1608 cm$^{-1}$ in case of [SF$_3$(C$_5$H$_5$N)$_2$][SbF$_6$]·CH$_2$Cl$_2$, to 1609 cm$^{-1}$ in case of [SF$_3$(C$_5$H$_5$N)$_2$][AsF$_6$]·CH$_2$Cl$_2$ and to 1608 cm$^{-1}$ in case of [SF$_3$(C$_5$H$_5$N)$_2$][SbF$_6$]·CH$_3$CN in the current study. The stretching frequencies of the C–H vibrations of pyridine are also shifted upon complex formation, e.g., the signal at 3088 cm$^{-1}$ in free pyridine is shifted to...
3116 cm\(^{-1}\) for \([\text{SF}_3(\text{C}_5\text{H}_5\text{N})_2][\text{SbF}_6]\cdot n\text{C}_5\text{H}_5\text{N},\) to 3111 cm\(^{-1}\) for \([\text{SF}_3(\text{C}_5\text{H}_5\text{N})_2][\text{AsF}_6]\cdot n\text{C}_5\text{H}_5\text{N},\) to 3116 cm\(^{-1}\) in case of \([\text{SF}_3(\text{C}_5\text{H}_5\text{N})_2][\text{SbF}_6]\cdot \text{CH}_2\text{Cl}_2,\) to 3107 cm\(^{-1}\) in case of \([\text{SF}_3(\text{C}_5\text{H}_5\text{N})_2][\text{AsF}_6]\cdot \text{CH}_2\text{Cl}_2\) and to 3113 cm\(^{-1}\) in case of \([\text{SF}_3(\text{C}_5\text{H}_5\text{N})_2][\text{SbF}_6]\cdot \text{CH}_3\text{CN.}\) A similar shift to 3124 cm\(^{-1}\) in the C–H stretching frequency was observed for C\(_5\)H\(_5\)N in BF\(_3\)·NC\(_5\)H\(_5\) adduct.

Figure 4.8 Raman spectrum of C\(_5\)H\(_5\)N, \([\text{SF}_3(\text{C}_5\text{H}_5\text{N})_2][\text{AsF}_6]\cdot \text{C}_5\text{H}_5\text{N},\) \([\text{SF}_3(\text{C}_5\text{H}_5\text{N})_2][\text{SbF}_6]\cdot \text{C}_5\text{H}_5\text{N}\) at −110 °C. Asterisks (*) denote bands arising from the FEP sample tube.
Table 4.11 Raman frequencies (relative intensities), cm\(^{-1}\) of SF\(_3\)SbF\(_6\), C\(_5\)H\(_5\)N and [SF\(_3\)(C\(_5\)H\(_5\)N)\(_2\)][SbF\(_6\)]\(_n\)C\(_5\)H\(_5\)N at –110 °C together with their tentative assignments.

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\(^a\) [SF\(_3\)(C\(_5\)H\(_5\)N)\(_2\)][SbF\(_6\)]\(_n\)C\(_5\)H\(_5\)N
The Raman spectrum was recorded in a glass NMR tube at –110 °C. The Raman spectrum was recorded in a ¼-in FEP tube at –110 °C. Signals observed at 294(8), 1213(15) cm$^{-1}$ in the spectrum of [SF$_3$(C$_5$H$_5$N)$_2$][SbF$_6$]·nC$_5$H$_5$N are overlapped with the bands of FEP sample tube. Signals observed at 387(5), 733(18), 1303(4), 1382(6) cm$^{-1}$ represents FEP. Pyridine bands have been assigned based on references 19–23. [SF$_3$][SbF$_6$] bands have been assigned based on references 2c.
Table 4.12 Raman frequencies (relative intensities), cm$^{-1}$ of [SF$_3$][AsF$_6$], C$_5$H$_5$N and [SF$_3$(C$_5$H$_5$N)$_2$][AsF$_6$]$\cdot$nC$_5$H$_5$N at $-110$ °C together with their tentative assignments.

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The Raman spectrum was recorded in a glass NMR tube at –110 °C. The Raman spectrum was recorded in a 1/4–in FEP tube at –110 °C. Signals observed at 733(51), 1219(29) cm\(^{-1}\) in Raman spectrum of [SF\(_3\)(C\(_5\)H\(_5\)N)]\(_2\)[AsF\(_6\)]\(\bullet\)nC\(_5\)H\(_5\)N are overlapped with the bands of FEP sample tube. Signals observed at 294(11), 387(13), 1305(5), 1383(13) cm\(^{-1}\) in Raman spectrum are of FEP sample tube. Pyridine bands have been assigned based on references 19–23. [SF\(_3\)][AsF\(_6\)] bands have been assigned based on references 2c.
Table 4.13. Raman frequencies (relative intensities), cm\(^{-1}\) of [SF\(_3\)][SbF\(_6\)], C\(_5\)H\(_5\)N and [SF\(_3\)(C\(_5\)H\(_5\)N)\(_2\)][SbF\(_6\)]·CH\(_3\)CN at –110 °C together with their tentative assignments.

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overtones and combination bands

ν(C-H) ν(C-H)
ν(C=C) ν(C=C)
ν(C=N) ν(C=N)
δ(C-H) δ(C-H)
in-plane ring-def in-plane ring-def
ν(C=N ring)
ν\(_s\)(C\(_5\)N ring)
| 604(3) | 634(8) | 617(8) | 605(4) | \(\delta(\text{SbF}_6)\) | \(\delta(\text{SbF}_6)\) |
| 578(1) | 552(20) | 533(sh) | 529(13) | 528(1) | \(\delta(\text{SF}_3)^*\) | \(\delta(\text{SF}_3)^*\) |
| 408(1) | 410(11) | 397(4) | 351(4) | out-of-plane ring def | 313(1) | 301(8) | 279(37) | 294(1) | 220(9) |

\(\text{a}\) The Raman spectrum was recorded in a glass NMR tube at –110 °C. \(\text{b}\) Signals observed at 384(14), 1219(23), 1375(12) cm\(^{-1}\) in the Raman spectrum of \([\text{SF}_3(\text{C}_5\text{H}_5\text{N})_2][\text{SbF}_6]\)·\(\text{CH}_3\text{CN}\) are overlapped with FEP signals. \(\text{c}\) Signals observed at 293(8), 733(25), 1307(1) cm\(^{-1}\) are of FEP. \(\text{d}\) Pyridine bands have been assigned based on references 19-23. \(\text{e}\) \([\text{SF}_3][\text{SbF}_6]\) bands have been assigned based on references 2c.
Table 4.14 Raman frequencies (relative intensities), cm\(^{-1}\) of [SF\(_3\)]/[SbF\(_6\)], C\(_5\)H\(_5\)N and [SF\(_3\)(C\(_5\)H\(_5\)N)]/[SbF\(_6\)]·CH\(_2\)Cl\(_2\) at \(-110\) °C together with their tentative assignments.

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The Raman spectrum was recorded in a glass NMR tube at –110 °C. Signals observed at 387(24), 1217(25) cm$^{-1}$ in the Raman spectrum of [SF$_3$(C$_5$H$_5$N)$_2$][SbF$_6$]·CH$_2$Cl$_2$ are overlapped with FEP signals. Signals from the FEP sample tube were observed at 292(10), 733(54), 1304(6), 1383(15) cm$^{-1}$. Pyridine bands have been assigned based on references 19-23. [SF$_3$][SbF$_6$] bands have been assigned based on references 2c.
Table 4.15 Raman frequencies (relative intensities), cm$^{-1}$ of [SF$_3$][AsF$_6$], C$_5$H$_5$N and [SF$_3$(C$_5$H$_5$N)$_2$][AsF$_6$]·CH$_2$Cl$_2$ at –110 °C together with their tentative assignments.

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The Raman spectrum was recorded in a glass NMR tube at –110 °C. * Signals observed 1217(21) cm⁻¹ in the Raman spectrum of [SF₃(C₅H₅N)]₂[AsF₆]·CH₂Cl₂ are overlapped with FEP signals. † The signals from the FEP sample tube were observed at 294(13), 387(13), 733(31), 1307(4), 1383(8) cm⁻¹. ‡ Pyridine bands have been assigned based on references 19-23. § [SF₃][AsF₆] bands have been assigned based on references 2c.
4.2.4.2 Raman spectroscopy of [SF$_3$(Phen)][SbF$_6$]·2CH$_2$Cl$_2$

The vibrational frequencies of [SF$_3$(Phen)][SbF$_6$]·2CH$_2$Cl$_2$ are listed in Table 4.16 together with their tentative assignments while the Raman spectrum is shown in Figure 4.9. The symmetric SF$_3$ stretch is situated at 832 cm$^{-1}$ indicating similar coordination strength of 1,10-phenanthroline with SF$_3^+$ cation in [SF$_3$(Phen)][SbF$_6$] as compared to the C$_5$H$_5$N coordination with SF$_3^+$ cation in [SF$_3$(C$_5$H$_5$N)$_2$][SbF$_6$]·nC$_5$H$_5$N for which the symmetric SF$_3$ stretch is at 812 cm$^{-1}$. The 1,10–phenanthroline ring stretching mode, also shifts from 1034 to 1057 cm$^{-1}$ upon adduct formation. This band has been shifted to 1050 cm$^{-1}$ in case of [Ag(phen)]$^+$ complex.$^{17}$ The A$_{1g}$ stretching mode of SbF$_6^-$ has been shifted insignificantly from 650 to 646 cm$^{-1}$. The same difference in the magnitude of the Raman shift of SbF$_6^-$ was found in [SF$_3$(C$_5$H$_5$N)$_2$][SbF$_6$]·nC$_5$H$_5$N salt indicating a similar lack of cation-anion interaction in [SF$_3$(Phen)][SbF$_6$]·2CH$_2$Cl$_2$ salt as is present in [SF$_3$(C$_5$H$_5$N)$_2$][SbF$_6$]·nC$_5$H$_5$N salt.
Figure 4.9 Raman spectrum of [SF$_3$][SbF$_6$], [SF$_3$(Phen)][SbF$_6$]-2CH$_2$Cl$_2$ and 1,10-phenanthroline (Phen) solids at −110 °C. Asterisks (*) denote bands arising from the FEP sample tube.
Table 4.16 Raman frequencies (relative intensities), cm\(^{-1}\) of \([\text{SF}_3][\text{SbF}_6]\), 1,10-Phenanthroline (Phen) and \([\text{SF}_3(\text{Phen})][\text{SbF}_6]\)-2CH\(_2\)Cl\(_2\) at –110 °C together with their tentative assignments.

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\(^a\) Corresponds to the spectra recorded in a previous study.
\(^b\) Corresponds to the spectra recorded in the current study.
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* The Raman spectrum was recorded in a glass NMR tube at –110 °C. b Signals observed at 292(37) and 1316(43) cm<sup>−1</sup> in the Raman spectrum of [SF<sub>3</sub>(Phen)][SbF<sub>6</sub>]·2CH<sub>2</sub>Cl<sub>2</sub> are overlapped with FEP signals. c Signals from the FEP sample tube were observed at 388(20), 733(71), 1215(18), 1383(23) cm<sup>−1</sup>. d 1,10-phenanthroline bands have been assigned based on references 24-25. e [SF<sub>3</sub>][SbF<sub>6</sub>] bands have been assigned based on references 2c. Signals from unreacted [SF<sub>3</sub>][SbF<sub>6</sub>] were obtained at 926(23), 939(37) and 955(20) cm<sup>−1</sup>.
4.2.4.3 Raman spectroscopy of \([\text{SF}_3(\text{CH}_3\text{CN})_2][\text{MF}_6]\) (M = Sb, As) salts

The Raman spectra for the \([\text{SF}_3(\text{CH}_3\text{CN})_2][\text{MF}_6]\) (M = Sb, As) salts are shown in Figure 4.10 along with the Raman spectrum of \(\text{CH}_3\text{CN}\). The vibrational frequencies of \([\text{SF}_3(\text{CH}_3\text{CN})_2][\text{SbF}_6]\) and \([\text{SF}_3(\text{CH}_3\text{CN})_2][\text{AsF}_6]\) are listed in Table 4.18 and 4.19, respectively. After adduct formation between \([\text{SF}_3][\text{MF}_6]\) (M = Sb, As) and \(\text{CH}_3\text{CN}\), diagnostic shifts of vibrational bands in the S–F stretching region of \(\text{SF}_3^+\) cation and of the C–N stretching mode of \(\text{CH}_3\text{CN}\) are expected. The most intense band in the S–F stretching region of the \([\text{SF}_3(\text{CH}_3\text{CN})_2][\text{MF}_6]\) in the Raman spectra appears at 900 cm\(^{-1}\) and can be assigned to \(\nu_s(\text{SF}_3)\) mode. This frequency is significantly lower than that of \([\text{SF}_3][\text{MF}_6]\) (M = As: 945 cm\(^{-1}\), M = Sb: 939 cm\(^{-1}\)). In addition to this band a number of other bands appear in this region. The band at 927 (\([\text{SF}_3(\text{CH}_3\text{CN})_2][\text{SbF}_6]\) / 926 (\([\text{SF}_3(\text{CH}_3\text{CN})_2][\text{AsF}_6]\)) has been tentatively assigned to the \(\nu(\text{C-C})\) mode of adducted \(\text{CH}_3\text{CN}\). A factor group analysis table (Table 4.17) was constructed for the \(\text{SF}_3^+\) group in \([\text{SF}_3(\text{CH}_3\text{CN})_2][\text{SbF}_6]\) to predict splitting of \(\text{SF}_3^+\) vibrational bands because of the solid-state structure. The analysis predicts two Raman active components for \(\nu_1\) and \(\nu_2\) while four components are expected for \(\nu_3\) and \(\nu_4\) in the Raman spectra of \([\text{SF}_3(\text{CH}_3\text{CN})_2][\text{SbF}_6]\). The large number of vibrational bands in the S–F stretching (besides the band at 900 cm\(^{-1}\)) likely arise from factor group splitting of \(\nu_s(\text{SF}_3)\) mode and the asymmetric \(\text{SF}_3\) stretching modes with their respective splitting. The Raman spectrum was recorded repeating the same reaction twice to verify that all the bands belong to \([\text{SF}_3(\text{CH}_3\text{CN})_2][\text{SbF}_6]\).
Table 4.17 Factor group analysis table for SF$_3$ group in [SF$_3$(CH$_3$CN)$_2$][SbF$_6$]

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<th>Crystal symmetry</th>
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<td></td>
</tr>
<tr>
<td>4T, 4v$_1$, 4v$_2$</td>
<td>A$_1$</td>
<td>A'</td>
</tr>
<tr>
<td></td>
<td></td>
<td>A''</td>
</tr>
<tr>
<td>C$_s$</td>
<td>A$_{1g}$</td>
<td>v$_1$, v$_2$, v$_3$, v$_4$, R, 2T</td>
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<tr>
<td></td>
<td>B$_{1g}$</td>
<td>v$_3$, v$_4$, 2R, T</td>
</tr>
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<td></td>
<td>B$_{2g}$</td>
<td>v$_1$, v$_2$, v$_3$, v$_4$, R, 2T</td>
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<td>B$_{1u}$</td>
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<td>B$_{3u}$</td>
<td>v$_1$, v$_2$, v$_3$, v$_4$, R, 2T</td>
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</table>

$\Gamma_{\text{vib}} = 2A_1 + 2E$

The Raman frequency of the v$_s$(SF$_3$) of [SF$_3$(CH$_3$CN)$_2$][MF$_6$] (M = Sb, As) salts is much larger compared to those in [SF$_3$(C$_5$H$_5$N)$_2$][MF$_6$]·C$_5$H$_5$N (M = Sb, As) salts because of lesser donor strength of CH$_3$CN compared to C$_5$H$_5$N. This comparison is also reflected in terms of the differences in the S–F bond lengths (Table 4.5). The C–N stretching mode of CH$_3$CN shifts from 2248 (neat CH$_3$CN) to 2271 cm$^{-1}$ for [SF$_3$(CH$_3$CN)$_2$][SbF$_6$] salt while to 2266 cm$^{-1}$ for [SF$_3$(CH$_3$CN)$_2$][AsF$_6$] salt. This is even a smaller complexation shift than that observed in the weakly coordinated WSF$_4$·CH$_3$CN complex (2286 cm$^{-1}$).$^{28}$ The Raman stretching frequencies for SbF$_6^-$ and AsF$_6^-$ shift slightly from 647 to 650 cm$^{-1}$ for SbF$_6^-$ and 680 to 683 cm$^{-1}$ for AsF$_6^-$ . The C–H stretch gets shifted by 10 cm$^{-1}$ to 2946 cm$^{-1}$ for [SF$_3$(CH$_3$CN)$_2$][SbF$_6$] salt while to 2955 cm$^{-1}$ for [SF$_3$(CH$_3$CN)$_2$][AsF$_6$] salt as compared to 2936 cm$^{-1}$ in free CH$_3$CN. This 10 cm$^{-1}$ shift is the same as has been observed for weakly coordinated WSF$_4$·CH$_3$CN adduct.$^{18}$
Figure 4.10 Raman spectrum of [SF$_3$][SbF$_6$], [SF$_3$(CH$_3$CN)$_2$][SbF$_6$], 
[SF$_3$(CH$_3$CN)$_2$][AsF$_6$] salts and CH$_3$CN at −110 °C. Asterisks (*) denote bands arising 
from the FEP sample tube.
Table 4.18 Raman frequencies (relative intensities), cm\(^{-1}\) of \([\text{SF}_3][\text{SbF}_6]\), CH\(_3\)CN and 
\([\text{SF}_3(\text{CH}_3\text{CN})_2][\text{SbF}_6]\) at \(-110\,^\circ\text{C}\) together with their tentative assignments.

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<th>Vibrational frequencies</th>
<th>Assignments</th>
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<td>389(14)</td>
<td>385(19)(^f)</td>
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\(^a\) The Raman spectrum was recorded in a glass NMR tube at \(-110\,^\circ\text{C}.\) \(^b\) Signals observed at 385(19) and 1377(17) cm\(^{-1}\) in the Raman spectrum of \([\text{SF}_3(\text{CH}_3\text{CN})_2][\text{SbF}_6]\) are overlapped with FEP signals. \(^c\) Signals from the FEP sample tube were observed at 733(15), 1215(1), 1305(1) cm\(^{-1}\). \(^d\) Acetonitrile bands have been assigned based on references 26. \(^e\) \([\text{SF}_3][\text{SbF}_6]\) bands have been assigned based on references 2c.
Table 4.19 Raman frequencies (relative intensities), cm\(^{-1}\) of [SF\(_3\)][AsF\(_6\)], CH\(_3\)CN and [SF\(_3\)(CH\(_3\)CN)\(_2\)][AsF\(_6\)] at \(-110\ °C\) together with their tentative assignments.

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\(^a\) The Raman spectrum was recorded in a glass NMR tube at \(-110\ °C\). \(^b\) Signals observed at 385(19) and 1381(16) cm\(^{-1}\) in the Raman spectrum of [SF\(_3\)(CH\(_3\)CN)\(_2\)][AsF\(_6\)] are overlapped with FEP signals. \(^c\) Signals from the FEP sample tube were observed at 733(37), 1215(7), 1305(11) cm\(^{-1}\). \(^d\) Acetonitrile bands have been assigned based on references 26. \(^e\) [SF\(_3\)][AsF\(_6\)] bands have been assigned based on references 2c.
**4.2.4.4 Raman spectroscopy of [SF$_2$(DMAP)$_2$][SbF$_6$]$_2$·CH$_3$CN**

The vibrational frequencies of [SF$_2$(DMAP)$_2$][SbF$_6$]$_2$·CH$_3$CN are listed in Table 4.20 and the Raman spectrum is shown in Figure 4.11. In the case of [SF$_2$(DMAP)$_2$][SbF$_6$]$_2$·CH$_3$CN, the S–F stretch is at 922 cm$^{-1}$, at a higher frequency in comparison to that of the [SF$_3$(Nitrogen-base)$_2$]$^+$ salts. This is the result of increased positive ionic charge of this fluorosulfur cation. The DMAP breathing C$_5$N mode is at 1016 cm$^{-1}$. This mode has been shifted from 998 to 1009 cm$^{-1}$ in the case of SF$_4$·DMAP adduct.$^3$ Signals attributable to CH$_3$CN were also observed. The C–N stretching mode appears at the same place as was found in uncomplexed CH$_3$CN, i.e., at 2248 cm$^{-1}$ indicating the presence of free CH$_3$CN. The Sb–F stretching frequency for SbF$_6^-$ shifts from 650 to 646 cm$^{-1}$ indicating a very weak interaction between [SF$_2$(DMAP)$_2$]$^{2+}$ cation and SbF$_6^-$ anion.
Figure 4.11 Raman spectrum of [SF$_3$][SbF$_6$], [SF$_2$(DMAP)$_2$][SbF$_6$]·CH$_3$CN and DMAP solids at –110 °C. Asterisks (*) denote bands arising from the FEP sample tube.
Table 4.20 Raman frequencies (relative intensities), cm\(^{-1}\) of [SF\(_3\)][SbF\(_6\)], DMAP and [SF\(_2\)(DMAP)\(_2\)][SbF\(_6\)]\(_2\)∙CH\(_3\)CN at −110 °C together with their tentative assignments.

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<td>δ(SbF₆)</td>
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<td>δ(SbF₆)</td>
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<td>481(11)</td>
<td>δ(sciss(SF₃))</td>
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<td>529(13)</td>
<td>δ(SF₃)</td>
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<tr>
<td>263(3)</td>
<td>δ(SbF₆)</td>
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<td>286(22)</td>
<td>δ(SbF₆)</td>
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<td>256(12)</td>
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* The Raman spectrum was recorded in a glass NMR tube at −110 °C. ** Signal observed at 382(25) cm⁻¹ in the Raman spectrum of [SF₃(DMAP)₂][SbF₆]₂·CH₃CN is overlapped with FEP signals. *** Signals from the FEP sample tube were observed at 294(16), 733(48), 1307(6), 1382(10) cm⁻¹. **DMAP bands have been assigned based on references 27. **[SF₃][SbF₆] bands have been assigned based on references 2c.
Table 4.21 Comparison of S–F stretching vibrational frequency

<table>
<thead>
<tr>
<th>Compounds</th>
<th>S–F stretching frequency, $\nu$ (cm$^{-1}$)</th>
</tr>
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<tbody>
<tr>
<td>$\gamma$-[SF$_3$][SbF$_6$]</td>
<td>939</td>
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<tr>
<td>[SF$_3$][AsF$_6$]</td>
<td>945</td>
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<tr>
<td>[SF$_3$(Py)$_2$][SbF$_6$]·CH$_2$Cl$_2$/$[$SF$_3$(Py)$_2$][AsF$_6$]·CH$_2$Cl$_2$</td>
<td>816/818</td>
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<tr>
<td>[SF$_3$(Py)$_2$][SbF$_6$]·CH$_3$CN</td>
<td>808, 828</td>
</tr>
<tr>
<td>[SF$_3$(Py)$_2$][SbF$_6$]·C$_5$H$_5$N/$[$SF$_3$(Py)$_2$][AsF$_6$]·C$_5$H$_5$N</td>
<td>815/812</td>
</tr>
<tr>
<td>[SF$_3$(CH$_3$CN)$_2$][SbF$_6$]/[$SF_3$(CH$_3$CN)$_2$][AsF$_6$]</td>
<td>900/900</td>
</tr>
<tr>
<td>[SF$_3$(Phen)][SbF$_6$]·2CH$_2$Cl$_2$</td>
<td>832</td>
</tr>
<tr>
<td>[SF$_2$(DMAP)$_2$][SbF$_6$]$_2$·CH$_3$CN</td>
<td>922</td>
</tr>
</tbody>
</table>

A comparison of S–F stretching vibrational frequencies of different fluorosulfur cationic species is presented in Table 4.21. The S–F stretching frequency for [SF$_3$][SbF$_6$] is present at 939 cm$^{-1}$. In the case of [SF$_3$(C$_5$H$_5$N)$_2$][SbF$_6$]·CH$_2$Cl$_2$, [SF$_3$(C$_5$H$_5$N)$_2$][SbF$_6$]·CH$_3$CN and [SF$_3$(C$_5$H$_5$N)$_2$][SbF$_6$]·C$_5$H$_5$N, the S–F stretch is shifted to 816, 808 and 815 cm$^{-1}$. The decrease in stretching frequency is a consequence of the weakening of the S–F bonds in the trifluorosulfur cationic species. This is also supported by the fact that the S–F bond lengths has been increased when SF$_3^+$ has formed adducts with nitrogen bases (Table 4.5).

Similar shifts in Raman frequencies have been observed for [SF$_3$(C$_5$H$_5$N)$_2$][AsF$_6$]·CH$_2$Cl$_2$ (818 cm$^{-1}$) and [SF$_3$(C$_5$H$_5$N)$_2$][AsF$_6$]·C$_5$H$_5$N (812 cm$^{-1}$) as compared to [SF$_3$][AsF$_6$] (945 cm$^{-1}$) for the same reason. In case of [SF$_3$(Phen)][SbF$_6$]·2CH$_2$Cl$_2$ the Raman signal for the symmetric SF$_3$ stretch has been shifted to 832 cm$^{-1}$ as compared to 939 cm$^{-1}$ in $\gamma$-[SF$_3$][SbF$_6$]. However, in the case of [SF$_3$(CH$_3$CN)$_2$][MF$_6$] where M = Sb, As, the S–F stretch is at 900 cm$^{-1}$. The difference in the SF$_3$ stretching frequency is directly related to the donor strengths of different nitrogen bases (Table 4.5). The higher the donor strength of the nitrogen base, the shorter the S–N distance, the longer the S–F distance and lower the value of the Raman frequency. In case of [SF$_2$(DMAP)$_2$][SbF$_6$]$_2$·CH$_3$CN, the value of
the Raman frequency is high i.e. 922 cm\(^{-1}\) although DMAP is a stronger base. This is due to an increase in the positive charge on fluorosulfur species from +1 to +2.

4.2.5 \(^{19}\)F NMR spectroscopy

4.2.5.1 \(^{19}\)F NMR spectroscopy of \([\text{SF}_3(\text{C}_5\text{H}_5\text{N})_2][\text{MF}_6]\cdot\text{C}_5\text{H}_5\text{N} \ (M = \text{Sb, As}), [\text{SF}_3(\text{CH}_3\text{CN})_2][\text{MF}_6] \ (M = \text{Sb, As}), \) and \([\text{SF}_3(\text{phen})][\text{SbF}_6]\cdot2\text{CH}_2\text{Cl}_2\)

The \(^{19}\)F NMR chemical shifts for \([\text{SF}_3][\text{SbF}_6]\) and \([\text{SF}_3][\text{AsF}_6]\) salts show a marked solvent dependence in solution. The \(^{19}\)F NMR chemical shifts for \([\text{SF}_3][\text{SbF}_6]\) and \([\text{SF}_3][\text{AsF}_6]\) salts in pyridine, acetonitrile and \(\text{SO}_2\) solvents are tabulated in Table 4.22. Dissolving the \([\text{SF}_3][\text{MF}_6]\) (M = Sb, As) salts in a nitrogen-base solvents such as \(\text{C}_5\text{H}_5\text{N}\) or \(\text{CH}_3\text{CN}\) results in low frequency \(^{19}\)F chemical shifts between 18.5 and 16.8 ppm in comparison to the values for \([\text{SF}_3][\text{MF}_6]\) (M = Sb, As) salts in \(\text{SO}_2(I)\) (31.5, 32.9 ppm), which is an inert solvent for \([\text{SF}_3][\text{MF}_6]\) (M = Sb, As) salts. Donation of the electron lone pair from nitrogen bases to the \(\text{SF}_3^+\) cation renders the S–F bond more ionic by increasing the electron density on sulfur, predicting increased shielding of the fluorine environments. Fast exchange between axial and equatorial fluorine environments result in the observation of only one \(^{19}\)F resonance (except for \([\text{SF}_3(\text{phen})][\text{SbF}_6]\cdot2\text{CH}_2\text{Cl}_2\)), even at temperatures as low as \(–40 \degree\text{C} \).
Table 4.22 $^{19}$F NMR chemical shifts (δ) of ionic species in different [SF$_3$]$^+$ and [SF$_2$]$^{2+}$ salts with different nitrogen bases at –30 °C

<table>
<thead>
<tr>
<th>Compound</th>
<th>Solvent</th>
<th>Chemical Shift (ppm, δ [SF$_3$]$^+$)</th>
<th>$^2J$(F–F) (Hz)</th>
<th>Chemical Shift (δ, ppm [MF$_6$]$^-$ (M = Sb, As))</th>
<th>$^1J$(F–M) (Hz) ($^3$M = $^{121}$Sb/$^{123}$Sb/$^{75}$As)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[SF$_3$][SbF$_6$]</td>
<td>SO$_2$(l)</td>
<td>31.5 (s)</td>
<td>–</td>
<td>–109.5</td>
<td>–</td>
</tr>
<tr>
<td>[SF$_3$][AsF$_6$]</td>
<td>SO$_2$(l)</td>
<td>32.9 (s)</td>
<td>–</td>
<td>–58.5</td>
<td>–</td>
</tr>
<tr>
<td>[SF$_3$(C$_5$H$_5$N)$_2$]</td>
<td>C$_5$H$_5$N</td>
<td>18.5 (s)</td>
<td>–</td>
<td>–121.3</td>
<td>Overlap</td>
</tr>
<tr>
<td>[SbF$_6$]:C$_5$H$_5$N</td>
<td>C$_5$H$_5$N</td>
<td>18.5 (s)</td>
<td>–</td>
<td>–64.4</td>
<td>930</td>
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<tr>
<td>[SF$_3$(C$_5$H$_5$N)$_2$]</td>
<td>CH$_3$CN</td>
<td>16.8 (s)</td>
<td>–</td>
<td>–123.3</td>
<td>Overlap</td>
</tr>
<tr>
<td>[SbF$_6$]</td>
<td>CH$_3$CN</td>
<td>18.8 (s)</td>
<td>–</td>
<td>–64.8</td>
<td>933</td>
</tr>
<tr>
<td>[SF$_3$(CH$_2$CN)$_2$]</td>
<td>CH$_3$CN</td>
<td>16.8 (s)</td>
<td>6.8</td>
<td>–116.7</td>
<td>1950/1013</td>
</tr>
<tr>
<td>[AsF$_6$]</td>
<td>CH$_3$CN</td>
<td>18.8 (s)</td>
<td></td>
<td>–</td>
<td>1946/930</td>
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<tr>
<td>[SF$_3$(Phen)]</td>
<td>CH$_2$Cl$_2$</td>
<td>27.3 ($d$), 60.3 ($t$)</td>
<td>6.8</td>
<td>–116.7</td>
<td>1950/1013</td>
</tr>
<tr>
<td>[SbF$_6$]:CH$_2$Cl$_2$</td>
<td>CH$_3$CN</td>
<td>52.6 (s)</td>
<td>–</td>
<td>–123.0</td>
<td>1946/930</td>
</tr>
</tbody>
</table>

Figure 4.12 Solution-state $^{19}$F NMR spectrum of (a) [SF$_3$(C$_5$H$_5$N)$_2$][AsF$_6$] and (b) [SF$_3$(C$_5$H$_5$N)$_2$][SbF$_6$] in liquid C$_5$H$_5$N at –30 °C.
The exchange generally results in relatively sharp $^{19}$F cation resonances. The $^{19}$F NMR spectrum of [SF$_3$(CH$_3$CN)$_2$][AsF$_6$] is the exception where a broad singlet is observed at 18.8 ppm ($\Delta\nu_{1/2} = 912$ Hz). This broadening is a result of slowing down the exchange between the cation fluorine environments likely as a consequence of strong cation anion contacts. The AsF$_6^-$ is somewhat more fluorobasic than SbF$_6^-$ and the sulfur in [SF$_3$(CH$_3$CN)$_2$]$^+$ is more electrophilic than in [SF$_3$(C$_5$H$_5$N)$_2$]$^+$. Therefore, the cation-anion interactions are the most severe in the [SF$_3$(CH$_3$CN)$_2$][AsF$_6$] among the salts in this chapter. For all adduct salts, coupling of $^{19}$F with the quadrupolar nuclei $^{75}$As and $^{121}$Sb/$^{123}$Sb were observed.

![Figure 4.13 Solution-state $^{19}$F NMR spectrum of (a) [SF$_3$(CH$_3$CN)$_2$][AsF$_6$] and (b) [SF$_3$(CH$_3$CN)$_2$][SbF$_6$] in liquid CH$_3$CN at –30 °C.](image)
The dissociation of the nitrogen-base from the $[\text{SF}_3(\text{Nitrogen-base})_2]^+$ adduct with subsequent rapid exchange with the nitrogen base solvent is hypothesized to be the mechanism of exchange of the axial and equatorial fluorine environments. This mechanism would go via a trigonal bipyramidal electron group geometry, which can scramble the axial and equatorial fluorine environments via the Berry pseudo rotation. The use of the chelating ligand 1,10-phenanthroline was expected to increase the kinetic stability of the adduct between $\text{SF}_3^+$ cation and the nitrogen base. The $^{19}\text{F}$ NMR spectrum of $[\text{SF}_3(\text{Phen})][\text{SbF}_6]$ salt in CH$_3$CN solvent gave rise to resonances at 22.7 and 56.1 ppm in a 2:1 ratio for the equatorial and axial fluorine environments, respectively, at $–35$ °C while in CH$_2$Cl$_2$ solvent the resonances are at 27.3 and 60.3 ppm for the equatorial and axial fluorine at $–40$ °C, respectively. In CH$_2$Cl$_2$ solvent, coupling was revealed. The axial fluorine is a triplet and the equatorial fluorine a doublet with a $^2$$\text{J}(^{19}\text{F}–^{19}\text{F})$ coupling constant of 6.8 Hz in CH$_2$Cl$_2$ solvent. Production of SF$_4$ may be the result of residual moisture in CH$_2$Cl$_2$ because no SF$_4$ signal was observed in well dried CH$_3$CN solvent (Figure 4.14). A two-dimensional $^{19}\text{F}–^{19}\text{F}$ magnitude COSY experiment clearly showed a correlation between the resonances at 27.3 and 60.3 ppm of $[\text{SF}_3(\text{Phen})]^+$ in the form of cross peaks. Furthermore, the same sign of the $^2$$\text{J}(^{19}\text{F}–^{19}\text{F})$ coupling constant for $[\text{SF}_3(\text{Phen})]^+$ and SF$_4$ was confirmed by 2D $^{19}\text{F}–^{19}\text{F}$ COSY45 experiment (Figure 4.16). The high resolution in the COSY45 showed the same leaning behaviour of the doublet and triplet for $[\text{SF}_3(\text{Phen})]^+$ in correspondence with the leaning behaviour of the two triplets for SF$_4$. This behaviour prove the same sign of $^2$$\text{J}(^{19}\text{F}–^{19}\text{F})$ coupling for $[\text{SF}_3(\text{Phen})]^+$ and SF$_4$. The $^{19}\text{F}$ signal for SbF$_6^-$ is at $–123.3$ ppm in the form of a broad pattern because of fast relaxation of the quadrupolar $^{121,123}\text{Sb}$ nuclei.
Figure 4.14 (a) Solution-state $^{19}\text{F}$ NMR spectrum of 1:1 ratio of $\left[\text{SF}_3\right]\left[\text{SbF}_6\right]$ and 1,10-phenanthroline in liquid CH$_3$CN at –35 °C (b) in liquid CH$_2$Cl$_2$ at –40 °C. The production of SF$_4$ in (b) is a result of the presence of moisture in CH$_2$Cl$_2$. 
Figure 4.15 Solution-state $^{19}\text{F}$$-^{19}\text{F}$ COSY NMR spectrum of 1:1 ratio of [SF$_3$][SbF$_6$] and 1,10-phenanthroline in liquid CH$_2$Cl$_2$ at $-40$ °C.

Figure 4.16 Solution-state $^{19}\text{F}$$-^{19}\text{F}$ COSY45 NMR spectrum of 1:1 ratio of [SF$_3$][SbF$_6$] and 1,10-phenanthroline in liquid CH$_2$Cl$_2$ at $-40$ °C.
4.2.5.2 $^{19}$F NMR spectroscopy of [SF$_2$(DMAP)$_2$][SbF$_6$]$_2$·CH$_3$CN

The $^{19}$F NMR chemical shift for the [SF$_2$(DMAP)$_2$]$^{2+}$ cation, as the product of the reaction of [SF$_3$][SbF$_6$] salt with DMAP in a 1:1 ratio in CH$_3$CN, is a singlet at 52.6 ppm due to the presence of only one fluorine environment. The chemical shift for this fluorosulfur (IV) cation has moved to higher frequency due to an increase in the positive ionic charge, i.e. +2, in comparison to the [SF$_3$(C$_5$H$_5$N)$_2$]$^+$ cation, which results in less polar S–F bonding. The SbF$_6^-$ anion signal is at –123.0 ppm with the values for $^1J$(Sb–$^{19}$F) and $^1J$(Sb–$^{19}$F) 1946 and 930 Hz as obtained by deconvolution, in agreement with the literature. The stoichiometry of the dismutation reaction (Eq 4) was confirmed by integrating the resonance at 52.6 ppm with respect to the two triplet resonances for SF$_4$ at 32.8 and 84.2 ppm. The integration shows 0.98:1.06:1.00 ratio for the resonances at 32.8, 52.6 and 84.2 ppm confirming the equimolar ratio of [SF$_2$(DMAP)$_2$]$^{2+}$ and SF$_4$.

Figure 4.17 Solution-state $^{19}$F NMR spectrum of 1:1 ratio of [SF$_3$][SbF$_6$] and 4-dimethylamino pyridine (DMAP) in liquid CH$_3$CN at –30 °C.
4.3 Conclusion and future directions

A series of adducts between [SF$_3$][MF$_6$] (M = Sb, As) and nitrogen bases was studied and conclusively characterized. The 1:2 adducts using C$_5$H$_5$N and CH$_3$CN were found to be stable at low temperature. For the bidentate ligand 1,10-phenanthroline, a 1:1 adduct was obtained. The synthesis and conclusive characterization of [SF$_3$(N-base)][MF$_6$] (M = Sb, As) is still pending. The reactions of the [SF$_3$(N-base)$_x$]$^+$ cation with highly Lewis acidic materials such as AsF$_5$ and SbF$_5$ can be studied to synthesize [SF$_2$(N-base)$_x$]$^{2+}$ compounds.

In the future, the nitrogen bases can be replaced with oxygen bases to study [SF$_3$(O-base)][MF$_6$] and [SF$_3$(O-base)$_2$][MF$_6$] (M = Sb, As) compounds to better understand the reactive intermediate species in the deoxofluorination reactions of carbonyl compounds.
References


Chapter-5

5. Synthesis and characterization of WOF₄SO₂, [(CH₃)₄N][WO₅], and CH₃CN·WOF₃(OCH₂CF₃)

5.1 Introduction

Tungsten oxytetrafluoride, WOF₄, is a moderately strong Lewis acid and can accept electrons from weak as well as strong nitrogen bases such as CH₃CN and C₅H₅N. The adducts of WOF₄ with C₅H₅N, i.e. WOF₄·nC₅H₅N (n = 1, 2) show characteristic W=O stretching frequencies of 996 cm⁻¹ (WOF₄·C₅H₅N) and 969 cm⁻¹ (WOF₄·2C₅H₅N) in the Raman spectra compared to 1056 cm⁻¹ for WOF₄. The ¹⁹F chemical shift of these adducts (63.9 ppm for WOF₄·C₅H₅N with ¹J(W-¹⁹F) of 67 Hz; 63.6 ppm for WOF₄·2C₅H₅N with ¹J(W-¹⁹F) of 67 Hz) appear at lower frequency compared to that of WOF₄ (70.5 ppm) in CH₂Cl₂ solvent.¹ ² X-ray crystallography showed the octahedral geometry of WOF₄·C₅H₅N and pentagonal bipyramidal geometry of WOF₄·2C₅H₅N.¹ ² The adduct formation of WOF₄ with CH₃CN was identified solely based on the ¹⁹F NMR spectroscopy results where a change in the chemical shift was observed for WOF₄ upon addition of one equivalent of CH₃CN from 69.0 ppm to 66.9 ppm with ¹J(W-¹⁹F) of 68 Hz using chloroform as solvent.¹⁰ The Lewis acidity of WOF₄ is also reflected by its tetrameric fluorine bridged structure in the solid state and in CH₂Cl₂ solvent.¹ The tetramer gets converted to monomeric WOF₄·CH₃CN in CH₃CN solvent. Furthermore, WOF₄ was found to be soluble in liquid SO₂. The observation of a narrow singlet at −73.9 ppm with ¹J(W-¹⁹F) coupling constant of 64 Hz at 28 °C suggests the monomeric nature of WOF₄ in SO₂.

Due to the Lewis acidic nature of WOF₄, F⁻ ion addition to WOF₄ results in the formation of WOF₅⁻ salts. The known WOF₅⁻ compounds are summarized in Table 5.1 with their characterization methods.
Table 5.1 Known WOF$_5^-$ compounds and their characterization techniques

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<tr>
<th>WOF$_5^-$ salts</th>
<th>Vibrational spectroscopy</th>
<th>NMR spectroscopy</th>
<th>X-ray diffractometry</th>
<th>Elemental analysis (EA)</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>[NO][WO$_F_5$]</td>
<td>Raman</td>
<td>Solution $^{19}$F NMR</td>
<td>Powder X-ray Diffraction</td>
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<td>[NF$_4$][WO$_F_5$]</td>
<td>IR &amp; Raman</td>
<td>Solution $^{19}$F NMR</td>
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<tr>
<td>[EMIM][WO$_F_5$]$^a$</td>
<td>IR &amp; Raman</td>
<td></td>
<td></td>
<td>EA</td>
<td>5</td>
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<tr>
<td>[As(Ph)$_4$][WO$_F_5$]</td>
<td></td>
<td>X-ray crystallography</td>
<td>(Disordered structure)</td>
<td>EA</td>
<td>8</td>
</tr>
</tbody>
</table>

$^a$ [EMIM] is 1-ethyl 3-methylimidazolium cation

WOF$_5^-$ salts have been prepared in several ways. For example, Hagiwara et al. reported the synthesis of the WOF$_5^-$ salt of 1-ethyl 3-methyl imidazolium (EMIM), i.e. [EMIM][WO$_F_5$], by the reaction of [EMIM][(HF)$_2$3F] with WOF$_4$ and characterized it by Raman spectroscopy.$^5$ Similarly, Wilson and Christe synthesized [NF$_4$][WO$_F_5$] by the reaction of [NF$_4$][HF$_2$] with WOF$_4$ in the presence of HF and characterized it by IR, Raman and solution $^{19}$F NMR spectroscopy.$^6$ Charpin et al. synthesized [NO][WO$_F_5$] by the decomposition of [NO]$_2$[WO$_F_6$], which was synthesized by the reaction of FNO and WOF$_4$, and characterized [NO][WO$_F_5$] by Raman and NMR spectroscopy, as well as by powder X-ray diffraction.$^7$ However, the only X-ray crystal structure known thus far for WOF$_5^-$ salt is of tetraphenylarsonium oxo-pentafluoro-tungstenate ([As(Ph)$_4$][WO$_F_5$]) which exhibits a 50:50% disorder between oxygen and the axial fluorine on tungsten$^8$ and therefore no ordered structure of the WOF$_5^-$ with accurate metric parameters is known prior to this work to clearly predicting the accurate distances to axial oxygen and fluorine. The [As(Ph)$_4$][WO$_F_5$] salt was synthesized by stirring 3.38 mmol of [As(Ph)$_4$][Cl$_5$W≡N–CCl$_3$]
with 24 mmol of AgF in 30 ml of CH$_3$CN and 0.06 g of water.\textsuperscript{6} A $^{19}$F and $^{129}$Xe solution NMR study showed that WOF$_4$ and XeF$_2$ form an adduct.\textsuperscript{9} A doublet for the terminal fluorine atoms on W and a quintet for the bridging fluorine atom was observed in the $^{19}$F solution NMR spectrum. $^{19}$F solution NMR spectroscopy data of the known WOF$_5^-$ systems and FXeFWOF$_4$ adduct are summarized in Table 5.2.

<table>
<thead>
<tr>
<th>WOF$_5^-$ salts</th>
<th>Solvent system</th>
<th>Temperature ($^\circ$C)</th>
<th>$^19$F (ppm)</th>
<th>$^2J^{(19F-19F)}$</th>
<th>$^1J^{(183W-19F)}$</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>[NO][WOF$_5$]</td>
<td>HF/ClF$_3$</td>
<td>10</td>
<td>+49.2, -145.7</td>
<td>57.5</td>
<td>70/55</td>
<td>7</td>
</tr>
<tr>
<td>[WOF$_5$]$^-$</td>
<td>HF/WOCl$_4$</td>
<td>RT</td>
<td>53.7, -104.0</td>
<td>55</td>
<td>72</td>
<td>3</td>
</tr>
<tr>
<td>XeF$_2$·WOF$_4$</td>
<td>SO$_2$ClF</td>
<td>-124</td>
<td>69.7, -166.8</td>
<td>55</td>
<td>-</td>
<td>18</td>
</tr>
<tr>
<td>KrF$_2$·WOF$_4$</td>
<td>SO$_2$ClF</td>
<td>-121</td>
<td>67.9, -26.1</td>
<td>48</td>
<td>-</td>
<td>18</td>
</tr>
<tr>
<td>[WOF$_5$]$^-$</td>
<td>CH$_3$CN</td>
<td>RT</td>
<td>48.4, -83.5</td>
<td>51.9</td>
<td>-</td>
<td>20</td>
</tr>
</tbody>
</table>

The value for the H–F bond dissociation enthalpy, (i.e., 568 kJ/mol at 25$^\circ$C) is among one of the highest known bond enthalpies. Thus, HF formation as the driving force has been utilized for substituting one or more fluorides from WF$_6$ with the $^-$OCH$_2$CF$_3$ nucleophilic ligand.\textsuperscript{10} F$_3$W(OCH$_2$CF$_3$) and cis-F$_4$W(OCH$_2$CF$_3$)$_2$ were prepared from WF$_6$ and CF$_3$CH$_2$OH in 1:1 and 1:2 stoichiometry and have been characterized by solution $^{19}$F NMR and Raman spectroscopy. cis-F$_4$W(OCH$_2$CF$_3$)$_2$ was also characterized by X-ray crystallography.\textsuperscript{10} A number of other substituents have been introduced in WF$_6$, i.e. the $^-OR$ groups with R = $^-CH_3$, $^-C_2H_5$ and $^-C_6H_5$.\textsuperscript{11,12,13,14} Instead of utilizing the alcohol, Noble and Winfield synthesized monosubstituted F$_5$W(OR) (R = $^-CH_3$, $^-C_2H_5$ and $^-C_6H_5$)
compounds by the reaction of WF$_6$ with dialkyl and diaryl sulphites.\textsuperscript{13} They were also able to obtain a series WF$_{6-n}$(OR)$_n$ ($R = \text{CH}_3, \text{C}_2\text{H}_5, \text{C}_6\text{H}_5$) to a maximum of four substituted fluorine atoms ($n = 4$) by reacting WF$_6$ with methylalkoxy and methylphenoxy silanes.\textsuperscript{11} They also obtained WF$_4$(OCH$_3$)$_2$ by the reaction of WF$_5$(OCH$_3$) with [(CH$_3$O)$_2$SO]. All of the WF$_6$ derivatives were identified by $^{19}$F NMR spectroscopy.

5.2 Results and discussion

5.2.1 Synthesis and properties of WOF$_4$SO$_2$, [(CH$_3$)$_4$N][WOF$_5$], and CH$_3$CN·WOF$_3$(OCH$_2$CF$_3$)

5.2.1.1 Synthesis and properties of WOF$_4$SO$_2$

The WOF$_4$SO$_2$ adduct was synthesized by the reaction of WOF$_4$ with excess SO$_2$ at low-temperature ($-30^\circ$C) according to the reaction equation 5.1. The resultant WOF$_4$SO$_2$ adduct is a white solid which is highly soluble in SO$_2$. Reaction (1) is reversible and neat WOF$_4$ was recovered after pumping off SO$_2$ to ambient temperature.

\[
\text{WOF}_4 + \text{SO}_2 \xleftrightarrow{-30 \, ^\circ \text{C}} \text{WOF}_4\text{SO}_2 \]

The $^{19}$F solution NMR spectroscopy of WOF$_4$ was performed using excess SO$_2$ as solvent at $-60^\circ$C. A single fluorine resonance at 74.9 ppm with tungsten satellites ($^1J(\text{W}^{183}-^{19}\text{F}) = 65.4$ Hz) was observed due to equivalent fluorine environments about tungsten. This signal compares well with the literature value (73.9 ppm).\textsuperscript{4}

5.2.1.2 Synthesis and properties of [(CH$_3$)$_4$N][WOF$_5$]

Tetramethylammonium oxypentafluorotungstate, [(CH$_3$)$_4$N][WOF$_5$], was synthesized by reacting a 1:1 molar ratio of [(CH$_3$)$_4$N][F] and WOF$_4$ at $-30$ °C in CH$_3$CN solvent and subsequently removing CH$_3$CN under dynamic vacuum as well as allowing the resultant
white solid to warm up to room temperature. The [(CH$_3$)$_4$N][WOF$_5$] salt is highly soluble in CH$_3$CN.

\[
\text{[(CH$_3$)$_4$N][F] + WOF}_4 \xrightarrow{-30 \, ^\circ\text{C}} \text{[(CH$_3$)$_4$N][WOF}_5]\]

The $^{19}$F NMR spectrum of [(CH$_3$)$_4$N][WOF$_5$] was recorded in CH$_3$CN solvent (Table 5.2). The $^{19}$F NMR spectrum using CH$_3$CN solvent shows a doublet at 48.2 ppm for the four equivalent equatorial fluorine atoms and a quintet at –82.8 ppm for axial fluorine (Figure 5.1). The observed $^2J(^{19}\text{F}\cdots{^{19}\text{F}})$ and $^1J(^{183}\text{W}\cdots{^{19}\text{F}})$ are in agreement with the literature value obtained for WOF$_5^–$ anion. The observed solvent dependence (see Table 5.2 and 5.3) of the chemical shift corresponding to the axial fluorine indicates strong F$_{ax}$--solvent interactions if solvents such as HF are used.

<table>
<thead>
<tr>
<th>Chemical shift (ppm)</th>
<th>Species</th>
<th>Solvent</th>
<th>Scalar-coupling($J$) (Hz)</th>
<th>Assignment(s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>48.2</td>
<td>F$_{eq}$</td>
<td>CH$_3$CN</td>
<td>52.1/71.5</td>
<td>$^2J(^{19}\text{F}\cdots{^{19}\text{F}})/^1J(^{183}\text{W}\cdots{^{19}\text{F}}_{eq})$</td>
</tr>
<tr>
<td>–82.8</td>
<td>F$_{ax}$</td>
<td>CH$_3$CN</td>
<td>52.1/52.7</td>
<td>$^2J(^{19}\text{F}\cdots{^{19}\text{F}})/^1J(^{183}\text{W}\cdots{^{19}\text{F}}_{ax})$</td>
</tr>
</tbody>
</table>

Figure 5.1. $^{19}$F NMR spectrum of [N(CH$_3$)$_4$][WOF$_5$] in CH$_3$CN solvent
Comparing the $^{19}$F chemical shifts of the four equatorial fluorine atoms in WOF$_4$ adducts, the trend of decreasing $^{19}$F chemical shifts with increasing donor strength of the Lewis base is observed (WOF$_4$·SO$_2$: 74.9 ppm, WOF$_4$·C$_5$H$_5$N: 63.9 ppm$^4$, WOF$_4$·F$^-$: 48.2 ppm).

5.2.1.3 Synthesis and properties of CH$_3$CN·WOF$_3$(OCH$_2$CF$_3$)

Tungsten oxytetrafluoride, WOF$_4$, was reacted with excess CF$_3$CH$_2$OH at ambient temperature in the absence of a solvent. Exclusively, the monosubstituted W(O)F$_2$(OCH$_2$CF$_3$), a colorless translucent liquid at room temperature, was obtained and characterized by Raman and $^{19}$F solution NMR spectroscopy. The state of matter of the related F$_5$W(OCH$_2$CF$_3$) has also been found to be liquid at room temperature.$^{10}$

$$\text{WOF}_4 + \text{CF}_3\text{CH}_2\text{OH} \rightarrow \text{W(O)F}_3(\text{OCH}_2\text{CF}_3) + \text{HF} \quad \text{.................................}(5.3)$$

The $^{19}$F solution NMR spectroscopy indicated the formation of W(O)F$_3$(OCH$_2$CF$_3$). The $^{19}$F solution NMR spectrum of W(O)F$_3$(OCH$_2$CF$_3$) was recorded using excess CF$_3$CH$_2$OH as solvent and is shown in Figure 5.3. The chemical shifts and the coupling constants are given in Table 5.4. The $^{19}$F AX$_2$ NMR spectrum comprises a doublet at 22.3 ppm with a $^2J(^{19}$F–$^{19}$F) coupling of 79.2 Hz and with tungsten satellites ($^1J(^{183}$W–$^{19}$F) = 72.6 Hz) for the two equivalent cis-fluorine and a triplet at 15.6 ppm with tungsten satellites ($^1J(^{183}$W–$^{19}$F) = 49.6 Hz) for one trans-fluorine. The $^{19}$F NMR spectrum is in agreement with a monomeric square pyramidal structure (Fig. 5.2). The size of the $^1J(^{183}$W–$^{19}$F) value is in agreement with the literature value obtained for mono substituted WF$_6$ products and for WOF$_5^-$ anion.$^8$
Figure 5.2 Wedge and dash diagram of $\text{W(O)F}_3(\text{OCH}_2\text{CF}_3)$

Figure 5.3 $^{19}\text{F}$ NMR spectrum of $\text{W(O)F}_3(\text{OCH}_2\text{CF}_3)$, *represents impurities

Table 5.4 $^{19}\text{F}$ chemical shifts for $\text{W(O)F}_3(\text{OCH}_2\text{CF}_3)$

<table>
<thead>
<tr>
<th>Chemical shift (ppm)$^a$</th>
<th>Species</th>
<th>Scalar-coupling($J$) (Hz)</th>
<th>Assignment(s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>22.3(d)</td>
<td>$^{19}\text{F}_{\text{cis}}$</td>
<td>79.2/72.6</td>
<td>$^2J( ^{19}\text{F}-^{19}\text{F})/^1J( ^{183}\text{W}-^{19}\text{F}_{\text{cis}})$</td>
</tr>
<tr>
<td>15.6(t)</td>
<td>$^{19}\text{F}_{\text{trans}}$</td>
<td>79.2/49.6</td>
<td>$^2J( ^{19}\text{F}-^{19}\text{F})/^1J( ^{183}\text{W}-^{19}\text{F}_{\text{trans}})$</td>
</tr>
<tr>
<td>-77.1(t)</td>
<td>$-\text{CF}_3$</td>
<td>7.8</td>
<td>$^3J( ^{1}\text{H}-^{19}\text{F})$</td>
</tr>
</tbody>
</table>

$^a$ d-doublet, t-triplet
Reacting W(O)F₃(OCH₂CF₃) with excess CH₃CN at ambient temperature yielded the CH₃CN·WOF₃(OCH₂CF₃) adduct. The resultant adduct is a white solid and is soluble in CH₂Cl₂, from which the crystals of CH₃CN·W(O)F₃(OCH₂CF₃) were grown.

\[ \text{W(O)F}_{3}(\text{OCH}_{2}\text{CF}_{3}) + \text{CH}_{3}\text{CN} \rightarrow \text{CH}_{3}\text{CN} \cdot \text{W(O)F}_{3}(\text{OCH}_{2}\text{CF}_{3}) \]

5.2.2 X-ray crystallography

5.2.2.1 X-ray crystallography of WOF₄SO₂

Crystals of WOF₄·SO₂ were grown from SO₂ at low temperature (−70 °C). WOF₄·SO₂ crystallizes in monoclinic space group \(P2_1/c\) with four formula units per unit cell (Table 5.5). The structural unit of WOF₄·SO₂ crystal structure is shown in Figure 5.4 while the bond lengths and bond angles are given in Table 5.6. In the crystal structure of WOF₄·SO₂ adduct, the SO₂ molecule is joined to WOF₄ with a weak coordinate W···O bond. The WOF₄·SO₂ adduct has a six coordinate W center with four fluorine atoms in the equatorial plane and the two oxygen atoms on the axial position, one strong covalent W1–O1 bond with a bond length of 1.658(5) Å, and a weak co-ordinate W1–O2 bond with a bond length of 2.381(5) Å. The O1–W1–O2 angle is essentially linear (179.2(2)°). The W–F bond lengths in WOF₄·SO₂ range from 1.841(4) to 1.859(4) Å. A meaningful comparison of bond lengths and angles with those of WOF₄ (determined in 1968 at ambient temperature) and WOF₄·C₅H₅N (determined in 1988 at 22 °C) is not possible because of the large uncertainties in the metric parameters of these two structures. The monomeric structure of WOF₄·SO₂ indicates the monomerization of the (WOF₄)₄ tetramer upon dissolution in SO₂.
Figure 5.4 Thermal ellipsoid plot of the structural unit of WOF₄SO₂ in the crystal structure of WOF₄SO₂ at 50% probability level.

Table 5.5 Crystallographic data for WOF₄SO₂, CH₃CN·WO₅(OCH₂CF₃) and [(CH₃)₄N][WO₅]

<table>
<thead>
<tr>
<th>Chemical formula</th>
<th>WOF₄SO₂</th>
<th>[(CH₃)₄N][WO₅]</th>
<th>CH₃CN·WO₅(OCH₂CF₃)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Crystal system</td>
<td>Monoclinic</td>
<td>Tetragonal</td>
<td>Monoclinic</td>
</tr>
<tr>
<td>Space group</td>
<td>P₂₁/c</td>
<td>P₄/n</td>
<td>P₂₁/c</td>
</tr>
<tr>
<td>a (Å)</td>
<td>7.7097(15)</td>
<td>8.205(3)</td>
<td>8.1236(12)</td>
</tr>
<tr>
<td>b (Å)</td>
<td>7.2274(14)</td>
<td>8.205(3)</td>
<td>12.7219(19)</td>
</tr>
<tr>
<td>c (Å)</td>
<td>10.244(2)</td>
<td>6.989(2)</td>
<td>8.9834(13)</td>
</tr>
<tr>
<td>α (°)</td>
<td>90</td>
<td>90</td>
<td>90</td>
</tr>
<tr>
<td>β (°)</td>
<td>90.530(2)</td>
<td>90</td>
<td>97.386(2)</td>
</tr>
<tr>
<td>γ (°)</td>
<td>90</td>
<td>90</td>
<td>90</td>
</tr>
<tr>
<td>Z</td>
<td>4</td>
<td>2</td>
<td>4</td>
</tr>
<tr>
<td>Formula weight (g mol⁻¹)</td>
<td>339.91</td>
<td>369.00</td>
<td>396.94</td>
</tr>
<tr>
<td>Calcd density (g cm⁻³)</td>
<td>3.956</td>
<td>2.604</td>
<td>2.864</td>
</tr>
<tr>
<td>T (°C)</td>
<td>−120</td>
<td>−120</td>
<td>−120</td>
</tr>
<tr>
<td>μ (mm⁻¹)</td>
<td>20.629</td>
<td>12.311</td>
<td>12.618</td>
</tr>
<tr>
<td>R₁⁺</td>
<td>0.0310</td>
<td>0.0209</td>
<td>0.0325</td>
</tr>
<tr>
<td>wR₂⁺</td>
<td>0.0479</td>
<td>0.0391</td>
<td>0.0646</td>
</tr>
</tbody>
</table>

* R₁ is defined as Σ||Fₒ| − |Fₑ||Σ|Fₒ| for I > 2σ(I). b wR₂ is defined as [Σ[w(Fₒ² − Fₑ²)²]/Σw(Fₒ²)²]½ for I > 2σ(I).
Table 5.6 Bond lengths (Å) and bond angles (°) of WOF₄SO₂ adduct

<table>
<thead>
<tr>
<th>Bond lengths (Å)</th>
<th>Bond angles (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>W1-O1 1.658(5)</td>
<td>O1-W1-F1 100.2(2)</td>
</tr>
<tr>
<td>W1-O2 2.381(5)</td>
<td>O1-W1-F2 101.2(2)</td>
</tr>
<tr>
<td>W1-F1 1.859(4)</td>
<td>O1-W1-F3 100.6(2)</td>
</tr>
<tr>
<td>W1-F2 1.841(4)</td>
<td>O1-W1-O2 179.2(2)</td>
</tr>
<tr>
<td>W1-F3 1.842(4)</td>
<td>F1-W1-F2 158.58(18)</td>
</tr>
<tr>
<td>W1-F4 1.855(4)</td>
<td>F1-W1-F3 87.65(18)</td>
</tr>
<tr>
<td>S1-O2 1.446(5)</td>
<td>F2-W1-F3 89.52(17)</td>
</tr>
<tr>
<td>S1-O3 1.410(5)</td>
<td>F2-W1-F4 88.12(18)</td>
</tr>
<tr>
<td></td>
<td>F3-W1-F4 157.99(18)</td>
</tr>
<tr>
<td></td>
<td>F1-W1-O2 79.30(17)</td>
</tr>
<tr>
<td></td>
<td>F2-W1-O2 79.30(17)</td>
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<tr>
<td></td>
<td>F3-W1-O2 79.99(17)</td>
</tr>
<tr>
<td></td>
<td>F4-W1-O2 78.07(17)</td>
</tr>
<tr>
<td></td>
<td>S1-O2-W1 141.3(3)</td>
</tr>
<tr>
<td></td>
<td>O3-S1-O2 117.6(3)</td>
</tr>
</tbody>
</table>

5.2.2.2 X-ray crystallography of [(CH₃)₄N][WOF₅]

Crystals of [(CH₃)₄N][WOF₅] were grown from anhydrous HF at low temperature (~70 °C). [(CH₃)₄N][WOF₅] crystallizes in the tetragonal space group P4/n with two formula units per unit cell (Table 5.4). The structural unit of [(CH₃)₄N][WOF₅] crystal is shown in Figure 5.5 while the bond lengths and bond angles are given in Table 5.7. The WOF₅⁻ is a distorted octahedron with the axial W–F bond (1.943(6) Å), which is trans to the W–O bond, being longer than the crystallographically equivalent equatorial W–F bonds (1.859(3) Å). This elongation is a consequence of the trans influence of the W–O bond that has significant double bond character (W1–O1 = 1.675(8) Å).
The O1–W1–F2 angle in the [WOF₅]⁻ anion is 180.0°. The W1–O1 bond length (1.675(8) Å) is longer than the W1–O1 bond length (1.658(5) Å) found in WOF₄·SO₂ (section 5.3.1) reflecting the higher Lewis basicity of naked F⁻ versus SO₂. The equatorial W–F bond lengths (1.859(3) Å) are comparable to those in [(Ph)₄As][WOF₅] (1.852(7) Å)⁸ and WOF₄·SO₂ (1.841(4) to 1.859(4) Å). The average of the W–F2 and W=O bond lengths in [(CH₃)₄N][WOF₅] (1.809 Å) is comparable to the average bond length of 1.822(13) Å for [(Ph)₄As][WOF₅], which exhibits a 50:50% disorder between these axial atoms. The O1–W1–F2 angle (180.0°) in [WOF₅]⁻ anion of [(CH₃)₄N][WOF₅] is perfectly linear and is comparable to the O–W–F1 angle in [(Ph)₄As][WOF₅] (180.0°)⁷ and O1–W–O2 angle in WOF₄·SO₂ (179.2(2)°) in section 5.2.2.1.
### Table 5.7 Bond lengths (Å) and Bond angles (°) in [(CH$_3$)$_4$N][WO$_F$$_5$]

<table>
<thead>
<tr>
<th>Bond lengths (Å)</th>
<th>Bond angles (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>W1-O1</td>
<td>1.675(8)</td>
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<tr>
<td>W1-F1</td>
<td>1.859(3)</td>
</tr>
<tr>
<td>W1-F1</td>
<td>1.859(3)</td>
</tr>
<tr>
<td>W1-F1</td>
<td>1.859(3)</td>
</tr>
<tr>
<td>W1-F1</td>
<td>1.859(3)</td>
</tr>
<tr>
<td>W1-F2</td>
<td>1.943(6)</td>
</tr>
<tr>
<td>N1-C1</td>
<td>1.496(4)</td>
</tr>
<tr>
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</tr>
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</table>

### 5.2.2.3 X-ray crystallography of CH$_3$CN-WOF$_3$(OCH$_2$CF$_3$)

Crystals of CH$_3$CN-WOF$_3$(OCH$_2$CF$_3$) were grown using CH$_2$Cl$_2$ solvent. The CH$_3$CN-WOF$_3$(OCH$_2$CF$_3$) crystallizes in monoclinic space group $P2_1/c$ with four formula units per unit cell (Table 5.4). The structural unit of the CH$_3$CN-WOF$_3$(OCH$_2$CF$_3$) crystal structure is shown in Figure 5.6 while the bond lengths and bond angles are given in Table 5.8. The WOF$_3$(OCH$_2$CF$_3$) moiety adopts a square pyramidal geometry as predicted by $^{19}$F NMR spectroscopy for WOF$_3$(OCH$_2$CF$_3$) (Figure 5.2) with F1,F2, F3 and O2 atoms in the equatorial plane about tungsten while O1 in the axial position. The CH$_3$CN molecule coordinates trans to the W=O bond with an almost linear O1–W1–N1 angle (178.7(2)°),
expanding the coordination number of tungsten to six. The W1–O1 bond length (1.686(2) Å) is the same size as that for [(CH₃)₄N][WOF₅] (1.675(8) Å). The equatorial W–F bond lengths in CH₃CN·WOF₃(OCH₂CF₃) (1.860(9) to 1.871(4) Å) are the same within 3σ as those in WOF₅⁻ anion.

Figure 5.6 Thermal ellipsoid plot of the structural unit of CH₃CN·WOF₃(OCH₂CF₃) in the X–ray structure of CH₃CN·WOF₃(OCH₂CF₃)
Table 5.8 Bond lengths (Å) and bond angles (°) for CH$_3$CN·WOF$_3$(OCH$_2$CF$_3$)

<table>
<thead>
<tr>
<th>Bond lengths (Å)</th>
<th>Bond angles (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>W1-O1</td>
<td>1.686(5)</td>
</tr>
<tr>
<td>W1-O2</td>
<td>1.844(5)</td>
</tr>
<tr>
<td>W1-F1</td>
<td>1.871(4)</td>
</tr>
<tr>
<td>W1-F2</td>
<td>1.863(4)</td>
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<td>W1-F3</td>
<td>1.860(4)</td>
</tr>
<tr>
<td>W1-N1</td>
<td>2.343(6)</td>
</tr>
<tr>
<td>C1-F4</td>
<td>1.325(9)</td>
</tr>
<tr>
<td>C1-F5</td>
<td>1.315(9)</td>
</tr>
<tr>
<td>C1-F6</td>
<td>1.326(9)</td>
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<tr>
<td>C1-C2</td>
<td>1.464(10)</td>
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<tr>
<td>C3-C4</td>
<td>1.447(10)</td>
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<tr>
<td>N1-C3</td>
<td>1.130(8)</td>
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<tr>
<td>C2-O2</td>
<td>1.397(8)</td>
</tr>
<tr>
<td>O1-W1-O2</td>
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</tr>
<tr>
<td>O1-W1-N1</td>
<td>178.7(2)</td>
</tr>
<tr>
<td>O1-W1-F1</td>
<td>99.1(2)</td>
</tr>
<tr>
<td>O1-W1-F2</td>
<td>99.2(2)</td>
</tr>
<tr>
<td>O1-W1-F3</td>
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<td>O2-W1-F1</td>
<td>90.9(2)</td>
</tr>
<tr>
<td>O2-W1-F2</td>
<td>162.2(2)</td>
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<tr>
<td>O2-W1-F3</td>
<td>91.6(2)</td>
</tr>
<tr>
<td>F1-W1-F2</td>
<td>84.9(2)</td>
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<td>161.1(2)</td>
</tr>
<tr>
<td>F2-W1-F3</td>
<td>86.9(2)</td>
</tr>
</tbody>
</table>

5.2.3 Raman spectroscopy

5.2.3.1 Raman spectroscopy of WOF$_4$SO$_2$ adduct

The Raman spectrum of WOF$_4$SO$_2$ together with that of solid WOF$_4$, i.e. (WOF$_4$)$_4$, is shown in Figure 5.7 and the Raman frequencies are listed in Table 5.10. After the adduct formation of WOF$_4$ with SO$_2$, the W=O stretch shifts from 1057 to 1041 cm$^{-1}$. Based on the crystal structure of WOF$_4$SO$_2$, a factor group analysis was performed for WOF$_4$ (Table 5.9). The factor group splitting of this mode into two Raman-active components was predicted and observed (1041 and 1048 cm$^{-1}$). This shift reflects a weakening of the axial W=O bond length in WOF$_4$SO$_2$ adduct. Similarly, the frequency of the symmetric WF$_4$ stretch shifts from 726 to 701/711 cm$^{-1}$. The splitting of this band into two Raman active components is predicted by the factor group analysis. The WF$_4$ asymmetrical stretching mode is predicted to split into four bands in the Raman spectrum, but only two bands are resolved (660 to 645 cm$^{-1}$). Solid SO$_2$ shows the asymmetric stretching frequency at 1351 cm$^{-1}$.
and 1341 cm$^{-1}$, symmetric stretch with a split at 1148 and 1144 cm$^{-1}$, and the bending mode at 523 and 537 cm$^{-1}$. After adduct formation, the SO$_2$ stretching frequencies appear at lower frequency ($\nu_s$(SO$_2$): 1142/1136 cm$^{-1}$ and $\nu_{as}$(SO$_2$): 1126 cm$^{-1}$) while the bending mode is shifted to higher frequency (534 cm$^{-1}$).

Figure 5.7. Raman spectra of (a) WOF$_4$ and (b) WOF$_4$·SO$_2$ adduct recorded in FEP reactor at −110 °C. '•' denotes the FEP signals and '+' denotes the SO$_2$ bands.

Table 5.9 Factor group analysis table for WOF$_4$ in WOF$_4$·SO$_2$

<table>
<thead>
<tr>
<th>Local symmetry</th>
<th>Site symmetry</th>
<th>Factor group symmetry</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C_{4v}$</td>
<td>$C_1$</td>
<td>$C_{2h}$</td>
</tr>
<tr>
<td>$4\nu_1, 4\nu_2, 4\nu_3$</td>
<td>$A_1$</td>
<td>$A_g$ $\nu_1, \nu_2, \nu_3, \nu_4, \nu_5, \nu_6, 2\nu_7, 2\nu_8, 2\nu_9$ Raman</td>
</tr>
<tr>
<td></td>
<td>$A_2$</td>
<td>$B_g$ $\nu_1, \nu_2, \nu_3, \nu_4, \nu_5, \nu_6, 2\nu_7, 2\nu_8, 2\nu_9$ Raman</td>
</tr>
<tr>
<td>$4\nu_4, 4\nu_5$</td>
<td>$B_1$</td>
<td>$A_u$ $\nu_1, \nu_2, \nu_3, \nu_4, \nu_5, \nu_6, 2\nu_7, 2\nu_8, 2\nu_9$ IR</td>
</tr>
<tr>
<td>$4\nu_6$</td>
<td>$B_2$</td>
<td>$B_u$ $\nu_1, \nu_2, \nu_3, \nu_4, \nu_5, \nu_6, 2\nu_7, 2\nu_8, 2\nu_9$ IR</td>
</tr>
<tr>
<td>$4\nu_7, 4\nu_8, 4\nu_9$</td>
<td>$E$</td>
<td></td>
</tr>
</tbody>
</table>
Table 5.10 Raman frequencies (relative intensities), cm$^{-1}$ of WOF$_4$, SO$_2$ and WOF$_4$SO$_2$ at –110 °C together with their assignments.

<table>
<thead>
<tr>
<th>Vibrational frequencies</th>
<th>Assignments</th>
</tr>
</thead>
<tbody>
<tr>
<td>SO$_2^a$</td>
<td>(WOF$_4$)$_b$</td>
</tr>
<tr>
<td>1351(3)</td>
<td>1326(24)</td>
</tr>
<tr>
<td>1340(4)</td>
<td></td>
</tr>
<tr>
<td>1148(100)</td>
<td>1142(63)</td>
</tr>
<tr>
<td>1144(69)</td>
<td>1136(54)</td>
</tr>
<tr>
<td>1057(100)</td>
<td>1048(27)</td>
</tr>
<tr>
<td>743(14)</td>
<td>711(9)</td>
</tr>
<tr>
<td>726(51)</td>
<td>701(43)</td>
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<td>704(1)</td>
<td>660(5)</td>
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<td>660(7)</td>
<td>608(5)</td>
</tr>
<tr>
<td>561(1)</td>
<td>578(2)</td>
</tr>
<tr>
<td>539(2)</td>
<td>518(3)</td>
</tr>
<tr>
<td>523(10)</td>
<td>534(4)</td>
</tr>
<tr>
<td>329(18)</td>
<td>316(21)</td>
</tr>
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<td>317(30)</td>
<td>312(27)</td>
</tr>
<tr>
<td>312(34)</td>
<td>294(8)</td>
</tr>
<tr>
<td>263(1)</td>
<td>246(5)</td>
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<tr>
<td>240(4)</td>
<td>224(3)</td>
</tr>
<tr>
<td>216(6)</td>
<td>205(7)</td>
</tr>
<tr>
<td>120(8)</td>
<td>123(6)</td>
</tr>
</tbody>
</table>

$^a$ Crystalline SO$_2$ assignment has been done at –78 °C in reference 9.$^{b,c}$ The Raman spectrum were recorded in a ¼–in FEP reactor at –110 °C. Signals from the FEP sample tube were observed at 294(8), 386(9), 733(29), 751(7), 1216(6), 1309(7), 1383(9) cm$^{-1}$. WOF$_4$ bands have been assigned based on references 7, 16, 17 and 18. Unreacted (WOF$_4$)$_4$ bands appeared at 1056(7) and 727(10) cm$^{-1}$.

5.2.3.2 Raman spectroscopy of [(CH$_3$)$_4$N][WO$_5$F$_3$]

The Raman spectrum of [(CH$_3$)$_4$N][WO$_5$F$_3$] is shown in Figure 5.8 and the Raman frequencies for [(CH$_3$)$_4$N][WO$_5$F$_3$] are tabulated in Table 5.11. The W=O stretching frequency for [(CH$_3$)$_4$N][WO$_5$F$_3$] is 985 cm$^{-1}$. This is in agreement with the literature value.
of W=O stretching frequency of WOF$_5^-$ anion in [EMIM][WOF$_5$]$^7$ (982 cm$^{-1}$) and [NF$_4$][WOF$_3$]$^{3,15}$ (996 cm$^{-1}$). This represents a dramatic decrease in W=O stretching frequency compared to WOF$_4$ (1056 cm$^{-1}$).$^{16}$ The adduct of WOF$_4$ with the much weaker Lewis base SO$_2$ results in a much smaller change in the $\nu_8$(W=O) frequency (1041 cm$^{-1}$). The equatorial WF$_4$ stretching bands appear at 681 and 587 cm$^{-1}$ in the Raman spectrum. This is in agreement what has been observed for [NO][WOF$_5$]$^7$ (684 cm$^{-1}$ for equatorial fluorine and 591 cm$^{-1}$ for axial fluorine) and [NF$_4$][WOF$_5$] (690 cm$^{-1}$ for equatorial fluorine and 613 cm$^{-1}$ for axial fluorine).$^{3,15}$ The WOF$_4$ bending frequency appears at 323 cm$^{-1}$. For [NO][WOF$_5$]$^6$, this frequency is 327 cm$^{-1}$ while for [NF$_4$][WOF$_5$] is 329 cm$^{-1}$.$^{3,15}$

![Raman spectra](image)

Figure 5.8. Raman spectra of (a) WOF$_4$ and (b) [(CH$_3$)$_4$N][WOF$_5$] in glass melting point capillaries at ambient temperature. [(CH$_3$)$_4$N]$^+$ bands also appear at 3041, 2992, 2964, 2818, 1466, 1417, 1174, 948, 753, and 374 cm$^{-1}$ in [(CH$_3$)$_4$N][WOF$_5$].
Table 5.11. Raman spectroscopic data for \([\text{N(CH}_3\text{)}_4][\text{WOF}_5]\) at ambient temperature

<table>
<thead>
<tr>
<th>Vibrational frequencies</th>
<th>Assignments</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>(WOF(_4))(_4^a)</strong></td>
<td><strong>[WOF(_5^-)]</strong></td>
</tr>
<tr>
<td>Frequencies in [EMIM][WOF(_5)](^b)</td>
<td>Frequencies in [EMIM][WOF(_5)]</td>
</tr>
<tr>
<td>1056(100)</td>
<td>985(100)</td>
</tr>
<tr>
<td>742(14)</td>
<td>681(57)</td>
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<td>726(51)</td>
<td>670(1)</td>
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<tr>
<td>661(7)</td>
<td>521(3)</td>
</tr>
<tr>
<td>329(68)</td>
<td>323(38)</td>
</tr>
</tbody>
</table>

\(^a\) WOF\(_4\) is a tetramer in solid state. \(^b\) [(CH\(_3\))\(_4\)]\(^+\) bands also appear at 3041, 2992, 2964, 2818, 1466, 1174, 948, 753, and 374 cm\(^{-1}\) in [(CH\(_3\))\(_4\)][WOF\(_5\)].
5.2.3.3 Raman spectroscopy of CH$_3$CN·WOF$_3$(OCH$_2$CF$_3$)

The Raman spectra for solid WOF$_4$, W(O)F$_3$(OCH$_2$CF$_3$) and CH$_3$CN·WOF$_3$(OCH$_2$CF$_3$) are shown in Figure 5.9 and the Raman frequencies are given in Table 5.12. For W(O)F$_3$(OCH$_2$CF$_3$), with a square pyramidal geometry, there is a significant difference in the W=O stretching frequency to that of solid WOF$_4$ ($\nu_s$(W=O) 1028 cm$^{-1}$ for W(O)F$_3$(OCH$_2$CF$_3$); $\nu_s$(W=O) 1056 cm$^{-1}$ for WOF$_4$). The $\nu_s$(WF$_2$-cis) symmetrical stretching bands appear at 701 and 711 cm$^{-1}$ in W(O)F$_3$(OCH$_2$CF$_3$), as compared to the WF$_4$ symmetrical stretching in neat WOF$_4$ (726 cm$^{-1}$). The W=O stretching frequency is further shifted to 1001 cm$^{-1}$ upon coordination of CH$_3$CN trans to the W=O bond. This shift (1001 cm$^{-1}$) towards lower frequency in W=O stretch of CH$_3$CN·W(O)F$_3$(OCH$_2$CF$_3$) is a consequence of donation of electron density from CH$_3$CN to W, resulting in a more ionic W–O bond. The WF$_2$ stretching mode for CH$_3$CN·WOF$_3$(OCH$_2$CF$_3$) (659 cm$^{-1}$) is also shifted to lower frequency upon CH$_3$CN coordination. For W(O)F$_3$(OCH$_2$CF$_3$), the CH$_2$ stretching and bending modes are between 2964 to 3013 cm$^{-1}$ and 1174 to 1444 cm$^{-1}$, respectively. These ranges have been shifted to 2953 to 3005 cm$^{-1}$ and 1129 to 1441 cm$^{-1}$ for stretching and bending modes in case of CH$_3$CN·WOF$_3$(OCH$_2$CF$_3$), respectively.
Figure 5.9 Comparison of the Raman spectra of WOF₄, W(O)F₃(OCH₂CF₃) and CH₃CN·WOF₃(OCH₂CF₃) at ambient temperature.

"*" denotes the FEP bands.
Table 5.12 Raman frequencies (relative intensities), cm$^{-1}$ of WOF$_4$, W(O)F$_3$(OCH$_2$CF$_3$) and CH$_3$CN-WOF$_3$(OCH$_2$CF$_3$) at room temperature together with their assignments.

<table>
<thead>
<tr>
<th>Vibrational frequencies</th>
<th>Assignments</th>
</tr>
</thead>
<tbody>
<tr>
<td>(WOF$_4$)$_4$</td>
<td>CH$_3$CN</td>
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<tr>
<td>2999(52)</td>
<td>3013(11)</td>
</tr>
<tr>
<td>2996(11)</td>
<td>2996(34)</td>
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<td>2936(90)</td>
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<td>2817(3)</td>
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<td>2732(5)</td>
<td>2341(3)</td>
</tr>
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<td>2293(4)</td>
<td>1444(14)</td>
</tr>
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<td>2248(100)</td>
<td>1400(2)</td>
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<td>240(4)</td>
<td>240(4)</td>
</tr>
</tbody>
</table>

*The Raman spectrum was recorded in a glass melting point capillary at ambient temperature. *b The Raman spectrum was recorded in a ¼–in FEP tube. Signals from the FEP sample tube were observed at 291(11), 386(20), 733(100), 1285(17), 1379(17) cm$^{-1}$. *c The Raman spectrum was recorded in a glass melting point capillary at ambient temperature. *d WOF$_4$ bands have been assigned based on references 7, 16, 17 and 18. CH$_3$CN bands have been assigned based on references 21.
5.3 Conclusion

For the first time, the WOF₄ SO₂ adduct was identified in the solid state and conclusively characterized by X-ray crystallography and Raman spectroscopy. The identification of this SO₂ solvate in the solid state suggests its presence in SO₂ solution.

There has been a lack of a high-quality X-ray structure of WOF₅⁻ salts in literature and the only crystal structure known to date is [As(Ph)₄][WO₅]. The crystal structure of [As(Ph)₄][WO₅] possess a 50:50% disorder between axial oxygen and fluorine on tungsten. The first X-ray structure of WOF₅⁻ in the form of [(CH₃)₄N][WO₅] salt without any disorder and more accurate metric parameters has been presented in the given chapter.

Attempts to derivatize WOF₄ with CF₃CH₂OH yielded only the mono-substituted WOF₃(OCH₂CF₃) compound which was identified by ¹⁹F NMR spectroscopy as a monomeric compound in CF₃CH₂OH solvent. The CH₃CN adduct of WOF₃(OCH₂CF₃), i.e. CH₃CN-WOF₃(OCH₂CF₃), was structurally characterized by X-ray crystallography.
References


Chapter-6

6. Structural characterization of perfluorocarboxylic acids and carboxylates of environmental concern

6.1 Introduction

Perfluoroorganocompounds are synthetic materials being used for many applications, e.g. the use of polytetrafluoroethylene in our daily life from greaseless screws to the non-stick black coating on the cookwares. Perfluorooctanoic acid (PFOA) and its salts are used as polymerization aid in the polymerization process of fluoropolymers.\(^1\) In spite of their usefulness, PFOA and its salts have posed environmental concern due to their non-biodegradability and bioaccumulative property in the environment.\(^2\) For example, researchers have linked exposure of 3-30 mg/l of PFOA and its salts, to inhibition of the thyroid hormone biosynthesis genes, birth defects (causes ovary degeneration in females), liver damage (ammonium salt of PFOA increased the weight of rat liver, and may induce peroxisomal fatty acid oxidation and impose oxidative stress through the alteration of cellular oxidative homeostasis in the liver), cancer (peroxisome proliferation is a key carcinogenic mechanism) and suppression of immunity (PFOA affects the lysozyme activity).\(^2\)

Important perfluoroalkanoic acids and their salts are perfluorooctanoic acid (PFOA), sodium perfluorooctanoate (SPFO), perfluorodecanoic acid (PFDA) and sodium perfluorobutyrate (SPFB).\(^3\,4\) Perfluorooctanoic acid, PFOA, is highly stable solid at 25 °C with a low vapor pressure of $1.65 \times 10^{-2}$ mm Hg (Screening Assessment Report, Health Canada, August 2012).\(^2\) Its vapor pressure increases close to its melting point (52–54 °C).\(^5\,6\) PFOA is readily soluble in CDCl$\textsubscript{3}$, D$_2$O and (CH$_3$)$_2$CO and 2,2,2-trifluoroethanol.
The sodium salt of perfluorooctanoic acid has been used as emulsifier to stabilize perfluorocarbon emulsions and is also one of the salt of environmental concern. It is a white powder having a melting point of 280 °C. This compound has been studied earlier in the form of inclusion complex with β-cyclodextrin using solid-state NMR techniques. Perfluorodecanoic acid (PFDA) is another member of long chain perfluoroalkanoic acid. It is a white powder having a melting point of 78 °C. Its usage includes as commercial wetting agent and flame retardant. Sodium perfluorobutyrate is white powder having melting point of 248 °C.

Perfluorinated materials are preferred over hydrocarbon analogues because of the higher surface activity in the stabilization of emulsions, e.g. the critical micelle concentration (cmc) of SPFO is 0.032 M as compared to 0.4 M of sodium octanoate. PFOA, SPFO, and SPFB have been studied by solution-state NMR spectroscopy, molecular orbital calculations, viscometry, differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), and powder X-ray diffraction as well as in the form of their inclusion complexes with other materials such as with β-cyclodextrin by solid-state NMR spectroscopy. Even after being so thoroughly studied, the solid-state information of these materials is limited because of the unavailability of exact structural parameters. To determine the exact dipolar coupling constant values between carbon and fluorine and between two fluorine atoms in space for solid-state NMR studies, it is necessary to have the X-ray characterization done for this compound. The single-crystal X-ray characterization of these perfluorinated materials has never been reported because of the difficulty associated with the crystallization of these materials. Here, we report the first X-ray crystallographic characterization for perfluorooctanoic acid (PFOA) as its hydrate PFOA·H₂O, sodium perfluorooctanoate (SPFO), perfluorodecanoic
acid (PFDA) as PFDA-H\textsubscript{2}O and sodium perfluorobutyrate (SPFB). Perfluorodecanoic acid (PFDA) was chosen in search for any sign of a different conformation of the long perfluoro chain in the perfluoroalkanoic acids. Because of today’s trend for using short chain perfluorocompounds as a replacement for the long chain ones, SPFB was chosen for the X-ray crystallography study.

6.2 X-ray crystal structure of perfluorooctanoic acid monohydrate (PFOA-H\textsubscript{2}O)

A sample of PFOA was used as received (Sigma-Aldrich), which was shown to contain H\textsubscript{2}O based on its infrared spectrum. Infrared spectroscopy on PFOA shows the presence of water by the observation of the broad O–H stretching bands at 3540 and 3464 cm\textsuperscript{-1}. Data obtained from thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) verifies the presence of water in the crystal lattice of PFOA. In the thermogravimetric analysis of PFOA, weight loss was observed at 100 °C due to the loss of water molecules associated with PFOA while in DSC measurement, the corresponding endothermic transition was observed at 110 °C reflecting the thermal phase transition.\textsuperscript{13}

![Infrared spectrum of perfluorooctanoic acid](image)

Figure 6.1 Infrared spectrum of perfluorooctanoic acid (a) complete spectrum (b) narrow range
Several attempts were made to grow crystals of PFOA from CH₂Cl₂, D₂O, and liquid SO₂ but these were unsuccessful. Crystals of PFOA·H₂O were obtained from its solution in 2,2,2-trifluoroethanol suggesting that PFOA usually exists in its monohydrated form as PFOA·H₂O. Efforts were made to get the anhydrous form of PFOA, instead of the monohydrate, by drying it completely under dynamic vacuum at 50 °C but water removal under vacuum remained unsuccessful since PFOA sublimed under dynamic vacuum above 50 °C. In the search for getting PFOA·nH₂O (n>1), crystal growth was attempted by dissolving PFOA·H₂O in excess D₂O, but crystals obtained from D₂O had the same unit cell as PFOA·H₂O as determined by X-ray crystallography. It should be noted that these crystals were of substantially poorer quality than grown from those CF₃CH₂OH.

PFOA·H₂O crystallizes in the monoclinic P2₁/c space group with four formula unit of PFOA·H₂O in the unit cell. The thermal ellipsoid plot of PFOA·H₂O is shown in Figure 6.2(a). The concise crystal data for PFOA·H₂O has been given in Table 6.1. The bond lengths and bond angles are given in Table 6.2.

Usually, carboxylic acids form hydrogen bonded dimers and crystallize without water molecules. In contrast, in PFOA·H₂O, water molecules were found between PFOA units in the crystal structure. Each water molecule is hydrogen bonded to two PFOA molecules resulting in a layered structure. The PFOA chains are aligned along the a-axis. The packing diagram of PFOA·H₂O (Figure 6.2b) shows two types of layers in the bc-plane of PFOA·H₂O. One is the fluorophilic layer generated by the regular arrangement of perfluoro chains and the other is the hydrophilic layer composed of the carboxylic acid groups and water. Such a layered structure was also observed for carboxylic acids (Fig 6.2c). The distance between the two opposite perfluoro chains (–CF₃ group to –CF₃ group) in the fluorophilic layer is 4.245(3) Å in perfluorooctanoic acid monohydrate while for
octanoic acid (Figure 6.2c) the distance between the two opposite alkyl chains (–CH$_3$ group to –CH$_3$ group) in the hydrophobic layer is 3.896(4) Å. The distance between two adjacent perfluorooctanoic molecules is 5.573(4) Å while the distance is 4.379(4) Å in case of octyl chains in octanoic acid. The reason being larger size and higher electronegativity of fluorine atom in comparison to hydrogen atom.

The three conformations found in hydrocarbons are syn, anti and gauche, of which the anti-configuration is the most stable conformation in hydrocarbon chains. But in the case of perfluorocarbons, a distorted anti conformation is preferred (Scheme-I) due to the electronic repulsion of fluorine atoms.$^{16}$ As a consequence, the perfluoro chains usually adopt a helical structure as observed for PFOA. The distorted anti conformation of the perfluoroctyl chain in PFOA·H$_2$O is in accordance with the results found on the basis of $^{19}$F–$^{19}$F COSY,$^{15}$ $^{19}$F–$^{19}$F NOESY NMR study,$^{15}$ AM-1 calculation which predict an anti conformation up to the perfluorocarbon chain length of eight.$^{15}$ The $^{19}$F solid-state study of PFOA on its inclusion complex with β-cyclodextrin demonstrated the acquisition of anti and gauche arrangements of PFOA in the complex with heating and cooling of the sample.$^{5}$
Table 6.1. Crystallographic data for perfluorooctanoic acid (PFOA) as PFOA·H$_2$O, perfluorodecanoic acid (PFDA) as PFDA·H$_2$O, sodium perfluorooctanoate (SPFO), and sodium perfluorobutyrate (SPFB)

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<td>b (Å)</td>
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$^a$ R$_1$ is defined as $\sum||F_o| - |F_c||/\sum|F_o|$ for $I > 2\sigma(I)$. $^b$ wR$_2$ is defined as $[\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$ for $I > 2\sigma(I)$.

(Scheme – I)
Two types of conformational Newman projections of perfluoro chains of PFOA (a) anti conformation (b) distorted anti conformation.
For the comparison of hydrogen bonding strength in the carboxylic acid monohydrates, the available structures in the literature were hydrated 4-bromo-6-oxotetrahydro-3H,8H-pyrano[3,4-d]pyrrolo[1,2-c][1,3]oxazole-8-carboxylic acid\textsuperscript{17} and hydrated 11-aminoundecanoic acid.\textsuperscript{18} The comparison with hydrated hydrogenated acid was done due to the lack of availability of the crystal structure hydrated perfluoroalkanoic acid in literature. The hydrogen bonding between the perfluorooctanoic acid and the water molecule is significantly stronger than in the two cited structures. The RO⋯O distance in PFOA·H\textsubscript{2}O is 2.503(2) Å, which is smaller than the RO⋯O distance of 2.794(3) Å found for 4-bromo-6-oxotetrahydro-3H,8H-pyrano[3,4-d]pyrrolo[1,2-c][1,3]oxazole-8-carboxylic acid monohydrate\textsuperscript{19} and 2.786(8) Å found for hydrated 11-aminoundecanoic acid.\textsuperscript{18} The carbon-fluorine bond lengths are in the expected range of 1.309(3) to 1.347(2) Å. The C–C–C bond angles vary from 113.10(15) to 115.06(17)° in the helical structure.
Figure 6.2 (a) Thermal ellipsoid plot of PFOA·H₂O at 50% probability level in the crystal structure of PFOA·H₂O (b) Arrangement of fluorophilic perfluoro chains having hydrophilic channel in PFOA·H₂O which includes water molecules between two perfluorooctanoic molecules and a distance of 4.245(3) Å between two opposite perfluoro chains and a distance of 5.573(4) Å (c) Arrangement of hydrophobic alkyl chains having hydrophilic channel octanoic acid. The distance between two opposite alkyl chains is 3.896(3) Å and the distance between two octanoic acid units is 4.379(4) Å (d) helical view of PFOA unit in PFOA·H₂O.
Table 6.2 Bond lengths and bond angles for PFOA·H₂O

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6.3 X-ray crystal structure of perfluorodecanoic acid monohydrate (PFDA·H₂O)

Attempts were made to grow the crystal of PFDA using CH₂Cl₂, D₂O, liquid SO₂, n-hexane, ethanol, isopropanol and n-butanol. Crystals of perfluorodecanoic acid (PFDA) were obtained only from its solution in n-butanol in its hydrated form as PFDA·H₂O. PFDA·H₂O crystallizes in the monoclinic P2₁/c space group with four formula unit of PFDA·H₂O in the unit cell. The thermal ellipsoid plot of PFDA·H₂O is shown in Figure 6.3(a). The concise crystal data for PFDA·H₂O has been given in Table 6.1. The bond lengths and bond angles are given in Table 6.3.
Figure 6.3 (a) Thermal ellipsoid plot of PFDA·H$_2$O at 50% probability level in the crystal structure of PFDA·H$_2$O (b) Arrangement of fluorophilic perfluoro chains having hydrophilic channel in PFDA·H$_2$O which includes water molecules between two perfluorooctanoic molecules and a distance of 4.801(8) Å between two opposite perfluoro chains and an interlayer distance of 5.935(7) Å (c) helical view of PFDA unit in PFDA·H$_2$O.

The –CF$_2$ groups, in perfluorodecanoic acid monohydrate, adopts a distorted anti conformation to form a helical structure just as they do in PFOA·H$_2$O. The C–F bond lengths in PFDA·H$_2$O range from 1.308(6) Å to 1.353(5) Å and the C–C–C bond angles range from 112.8(4) to 115.5(5)°. The C–F bond lengths and bond angles in PFDA·H$_2$O are similar to what have been found for PFOA·H$_2$O (1.309(3) to 1.342(2) Å). The water molecule is hydrogen bonded with two PFDA molecules resulted in a layered structure. Due to the hydrogen bonding between the water molecule and the perfluorodecanoic acid, the RO⋯O distance is 2.486(5) Å which is similar to what has been found in the case of
PFOA·H₂O (2.503(2) Å) but smaller than the RO···O distance of 2.794(3) Å found for 4-bromo-6-oxotetrahydro-3H,8H-pyrano [3,4-d] pyrrolo [1,2-c] [1,3] oxazole-8-carboxylic acid monohydrate and 2.786(8) Å found in case of the hydrated 11-aminoundecanoic acid.

In the packing diagram of PFDA·H₂O (Figure 6.3b) two layers, i.e. a fluorophilic and a hydrophilic layer, are observed. The distance between parallel perfluoro chains is 5.935(7) Å and the distance between the perfluoro chains (between the carbons of two consecutive –CF₃ groups) is 4.801(8) Å.

Table 6.3 Bond lengths (Å) and bond angles (°) for PFDA·H₂O

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6.4 X-ray crystal structure of sodium perfluorooctanoate (SPFO)

The crystal growth for SPFO was attempted from CH₂Cl₂, D₂O, 2,2,2-trifluoroethanol, methanol, and ethanol but the crystals suitable for X-ray diffraction of SPFO were obtained from its solution in ethanol. SPFO crystallizes in the monoclinic P2₁/c space group with four formula unit of SPFO in the unit cell. The thermal ellipsoid plot of SPFO is shown in Figure 6.4(a). The concise crystal data for SPFO has been given in Table 6.1. The bond lengths and bond angles are given in Table 6.4. The perfluoro chain of SPFO adopts the distorted anti conformation to form the helical structure in the same manner as they do in PFOA·H₂O. The C–F bond lengths in SPFO range from 1.311(9) Å to 1.359(8) Å while the bond angles range from 116.0(8) to 117.6(7)° in SPFO.

The RO···O distance found between two SPFO units is 3.570(9) Å, reflecting strong interactions between two SPFO units. Furthermore, the DSC and TGA measurements do not show any transition or weight loss around 100 °C, presenting support for the absence of water as observed in the crystal structure of SPFO.¹⁹

The packing diagram of SPFO (Figure 6.4b) shows two different types of layers, one is the fluorophilic layer and the other is hydrophilic. The distance between the fluorocarbon chains (from one carbon of the first chain to the parallel carbon of the second chain) is 5.65(1) Å and the distance between the perfluoro chains (between the carbons of two consecutive –CF₃ groups) is 4.82(2) Å.
Figure 6.4 (a) Thermal ellipsoid plot of SPFO at 50% probability level in the crystal structure of SPFO (b) Arrangement of the hydrophilic and fluorophilic layers in SPFO. Packing arrangement of SPFO in unit cell with a distance of 4.82(2) Å between two opposite perfluoro chains and an interlayer distance of 5.65(1) Å (c) helical view of perfluoro chain in SPFO.
Table 6.4 Bond lengths (Å) and bond angles (°) for SPFO

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6.5 X-ray crystal structure of sodium perfluorobutyrate (SPFB)

The crystals of SPFB were obtained from its solution in ethanol. SPFB crystallizes in the monoclinic $C2/c$ space group with eight formula unit of SPFB in the unit cell. The thermal ellipsoid plot of SPFB is shown in Figure 6.5 at 50% probability level. The concise crystal data for SPFO has been given in Table 6.1. The bond lengths and bond angles are given in Table 6.5.

Sodium perfluorobutyrate chains arrange themselves along $a$-axis in the unit cell. The usual distorted anti conformation is adopted by the perfluoro chains in the same manner.
as they do in SPFO. The C–F bond lengths in SPFB range from 1.312(6) Å to 1.370(5) Å and the C–C–C bond angles are 114.3(4) to 118.7(5)°. The C–F bond lengths in SPFB are similar to what have been found for SPFO (1.311(9) to 1.359(8) Å). Similarly, the bond angles are also similar to what were found for PFOA (116.0(8) to 117.6(7)°) in section 6.3.1. The RO···O distance between two SPFB molecule is 3.499(5) Å also similar to what has been found in the case of SPFO (3.570(9) Å).

Figure 6.5 (a) Thermal ellipsoid plot of SPFB at 50% probability level in the crystal structure of SPFB (b) Arrangement of the hydrophilic and fluorophilic layers in SPFB with a distance of 4.585(8) Å between two opposite perfluoro chains and an interlayer distance of 5.791(9) Å.
Table 6.5 Bond lengths (Å) and bond angles (°) for SPFB

<table>
<thead>
<tr>
<th>Bond lengths (Å)</th>
<th>Bond angles (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C1-F1</td>
<td>1.312(7)</td>
</tr>
<tr>
<td>C1-F2</td>
<td>1.320(7)</td>
</tr>
<tr>
<td>C1-F3</td>
<td>1.312(6)</td>
</tr>
<tr>
<td>C2-F4</td>
<td>1.345(5)</td>
</tr>
<tr>
<td>C2-F5</td>
<td>1.340(6)</td>
</tr>
<tr>
<td>C3-F6</td>
<td>1.353(5)</td>
</tr>
<tr>
<td>C3-F7</td>
<td>1.370(5)</td>
</tr>
<tr>
<td>C4-O1</td>
<td>1.241(5)</td>
</tr>
<tr>
<td>C4-O2</td>
<td>1.237(5)</td>
</tr>
<tr>
<td>O1-Na1A</td>
<td>2.370(4)</td>
</tr>
<tr>
<td>O2-Na1</td>
<td>2.293(4)</td>
</tr>
<tr>
<td>C1-C2-C3</td>
<td>118.7(5)</td>
</tr>
<tr>
<td>C2-C3-C4</td>
<td>114.3(4)</td>
</tr>
<tr>
<td>C3-C4-O1</td>
<td>114.8(4)</td>
</tr>
<tr>
<td>C3-C4-O2</td>
<td>116.3(4)</td>
</tr>
<tr>
<td>O1-C4-O2</td>
<td>128.9(4)</td>
</tr>
<tr>
<td>F1-C1-F2</td>
<td>107.8(5)</td>
</tr>
<tr>
<td>F1-C1-F3</td>
<td>106.9(5)</td>
</tr>
<tr>
<td>F2-C1-F3</td>
<td>107.9(5)</td>
</tr>
<tr>
<td>F4-C2-F5</td>
<td>106.7(4)</td>
</tr>
<tr>
<td>F6-C3-F7</td>
<td>105.1(3)</td>
</tr>
<tr>
<td>C4-O2-Na1</td>
<td>123.6(3)</td>
</tr>
</tbody>
</table>

In the packing diagram of SPFO (Figure 6.5b), there are two different types of layers, fluorophilic and hydrophilic. The interlayer distance between the fluorocarbon chains is 5.791(9) Å and the distance between two consecutive perfluoro chains (between the carbons of two consecutive –CF<sub>3</sub> groups) is 4.585(8) Å.

6.6 Conclusion

The X-ray crystallography of perfluoro carboxylic acids and carboxylates without any hydrogen atom in the chain (except for carboxylic acid group) is being reported for the first time. Future work may include efforts to get the anhydrous crystal structures of carboxylic acids.
References:


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Chapter-7

7. Properties of 1-ethyl-3-methyl imidazolium bifluoride (EMIMHF$_2$)

7.1 Introduction

Ionic liquids/room temperature molten salts have their primary importance as non-volatile, non-flammable and unreactive liquids. These liquids usually have very high thermal, chemical and electrochemical stability.$^{1,2}$ Among the available ionic liquids, imidazolium cation-based ionic liquids are very important because of the resistance of these cations towards reduction.$^{3,4,5}$ Imidazolium ionic liquids have melting points below 100 °C, low viscosity, and high conductivity which can be explained in terms of charge delocalization on the imidazolium ring.$^{3,4,5}$ Because of these valuable properties, the detailed study of structural and dynamical properties of ionic liquids are of high importance not only from the theoretical point of view to understand their fundamental properties but also for their applications. Ionic liquids such as imidazolium tetrafluoroborate have been studied in the polymer composite form for the application as electrolytes in fuel cells.$^7$ One study based on the Radial Density Function (RDF) analysis (simulation work) states that the imidazolium cations, e.g. 1-butyl 3-methylimidazolium cation, have faster self-diffusion coefficients than their counter anions, e.g. BF$_4^-$, inside the Nafion network.$^7$

Electrolytic studies on salts such as KHF$_2$ revealed that the protons present in this solid are responsible for the conduction of current ($\text{H}_2$ is generated at the anode as a result of electrolysis and $\text{F}_2$ is generated at the cathode).$^6$ A series of imidazolium fluorohydrogenate [F(HF)$_n$]$^{-}(n = 1–2.6)$ salts ranging from liquid to solid at ambient temperature was synthesized by Rika Hagiwara et al. and were shown to be ionic liquids with very high conductivities.$^{8,9,10}$ These fluorohydrogenate ionic liquids were studied using the pulse field gradient solution NMR technique to explore the conductivity
mechanism and it was proposed that the dispersion of the anionic charge over a larger fluorohydrogenate anion results in faster migration of that anion.\textsuperscript{11,12}

In the solid state, such ionic liquids usually exhibit restricted motion, especially translational motion. Some motion, however, can be observed due to rotation of the alkyl groups, inversion of the rings in the molecule, migration of labile hydrogens and internal rotation of small molecules within larger structures. The focus of the present study is to analyze 1-ethyl-3-methylimidazolium bifluoride with solid-state NMR techniques to characterize important structural and dynamical properties.

7.2 Results and discussion

7.2.1 X-ray crystallography

The HF\textsubscript{2}– anion is of significant interest because it contains the strongest hydrogen bond known and it may exist either in the symmetric or unsymmetric form depending on the symmetry of the surrounding crystal field. 1-ethyl-3-methylimidazolium bifluoride (EMIMHF\textsubscript{2}) was found to exist in two different modifications, a low-temperature phase and a room-temperature phase.\textsuperscript{9} The low-temperature structure is discussed in the present study by X-ray crystallography, whereas the room temperature modification has been reported previously.\textsuperscript{9}
The low temperature phase of 1-ethyl-3-methylimidazolium bifluoride (EMIMHF$_2$) crystallizes in triclinic space group $P\bar{1}$ with two molecular units in the unit cell. The concise crystallographic data has been given in Table 7.1 while the bond lengths and bond angles are given in Table 7.2. The crystallographic data for two different phases of [EMIM][HF$_2$] are compared in Table 7.1. The crystallography for room-temperature [EMIM][HF$_2$] was performed at 25 °C$^9$ while the data set for the low-temperature phase was collected at –120 °C. Because of poorer crystal quality, the uncertainties associated with the unit cell dimensions of the low temperature phase of 1-ethyl-3-methylimidazolium bifluoride are higher compared to the uncertainties associated with the known unit cell dimensions of ambient temperature phase of 1-ethyl-3-methylimidazolium bifluoride. The volume for the low-temperature phase is, as expected, smaller than that of the room-temperature phase.$^9$
Table 7.1 Selected crystallographic data for [EMIM][HF$_2$], for symmetric and unsymmetric HF$_2$.

<table>
<thead>
<tr>
<th></th>
<th>[EMIM][HF$_2$] (Unsymmetric HF$_2$– unit)</th>
<th>[EMIM][HF$_2$]$^c$ (Symmetric HF$_2$– unit)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chem formula</td>
<td>C$<em>6$H$</em>{12}$N$_2$F$_2$</td>
<td>C$<em>6$H$</em>{12}$N$_2$F$_2$</td>
</tr>
<tr>
<td>Crystal system</td>
<td>Triclinic</td>
<td>Monoclinic</td>
</tr>
<tr>
<td>Space group</td>
<td>P–I</td>
<td>$P2_1/m$</td>
</tr>
<tr>
<td>a (Å)</td>
<td>6.710(12)</td>
<td>7.281(1)</td>
</tr>
<tr>
<td>b (Å)</td>
<td>7.234(13)</td>
<td>6.762(1)</td>
</tr>
<tr>
<td>c (Å)</td>
<td>8.354(15)</td>
<td>8.403(1)</td>
</tr>
<tr>
<td>α (°)</td>
<td>72.359(18)</td>
<td></td>
</tr>
<tr>
<td>β (°)</td>
<td>78.343(18)</td>
<td>107.26(1)</td>
</tr>
<tr>
<td>γ (°)</td>
<td>88.72(2)</td>
<td></td>
</tr>
<tr>
<td>V (Å$^3$)</td>
<td>378.1(12)</td>
<td>395.09(18)</td>
</tr>
<tr>
<td>Z</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>mol wt (g mol$^{-1}$)</td>
<td>150.17</td>
<td>150.17</td>
</tr>
<tr>
<td>$\rho_{\text{calcd}}$ (g cm$^{-3}$)</td>
<td>1.26</td>
<td>1.26</td>
</tr>
<tr>
<td>T (°C)</td>
<td>–120</td>
<td>25</td>
</tr>
<tr>
<td>$R_1^a$</td>
<td>0.0540</td>
<td>0.062</td>
</tr>
<tr>
<td>w$R_2^b$</td>
<td>0.1443</td>
<td>0.169</td>
</tr>
</tbody>
</table>

$^a$ $R_1$ is defined as $\Sigma||F_o| - |F_c||/\Sigma|F_o|$ for $I > 2\sigma(I)$. $^b$ w$R_2$ is defined as $[\Sigma w(F_o^2 - F_c^2)^2]/\Sigma w(F_o^2)^{1/2}$ for $I > 2\sigma(I)$. $^c$ EMIMHF$_2$ structure details has been taken from reference 9.

Table 7.2 Bond lengths (Å) and Bond angles (°) in 1-ethyl-3-methylimidazolium bifluoride (EMIMHF$_2$) crystal

<table>
<thead>
<tr>
<th>Bond lengths (Å)</th>
<th>Bond angles (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>N1-C1</td>
<td>1.331(3)</td>
</tr>
<tr>
<td>N1-C3</td>
<td>1.379(4)</td>
</tr>
<tr>
<td>N1-C4</td>
<td>1.472(3)</td>
</tr>
<tr>
<td>N2-C1</td>
<td>1.329(3)</td>
</tr>
<tr>
<td>N2-C2</td>
<td>1.377(3)</td>
</tr>
<tr>
<td>N2-C6</td>
<td>1.459(4)</td>
</tr>
<tr>
<td>F1-H10</td>
<td>1.27(4)</td>
</tr>
<tr>
<td>F2-H10</td>
<td>1.00(4)</td>
</tr>
</tbody>
</table>
In the low-temperature phase of [EMIM][HF$_2$], the hydrogen atom in HF$_2^-$ could be found in the difference map and its location was freely refined showing an unsymmetric HF$_2^-$ anion. The unsymmetric F–H⋯F unit (F1–H10: 1.27(4) Å; F2–H10: 1.00(4) Å) is not perfectly linear (168.3°). The F⋯F distance of 2.257(4) Å in EMIMHF$_2$ is fairly close to what has been observed in the case of other bifluoride salts ([{(CH$_3$)$_4$N}][HF$_2$]: 2.213(4) Å; [p-toludinium][HF$_2$]: 2.260(4) Å).$^{14,15,16,17}$ The geometrical parameters for the EMIM$^+$ cation are in agreement with the known EMIMHF$_2$ crystal structure at 25 °C.$^9$ EMIMHF$_2$ crystallizes in a layered structure made up of EMIM$^+$ cation and HF$_2^-$ anion. The distance between the planes of two imidazolium rings is 3.331 Å (Figure 7.2).

![Figure 7.2 Thermal ellipsoid plot of 1-ethyl-3-methylimidazolium bifluoride at 50% probability level in the crystal structure of 1-ethyl-3-methylimidazolium bifluoride (EMIMHF$_2$)](image)

The H⋯F contacts between HF$_2^-$ and protons of the imidazolium ring in EMIMHF$_2$ are 2.001 Å (H1⋯F2), 2.116 Å (H2⋯F1) and 2.114 Å (H3⋯F1) which are less than the sum of the van der Waal’s radii (2.67 Å) and compare well with the room temperature structure. The local environment of HF$_2^-$ is very similar to that in the room temperature structure.
7.2.2 Solution and Solid State NMR spectroscopy of 1-ethyl-3-methylimidazolium bifluoride

![Structure of EMIMHF2](image)

(Scheme-I)

7.2.2.1 $^1$H and $^{13}$C NMR spectroscopy

The comparison of solution- and solid-state $^1$H NMR spectra of EMIMHF$_2$ is shown in Figure 7.3. Figure 7.3(a) shows the solution-state NMR spectrum in DMSO-d$_6$ solvent while 7.3 (b) shows the solid-state MAS NMR spectrum. Due to the broad resonances in the $^1$H MAS NMR spectrum, the solid-state spectrum was deconvolved with different contributions based on the available features in the spectrum and the areas of the contributions were compared. It was difficult to separate the 2'–CH$_2$ and 1''–CH$_3$ contributions and thus the sum of these contributions was deconvolved as a single peak. The areas for the imidazolium proton contributions of imidazolium rings agrees well with the number of protons present. The small sharp signals in the solid-state NMR spectrum signals point to different mobile contributions present in the imidazolium cation. The broad signal at 8.19 ppm might be due to the background signal from the Torlon cap of the rotor. The chemical shifts for the protons in the solid state are close to those obtained in the solution NMR experiment.
Figure 7.3 $^1$H MAS NMR spectroscopy of 1-ethyl-3-methylimidazolium bifluoride (a) in solution state using DMSO-d$_6$ as solvent at 20 °C (b) solid-state $^1$H NMR spectrum with deconvolution at 14 kHz MAS spinning rate at –40 °C.

The chemical shifts for the methyl group on the imidazolium ring is shifted to higher frequency due to their attachment to the more electronegative nitrogen atom in the 1-ethyl 3-methyl imidazolium ring when compared to the methyl group on the alkyl chain. The 4,5...
ring proton positions are in the range of aromatic protons (6.0 to 8.0 ppm) while the proton on the 2-position is shifted out of aromatic range because of its connectivity to two more electronegative nitrogen atoms. The HF$_2^-$ signal appears at the highest frequency compared to the other proton signals in EMIMHF$_2$ due to the highest electronegativity of the fluorine atoms.

Table 7.3 Comparison of $^1$H NMR chemical shifts of EMIMHF$_2$ in solution and solid state

<table>
<thead>
<tr>
<th>Solvent: DMSO-d$_6$</th>
<th>Solution State (21 °C)</th>
<th>Solid State (−40 °C)</th>
<th>Assignments</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\delta$ (ppm)</td>
<td>$^2$$^2$$^J$(H-H), Hz</td>
<td>$\delta$ (ppm); Integration (Area)</td>
<td></td>
</tr>
<tr>
<td>1.40 (triplet)</td>
<td>7.1</td>
<td>1.23; 2.84</td>
<td>−CH$_3$ (1’)</td>
</tr>
<tr>
<td>3.85 (singlet)</td>
<td>-</td>
<td>4.11; 4.77</td>
<td>−CH$_3$ (1”)</td>
</tr>
<tr>
<td>4.19 (quartet)</td>
<td>7.2</td>
<td>−CH$_2$ (2’)</td>
<td></td>
</tr>
<tr>
<td>7.81 (doublet)</td>
<td>27.7</td>
<td>8.03; 1.76</td>
<td>−CH (4,5)</td>
</tr>
<tr>
<td>9.46 (singlet)</td>
<td>-</td>
<td>10.97; 1.10</td>
<td>−CH (2)</td>
</tr>
<tr>
<td>16.10 (singlet)</td>
<td>-</td>
<td>17.24; 1.00</td>
<td>HF$_2^-$</td>
</tr>
</tbody>
</table>

The $^{13}$C NMR chemical shifts for the 1-ethyl-3-methylimidazolium cation unit in the solution and solid state are given in Table 7.4 and the spectra are shown in Figure 7.4. In the solid-state NMR spectrum, there are some broad features underneath the imidazolium cation signals and the methylene signal of the ethyl chain is probably due to the contribution from the less mobile imidazolium part.
Figure 7.4 (a) $^{13}\text{C}\{^1\text{H}\}$ solution NMR spectroscopy of 1-ethyl-3-methylimidazolium bifluoride in DMSO-d6 solvent at 20 °C (b) $^{13}\text{C}\{^1\text{H}–^{13}\text{C}\}$ CP with 1 ms contact time NMR spectroscopy of 1-ethyl-3-methylimidazolium bifluoride in the solid state at 9 kHz spinning rate at –40 °C.
Table 7.4 Comparison of $^{13}$C NMR chemical shifts of EMIMHF$_2$ in solution and solid state

<table>
<thead>
<tr>
<th>Solvent – DMSO</th>
<th>Solution state (20 °C)</th>
<th>Solid state (–40 °C)</th>
<th>Assignments</th>
</tr>
</thead>
<tbody>
<tr>
<td>δ (ppm)</td>
<td>δ (ppm)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>15.13</td>
<td>12.6</td>
<td>–CH$_3$ (1’)</td>
<td></td>
</tr>
<tr>
<td>35.57</td>
<td>36.0</td>
<td>–CH$_3$ (1’’)</td>
<td></td>
</tr>
<tr>
<td>44.03</td>
<td>45.3</td>
<td>–CH$_2$ (2’)</td>
<td></td>
</tr>
<tr>
<td>122.0</td>
<td>122.4</td>
<td>–CH (5)</td>
<td></td>
</tr>
<tr>
<td>123.6</td>
<td>123.8</td>
<td>–CH (4)</td>
<td></td>
</tr>
<tr>
<td>136.6</td>
<td>136.4</td>
<td>–CH (2)</td>
<td></td>
</tr>
</tbody>
</table>

7.2.2.2 $^{19}$F NMR spectroscopy

The $^{19}$F NMR chemical shift for the bifluoride (HF$_2^-$) unit is found at –141.2 ppm of a solution of EMIMHF$_2$ in DMSO-d6 solvent at 21 °C (Figure 7.5(a)). The direct polarization experiment on $^{19}$F in solid state at –15 °C provided no discernable or very weak fluorine signal for HF$_2^-$ because of the large $^{19}$F background signal coming from the FEP material used to make the insert (Figure 7.6). Thus, the $^1$H–to–$^{19}$F cross polarization technique was applied to filter out the FEP signals. Two isotropic fluorine signals were observed at –141.2 and –144.8 ppm using a short contact time of 50 μs as shown in Figure 7.5 (c) while only one isotropic fluorine signal at –141.2 ppm was obtained using a longer contact time (160 μs) as shown in Figure 7.5 (b). The presence of two fluorine signals with short contact time indicates the presence of two different fluorine environments: one which is less mobile and the other which is more mobile.
Figure 7.5 (a) $^{19}\text{F}$ signal in solution state using DMSO-d6 solvent and $^{19}\text{F}[^1\text{H}\text{-to-}^{19}\text{F CP}]$ MAS NMR spectra with (b) 160 μs and (c) 50 μs contact time NMR spectroscopy of 1-ethyl-3-methylimidazolium bifluoride in the solid state at 14 kHz spinning rate at –40 °C. The isotropic signal is at –141.2 ppm for 160 μs contact time while with 50 μs contact time, two signals were obtained at –141.2 and –144.8 ppm respectively.
Figure 7.6 $^{19}$F DP NMR spectrum in solid state using different spinning rate at $-40 \, ^{\circ}C$.

7.2.3 $^1$H–to–$^{19}$F and $^{19}$F–to–$^1$H CP build-up experiments with magic angle spinning

7.2.3.1 $^1$H–to–$^{19}$F CP build-up experiment and simulation of the spectra

The $^1$H–to–$^{19}$F CP build-up curve shows the presence of two different types of fluorine environments at contact time periods between 10 μs to 180 μs (Figure 7.7). The intensity of the $^{19}$F signal at $-144.8$ ppm builds up until a contact time of 60 μs and then decreases until it vanishes at 160 μs. The signal at $-141.2$ ppm (more mobile phase) increases gradually up to 200 μs and then decreases (Figure 7.8). This signal is taking longer time to build up, and is considered to represent a more mobile environment. The signal at $-144.8$ ppm represents the less mobile environment.
Figure 7.7 (a) $^1$H to $^{19}$F CP build-up curve over a range 10 to 500 μs of contact-time periods in the steps of 10 μs interval  (b) Extension of $^1$H to $^{19}$F CP build up curve for the contact time over a range of 10 to 180 μs.

Figure 7.8 $^1$H to $^{19}$F CP build-up curve over a range of 0 to 300 μs contact-time periods for $^{19}$F signal at (a) –141.2 ppm (more mobile component) and (b) at –144.8 ppm (less mobile component).
The $^{19}\text{F}$ NMR spectra obtained in the $^{1}\text{H}$–to–$^{19}\text{F}$ CP build up array were simulated using the SIMPSON software.\textsuperscript{18} For simulating the resultant spectra, the maximum value for the chemical shielding anisotropy (CSA) for the $^{19}\text{F}$ and $^{1}\text{H}$ shielding tensors were taken from the solid-state NMR work on KHF\textsubscript{2} by Hecke et al.\textsuperscript{19,20} Smaller CSA value can arise because of motional scaling. Unfortunately, $^{1}\text{H}\{^{19}\text{F}\}$ and $^{19}\text{F}\{^{1}\text{H}\}$ decoupling did not work in the present work. Hence, the dipolar coupling values between H–F and F–F were calculated based on the crystal structure parameters obtained by Hagiwara for EMIMHF\textsubscript{2} at 25 °C.\textsuperscript{9} The Euler angle ($\beta$) (defining the displacement of the object from z-axis in the principal axis system) used in the simulation work was then varied to match the simulated spectra with the experimental one. Due to the presence of overlap of the signals, distortion in the base line and contribution from FEP signal, the experimental spectra were first deconvolved (Figure 7.9) and then matched with the simulation results. The results obtained from the simulation work are summarized in Table 7.5.
Figure 7.9 $^1$H–$^{19}$F CP MAS NMR simulated and experimental spectra for (a) 60 μs and (b) 160 μs at 14 kHz MAS spinning rate.
Table 7.5 SIMPSON simulation results for the $^{19}$F and $^1$H tensors of HF$_2^-$ anion in EMIMHF$_2$

<table>
<thead>
<tr>
<th>Contact time (μs)</th>
<th>60</th>
<th>160</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nucleus</td>
<td>$^1$H</td>
<td>$^{19}$F</td>
</tr>
<tr>
<td>CSA (ppm)$^a$</td>
<td>44</td>
<td>74</td>
</tr>
<tr>
<td>H–F dipolar coupling (kHz)$^b$</td>
<td>68.8</td>
<td>68.8</td>
</tr>
<tr>
<td>F–F dipolar coupling (kHz)$^c$</td>
<td>10.7</td>
<td>10.7</td>
</tr>
<tr>
<td>Angle, β (°)$^d$</td>
<td>140</td>
<td>140</td>
</tr>
<tr>
<td>Asymmetry (η)$^e$</td>
<td>0.3</td>
<td>0.3</td>
</tr>
</tbody>
</table>

The uncertainties associated with the $^{19}$F CSA,$^a$ $^1$H–$^{19}$F dipolar couplings and $^{19}$F–$^{19}$F dipolar couplings,$^b,c$ asymmetry$^e$ and β$^d$ angle are ±3 ppm, ±0.5 kHz, ±0.1 and ±5°, respectively.

The results obtained from simulating the $^{19}$F and $^1$H tensors of HF$_2^-$ anion in EMIMHF$_2$ suggest the presence of H$_2$F$_3^-$ and H$_3$F$_4^-$ anions beside HF$_2^-$ (scheme II). The dipolar coupling values, asymmetry and CSA values for $^{19}$F tensor are different for the non-linear bifluoride contributions compared to the linear bifluoride contribution (CSA: 74.0 versus 84.0 ppm; $^1$H–$^{19}$F dipolar coupling: 68.8 versus 88.8 kHz). It indicates the deviation of $^{19}$F tensors from linearity for different fluorohydrogenate anions contributions in EMIMHF$_2$, which might be present as an impurity from the starting material EMIM(HF)$_2$.3. It should be noted that the fluorine in HF$_2^-$ and μ (bridging) fluorine in H$_2$F$_3^-$ and H$_3$F$_4^-$ anions (Scheme II) have one, two and three neighboring protons, respectively. Thus, in the $^1$H-to-$^{19}$F CP build-up experiment, the $^{19}$F signal for H$_3$F$_4^-$ anion will experience more efficient cross polarization from $^1$H and will appear at the short contact times followed by the H$_2$F$_3^-$ and HF$_2^-$ at the longer contact time periods.

It was noticed in the simulations that a perfect match between the experimental and the simulated spectrum is difficult to obtain where the experimental spectrum represents a combination of different contributions.
7.2.3.2 $^{19}$F–to–$^1$H CP build up experiment

The $^{19}$F–to–$^1$H CP build up curve is shown in Figure 7.10 (a). The intensity of the bifluoride signal gradually decreases as the contact time increases while the intensities for the basal protons of the imidazolium cation increases gradually at the same time. The intensity for the imidazolium protons is shown in Figure 7.10 (b) which shows an increase with the increasing contact time while the intensity of the bifluoride proton signal is showing a decrease as shown in Figure 7.10 (c). The increase in intensity for the protons of the imidazolium ring indicates the more dynamic behavior of imidazolium cation as compared to the bifluoride anion because the more dynamic contribution takes more time in signal build-up whereas the less dynamic contribution builds up very fast. Initially, only the signals from HF$_2^-$ will show up at short contact times because of the strong covalent bonding between proton and fluorine. As the contact period is increased, the imidazolium proton signals come up due to the short contacts between $^1$H of imidazolium ring and the $^{19}$F of HF$_2^-$. 

(Scheme-II) The geometries for HF$_2^-$, H$_2$F$_3^-$ and H$_3$F$_4^-$ anions.
Figure 7.10 (a) The plot of intensity of the EMIMHF$_2$ proton signals over a range 10 – 250 μs of contact-time periods in the steps of 10 μs interval in $^{19}$F–to–$^1$H CP build-up (b) expansion of the isotropic signal of array shown in 7.10a (c) $^1$H imidazolium ring protons signal increasing intensity and $^1$H signal decreasing intensity of the bifluoride protons as a function of contact time.
The $^1$H NMR spectra obtained in the $^{19}$F–to–$^1$H CP build up array were simulated using the SIMPSON software. The values for CSA, $^1$H–$^{19}$F dipolar coupling obtained in the $^{19}$F simulation was used for simulating the $^1$H experimental spectrum. The simulated spectrum at 160 μs is shown in the following figure 7.11.

![Figure 7.11 $^{19}$F–to–$^1$H CP MAS NMR spectra simulation for 160 μs contact time and at 14 kHz MAS spinning rate](image)

**7.2.4 Dipolar-dephasing experiments with magic angle spinning**

Dipolar-dephasing experiments were performed on the $^{13}$C resonance by applying a variable delay on the $^1$H resonance in the $^1$H–to–$^{13}$C cross-polarization NMR experiment. It provides a direct measure of the dipolar coupling strength of C–H bond associated with the particular carbon nucleus. The magic angle spinning removes the chemical shielding anisotropy yielding narrow $^{13}$C resonances. The $^{13}$C–$^1$H dipolar coupling has an $1/r^3$ dependence, where $r$ is the inter-nuclear distance between carbon and proton. This coupling strength is greater for the carbons directly bonded to protons as compared to the protons on the neighboring carbons. Thus, for a short dephasing delay only the directly bonded proton-carbon couple will be affected and the signal will disappear after the coupling strength of $^{13}$C–$^1$H bond length is passed. If the signal is still present, it indicates the occurrence of
some dynamical process related to the mobility for that particular $^{13}\text{C}$$^{–}$1$^1\text{H}$ bond. The $^{13}\text{C}$$^{–}$1$^1\text{H}$ dipolar coupling is responsible for the rapid $T_2$ relaxation of the $^{13}\text{C}$. If an array of spectra is collected with this experiment, the different types of $^{13}\text{C}$ environments can be distinguished based on their relaxation rates and the shape of the curves. The dipolar dephasing experiments were performed on the imidazolium ring of the EMIMH$\text{F}_2$ at $–40\, ^\circ\text{C}$ (Figure 7.12). The $^{13}\text{C}$ signals at $121.3\, \text{ppm}$ and $123.4\, \text{ppm}$ persisted even after the application of the required total dephasing delay, which was calculated based on the internuclear C–H distance ($1.09\, \text{Å}$ for aromatic ring systems). Based on this distance the carbon signal should dephase in about $42\, \mu\text{s}$ but the imidazolium carbon signals at 4 and 5 position survive even after this dephasing time period up to about $60\, \mu\text{s}$. The persistence of the signal after total dephasing delay indicated the presence of molecular dynamics in the imidazolium ring at $–40\, ^\circ\text{C}$. The presence of dynamics in the imidazolium ring was confirmed on repeating this experiment by warming up the sample. As a consequence of higher temperature, the dephasing time of the imidazolium carbon signals increased a bit.

![Figure 7.12 Dipolar dephasing experiments with magic angle spinning of 1-ethyl-3-methylimidazolium bifluoride at MAS 9 kHz and $–40\, ^\circ\text{C}$.](image)
It is evident from the results of dipolar dephasing experiments (Figure 7.13) that the highly mobile –CH\sub{3} groups on the imidazolium cation as well as on the alkyl chain dephase very slowly because of rapid motion of the methyl group. The imidazolium ring protons dephase relatively faster compared to the –CH\sub{3} groups because of the less dynamics of the ring system whereas the –CH\sub{2} group dephase very rapidly due to its comparatively more rigid nature as compared to the –CH\sub{3} group and because of its direct attachment to the nitrogen of the imidazolium ring.
7.3 Conclusion

Based on the results from simulations of 1D $^1$H and $^{19}$F spectra and dipolar-dephasing experiments, it can be concluded that the presence of dynamics is evident for the 1-ethyl-3-methylimidazolium cation in EMIMHF$_2$ at 14.0 kHz at –40 °C. The simulation results suggests the presence of some kind of agglomerated domain structure for the fluorohydrogenate anions in the form of H$_2$F$_3^−$ and H$_3$F$_4^−$ anions besides HF$_2^−$ and thus signifies the importance of CP dynamics in detecting impurities in the material.
References


8. Conclusion and future directions

The crystal structures of two modifications of \([\text{SF}_3][\text{SbF}_6]\) (γ- and α-phases) and of \([\text{SF}_3][\text{AsF}_6]\) were characterized. The structure for the β-phase of \([\text{SF}_3][\text{SbF}_6]\) still needs to be conclusively characterized. Deoxofluorination reactions for two ketones, two carboxylic acids and an alcohol were done from \([\text{SF}_3][\text{SbF}_6]\) and \([\text{SF}_3][\text{AsF}_6]\) using \(\text{SO}_2\), \(\text{CH}_3\text{CN}\), and \(\text{CH}_2\text{Cl}_2\) solvents. More substrates need to be used for a complete establishment of the use of \([\text{SF}_3][\text{SbF}_6]\) and \([\text{SF}_3][\text{AsF}_6]\) as deoxofluorinating reagents in organic chemistry. A series of adducts between \([\text{SF}_3][\text{MF}_6]\) (\(M = \text{Sb, As}\)) and nitrogen bases were studied and conclusively characterized. The 1:2 ratio between the \(\text{SF}_3^+\) cation of \([\text{SF}_3][\text{MF}_6]\) (\(M = \text{Sb, As}\)) salts and nitrogen ligands was conclusively shown at low temperature. The synthesis and conclusive characterization of a 1:1 adduct of \([\text{SF}_3][\text{MF}_6]\) (\(M = \text{Sb, As}\)) salts and nitrogen bases is still pending. The reactions of \([\text{SF}_3(\text{N-base})_x]^+\) cation with highly Lewis acidic compounds, such as \(\text{AsF}_5\) and \(\text{SbF}_5\), can be studied to explore the synthesis of \([\text{SF}_2(\text{N-base})_x]^{2+}\) compounds. The nitrogen bases can be replaced with oxygen bases to study \([\text{SF}_3(\text{O-base})][\text{MF}_6]\) and \([\text{SF}_3(\text{O-base})_2][\text{MF}_6]\) (\(M = \text{Sb, As}\)) compounds to better understand the reactive intermediate species in the deoxofluorination reactions of carbonyl compounds.

The \(\text{WOF}_4\cdot\text{SO}_2\) adduct was identified in the solid state and conclusively characterized by X-ray crystallography and Raman spectroscopy. The first X-ray structure of \(\text{WOF}_5^-\) in the form of \([(\text{CH}_3)_4\text{N}][\text{WOF}_5]\) was characterized without any disorder and more accurate metric parameters. The mono substituted product of \(\text{WOF}_4\) with \(\text{CF}_3\text{CH}_2\text{OH}\), i.e. \(\text{WOF}_3(\text{OCH}_2\text{CF}_3)\) was conclusively characterized as its \(\text{CH}_3\text{CN}\) adduct, i.e. \(\text{CH}_3\text{CN}\cdot\text{WOF}_3(\text{OCH}_2\text{CF}_3)\). Attempts should be made to synthesize the products in which
more fluorine atoms can be substituted from WOF$_4$. Also the chemistry of WOF$_4$ involving the driving force of H–F bond formation can be extended to different aliphatic and aromatic alcohols.

The first X-ray crystallographic results for perfluoro carboxylic acids and carboxylates have been reported. Future work may include efforts to get the anhydrous crystal structures of these perfluoro carboxylic acids to explore their dimeric form.

The solid state NMR spectroscopy for the EMIMHF$_2$ imidazolium ionic liquid provided the indications of dynamics and sources of impurity present in this salt.
APPENDIX

Appendix – Chapter 3

Table 3A1. Crystal data and structure refinement for [SF₃][AsF₆]

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<th>Empirical formula</th>
<th>F₂SAs</th>
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<td>143(2)</td>
</tr>
<tr>
<td>Wavelength, pm</td>
<td>71.073</td>
</tr>
<tr>
<td>Crystal System</td>
<td>Orthorhombic</td>
</tr>
<tr>
<td>Space group</td>
<td>Cmc2₁</td>
</tr>
<tr>
<td>Unit cell dimensions, Å</td>
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</tr>
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<td>a = 20.308(14)</td>
<td>b = 8.369(6)</td>
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<tr>
<td>c = 11.091(7)</td>
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</tr>
<tr>
<td>Z</td>
<td>8</td>
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<td>Density(calculated), mg mm⁻³</td>
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<td>F(000)</td>
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<td>Crystal size, mm³</td>
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<td>Refine diff density_min</td>
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Table 3A2. Crystal data and structure refinement for γ-[SF₃][SbF₆]

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<td>Temperature, K</td>
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</tr>
<tr>
<td>Wavelength, pm</td>
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</tr>
<tr>
<td>Crystal System</td>
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</tr>
<tr>
<td>Space group</td>
<td>( P2_1/n )</td>
</tr>
<tr>
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<td>Unit cell dimensions, Å</td>
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</tr>
<tr>
<td></td>
<td>( b = 10.5450(13) )</td>
</tr>
<tr>
<td></td>
<td>( c = 8.0879(10) )</td>
</tr>
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<td>c = 11.19(2)</td>
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<td>(calculated), mg mm⁻³</td>
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<td>−13 ≤ l ≤ 10</td>
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## Appendix – Chapter 4

Table 4A1. Crystal data and structure refinement for [SF₅(C₅H₅N)₂][SbF₆]·CH₂Cl₂

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<th>Description</th>
<th>Value</th>
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<td><strong>Empirical formula</strong></td>
<td>C₁₁H₁₂Cl₂F₉N₂Sb</td>
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<tr>
<td><strong>Temperature, K</strong></td>
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</tr>
<tr>
<td><strong>Wavelength, pm</strong></td>
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</tr>
<tr>
<td><strong>Crystal System</strong></td>
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</tr>
<tr>
<td><strong>Space group</strong></td>
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<td><strong>Angle-β,°</strong></td>
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<td><strong>Z</strong></td>
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<td><strong>Density (calculated), mg mm⁻³</strong></td>
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Table 4A2. Crystal data and structure refinement for [SF$_3$(C$_5$H$_5$N)$_2$][AsF$_6$]-CH$_2$Cl$_2$

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<td>Formula weight, g mol$^{-1}$</td>
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<td>Temperature, K</td>
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<tr>
<td>Wavelength, pm</td>
<td>71.073</td>
</tr>
<tr>
<td>Crystal System</td>
<td>Monoclinic</td>
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<tr>
<td>Space group</td>
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<td></td>
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<td></td>
<td>c = 14.118(3) Å</td>
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<td>Crystal size, mm$^3$</td>
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<td>–16 ≤ k ≤ 16,</td>
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222
Table 4A3. Crystal data and structure refinement for [SF$_3$(C$_5$H$_5$N)$_2$][SbF$_6$]·C$_5$H$_5$N

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</tr>
<tr>
<td>Crystal System</td>
<td>Monoclinic</td>
</tr>
<tr>
<td>Space group</td>
<td>C2/c</td>
</tr>
<tr>
<td>Angle-$\beta$, $^\circ$</td>
<td>125.1550(10)$^\circ$</td>
</tr>
<tr>
<td>Unit cell dimensions, Å</td>
<td></td>
</tr>
<tr>
<td>a</td>
<td>26.913(3)</td>
</tr>
<tr>
<td>b</td>
<td>8.5689(10)</td>
</tr>
<tr>
<td>c</td>
<td>18.447(2)</td>
</tr>
<tr>
<td>Volume, $10^2$ Å$^3$</td>
<td>34.782(7)</td>
</tr>
<tr>
<td>Z</td>
<td>8</td>
</tr>
<tr>
<td>Density (calculated), mg mm$^{-3}$</td>
<td>2.0690</td>
</tr>
<tr>
<td>Absorption coefficient, mm$^{-1}$</td>
<td>3.540</td>
</tr>
<tr>
<td>F(000)</td>
<td>3040</td>
</tr>
<tr>
<td>Crystal size, mm$^3$</td>
<td>0.25 × 0.30 × 0.38</td>
</tr>
<tr>
<td>Theta range for data collection</td>
<td>1.85$^\circ$ – 27.53$^\circ$</td>
</tr>
<tr>
<td>Index ranges</td>
<td>–34 ≤ h ≤ 34,</td>
</tr>
<tr>
<td></td>
<td>–11 ≤ k ≤ 11,</td>
</tr>
<tr>
<td></td>
<td>–23 ≤ l ≤ 23</td>
</tr>
<tr>
<td>Reflections collected</td>
<td>19324</td>
</tr>
<tr>
<td>Independent reflections</td>
<td>4007 [R$_{int}$ = 0.0257]</td>
</tr>
<tr>
<td>Completeness to theta[27.55$^\circ$]</td>
<td>99.9%</td>
</tr>
<tr>
<td>Refinement method</td>
<td>Full matrix Least-squares on F$^2$</td>
</tr>
<tr>
<td>Data/restraints/parameters</td>
<td>4007 / 0 / 250</td>
</tr>
<tr>
<td>Goodness-of-fit on F$^2$</td>
<td>0.986</td>
</tr>
<tr>
<td>Refine diff density_max</td>
<td>0.464</td>
</tr>
<tr>
<td>Refine diff density_min</td>
<td>–0.444</td>
</tr>
</tbody>
</table>
Table 4A4. Crystal data and structure refinement for [SF₃(C₅H₅N)₂][AsF₆]·C₅H₅N

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Empirical formula</td>
<td>C₁₅H₁₅AsF₉N₃S</td>
</tr>
<tr>
<td>Formula weight, g mol⁻¹</td>
<td>515.29</td>
</tr>
<tr>
<td>Temperature, K</td>
<td>153(2)</td>
</tr>
<tr>
<td>Wavelength, pm</td>
<td>71.073</td>
</tr>
<tr>
<td>Crystal System</td>
<td>Monoclinic</td>
</tr>
<tr>
<td>Space group</td>
<td>C2/c</td>
</tr>
<tr>
<td>Angle-β,°</td>
<td>124.417(4)°</td>
</tr>
<tr>
<td>Unit cell dimensions, Å</td>
<td></td>
</tr>
<tr>
<td>a = 26.704(10)</td>
<td></td>
</tr>
<tr>
<td>b = 8.521(3)</td>
<td></td>
</tr>
<tr>
<td>c = 17.984(7)</td>
<td></td>
</tr>
<tr>
<td>Volume, 10² Å³</td>
<td>33.76(2)</td>
</tr>
<tr>
<td>Z</td>
<td>8</td>
</tr>
<tr>
<td>Density (calculated), mg mm⁻³</td>
<td>1.9541</td>
</tr>
<tr>
<td>Absorption coefficient, mm⁻¹</td>
<td>4.406</td>
</tr>
<tr>
<td>F(000)</td>
<td>2752</td>
</tr>
<tr>
<td>Crystal size, mm³</td>
<td>0.21 × 0.25 × 0.46</td>
</tr>
<tr>
<td>Theta range for data collection</td>
<td>1.85° – 20.16°</td>
</tr>
<tr>
<td>Index ranges</td>
<td>-25 ≤ h ≤ 25,</td>
</tr>
<tr>
<td></td>
<td>-8 ≤ k ≤ 8,</td>
</tr>
<tr>
<td></td>
<td>-17 ≤ l ≤ 17</td>
</tr>
<tr>
<td>Reflections collected</td>
<td>9936</td>
</tr>
<tr>
<td>Independent reflections</td>
<td>1620 [R_int = 0.0836]</td>
</tr>
<tr>
<td>Completeness to theta[27.55°]</td>
<td>100.0%</td>
</tr>
<tr>
<td>Refinement method</td>
<td>Full matrix Least-squares on F²</td>
</tr>
<tr>
<td>Data/restraints/parameters</td>
<td>1620 / 0 / 250</td>
</tr>
<tr>
<td>Goodness-of-fit on F²</td>
<td>1.044</td>
</tr>
<tr>
<td>Refine diff density_max</td>
<td>0.311</td>
</tr>
<tr>
<td>Refine diff density_min</td>
<td>-0.429</td>
</tr>
<tr>
<td>Table 4A5. Crystal data and structure refinement for [SF$_3$(C$_5$H$_5$N)$_2$][SbF$_6$]-CH$_3$CN</td>
<td></td>
</tr>
<tr>
<td>---------------------------------</td>
<td>------------------</td>
</tr>
<tr>
<td><strong>Empirical formula</strong></td>
<td>C$<em>{12}$H$</em>{13}$F$_9$N$_3$SSb</td>
</tr>
<tr>
<td>Formula weight, g mol$^{-1}$</td>
<td>524.071</td>
</tr>
<tr>
<td>Temperature, K</td>
<td>153(2)</td>
</tr>
<tr>
<td>Wavelength, pm</td>
<td>71.073</td>
</tr>
<tr>
<td>Crystal System</td>
<td>Triclinic</td>
</tr>
<tr>
<td>Space group</td>
<td>P$–1$</td>
</tr>
<tr>
<td>Angle-$\alpha$,°</td>
<td>71.363(2)$^\circ$</td>
</tr>
<tr>
<td>Angle-$\beta$,°</td>
<td>78.440(2)$^\circ$</td>
</tr>
<tr>
<td>Angle-$\gamma$,°</td>
<td>79.556(2)$^\circ$</td>
</tr>
<tr>
<td>Unit cell dimensions, Å</td>
<td>a = 7.6743(15)</td>
</tr>
<tr>
<td></td>
<td>b = 9.0613(18)</td>
</tr>
<tr>
<td></td>
<td>c = 14.160(3)</td>
</tr>
<tr>
<td>Volume, 10$^2$ Å$^3$</td>
<td>9.068(3)</td>
</tr>
<tr>
<td>Z</td>
<td>2</td>
</tr>
<tr>
<td>Density (calculated), mg mm$^{-3}$</td>
<td>1.8497</td>
</tr>
<tr>
<td>Absorption coefficient, mm$^{-1}$</td>
<td>3.569</td>
</tr>
<tr>
<td>F(000)</td>
<td>848</td>
</tr>
<tr>
<td>Crystal size, mm$^3$</td>
<td>0.77 $\times$ 0.15 $\times$ 0.24</td>
</tr>
<tr>
<td>Theta range for data collection</td>
<td>1.54° – 27.79°</td>
</tr>
<tr>
<td>Index ranges</td>
<td>$–10 \leq h \leq 10$, $–11 \leq k \leq 11$, $–18 \leq l \leq 18$</td>
</tr>
<tr>
<td>Reflections collected</td>
<td>10923</td>
</tr>
<tr>
<td>Independent reflections</td>
<td>4223 [R$_{int}$ = 0.0354]</td>
</tr>
<tr>
<td>Completeness to theta[27.55°]</td>
<td>98.4%</td>
</tr>
<tr>
<td>Refinement method</td>
<td>Full matrix Least-squares on F$^2$</td>
</tr>
<tr>
<td>Data/restraints/parameters</td>
<td>4223 / 0 / 240</td>
</tr>
<tr>
<td>Goodness-of-fit on F$^2$</td>
<td>1.029</td>
</tr>
<tr>
<td>Refine diff density_max</td>
<td>2.196</td>
</tr>
<tr>
<td>Refine diff density_min</td>
<td>–0.638</td>
</tr>
</tbody>
</table>
Table 4A6. Crystal data and structure refinement for [SF$_3$(CH$_3$CN)$_2$][SbF$_6$]

<table>
<thead>
<tr>
<th>Empirical formula</th>
<th>C$_4$H$_6$F$_9$N$_2$SSb</th>
</tr>
</thead>
<tbody>
<tr>
<td>Formula weight, g mol$^{-1}$</td>
<td>406.92</td>
</tr>
<tr>
<td>Temperature, K</td>
<td>153(2)</td>
</tr>
<tr>
<td>Wavelength, pm</td>
<td>71.073</td>
</tr>
<tr>
<td>Crystal System</td>
<td>Orthorhombic</td>
</tr>
<tr>
<td>Space group</td>
<td>Pnma</td>
</tr>
<tr>
<td>Unit cell dimensions, Å</td>
<td></td>
</tr>
<tr>
<td>a</td>
<td>13.546(13)</td>
</tr>
<tr>
<td>b</td>
<td>12.717(12)</td>
</tr>
<tr>
<td>c</td>
<td>6.992(7)</td>
</tr>
<tr>
<td>Volume, $10^2$ Å$^3$</td>
<td>12.04(2)</td>
</tr>
<tr>
<td>Z</td>
<td>4</td>
</tr>
<tr>
<td>Density (calculated), mg mm$^{-3}$</td>
<td>2.1634</td>
</tr>
<tr>
<td>Absorption coefficient, mm$^{-1}$</td>
<td>3.816</td>
</tr>
<tr>
<td>F(000)</td>
<td>1020</td>
</tr>
<tr>
<td>Crystal size, mm$^3$</td>
<td>$0.09 \times 0.15 \times 0.18$</td>
</tr>
<tr>
<td>Theta range for data collection</td>
<td>$3.01^\circ - 27.81^\circ$</td>
</tr>
<tr>
<td>Index ranges</td>
<td>$-17 \leq h \leq 17$, $-16 \leq k \leq 16$, $-9 \leq l \leq 9$</td>
</tr>
<tr>
<td>Reflections collected</td>
<td>13609</td>
</tr>
<tr>
<td>Independent reflections</td>
<td>1486 [R$_{int} = 0.0261$]</td>
</tr>
<tr>
<td>Completeness to theta[27.55°]</td>
<td>99.9%</td>
</tr>
<tr>
<td>Refinement method</td>
<td>Full matrix Least-squares on F$^2$</td>
</tr>
<tr>
<td>Data/restraints/parameters</td>
<td>1486 / 0 / 87</td>
</tr>
<tr>
<td>Goodness-of-fit on F$^2$</td>
<td>2.329</td>
</tr>
<tr>
<td>Refine diff density_max</td>
<td>0.549</td>
</tr>
<tr>
<td>Refine diff density_min</td>
<td>$-0.382$</td>
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</tbody>
</table>
Table 4A7. Crystal data and structure refinement for [SF₅(Phen)][SbF₆]·CH₂Cl₂

<table>
<thead>
<tr>
<th></th>
<th>C_{14}H_{16}Cl_{4}F_{9}N_{2}Sb</th>
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</thead>
<tbody>
<tr>
<td>Empirical formula</td>
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</tr>
<tr>
<td>Formula weight, g mol⁻¹</td>
<td>684.922</td>
</tr>
<tr>
<td>Temperature, K</td>
<td>153(2)</td>
</tr>
<tr>
<td>Wavelength, pm</td>
<td>71.073</td>
</tr>
<tr>
<td>Crystal System</td>
<td>Monoclinic</td>
</tr>
<tr>
<td>Space group</td>
<td>P2₁/c</td>
</tr>
<tr>
<td>Angle-β,°</td>
<td>94.5460(10)°</td>
</tr>
<tr>
<td>Unit cell dimensions, Å</td>
<td></td>
</tr>
<tr>
<td>a</td>
<td>13.2776(11)</td>
</tr>
<tr>
<td>b</td>
<td>9.0216(8)</td>
</tr>
<tr>
<td>c</td>
<td>18.6778(16)</td>
</tr>
<tr>
<td>Volume, 10² Å³</td>
<td>22.303(3)</td>
</tr>
<tr>
<td>Z</td>
<td>4</td>
</tr>
<tr>
<td>Density (calculated), mg mm⁻³</td>
<td>1.9658</td>
</tr>
<tr>
<td>Absorption coefficient, mm⁻¹</td>
<td>1.891</td>
</tr>
<tr>
<td>F(000)</td>
<td>1308</td>
</tr>
<tr>
<td>Crystal size, mm³</td>
<td>0.33 × 0.13 × 0.07</td>
</tr>
<tr>
<td>Theta range for data collection</td>
<td>1.54° – 27.61°</td>
</tr>
<tr>
<td>Index ranges</td>
<td></td>
</tr>
<tr>
<td>-17 ≤ h ≤ 17,</td>
<td></td>
</tr>
<tr>
<td>-11 ≤ k ≤ 11,</td>
<td></td>
</tr>
<tr>
<td>-24 ≤ l ≤ 24</td>
<td></td>
</tr>
<tr>
<td>Reflections collected</td>
<td>25476</td>
</tr>
<tr>
<td>Independent reflections</td>
<td>5153 [R_{int} = 0.0536]</td>
</tr>
<tr>
<td>Completeness to theta[27.55°]</td>
<td>99.4%</td>
</tr>
<tr>
<td>Refinement method</td>
<td>Full matrix Least-squares on F²</td>
</tr>
<tr>
<td>Data/restraints/parameters</td>
<td>5153 / 0 / 281</td>
</tr>
<tr>
<td>Goodness-of-fit on F²</td>
<td>1.016</td>
</tr>
<tr>
<td>Refine diff density_max</td>
<td>1.360</td>
</tr>
<tr>
<td>Refine diff density_min</td>
<td>-0.529</td>
</tr>
</tbody>
</table>
Table 4A8. Crystal data and structure refinement for [SF₂(DMAP)₂][SbF₆]₂·CH₃CN

<table>
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<th>Property</th>
<th>Value</th>
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</thead>
<tbody>
<tr>
<td>Empirical formula</td>
<td>C₁₅H₂₃F₁₄N₅SSb₂</td>
</tr>
<tr>
<td>Formula weight, g mol⁻¹</td>
<td>814.948</td>
</tr>
<tr>
<td>Temperature, K</td>
<td>153(2)</td>
</tr>
<tr>
<td>Wavelength, pm</td>
<td>71.073</td>
</tr>
<tr>
<td>Crystal System</td>
<td>Monoclinic</td>
</tr>
<tr>
<td>Space group</td>
<td>C₂/c</td>
</tr>
<tr>
<td>Angle-β,°</td>
<td>107.0°</td>
</tr>
<tr>
<td>Unit cell dimensions, Å</td>
<td>a = 12.806(8)</td>
</tr>
<tr>
<td></td>
<td>b = 10.699(7)</td>
</tr>
<tr>
<td></td>
<td>c = 22.056(15)</td>
</tr>
<tr>
<td>Volume, 10² Å³</td>
<td>28.92(3)</td>
</tr>
<tr>
<td>Z</td>
<td>4</td>
</tr>
<tr>
<td>Density (calculated), mg mm⁻³</td>
<td>1.8038</td>
</tr>
<tr>
<td>Absorption coefficient, mm⁻¹</td>
<td>3.193</td>
</tr>
<tr>
<td>F(000)</td>
<td>2268</td>
</tr>
<tr>
<td>Crystal size, mm³</td>
<td>0.21 × 0.22 × 0.36</td>
</tr>
<tr>
<td>Theta range for data collection</td>
<td>1.93° – 27.64°</td>
</tr>
<tr>
<td>Index ranges</td>
<td>−16 ≤ h ≤ 16,</td>
</tr>
<tr>
<td></td>
<td>−13 ≤ k ≤ 13,</td>
</tr>
<tr>
<td></td>
<td>−28 ≤ l ≤ 28</td>
</tr>
<tr>
<td>Reflections collected</td>
<td>9249</td>
</tr>
<tr>
<td>Independent reflections</td>
<td>2369 [R_m = 0.0742]</td>
</tr>
<tr>
<td>Completeness to theta [27.55°]</td>
<td>70.6%</td>
</tr>
<tr>
<td>Refinement method</td>
<td>Full matrix Least-squares on F²</td>
</tr>
<tr>
<td>Data/restraints/parameters</td>
<td>2369 / 0 / 190</td>
</tr>
<tr>
<td>Goodness-of-fit on</td>
<td>F² 1.013</td>
</tr>
<tr>
<td>Refine diff density_max</td>
<td>0.760</td>
</tr>
<tr>
<td>Refine diff density_min</td>
<td>−0.755</td>
</tr>
</tbody>
</table>
Table 4A9. Crystal data and structure refinement for [SF(DMAP)$_4$]$_2$[SbF$_6$]$_3$·2CH$_3$CN

<table>
<thead>
<tr>
<th>Empirical formula</th>
<th>C$<em>{60}$H$</em>{86}$F$<em>{20}$N$</em>{18}$S$_2$Sb$_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Formula weight, g mol$^{-1}$</td>
<td>1868.852</td>
</tr>
<tr>
<td>Temperature, K</td>
<td>153(2)</td>
</tr>
<tr>
<td>Wavelength, pm</td>
<td>71.073</td>
</tr>
<tr>
<td>Crystal System</td>
<td>Monoclinic</td>
</tr>
<tr>
<td>Space group</td>
<td>C2/c</td>
</tr>
<tr>
<td>Angle-β,$^\circ$</td>
<td>107.4588(14)$^\circ$</td>
</tr>
<tr>
<td>Unit cell dimensions, Å</td>
<td>a = 16.0316(18), b = 17.4013(19), c = 19.832(2)</td>
</tr>
<tr>
<td>Volume, 10$^2$ Å$^3$</td>
<td>52.777(10)</td>
</tr>
<tr>
<td>Z</td>
<td>4</td>
</tr>
<tr>
<td>Density (calculated), mg mm$^{-3}$</td>
<td>2.2667</td>
</tr>
<tr>
<td>Absorption coefficient, mm$^{-1}$</td>
<td>2.333</td>
</tr>
<tr>
<td>F(000)</td>
<td>3040</td>
</tr>
<tr>
<td>Crystal size, mm$^3$</td>
<td>0.15 × 0.19 × 0.33</td>
</tr>
<tr>
<td>Theta range for data collection</td>
<td>1.77$^\circ$ – 27.57$^\circ$</td>
</tr>
<tr>
<td>Index ranges</td>
<td>–20 ≤ h ≤ 20, –22 ≤ k ≤ 22, –25 ≤ l ≤ 25</td>
</tr>
<tr>
<td>Reflections collected</td>
<td>29235</td>
</tr>
<tr>
<td>Independent reflections</td>
<td>5913 [R$_{int}$ = 0.0718]</td>
</tr>
<tr>
<td>Completeness to theta [27.55$^\circ$]</td>
<td>96.8%</td>
</tr>
<tr>
<td>Refinement method</td>
<td>Full matrix Least-squares on F$^2$</td>
</tr>
<tr>
<td>Data/restraints/parameters</td>
<td>5913 / 0 / 370</td>
</tr>
<tr>
<td>Goodness-of-fit on F$^2$</td>
<td>1.113</td>
</tr>
<tr>
<td>Refine diff density_max</td>
<td>1.461</td>
</tr>
<tr>
<td>Refine diff density_min</td>
<td>–1.149</td>
</tr>
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Appendix – Chapter 5

<table>
<thead>
<tr>
<th>Table 5A1. Crystal data and structure refinement for WOF₄·SO₂</th>
</tr>
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<tbody>
<tr>
<td><strong>Empirical formula</strong></td>
</tr>
<tr>
<td><strong>Formula weight, g mol⁻¹</strong></td>
</tr>
<tr>
<td><strong>Temperature, K</strong></td>
</tr>
<tr>
<td><strong>Wavelength, pm</strong></td>
</tr>
<tr>
<td><strong>Crystal System</strong></td>
</tr>
<tr>
<td><strong>Space group</strong></td>
</tr>
<tr>
<td><strong>Angle-α,°</strong></td>
</tr>
<tr>
<td><strong>Angle-β,°</strong></td>
</tr>
<tr>
<td><strong>Angle-γ,°</strong></td>
</tr>
<tr>
<td><strong>Unit cell dimensions, Å</strong></td>
</tr>
<tr>
<td>a</td>
</tr>
<tr>
<td>b</td>
</tr>
<tr>
<td>c</td>
</tr>
<tr>
<td><strong>Volume, 10² Å³</strong></td>
</tr>
<tr>
<td><strong>Z</strong></td>
</tr>
<tr>
<td><strong>Density (calculated), mg mm⁻³</strong></td>
</tr>
<tr>
<td><strong>Absorption coefficient, mm⁻¹</strong></td>
</tr>
<tr>
<td><strong>F(000)</strong></td>
</tr>
<tr>
<td><strong>Crystal size, mm³</strong></td>
</tr>
<tr>
<td><strong>Theta range for data collection</strong></td>
</tr>
<tr>
<td><strong>Index ranges</strong></td>
</tr>
<tr>
<td>-10 ≤ h ≤ 10,</td>
</tr>
<tr>
<td>-9 ≤ k ≤ 9,</td>
</tr>
<tr>
<td>-13 ≤ l ≤ 13</td>
</tr>
<tr>
<td><strong>Reflections collected</strong></td>
</tr>
<tr>
<td><strong>Independent reflections</strong></td>
</tr>
<tr>
<td><strong>Completeness to theta[27.55°]</strong></td>
</tr>
<tr>
<td><strong>Refinement method</strong></td>
</tr>
<tr>
<td><strong>Data/restraints/parameters</strong></td>
</tr>
<tr>
<td><strong>Goodness-of-fit on F²</strong></td>
</tr>
<tr>
<td><strong>Refine diff density_max</strong></td>
</tr>
<tr>
<td><strong>Refine diff density_min</strong></td>
</tr>
</tbody>
</table>
Table 5A2. Crystal data and structure refinement for [(CH₃)₄N][WO₅F₃]

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Empirical formula</td>
<td>C₄H₁₂N₁W₁OF₅</td>
</tr>
<tr>
<td>Formula weight, g mol⁻¹</td>
<td>369.00</td>
</tr>
<tr>
<td>Temperature, K</td>
<td>153(2)</td>
</tr>
<tr>
<td>Wavelength, pm</td>
<td>71.073</td>
</tr>
<tr>
<td>Crystal System</td>
<td>Tetragonal</td>
</tr>
<tr>
<td>Space group</td>
<td>P4/n</td>
</tr>
<tr>
<td>Angle-α,°</td>
<td>90°</td>
</tr>
<tr>
<td>Angle-β,°</td>
<td>90°</td>
</tr>
<tr>
<td>Angle-γ,°</td>
<td>90°</td>
</tr>
<tr>
<td>Unit cell dimensions, Å</td>
<td>a = 8.205(3)</td>
</tr>
<tr>
<td></td>
<td>b = 8.205(3)</td>
</tr>
<tr>
<td></td>
<td>c = 6.989(2)</td>
</tr>
<tr>
<td>Volume, 10² Å³</td>
<td>470.5(3)</td>
</tr>
<tr>
<td>Z</td>
<td>2</td>
</tr>
<tr>
<td>Density (calculated), mg mm⁻³</td>
<td>2.604</td>
</tr>
<tr>
<td>Absorption coefficient, mm⁻¹</td>
<td>12.311</td>
</tr>
<tr>
<td>F(000)</td>
<td>340</td>
</tr>
<tr>
<td>Crystal size, mm³</td>
<td>0.05 × 0.08 × 0.11</td>
</tr>
<tr>
<td>Theta range for data collection</td>
<td>2.92° – 27.47°</td>
</tr>
<tr>
<td>Index ranges</td>
<td>−10 ≤ h ≤ 10,</td>
</tr>
<tr>
<td></td>
<td>−10 ≤ k ≤ 10,</td>
</tr>
<tr>
<td></td>
<td>−9 ≤ l ≤ 9</td>
</tr>
<tr>
<td>Reflections collected</td>
<td>5020</td>
</tr>
<tr>
<td>Independent reflections</td>
<td>537 [R_{int} = 0.0514]</td>
</tr>
<tr>
<td>Completeness to theta [27.55°]</td>
<td>98.7%</td>
</tr>
<tr>
<td>Refinement method</td>
<td>Full matrix Least-squares on F²</td>
</tr>
<tr>
<td>Data/restraints/parameters</td>
<td>537 / 0 / 32</td>
</tr>
<tr>
<td>Goodness-of-fit on F²</td>
<td>1.105</td>
</tr>
<tr>
<td>Refine diff density_max</td>
<td>1.745</td>
</tr>
<tr>
<td>Refine diff density_min</td>
<td>−0.436</td>
</tr>
</tbody>
</table>
### Table 5A3. Crystal data and structure refinement for CH$_3$CN-WOF$_3$(OCH$_2$CF$_3$)

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Empirical formula</strong></td>
<td>C$_4$H$_5$N$_1$W$_1$O$_2$F$_6$</td>
</tr>
<tr>
<td><strong>Formula weight, g mol$^{-1}$</strong></td>
<td>396.94</td>
</tr>
<tr>
<td><strong>Temperature, K</strong></td>
<td>153(2)</td>
</tr>
<tr>
<td><strong>Wavelength, pm</strong></td>
<td>71.073</td>
</tr>
<tr>
<td><strong>Crystal System</strong></td>
<td>Monoclinic</td>
</tr>
<tr>
<td><strong>Space group</strong></td>
<td>$P2_1/c$</td>
</tr>
<tr>
<td><strong>Angle-$\alpha$,°</strong></td>
<td>90°</td>
</tr>
<tr>
<td><strong>Angle-$\beta$,°</strong></td>
<td>97.386(2)°</td>
</tr>
<tr>
<td><strong>Angle-$\gamma$,°</strong></td>
<td>90°</td>
</tr>
<tr>
<td><strong>Unit cell dimensions, Å</strong></td>
<td>$a = 8.1236(12)$</td>
</tr>
<tr>
<td></td>
<td>$b = 12.7219(19)$</td>
</tr>
<tr>
<td></td>
<td>$c = 8.9834(13)$</td>
</tr>
<tr>
<td><strong>Volume, 10$^2$ Å$^3$</strong></td>
<td>920.7(2)</td>
</tr>
<tr>
<td><strong>Z</strong></td>
<td>4</td>
</tr>
<tr>
<td><strong>Density (calculated), mg mm$^{-3}$</strong></td>
<td>2.864</td>
</tr>
<tr>
<td><strong>Absorption coefficient, mm$^{-1}$</strong></td>
<td>12.618</td>
</tr>
<tr>
<td><strong>F(000)</strong></td>
<td>720</td>
</tr>
<tr>
<td><strong>Crystal size, mm$^3$</strong></td>
<td>$0.10 \times 0.04 \times 0.21$</td>
</tr>
<tr>
<td><strong>Theta range for data collection</strong></td>
<td>$2.53° - 27.49°$</td>
</tr>
<tr>
<td><strong>Index ranges</strong></td>
<td>$-10 \leq h \leq 10,$</td>
</tr>
<tr>
<td></td>
<td>$-16 \leq k \leq 16,$</td>
</tr>
<tr>
<td></td>
<td>$-11 \leq l \leq 11$</td>
</tr>
<tr>
<td><strong>Reflections collected</strong></td>
<td>10600</td>
</tr>
<tr>
<td><strong>Independent reflections</strong></td>
<td>2117 [R$_{int} = 0.0664$]</td>
</tr>
<tr>
<td><strong>Completeness to theta[27.55°]</strong></td>
<td>99.8%</td>
</tr>
<tr>
<td><strong>Refinement method</strong></td>
<td>Full matrix Least-squares on F$^2$</td>
</tr>
<tr>
<td><strong>Data/restraints/parameters</strong></td>
<td>2117 / 0 / 129</td>
</tr>
<tr>
<td><strong>Goodness-of-fit on F$^2$</strong></td>
<td>1.109</td>
</tr>
<tr>
<td><strong>Refine diff density_max</strong></td>
<td>1.674</td>
</tr>
<tr>
<td><strong>Refine diff density_min</strong></td>
<td>$-1.680$</td>
</tr>
</tbody>
</table>
### Appendix – Chapter 6

Table 6A1. Crystal data and structure refinement for PFOA-H$_2$O

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Empirical formula</strong></td>
<td>C$_8$H$_3$O$<em>3$F$</em>{15}$</td>
</tr>
<tr>
<td><strong>Formula weight, g mol$^{-1}$</strong></td>
<td>432.10</td>
</tr>
<tr>
<td><strong>Temperature, K</strong></td>
<td>153(2)</td>
</tr>
<tr>
<td><strong>Wavelength, pm</strong></td>
<td>71.073</td>
</tr>
<tr>
<td><strong>Crystal System</strong></td>
<td>Monoclinic</td>
</tr>
<tr>
<td><strong>Space group</strong></td>
<td>$P2_1/c$</td>
</tr>
<tr>
<td><strong>Angle-$\alpha$,^\circ$</strong></td>
<td>90$^\circ$</td>
</tr>
<tr>
<td><strong>Angle-$\beta$,^\circ$</strong></td>
<td>91.215(8)$^\circ$</td>
</tr>
<tr>
<td><strong>Angle-$\gamma$,^\circ$</strong></td>
<td>90$^\circ$</td>
</tr>
<tr>
<td><strong>Unit cell dimensions, Å</strong></td>
<td></td>
</tr>
<tr>
<td>$a$</td>
<td>22.752(14)</td>
</tr>
<tr>
<td>$b$</td>
<td>5.309(3)</td>
</tr>
<tr>
<td>$c$</td>
<td>11.026(7)</td>
</tr>
<tr>
<td><strong>Volume, 10$^2$ Å$^3$</strong></td>
<td>1331.5(15)</td>
</tr>
<tr>
<td><strong>Z</strong></td>
<td>4</td>
</tr>
<tr>
<td><strong>Density (calculated), mg mm$^{-3}$</strong></td>
<td>2.155</td>
</tr>
<tr>
<td><strong>Absorption coefficient, mm$^{-1}$</strong></td>
<td>0.290</td>
</tr>
<tr>
<td><strong>F(000)</strong></td>
<td>840</td>
</tr>
<tr>
<td><strong>Crystal size, mm$^3$</strong></td>
<td>0.132 × 0.266 × 0.560</td>
</tr>
<tr>
<td><strong>Theta range for data collection</strong></td>
<td>2.92$^\circ$ – 27.47$^\circ$</td>
</tr>
<tr>
<td><strong>Index ranges</strong></td>
<td></td>
</tr>
<tr>
<td>–10 $\leq$ h $\leq$ 10,</td>
<td></td>
</tr>
<tr>
<td>–10 $\leq$ k $\leq$ 10,</td>
<td></td>
</tr>
<tr>
<td>–9 $\leq$ l $\leq$ 9</td>
<td></td>
</tr>
<tr>
<td><strong>Reflections collected</strong></td>
<td>5020</td>
</tr>
<tr>
<td><strong>Independent reflections</strong></td>
<td>537 [R$_{int}$ = 0.0514]</td>
</tr>
<tr>
<td><strong>Completeness to theta [27.55$^\circ$]</strong></td>
<td>98.7%</td>
</tr>
<tr>
<td><strong>Refinement method</strong></td>
<td>Full matrix Least-squares on F$_2$</td>
</tr>
<tr>
<td><strong>Data/restraints/parameters</strong></td>
<td>537 / 0 / 32</td>
</tr>
<tr>
<td><strong>Goodness-of-fit on F$^2$</strong></td>
<td>1.105</td>
</tr>
<tr>
<td><strong>Refine diff density_max</strong></td>
<td>1.745</td>
</tr>
<tr>
<td><strong>Refine diff density_min</strong></td>
<td>–0.436</td>
</tr>
<tr>
<td>Table 6A2. Crystal data and structure refinement for SPFO</td>
<td></td>
</tr>
<tr>
<td>---------------------------------------------------------</td>
<td></td>
</tr>
<tr>
<td><strong>Empirical formula</strong></td>
<td>C₈O₃F₁₅Na</td>
</tr>
<tr>
<td>Formula weight, g mol⁻¹</td>
<td>452.05</td>
</tr>
<tr>
<td>Temperature, K</td>
<td>153(2)</td>
</tr>
<tr>
<td>Wavelength, pm</td>
<td>71.073</td>
</tr>
<tr>
<td>Crystal System</td>
<td>Monoclinic</td>
</tr>
<tr>
<td>Space group</td>
<td>P2₁/c</td>
</tr>
<tr>
<td>Angle-α,°</td>
<td>90°</td>
</tr>
<tr>
<td>Angle-β,°</td>
<td>95.472(18)°</td>
</tr>
<tr>
<td>Angle-γ,°</td>
<td>90°</td>
</tr>
<tr>
<td>Unit cell dimensions, Å</td>
<td>a = 22.43(4)</td>
</tr>
<tr>
<td></td>
<td>b = 5.878(11)</td>
</tr>
<tr>
<td></td>
<td>c = 9.626(17)</td>
</tr>
<tr>
<td>Volume, 10² Å³</td>
<td>1263.0(4)</td>
</tr>
<tr>
<td>Z</td>
<td>4</td>
</tr>
<tr>
<td>Density (calculated), mg mm⁻³</td>
<td>2.291</td>
</tr>
<tr>
<td>Absorption coefficient, mm⁻¹</td>
<td>0.318</td>
</tr>
<tr>
<td>F(000)</td>
<td>828</td>
</tr>
<tr>
<td>Crystal size, mm³</td>
<td>0.126 × 0.147 × 0.409</td>
</tr>
<tr>
<td>Theta range for data collection</td>
<td>1.82° – 18.30°</td>
</tr>
<tr>
<td>Index ranges</td>
<td>−19 ≤ h ≤ 19,</td>
</tr>
<tr>
<td></td>
<td>−105 ≤ k ≤ 5,</td>
</tr>
<tr>
<td></td>
<td>−8 ≤ l ≤ 8</td>
</tr>
<tr>
<td>Reflections collected</td>
<td>4967</td>
</tr>
<tr>
<td>Independent reflections</td>
<td>913 [R(int) = 0.0946]</td>
</tr>
<tr>
<td>Completeness to theta [27.55°]</td>
<td>99.7%</td>
</tr>
<tr>
<td>Refinement method</td>
<td>Full matrix Least-squares on F²</td>
</tr>
<tr>
<td>Data/restraints/parameters</td>
<td>913 / 0 / 236</td>
</tr>
<tr>
<td>Goodness-of-fit on F²</td>
<td>1.421</td>
</tr>
<tr>
<td>Refine diff density_max</td>
<td>0.253</td>
</tr>
<tr>
<td>Refine diff density_min</td>
<td>−0.222</td>
</tr>
<tr>
<td>Property</td>
<td>Value</td>
</tr>
<tr>
<td>--------------------------------------</td>
<td>------------------------------------------------</td>
</tr>
<tr>
<td>Empirical formula</td>
<td>C_{10}H_{13}O_{3}F_{19}</td>
</tr>
<tr>
<td>Formula weight, g mol(^{-1})</td>
<td>532.12</td>
</tr>
<tr>
<td>Temperature, K</td>
<td>153(2)</td>
</tr>
<tr>
<td>Wavelength, pm</td>
<td>71.073</td>
</tr>
<tr>
<td>Crystal System</td>
<td>Monoclinic</td>
</tr>
<tr>
<td>Space group</td>
<td>(P2_1/c)</td>
</tr>
<tr>
<td>Angle-(\alpha)(^{\circ})</td>
<td>90(^{\circ})</td>
</tr>
<tr>
<td>Angle-(\beta)(^{\circ})</td>
<td>95.350(4)(^{\circ})</td>
</tr>
<tr>
<td>Angle-(\gamma)(^{\circ})</td>
<td>90(^{\circ})</td>
</tr>
<tr>
<td>Unit cell dimensions, Å</td>
<td>a = 27.035(10) \hspace{1cm} b = 5.396(2) \hspace{1cm} c = 10.944(4)</td>
</tr>
<tr>
<td>Volume, (10^2) Å(^3)</td>
<td>1589.6(11)</td>
</tr>
<tr>
<td>(Z)</td>
<td>4</td>
</tr>
<tr>
<td>Density (calculated), mg mm(^{-3})</td>
<td>2.223</td>
</tr>
<tr>
<td>Absorption coefficient, mm(^{-1})</td>
<td>0.300</td>
</tr>
<tr>
<td>(F(000))</td>
<td>1032</td>
</tr>
<tr>
<td>Crystal size, mm(^3)</td>
<td>0.106 × 0.218 × 0.778</td>
</tr>
<tr>
<td>Theta range for data collection</td>
<td>2.27(^{\circ}) – 27.47(^{\circ})</td>
</tr>
<tr>
<td>Index ranges</td>
<td>(-34 \leq h \leq 34,) \hspace{1cm} (-6 \leq k \leq 6,) \hspace{1cm} (-14 \leq l \leq 14)</td>
</tr>
<tr>
<td>Reflections collected</td>
<td>16265</td>
</tr>
<tr>
<td>Independent reflections</td>
<td>3589 [R(int) = 0.0407]</td>
</tr>
<tr>
<td>Completeness to theta [27.55(^{\circ})]</td>
<td>99.0%</td>
</tr>
<tr>
<td>Refinement method</td>
<td>Full matrix Least-squares on (F^2)</td>
</tr>
<tr>
<td>Data/restraints/parameters</td>
<td>3589 / 0 / 302</td>
</tr>
<tr>
<td>Goodness-of-fit on (F^2)</td>
<td>1.108</td>
</tr>
<tr>
<td>Refine diff density_max</td>
<td>0.660</td>
</tr>
<tr>
<td>Refine diff density_min</td>
<td>(-0.565)</td>
</tr>
</tbody>
</table>
Table 6. Crystal data and structure refinement for SPFB

<table>
<thead>
<tr>
<th>Empirical formula</th>
<th>C₄F₇O₂Na</th>
</tr>
</thead>
<tbody>
<tr>
<td>Formula weight, g mol⁻¹</td>
<td>236.02</td>
</tr>
<tr>
<td>Temperature, K</td>
<td>153(2)</td>
</tr>
<tr>
<td>Wavelength, pm</td>
<td>71.073</td>
</tr>
<tr>
<td>Crystal System</td>
<td>Monoclinic</td>
</tr>
<tr>
<td>Space group</td>
<td>P2₁/c</td>
</tr>
<tr>
<td>Angle-α,°</td>
<td>90°</td>
</tr>
<tr>
<td>Angle-β,°</td>
<td>99.069(8)°</td>
</tr>
<tr>
<td>Angle-γ,°</td>
<td>90°</td>
</tr>
<tr>
<td>Unit cell dimensions, Å</td>
<td>a = 25.99(2)</td>
</tr>
<tr>
<td></td>
<td>b = 6.113(5)</td>
</tr>
<tr>
<td></td>
<td>c = 9.181(7)</td>
</tr>
<tr>
<td>Volume, 10² Å³</td>
<td>1440.4(19)</td>
</tr>
<tr>
<td>Z</td>
<td>4</td>
</tr>
<tr>
<td>Density (calculated), mg mm⁻³</td>
<td>1.048</td>
</tr>
<tr>
<td>Absorption coefficient, mm⁻¹</td>
<td>0.326</td>
</tr>
<tr>
<td>F(000)</td>
<td>912</td>
</tr>
<tr>
<td>Crystal size, mm³</td>
<td>0.106 × 0.109 × 0.263</td>
</tr>
<tr>
<td>Theta range for data collection</td>
<td>1.59° – 21.30°</td>
</tr>
<tr>
<td>Index ranges</td>
<td>–26 ≤ h ≤ 21,</td>
</tr>
<tr>
<td></td>
<td>–6 ≤ k ≤ 6,</td>
</tr>
<tr>
<td></td>
<td>–9 ≤ l ≤ 9</td>
</tr>
<tr>
<td>Reflections collected</td>
<td>2333</td>
</tr>
<tr>
<td>Independent reflections</td>
<td>806 [R(int) = 0.0279]</td>
</tr>
<tr>
<td>Completeness to theta [27.55°]</td>
<td>99.1%</td>
</tr>
<tr>
<td>Refinement method</td>
<td>Full matrix Least-squares on F²</td>
</tr>
<tr>
<td>Data/restraints/parameters</td>
<td>806 / 0 / 128</td>
</tr>
<tr>
<td>Goodness-of-fit on F²</td>
<td>3.078</td>
</tr>
<tr>
<td>Refine diff density_max</td>
<td>0.384</td>
</tr>
<tr>
<td>Refine diff density_min</td>
<td>–0.254</td>
</tr>
</tbody>
</table>