

DONOR-STABILISED FLUORIDO CATIONS OF GROUPS 15 AND 16

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Abstract

The fluoride-ion donor properties of the strong Lewis-acids SbF_5 and AsF_5 were investigated. In the presence of the bidentate nitrogen base 1,10-phenanthroline (phen) SbF_5 and AsF_5 were found to autoionise generating $[\text{PnF}_4(\text{phen})][\text{PnF}_6]$ ($\text{Pn} = \text{As}$ or Sb) salts; this is the first time that SbF_5 has demonstrated the ability to act as a fluoride-ion donor. In the presence of the more flexible nitrogen base 2,2'-bipyridine (bipy), SbF_5 was again found to autoionise yielding $[\text{SbF}_4(\text{bipy})][\text{SbF}_6]$, whereas AsF_5 forms the neutral adduct $(\text{AsF}_5)_2 \cdot \text{bipy}$. In the presence of the tridentate base 2,2':6',2''-terpyridine (terpy) SbF_5 autoionises to form $[\text{SbF}_4(\text{terpy})][\text{SbF}_6]$; the $[\text{SbF}_4(\text{terpy})]^+$ cation is the first structurally characterised fluoro $\text{Sb}(\text{V})$ complex with a coordination number of seven and adopts a heavily distorted pentagonal bipyramidal geometry. The structure and bonding in these unique systems was studied using a combination of spectroscopic, crystallographic and computational techniques.

The $[\text{SF}_3]^+$ cation forms 1:1 adducts with pyridine and 4-dimethylaminopyridine (DMAP) which adopt different structures. Whereas pyridine coordinates in the axial position of the seesaw-geometry, DMAP is located in the equatorial position. The latter structure leads to facile dismutation to the $[\text{SF}_2(\text{dmap})_2]^{2+}$ cation and SF_4 , while $[\text{SF}_3(\text{py})]^+$ is stable towards dismutation. Further dismutation afforded the square-pyramidal $[\text{SF}(\text{dmap})_4]^{3+}$ cation. Attempts to form adducts of $[\text{SF}_3]^+$ cation with triphenylphosphine oxide, resulted in deoxofluorination.

Contributions of Authors

The following research chapters have been based on the following publications, the contents of which are reproduced with permission from the corresponding publishers:

Chapter 2 – O'Donnell, F.; Turnbull, D.; Wetmore, S. D.; Gerken, M. *Chem. - A Eur. J.*, **2021**, 27, 16334–16337.

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In Chapter 2 I am responsible for all of the synthesis, spectroscopic characterisation and computational work. D. T. performed the crystallographic characterisation. S. D. W. provided guidance for the computational work.

In Chapters 3 & 4 I am responsible for all of the experimental and computational work. S. D. W. provided guidance for the computational work.

In Chapter 5 P. C. synthesised and characterised the $[\text{SF}_2(\text{dmap})_2][\text{SbF}_6]_2$ salt and obtained the crystal structure of $[\text{SF}(\text{dmap})_4][\text{SbF}_6]_3$. Y. Y. performed preliminary work studying the direct combination of $[\text{SF}_3][\text{AsF}_6]$ with an equimolar amount of pyridine. I am responsible for all the other experimental work in this chapter. D. T. performed the DLPNO-CCSD(T)

calculations for which I analysed and interpreted the results, I am responsible for all of the other computational work in this chapter. S. D. W. provided guidance for the computational work.

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List of Abbreviations

General

A	central atom
AIM	atoms in molecules
ax	axial
DFT	density functional theory
E	lone pair domain
e	elementary charge
eq	equatorial
eq.	equation
FEP	tetrafluoroethene-hexafluoropropene copolymer
FIA	fluoride-ion affinity
HOMO	highest occupied molecular orbital
LUMO	lowest unoccupied molecular orbital
Pn	group 15 element
NBO	natural bond orbital
NPA	natural population analysis
QTAIM	quantum theory of atoms in molecules
RT	room temperature
VSEPR	valence shell electron pair repulsion
WBI	Wiberg bond index
X	bonding pair domain

Ligands/solvents

aHF	anhydrous hydrogen fluoride
bipy	bipyridine
DMAP	4-dimethylaminopyridine
DMF	dimethylformamide
DMSO	dimethyl sulfoxide
f-bipy	fluro-bipyridine

phen	1,10-phenanthroline
py	pyridine
terpy	2,2';6',2''-terpyridine
NMR Spectroscopy	
d	doublet
I	nuclear spin quantum number
J	scalar coupling constant
m	multiplet
NMR	nuclear magnetic resonance
ppm	parts per million
s	singlet
t	triplet
δ	chemical shift
X-ray Crystallography	
a, b, c, α , β , γ	cell dimensions
F(000)	electrons per unit cell
GooF	goodness of fit
R1	R-factor (agreement index)
T	temperature
V	cell volume
wR2	weighted R-factor
Z	molecules per unit cell
λ	wavelength
μ	absorption coefficient
ρ_{calc}	calculated density

Chapter 1–Introduction

1.1 Valence Shell Electron Pair Repulsion Model

The understanding of molecular geometry is a foundational aspect of modern inorganic chemistry, as the geometry of a species influences its reactivity and physical properties. Among the most useful tools for predicting and rationalising geometries in main-group compounds is the Valence Shell Electron Pair Repulsion (VSEPR) model. The VSEPR model, originally developed by Gillespie and Nyholm in 1957,¹ predicts molecular geometries based on the repulsion between electron pair domains around a central atom. The model classifies molecular shapes using the AXE notation, where A is the central atom, X represents bonding pair domains, and E denotes lone pair domains.

Although initially empirical, VSEPR has been supported by quantum mechanical calculations that confirm the spatial arrangement of electron density.² However, its limitations become evident outside the p-block where d or f-orbital participation can play a significant role in bonding. For example, transition metal fluoro complexes often involve d-orbital participation, which can lead to distinct bonding features, such as ligand field stabilisation, π -backbonding (the fluoro ligands do not participate in π -backbonding), and unique electronic transitions.

X-ray crystallography remains the usual gold standard for determining solid-state structures and confirming geometric predictions made by the VSEPR model, while other structural characterisation techniques are also available and can provide detailed geometric information, such as gas-phase electron diffraction, neutron diffraction and, more recently,

electron crystallography. X-ray crystallography can provide accurate bond lengths, angles, and coordination numbers, crucial for evaluating the predictions of the VSEPR model. In the absence of X-ray diffraction data spectroscopic methods can also provide valuable insights into the geometry of a specific complex. Of particular use is multinuclear NMR spectroscopy which allows for the identification of specific parts of a molecule and how those individual parts connect together in order to build a complete model for the compound. There are two key observables from NMR spectroscopy that aid in the structural determination of a compound, the first is chemical shift (δ). A chemical shift is the resonance frequency of a nucleus in a magnetic field relative to a reference compound. Structural features of the molecule affect the precise magnitude of the magnetic field experienced by a specific nucleus; this means that nuclei in different chemical environments will give rise to different chemical shifts. Chemical shifts provide a lot of insight into the local electronic environment around a nucleus such as the bonding and hybridisation state. The second key observable is spin-spin coupling (J), which is the interaction of magnetically non-equivalent nuclear spins through chemical bonds. Magnetically non-equivalent neighbouring nuclear spins generate their own magnetic fields which can either align with or against the external field. This leads to multiple effective magnetic fields experienced by the nucleus of interest, which, in turn, leads to multiple resonant frequencies splitting the signal observed in the NMR spectrum into multiple lines. The multiplicity of the resultant signal is given by the equation $2nI+1$ (n = number of interacting neighbouring spins, I = nuclear spin quantum number of the interacting neighbouring spins). The magnitude of J , reported in Hz, depends on the number of bonds and the dihedral angle between the interacting spins. Based on the

multiplicity of the signals and the magnitude of J it is possible to elucidate the connectivity of the different chemical environments. The structural determination of a compound using NMR spectroscopy is complicated by dynamic effects such as the intramolecular exchange of distinct chemical environments which can cause the averaging of multiple resonances into a single resonance, with each chemical environment no longer showing a distinct chemical shift. Exchange can also cause substantial line broadening; so, the multiplicity of the signals is no longer visible precluding the measurement of J values. The infrared (IR) and Raman spectroscopies are also useful as they provide important information about the symmetry of the structure. Computational methods such as Density Functional Theory (DFT) and related methods are indispensable in modern structural chemistry. They allow for geometry optimisation, vibrational analysis, and detailed bonding analysis (*e.g.*, natural bond orbital (NBO) and quantum theory of atoms in molecules (QTAIM)). Computational studies have clarified the nature of bonding in main-group fluorido species, confirming the presence of three centre-four electron (3c-4e) bonds and validating the predictions of the VSEPR model.

1.2. Four-Coordinate Main-Group Fluorido Complexes

Four-coordinate fluorido complexes of main-group elements exhibit three primary geometries that are well explained by the VSEPR model and supported by experimental and computational studies. These include tetrahedral (AX_4), disphenoidal/seesaw (AX_4E) and square planar (AX_4E_2) (Figure 1.1).

The tetrahedral geometry is the most common and occurs when a main-group element forms four equivalent M–F bonds without lone pairs on the central atom. Notable examples include $[\text{BF}_4]^-$, SiF_4 , and CF_4 , which adopt nearly ideal tetrahedral structures. Crystallographic data show B–F bond distances around 1.40 Å in $[\text{BF}_4]^-$ and Si–F distances of ~1.54 Å in SiF_4 , with minimal bond angle distortions.³

In cases where one lone pair is present as in the group-16 tetrafluorides SF_4 and SeF_4 , the structure becomes seesaw-shaped (AX_4E). The VSEPR model predicts that the lone pair occupies an equatorial position of a trigonal bipyramid to minimise repulsion. Experimental confirmation of the seesaw structure in SF_4 and SeF_4 comes from X-ray diffraction studies, where two fluorido ligands occupy axial positions and two occupy equatorial positions with the third equatorial position being occupied by the stereochemically active lone pair.^{4,5} Interestingly the heavier chalcogen tetrafluoride TeF_4 is polymeric in the solid state where TeF_3^+ units are bridged by two F^- ions. Spectroscopic evidence reinforces these structural assignments. Tetrahedral species show a single sharp ^{19}F NMR resonance, while AX_4E geometries display separate resonances due to axial and equatorial F environments at low temperatures. However, AX_4E molecules frequently display only a single resonance at ambient temperature due to Berry pseudorotation, which is an intramolecular exchange of the axial and equatorial environments.

In cases where two lone pairs are present as in XeF_4 the structure becomes square planar (AX_4E_2) where the central atom and the surrounding atoms are all coplanar.⁶ This geometry is rare in main-group compounds but is more common in transition metal complexes especially for d^8 metals where favourable ligand field stabilisation energies

prefer this geometry over tetrahedral geometry. A classic example of a square planar transition metal complex is *cis*-platin $[(\text{Cl})_2\text{Pt}(\text{NH}_3)_2]$ which features a Pt^{2+} (d^8) centre.⁷

From a bonding model perspective, tetrahedral fluorides like $[\text{BF}_4]^-$ and CF_4 are best described with localised sp^3 hybrid orbitals. Heavier analogues like SnF_4 display more ionic character. In AX_4E species like SeF_4 the equatorial bonds are best described with localised sp^2 hybrid orbitals while the axial bonds are better described by a three-centre four-electron (3c-4e) bonding model.⁸

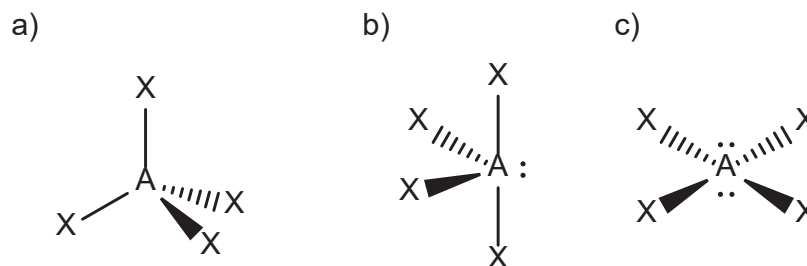


Figure 1.1. Three possible four-coordinate geometries predicted by VSEPR: (a) tetrahedral, (b) disphenoidal/seesaw, and (c) square planar.

1.3 Five-Coordinate Main-Group Fluorido Complexes

Five-coordinate main-group fluorido complexes predominantly adopt either trigonal bipyramidal or square pyramidal geometries (Figure 1.2). The determining factor between these geometries is often the presence of lone pairs, ligand sterics, and electronic effects.

Trigonal bipyramidal geometries are exemplified by PF_5 and AsF_5 , both of which display rapid pseudorotation in the gas phase. X-ray diffraction confirms ideal trigonal bipyramidal geometry in the solid state, with axial M–F bonds typically being longer. For

instance, in PF_5 , the axial P–F bond lengths are 1.593(5) Å while equatorial bonds are slightly shorter (1.538(5) Å).⁹ In species like PF_5 , the bonding is best described via 3c-4e interactions among the central atom and axial fluorines leading to more ionic axial P–F bonds causing the elongation of these bonds as seen in the solid-state structure.

In contrast, square pyramidal geometries emerge when one lone pair is present (AX_5E). The classic example for such species is IF_5 , which exhibits I–F bond lengths ranging from 1.75(3)–1.97(3) Å, with a shorter apical I–F bond length *trans* to the lone pair.¹⁰ The presence of the apical lone pair causes a displacement of the basal fluorido ligands away from the lone pair leading to a slight contraction of the $\text{F}_{\text{apical}}\text{--I--F}_{\text{basal}}$ angle (81.9(4)°) compared to the idealised value of 90°.

Computational analyses support these interpretations. DFT studies of IF_5 and PF_5 show good agreement with experimental geometries and identify low-lying transition states for pseudorotation in PF_5 .^{11,12} Natural population analyses reveal significant electron density in nonbonding orbitals of IF_5 , validating the role of stereochemically active lone pairs in shaping geometry.¹³

Compounds of the form AX_5E_2 are also known, but rare, and are best exemplified by $[\text{XeF}_5]^-$ which adopts a pentagonal planar geometry with all five atoms being coplanar with each other. The Xe–F distances are 1.979(2)–2.034(2) Å and the bond angles all lie close to the idealised value of 72°.¹⁴

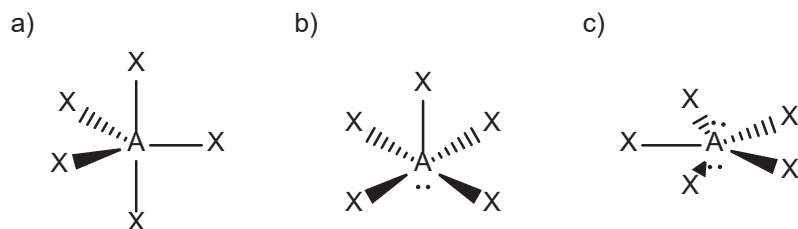


Figure 1.2. Three possible five-coordinate geometries predicted by VSEPR: (a) trigonal bipyramidal, (b) square pyramidal, and (c) pentagonal planar.

1.4 Six-Coordinate Complexes

Octahedral (AX_6) geometries dominate six-coordinate fluoro species, particularly for group 16 compounds such as sulfur (SF_6), selenium (SeF_6) and tellurium hexafluorides (TeF_6). Among these, SF_6 is a textbook example of a perfectly symmetrical octahedron with equivalent S–F bond lengths 1.561(3) Å and no lone pairs.¹⁵ The molecule is electronically saturated and highly inert, consistent with its use as a dielectric gas and its low reactivity. In contrast, the group-18 analogue XeF_6 in the gas-phase adopts distorted octahedral geometries due to the presence of a stereochemically active lone pair (Figure 1.3). Xenon hexafluoride, formally AX_6E , is often described as a distorted octahedron or a monocapped octahedron, depending on the interpretation of the lone pair's spatial influence.¹⁶ In solution XeF_6 is found to form fluorine-bridged $[XeF_6]_4$ tetramers and in the solid state it forms tetramers or hexamers of $[XeF_5]^+$ linked by F^- . In some AX_6E systems it has been observed that the lone pair is no longer stereochemically active and does not seem to influence the geometry as would be expected in the classic VSEPR model, resulting in octahedral species.^{17,18} For example, $[BrF_6]^-$ adopts the octahedral geometry while $[IF_6]^-$ adopts a distorted monocapped octahedral geometry similar to that observed in XeF_6 .¹⁹ Christie and co-workers rationalised this result on a purely steric basis arguing that the Br atom in

$[\text{BrF}_6]^-$ is coordinatively saturated and unable to accommodate a seventh ligand/electron group around it, forcing the lone pair to be sterically inactive.²⁰ In contrast, the larger iodine atom has been shown to be able to accommodate up to eight fluorido ligands as seen in the $[\text{IF}_8]^-$ anion, therefore, there is enough space around the central I atom for the lone pair to be sterically active. In contrast Seppelt offered an electronic argument stating that the 4s electrons of Br in $[\text{BrF}_6]^-$ are strongly bound as a result of poor shielding of the nuclear charge from the filled 3d orbitals.²¹ Thus, the 4s electrons are effectively “core-like” and not engaged in bonding to the fluorido ligands in $[\text{BrF}_6]^-$ which occurs exclusively through the three 4p orbitals for which a regular octahedral geometry would be expected. Intrinsic bond orbital calculations support this hypothesis predicting that the 4s contribution to Br–F bonds are 37% in $[\text{BrF}_6]^+$, dropping to 20% for the axial Br–F bond and 3% for the equatorial bonds in BrF_5 and 0% in $[\text{BrF}_6]^-$.¹⁹ DFT calculations predict that a $[\text{BrF}_6]^-$ structure with perfect O_h point group symmetry is a minimum, while in $[\text{IF}_6]^-$ the minimum was found to a C_1 symmetric structure while the O_h structure was found to be a transition state and 14 kJ mol⁻¹ higher in energy.

Another possible six-coordinate geometry is trigonal prismatic. While molecular main-group compounds tend not to adopt this geometry, it is seen primarily in complexes with high-oxidation-state transition metals such as the hexamethyl transition metal compounds $\text{W}(\text{CH}_3)_6$ and $\text{Re}(\text{CH}_3)_6$. In these systems the trigonal prismatic geometry improves overlap between ligand orbitals and metal d-orbitals, it particularly improves the agostic C–H→M interactions which help stabilise the structure.^{22–24}

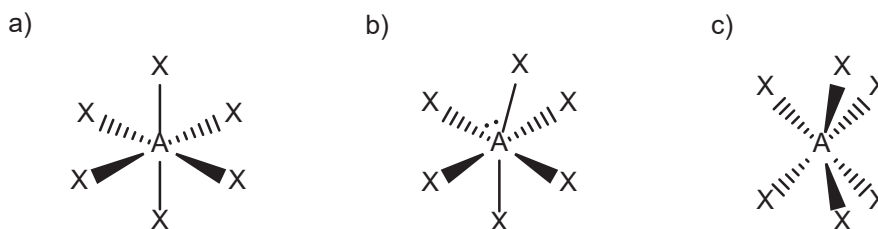


Figure 1.3. Three possible six-coordinate geometries predicted by VSEPR: (a) octahedral, (b) distorted octahedral geometry like that observed in $\text{XeF}_{6(g)}$, and (c) trigonal prismatic.

1.5 Seven-Coordinate Complexes

Seven-coordinate main-group complexes are rare, as a majority of main-group elements are not large enough to accommodate seven ligands around them. The most studied example of a heptacoordinate main-group compound is IF_7 , which adopts a pentagonal bipyramidal geometry (Figure 1.4), as predicted by VSEPR (AX_7). Due to the high level of ligand congestion in the equatorial plane the I-F_{eq} bonds are notably elongated compared to the I-F_{ax} bonds.²⁵ The structure was found to be highly fluxional undergoing a dynamic puckering of the congested pentagonal plane, it was also found to undergo Bartell pseudorotation in solution where the axial and equatorial environments exchange similar to Berry pseudorotation observed in trigonal bipyramidal species causing an equivalence of the two environments in ^{19}F NMR experiments. The same geometry is also observed in the crystal structure of the isoelectronic anion $[\text{TeF}_7]^-$. While $[\text{SbF}_7]^{2-}$ has not been structurally characterised, vibrational spectroscopy and quantum chemical calculations predict it also adopts a pentagonal bipyramidal geometry.²⁶⁻³⁰ In contrast the heptacoordinate transition metal fluorides $[\text{MoF}_7]^-$ and $[\text{WF}_7]^-$ adopt monocapped octahedral geometries.³¹ The $[\text{XeF}_7]^-$ anion in $[\text{Cs}][\text{XeF}_7]$ is an example of a main-group species which adopts a monocapped octahedral geometry; however, the Xe^{VI} centre still

possesses a valence lone pair, which is stereochemically inactive.³² The related $[\text{Xe}_2\text{F}_{13}]^-$ anion which can be described as a XeF_6 molecule bridged by two long Xe–F bonds to an $[\text{XeF}_7]^-$ anion, where the $[\text{XeF}_7]^-$ anion in this system adopts a monocapped trigonal prismatic geometry.

Computational investigations underscore the challenges in stabilising seven-coordinate geometries. DFT and ab initio calculations reveal the importance of dispersion and relativistic corrections, especially for heavier elements.³³ Natural bond orbital (NBO) and atoms-in-molecules (AIM) analyses confirm the dominance of polar covalent interactions and the secondary role of non-bonding electron density in shaping geometry.³⁴

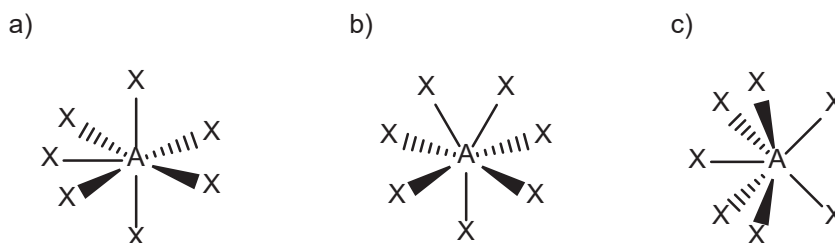


Figure 1.4. Three possible seven-coordinate geometries predicted by VSEPR: (a) pentagonal bipyramidal, (b) monocapped octahedral, and (c) monocapped trigonal prismatic.

Overall, the primary differences between main-group fluorides and transition metal fluorides stem from the electronic structure of the central atom, main-group fluoro complexes emphasise electron-pair repulsion and multicentred bonding, while transition metal complexes reflect the dominance of d-orbital ligand field effects.

1.6 Main-group Fluorido Cations Stabilised by Neutral Donors

Cations by their very nature are electron deficient. Fluorido ligands, due to their high electronegativity and polarising power, exacerbate this electrophilicity, increasing the reactivity of these cations. A variety of cationic fluorido species can be prepared via the use of strong fluoride-ion acceptors, such as BF_3 or SbF_5 . In some of the resulting compounds, such as $[\text{SF}_3][\text{BF}_4]$ and $[\text{XeF}][\text{SbF}_6]$, strong cation-anion interactions are presents, and such species cannot be described as purely ionic compounds with ‘naked’ fluorido cations. Therefore, to facilitate the isolation and study of these reactive cationic species it is useful to try to quench this electrophilicity. One highly effective method to achieve this is the use a neutral Lewis base which can donate electron density to the cationic centre and stabilise it. Examples of this method are discussed below and show how this is an effective strategy which has been used throughout the p-block.

Group 13 (B, Al)

Three-coordinate boron cations (borenium cations) with terminal fluorido ligands (difluoroborenium species) require strong donors for stabilisation. The use of hexaphenyl carbodiphosphorane ($\text{C}(\text{PPh}_3)_2$, CDP) allows for the stabilisation of the highly reactive difluoroborenium $[\text{CDP}-\text{BF}_2]^+$ cation (Figure 1.5) reported by Münzer *et al.*³⁵ X-ray crystallography shows a planar boron centre bonded to two fluorido ligands and the carbon donor of CDP, with B–F distances 1.326(4)–1.336(4) Å and a C–B bond length of 1.514(4) Å, and a F–B–F bond angle of 114.0°. In 2016, Levason, Reid and co-workers utilised the autoionisation of BF_3 in the presence of bidentate phosphines and arsines to form $[\text{BF}_2\{o\text{-C}_6\text{H}_4(\text{PMe}_2)_2\}][\text{BF}_4]$ and $[\text{BF}_2\{o\text{-C}_6\text{H}_4(\text{AsMe}_2)_2\}][\text{BF}_4]$ which feature four-coordinate boron centres.³⁶ They fortuitously obtained a crystal of $[\text{BF}_2\{o\text{-C}_6\text{H}_4(\text{PMe}_2)_2\}][\text{B}_2\text{F}_7]$

which contains B–F bond lengths (1.353(5) Å) that are longer than those found in the $[\text{CDP-BF}_2]^+$ cation reflective of the higher coordination number. Displacement reactions of $\text{py} \cdot \text{BF}_2\text{X}$ (py = pyridine; X = Cl or Br) with an excess of pyridine leads to $[\text{py}_2 \cdot \text{BF}_2]^+$ cations; pyridine can subsequently be displaced by a bidentate ligand giving the $[\text{BF}_2\{\text{Me}_2\text{N}(\text{CH}_2)_2\text{NMe}_2\}]^+$ cation.³⁷⁻³⁹

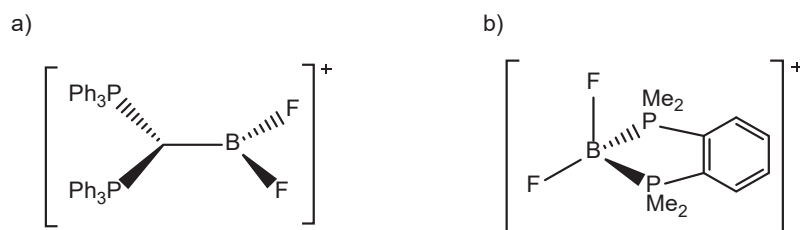
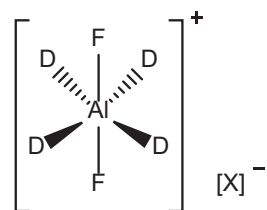


Figure 1.5. Structures of (a) $[\text{CDP-BF}_2]^+$ and (b) $[\text{BF}_2\{\text{o-C}_6\text{H}_4(\text{PMe}_2)_2\}]^+$.

Aluminium(III) can also form difluorido cations, which are more common than the boron analogues. Fluoride-ion abstraction or exchange reactions can produce $[\text{AlF}_2]^+$ adducts. Kemnitz *et al.* first showed that $(\text{CH}_3)_3\text{SiF}$ fluorination of $\text{AlCl}_3 \cdot 3\text{py}$ in pyridine solvent replaces two Cl by F, yielding crystalline $[\text{AlF}_2(\text{py})_4][\text{Cl}]$, an ionic salt with a $[(\text{py})_4\text{AlF}_2]^+$ cation.⁴⁰ In the solid state, the Al centre is octahedral (*trans*- AlF_2 unit with 4 equatorial py as shown in Figure 1.6). The ^{19}F solid-state NMR spectrum shows a dramatic change: the quadrupolar coupling for ^{27}Al in $[(\text{py})_4\text{AlF}_2]^+$ is ≈ 16 MHz versus only 0.24 MHz in the isostructural $[(\text{py})_4\text{AlCl}_2]^+$. This reflects the much higher electronegativity of F compared to Cl. Building on this, $[\text{AlF}_2(\text{py})_4][\text{Br}]$ and $[\text{AlF}_2(\text{py})_4][\text{I}]$ were made similarly. All have the same octahedral *trans*- $[\text{AlF}_2(\text{py})_4]^+$ cation. The hydrated species $[\text{AlF}_2(\text{H}_2\text{O})_4]^+$ was crystallographically identified.⁴¹ It is formed by hydrolysing $[\text{AlF}_2(\text{py})_4]^+$ and retains the *trans* configuration of the F–Al–F unit. The X-ray crystal structure shows four water ligands in an approximate square plane and two *trans* fluorido

ligands. This confirms that even weaker donors like H₂O can stabilise [AlF₂]⁺. To date no structurally characterised cations derived from gallium, indium or thallium have been reported.



D = pyridine or H₂O.
X = Cl, Br, I

Figure 1.6. Structure of [AlF₂D₄][X] salts.

Group 14 (Si, Ge, Sn)

The autoionisation of SiF₄ in the presence of 1,4,7-trimethyl-1,4,7-triazacyclononane (Me₃tacn) forms the [SiF₃(Me₃tacn)][SiF₅] salt.⁴² This is a rather unexpected result as the displacement of F⁻ by neutral ligands is occurring under such mild conditions. The [SiF₃(Me₃tacn)]⁺ cation adopts a distorted octahedral geometry with the tridentate Me₃tacn ligand coordinating facially (Figure 1.7). The cation contains crystallographic threefold rotational symmetry resulting in all the Si–F bond lengths being equivalent (1.629(3) Å).

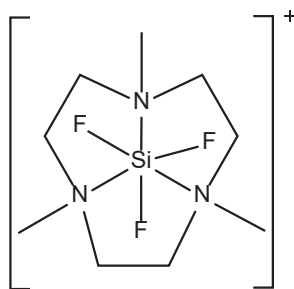


Figure 1.7. Structure of [SiF₃(Me₃tacn)]⁺.

The reaction of $\text{GeF}_4(\text{PMe}_3)_2$ with $(\text{CH}_3)_3\text{SiO}_3\text{SCF}_3$ (TMSOTf) yields neutral compounds of the form $[\text{GeF}_{4-n}(\text{PMe}_3)_2(\text{OTf})_n]$ ($n = 1-3$). The trifluorido germanium compound $[\text{GeF}_3(\text{PMe})_2(\text{OTf})]$ undergoes rapid reductive defluorination in solution to produce the Ge(II) salt $[\text{Ge}(\text{PMe}_3)_3][\text{OTf}]_2$ featuring a Ge^{2+} centre and $[\text{FPMe}_3]^+$ and other unidentified by-products. The use of the bulkier phosphine ligand P^iPr_3 leads to an ionic species $[\text{GeF}_3(\text{P}^i\text{Pr}_3)_2][\text{OTf}]$ featuring a trigonal bipyramidal $[\text{GeF}_3(\text{P}^i\text{Pr}_3)_2]^+$ cation.⁴³ The use of the bidentate phosphine $o\text{-C}_6\text{H}_4(\text{PMe}_2)_2$ produces a similar result to the PMe_3 system with trifluorido species being unstable towards reductive defluorination in solution producing $[\text{Ge}(o\text{-C}_6\text{H}_4(\text{PMe}_2)_2)_2(\text{OTf})][\text{OTf}]$. Similar reactions between $\text{GeF}_4 \cdot 2\text{CH}_3\text{CN}$ and neutral oxygen and nitrogen donor ligands with TMSOTf in a 1:1:1 stoichiometry generate $[\text{GeF}_3(\text{L})_2][\text{OTf}]$ ($\text{L} = \text{DMSO}, \text{DMF}, \text{py}, \text{pyridine N-oxide}, \text{OPPh}_3 \text{ and } \text{OPMe}_3$) salts with no evidence of reductive defluorination occurring.⁴⁴ The reaction of $[\text{GeF}_4(\text{MeCN})_2]$ with TMSOTf in CH_2Cl_2 solution, followed by the addition of 2,2':6',2''-terpyridine (terpy) formed *mer*- $[\text{GeF}_3(\text{terpy})][\text{OTf}]$, whilst a similar reaction with $\text{Me}_3\text{-tacn}$ in CH_3CN solution produced *fac*- $[\text{GeF}_3(\text{Me}_3\text{-tacn})][\text{OTf}]$. The use of tetraaza macrocycles such as 1,4,7,10-tetramethyl-1,4,7,10-tetra-azacyclododecane ($\text{Me}_4\text{-cyclen}$) and 1,4,8,11-tetramethyl-1,4,8,11-tetra-azacyclotetradecane ($\text{Me}_4\text{-cyclam}$) with $[\text{GeF}_4(\text{CH}_3\text{CN})_2]$ and two equivalents of TMSOTf lead to the clean formation of *cis*- $[\text{GeF}_2(\text{Me}_4\text{-cyclen})][\text{OTf}]_2$ and *trans*- $[\text{GeF}_2(\text{Me}_4\text{-cyclam})][\text{OTf}]_2$ featuring donor-stabilised $[\text{GeF}_2]^{2+}$ dications. The oxidative fluorination of the Ge(II) dicationic complex $[\text{GeBIMEt}_3]^{2+}$ ($\text{BIMEt}_3 = \text{tris}(1\text{-ethyl-benzoimidazol-2-ylmethyl})\text{amine}$) with Selectfluor generates the Ge(IV) cation $[\text{BIMEt}_3\text{GeF}_2]^{2+}$. Abstraction of a fluoride ion is possible using TMSOTf to give the $[\text{BIMEt}_3\text{GeF}]^{3+}$ trication (Figure 1.8).⁴⁵

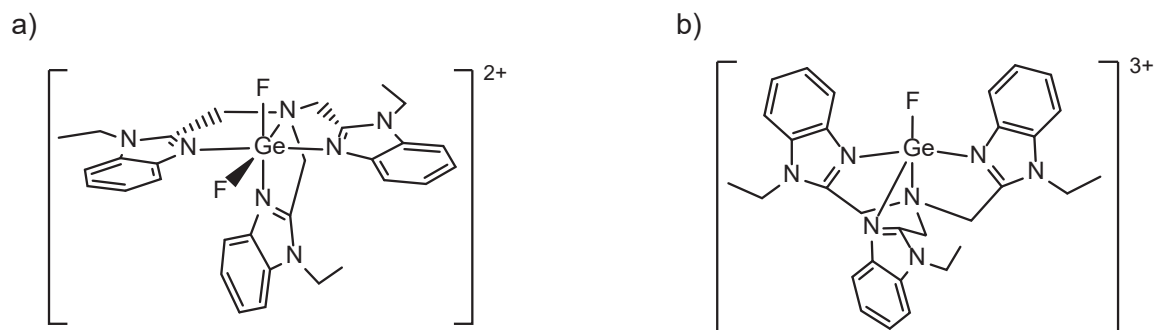


Figure 1.8. Structures of (a) $[BIMeEt_3GeF_2]^{2+}$ and (b) $[BIMeEt_3GeF]^{3+}$.

The behaviour of phosphine adducts of SnF_4 toward TMSOTf has been studied in a manner similar to that of the Ge analogue. When $SnF_4(PMe_3)_2$ is reacted with TMSOTf it forms neutral $[SnF_{4-n}(PMe_3)_2(OTf)_n]$ ($n = 1-3$) species which undergo reductive defluorination in solution to form the Sn(II) complexes $Sn(PMe_3)_2(OTf)_2$, Sn_3F_5OTf as well as $[FPMe_3]^+$.⁴⁶ However, unlike the germanium analogues the triflates are covalently bound to the tin centre. The crystal structure of $[SnF_3(PMe_3)_2(OTf)]$ reveals the three fluorines in a meridional arrangement with mutually *trans* PMe_3 ligands. Multinuclear NMR studies showed that the *trans* arrangement of the phosphine ligands is conserved across the entire $[SnF_{4-n}(PMe_3)_2(OTf)_n]$ ($n = 1-3$) series in solution. The use of the bulkier phosphine P^iPr_3 produces similar neutral adducts, though at room temperature NMR studies suggest that the partial dissociation of one triflate is occurring generating small quantities of a $[Sn(P^iPr_3)_2(OTf)][OTf]$ salt in solution. The use of harder monodentate oxygen and nitrogen bases provides a cleaner route to donor-stabilised cations. Starting from the neutral adduct SnF_4L_2 ($L = DMSO, py, pyridine-N-oxide, DMF, OPPh_3$) the equimolar reaction with TMSOTf and a further equivalent of L gives $[SnF_3L_3][OTf]$ salts (Figure 1.9). Both *fac* and *mer*-isomers were observed in solution by NMR spectroscopy. A further fluoride ion could be abstracted from the $[SnF_3(OPPh_3)_3]^+$ cation in the presence

of TMSOTf and a further equivalent OPPh₃ to form the [SnF₂(OPPh₃)₄]²⁺ dication; in solution this species exists as a mixture of *cis* and *trans*-isomers and a crystal structure of the *trans*-isomer was also obtained. As of yet there are no examples of a donor-stabilised cationic lead fluoro compound.

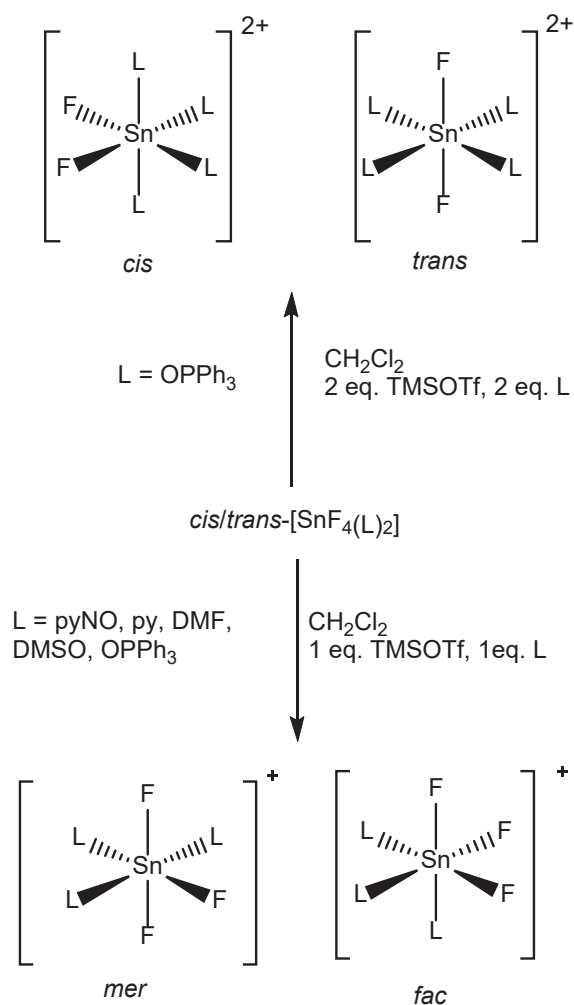


Figure 1.9. The reactivity of neutral [SnF₄(L)₂] (L = pyridine-N-oxide, py, DMF, DMSO, OPPh₃) toward 1 and 2 equivalents of TMSOTf. Based on ref. 46.

Group 15 (N, P, As, Sb)

Among the pnictogens, nitrogen (V) forms the known tetrafluoroammonium cation $[\text{NF}_4]^+$ (e.g. in $[\text{NF}_4][\text{SbF}_6]$),^{47,48} but this species is not stabilised by a neutral donor, as it is coordinatively saturated. The attempts to prepare NF_5 have been unsuccessful.

No examples of a donor-stabilised cationic P(III) fluoride are known, but there are examples of such P(V) species. In the presence of bidentate N or P-bases such as 2,2'-bipyridine (bipy), 4-fluoro-2,2'-bipyridine (f-bipy), 1,10-phenanthroline (phen), *o*- $\text{C}_6\text{H}_4(\text{PMe}_2)_2$ and *o*- $\text{C}_6\text{H}_4(\text{PPh}_2)_2$, PF_5 undergoes autoionisation to form $[\text{PF}_4(\text{L-L})][\text{PF}_6]$ ($\text{L-L} = \text{bipy, f-bipy, phen, } o\text{-C}_6\text{H}_4(\text{PMe}_2)_2 \text{ and } o\text{-C}_6\text{H}_4(\text{PPh}_2)_2$) salts.^{49,50} The $[\text{PF}_4(\text{L-L})]^+$ cation adopts a distorted octahedral geometry as determined by multinuclear NMR spectroscopy and the crystal structure of $[\text{PF}_4\{o\text{-C}_6\text{H}_4(\text{PMe}_2)_2\}][\text{PF}_6]$.

The reaction of AsF_3 with SbF_5 has previously been studied, and the solid-state structure of the product was investigated using X-ray diffraction, however, it is unclear from the structure whether it is a molecule adduct of the form $\text{AsF}_3 \cdot \text{SbF}_5$ or a $[\text{AsF}_2][\text{SbF}_6]$ salt.⁵¹ No examples of donor-stabilised cationic As(III) fluorides are known and As(V) examples are the subject of Chapter 4.

In the case of Sb(III) the neutral adduct $\text{SbF}_3(\text{bipy})$ can undergo sequential fluoride-ion abstraction by TMSOTf leading to the formation of salts of a donor-stabilised monocation ($[\text{SbF}_2(\text{bipy})][\text{OTf}]$), dication $[\text{SbF}(\text{bipy})_2][\text{OTf}]_2$ and even a trication $[\text{Sb}(\text{bipy})_3][\text{OTf}]_3$.⁵² In the monocation, the bipy ligand binds asymmetrically to the Sb centre with one long Sb–N bond (2.3719(18) Å) and one shorter (2.2302(18) Å); the two fluorido ligands are mutually *cis* to each other. The Sb centre also engages in weak

interactions with one oxygen atom of the anion and a fluorine of a neighbouring $[\text{SbF}_2]^+$ unit imposing a distorted octahedral geometry overall at the Sb centre. The structure of the trication was also determined by X-ray diffraction. It features a $[\text{Sb}]^{3+}$ cation chelated by two bidentate bipy ligands. The antimony centre also shows weak contacts with three oxygen atoms of the triflate anions. Another example of a donor-stabilised Sb(III) fluoride was found when reacting $\text{SbF}_2(\text{OTf})$ or $\text{SbF}(\text{OTf})_2$ with 1,2-bis[(2,6-diisopropylphenyl)imino]acenaphthene ($^{\text{Dipp}}\text{BIAN}$) which affords $[\text{SbF}_2(^{\text{Dipp}}\text{BIAN})][\text{OTf}]$ and $[\text{SbF}(^{\text{Dipp}}\text{BIAN})][\text{OTf}]_2$, respectively (Figure 1.10).⁵³ The Sb centre in $[\text{SbF}_2(^{\text{Dipp}}\text{BIAN})]^+$ adopts a distorted square pyramidal geometry with one fluorido ligand in the axial position, the equatorial positions are occupied by the remaining fluorido ligand, the two-nitrogen donors and a long contact to the oxygen of the triflate anion. The Sb centre deviates from the BIAN ($\text{N}=\text{C}-\text{C}=\text{N}$) plane by 15° . The Sb–N bond *trans* to the fluorido ligands is dramatically elongated (2.6066(14) Å) compared to the other Sb–N bond length (2.2902(14) Å) which is comparable to the shorter Sb–N bond found in $[\text{SbF}_2(\text{bipy})]^+$. In the $[\text{SbF}(^{\text{Dipp}}\text{BIAN})][\text{OTf}]_2$ salt the Sb centre also adopts a distorted square pyramidal geometry with the fluorido ligand in an axial position. The Sb centre in the dication sits in the $\text{N}=\text{C}-\text{C}=\text{N}$ plane with two long contacts to the triflate anions. The fluorine substituent in $[\text{SbF}(^{\text{Dipp}}\text{BIAN})][\text{OTf}]_2$ can be readily replaced with an azide or cyanide group through the use of TMSX ($\text{X} = \text{N}_3$ or CN); these are the first examples of dicationic azido or cyano complexes.

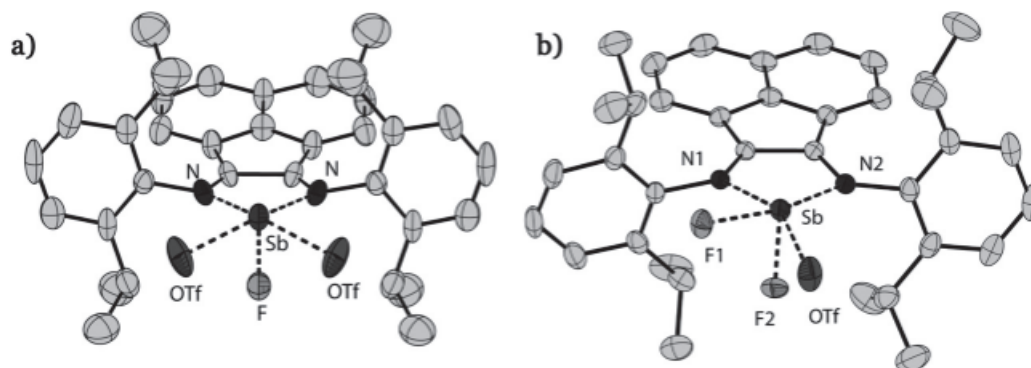


Figure 1.10. Thermal ellipsoid plots (50% probability level) of (a) $[\text{SbF}(\text{DippBIAN})][\text{OTf}]_2$, and (b) $[\text{SbF}_2(\text{DippBIAN})][\text{OTf}]$. Taken from ref. 53

Group 16

Oxonium cations $[\text{R}_3\text{O}]^+$ (like $[\text{OEt}_2\text{H}]^+$) have a rich chemistry, but no isolable cationic O–F species of the form $\text{L} \rightarrow \text{O} \rightarrow \text{F}$ exist. Sulfur tetrafluoride reacts with fluoride-ion acceptors to form $[\text{SF}_3][\text{LA} \rightarrow \text{F}]$ ($\text{LA} = \text{SbF}_5, \text{AsF}_5, \text{IrF}_5, \text{BF}_3, \text{PF}_5, \text{GeF}_4$ and AsF_3) or $[\text{SF}_3][\text{M}_2\text{O}_2\text{F}_9]$ ($\text{M} = \text{W}$ or Mo) salts.^{54–60} The $[\text{SF}_3]^+$ cation adopts a trigonal pyramidal geometry and forms appreciable cation-anion contacts resulting in hexacoordinate sulfur centres except in $[\text{SF}_3][\text{Mo}_2\text{O}_2\text{F}_9]$ where the coordination number at sulfur is increased to seven. In recent years the Lewis acidity of $[\text{SF}_3]^+$ towards nitrogen bases has been explored and lead to the isolation of numerous $[\text{SF}_3(\text{L})_2]^+$ ($\text{L} = \text{py}, \text{CH}_3\text{CN}$ or F_3SN) adducts and $[\text{SF}_3(\text{phen})]^+$.^{61,62} Cationic adducts of $[\text{SF}_3]^+$ with nitrogen bases are discussed in detail in Chapter 5. Gas-phase studies have identified small sulfur based cations such as $[\text{FSO}]^+$ and $[\text{FSO}_2]^+$, however, they have yet to be isolated in the bulk phase and no examples of donor-stabilised versions of these cations.⁶³ Likewise no examples for S(VI) or S(II) fluorides although $[\text{SF}_5]^+$ has been observed via mass spectrometric methods a $[\text{SF}_5]^+$ salt has yet to

be isolated.⁶⁵ Analogous comments apply to selenium and tellurium. No known neutral-donor complexes of Se or Te fluorides have been characterised.

Group 17

The species $[\text{F}_2]^+$ has been observed by mass spectrometric method and studied computationally but is too reactive to be isolated in the bulk phase.^{65,66} The N-fluoropyridinium cation $[\text{py}-\text{F}]^+$ represents an interesting case as the positive charge resides mainly on N, however, the $[\text{py}_2\text{F}]^+$ could be considered a donor-stabilised cation so warrants discussion here. The monopyridine $[\text{py}-\text{F}]^+$ cation is a widely used electrophilic fluorinating agent.^{67,68} Coordination to a second pyridine is possible to form $[\text{py}_2\text{F}]^+$ but the interaction to the second pyridine is weak due to the bond polarity inversion, leading to asymmetric binding with one short N–F bond and the other very long forming essentially $[\text{py}-\text{F}]^+$ plus a weak interaction with the second pyridine. NMR and computational studies show $[\text{py}-\text{F}]^+$ is highly fluorophilic and strongly polarised.⁶⁹

Chloronium ions have recently been isolated and structurally characterised, Riedel *et al.* reported the first crystal structures of mono and bis(pyridine)chloronium salts.⁷⁰ The bis(pyridine) cation is synthesised at low temperature in propionitrile reacting pyridine, Cl_2 and NaBF_4 yielding $[\text{py}-\text{Cl}-\text{py}][\text{BF}_4]$ it displays an essential linear N–Cl–N motif with one long N–Cl bond (2.232(6) Å) and one short N–Cl bond (1.793(5) Å). The reaction of two equivalents of ClF with AsF_5 yields the $[\text{Cl}_2\text{F}][\text{AsF}_6]$ salt. This salt can subsequently be reacted with perfluoropyridine in anhydrous HF (aHF) to afford $[\text{F}_5\text{C}_5\text{N}-\text{Cl}][\text{AsF}_6]$ as the first example of a monopyridine chloronium cation. The N–Cl bond length (1.696(3) Å) is substantially shorter than those found in the bis-pyridine system. Analogous bromonium and iodonium cations stabilised with pyridine are known in the case of $[\text{py}-\text{I}-\text{py}]^+$

(Barluenga's reagent) is used in organic chemistry as a halogenation or oxidation reagent and commonly used as a model system to investigate halogen-bonding.⁷¹⁻⁷⁶ Higher oxidation state cationic interhalogen fluorides exist though they are typically donor free species, additionally, their highly oxidising nature often makes them incompatible with organic material.

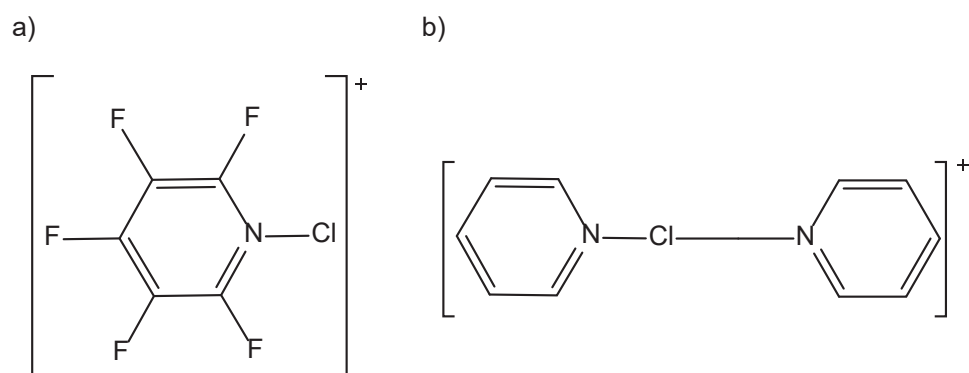


Figure 1.11. The structures of (a) $[F_5C_5N-Cl]^+$ and (b) $[py_2Cl]^+$.

Group 18

The chemistry of krypton is dominated by krypton difluoride (KrF_2). Strong fluoride-ion acceptors such as AsF_5 , SbF_5 or BiF_5 can be used to generate the extremely potent fluorinating and oxidising $[KrF]^+$ and $[Kr_2F_3]^+$ cations.⁷⁷⁻⁸¹ The $[Kr_2F_3]^+$ cation can be thought of as the KrF_2 adduct of $[KrF]^+$. The $[Kr_2F_3]^+$ cation has a V-shaped fluorine-bridged geometry (Figure 1.12). The terminal $Kr-F$ bonds in $[Kr_2F_3]_2[SbF_6]_2 \cdot KrF_2$ (1.787(4)-1.805(5) Å) are appreciably shorter than the more polarised bridging $Kr-F$ bonds (2.041(4)-2.065(4) Å) and comparable to those found in $[KrF]^+$ ($[KrF][SbF_6] = 1.765(3)$ Å).⁸³ The $Kr-F-Kr$ angle in $[Kr_2F_3]^+$ varies considerably between the different salts ranging from $126.0(2)^\circ$ in $[Kr_2F_3]_2[SbF_6]_2 \cdot KrF_2$ to $142.5(3)^\circ$ in $[Kr_2F_3][SbF_6] \cdot KrF_2$. Cationic adducts of $[KrF]^+$ with oxidatively resistant nitriles can be accessed by reacting

the protonated nitrile with KrF₂ in aHF or BrF₅ solvent losing an equivalent of HF and producing the desired [RC≡NKrF]⁺ (R = H, CF₃, C₂F₅ or *n*-C₃F₇) cation. The [HC≡NKrF]⁺ cation represented the first example of Kr bonding to an element other than F.^{84,85}

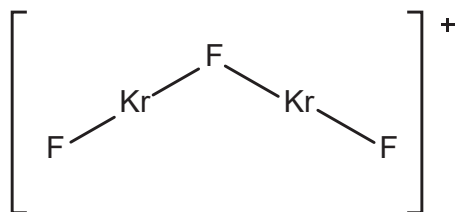
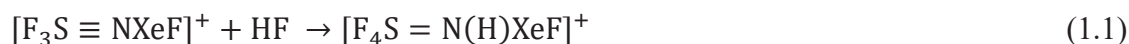


Figure 1.12. The V-shaped [Kr₂F₃]⁺ cation.

The chemistry of xenon is far more developed than that of krypton; xenon exists in multiple oxidation states (0, +1/2, +2, +4, +6, +8). Analogous to its krypton counterpart XeF₂ reacts with strong Lewis acids such as AsF₅, SbF₅ to form [XeF]⁺ and [Xe₂F₃]⁺.⁸⁶ Like its krypton analogue, [Xe₂F₃]⁺ has a V-shaped geometry with shorter terminal Xe–F bonds ([Xe₂F₃][AsF₆] Xe–F_t = 1.873(6) Å; Xe–F_b = 2.212(5) Å) and longer bridging Xe–F bonds. Again, the Xe–F_b–Xe angle shows significant variation over the different salts ranging from 160.3(3)° in [Xe₂F₃][SbF₆] to 139.8(8)° in the trigonal phase of [Xe₂F₃][AsF₆].⁸³ Due to the less oxidising nature of Xe(II) compared to Kr(II), [XeF]⁺ is compatible with a greater number organic N-bases, such as HCN, CH₃CN, F₅C₅N or *s*-C₃F₃N₃.^{84,87,88} Adduct formation with inorganic bases such as N≡SF₃ is also possible. The [F₃S≡N–XeF][AsF₆] salt is synthesised by the direct combination of [XeF][AsF₆] with F₃S≡N in BrF₅ solvent. The use of aHF solvent causes the adduct to undergo two consecutive additions of HF across the S≡N bond and subsequent HF elimination to form [F₄S=N–Xe]⁺ and [F₅SN(H)–Xe]⁺ (eq. 1.1–1.3).⁹⁰ Sulfuryl chloride fluoride typically thought to be a poor Lewis base was found to form an adduct with [XeOTeF₅][Sb(OTeF₅)₆]; SO₂ClF binds to the xenon centre through an oxygen atom. The solid-state structure of

$[(\text{SO}_2\text{ClF})\text{XeOTeF}_5][\text{Sb}(\text{OTeF}_5)_6]$ shows a long Xe–OS(O)ClF bond length of 2.479(4) Å much longer than the Xe–OTeF₅ bond length of 1.969(4) Å reflective of the weak interaction.⁹¹ The cationic adduct readily dissociates at temperatures as low as –80 °C, as evidenced by multinuclear NMR spectroscopy



An example of a Xe(IV) donor-stabilised cation is generated when $\text{OXeF}_2 \cdot \text{xHF}$ was dissolved in SbF_5/aHF solvent mixture and yielded crystals of $[\text{H}_5\text{F}_4][\text{SbF}_6] \cdot 2[\text{XeF}_3 \cdot \text{HF}][\text{Sb}_2\text{F}_{11}]$, $[\text{XeF}_3 \cdot \text{HF}][\text{Sb}_2\text{F}_{11}]$, and $[\text{XeF}_3][\text{SbF}_6]$, providing two rare examples of HF coordinating to a $[\text{XeF}_3]^+$ cation. The $[\text{XeF}_3]^+$ cation in both cases adopts a T-shaped primary coordination (AX_3E_2 VSEPR arrangement) to xenon with a longer secondary contact to the fluorine of HF or $[\text{SbF}_6]^-$ in the case of $[\text{XeF}_3][\text{SbF}_6]$.⁹² There are examples of lower oxidation state xenon fluorides coordinating to higher oxidation state cationic xenon fluorides, such as in $[\text{F}_5\text{Xe}(\text{FXeF})\text{XeF}_5][\text{AsF}_6]_2$, $[\text{F}_5\text{Xe}(\text{XeF}_2)][\text{AsF}_6]$, and $[\text{F}_5\text{Xe}(\text{XeF}_2)_2][\text{AsF}_6]$ which have been structurally characterised and $[\text{F}_5\text{Xe}(\text{XeF}_2)][\text{RuF}_6]$ which was characterised by Raman spectroscopy.⁹³ In 2021 Schrobilgen *et al.* reported the mixed noble gas compounds $[\text{XeF}_5(\text{KrF}_2)][\text{AsF}_6]$ and $[\text{XeF}_5(\text{KrF}_2)_2][\text{AsF}_6]$ which feature KrF_2 acting as a base towards $[\text{XeF}_5]^+$.⁹⁴ The Lewis acidity of $[\text{XeF}_5]^+$ is sufficiently high that KrF_2 will coordinate to it, yet not sufficiently Lewis acidic that it will abstract a fluoride from KrF_2 . Quantum chemical calculations suggest that the interaction between $[\text{XeF}_5]^+$ and KrF_2 is almost entirely electrostatic in

nature and is best described as a σ -hole interaction. In the same study they also reported $[\text{F}_5\text{Xe}(\text{FH})][\text{AsF}_6]$ and $[\text{F}_5\text{Xe}(\text{FH})][\text{SbF}_6]$ which are rare example of HF coordinating to Xe(VI).

1.7 Objectives of Research

The primary objective of this research is to synthesise and isolate cationic main-group fluoro species that are stabilised with neutral Lewis bases and study the structure and bonding of the resulting donor-stabilised cations. Donor-stabilised $[\text{PnF}_4]^+$ ($\text{Pn} = \text{As}$ or Sb) cations were chosen as synthetic targets as the parent pentafluorides are well known to act as strong fluoride-ion acceptors, yet their fluoride-ion donor properties have not been sufficiently explored. In fact, there is only one report of AsF_5 acting as a fluoride-ion donor in the $[\text{AsF}_4][\text{PtF}_6]$ salt, the characterisation of which was based on vibrational spectroscopy, and there are no examples of SbF_5 acting as a fluoride-ion donor.⁹⁵ Additionally cationic adducts of $[\text{SF}_3]^+$ were chosen as synthetic targets as 1:1 adducts with organic bases are invoked in the most widely accepted mechanism for deoxofluorination of carbonyl $\text{C}=\text{O}$ bonds using SF_4 . A better understanding of these species will lead to a greater understanding of the deoxofluorination mechanism.

Antimony pentafluoride readily forms neutral adducts with a variety of N-donors such as pyridines and nitriles; however, no cationic species derived from SbF_5 have previously been reported. Donor-stabilised cations of the lighter group 15 pentafluoride PF_5 can be accessed by exploiting its autoionisation in the presence of bidentate N or P-donor ligands to form $[\text{PF}_4(\text{L}-\text{L})][\text{PF}_6]$ salts.^{49,50} Similar behaviour is also observed for the

transition metal pentafluorides of TaF₅ and NbF₅.⁹⁶ It was rationalised that similar behaviour might also be observed in SbF₅. Chapter 2 aims to test whether the autoionisation of SbF₅ in the presence of bidentate N-bases is a viable route to access [SbF₄(L–L)][SbF₆] salts. This will be done by studying the reaction of SbF₅ with the bidentate N-bases phen and bipy in a suitably oxidatively resistant solvent.

Chapter 3 aims to explore the reactivity of SbF₅ in the presence of a tridentate nitrogen base. Antimony pentafluoride shows a strong preference for hexacoordination as it oligomerises to form *cis*-linked SbF₆ octahedra in both its solid and liquid forms. Heptacoordination is possible as seen in [SbF₇]^{2–} salts, but these salts are rare. Therefore, in the presence of the tridentate base terpy, will SbF₅ autoionise to form a hexacoordinate [SbF₃(terpy)]²⁺ dication or would it form a heptacoordinate [SbF₄(terpy)]⁺ cation? Alternatively the conformational flexibility of terpy means it could bind in a κ² mode instead of κ³ which would result in a hexacoordinate [SbF₄(κ²-terpy)]⁺ cation.

Chapter 4 aims to look at the propensity of AsF₅ to autoionise in the presence of phen and bipy, then compare this reactivity to the analogous reactions studied in Chapter 2. The higher fluoride-ion affinity of SbF₅ compared to AsF₅ can be exploited to try access mixed arsenic/antimony salts [AsF₄(L–L)][Sb_nF_{5n+1}]. Neutral AsF₅ and SbF₅ are strong Lewis acids, therefore, the “naked” [AsF₄]⁺ and [SbF₄]⁺ cations are predicted to be extremely potent Lewis acids. Attempts to quantify the Lewis acidity of [AsF₄]⁺ and [SbF₄]⁺ will be achieved through the calculation of the fluoride-ion affinities of these donor-free cations in both the gas-phase and solution using DFT methods.

Since the late 1950s SF₄ has been known to act as a deoxofluorinating agent towards C=O bonds, however, the precise mechanism for this reaction is not yet fully understood.

The active species in this reaction is believed to be $[\text{SF}_3]^+$ and the proposed first step of this reaction is the formation of a 1:1 adduct between $[\text{SF}_3]^+$ and the carbonyl oxygen.⁹⁷ Previous work in the group studied the Lewis acidity of $[\text{SF}_3]^+$ towards two nitrogen donors resulting in $[\text{SF}_3(\text{L})_2]^+$ ($\text{L} = \text{py}$ or CH_3CN) or $[\text{SF}_3(\text{phen})]^+$ salts, while attempts to isolate adducts of $[\text{SF}_3]^+$ with ketones proved unsuccessful.⁹⁸ It was rationalised that the use of a stronger oxygen bases could facilitate the isolation of an $[\text{SF}_3]^+$ adduct with an oxygen base. Phosphine oxides such as OPPh_3 have a considerably larger BF_3 affinity than ketones such as acetone (OPPh_3 BF_3 affinity = 103.3 ± 1.50 ; acetone BF_3 affinity = 76.07 ± 0.33) and therefore, represent a promising class of compounds that could be utilised to study the interaction between $[\text{SF}_3]^+$ and an O-base. Chapter 5 aims to isolate 1:1 adducts of $[\text{SF}_3]^+$ with both N-donors (py and DMAP) and O-donor (OPPh_3) and study the effect that adduct formation has on the structure and bonding of the $[\text{SF}_3]^+$ cation. The direct combination of $[\text{SF}_3][\text{PnF}_6]$ ($\text{Pn} = \text{As}$ or Sb) with the organic base of choice should yield the desired $[\text{SF}_3(\text{L})]^+$ ($\text{L} = \text{py}$, DMAP or OPPh_3) cation. Alternatively $[\text{SF}_3(\text{L})]^+$ cations could be synthesised through the reaction of SF_4 with $[\text{TMS}(\text{L})][\text{OTf}]$, where the $[\text{TMS}(\text{L})][\text{OTf}]$ salt acts as both the fluoride-ion acceptor and the source of the Lewis base.

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Chapter 2 – Donor-stabilised $[\text{SbF}_4]^+$: SbF_5 as a Fluoride-Ion Donor*

2.1 Abstract

Antimony pentafluoride is a strong Lewis acid and fluoride-ion acceptor that has not previously demonstrated any discreet fluoride-ion donor properties. The first donor-stabilised $[\text{SbF}_4]^+$ cations were prepared from the autoionisation of SbF_5 in the presence of bidentate N-donor ligands 2,2'-bipyridine (bipy) and 1,10-phenanthroline (phen) as their $[\text{SbF}_6]^-$ salts. The $[\text{SbF}_4(\text{N-N})][\text{Sb}_2\text{F}_{11}]$ (N-N = bipy, phen) salts were synthesised by the addition of one equivalent of $\text{SbF}_5 \cdot \text{SO}_2$ to $[\text{SbF}_4(\text{N-N})][\text{SbF}_6]$ in liquid SO_2 . The salts show remarkable stability and were characterised by Raman spectroscopy and multinuclear NMR spectroscopy. The crystal structures of $[\text{SbF}_4(\text{phen})][\text{SbF}_6] \cdot 3\text{CH}_3\text{CN}$ and $[\text{SbF}_4(\text{phen})][\text{SbF}_6] \cdot 2\text{SO}_2$ were determined, showing distorted octahedral cations. DFT calculations and NBO analyses reveal that significant degree of electron-pair donation from N to Sb stabilizes $[\text{SbF}_4]^+$ with the Sb–N bond strength being ca. $2/3$ of that of the Sb–F bonds in these cations and the cationic charge being primarily ligand-centred.

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2.2 Introduction

Antimony pentafluoride, SbF_5 , is one of the strongest F^- acceptors currently known, forming highly stable $[\text{Sb}_n\text{F}_{5n+1}]^-$ ($n = 1-4$) anions. Its solutions in anhydrous HF (aHF) are some of the strongest recorded Bronsted superacids. Antimony pentafluoride is also the benchmark for Lewis superacidity, as molecular Lewis acids with fluoride-ion affinities (FIAs) greater than monomeric SbF_5 in the gas phase (calcd. 501 kJ mol^{-1} , exptl. $506 \pm 60 \text{ kJ mol}^{-1}$) are considered Lewis superacids.¹⁻³ The formation of polynuclear anions, however, can drive the already extreme FIA of SbF_5 even higher.⁴

Thus, it is unsurprising that, aside from self-association of solid and liquid SbF_5 to form *cis*-linked SbF_6 octahedra, the ability of SbF_5 to act as a discrete F^- donor is hitherto unknown. However, the lighter pnictogen pentafluorides, PF_5 and AsF_5 , have both previously demonstrated the ability to act as F^- donors and form $[\text{PnF}_4]^+$ cations ($\text{Pn} = \text{P}$ and As).^{5,6} In fact, the entire series of $[\text{PX}_4]^+$ ($\text{X} = \text{F},^5 \text{Cl},^7 \text{Br},^8 \text{I}^{9,10}$) and their arsonium analogues are known.^{6,11-16} Conversely, only $[\text{NF}_4]^+$,^{17,18} $[\text{NCl}_4]^+$,¹⁹ $[\text{SbCl}_4]^+$ ²⁰⁻²² and $[\text{SbBr}_4]^+$ ^[21] have been isolated for nitrogen and antimony, while no analogous bismuth cations have been reported. We therefore targeted the isolation and characterisation of $[\text{SbF}_4]^+$ cations upon stabilisation via neutral N-donors to explore the F^- donor properties of SbF_5 .

Fluoride-ion abstraction from the parent pentafluoride using a strong F^- acceptor was used to synthesise both $[\text{PF}_4]^+$ and $[\text{AsF}_4]^+$ salts. The reaction of SbF_5 with an excess of PF_5 at ambient temperature quantitatively yields $[\text{PF}_4][\text{Sb}_3\text{F}_{16}]$.⁵ The only example of an $[\text{AsF}_4]^+$ salt is $[\text{AsF}_4][\text{PtF}_6]$, as identified by vibrational spectroscopy, and was formed during electrical resistance heating of Pt wire under an atmosphere of AsF_5 and F_2 .⁶ The

generation of Lewis-superacidic PtF_5 (calcd. FIA = 546 kJ mol^{-1})²³ was necessary to abstract F^- from the weak donor AsF_5 . Due to the non-existence of parent NF_5 , $[\text{NF}_4]^+$ cations were instead prepared via the reaction of NF_3 , F_2 , and a strong Lewis acid (BF_3 , GeF_4 , PF_5 , AsF_5 , SbF_5) under UV photolytic conditions.¹⁷

Ligand-induced autoionisation has been observed upon reaction of PF_5 with bidentate N- and P-donors (L–L), yielding $[\text{PF}_4(\text{L–L})][\text{PF}_6]$ salts stabilised by 2,2'-bipyridine (bipy), 1,10-phenanthroline (phen), 4-fluoro-2,2'-bipyridine, *o*- $\text{C}_6\text{H}_4(\text{PMe}_2)_2$, and *o*- $\text{C}_6\text{H}_4(\text{PPh}_2)_2$.^{24,25} Facile ligand-induced autoionisation has also been observed for the transition-metal pentafluorides MF_5 ($\text{M} = \text{Nb}, \text{Ta}$) in the presence of bi- as well as monodentate donors.^{26–28} Given that MF_5 are strong acids that show similar aggregation behaviour to SbF_5 in the solid and liquid state, we rationalised that SbF_5 might undergo an analogous autoionisation under appropriate conditions, providing a route to donor-stabilised $[\text{SbF}_4]^+$ cations.

2.3 Results and Discussion

The reaction of SbF_5 with N–N ($\text{N–N} = \text{bipy}, \text{phen}$) in a 2:1 molar ratio in SO_2ClF at ambient temperature produces $[\text{SbF}_4(\text{N–N})][\text{SbF}_6]$ as off-white powders in near quantitative yields (eq. 2.1). The insolubility of the ionic product in SO_2ClF is likely what drives its formation. The resulting powders were found to be insoluble in CH_2Cl_2 and CFC_l_3 but soluble in SO_2 , CH_3CN and aHF. Addition of $\text{SbF}_5 \cdot \text{SO}_2$ in SO_2 did not result in F^- abstraction to form dications but instead afforded the pale yellow $[\text{Sb}_2\text{F}_{11}]^-$ salts (eq. 2.2).



The salts are moisture-sensitive but can be stored for at least three months at ambient temperature under dry N₂ without decomposition. This stability is notable, considering that SbF₅ is strongly oxidising (*e.g.*, oxidising alkanes under mild conditions) and thus largely incompatible with organic materials under ambient conditions. Neutral SbF₅ adducts with organic bases, *e.g.* nitriles, have been observed to decompose under ambient conditions.²⁹

Crystals of the [SbF₄(phen)]⁺ salts can be grown from concentrated solutions of CH₃CN at –40 °C for 16 h, yielding [SbF₄(phen)][SbF₆]·3CH₃CN, or by the slow evacuation of an SO₂ solution at –70 °C, resulting in crystals of [SbF₄(phen)][SbF₆]·2SO₂. The solvent molecules of crystallisation can easily be removed from either lattice under dynamic vacuum at ambient temperature, resulting in white powders.

The [SbF₄(phen)][SbF₆]·3CH₃CN and [SbF₄(phen)][SbF₆]·2SO₂ solvates crystallise in the monoclinic space groups *P*2₁/*m* and *P*2₁/*c*, respectively. The metric parameters of [SbF₄(phen)]⁺ do not differ notably between the two crystals structures, thus, only [SbF₄(phen)][SbF₆]·3CH₃CN will be discussed further. The structure of the cation in [SbF₄(phen)][SbF₆]·3CH₃CN is shown in Figure 2.1 and the key metric parameters are listed in Table 2.1. No appreciable cation-anion interactions are observed in the crystal structures. The [SbF₄(phen)]⁺ cation displays a distorted octahedral geometry around the central Sb atom with the F(1)–Sb(1)–F(2) axis lying in a crystallographic mirror plane. The equatorial Sb(1)–F_{eq} bonds (1.8683(12) Å) that are *trans* to the Sb–N bonds are comparable

to Sb–F_{ax} (1.8763(12), 1.8783(17) Å). Interestingly, the Sb–F bond lengths in the cation are not substantially different from those in the [SbF₆][–] anion (av. Sb(2)–F = 1.8726 Å), but are notably shorter than in the related bipy-stabilised Sb^{III} cation, [SbF₂(bipy)]⁺ (1.9332(18)–1.9387(13) Å).³⁰ The Sb(1)–N(1) bond lengths (2.1126(16) Å) are comparable to those found in the neutral adducts of SbF₅ with nitriles (SbF₅·NCH: 2.132(3) Å, SbF₅·NCC(CH₃)₃: 2.104(6) Å),²⁹ but are significantly shorter than in bipy complexes of Sb^{III} cations ([SbF₂(bipy)]⁺: 2.2302(18)–2.3719(18) Å, [Sb(bipy)₂]³⁺: 2.2333(12)–2.3322(12) Å).³⁰ The small bite angle of phen (78.93(8)°) causes a slight widening of the F(3)–Sb(1)–F(3') (97.61(8)°) and F(3)–Sb(1)–N(1) (91.73(6)°) angle from 90°. The F(1)–Sb(1)–F(2) (179.12(7)°) moiety is essentially linear.

Gas-phase geometry optimisation of [SbF₄(phen)]⁺ reproduces the experimental structures with minor variations in bond lengths and angles, the most notable being the overestimation of the Sb–N bond length (2.180 vs. 2.1126(16) Å) and bending of the F(1)–Sb–F(2) bond angle (171.33°). The geometric features about Sb(1) in [SbF₄(phen)]⁺ are reproduced almost identically in the optimised structure of [SbF₄(bipy)]⁺ (Table 1).

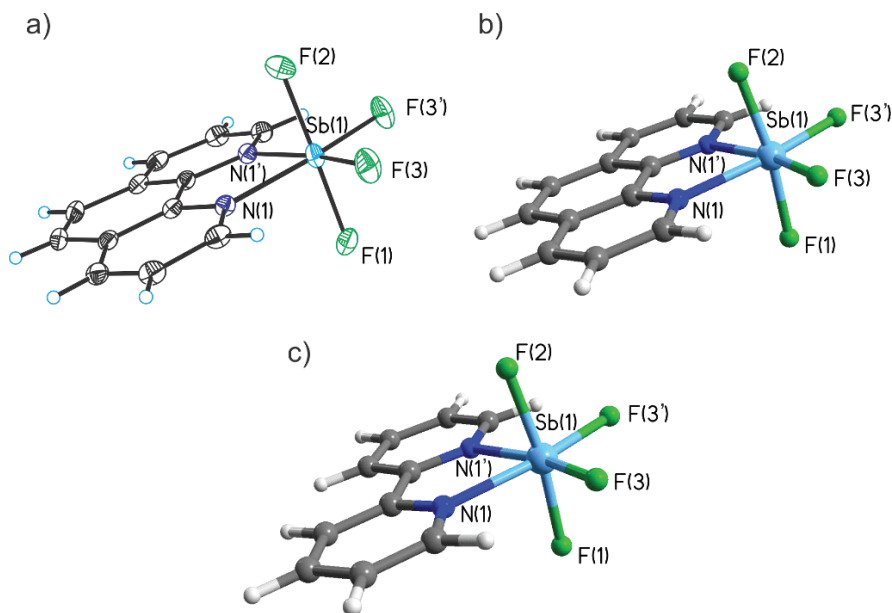


Figure 2.1. (a) Thermal ellipsoid plot (50% probability level) of [SbF₄(phen)][SbF₆]·3CH₃CN. (b) Optimised gas-phase geometry of [SbF₄(phen)]⁺ using the B3LYP functional with the aug-cc-pVTZ-PP (Sb) and aug-cc-pVTZ (C, H, N, F) basis sets. (c) Optimised gas-phase geometry of [SbF₄(bipy)]⁺ using the B3LYP functional with the aug-cc-pVTZ-PP (Sb) and aug-cc-pVTZ (C, H, N, F) basis sets.

Table 2.1. Selected bond lengths [Å] and angles [°] of [SbF₄(phen)]⁺

	[SbF ₄ (phen)] ⁺		[SbF ₄ (bipy)] ⁺
	Exptl. ^[a]	Calcd. ^[b]	Calcd. ^[b]
Sb(1)–F(1)	1.8763(12)	1.897	1.897
Sb(1)–F(2)	1.8783(17)	1.897	1.897
Sb(1)–F(3)	1.8683(12)	1.882	1.882
Sb(1)–N(1)	2.1126(16)	2.180	2.171
F(1)–Sb(1)–F(2)	179.12(7)	171.33	171.85
F(3)–Sb(1)–F(3')	97.61(8)	101.67	101.48
N(1)–Sb(1)–N(1')	78.93(8)	76.75	76.04
F(3)–Sb(1)–N(1)	91.73(6)	90.79	91.24

[a] From [SbF₄(phen)][SbF₆]·3CH₃CN. [b] Calculated using the B3LYP functional with the aug-cc-pVTZ-PP (Sb) and aug-cc-pVTZ (C, H, N, F) basis sets.

The Raman spectra for [SbF₄(N–N)]⁺ as their [SbF₆][–] and [Sb₂F₁₁][–] salts were acquired on solid samples and the partial Raman spectrum of [SbF₄(phen)][SbF₆] is shown in Figure 2.2. Quantum-chemical calculations were used to aid the assignment of

vibrational frequencies of the cations. The symmetric equatorial and axial Sb–F stretching frequencies (Table 2.2) are observed at 600–700 cm^{-1} , typical of octahedral Sb^{V} fluorides.^{31,32} The splitting of the $\nu_{\text{s}}(\text{SbF}_{2\text{ax}})$ mode in $[\text{SbF}_4(\text{phen})][\text{SbF}_6]$ and $[\text{SbF}_4(\text{bipy})][\text{Sb}_2\text{F}_{11}]$ is likely due to vibrational coupling within unit cells. The stretching modes of phen and bipy are considerably blue shifted in the cations with respect to the free bases. The most notable examples are in the symmetric ring breathing modes; in $[\text{SbF}_4(\text{phen})]^+$ this mode is observed at 1077 and 1066 cm^{-1} (calcd. 1088) while in free phen this mode occurs at 1035 and 1039 cm^{-1} (calcd. 1058). The symmetric ring breathing mode of bipy is tentatively assigned to the band at 1048 cm^{-1} (calcd. 1057) in $[\text{SbF}_4(\text{bipy})]^+$ and occurs at 995 cm^{-1} (calcd. 1010) in free bipy. Full lists of vibrational frequencies and assignments are given in Appendix A (Tables A3 and A4).

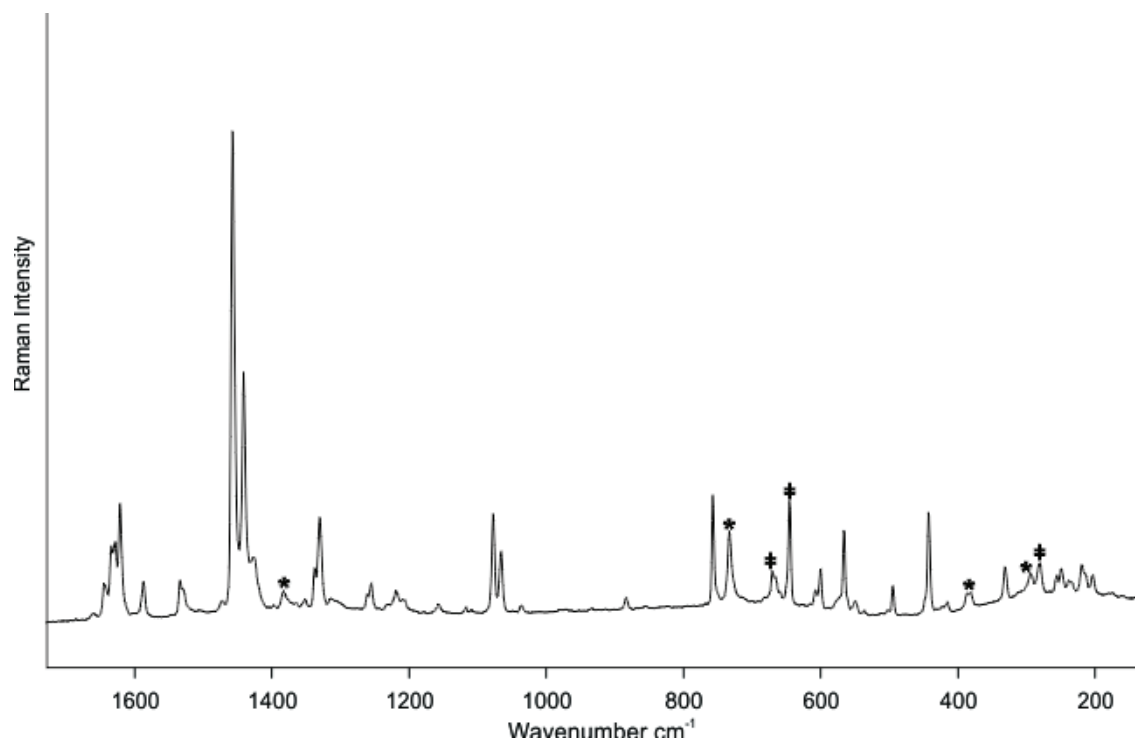


Figure 2.2. The partial Raman spectrum of $[\text{SbF}_4(\text{phen})][\text{SbF}_6]$, recorded in a $\frac{1}{4}$ ''-o.d. FEP sample tube at $-100\text{ }^\circ\text{C}$. Asterisks (*) and double daggers (‡) denote bands arising from the FEP sample tube and $[\text{SbF}_6]^-$ anion, respectively.

Table 2.2. Selected vibrational frequencies (cm^{-1}) for $[\text{SbF}_4(\text{N}-\text{N})][\text{SbF}_6]$ (N-N = phen, bipy).

	$[\text{SbF}_4(\text{phen})]^+$				$[\text{SbF}_4(\text{bipy})]^+$			
	obsd. ^[a]	obsd. ^[b]	calcd. ^[c]	obsd. ^[d]	obsd. ^[e]	calcd. ^[c]		
$\nu_s(\text{SbF}_{2\text{eq}})$	670(7)	668(20)	657(12)[99]	663(17)	662(41)	654(18)[70]		
$\nu_s(\text{SbF}_{2\text{ax}})$	607sh/600(7)	607(18)	603(17)[1]	605(10)	607(33)/601sh	603(14)[<1]		
Symmetric ring-breathing mode	1077(21)/1066(13)	1077(27)/1066(18)	1088(53)[1]	1048(56)	1049(60)	1057(113)[31]		

[a]. From $[\text{SbF}_4(\text{phen})][\text{SbF}_6]$ recorded in a $\frac{1}{4}$ " -o.d. FEP sample tube at -100°C . Normalised Raman intensities are given in parentheses. Shoulders are denoted sh. [b]. From $[\text{SbF}_4(\text{phen})][\text{Sb}_2\text{F}_{11}]$ recorded in a flame sealed melting point capillary at ambient temperature. [c]. Calculated using the B3LYP functional with the aug-cc-pVTZ-PP (Sb) and aug-cc-pVTZ (C, H, N, F) basis sets. Absolute Raman intensities ($\text{\AA}^4\text{u}^{-1}$) are given in parentheses and IR intensities (km mol^{-1}) are given in square brackets [d]. From $[\text{SbF}_4(\text{bipy})][\text{SbF}_6]$ recorded in a $\frac{1}{4}$ " -o.d. FEP sample tube at -100°C . [e]. $[\text{SbF}_4(\text{bipy})][\text{Sb}_2\text{F}_{11}]$ recorded in a flame sealed melting point capillary at ambient temperature.

The ^{19}F NMR spectra of $[\text{SbF}_4(\text{N-N})][\text{SbF}_6]$ in CH_3CN at $-40\text{ }^\circ\text{C}$ are dominated by the overlapping equal-intensity sextet and octet that is characteristic of $[\text{SbF}_6]^-$ [^{121}Sb $I = 5/2$, $^1J(^{19}\text{F}-^{121}\text{Sb}) = 1958\text{ Hz}$; ^{123}Sb $I = 7/2$, $^1J(^{19}\text{F}-^{123}\text{Sb}) = 1041\text{ Hz}$]. The resolution of these multiplets suggests the absence of cation-anion interactions in solution. Resonances attributable to the cation were not observed in either spectrum. This is consistent with intermediate quadrupolar relaxation of $^{121,123}\text{Sb}$ on the NMR timescale causing extreme broadening of the cation ^{19}F resonances, rendering them indistinguishable from the baseline. In the ^{19}F NMR spectra of $[\text{Sb}^{\text{III}}\text{F}_{3-n}(\text{bipy})_m]^{n+}$ ($n = 1,2$; $m = 2,1$), only broad singlets arising from the low-symmetry cations were observed.³⁰ The symmetry of the distorted octahedral environment about Sb^{V} in the cations is sufficiently high to prevent rapid quadrupolar relaxation and broaden the ^{19}F resonances beyond observability; J coupling to the $^{121,123}\text{Sb}$ nuclei, however, still being quadrupole-collapsed. Identification of the two expected broad cation resonances (axial and equatorial) is also hampered by the overlapping anion signals.

The $[\text{SbF}_4(\text{N-N})][\text{Sb}_2\text{F}_{11}]$ salts are incompatible with CH_3CN , leading to cleavage of the dinuclear anion, as shown by NMR spectroscopy. The $[\text{SbF}_4(\text{N-N})][\text{Sb}_2\text{F}_{11}]$ salts, however, are stable in SO_2 solutions. The ^{19}F NMR spectrum of $[\text{SbF}_4(\text{bipy})][\text{Sb}_2\text{F}_{11}]$ (Figure 2.3) at $-70\text{ }^\circ\text{C}$ contains the three singlet resonances expected for the $[\text{Sb}_2\text{F}_{11}]^-$ anion. Rather than the expected 1:8:2 ratio, an integral ratio of ca. 1:8:3.6 suggests that the axial fluorine F_{ax} environment of the cation, observed as a shoulder, overlaps with the terminal F_{ax} environment of the anion (-133.1 ppm). The additional broad singlet at -98.4 ppm (2F ; $\nu_{1/2} = 605\text{ Hz}$) is assigned to the F_{eq} environment of the cation based on the slightly greater covalency of the Sb-F bonds compared to the axial Sb-F bonds. The low-

temperature ^{19}F NMR spectrum of $[\text{SbF}_4(\text{phen})][\text{Sb}_2\text{F}_{11}]$ contained only the expected anion resonances in approximately 1:8:2 ratio and no discernible cation resonances were observed.

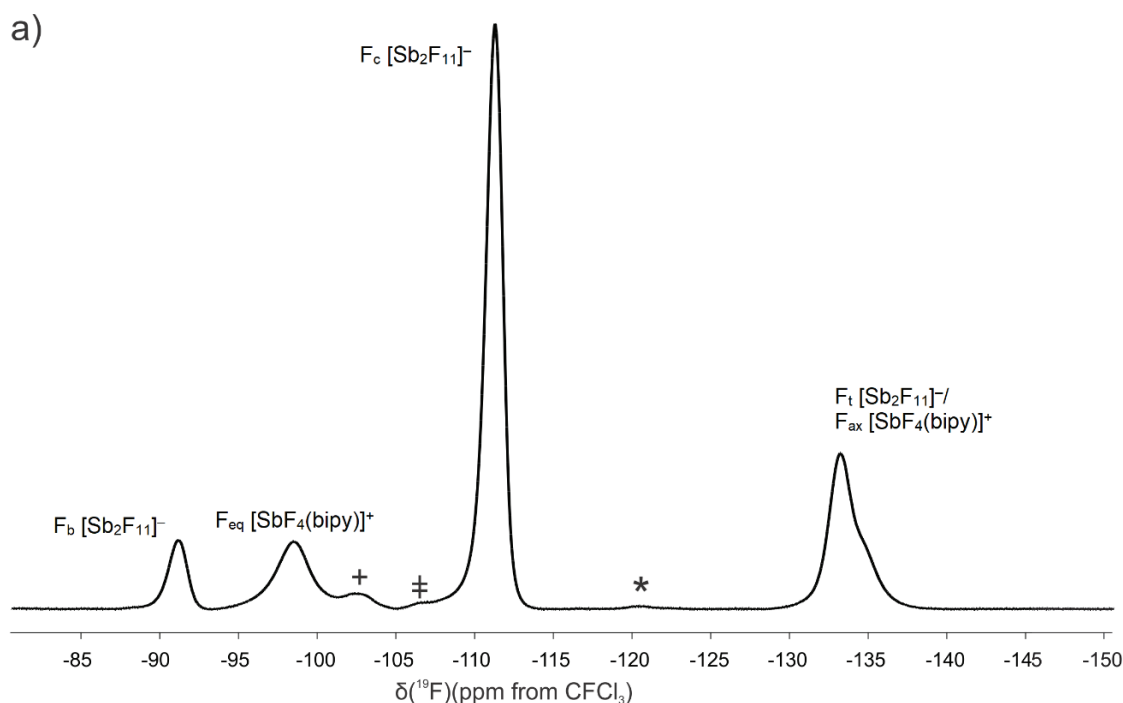


Figure 2.3. (a) ^{19}F NMR spectrum of $[\text{SbF}_4(\text{bipy})][\text{Sb}_2\text{F}_{11}]$ in SO_2 at $-70\text{ }^\circ\text{C}$. (+), ($\ddagger$) and (*) denotes $\text{SbF}_5 \cdot \text{SO}_2$, $[\text{H-bipy}][\text{SbF}_6]$ and an unknown impurity respectively.

Recording the ^{19}F NMR spectra at ambient temperature resulted in linewidth narrowing in the $[\text{SbF}_6]^-$ multiplets as well as broadening of the $[\text{Sb}_2\text{F}_{11}]^-$ singlets, consistent with the expected decrease in quadrupolar relaxation rate of $^{121,123}\text{Sb}$ at elevated temperatures. No discernable cation resonances were observed in the spectra, even for $[\text{SbF}_4(\text{bipy})][\text{Sb}_2\text{F}_{11}]$, due to this line broadening.

The optimised gas-phase geometries of SbF_5 , $[\text{SbF}_4]^+$ and $[\text{SbF}_6]^-$ are shown in Figure 2.11. Natural bond orbital (NBO) analysis was used to investigate the bonding in $[\text{SbF}_4]^+$ cations. As expected, the natural population analysis (NPA) charge on Sb^{V} increases upon F^- abstraction from monomeric SbF_5 (3.04) to the hypothetical tetrahedral

$[\text{SbF}_4]^+$ (3.08) cation (Table 2.3). However, the size of the increase is surprisingly small due to compensation by increased covalent Sb–F bonding. The opposite is true for $[\text{SbF}_4(\text{N–N})]^+$, in which the NPA charge on Sb^{V} decreases upon F^- abstraction due to considerable electron-pair donation from the nitrogen bases; a charge of 0.74 e is donated from the N-donor to the $[\text{SbF}_4]^+$ moiety (See Table A5 for full list of NPA charges). The lower Wiberg bond indices (WBI) for the Sb–F bonds in $[\text{SbF}_4(\text{N–N})]^+$ ($\text{Sb–F}_{\text{ax}} = 0.51$, $\text{Sb–F}_{\text{eq}} = 0.54$) compared to neutral SbF_5 ($\text{Sb–F}_{\text{ax}} = 0.55$, $\text{Sb–F}_{\text{eq}} = 0.57$) indicate increased ionicity in the Sb–F bonds of the cations, which is paralleled by increased NPA charges on the fluorine atoms. The Sb–F bonding in $[\text{SbF}_4(\text{N–N})]^+$ is not as ionic as in $[\text{SbF}_6]^-$, which displays the lowest Sb–F WBI and highest NPA charge on F out of all the systems studied. The Sb–N WBIs of $[\text{SbF}_4(\text{N–N})]^+$ are more than $2/3$ of those of the Sb–F bonds, suggesting a significant degree of covalency. The strength of the Sb–N interaction reflects the extreme electrophilicity of the ‘naked’ $[\text{SbF}_4]^+$ cation. The $\sigma(\text{lp}(\text{N}) \rightarrow \text{lv}(\text{Sb}))$ energy for a single Sb–N interaction, however, is greater in $[\text{SbF}_4(\text{phen})]^+$ (1731 kJ mol⁻¹) compared to $[\text{SbF}_4(\text{bipy})]^+$ (1629 kJ mol⁻¹), revealing marginally stronger dative interactions in the former. The Sb–F bonds in $[\text{SbF}_4(\text{N–N})]^+$ possess significant π contributions to covalent bonding, according to the second-order perturbation analysis (15–18% per bond, Table 2.4). Meanwhile, the π component of the Sb–F bonds in SbF_5 , $[\text{SbF}_4]^+$ and $[\text{SbF}_6]^-$ are negligible (<2%). The high degree of covalent Sb–N bonding, satiating the extreme electron deficiency of $[\text{SbF}_4]^+$, could rationalise the unexpected stability of these cations.

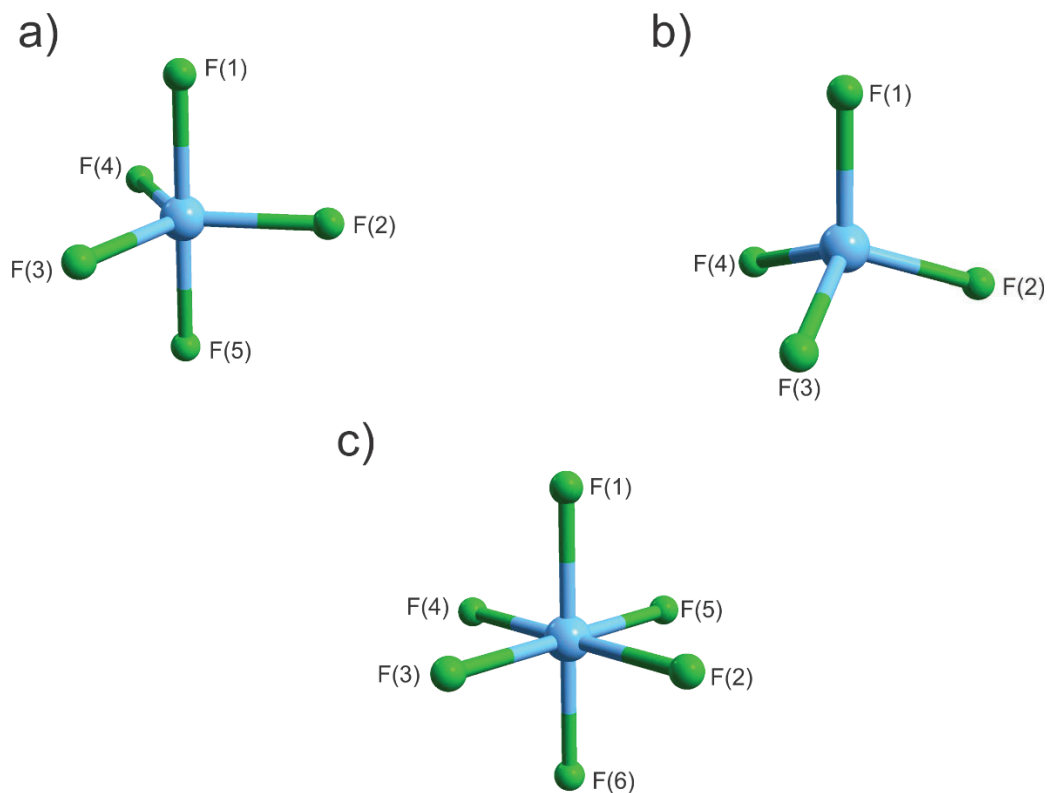


Figure 2.4. Optimised gas-phase geometries for (a) SbF_5 (b) $[\text{SbF}_4]^+$ and (c) $[\text{SbF}_6]^-$. Calculated using the B3LYP functional with the aug-cc-pVTZ-PP (Sb) and aug-cc-pVTZ (F) basis sets. Atom Labelling corresponds to that used for the NBO calculations.

Table 2.3. NPA charges and WBIs for various Sb^{V} fluorides^[a]

	NPA Charge		WBI	
	Sb	F	Sb–F	Sb–N
SbF_5	3.04	–0.61	0.55–0.57	
$[\text{SbF}_4]^+$	3.08	–0.52	0.68	
$[\text{SbF}_6]^-$	3.04	–0.67	0.47	
$[\text{SbF}_4(\text{phen})]^+$	2.92	–0.63 – –0.62	0.51–0.54	0.37
$[\text{SbF}_4(\text{bipy})]^+$	2.92	–0.63 – –0.62	0.51–0.54	0.37

[a]. Calculated using the B3LYP functional with the aug-cc-pVTZ-PP (Sb) and aug-cc-pVTZ (C, H, N, F) basis sets.

Table 2.4. Energies ($E(2)$, kJ mol^{-1}) of the Sb–N and Sb–F interactions in the $[\text{SbF}_4(\text{phen})]^+$ and $[\text{SbF}_4(\text{bipy})]^+$ cations.^[a]

	$\sigma(\text{lp}(\text{N}) \rightarrow \text{lv}(\text{Sb}))$	$\sigma(\text{lp}(\text{F}) \rightarrow \text{lv}(\text{Sb}))$	$\Sigma_{\pi}(\text{lp}(\text{F}) \rightarrow \text{lv}(\text{Sb}))$	$\Sigma_{\text{T}}(\text{lp}(\text{F}) \rightarrow \text{lv}(\text{Sb}))$
$[\text{SbF}_4(\text{phen})]^+$				
Sb–N(1)	1731			
Sb–N(2)	1731			
Sb–F(1)		1319	233	1552
Sb–F(2)		1319	233	1552
Sb–F(3)		1145	249	1394
Sb–F(4)		1145	249	1394
$[\text{SbF}_4(\text{bipy})]^+$				
Sb–N(1)	1629			
Sb–N(2)	1629			
Sb–F(1)		1311	241	1552
Sb–F(2)		1311	241	1552
Sb–F(3)		1137	248	1393
Sb–F(4)		1137	248	1393

[a] Calculated using the B3LYP functional with the aug-cc-pVTZ-PP (Sb) and aug-cc-pVTZ (C, H, N, F) basis sets. (lp) and (lv) denote lone pair and lone valence, respectively.

Molecular orbital calculations (Figure 2.5) reveal that the HOMO and LUMO of $[\text{SbF}_4(\text{N–N})]^+$ are primarily ligand-based. The Sb–N bonding interactions consist of $\sigma(\text{sp}^2(\text{N})\text{--p}(\text{Sb}))$ interactions when the Sb–N are out of phase with respect to one another (HOMO–4) and $\sigma(\text{sp}^2(\text{N})\text{--s}(\text{Sb}))$ interactions when the bonds are in phase (HOMO–5).

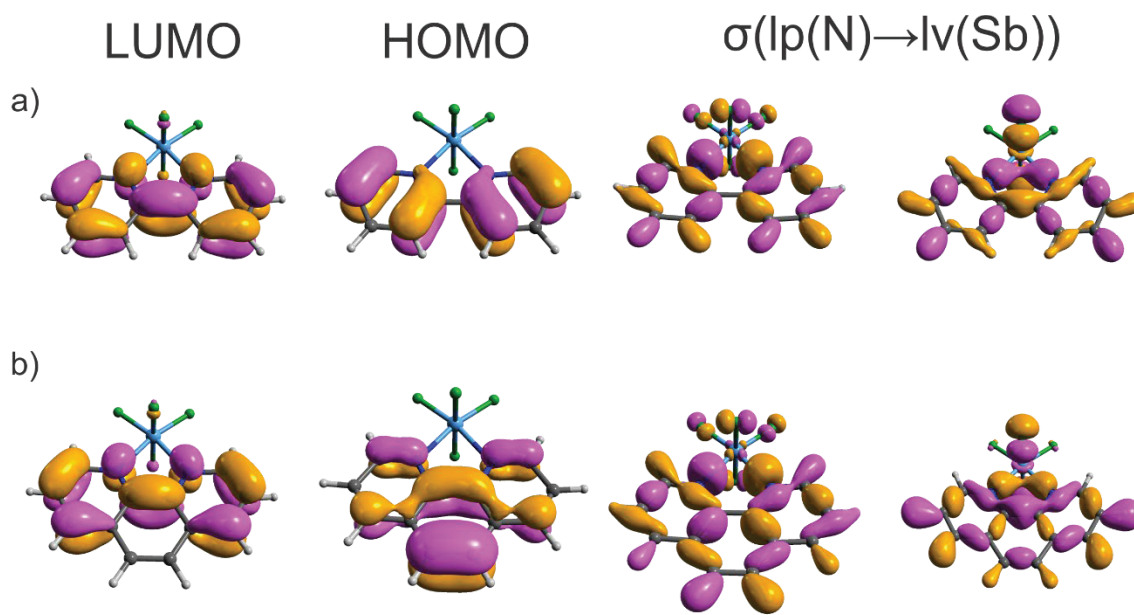


Figure 2.5. Selected molecular orbitals of a) $[\text{SbF}_4(\text{bipy})]^+$ and b) $[\text{SbF}_4(\text{phen})]^+$. Isosurfaces are drawn at $0.04 \text{ e } \alpha_0^{-3}$.

2.4 Conclusions

In conclusion, by exploiting the autoionisation of SbF_5 in the presence of bidentate N-donor ligands, we were able to synthesise and isolate the first examples of donor-stabilised $[\text{SbF}_4]^+$ cations and demonstrate the ability of SbF_5 to act as a F^- donor. The $[\text{SbF}_4(\text{N}-\text{N})]^+$ cations adopt a distorted octahedral geometry in the solid state and in solution. Quantum-chemical calculations reveal that significant σ -electron density from the N-donor ligands is imparted to $[\text{SbF}_4]^+$ upon ligand-induced ionisation, paralleled by an increase in ionicity of the Sb–F bonds, resulting in thermally robust cations derived from strongly Lewis acidic, highly reactive SbF_5 .

2.5 Experimental

2.5.1 General Methods

Caution! Elemental F_2 and SbF_5 are highly toxic and corrosive, rapidly evolving HF upon exposure to moisture. Appropriate safety measures should be taken during their handling.

All reactions were carried out in heat-sealed $\frac{1}{4}$ "-o.d. FEP reactors which were connected to either stainless-steel or Kel-F valves via flared fittings and passivated with 100% F_2 . Volatile materials were distilled on a Pyrex vacuum line equipped with high-vacuum PTFE valves (Chemglass). Solid materials were handled in a dry box (Omni Lab, Vacuum Atmospheres) under an atmosphere of dry N_2 .

Acetonitrile was dispensed from a solvent purification system (M. Braun MB-SPS) onto 3-Å molecular sieves and distilled again onto fresh sieves. Benzene was distilled from a solvent purification system (M. Braun MB-SPS) onto CaH_2 , then distilled again onto fresh 4-Å molecular sieves. Sulfur dioxide (Matheson) was dried over CaH_2 . Antimony pentafluoride (Galaxy chemicals) was purified by distillation. Sulfuryl chloride fluoride (Ozark fluoride specialties) was distilled onto 4-Å molecular sieves to remove SO_2 (confirmed by gas-phase IR spectroscopy) and then distilled onto dried KF; the purified SO_2ClF contains an impurity of SO_2F_2 . 2,2'-Bipyridine (bipy) (Sigma-Aldrich, $\geq 99\%$) was dried by sublimation under dynamic vacuum at 100 °C. 1,10-Phenanthroline (phen) (Sigma-Aldrich, $\geq 99\%$) was recrystallised from dried benzene. The $SbF_5 \cdot SO_2$ adduct was prepared as previously described.³³

2.5.2 Synthesis

[SbF₄(phen)][SbF₆]

In a typical experiment, SbF₅ (0.170 g, 0.783 mmol) and SO₂ClF (1.21 g) were distilled into a ¼”o.d FEP reactor at –196 °C, forming a clear and colourless solution. In a dry box, the solution was frozen in a Dewar containing liquid-nitrogen-cooled copper BBs and charged with 1,10-phenanthroline (0.0707 g, 0.392 mmol). The reactor was removed from the dry box and warmed to ambient temperature over the course of two minutes, briefly resulting in a yellow suspension. After agitating the reactor at ambient temperature for ca. 30 s, a fine white precipitate was formed and the yellow colour of the supernatant was lost, leaving a colourless supernatant. The reactor was agitated for a further 10 min before being cooled to –40 °C, followed by removal of volatile material at this temperature over 30 min under dynamic vacuum. The reactor was subsequently warmed to ambient temperature under dynamic vacuum for a further 10 minutes, yielding [SbF₄(phen)][SbF₆] (0.232 g, 0.378 mmol, 96% yield) as an off-white powder. The NMR spectrum (Figure S3) reveals traces of SO₂ClF (3 mol%), SOF₂ (0.75 mol%), SO₂F₂ (0.09 mol%). The residual SO₂ClF could not be removed despite pumping on the sample under dynamic vacuum at ambient temperature; the SO₂F₂ is an impurity in the SO₂ClF solvent. Thionyl fluoride is likely present due to traces of SO₂ in the SO₂ClF solvent being fluorinated during the reaction.

NMR (ppm, –40 °C, CH₃CN, unlocked)

¹⁹F: 98.6 (s, SO₂ClF), 70.4 (s, SOF₂), 34.3 (s, SO₂F₂), –107.6 (s, [H–phen][SbF₆]), –123.3 (m, 6F, [SbF₆][–]), ¹J(¹⁹F–¹²¹Sb) = 1958 Hz, ¹J(¹⁹F–¹²³Sb) = 1041 Hz).

^1H : 9.23 (d, H1; $^3J(\text{H1-H2}) = 5.25 \text{ Hz}$), 9.15 (d, H3; $^3J(\text{H3-H2}) = 8.52 \text{ Hz}$), 8.29 (m H2/H6)

Atom labelling is as in Figure 2.6 below.

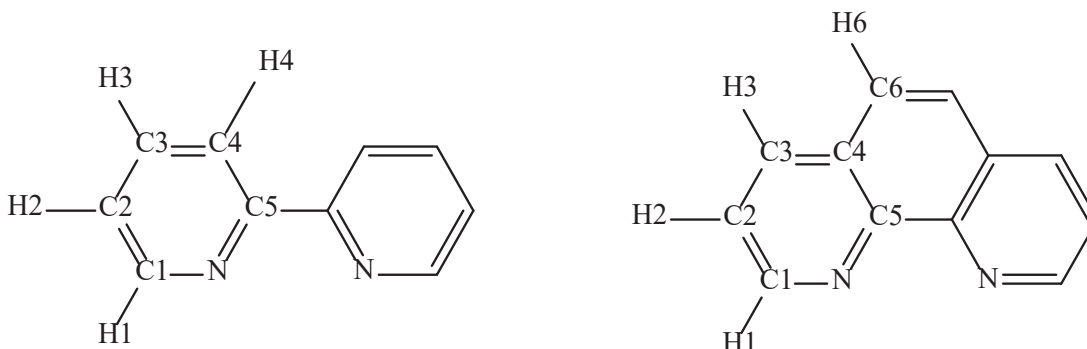


Figure 2.6. Atom labelling used for bipy and phen.

[SbF₄(bipy)][SbF₆]

In a typical experiment, SbF₅ (0.0970 g, 0.450 mmol) and SO₂ClF (1.18 g) were distilled into a ¼”o.d FEP reactor at –196 °C, forming a clear and colourless solution. In a dry box the solution was frozen in a Dewar containing liquid-nitrogen-cooled copper BBs and charged with 2,2'-bipyridine (0.0361 g, 0.231 mmol). The reactor was removed from the dry box and warmed to ambient temperature over the course of two minutes, briefly resulting in a yellow suspension. After agitating the reactor at ambient temperature for ca. 30 s, a fine white precipitate formed and the yellow colour of the supernatant was lost leaving a colourless supernatant. The reactor is agitated for a further 10 min before being cooled to –40 °C, followed by removal of volatile material at this temperature over 30 min under dynamic vacuum. The reactor was then warmed to 90 °C in an oil bath for 2 h under dynamic vacuum causing any free bipy to sublime. The product was isolated in a dry box by cutting the reactor below the point where the 2,2'-bipyridine sublimed, resulting in

[SbF₄(bipy)][SbF₆] (0.123 g, 0.210 mmol, 93.3% yield) as an off-white powder. The NMR spectrum (Figure S4) revealed traces of SO₂ClF (2 mol%) and SO₂F₂ (0.52 mol%). An additional doublet and quartet were observed in the fluorine-on-antimony region at –108 and –117 ppm respectively. The resonance at –117 ppm overlaps with the [SbF₆][–] anion. These multiplet can tentatively be assigned to a SbF₅ adduct, possibly to the neutral adduct SbF₅-bipy-SbF₅.

NMR (ppm, –40 °C, CH₃CN, unlocked)

¹⁹F: 98.6 (s, SO₂ClF); 34.3 (s, SO₂F₂), –107.3 (s, [H–bipy][SbF₆]), –108.2 (d; J = 99 Hz), –117.1 (q; J = 93 Hz), –123.3 (m, 6F, [SbF₆][–] , ¹J(¹⁹F–¹²¹Sb) = 1958 Hz, ¹J(¹⁹F–¹²³Sb) = 1041 Hz)

¹H: 8.96 (d, H1; ³J(H1–H2) = 5.50 Hz), 8.78 (d H4; ³J(H3–H4) = 7.97 Hz), 8.69 (t, H3), 8.16(t, H2).

Atom labelling as shown in Figure 2.6

[SbF₄(phen)][Sb₂F₁₁]

In a dry box, a ¼”o.d FEP reactor was charged with [SbF₄(phen)][SbF₆] (0.0889 g, 0.145 mmol) and SbF₅·SO₂ (0.0408 g, 0.145 mmol) at –80 °C in a Dewar containing liquid-nitrogen-cooled copper BBs. The reactor was kept at –80 °C until SO₂ was distilled onto the solids at –196 °C. The reactor was subsequently warmed up to –70 °C and agitated, forming a yellow solution. The reactor was then warmed up to ambient temperature over the course of two minutes and periodically agitated for a further 10 min. Volatile material was then removed *in vacuo* at –70 °C leaving a brown oil, warming to ambient temperature under dynamic vacuum removed the residual solvent, yielding [SbF₄(phen)][Sb₂F₁₁] (0.112 g, 0.135 mmol, 93% yield) as a light-yellow powder.

NMR (ppm, $-70\text{ }^{\circ}\text{C}$, SO_2 , unlocked)

^{19}F : -92.0 (s, $[\text{Sb}_2\text{F}_{11}]^-$, F_b), -101.8 (s, $\text{SbF}_5 \cdot \text{SO}_2$), -104.7 (s, $\text{SbF}_5 \cdot \text{SOF}_2$), -107.1 (s, $[\text{H-phen}][\text{SbF}_6]$), -111.2 (s, $[\text{Sb}_2\text{F}_{11}]^-$, F_c), -133.1 (s, $[\text{Sb}_2\text{F}_{11}]^-$, F_t)

^1H : 10.22 (s, H1/H3), 9.38 (m, H2/H6)

Atom labelling as shown in Figure 2.6

$[\text{SbF}_4(\text{bipy})][\text{Sb}_2\text{F}_{11}]$

In a dry box, a $\frac{1}{4}$ " o.d FEP reactor was charged with $[\text{SbF}_4(\text{bipy})][\text{SbF}_6]$ (0.0938 g, 0.159 mmol) and $\text{SbF}_5 \cdot \text{SO}_2$ (0.0444 g, 0.158 mmol) at $-80\text{ }^{\circ}\text{C}$ in a Dewar containing liquid-nitrogen-cooled copper BBs. The reactor was kept at $-80\text{ }^{\circ}\text{C}$ until SO_2 was distilled onto the solids at $-196\text{ }^{\circ}\text{C}$. The reactor was subsequently warmed up to $-70\text{ }^{\circ}\text{C}$ and agitated forming a yellow solution. The reactor was then warmed up to ambient temperature over the course of two minutes and periodically agitated for a further 10 min. Volatile material was then removed *in vacuo* at $-70\text{ }^{\circ}\text{C}$ leaving a brown oil. Warming to ambient temperature under dynamic vacuum removed the residual solvent, yielding $[\text{SbF}_4(\text{bipy})][\text{Sb}_2\text{F}_{11}]$ (0.123 g, 0.153 mmol, 97% yield) as a light-yellow powder.

^{19}F : -91.1 (s, $[\text{Sb}_2\text{F}_{11}]^-$, F_b), -98.4 (s, $[\text{SbF}_4(\text{bipy})]^+$, F_{eq}), -102.5 (s, $\text{SbF}_5 \cdot \text{SO}_2$), -107.0 (s, $[\text{H-bipy}][\text{SbF}_6]$), -111.2 (s, $[\text{Sb}_2\text{F}_{11}]^-$, F_c), -133.1 (s, $[\text{Sb}_2\text{F}_{11}]^-$, F_t ; sh, $[\text{SbF}_4(\text{bipy})]^+$, F_{ax}).

^1H : 9.27 (d, H1 , $^3\text{J}(\text{H1-H2}) = 5.42\text{ Hz}$), 9.05 (m, H3/H4), 8.56 (t, H2)

Atom labelling as shown in Figure 2.6

2.5.3 X-ray Crystallography

Crystal Growth and Mounting

Crystals of $[\text{SbF}_4(\text{phen})][\text{SbF}_6] \cdot 2\text{CH}_3\text{CN}$ were grown by dissolving $[\text{SbF}_4(\text{phen})][\text{SbF}_6]$ in the minimum amount of CH_3CN necessary for complete dissolution to occur at ambient temperature. The solution was then stored at $-40\text{ }^\circ\text{C}$ for 16 h, resulting in small pale-yellow blocks.

Crystals of $[\text{SbF}_4(\text{phen})][\text{SbF}_6] \cdot 2\text{SO}_2$ were grown by dissolving $[\text{SbF}_4(\text{phen})][\text{SbF}_6]$ in the minimum amount of SO_2 necessary for complete dissolution to occur at ambient temperature. The solution was then cooled to $-70\text{ }^\circ\text{C}$ and volatiles were removed at this temperature slowly over 4 h, resulting in small pale-yellow blocks.

Despite repeated attempts, crystals of $[\text{SbF}_4(\text{bipy})][\text{SbF}_6]$ suitable for single crystal X-ray diffraction could not be grown.

Data Collection and Reduction

The crystals were centered on a Rigaku SuperNova diffractometer equipped with a Dectris Pilatus 3R 200K-A hybrid-pixel-array detector, a four-circle κ goniometer, an Oxford Cryostream 800, and sealed $\text{MoK}\alpha$ and $\text{CuK}\alpha$ X-ray sources. Data were collected using the $\text{MoK}\alpha$ source ($\lambda = 0.71073\text{ \AA}$) at $-173\text{ }^\circ\text{C}$. Crystals were screened for quality before a pre-experiment was run to determine the unit cell, and a data-collection strategy was calculated based on the determined unit cell and intensity of the preliminary data. This strategy was optimised to collect five-fold redundant data at a resolution of $0.77\text{ \AA}$. The data were processed using CrysAlisPro,³⁴ which applied necessary Lorentz and polarisation

corrections to the integrated data and scaled the data. A numerical (Gaussian-grid) absorption correction was generated based upon the indexed faces of the crystal.

Structure Solution and Refinement

Atom positions were determined using the intrinsic phasing method (ShelXT)³⁵ and were refined using least-squares refinement (ShelXL).³⁶ Non-hydrogen atoms were refined anisotropically and recommended weights for the atoms were determined before hydrogen atoms were introduced using a riding model (HFIX). Structure solution and refinement were performed with the aid of Olex2 (version 1.2).³⁷

2.5.4 Raman Spectroscopy

The Raman spectra of all samples were recorded on solid samples in either flame-sealed m.p. capillaries or 1/4"-o.d. FEP reactors using a Bruker RFS-100 Raman spectrometer outfitted with a quartz beam-splitter and liquid-N₂-cooled germanium detector. The 1064-nm line of a Nd:YAG laser was used for excitation of the sample, and backscattered (180°) radiation was sampled. The usable Stokes range of the collected data was 85–3500 cm⁻¹ with a resolution of 2 cm⁻¹. The laser power was typically set to 200 mW. All Raman spectra are shown in Appendix A (Figures A1–A4)

2.5.5 NMR Spectroscopy

The NMR spectra for all samples were recorded in heat-sealed 4-mm-o.d. FEP tubes sheathed in 5-mm-o.d. glass inserts using a Bruker Avance II 300 MHz spectrometer equipped with a 5-mm broadband probe. Spectra were recorded unlocked in dilute CH₃CN solutions at -40 °C ([SbF₆]⁻ salts) or SO₂ solutions at -70 °C ([Sb₂F₁₁]⁻ salts) and

referenced externally to CFCl_3 (^{19}F) and $\text{Si}(\text{CH}_3)_4$ (^1H) at 20 °C. All NMR spectra are shown in Appendix A (Figures A5–A9)

2.5.6 Computational Details

Calculations were performed using the B3LYP functional as implemented in Gaussian 16 (revision D.01).³⁸ The aug-cc-pVTZ basis set and associated pseudopotentials were used for Sb,³⁹ while the aug-cc-pVTZ basis set was used for all other atoms. The geometries were optimized using analytic-gradient methods, resulting in stationary points with no imaginary frequencies. All subsequent calculations were performed on these optimized geometries. The NBO analyses were performed using NBO (version 6.0),⁴⁰ and GaussView (version 6.0)⁴¹ was used to visualize the vibrational modes and aid in their description.

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Chapter 3 – Synthesis and Characterization of $[\text{SbF}_4(\text{terpy})]^+[\text{SbF}_6]^-$, Heptacoordination About $\text{Sb}^{\text{V}*}$

3.1 Abstract.

The strong fluoride-ion acceptor SbF_5 reacts with the tridentate ligand 2,2':6',2''-terpyridine (terpy), yielding the autoionization product $[\text{SbF}_4(\text{terpy})][\text{SbF}_6]$. The $[\text{SbF}_4(\text{terpy})]^+$ cation is the first example of a crystallographically verified seven-coordinate fluoroantimony(V) complex and exhibits a distorted pentagonal bipyramidal geometry.

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3.2 Introduction

Antimony pentafluoride is well known as a strong Lewis acid and fluoride-ion acceptor; in fact, monomeric SbF_5 in the gas phase is used as the benchmark for Lewis superacidity.¹ The already considerable fluoride-ion affinity (FIA) of monomeric SbF_5 is further increased when utilizing oligomeric SbF_5 yielding polynuclear anions $[\text{Sb}_n\text{F}_{5n+1}]^-$ where $n > 1$).² In addition to its strong Lewis acidity, SbF_5 solutions in anhydrous HF (aHF) are known to be some of the strongest recorded Brønsted superacids.³ We recently found that in the presence of bidentate nitrogen bases, such as 1,10-phenanthroline (phen) or 2,2'-bipyridine (bipy) SbF_5 will autoionize to form $[\text{SbF}_4(\text{N}-\text{N})][\text{SbF}_6]$ ($\text{N}-\text{N}$ = phen or bipy) salts.⁴ They were the first examples of SbF_5 acting as a fluoride-ion donor. Similar ligand-induced autoionisation has also been observed for the lighter group-15 pentafluorides PF_5 and AsF_5 in the presence of phen; interestingly, the use of the conformationally flexible bipy ligand resulted in the autoionisation of PF_5 , but not for AsF_5 where the 2:1 neutral adduct $(\text{AsF}_5)_2 \cdot \text{bipy}$ was the product.^{5,6} Bidentate phosphorus bases such as $o\text{-C}_6\text{H}_4(\text{PMe}_2)_2$, and $o\text{-C}_6\text{H}_4(\text{PPh}_2)_2$ have also been shown to induce autoionisation in PF_5 .⁷

Antimony pentafluoride shows a strong, almost exclusive, preference for hexacoordination, which is reflected in self-association to form *cis*-linked SbF_6 octahedra in both its solid and liquid forms. The $[\text{Sb}_n\text{F}_{5n+1}]^-$ anions ($n = 2$ to 4) also form chains of fluorine-bridged $[\text{SbF}_6]^-$ octahedra. The Lewis acidity of $[\text{SbF}_6]^-$, however, is still sufficiently high to accept a second fluoride ion to form the $[\text{SbF}_7]^{2-}$ dianion, when using the rigorously anhydrous fluoride-ion sources KF , CsF and $[\text{N}(\text{CH}_3)_4]\text{F}$. This heptacoordinate anion demonstrates the highest coordination number that has been achieved in a binary antimony halide.⁸ While $[\text{SbF}_7]^{2-}$ salts have not been structurally

characterised, quantum chemical calculations predict that the $[\text{SbF}_7]^{2-}$ dianion adopts a pentagonal bipyramidal geometry.

Excluding cluster compounds such as $[\text{Rh}_{12}\text{Sb}(\text{CO})_{27}]^{3-}$ where the antimony atom resides in the central cavity of the cluster. Structurally authenticated molecular seven-coordinate antimony(V) complexes are rare and are almost exclusively arylantimony carboxylato derivatives (Figure 3.1).⁹ Compounds **1-6** are formed by the reaction of arylantimony(V) halides with the respective carboxylate. The presence of adventitious water resulted in formation of the oxygen-bridged species **1** and **2**, while anhydrous conditions led to the formation of the mononuclear compounds **3-6**.¹⁰⁻¹⁵ Compound **7** was formed by the reaction of Ph_3Sb with 1-adamantylcarboxylic acid in the presence of H_2O_2 .¹⁶ The mixed valence Sb(III)/Sb(V) compound **8** was formed in the reaction of SbCl_3 with pyridine 2,6-dicarboxylic acid in aqueous solution.¹⁷ In all of the crystallographically characterised heptacoordinate Sb(V) complexes, except **3** and **8**, the carboxylate ligand binds in an unsymmetric fashion with one set of short Sb–O bonds and one notably longer set. In compounds **1-7** five of the bonds to the central Sb atom lie in the same plane, however, the bond angle between the remaining two ligands always deviates significantly from linearity; therefore, the geometry around the central Sb atoms in these compounds is best described as a heavily distorted pentagonal bipyramid. The Sb centres in the binuclear compound **8** also adopt a pentagonal bipyramidal geometry with only minor deviations from the idealised bond angles.

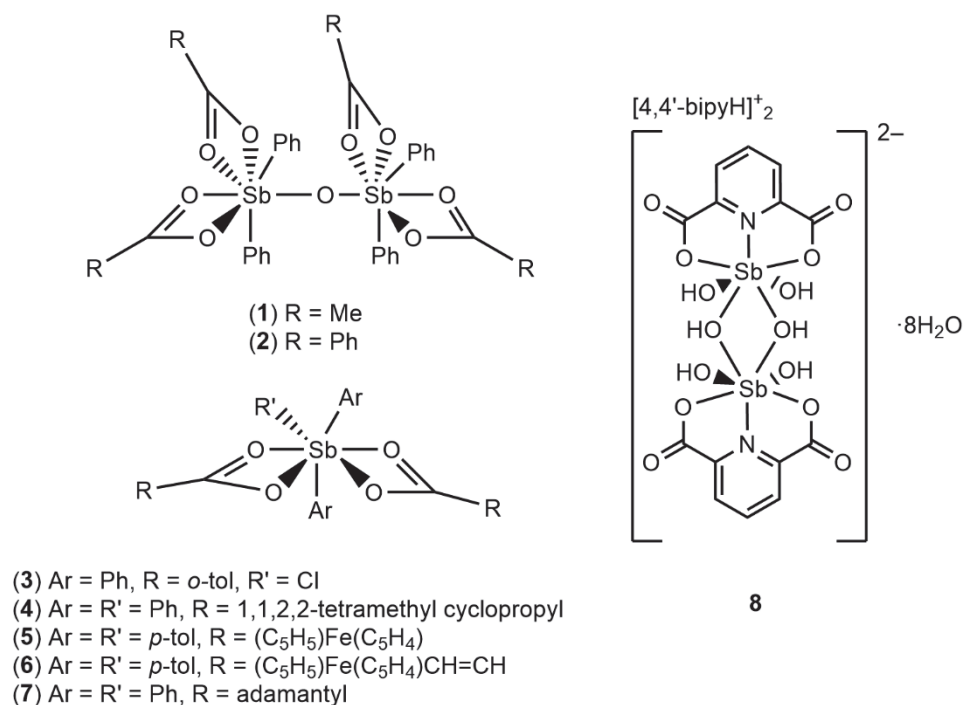


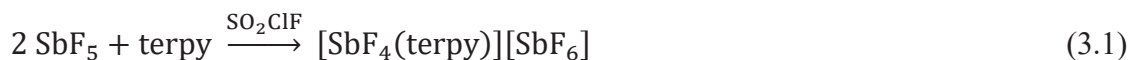
Figure 3.1. Crystallographically characterised hepta-coordinate Sb(V) compounds. Average Sb–O_{carboxylato} bond lengths [Å]: [1] 2.171(7), 2.411(7);¹⁰ [2] 2.188(3), 2.420(5);¹¹ [3] 2.255(3);¹² [4] 2.105(4), 2.800(5);¹³ [5] 2.129(4), 2.851(3);¹⁴ [6] 2.111(6), 2.952(1);¹⁵ [7] 2.154(7), 2.570(7);¹⁶ [8] 2.245(7) Å.¹⁷

No previous examples of a fluoro Sb(V) compound with a coordination number of seven has been structurally characterised. Exploiting the ligand-induced autoionisation of SbF₅ in the presence of a tridentate nitrogen base was studied as a potential route to a heptacoordinate [SbF₄(N–N–N)]⁺ cation. 2,2':6',2''-Terpyridine (terpy) was chosen as the tridentate base because it can possibly relieve steric crowding around the Sb centre via κ²-coordination due to its conformational flexibility.

3.3 Results and Discussions

The reaction of SbF₅ with terpy in a 2:1 molar ratio in SO₂ClF (eq. 3.1) at ambient temperature afforded [SbF₄(terpy)][SbF₆] as an off-white powder in near quantitative yield.

The resulting powder was found to be soluble in SO₂ and CH₃CN, but insoluble in CH₂Cl₂ and pentane. The product is moisture sensitive, but stable at ambient temperature under a dry N₂ atmosphere for at least 5 months.



Crystals of [SbF₄(terpy)][SbF₆]·CH₃CN were grown from a concentrated CH₃CN solution at –40 °C over the course of 16 hours. The salt crystallises in the monoclinic space group *P*2₁/*c* and contains one formula unit in the asymmetric unit. No appreciable anion-cation interactions are present in the structure. The CH₃CN molecule of crystallisation can easily be removed under dynamic vacuum at ambient temperature resulting in an off-white powder. The structure of the [SbF₄(terpy)]⁺ cation is shown in Figure 3.2 and the key metric parameters are listed in Table 3.1. Additionally, the gas-phase structure of [SbF₄(terpy)]⁺ was optimised using density functional theory (DFT) methods (B3LYP functional), generally reproducing the cation geometry well. The [SbF₄(terpy)]⁺ cation represents the first crystallographically characterised fluoro antimony species with a coordination number of 7. It adopts a distorted pentagonal bipyramidal geometry around the central Sb atom with two fluoro ligands in the axial positions (exptl. F(1)–Sb–F(2): 175.49(5)°) and the remaining two fluoro ligands and the nitrogen donor atoms of the terpy ligand located in the equatorial positions, confirming the tendency of heptacoordinate main-group species to adopt a pentagonal bipyramidal geometry motif, as observed for IF₇ and [pip][TeF₇] (pip = 1,1,3,3,5,5 hexamethylpiperidinium).^{18,19} The axial Sb–F bonds (exptl. 1.8851(10), 1.8857(10) Å; calcd. 1.893, 1.894 Å) in [SbF₄(terpy)]⁺ are slightly shorter than the equatorial Sb–F bonds (exptl. 1.9141(10), 1.9181(10) Å; calcd. 1.905 Å) as a consequence of steric crowding. Both sets of Sb–F bond lengths are elongated compared to

$[\text{SbF}_4(\text{phen})]^+$ ($\text{Sb}-\text{F}_{\text{ax}} = 1.8763(12), 1.8783(17) \text{ \AA}$; $\text{Sb}-\text{F}_{\text{eq}} = 1.8683(12) \text{ \AA}$) because of the increased coordination number. Three distinct $\text{Sb}-\text{N}$ bond lengths are observed ($\text{Sb}-\text{N}(1) = 2.2563(13) \text{ \AA}$, $\text{Sb}-\text{N}(2) = 2.2248(12) \text{ \AA}$, $\text{Sb}-\text{N}(3) = 2.2684(13) \text{ \AA}$) with the $\text{Sb}-\text{N}$ bond to the central pyridine ring of terpy being the shortest. As expected, based on the higher coordination number, the $\text{Sb}-\text{N}$ bonds in $[\text{SbF}_4(\text{terpy})]^+$ are longer than those found in $[\text{SbF}_4(\text{phen})]^+$ ($2.1126(16) \text{ \AA}$). Calculation overestimates the $\text{Sb}-\text{N}$ bond lengths by 0.06 to 0.12 $\text{\AA}$. Interestingly, with the dative bond to the central pyridine predicted to be longer than the other two. The overestimation of dative bond lengths from N-donor ligands by DFT calculations was previously found in $[\text{SbF}_4(\text{phen})]^+$; as well as in neutral SF_4 adducts with $\text{N}(\text{C}_2\text{H}_5)_3$ and various pyridine derivatives.^{20,21} As a consequence of the longer $\text{Sb}-\text{N}$ bonds, the calculated $\text{F}(1)-\text{Sb}(1)-\text{F}(2)$ angle (167.51°) deviates further from the idealised value than the experimental structure due to bending away from the more tightly bonded equatorial fluorines. The sum of the equatorial angles (exptl. $364.09(6)^\circ$; calcd. 363.08°) is close to the expected value of 360° for a planar arrangement; however, the puckering of the equatorial plane is represented by $\text{F}(3)$ and $\text{F}(4)$ deviating from the best $\text{N}(1)-\text{N}(2)-\text{N}(3)$ plane by 26.75° . Terpy has previously been reacted with the lower-oxidation-state antimony fluoride, SbF_3 , yielding the neutral $\text{SbF}_3 \cdot \text{terpy}$ adduct which can be considered to have a pseudo-pentagonal bipyramidal coordination around the central Sb atom, where the axial positions are occupied by one of the fluorido ligands and a stereochemically active lone pair.²² The $\text{Sb}-\text{F}$ bonds in the $[\text{SbF}_4(\text{terpy})]^+$ cation are notably shorter than those in $\text{SbF}_3 \cdot \text{terpy}$ ($\text{Sb}-\text{F}_{\text{ax}} = 1.904(7), 1.912(7) \text{ \AA}$; $\text{Sb}-\text{F}_{\text{eq}} = 1.963(7)-1.993(9) \text{ \AA}$) reflecting the stronger bonds to the more electron-poor Sb^{V} centre. Similarly, the $\text{Sb}-\text{N}$ bonds are shorter than those found in $\text{SbF}_3 \cdot \text{terpy}$ ($2.606(12)-2.715(10) \text{ \AA}$).

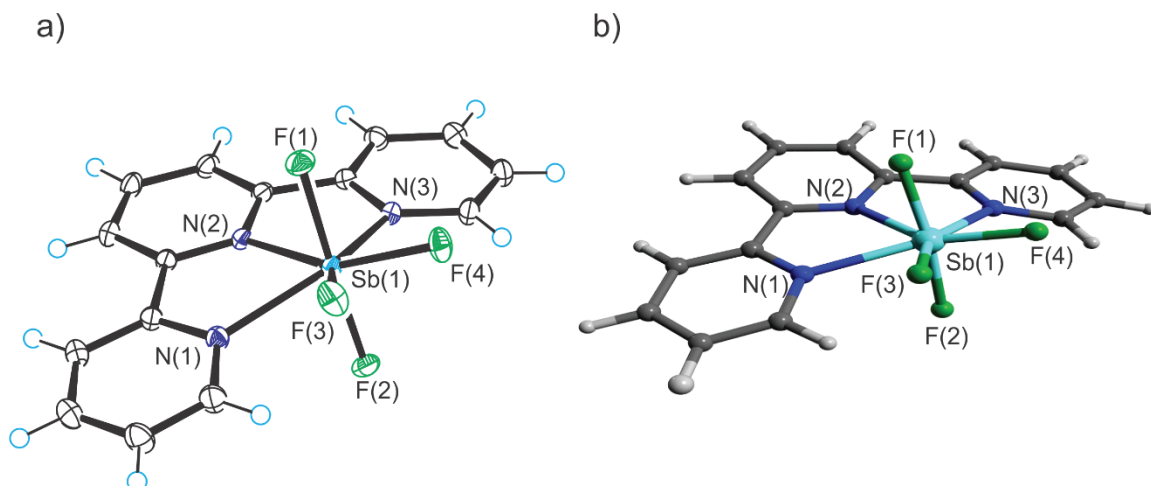


Figure 3.2. (a) Thermal ellipsoid plot (50% probability level) of $[\text{SbF}_4(\text{terpy})]^+$ from $[\text{SbF}_4(\text{terpy})][\text{SbF}_6] \cdot \text{CH}_3\text{CN}$. (b) Optimised gas-phase structure of $[\text{SbF}_4(\text{terpy})]^+$.

Table 3.1. Selected bond lengths (Å) and angles (°) of $[\text{SbF}_4(\text{terpy})]^+$.

$[\text{SbF}_4(\text{terpy})]^+$		
	Exptl.	Calcd. ^[a]
Sb(1)–F(1)	1.8851(10)	1.894
Sb(1)–F(2)	1.8857(9)	1.893
Sb(1)–F(3)	1.9181(10)	1.905
Sb(1)–F(4)	1.9141(10)	1.905
Sb(1)–N(1)	2.2563(13)	2.329
Sb(1)–N(2)	2.2248(12)	2.346
Sb(1)–N(3)	2.2684(13)	2.329
F(1)–Sb(1)–F(2)	175.49(5)	167.51
F(3)–Sb(1)–F(4)	75.97(4)	79.88
F(3)–Sb(1)–N(1)	74.67(4)	73.67
N(1)–Sb(1)–N(2)	70.76(4)	67.93
N(2)–Sb(1)–N(3)	70.09(5)	67.93
N(3)–Sb(1)–F(4)	72.61(4)	73.67

[a] Calculated using the B3LYP-D3(BJ) functional using the def2-TZVPPD-PP (Sb) and def2-TZVPPD (C, H, N, F) basis set.

Whereas $[\text{SbF}_7]^{2-}$ salts could not be studied in solutions by ^{19}F NMR spectroscopy due to solvolysis reactions in aHF and SO_2 (eq. 3.2 & 3.3), solutions of $[\text{SbF}_4(\text{terpy})][\text{SbF}_6]$ were characterised by NMR spectroscopy. The ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra exhibit high-frequency shifts of the terpy signals consistent with complex formation (spectra are shown in Appendix B). The ^{19}F NMR spectrum of $[\text{SbF}_4(\text{terpy})][\text{SbF}_6]$ recorded in CH_3CN at -40°C (Figure 3.3) shows two broad singlets at -67.9 ppm (2F; $\Delta\nu_{1/2} = 313$ Hz) and -82.4 ppm

($2F$; $\Delta\nu_{1/2} = 440$ Hz) that can be attributed to the F_{ax} and F_{eq} environments of the cation, respectively, based on DFT calculations which predict F_{ax} to be the more deshielded environment (See section 3.5.6 Table 3.4). The F_{ax} and F_{eq} signals occur at higher frequencies than in the related $[SbF_4(bipy)][Sb_2F_{11}]$ salt ($F_{ax} = -98.4$; $F_{eq} = -133.1$ ppm). Due to the low symmetry of the cation any J coupling information is lost as the signals are broadened by coupling to rapid quadrupolar relaxed $^{121/123}Sb$ nuclei. Also present is the overlapping equal intensity sextet and octet indicative of the $[SbF_6]^-$ anion [^{121}Sb $I = 5/2$, $^1J(^{19}F-^{121}Sb) = 1950$ Hz; ^{123}Sb $I = 7/2$, $^1J(^{19}F-^{123}Sb) = 1051$ Hz]. The well-resolved sextet and octet suggests a lack of anion-cation interactions in solution. The NMR spectra are in agreement with the solid-state structure of $[SbF_4(terpy)][SbF_6]$. An impurity $[Hterpy][SbF_6]$ was observed in the NMR spectra, where the $[Hterpy]^+$ hydrogen-bonds to the $[SbF_6]^-$ anion, causing a distortion from the ideal octahedral geometry and is a product of accidental hydrolysis.



$M = K, Cs, N(CH_3)_4$

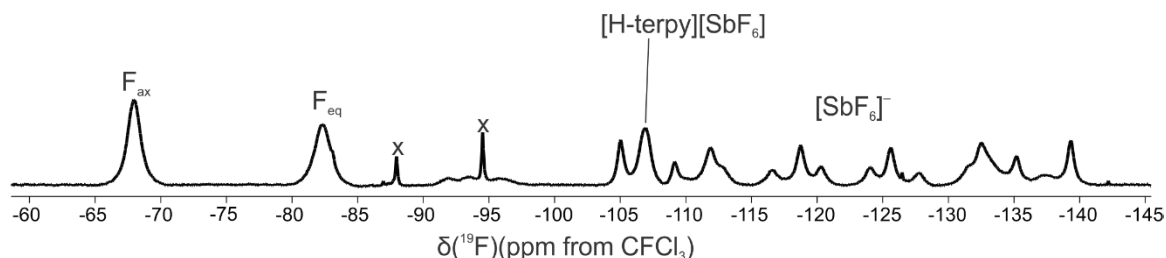


Figure 3.3. ^{19}F NMR spectrum of $[SbF_4(terpy)][SbF_6]$ recorded in CH_3CN at -40 °C. (x) denotes unknown impurity possibly resulting from fluorination of the terpy ligand.

Solid $[\text{SbF}_4(\text{terpy})][\text{SbF}_6]$ was characterised by Raman spectroscopy (Figure 3.4) and quantum chemical calculations were used to aid the assignment of vibrational modes. Key modes and assignments are listed in Table 3.2, a full list of vibrational frequencies and assignments are available in Appendix B. Despite the difference in geometry and coordination number, the symmetric axial and equatorial Sb–F stretching frequencies of $[\text{SbF}_4(\text{terpy})]^+$ are comparable to the octahedral $[\text{SbF}_4(\text{phen})]^+$ ($\nu_s(\text{SbF}_{2\text{ax}}) = 607/600 \text{ cm}^{-1}$, $\nu_s(\text{SbF}_{2\text{eq}}) = 670 \text{ cm}^{-1}$), $[\text{SbF}_4(\text{bipy})]^+$ ($\nu_s(\text{SbF}_{2\text{ax}}) = 605 \text{ cm}^{-1}$, $\nu_s(\text{SbF}_{2\text{eq}}) = 663 \text{ cm}^{-1}$) cations as well as the symmetric axial Sb–F stretch of K_2SbF_7 (604 cm^{-1}); however, the symmetric equatorial Sb–F stretch in K_2SbF_7 (517 cm^{-1}) occurs at a substantially lower frequency, presumably due to the high charge density in the equatorial plane and electrostatic repulsion of the equatorial fluoro ligands. Key vibrational modes of the terpy ligand in $[\text{SbF}_4(\text{terpy})]^+$ are blue shifted relative to the free base, indicative of a Lewis acid-base interaction. This is best demonstrated by the symmetric ring-breathing mode where the three rings are undergoing in-phase ring breathing; this mode occurs at 1030 cm^{-1} (calcd. 1044 cm^{-1}) in $[\text{SbF}_4(\text{terpy})]^+$ compared to 996 cm^{-1} (calcd. 1013 cm^{-1}) in free terpy.

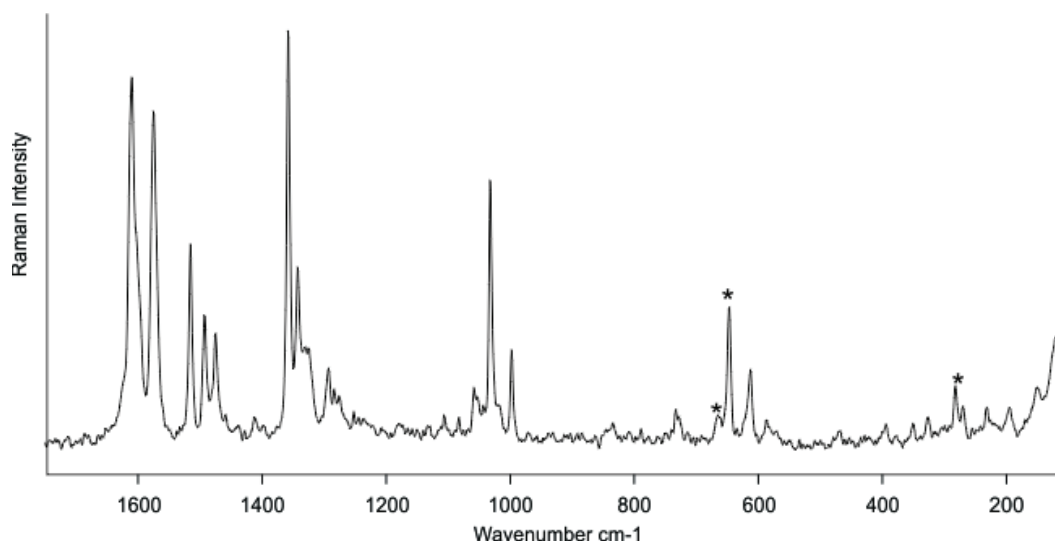


Figure 3.4. Partial Raman spectrum of $[\text{SbF}_4(\text{terpy})][\text{SbF}_6]$. Asterisks (*) denotes bands corresponding to the $[\text{SbF}_6]^-$ anion.

Table 3.2. Selected vibrational frequencies (cm^{-1}) of $[\text{SbF}_4(\text{terpy})]^+$

	$[\text{SbF}_4(\text{terpy})]^+$	
	Exptl.	Calcd. ^[a]
$\nu_{\text{as}}(\text{SbF}_{2\text{ax}})$	-	663(1)[87]
$\nu_{\text{s}}(\text{SbF}_{2\text{ax}})$	610(19)	589(22)[<1]
$\nu_{\text{s}}(\text{SbF}_{2\text{eq}})$	659(sh)	623(15)[81]
$\nu_{\text{as}}(\text{SbF}_{2\text{eq}})$	-	586(<1)[55]
Symmetric ring-breathing mode	1030(64)	1044(150)[4]

Normalised Raman intensities given in parenthesis. [a] Calculated using the B3LYP-D3(BJ) functional using the def2-TZVPPD-PP (Sb) and def2-TZVPPD (C, H, N, F) basis set. Absolute Raman intensities ($\text{\AA}^4 \text{u}^{-1}$) are given in parentheses and IR intensities (km mol^{-1}) given in square brackets.

Natural bond order (NBO) analysis was used to gain a better understanding of the bonding in $[\text{SbF}_4(\text{terpy})]^+$ and how it compares to the hexacoordinate $[\text{SbF}_4(\text{phen})]^+$ and $[\text{SbF}_4(\text{bipy})]^+$ cations. All the donor-stabilised cations show a decrease in the Natural Population Analysis (NPA) charge on Sb compared to neutral SbF_5 (3.04). This is a result of the nitrogen bases donating considerable amounts of electron density to stabilise the highly electrophilic $[\text{SbF}_4]^+$ centre. As expected, there is a slightly larger decrease in NPA charge on Sb in $[\text{SbF}_4(\text{terpy})]^+$ (2.88) compared to $[\text{SbF}_4(\text{N-N})]^+$ (2.92) due to increased electron density donation from the tridentate base compared to the bidentate bases (Table 3.3). Whereas the Sb-F_{ax} bonds in the hexacoordinate and heptacoordinate cations are similar and weaker than in monomeric SbF_5 (Wiberg bond indices: $\text{SbF}_5 = 0.55$; $[\text{SbF}_4(\text{N-N})]^+ = 0.51$; $[\text{SbF}_4(\text{terpy})]^+ = 0.49$), the weakening of the Sb-F_{eq} bond compared to SbF_5 is more substantial in $[\text{SbF}_4(\text{terpy})]^+$, likely because of the steric crowding in the equatorial plane (WBI: $\text{SbF}_5 = 0.57$; $[\text{SbF}_4(\text{N-N})]^+ = 0.54$; $[\text{SbF}_4(\text{terpy})]^+ = 0.50$). Due to the distorted pentagonal bipyramidal geometry of the $[\text{SbF}_4(\text{terpy})]^+$ cation there is less efficient orbital overlap between the nitrogen donors and the central Sb atom compared to the octahedral cations, resulting in the lowest level of covalency. The distinction between the pendant N-donors N(1)/N(3) which have slightly more covalent interactions (WBI = 0.30) and the central N-donor N(2) (WBI = 0.27) reflects the predicted bond lengths, which, as stated above, show the opposite trend compared to the experimental structure.

Table 3.3. NPA charges and Wiberg bond indices (WBI) for various Sb(V) fluorides. ^[a]

	NPA Charge		WBI	
	Sb	F	Sb–F	Sb–N
SbF ₅	3.04	–0.61	0.55-0.57	
[SbF ₄ (phen)] ⁺	2.92	–0.63- –0.62	0.51-0.54	0.37
[SbF ₄ (bipy)] ⁺	2.92	–0.63- –0.62	0.51-0.54	0.37
[SbF ₄ (terpy)] ⁺	2.88	–0.65- –0.63	0.49-0.50	0.27-0.30

[a] Calculated using the B3LYP-D3(BJ) functional using the def2-TZVPPD-PP (Sb) and def2-TZVPPD (C, H, N, F) basis set.

3.4 Conclusion

In summary SbF₅ autoionises in the presence of the tridentate nitrogen base terpy to form the heptacoordinate [SbF₄(terpy)]⁺ cation as its [SbF₆][–] salt. This is the first structurally characterised fluoro Sb(V) complex with a coordination number of seven and a distorted pentagonal bipyramidal geometry. The stability of the [SbF₄(terpy)]⁺ cation is promising towards expanding the chemistry of heptacoordinate Sb^V compounds.

3.5 Experimental

3.5.1 General Methods

Caution! SbF₅ is highly toxic and corrosive, rapidly evolving HF upon exposure to moisture. Appropriate safety measures should be taken when handling it.

All reactions were carried out in heat-sealed ¼”-o.d. FEP reactors which were connected to either stainless-steel or Kel-F valves via flared fittings. Volatile materials were distilled on a Pyrex vacuum line equipped with high-vacuum PTFE valves (Chemglass). Solid materials were handled in a dry box (Omni Lab, Vacuum Atmospheres) under an atmosphere of dry N₂.

Acetonitrile, dichloromethane and pentane were dispensed from a solvent purification system (M. Braun MB-SPS) onto 3-Å molecular sieves and distilled again onto fresh sieves. Sulfur dioxide (Matheson) was dried over CaH₂. Antimony pentafluoride (Galaxy chemicals) was purified by distillation. Sulfuryl chloride fluoride (Ozark fluoride specialties) was distilled onto 4-Å molecular sieves to remove SO₂ (confirmed by gas-phase IR spectroscopy) and then distilled onto dried KF; the purified SO₂ClF contains an impurity of SO₂F₂ which does not interfere with the chemistry. 2,2':6',2''-Terpyridine (terpy) (sigma-aldrich 98%) was purified by sublimation under dynamic vacuum (3 mTorr) at 100 °C. The SbF₅·SO₂ adduct was prepared as previously described.²³

3.5.2 Synthesis

[SbF₄(terpy)][SbF₆]

In a typical experiment SbF₅ (0.247 g, 1.14 mmol) and SO₂ClF (ca. 1 g) were distilled into a ¼”-o.d FEP reactor at -196 °C, forming a clear and colourless solution. In a dry box the solution was frozen in a Dewar containing liquid-nitrogen-cooled copper BBs and charged with terpy (0.130 g, 0.556 mmol). The reactor was removed from the dry box and warmed to ambient temperature over the course of two minutes, forming a yellow suspension. After agitating the reactor for ca. 5 min at ambient temperature a white

precipitate was formed and the supernatant loses its yellow colour, leaving a colourless supernatant. The reactor was agitated for a further 10 min at ambient temperature then cooled to $-40\text{ }^{\circ}\text{C}$ and volatiles were removed under dynamic vacuum. The reactor was then warmed to $40\text{ }^{\circ}\text{C}$ in a hot water bath and was under dynamic vacuum for a further 15 min yielding $[\text{SbF}_4(\text{terpy})][\text{SbF}_6]$ as an off-white powder (0.715 g, 1.07 mmol, 94% yield).

NMR (ppm, $-40\text{ }^{\circ}\text{C}$, CH_3CN , unlocked)

^{19}F : -67.9 (s, $\text{SbF}_{2\text{ax}} [\text{SbF}_4(\text{terpy})]^+$), -82.4 (s, $\text{SbF}_{2\text{eq}} [\text{SbF}_4(\text{terpy})]^+$), -107.0 (s, $[\text{H-terpy}][\text{SbF}_6]$), -122.2 (m, 6F, $[\text{SbF}_6]^-$ $^1J(^{19}\text{F}-^{121}\text{Sb}) = 1950\text{ Hz}$, $^1J(^{19}\text{F}-^{123}\text{Sb}) = 1051\text{ Hz}$).

^1H : 9.42 (s, $\text{H}3'/\text{H}5'$), 8.91 (s, $\text{H}4'/3/3''$), 8.76 (s, $\text{H}4/4''$), 8.64 (s, $\text{H}6/6''$), 8.16 (s, $\text{H}5/5''$)

^{13}C : 151.3 (s, $\text{C}2/2''$), 149.6 (s, $\text{C}2'/6'$), 147.3 (s, $\text{C}6/6''$), 141.2 (s, $\text{C}4'$), 140.3 (s, $\text{C}4/4''$), 131.3 (s, $\text{C}5/5''$), 126.2 (s, $\text{C}3'/5'$), 124.8 (s, $\text{C}3/3''$)

3.5.3. X-Ray Crystallography

The reactors containing the crystals were cut on an aluminium trough that was positioned close to the diffractometer and cooled to approximately $-80\text{ }^{\circ}\text{C}$ by a stream of cold, dry N_2 . Once the crystals were deposited onto the trough, the selected crystal was affixed to a Nylon cryo-loop submerged in perfluorinated polyether oil (Fomblin Z-25) and transferred to the goniometer using liquid N_2 -cooled cryo-tongs. The crystals were centered on a Rigaku SuperNova diffractometer equipped with a Dectris Pilatus 3R 200 K-A hybrid-pixel-array detector, a four-circle κ goniometer, an Oxford Cryostream 800 cooling device, and sealed $\text{MoK}\alpha$ and $\text{Cu K}\alpha$ X-ray sources. Data were collected using the $\text{MoK}\alpha$ source at $-173\text{ }^{\circ}\text{C}$. Crystals were screened for quality before a pre-experiment was run to determine the unit cell, and data was collected on a full hemisphere at a resolution of 0.70

Å. The data were processed using CrysAlisPro,²⁴ which applied necessary Lorentz and polarization corrections to the integrated data and scaled the data. A numerical (Gaussian-grid) absorption correction was generated on the basis of the indexed faces of the crystal. Atom positions were determined using the intrinsic phasing method (ShelXT)²⁵ and refined using least-squares refinement (ShelXL).²⁶ Non-hydrogen atoms were refined anisotropically, and recommended weights for the atoms were determined before hydrogen atoms were introduced using a riding model (HFIX). Structure solution and refinement were performed with the aid of Olex2 (version 1.5).²⁷

3.5.4. Raman Spectroscopy

Raman spectra of all samples were recorded on solid samples in flame-sealed m.p. capillaries using a Bruker RFS-100 Raman spectrometer outfitted with a quartz beam-splitter and liquid-N₂-cooled germanium detector. The 1064-nm line of a Nd:YAG laser was used for excitation of the sample, and backscattered (180°) radiation was sampled. The usable Stokes range of the collected data was 85–3500 cm⁻¹ with a resolution of 2 cm⁻¹. The laser power was typically set to 100 mW.

3.5.5 NMR Spectroscopy

The NMR spectra for all samples were recorded in heat-sealed 4-mm-o.d. FEP tubes sheathed in 5-mm-o.d. glass inserts using a Bruker Avance II 300 MHz spectrometer equipped with a 5-mm broadband probe. Spectra were recorded unlocked in dilute CH₃CN solutions at -40 °C ([SbF₄(terpy)][SbF₆]) and referenced externally to CFC₃ (¹⁹F) and Si(CH₃)₄ (¹H and ¹³C{¹H}) at 20 °C. It was found that [SbF₄(terpy)][SbF₆] slowly precipitated out of CH₃CN solution during the acquisition of the ¹³C{¹H} NMR spectrum,

to prevent precipitation the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of $[\text{SbF}_4(\text{terpy})][\text{SbF}_6]$ was recorded in SO_2 at $-30\text{ }^\circ\text{C}$. The ^1H & ^{13}C NMR are shown in Appendix B (Figures B.2 & B.3)

3.5.6. Computational details

Calculations were performed using the B3LYP-D3BJ and TPSSSTPSS-D3BJ functionals as implemented in Gaussian 16 (revision D.01).⁶ The geometries were optimized using analytic-gradient methods, resulting in stationary points with no imaginary frequencies. All subsequent calculations were performed on these optimized geometries without imposing any symmetry. The B3LYP-D3BJ/def2tzvppd-PP⁷ level of theory was used for Sb, while the def2tzvppd basis set was used for all other atoms in geometry optimizations and frequency calculations. The NBO analyses were performed using NBO (version 6.0),⁸ and GaussView (version 6.0)⁹ was used to visualize the vibrational modes and aid in their description. The nuclear shielding tensors were calculated using the GIAO method at the TPSSSTPSS-D3BJ/def2tzvppd level of theory in CH_3CN using the IEFPCM solvent model. The equation $\delta = \sigma_{\text{CFCl}_3} - \sigma_{\text{F}}$ was used to determine the chemical shifts from the calculated shielding values of CFCl_3 and the fluorine environment of interest.

3.5.7. NMR Shift Calculations

In spite of the high level of agreement, the assignment of the axial and equatorial fluorine environments for the $[\text{SbF}_4(\text{terpy})]^+$ cation remains tentative based on the fact that calculation of accurate ^{19}F NMR chemical shifts is not trivial.

Table 3.4. Experimental and calculated chemical shifts (ppm) for $[\text{SbF}_4(\text{terpy})]^+$

$[\text{SbF}_4(\text{terpy})]^{+[\text{a}]}$		
	F_{ax}	F_{eq}
Exptl.	−67.9	−82.4
Calcd. ^[b]	−65	−70

[a] From $[\text{SbF}_4(\text{terpy})][\text{SbF}_6]$ in CH_3CN at $-40\text{ }^\circ\text{C}$. [b] Calculated at the TPSSTPSS-D3BJ/def2tzvppd level of theory.

3.6 References

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Chapter 4 – Fluoride-Ion Donor Properties of AsF₅*

4.1 Abstract

Arsenic pentafluoride undergoes ligand-induced autoionization in the presence of 1,10-phenanthroline (phen) in SO₂ClF solution to form the donor-stabilized [AsF₄(phen)][AsF₆] salt. Reacting [AsF₄(phen)][AsF₆] with the strong Lewis acid SbF₅·SO₂ yields the mixed arsenic-antimony salt [AsF₄(phen)][Sb₂F₁₁]. These salts are the first examples of crystallographically characterized donor-stabilized [AsF₄]⁺ cations. The analogous reaction of AsF₅ and 2,2'-bipyridine (bipy) does not result in autoionization but leads to the formation of a 2:1 neutral adduct (AsF₅)₂·bipy. The gas-phase and solution fluoride-ion affinities (FIA) of [AsF₄]⁺ and [SbF₄]⁺ were calculated revealing them to be incredibly strong Lewis acids. DFT calculations and NBO analysis show that significant electron-pair donation from phen to the As center in [AsF₄(phen)]⁺ is occurring and quenching the extreme electrophilicity of the [AsF₄]⁺ cation.

*Based on the following publication: O'Donnell, F.; Wetmore, S. D.; Gerken, M. *Inorg. Chem.*

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4.2 Introduction

Arsenic pentafluoride is a colorless gas containing monomeric trigonal bipyramidal molecules under standard conditions. It is a strong F^- acceptor forming stable $[AsF_6]^-$ anions and in some cases $[As_2F_{11}]^-$ anions. The $[As_2F_{11}]^-$ anion was first observed in 1969 via low temperature IR¹ and NMR² spectroscopies, however, it was not structurally characterized until 1999 as its $[(MeS)_2CSX]^+$ ($X = H$ or D)³ and $[(m-CF_3C_6H_4)(C_6H_5)CF]^+$ salts.⁴ In contrast, the heavier group-15 pentafluoride SbF_5 is a highly viscous colorless liquid under standard conditions consisting of chains of cis-linked SbF_6 octahedra; it is an even stronger F^- acceptor than AsF_5 forming stable polynuclear $[Sb_nF_{5n+1}]^-$ ($n = 1-4$) anions. The lightest group-15 pentafluoride PF_5 , like AsF_5 , is also a colorless monomeric gas with a trigonal bipyramidal molecular geometry and is the weakest F^- acceptor of the three, forming $[PF_6]^-$ anions, with no known examples of a $[P_2F_{11}]^-$ anion. The propensity for group-15 pentafluorides of phosphorus, arsenic, and antimony to form fluorine-bridged oligomers scales with their fluoride-ion affinities (FIA) (PF_5 calcd. 382 kJ mol^{-1} ; AsF_5 : exptl. $421 \pm 22\text{ kJ mol}^{-1}$, calcd. 435 kJ mol^{-1} ; SbF_5 : exptl. $506 \pm 60\text{ kJ mol}^{-1}$, calcd. 495 kJ mol^{-1}).^{5,6}

The fluoride-ion donor properties of AsF_5 are much less explored than its fluoride-ion acceptor properties; in fact, there has only been one previous report of AsF_5 acting as a fluoride-ion donor. Electrical resistive heating of a platinum wire under an atmosphere of AsF_5 and F_2 leading to the formation $[AsF_4][PtF_6]$ as characterized by vibrational spectroscopy.^{7,8} Fluoroarsonium(V) cations have also been accessed with methyl substituents on As. The $[CH_3AsF_3][AsF_6]$ salt was obtained as a by-product in the reaction of $(CH_3)_3SiNCNSi(CH_3)_3$ with AsF_5 in anhydrous HF at $-70\text{ }^\circ\text{C}$; it was hypothesized that

the trifluoromethylarsonium cation was formed from the reaction intermediates AsF_3 and FCH_3 in the presence of AsF_5 .⁹ The dimethyl-substituted salts, $[(\text{CH}_3)_2\text{AsF}_2][\text{PnF}_6]$, $\text{Pn} = \text{As}, \text{Sb}$, were prepared from $(\text{CH}_3)_2\text{AsOOH}$ and PnF_5 in anhydrous HF at $-78\text{ }^\circ\text{C}$.¹⁰ The $[\text{AsF}_6]^-$ salt was also prepared by fluorination of $(\text{CH}_3)_2\text{AsF}$ with F_2 in the presence of AsF_5 in CFCl_3 solvent.¹¹ The crystal structures of $[\text{CH}_3\text{AsF}_3][\text{AsF}_6]$ and $[(\text{CH}_3)_2\text{AsF}_2][\text{SbF}_6]$ showed cations distorted from tetrahedral symmetry with $\text{As}\cdots\text{F}$ cation-anion contacts.

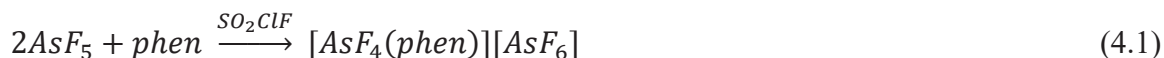
We recently showed that donor-stabilized $[\text{SbF}_4]^+$ cations could be accessed through the ligand-induced autoionization of SbF_5 in the presence of the bidentate nitrogen bases 1,10-phenanthroline (phen) or 2,2'-bipyridine (bipy) in SO_2ClF solvent.¹² Similar reactivity has also been observed with PF_5 and a variety of bidentate N- and P-donors (L–L) such as bipy, phen, 4-fluoro-2,2'-bipyridine, $o\text{-C}_6\text{H}_4(\text{PMe}_2)_2$, and $o\text{-C}_6\text{H}_4(\text{PPh}_2)_2$ yielding $[\text{PF}_4(\text{L}–\text{L})][\text{PF}_6]$ salts.^{13,14} The group 5 transition metal pentafluorides MF_5 ($\text{M} = \text{Nb}, \text{Ta}$) are also known to undergo facile ligand-induced autoionization with a number of mono- and bidentate donors.^{15–17} The propensity for AsF_5 to autoionize was studied in the presence of bidentate ligands.

4.3 Results and discussion

4.3.1 Synthesis and properties of $[\text{AsF}_4(\text{phen})][\text{AsF}_6]$, $[\text{AsF}_4(\text{phen})][\text{Sb}_2\text{F}_{11}]$ and $(\text{AsF}_5)_2\cdot\text{bipy}$.

The reaction of AsF_5 with phen in SO_2ClF in a 2:1 molar ratio produces $[\text{AsF}_4(\text{phen})][\text{AsF}_6]$ in near quantitative yield as an off-white powder (eq 4.1). The insolubility of the ionic product in SO_2ClF is likely an important factor that drives the

reaction. The resulting powder is soluble in SO₂ and CH₃CN. The salt was found to be stable at ambient temperature under an inert atmosphere for at least two months. This thermal stability is notable as previously studied neutral AsF₅ adducts of organic nitriles were found to decompose within 30 minutes at ambient temperature.¹⁸ A similar level of thermal stability was also observed for [SbF₄(phen)]⁺ and [SbF₄(bipy)]⁺ salts.⁹ Unlike neutral AsF₅, the salt does not react violently with water, as the equimolar reaction of [AsF₄(phen)][AsF₆] with H₂O in CH₃CN at ambient temperature for ca. 1 hour results in some hydrolysis of the salt generating small quantities of [Hphen][AsF₆] (≈10 mol%) while the remaining [AsF₄(phen)][AsF₆] is left unreacted as evidenced by Raman and NMR spectroscopies.¹⁹



The addition of a slight excess of SbF₅·SO₂ (2.7 equivalents) to [AsF₄(phen)][AsF₆] in SO₂ yields the mixed arsenic-antimony salt [AsF₄(phen)][Sb₂F₁₁] as a yellow powder (eq 4.2). The resulting product was found to be soluble in SO₂, while the dinuclear [Sb₂F₁₁][−] anion dissociates in CH₃CN into [SbF₆][−] and SbF₅·CH₃CN. The reaction of [AsF₄(phen)][AsF₆] with an excess of neat SbF₅ produces an intractable mixture of products possibly resulting from the oxidation of the organic base.



The reaction of two molar equivalents of AsF₅ with bipy in SO₂ClF forms the neutral 2:1 adduct (AsF₅)₂·bipy in a quantitative yield as a white powder (eq 4.3). The resulting powder was found to be soluble in CH₃CN, while insoluble in SO₂ and CH₂Cl₂. The neutral adduct is stable at ambient temperature under an inert atmosphere for at least two weeks. No evidence for an autoionization product was found.



Despite repeated attempts we were unable to stabilize an $[\text{AsF}_4]^+$ or $[\text{SbF}_4]^+$ cation using monodentate ligands such as pyridine or 4-dimethylaminopyridine (DMAP). Based on conductivity measurements Kolditz and Rehak suggested that in CH_3CN solutions of AsF_5 , an equilibrium between neutral AsF_5 and autoionized $[\text{AsF}_4(\text{CH}_3\text{CN})_2][\text{AsF}_6]$ is operating, however, the existence of $[\text{AsF}_4(\text{CH}_3\text{CN})_2][\text{AsF}_6]$ has never been substantiated.²⁰

Fluoride-ion abstraction from AsF_5 can also be achieved via the use of trimethylsilyl trifluoromethanesulfonate (TMSOTf) in the presence of phen, however, it was found during the equimolar reaction of AsF_5 , phen and TMSOTf in CH_2Cl_2 that autoionization was a competing reaction leading to the formation of mixtures of $[\text{OTf}]^-$ and $[\text{AsF}_6]^-$ salts of $[\text{AsF}_4(\text{phen})]^+$ in an approximate 1:0.7 ratio ($[\text{OTf}]:[\text{AsF}_6]$) based on ^{19}F NMR spectroscopy. The similar solubilities of the two salts in common solvents precluded the isolation of $[\text{AsF}_4(\text{phen})][\text{OTf}]$ as a pure compound.

4.3.2 Crystal and molecular structures.

The structures of $[\text{AsF}_4(\text{phen})][\text{AsF}_6] \cdot 2.5\text{SO}_2$, $[\text{AsF}_4(\text{phen})][\text{Sb}_2\text{F}_{11}]$ and $(\text{AsF}_5)_2 \cdot \text{bipy}$ were elucidated via X-ray crystallography. In addition, the gas-phase geometries of $[\text{AsF}_4(\text{phen})]^+$ and $(\text{AsF}_5)_2 \cdot \text{bipy}$ were optimized using DFT methods (B3LYP functional) resulting in stationary points whose geometries are in excellent agreement with the experimental structures. Full crystallographic data collection and refinement parameters are given in Appendix C (Table C1).

Colourless blocks of $[\text{AsF}_4(\text{phen})][\text{AsF}_6] \cdot 2.5\text{SO}_2$ were grown by the slow evacuation of an $\text{SO}_2/\text{SO}_2\text{ClF}$ solvent mixture at -70°C . The salt crystallizes in the triclinic

space group $P\bar{1}$, with two $[\text{AsF}_4(\text{phen})][\text{AsF}_6]$ moieties in the asymmetric unit. The crystal lattice consists of alternating layers of antiparallel offset π - π stacked $[\text{AsF}_4(\text{phen})][\text{AsF}_6]$ and SO_2 (Figure 4.1). The centroid-centroid distance between the two $[\text{AsF}_4(\text{phen})]^+$ cations is 3.518 Å, which falls within the typical range of 3.3–3.8 Å for complexes with nitrogen containing aromatic ligands.²¹ No appreciable anion-cation interactions are observed in the crystal structure.

Pale yellow plates of $[\text{AsF}_4(\text{phen})][\text{Sb}_2\text{F}_{11}]$ (Figure 4.2) were grown by the slow removal of volatiles from an $\text{SO}_2/\text{SO}_2\text{ClF}$ solvent mixture at -70°C . The salt crystallizes in the monoclinic space group $P2_1/n$, with one crystallographically independent formula unit in the asymmetric unit. There are no appreciable anion-cations interactions or π - π stacking between cations in the crystal structure.

The metric parameters for $[\text{AsF}_4(\text{phen})]^+$ do not differ substantially between either the $[\text{AsF}_6]^-$ or $[\text{Sb}_2\text{F}_{11}]^-$ salts, thus, only the $[\text{AsF}_4(\text{phen})][\text{AsF}_6]\cdot 2.5\text{SO}_2$ structure will be discussed further. Table 4.1 contains the key bond lengths and angles of the $[\text{AsF}_4(\text{phen})]^+$ cation. The cation adopts a distorted octahedral geometry around the central arsenic atom. The two equatorial As–F_{eq} bonds *trans* to the nitrogen donors are slightly contracted (1.6976(13)–1.7063(13) Å) compared to axial As–F_{ax} bonds (1.7227(14)–1.7241(14) Å), all the As–F bonds in $[\text{AsF}_4(\text{phen})]^+$ are longer than those in the related $[\text{CH}_3\text{AsF}_3]^+$ cation (1.647(2)–1.653(2) Å). It is also worth noting that the As–F bond lengths in the cation are not substantially different from those in the hexafluorido arsenate anion (av. As–F $[\text{AsF}_6]^-$ = 1.7143(15) Å) which can be attributed to the large degree of compensatory electron density donation from the nitrogen base (see computational results). There is a slight asymmetry in the As–N bond lengths (1.9502(17)–1.9608(16) Å) with one longer and one

shorter As–N bond a feature, which is not reproduced in the optimized gas-phase geometry where the As–N bond lengths are identical. The As–N bonds lengths in $[\text{AsF}_4(\text{phen})]^+$ are comparable to those found in neutral adducts of AsF_5 with nitriles ($\text{AsF}_5 \cdot \text{NCH}$: 1.983(3) Å, $\text{AsF}_5 \cdot \text{NCC}(\text{CH}_3)_3$: 1.969(2) Å).¹⁸ The small bite angle of phen (83.22(7)°) causes a slight widening of the F(3)–As(1)–F(4) (93.95(7)°) angle from 90°. There is a near-linear arrangement of the F(1)–As(1)–F(2) (175.38(6)°) moiety.

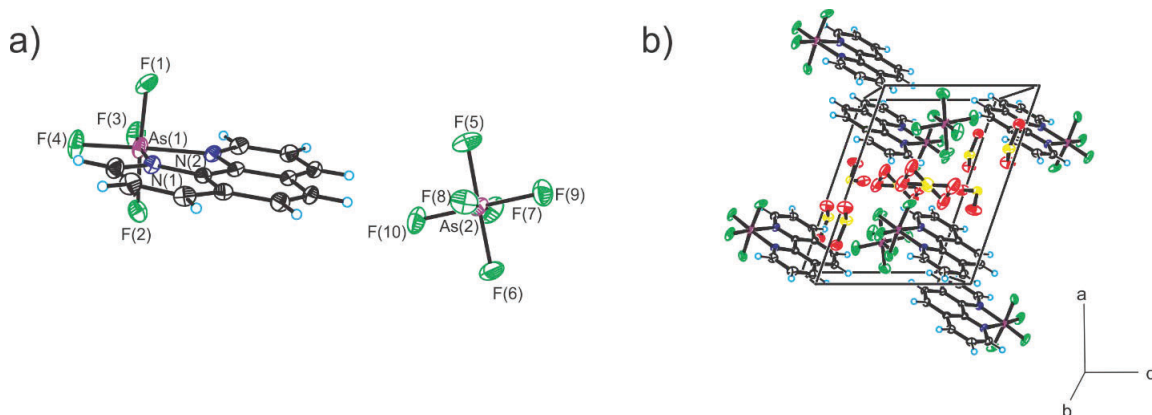


Figure 4.1. (a) Thermal ellipsoid plot (50% probability level) of one of the crystallographically independent $[\text{AsF}_4(\text{phen})][\text{AsF}_6]$ ion pair in $[\text{AsF}_4(\text{phen})][\text{AsF}_6] \cdot 2.5\text{SO}_2$. (b) Packing diagram of $[\text{AsF}_4(\text{phen})][\text{AsF}_6] \cdot 2.5\text{SO}_2$ viewed along the b axis.

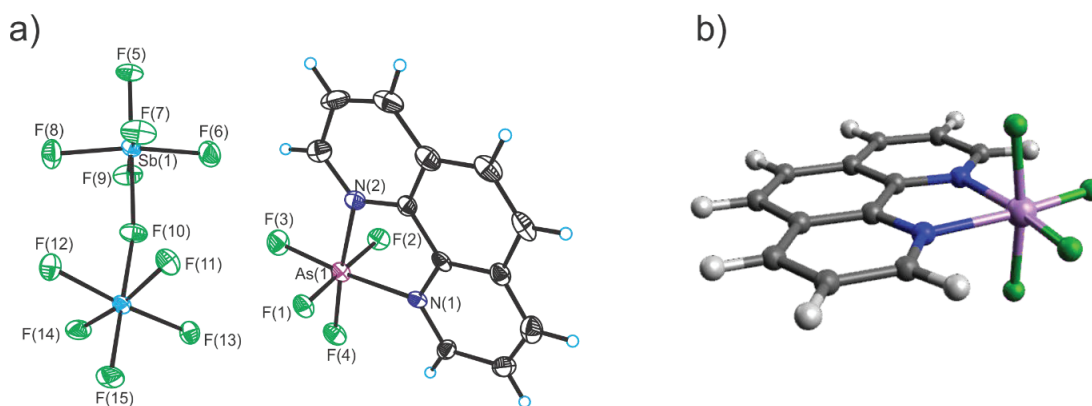


Figure 4.2. (a) Thermal ellipsoid plot (50% probability level) of $[\text{AsF}_4(\text{phen})][\text{Sb}_2\text{F}_{11}]$. (b) Optimized gas-phase geometry of $[\text{AsF}_4(\text{phen})]^+$ calculated using the B3LYP functional with the aug-cc-pVTZ-PP (As) and aug-cc-pVTZ (C, H, F, N) basis sets.

Table 4.1. Selected bond lengths [Å] and angles [°] for [AsF₄(phen)]⁺

	Exptl.		Calcd. ^[a]
	[AsF ₄ (phen)][AsF ₆]	[AsF ₄ (phen)][Sb ₂ F ₁₁]	[AsF ₄ (phen)] ⁺
As–F _{eq}	1.6976(13), 1.7063(13)	1.700(4), 1.7003(4)	1.711
As–F _{ax}	1.7227(14), 1.7241(14)	1.722(4)	1.733
As–N	1.9502(17), 1.9608(16)	1.952(6), 1.979(6)	2.026
F _{eq} –As–F _{eq}	93.95(7)	94.8(2)	97.52
F _{ax} –As–F _{ax}	175.38(6)	176.1(2)	171.82
N–As–N	83.22(7)	82.5(2)	80.89

[a] Calculated using the B3LYP functional with the aug-cc-pVTZ-PP (As) and aug-cc-pVTZ (C, H, F, N) basis sets.

Crystals of (AsF₅)₂·bipy were grown from the vapor diffusion of SO₂ into a CH₃CN solution at 0 °C over the course of 5 hours yielding clear, colorless plates. The compound crystallizes in the orthorhombic space group *Pbca*, with one formula unit in the asymmetric unit (Figure 4.3). Both arsenic centers display an octahedral geometry, with one fluorido ligand *trans* to the nitrogen donor atom of bipy and four fluorido ligands *cis* to the nitrogen donor atom. The two rings of bipy are essentially orthogonal to each other with the N(1)–C(5)–C(10)–N(2) dihedral angle being 99.0(3)°. The As–F bond lengths *trans* (1.7122(14)–1.7179(13) Å) to the nitrogen donor are indistinguishable from those *cis* (1.7165(14)–1.7249(13)) to the nitrogen donor (Table 2); the same trend was observed in the neutral adducts of AsF₅ with nitriles.¹⁸ The As–N bonds lengths (1.9916(19)–2.0094(19) Å) are somewhat shorter than those found in the 2:1 neutral adduct (AsF₅)₂·(CN)₂CH₂ (2.042(3)–2.068(3) Å) and somewhat longer than those found in

$[\text{AsF}_4(\text{phen})]^+$.¹⁸ The bond angles around the arsenic atom do not deviate significantly from the expected values for an octahedral arsenic center.

Table 4.2. Selected bond length [$\text{\AA}$] of $(\text{AsF}_5)_2\cdot\text{bipy}$

	Exptl.	Calcd. ^[a]
As–F _{trans}	1.7122(14)–1.7179(13)	1.711
As–F _{cis}	1.7165(14)–1.7249(13)	1.730–1.744
As–N	1.9916(19)–2.0094(19)	2.123

[a] Calculated using the B3LYP functional with the aug-cc-pVTZ-PP (As) and aug-cc-pVTZ (C, H, F, N) basis sets.

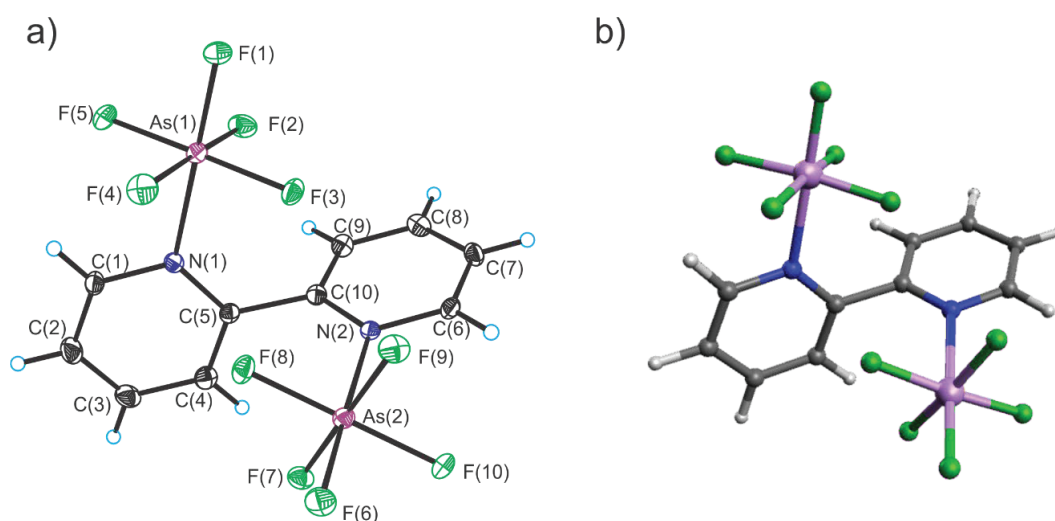


Figure 4.3. (a) Thermal ellipsoid plot (50% probability level) of $(\text{AsF}_5)_2\text{bipy}$. (b) Optimized gas-phase geometry of $(\text{AsF}_5)_2\text{bipy}$. Calculated using the B3LYP functional with the aug-cc-pVTZ-PP (As) and aug-cc-pVTZ (C, H, F, N) basis sets.

4.3.3 ^{19}F NMR spectroscopy.

The nature of $[\text{AsF}_4(\text{phen})]^+$ and $(\text{AsF}_5)_2\cdot\text{bipy}$ in solution was studied by NMR spectroscopy. The ^{19}F NMR spectrum of $[\text{AsF}_4(\text{phen})][\text{AsF}_6]$ (Figure 4.4) recorded in SO_2 at $-60\text{ }^\circ\text{C}$ shows the characteristic equal-intensity quartet at $\delta(^{19}\text{F}) = -56.6\text{ ppm}$ [$^1J(^{19}\text{F}-$

$^{75}\text{As}) = 941 \text{ Hz}]$ of the $[\text{AsF}_6]^-$ anion, the resolution of which suggests a lack of anion-cation interactions in solution. Also present are two broad singlets at -36.6 ppm (2F ; $\Delta\nu_{1/2} = 1310 \text{ Hz}$) and -79.7 ppm (2F ; $\Delta\nu_{1/2} = 1370 \text{ Hz}$) which have been tentatively assigned to the F_{ax} and F_{eq} environments of the cation, respectively, based on the assignments of SF_4 , where the more ionic axial S–F environments resonate at a higher frequency than the more covalent equatorial S–F environments,^{22,23} as well as quantum chemical calculations of the chemical shifts which predict that F_{ax} is the more deshielded environment (see section 4.5.6 Computational Methods for more detailed discussion of the chemical shift calculations). Due to the lower symmetry of the cation, the resonances are broadened as a result of the rapid quadrupolar relaxation of the ^{75}As nuclei collapsing any J -coupling information. Recording the spectrum at ambient temperature results in a narrowing of the linewidth of the $[\text{AsF}_6]^-$ quartet and a failure to observe the cation resonances, consistent with the expected decrease in the rate of quadrupolar relaxation of the ^{75}As nuclei at elevated temperatures which results in further broadening of the ^{19}F resonances. Similar behavior was observed for the ^{19}F resonances of the $[\text{SbF}_4(\text{phen})]^+$ cation.⁹ The F_{ax} and F_{eq} environments of $[\text{AsF}_4(\text{phen})]^+$ (Figure 4.4) also appear as broad quadrupolar collapsed singlets (F_{ax} : -39.0 ppm , $\Delta\nu_{1/2} = 510 \text{ Hz}$; F_{eq} : -79.0 ppm , $\Delta\nu_{1/2} = 550 \text{ Hz}$) in the ^{19}F NMR spectrum of $[\text{AsF}_4(\text{phen})][\text{Sb}_2\text{F}_{11}]$ at $-65 \text{ }^\circ\text{C}$ in SO_2 . Also observable in the spectrum is unreacted $\text{SbF}_5 \cdot \text{SO}_2$ as well as the characteristic three singlet resonances expected for the $[\text{Sb}_2\text{F}_{11}]^-$ anion.

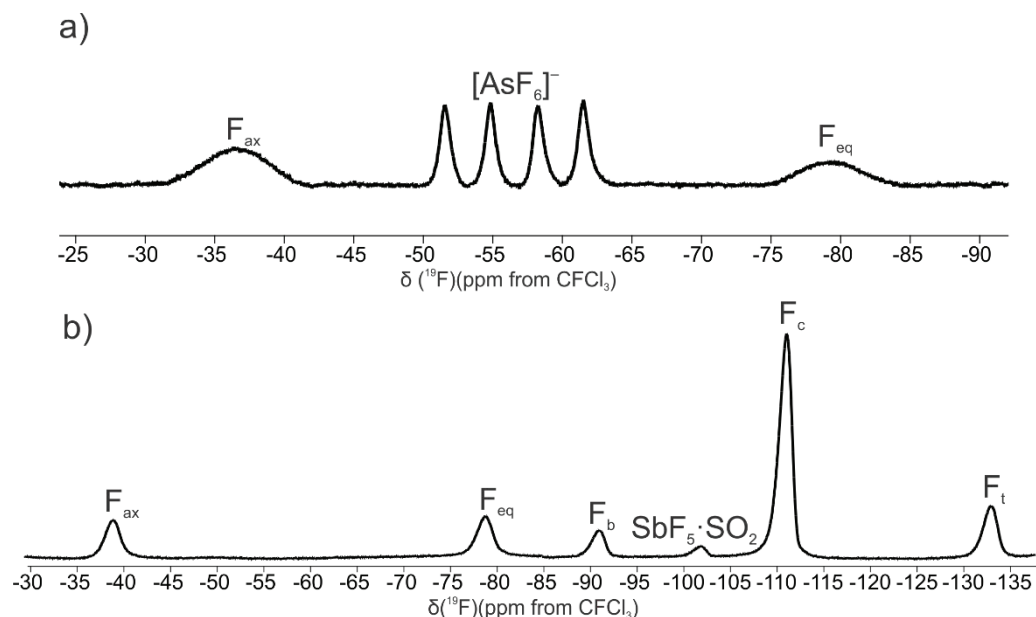


Figure 4.4. (a) The ^{19}F NMR spectrum of $[\text{AsF}_4(\text{phen})][\text{AsF}_6]$ recorded in SO_2 at $-60\text{ }^\circ\text{C}$. (b) The ^{19}F NMR spectrum of $[\text{AsF}_4(\text{phen})][\text{Sb}_2\text{F}_{11}]$ recorded in SO_2 at $-65\text{ }^\circ\text{C}$.

The ^{19}F NMR spectrum of $(\text{AsF}_5)_2\cdot\text{bipy}$ (Figure 4.5) was recorded in CH_3CN at $-40\text{ }^\circ\text{C}$, it shows a partially quadrupolar collapsed doublet at -49.0 ppm (8F ; $\Delta\nu_{1/2} = 300\text{ Hz}$) and partially quadrupolar collapsed quintet at -73.9 ppm (2F ; $\Delta\nu_{1/2} = 410\text{ Hz}$). This indicates an AX_4 spin system and is consistent with two equivalent octahedrally coordinated arsenic centers with one fluoro ligand *trans* to the nitrogen donor and four *cis* to the nitrogen donor. Resolution enhancement of the spectrum by Gaussian multiplication of the FID enabled measurement of the ^{19}F – ^{19}F J -coupling constants ($^2J_{\text{FF}} = 87.8\text{ Hz}$). The small shoulder at -50.2 ppm corresponds to $\text{AsF}_5\cdot\text{CH}_3\text{CN}$. Presence of trace moisture causes the hydrolysis of AsF_5 releasing HF which can then add across the As – N bond forming impurities of $[\text{H-bipy}][\text{AsF}_6]$ (12 mol %) as observed in the ^{19}F and ^1H NMR spectra. Upon warming the sample to ambient temperature both *trans* and *cis* (relative to the nitrogen donor) resonances broaden out to fully quadrupolar collapsed singlets.

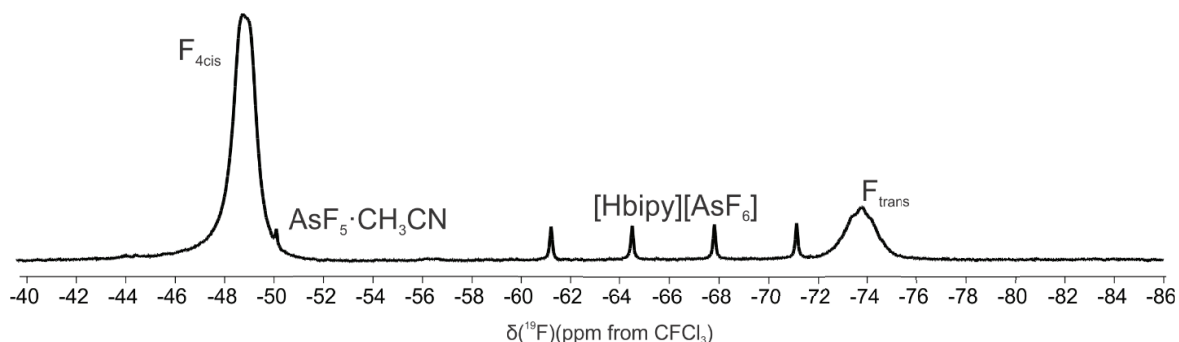


Figure 4.5. The ^{19}F NMR spectrum of $(\text{AsF}_5)_2\cdot\text{bipy}$ recorded in CH_3CN at -40°C . The $[\text{Hbipy}][\text{AsF}_6]$ impurity formed via hydrolysis and present in 12 mol % quantity relative to $(\text{AsF}_5)_2\cdot\text{bipy}$.

4.3.4 Raman Spectroscopy

The Raman spectra for $[\text{AsF}_4(\text{phen})][\text{AsF}_6]$, $[\text{AsF}_4(\text{phen})][\text{Sb}_2\text{F}_{11}]$ and $(\text{AsF}_5)_2\cdot\text{bipy}$ were acquired on solid samples in flame-sealed melting point capillaries at ambient temperature. Quantum chemical calculations were used to aid the assignments of vibrational frequencies. Key modes and assignments are listed in Table 4.3 and full lists of vibrational frequencies and assignments are given in Appendix C (Tables C.2 & C.3)

Vibrational spectroscopic studies of nitrogen containing heterocycles have frequently been used to assess Lewis acidic sites. Upon interaction with a Lewis acid many ligand bands experience considerable blue shift. In Raman spectroscopy, the intense band of the ring breathing mode of pyridine experiences a larger blue shift with stronger interactions of pyridine with a Lewis acid due to greater charge transfer from the nitrogen lone pair to the Lewis acid site.^{24–27} Previous quantum chemical studies on pyridine suggested that the origin of the blue shift of the ring breathing mode upon interaction with a Lewis acid is due to significant changes in σ electron density accompanied by polarization of the π -electron density towards the nitrogen atom.^{24,28} This polarization of electron density is thought to result in greater ionic attraction between the nitrogen and the bonded

carbon atoms, increasing the frequency of the vibrational mode. Calculations also suggested that the high-frequency shift of the ring breathing mode may also be caused by coupling with in-plane C–H bending modes.²⁸ The stretching frequencies for the phen ligand in $[\text{AsF}_4(\text{phen})]^+$ (Figure 4.6) are blue shifted relative to the free base indicating an interaction with a Lewis acid. The most pertinent example being the symmetric ring breathing mode which occurs at 1080 and 1066 cm^{-1} in $[\text{AsF}_4(\text{phen})][\text{AsF}_6]$ and occurs at 1039 and 1035 cm^{-1} in free phen. The origin of the splitting of this mode is not fully understood nor is it predicted by DFT calculations. An almost identical shift of the symmetric ring breathing mode of phen was observed in $[\text{SbF}_4(\text{phen})]^+$ (1077 and 1066 cm^{-1}) seemingly contradictorily suggesting similar levels of interaction between phen and the $[\text{PnF}_4]^+$ cations despite the much greater Lewis acidity of the $[\text{SbF}_4]^+$ cation. The symmetric As–F stretching frequencies are observed 715–620 cm^{-1} inside the typical range for an octahedral As^{V} fluoride.²⁹

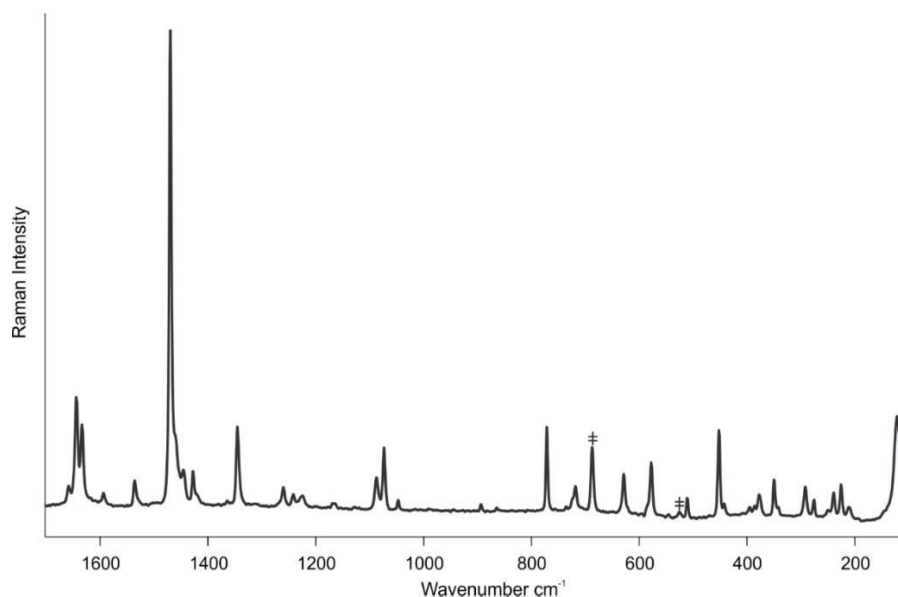


Figure 4.6. Raman spectrum of $[\text{AsF}_4(\text{phen})][\text{AsF}_6]$ recorded in a flame sealed melting point capillary tube at ambient temperature. Double daggers (‡) denote bands arising from the $[\text{AsF}_6]^-$ anion.

The key stretching frequencies of the bipy ligand in $(\text{AsF}_5)_2\cdot\text{bipy}$ (Figure 4.7) exhibit a hypsochromic shift indicating the formation of a Lewis acid-base adduct. The most notable example is the symmetric ring breathing mode which in $(\text{AsF}_5)_2\cdot\text{bipy}$ occurs at 1039 cm^{-1} (calcd. 1046 cm^{-1}), compared to 995 cm^{-1} (calcd. 1010 cm^{-1}) in the free base. The size of this shift (44 cm^{-1}) indicates a very strong interaction between the Lewis basic bipy and Lewis acidic AsF_5 .

The As–F stretching modes in $(\text{AsF}_5)_2\cdot\text{bipy}$ ($\nu(\text{AsF}_{\text{ax}}) = 691$; $\nu_{\text{s}}(\text{AsF}_{4\text{eq}}) = 638, 632$; $\nu_{\text{as}}(\text{AsF}_{4\text{eq}}) = 591\text{ cm}^{-1}$) occur at substantially lower frequencies than previously observed for neutral AsF_5 adducts with weaker bases such as, ketones,³⁰ nitriles,^{31,32} carbonyl halides,³³ 1,3,5-triazine,³⁴ POF_3 ,³⁵ SO_2 ,³⁵ SOF_2 ,³⁵ and SO_2F_2 ,³⁵ however, the stretching modes are comparable to $\text{AsF}_5\cdot\text{py}$ ($\nu(\text{AsF}_{\text{ax}}) = 699$; $\nu_{\text{s}}(\text{AsF}_{4\text{eq}}) = 632$; $\nu_{\text{as}}(\text{AsF}_{4\text{eq}}) = 586\text{ cm}^{-1}$). This highlights the reciprocal relationship between the donor strength of the ligand and As–F stretching frequencies with stronger donor ligands causing lower As–F stretching frequencies in neutral adducts of AsF_5 .

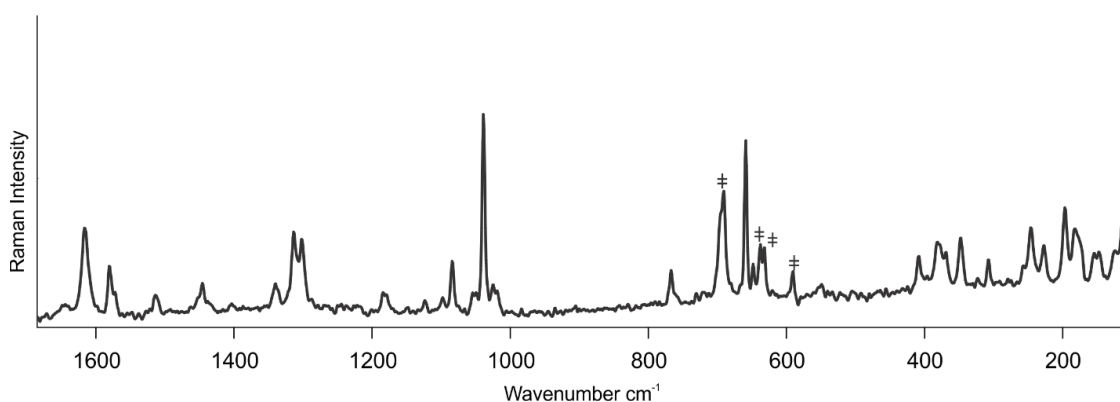


Figure 4.7. Raman spectrum of $(\text{AsF}_5)_2\cdot\text{bipy}$, recorded in a flame sealed melting point capillary tube at ambient temperature. Double daggers (‡) denote $\nu(\text{As-F})$ bands.

Table 4.3. Selected vibrational frequencies (cm^{-1}) for $[\text{AsF}_4(\text{phen})]^+$ and $(\text{AsF}_5)_2\cdot\text{bipy}$.

	$[\text{AsF}_4(\text{phen})]^+$			$(\text{AsF}_5)_2\cdot\text{bipy}$	
	$[\text{AsF}_6]^-$	$[\text{Sb}_2\text{F}_{11}]^-$			
	obsd.	obsd.	calcd. ^[a]	obsd.	calcd. ^[a]
$\nu_{\text{as}}(\text{AsF}_{2\text{ax}})$	728(4)	-	723(1)[110]		
$\nu_{\text{as}}(\text{AsF}_{2\text{eq}})$	-	-	716(1)[65]		
$\nu_{\text{s}}(\text{AsF}_{2\text{eq}})$	711(7)	713(9)	709(10)[140]		
$\nu_{\text{s}}(\text{AsF}_{2\text{ax}})$	621(21)	626(12)	620(16)[0]		
$\nu(\text{AsF}_{\text{trans}})$				691(63)	713(13)[206]
$\nu_{\text{s}}(\text{AsF}_{4\text{cis}})$				638(35) 632(34)	632(1)[1] 632(40)[8]
$\nu_{\text{as}}(\text{AsF}_{4\text{cis}})$				591(22)	577(1)[4] 577(2)[<1]
Symmetric	1080(9)	1076(10)	1086(52)[2]	1039(100)	1046(43)[10]
ring-breathing	1066(16)	1062(12)			
mode					

[a]. Calculated using the B3LYP functional with the aug-cc-pVTZ-PP (As) and aug-cc-pVTZ (C, H, F, N) basis sets. Absolute Raman intensities ($\text{\AA}^4 \text{u}^{-1}$) are given in parentheses and IR intensities (km mol^{-1}) are given in square brackets.

4.3.5 Computational results

NBO Analysis. Natural bond order (NBO) analysis was used to gain a better understanding of the effect that fluoride-ion abstraction has on the bonding in arsenic(V) fluoride species as well as the differences in bonding in a neutral adduct and a donor-stabilized cation. We used $\text{AsF}_5\cdot\text{py}$ (py = pyridine) as a model compound for $(\text{AsF}_5)_2\cdot\text{bipy}$. The key natural population analysis (NPA) charges and Wiberg bond indices (WBI) for AsF_5 , $\text{AsF}_5\cdot\text{py}$, $[\text{AsF}_4]^+$, $[\text{AsF}_4(\text{phen})]^+$ and $[\text{AsF}_6]^-$ are given in Table 4.4.

As expected, abstraction of a fluoride ion from AsF_5 to form free $[\text{AsF}_4]^+$ results in an increase in the NPA charge on As, however, the size of this increase (0.08 e) is rather small due to the increased covalency of the As–F bonds in $[\text{AsF}_4]^+$. An even smaller increase in NPA charge (0.04 e) was found during the abstraction of a fluoride ion from SbF_5 to form $[\text{SbF}_4]^+$ suggesting a greater increase in the covalency of the Sb–F bonds compared to the As–F bonds upon fluoride-ion abstraction. The opposite is found for the donor-stabilized $[\text{AsF}_4(\text{phen})]^+$ cation in which the NPA charge (2.55) on As^{V} decreases upon fluoride-ion abstraction due to the considerable electron pair donation from the phen ligand (0.70 e). Analogous levels of electron pair donation were found (0.74 e) in the donor-stabilized $[\text{SbF}_4(\text{N–N})]^+$ (N–N = phen or bipy) cations. A similar effect is observed upon adduct formation with the NPA charge on $\text{AsF}_5\cdot\text{py}$ (2.61) being lower than that in free AsF_5 (2.70) as a result of electron density donation from pyridine to the Lewis acidic arsenic center. The decrease in NPA charge in the neutral adduct is not as severe as in $[\text{AsF}_4(\text{phen})]^+$ reflecting the greater electrophilicity of the arsenic atom in the cation. The Wiberg bond indices (WBI) of the As–N bond in both $[\text{AsF}_4(\text{phen})]^+$ (0.43) and $\text{AsF}_5\cdot\text{py}$ (0.41) are greater than 2/3 of the As–F bond WBIs, highlighting the high degree of covalency in the dative As–N bonds. Electron density donation from a nitrogenous base to an As^{V} fluoride was found to cause a slight increase in the ionic character of the As–F bonds as evidenced by the decreased WBI and increased NPA charge on the fluorido ligands of $[\text{AsF}_4(\text{phen})]^+$ (WBI: $\text{As–F}_{\text{ax}} = 0.57$, $\text{As–F}_{\text{eq}} = 0.61$. NPA: $F_{\text{ax}} = -0.56$, $F_{\text{eq}} = -0.55$) and $\text{AsF}_5\cdot\text{py}$ (WBI: $\text{As–F}_{\text{ax}} = 0.56$, $\text{As–F}_{\text{eq}} = 0.61$. NPA: $F_{\text{ax}} = -0.56$, $F_{\text{eq}} = -0.59$) compared to AsF_5 (WBI: $\text{As–F}_{\text{ax}} = 0.61$, $\text{As–F}_{\text{eq}} = 0.66$. NPA: $F_{\text{ax}} = -0.55$, $F_{\text{eq}} = -0.53$). The As–F bonds in $[\text{AsF}_6]^-$ (WBI As–F = 0.54. NPA F = -0.61) were by a small margin the

most ionic of all the species studied. Interestingly, there is an almost identical level of covalency in the As–F bonds in the neutral adduct and the donor-stabilized cation. Second-order perturbation analysis shows that the π contributions to covalent bonding in the As–F bonds in the donor-stabilized cation are much higher (6-10%) than in the neutral adduct (<2%), which has a negligible π -component to its As–F bonds (Table 4.5).

Table 4.4. NPA charges and WBI for AsF₅, AsF₅·py, [AsF₄]⁺, [AsF₄(phen)]⁺ and [AsF₆][−]

	NPA Charge		WBI	
	As	F	As–F	As–N
AsF ₅	2.70	−0.53 to −0.55	0.61 to 0.66	–
[AsF ₄] ⁺	2.78	−0.44	0.77	–
[AsF ₆] [−]	2.65	−0.61	0.54	–
[AsF ₄ (phen)] ⁺	2.55	−0.55 to −0.56	0.57 to 0.61	0.43
AsF ₅ ·py	2.61	−0.56 to −0.59	0.56 to 0.61	0.41

Table 4.5. Energies ($E(2)$, kJ mol^{-1}) of the As–N and As–F interactions in the $[\text{AsF}_4(\text{phen})]^+$ and $\text{AsF}_5\cdot\text{py}$ cations.^[a]

	$\sigma(\text{lp}(\text{N})\rightarrow\text{lv}(\text{As}))$	$\sigma(\text{lp}(\text{F})\rightarrow\text{lv}(\text{As}))$	$\Sigma_{\pi}(\text{lp}(\text{F})\rightarrow\text{lv}(\text{As}))$	$\Sigma_{\tau}(\text{lp}(\text{F})\rightarrow\text{lv}(\text{As}))$
$[\text{AsF}_4(\text{phen})]^+$				
As–N(1)	520			
As–N(2)	520			
As–F(1)		2370	155	2525
As–F(2)		2370	155	2525
As–F(3)		2073	238	2311
As–F(4)		2073	238	2311
$\text{AsF}_5\cdot\text{py}$				
As–N(1)	399			
As–F(1)		1898	20	1918
As–F(2)		1699	26	1725
As–F(3)		1699	26	1725
As–F(4)		1699	26	1725
As–F(5)		1699	26	1725

[a] Calculated using the B3LYP functional with the aug-cc-pVTZ-PP (Sb) and aug-cc-pVTZ (C, H, N, F) basis sets. (lp) and (lv) denote lone pair and lone valence, respectively.

Molecular orbitals. Molecular-orbital calculations were employed to investigate the nature of the HOMO and LUMO as well as the As–N bonding interactions in $[\text{AsF}_4(\text{phen})]^+$ and $(\text{AsF}_5)_2\cdot\text{bipy}$ (Figure 4.8). The HOMO and LUMO of $[\text{AsF}_4(\text{phen})]^+$ and $(\text{AsF}_5)_2\cdot\text{bipy}$ are primarily π -bonding orbitals on the nitrogen base. The HOMO–LUMO gap in $[\text{AsF}_4(\text{phen})]^+$ is 4.39 eV (282 nm), while there is a larger HOMO–LUMO gap of 5.64 eV (220 nm) in $(\text{AsF}_5)_2\cdot\text{bipy}$. The As–N bonding interactions in $[\text{AsF}_4(\text{phen})]^+$

consist of $\sigma(\text{sp}^2(\text{N})-\text{p}(\text{As}))$ interactions when the As–N are out of phase with respect to one another (HOMO-4) and $\sigma(\text{sp}^2(\text{N})-\text{s}(\text{As}))$ interactions when the bonds are in phase (HOMO-5). The in-phase and out-of-phase As–N bonding interactions in $(\text{AsF}_5)_2\cdot\text{bipy}$ are the HOMO-4 and HOMO-5, respectively.

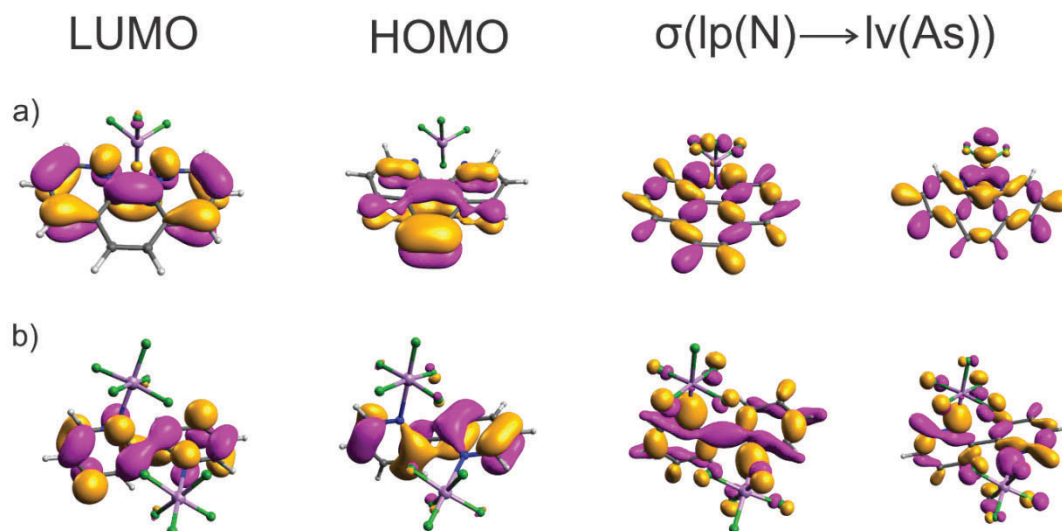


Figure 4.8. Selected molecular orbitals of a) $[\text{AsF}_4(\text{phen})]^+$ and b) $(\text{AsF}_5)_2\text{bipy}$. Isosurfaces are drawn at $0.04 \text{ e } \alpha_0^{-3}$

Fluoride-Ion Affinities. The fluoride-ion affinities (FIA) were calculated for $[\text{AsF}_4]^+$ and the hypothetical $[\text{SbF}_4]^+$ cation values are given in Table 4.6. The FIAs were calculated via an isodesmic reaction referenced to the TMSF/TMS^+ anchor point at the DSD-PBEP86-D3BJ/def2-QZVPP level of theory.^{6,36} Neutral monomeric SbF_5 in the gas phase (calcd. FIA = 495 kJ mol^{-1}) is used as the benchmark for Lewis superacidity with molecular Lewis acids that have a FIA greater than monomeric SbF_5 in the gas phase are considered Lewis superacids.³⁷ Neutral AsF_5 (calcd. FIA = 435 kJ mol^{-1}) is not Lewis superacidic but is still considered a strong Lewis acid. The calculated FIAs of free gas-phase $[\text{SbF}_4]^+$ (1053 kJ mol^{-1}) and $[\text{AsF}_4]^+$ (1013 kJ mol^{-1}) indicate that fluoride-ion

abstraction from the neutral parent pentafluoride leads to incredibly strong Lewis superacids. The FIA of $[\text{AsF}_4]^+$ is greater than that of the Lewis superacid PtF_5 (FIA = 546 kJ mol^{-1})³⁸ which calls into question the stability of the $[\text{AsF}_4][\text{PtF}_6]$ salt and a reinvestigation of this system could be warranted. The high degree of covalent Pn–N bonding in the donor-stabilized $[\text{AsF}_4(\text{phen})]^+$, $[\text{SbF}_4(\text{phen})]^+$ and $[\text{SbF}_4(\text{bipy})]^+$ cations quenching the extreme electron deficiency of the free $[\text{PnF}_4]^+$ cations is likely the source of the surprising stability of these donor-stabilised cations.¹² Second-order perturbation theory analysis shows the strength of the $\sigma(\text{lp}(\text{N}) \rightarrow \text{lv}(\text{Pn}))$ in $[\text{SbF}_4(\text{phen})]^+$ (1731 kJ mol^{-1}) compared to $[\text{AsF}_4(\text{phen})]^+$ (520 kJ mol^{-1}) which highlights a much stronger interaction between Sb and phen than in the As system reflecting the greater Lewis acidity of the Sb analogue.

The solvent corrected FIA_{solv} were calculated using the equation $\text{FIA}_{\text{solv}} = \text{FIA} - [\Delta E_{\text{solv}}(\text{LA-F}) - \Delta E_{\text{solv}}(\text{LA}) - \Delta E_{\text{solv}}(\text{F}^-)]$ (LA = Lewis acid, LA–F = fluoride adduct of the Lewis acid and F^- = free fluoride anion).^{6,39} The solvation energies were calculated using integral equation formalism polarisable continuum model (IEFPCM) in CH_3CN as implemented in Gaussian 16 at the DSD-PBEP86-D3BJ/def2-QZVPP level of theory. As expected, the FIAs of $[\text{AsF}_4]^+$ and $[\text{SbF}_4]^+$ in CH_3CN are drastically diminished compared to the gas-phase ($\text{FIA}_{\text{solv}} [\text{AsF}_4]^+ = 407 \text{ kJ mol}^{-1}$; $[\text{SbF}_4]^+ = 444 \text{ kJ mol}^{-1}$), due to the large solvation energies of the cations and the fluoride anion. The much lower solvation energies for the neutral parent pentafluorides means their FIAs in CH_3CN are attenuated to a much smaller degree ($\text{FIA}_{\text{solv}} \text{AsF}_5 = 297 \text{ kJ mol}^{-1}$; $\text{SbF}_5 = 335 \text{ kJ mol}^{-1}$). It should be noted that unlike the gas-phase FIA, the FIA_{solv} values are not absolute and are also strongly affected by the difficulty in modelling the free energy of the free fluoride anion.

Table 4.6. The calculated fluoride-ion affinities for neutral PnF_5 and $[\text{PnF}_4]^+$ cations (Pn = As, Sb).

Gas-phase	
Compound	Fluoride-ion affinity (kJ mol^{-1})
$\text{AsF}_5^{[\text{a}]}$	435
$\text{SbF}_5^{[\text{a}]}$	495
$[\text{AsF}_4]^{+[\text{b}]}$	1013
$[\text{SbF}_4]^{+[\text{b}]}$	1053
In CH_3CN	
Compound	Fluoride-ion affinity (kJ mol^{-1})
$\text{AsF}_5^{[\text{b}]}$	297
$\text{SbF}_5^{[\text{b}]}$	335
$[\text{AsF}_4]^{+[\text{b}]}$	407
$[\text{SbF}_4]^{+[\text{b}]}$	444

[a]. From ref. 6. [b]. Present study calculated at the DSD-PBEP86-D3BJ/def2-QZVPP level of theory.

Autoionization vs. Adduct formation. To probe why AsF_5 forms a 2:1 neutral adduct with bipy and does not autoionize we studied the two reactions computationally at the PBE0(D3BJ)/def2-QZVPP level of theory. In the gas-phase, adduct formation was predicted to be exergonic ($\Delta_r G = -123 \text{ kJ mol}^{-1}$) while autoionization is an endergonic process ($\Delta_r G = 129 \text{ kJ mol}^{-1}$). Because AsF_5 is a strong Lewis acid and CH_3CN is a coordinating solvent, $\text{AsF}_5 \cdot \text{CH}_3\text{CN}$ was used as a more realistic starting reagent in the calculations of the Gibbs free energies of reaction, resulting in less exergonic adduct formation in the gas-phase adduct ($\Delta_r G = -63.0 \text{ kJ mol}^{-1}$) while autoionization remains an endergonic process ($\Delta_r G = 190 \text{ kJ mol}^{-1}$). Inclusion of the IEFPCM implicit solvent model

for a CH₃CN solution yielded a slightly less favorable adduct formation reaction ($\Delta_r G = -59.0 \text{ kJ mol}^{-1}$), while the autoionization product [AsF₄(bipy)]⁺ did not optimize to a minimum but was instead found to be a transition state. The imaginary frequency corresponds to a twisting of the two rings of bipy coupled with a rocking motion of the AsF_{2ax} moiety, suggesting that bipy is unable to adopt a planar bidentate binding mode in solution likely due to steric crowding around the As center. The twisting of the two rings of bipy to render them normal to each other and acting as monodentate donors reduces steric hinderance around the As center and is therefore the favored binding mode. The lack of conformational flexibility in phen prevents this twisting from occurring and forces phen to act as a planar bidentate donor in the [AsF₄(phen)]⁺ cation. The larger atomic radius of Sb means that it is able to accommodate a planar bidentate binding mode of bipy to form the autoionized [SbF₄(bipy)]⁺ cation. The formation of (SbF₅)₂·bipy was not observed under the reaction conditions used.

4.4 Conclusion

In summary through the use of the rigid bidentate base phen we could extend the autoionization chemistry from SbF₅ to its lighter congener to generate a donor-stabilized [AsF₄]⁺, the first example of a crystallographically characterized [AsF₄]⁺ cation. The [AsF₄(phen)]⁺ cation adopts a distorted octahedral geometry in the solid state and in solution. Quantum chemical calculations were used to calculate fluoride-ion affinities of free [AsF₄]⁺ and [SbF₄]⁺ revealing the Lewis superacidic nature of these cations in the gas phase.

In contrast to SbF_5 , the use of the more flexible bidentate base bipy does not result in autoionization but leads to the formation of the 2:1 neutral adduct $(\text{AsF}_5)_2 \cdot \text{bipy}$. Each As atom displays an octahedral geometry, the two pyridine rings of the bipy ligand are arranged orthogonally to each other. Density functional theory calculations demonstrate the significant degree of σ -electron density transferred from the nitrogen bases to As in both a donor-stabilized cation and a neutral adduct, as well as the increased ionicity of the As–F bonds following this transfer of electron density. It is likely that BiF_5 also undergoes a similar ligand-induced autoionization and plans to investigate the reactivity of BiF_5 in the presence of bidentate nitrogen bases are ongoing in our lab. The highly oxidizing nature of BiF_5 , however, might mean that a $[\text{BiF}_4]^+$ cation is incompatible with organic bases.

4.5 Experimental Section

4.5.1 General Methods.

Caution! Elemental F_2 and AsF_5 are highly toxic and corrosive, rapidly evolving HF upon exposure to moisture. Appropriate safety measures should be taken during their handling.

All reactions were carried out in heat-sealed 1/4" o.d. FEP reactors that were connected to either 316-stainless-steel or Kel-F valves via flared fittings and passivated with F_2 (100%, Linde Gas). Sulfur dioxide, sulfuryl chloride fluoride and acetonitrile were distilled on a Pyrex vacuum line equipped with high-vacuum PTFE valves (Chemglass). Arsenic pentafluoride was distilled through a nickel/316 stainless-steel vacuum line equipped with 316 stainless-steel valves (Autoclave Engineers) and pre-passivated with F_2 .

Solid materials were handled in a drybox (Omni Lab, Vacuum Atmospheres) under an atmosphere of dry N₂.

Acetonitrile was distilled from a solvent purification system (M. Braun MB-SPS) onto 3-Å molecular sieves and distilled again onto fresh sieves. Benzene was distilled from a solvent purification system (M. Braun MB-SPS) onto CaH₂, then distilled again onto fresh 4-Å molecular sieves. Sulfur dioxide (Matheson) was dried over CaH₂. Antimony pentafluoride (Galaxy chemicals) was purified by distillation. Sulfuryl chloride fluoride (Ozark fluoride specialties) was distilled onto 4-Å molecular sieves to remove SO₂ (confirmed by gas-phase IR spectroscopy) and then distilled onto dried KF; the purified SO₂ClF contains an impurity of SO₂F₂. 2,2'-Bipyridine (bipy) (Sigma-Aldrich, ≥ 99%) was dried by sublimation under dynamic vacuum at 100 °C. 1,10-Phenanthroline (phen) (Sigma-Aldrich, ≥ 99%) was recrystallized from dried benzene. The SbF₅·SO₂⁴⁰ adduct and AsF₅⁴¹ were prepared as previously described.

4.5.2 Synthesis and crystal growth

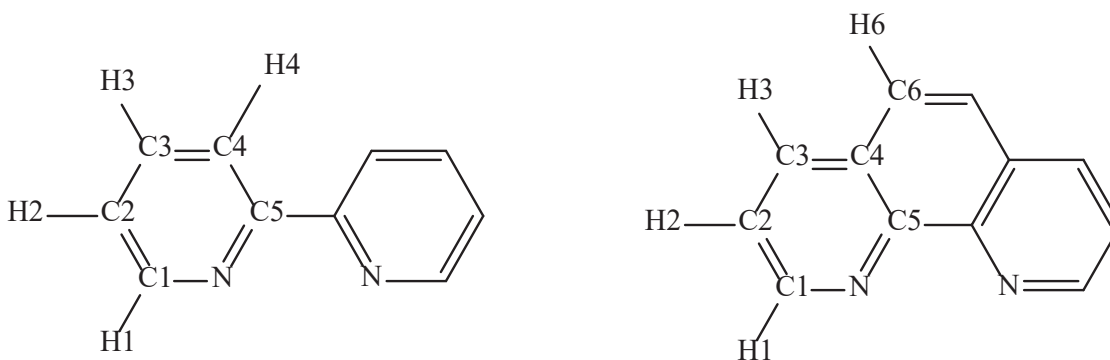


Figure 4.9. Atom labelling used for bipy and phen

[AsF₄(phen)][AsF₆].

In a drybox a 1/4'' o.d FEP reactor was loaded with phen (0.0293 g, 0.163 mmol). Sulfuryl chloride fluoride (ca. 0.5 mL) was then distilled into the reactor at $-196\text{ }^{\circ}\text{C}$ and the mixture was warmed to ambient temperature resulting in a suspension. A slight excess of AsF₅ (0.773 g, 0.455 mmol) was then distilled into the reactor at $-196\text{ }^{\circ}\text{C}$, the mixture was slowly warmed up to ambient temperature over the course of five minutes resulting in a pale-yellow suspension. After agitating the mixture for ca. 30 s a fine white precipitate was formed and the yellow color of the supernatant was lost, leaving a colorless supernatant. The reactor was agitated for a further 10 minutes before being cooled to $-40\text{ }^{\circ}\text{C}$, followed by removal of volatile material at this temperature. The reactor was subsequently warmed to $40\text{ }^{\circ}\text{C}$ in a warm water bath under dynamic vacuum for a further 30 minutes, yielding [AsF₄(phen)][AsF₆] (0.080 g, 0.15 mmol, 94% yield) as an off-white powder. Crystals suitable for single-crystal X-ray diffraction were grown by charging a 1/4'' o.d FEP reactor in the drybox with [AsF₄(phen)][AsF₆] (ca. 0.015 g), then dissolved in the minimum amount of SO₂ required for complete dissolution to occur at ambient temperature. Immediately after the SO₂ is added SO₂ClF (approximately 1/4 volume of SO₂) is distilled into the reactor at $-196\text{ }^{\circ}\text{C}$; the mixture is then allowed to warm to ambient temperature affording a layered solution with pale yellow SO₂ layer on the bottom and colorless SO₂ClF layer on top. Once it reaches room temperature the reactor is agitated to mix the two layers, then cooled to $-70\text{ }^{\circ}\text{C}$ and volatile material is removed slowly over the course of 5 hours at this temperature under dynamic vacuum yielding colorless blocks of [AsF₄(phen)][AsF₆]·2.5SO₂. NMR data in SO₂ at $-60\text{ }^{\circ}\text{C}$ $\delta(^{19}\text{F})$: -36.6 (br, s, [AsF₄(phen)]⁺ F_{ax}), -56.6 (q, [¹J(¹⁹F–⁷⁵As) = 941 Hz] [AsF₆][−]), -79.7 (br, s, [AsF₄(phen)]⁺ F_{eq}); $\delta(^1\text{H})$

9.77 (s, H1), 9.63 (s, H3), 8.83 (s, H2/H6); δ (^{13}C recorded at $-30\text{ }^{\circ}\text{C}$) -149.1 (C1), -147.3 (C5), -145.6 (C3), -130.8 (C4), -129.8 (C6), -128.9 (C2). Elemental analysis calcd for $\text{C}_{12}\text{H}_8\text{As}_2\text{F}_{10}\text{N}_2$ (520.0326): C, 27.72; H, 1.55; N, 5.39. Found: C, 27.57; H, 1.76; N, 5.59. Atom labelling as shown in Figure 4.9.

[AsF₄(phen)][Sb₂F₁₁].

In the drybox a 1/4'' o.d. FEP reactor was loaded with [AsF₄(phen)][AsF₆] (0.0479g, 0.0921 mmol) and SbF₅·SO₂ (0.0717 g, 0.249 mmol). Sulfur dioxide (ca. 0.5 mL) was then distilled onto the solids at $-196\text{ }^{\circ}\text{C}$, the mixture was then warmed to ambient temperature producing a yellow solution. The reactor was subsequently sonicated for 10 minutes, then cooled to $-70\text{ }^{\circ}\text{C}$ followed by removal of volatiles at this temperature under dynamic vacuum. The reactor was warmed to ambient temperature under dynamic vacuum for a further 10 minutes yielding [AsF₄(phen)][Sb₂F₁₁] (0.068 g, 0.087 mmol, 94%) as a yellow powder. Crystal suitable for single-crystal X-ray diffraction were grown in an analogous manner to that of [AsF₄(phen)][AsF₆] yielding yellow plates of [AsF₄(phen)][Sb₂F₁₁] NMR data in SO₂ at $-65\text{ }^{\circ}\text{C}$ δ (^{19}F): -39.0 (br, s, [AsF₄(phen)]⁺ F_{ax}), -79.0 (br, s, [AsF₄(phen)]⁺ F_{eq}), -91.3 (s, [Sb₂F₁₁]⁻ F_b) -102.2 (s, SbF₅·SO₂), -111.4 (s, [Sb₂F₁₁]⁻ F_c), -133.3 (s, [Sb₂F₁₁]⁻ F_t); δ (^1H) 9.76 (d, H1, $^3J(\text{H1-H2}) = 3.15\text{ Hz}$), 9.61 (d, H3, $^3J(\text{H2-H3}) = 7.69\text{ Hz}$), 8.83 (m H2/H6); δ (^{13}C recorded at $-30\text{ }^{\circ}\text{C}$) -149.1 (C1), -147.9 (C5), -145.7 (C3), -130.8 (C4), -129.8 (C6), -129.0 (C2).

Atom labelling as shown in Figure 4.9

Synthesis of (AsF₅)₂·bipy.

In the drybox a 1/4'' o.d. FEP reactor was loaded with bipy (0.137 g, 0.877 mmol). Sulfuryl chloride fluoride (ca. 0.5 mL) was then distilled into the reactor at $-196\text{ }^{\circ}\text{C}$, the

resulting mixture is then allowed to warm to ambient temperature affording a pale-yellow solution after some agitation. An excess of AsF_5 (0.417 g, 2.46 mmol) was then distilled in the reactor at $-196\text{ }^\circ\text{C}$, the mixture was warmed to $-60\text{ }^\circ\text{C}$ in an ethanol bath resulting in the immediate precipitation of a white powder. The reactor was then warmed to ambient temperature and agitated for 10 minutes after which the reactor was cooled to $-40\text{ }^\circ\text{C}$ and volatiles were removed at this temperature under dynamic vacuum. The reactor was subsequently warmed to $40\text{ }^\circ\text{C}$ in a warm water bath under dynamic vacuum for a further 30 minutes, yielding $(\text{AsF}_5)_2\cdot\text{bipy}$ (0.425 g, 0.857 mmol, 98%) as an off-white powder. Crystals suitable for single-crystal X-ray diffraction were grown by loading a 1/4'' o.d. FEP reactor in the drybox with $(\text{AsF}_5)_2\cdot\text{bipy}$ (ca. 0.015 g), then dissolving in the minimum amount of CH_3CN necessary for complete dissolution to occur. The reactor is then cooled to $0\text{ }^\circ\text{C}$ in an ice water bath and 1 atm of SO_2 is expanded into the glass vacuum line. The SO_2 is then allowed to vapour diffuse into the CH_3CN solution for four hours after which time colourless plate crystals had appeared. NMR data in CH_3CN at $-40\text{ }^\circ\text{C}$ δ (^{19}F): -49.0 (d, $^2J_{\text{FF}} = 87.8\text{ Hz}$, $(\text{AsF}_5)_2\cdot\text{bipy F}_{\text{eq}}$), -50.2 (s, $\text{AsF}_5\cdot\text{CH}_3\text{CN}$), -66.3 (q, [$^1J(^{19}\text{F}-^{75}\text{As}) = 933\text{ Hz}$], $[\text{Hbipy}][\text{AsF}_6]$), -73.9 (m, $(\text{AsF}_5)_2\cdot\text{bipy F}_{\text{ax}}$); δ (^1H) 9.01 (d, $^2J_{\text{HH}} = 6.1\text{ Hz}$, H1), 8.35 (t, $^2J_{\text{HH}} = 7.6\text{ Hz}$, H3), 7.89 (m, H2/H4); δ (^{13}C recorded at $-30\text{ }^\circ\text{C}$), -150.6 (C5), -148.4 (C1), -146.0 (C3), -132.5 (C2), -129.2 (C4).

Atom labelling as shown in Figure 4.9

Attempted synthesis of $[\text{AsF}_4(\text{phen})][\text{OTf}]$.

In the drybox a 1/4'' o.d. FEP reactor was loaded with phen (0.052 g, 0.29 mmol). Dichloromethane (ca. 0.4 mL) was then distilled into the reactor at $-196\text{ }^\circ\text{C}$ and the mixture is allowed to warm to ambient temperature affording a pale-yellow solution after some

agitation. The reactor was then cooled back down to $-196\text{ }^{\circ}\text{C}$ and trimethylsilyl trifluoromethanesulfonate (TMSOTf) (0.063 g, 0.28 mmol) was distilled in the reactor at this temperature, the frozen solution was then warmed to ambient temperature maintaining its yellow color. Arsenic pentafluoride (0.049 g, 0.29 mmol) was then distilled into the at $-196\text{ }^{\circ}\text{C}$ and then slowly warmed to ambient temperature over the course of 10 minutes resulting in a slight darkening of the yellow color. The solution was agitated for 30 minutes and then left at ambient temperature for 16 hours. After 16 hours a white precipitate had formed. The reactor was then cooled to $-70\text{ }^{\circ}\text{C}$ and volatiles were removed at this temperature under dynamic vacuum over the course of four hours yielding a mixture of $[\text{AsF}_4(\text{phen})][\text{OTf}]$ and $[\text{AsF}_4(\text{phen})][\text{AsF}_6]$ (0.122 g) as an off-white powder.

4.5.3 X-ray Crystallography.

The reactors containing the crystals were cut on an aluminum trough that was positioned close to the diffractometer and cooled to ca. $-80\text{ }^{\circ}\text{C}$ by a stream of cold, dry N_2 . Once the crystals were deposited onto the trough, the selected crystal was affixed to a Nylon cryo-loop submerged in perfluorinated polyether oil (Fomblin Z-25) and transferred to the goniometer using liquid- N_2 -cooled cryo-tongs. The crystals were centered on a Rigaku SuperNova diffractometer equipped with a Dectris Pilatus 3R 200 K-A hybrid-pixel-array detector, a four-circle κ goniometer, an Oxford Cryostream 800 cooling device, and sealed $\text{MoK}\alpha$ and $\text{CuK}\alpha$ X-ray sources. Data were collected using both the $\text{MoK}\alpha$ source and $\text{CuK}\alpha$ source at $-173\text{ }^{\circ}\text{C}$. Crystals were screened for quality before a pre-experiment was run to determine the unit cell, and a data-collection strategy was calculated based on the determined unit cell and intensity of the preliminary data. This strategy was optimized to collect 5-fold redundant data at a resolution of $0.77\text{ \AA}$. The data were

processed using CrysAlisPro,⁴² which applied necessary Lorentz and polarization corrections to the integrated data and scaled the data. A numerical (Gaussian-grid) absorption correction was generated based upon the indexed faces of the crystal. Atom positions were determined using the intrinsic phasing method (ShelXT)⁴³ and were refined using least-squares refinement (ShelXL).⁴⁴ Non-hydrogen atoms were refined anisotropically, and recommended weights for the atoms were determined. Structure solution and refinement were performed with the aid of Olex2 (version 1.5).⁴⁵

4.5.4 Raman Spectroscopy

The Raman spectra were recorded using a Bruker RFS-100 Raman spectrometer outfitted with a quartz beam-splitter and liquid-N₂-cooled germanium detector. The 1064-nm line of a Nd:YAG laser was used for excitation of the sample, and backscattered (180°) radiation was sampled. The usable Stokes range of the collected data was 85–3500 cm⁻¹ with a resolution of 2 cm⁻¹. The laser power was typically set for 100 mW.

4.5.5 NMR spectroscopy

The ¹⁹F, ¹³C{¹H}, and ¹H NMR spectra were recorded in heat-sealed 4 mm o.d. FEP tubes sheathed in a 5 mm o.d. glass insert using a Bruker Avance II 300 MHz spectrometer equipped with a 5mm broadband probe. Spectra were recorded unlocked in dilute CH₃CN solutions at -40 °C ((AsF₅)₂·bipy) and in dilute SO₂ solutions at -60 °C ([AsF₄(phen)][AsF₆]) or -65 °C ([AsF₄(phen)][Sb₂F₁₁]) and referenced externally to CFC₃ (¹⁹F) and Si(CH₃)₄ (¹H) at 22 °C. All ¹³C{¹H} NMR spectra were recorded at -30 °C and referenced externally to Si(CH₃)₄ (¹³C) at 22 °C. The ¹H & ¹³C NMR spectra and the ¹⁹F NMR spectrum of (AsF₅)₂·bipy after Gaussian multiplication of the FID are shown in Appendix C (Figures C.1–C.7).

4.5.6 Computational methods

Calculations were performed using the B3LYP-D3BJ, PBE0-D3BJ and DSD-PBEP86-D3BJ functionals as implemented in Gaussian 16 (revision D.01).⁴⁷ The geometries were optimized using analytic-gradient methods, resulting in stationary points with no imaginary frequencies except for the hypothetical $[\text{AsF}_4(\text{bipy})][\text{AsF}_6]$. All subsequent calculations were performed on these optimized geometries without imposing any symmetry. The B3LYP-D3BJ/aug-cc-pVTZ-PP level of theory was used for As, while the aug-cc-pVTZ basis set was used for all other atoms in geometry optimizations and frequency calculations discussed in the crystal and molecular structure and Raman spectroscopy sections. In the determination of FIA all species were geometry optimized using the PBE0-D3BJ/def2tzvppd-PP level of theory for As and PBE0-D3BJ/def2tzvppd level of theory for all other atoms. Single point energy calculations were performed at the DSD-PBEP86-D3BJ/def2-QZVPP level of theory.⁴⁸ The solvent corrected FIA were calculated using IEFPCM in CH_3CN as implemented in Gaussian 16. The NBO analyses were performed using NBO (version 6.0),⁴⁹ and GaussView (version 6.0)⁵⁰ was used to visualize the vibrational modes and aid in their description.

4.5.7 NMR chemical shift calculations

The geometries of $[\text{AsF}_4(\text{phen})]^+$ and SF_4 (and CFCl_3) were optimized at the B3LYP-D3BJ/ def2tzvppd-PP level of theory for As and B3LYP-D3BJ/ def2tzvppd for all other atoms, in CH_3CN using the IEFPCM solvent model as implemented in Gaussian 16, resulting in stationary points with no imaginary frequencies. The nuclear shielding tensors were calculated using the GIAO method at the TPSS/TPSS-D3BJ/def2tzvppd level of theory in CH_3CN using the IEFPCM solvent model. The equation $\delta = \sigma_{\text{CFCl}_3} - \sigma_{\text{F}}$ was

used to determine the chemical shifts from the calculated shielding values of CFCl_3 and the fluorine environment of interest. Table S7 shows experimental and calculated chemical shifts for $[\text{AsF}_4(\text{phen})]^+$ and SF_4 . In spite of the high level of agreement, the assignment of the axial and equatorial fluorine environments for the $[\text{AsF}_4(\text{phen})]^+$ cation remains tentative based on the fact that calculation of accurate ^{19}F NMR chemical shifts is not trivial.

Table 4.7. Experimental and calculated chemical shift values in ppm for $[\text{AsF}_4(\text{phen})]^+$ and SF_4 .

	$[\text{AsF}_4(\text{phen})]^+ \text{ [a]}$		$\text{SF}_4 \text{ [b]}$	
	F_{ax}	F_{eq}	F_{ax}	F_{eq}
Exptl.	-39.0	-79.0	93.0	34.2
Calcd.	-47	-87	92	38
Calcd. ^[c]			99.4	28.9

[a] Experimental values from $[\text{AsF}_4(\text{phen})][\text{Sb}_2\text{F}_{11}]$ recorded in SO_2 at -65°C . [b] Experimental values for gaseous SF_4 taken from reference 22. [c] Calculated values from reference 23.

4.6 References

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Chapter 5 – Synthesis and Reactivity of $[\text{SF}_3]^+$ Adducts with Organic Bases*

5.1 Abstract

The 1:1 adduct of $[\text{SF}_3]^+$ with pyridine was obtained from the reaction of SF_4 with $[(\text{CH}_3)_3\text{Si}(\text{NC}_5\text{H}_5)][\text{O}_3\text{SCF}_3]$ ($[(\text{CH}_3)_3\text{Si}(\text{py})][\text{OTf}]$) as the $[\text{SF}_3(\text{py})][\text{OTf}]$ salt in near quantitative yields. The analogous reaction of SF_4 with $[(\text{CH}_3)_3\text{Si}(4\text{-NC}_5\text{H}_5\text{N}(\text{CH}_3)_2)][\text{OTf}]$ ($[(\text{CH}_3)_3\text{Si}(\text{dmap})][\text{OTf}]$) resulted in the formation of a small amount of $[\text{SF}_3(\text{dmap})][\text{OTf}]$, which was found to undergo facile dismutation to $[\text{SF}_2(\text{dmap})_2][\text{OTf}]_2$ and SF_4 as the major products of the reaction. NMR spectroscopic data suggest that $[\text{SF}_3(\text{dmap})]^+$ adopts a seesaw structure with DMAP in the equatorial position, which is in contrast to the axial position of pyridine in $[\text{SF}_3(\text{py})]^+$. Quantum chemical calculations show that in the gas-phase the axial isomer of $[\text{SF}_3(\text{py})]^+$ is the more stable configuration by 28 kJ mol^{-1} , whereas the axial and equatorial isomers of $[\text{SF}_3(\text{dmap})]^+$ were found to be essentially isoenergetic with $< 2 \text{ kJ mol}^{-1}$ difference between the two isomers. The reaction of $[\text{SF}_3][\text{SbF}_6]$ with DMAP allowed for the isolation of $[\text{SF}_2(\text{dmap})_2][\text{SbF}_6]_2$ without any evidence of the monocation. In CH_3CN solution, $[\text{SF}_2(\text{dmap})_2]^{2+}$ was found to undergo further ligand scrambling leading to the precipitation of $[\text{SF}(\text{dmap})_4]^{3+}$ salts. Attempts to form a 1:1 adduct between $[\text{SF}_3]^+$ and OPPh_3 resulted instead in the deoxofluorination of OPPh_3 forming $[\text{FPPH}_3]^+$ salts.

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5.2 Introduction

Sulfur tetrafluoride has been documented to act as a fluoride-ion donor towards strong fluoride-ion acceptors, leading to a series of $[\text{SF}_3]^+$ salts. The order of stability with respect to reversion back to SF_4 and the Lewis acid was found to be $[\text{SF}_3][\text{SbF}_6] > [\text{SF}_3][\text{AsF}_6] > [\text{SF}_3][\text{IrF}_6] > [\text{SF}_3][\text{BF}_4] > [\text{SF}_3][\text{PF}_6] > [\text{SF}_3]_2[\text{GeF}_6] > [\text{SF}_3][\text{AsF}_4]$.¹⁻⁵ The trigonal pyramidal $[\text{SF}_3]^+$ cation is electrophilic and has three σ -holes opposite the three S–F bonds. As a result, the crystal structures of the $[\text{BF}_4]^-$ and $[\text{GeF}_6]^{2-}$ salts show the anions coordinating to the three σ -holes on $[\text{SF}_3]^+$ via fluorine atoms, resulting in distorted octahedrally coordinated sulfur centers; these anion-cation contacts are examples of chalcogen-bonding interactions. Some salts were found to incorporate HF into their structures such as $[\text{SF}_3][\text{SbF}_6] \cdot \text{HF}$ ⁶ and $[\text{SF}_3][\text{W}_2\text{O}_2\text{F}_9] \cdot \text{HF}$ ⁷ in which HF occupies one of the chalcogen-bonding sites. The $[\text{SF}_3][\text{Mo}_2\text{O}_2\text{F}_9]$ salt is currently the only example where the coordination of the sulfur center is extended to heptacoordination.⁷

Combined mass spectrometric and computational studies found that gaseous $[\text{SF}_3]^+$ acts as an electrophilic fluorinating agent towards five-membered heterocycles, however, it formed adducts with pyridine and CH_3CN .⁸⁻¹⁰ The $[\text{SF}_3]^+$ cation has been shown to form discrete adducts in solution and the solid state with pyridine, 1,10-phenanthroline (phen), CH_3CN and NSF_3 .^{11,12} The interactions with the weaker N-bases (CH_3CN and NSF_3) in $[\text{SF}_3(\text{N-base})_2]^+$ are electrostatic in nature and best described as non-covalent chalcogen-bonding interactions. Such interactions do not have a significant effect on the structure of the $[\text{SF}_3]^+$ cation which maintains its trigonal pyramidal geometry. The third chalcogen bonding site is occupied by the $[\text{PnF}_6]^-$ (Pn = As or Sb) anion resulting in hexacoordinate sulfur centers. The use of stronger N-bases (pyridine and phen), on the other hand, results

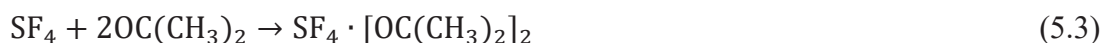
in two S---N dative interactions with a significant degree of covalency causing a change in the geometry and electronic structure of the cation such that it can no longer act as a third chalcogen bond donor, resulting in pentacoordinate square pyramidal cations. These salts that contain N-donor ligands are thermally unstable and were found to decompose into unidentified products at room temperature (RT).

The use of SF₄ as a deoxofluorinating agent was first reported in 1958 at Dupont's experimental station.¹³ It was subsequently found that the presence of HF dramatically improves the rate of deoxofluorination of carbonyl compounds using SF₄, and to achieve good yields stoichiometric amounts or in some cases a large excess of HF is required.¹⁴ Conductivity studies of SF₄ in anhydrous HF (aHF) revealed that SF₄ acts as a weak fluoride-ion donor towards HF (eq 5.1), the equilibrium constant for this process was found to be $K = 4 \pm 2 \times 10^{-2}$ at 0 °C,¹⁵ therefore, it has been proposed that [SF₃]⁺ is the active species during the deoxofluorination of carbonyl groups by SF₄. The first step of the mechanism has presumed to be the formation of a 1:1 adduct between [SF₃]⁺ and the carbonyl oxygen.¹⁶ Previous attempts to isolate adducts of [SF₃]⁺ with ketones have proved unsuccessful; the use of aHF solvent resulted in the protonation of the ketone and the generation of SF₄ instead.¹⁷



A sample of SF₄ dissolved in acetone and warmed to RT for an hour showed no evidence of deoxofluorination, further indication that SF₄ is not the active species in deoxofluorination. At low temperatures ca. -100 °C it is possible to isolate the [SF₄·O=C(CH₃)₂]₂ and SF₄·(O=C(CH₃)₂)₂ adducts (eq 5.2 and 5.3), the former of which was crystallographically characterized.¹⁸ The hydrolysis of a sample of SF₄ in the presence

of 2-adamantanone led to the fortuitous growth of a crystal of $\text{SF}_4 \cdot \text{O}=\text{C}_{10}\text{H}_{14} \cdot \text{HF}$ which is a coordination polymer consisting of alternating SF_4 , $\text{O}=\text{C}_{10}\text{H}_{14}$ and HF molecules. This structure represents one interaction modality possible for the deoxofluorination of 2-adamantanone.¹⁸ However, the structure of SF_4 did not change to any significant extent. The SF_4 molecule acts as a double chalcogen bond donor towards the carbonyl oxygen and the fluorine of HF . This was the first structure to contain an $\text{O}-\text{HF}-\text{SF}_4$ linkage where the HF molecule is bridging from the sulfur atom of SF_4 to carbonyl oxygen. This contrasts the behavior of SF_4 adducts with nitrogen bases which are solvolyzed by HF protonating the N-base and forming $\text{F}_4\text{S}-\text{F}-\text{HN}$ linkages in the solid state involving fluoride.^{19–22}

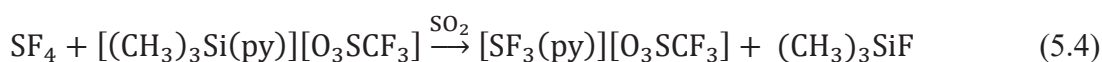


As the mechanism for deoxofluorination invokes 1:1 adducts of $[\text{SF}_3]^+$ with organic bases, the present study looks at the formation of 1:1 adducts of $[\text{SF}_3]^+$ with pyridine (py) and the much stronger nitrogen base 4-dimethylaminopyridine (DMAP) and the effect that adduct formation has on the structure and bonding of the $[\text{SF}_3]^+$ cation. Due to the paucity of information on $[\text{SF}_3]^+$ adducts with oxygen bases and the inability to isolate adducts with ketones such as acetone in previous work in our lab, we attempted to bridge this gap using a phosphine oxide, which is a much stronger Lewis base than acetone (BF_3 affinity acetone = $76.03 \pm 0.21 \text{ kJ mol}^{-1}$; BF_3 affinity $\text{O}=\text{PPh}_3$ = $103.3 \pm 1.50 \text{ kJ mol}^{-1}$), in hopes that using a stronger Lewis base helps facilitate the isolation of an adduct.²³ Triphenylphosphine oxide is a stable solid and has been used as a ligand in coordination chemistry.

5.3 Results and discussion

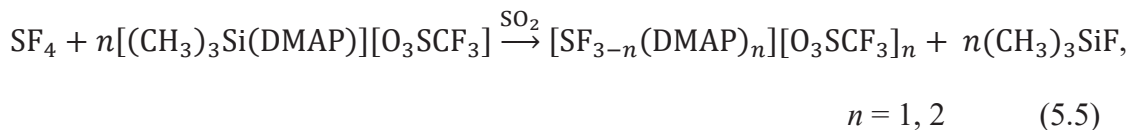
5.3.1 Synthesis and Properties of $[\text{SF}_3(\text{L})]^+$ (L = py, DMAP) and Attempted Synthesis of $[\text{SF}_3(\text{OPPh}_3)]^+$.

Initial attempts to synthesize a 1:1 adduct of $[\text{SF}_3]^+$ with pyridine involved the reaction of $[\text{SF}_3][\text{AsF}_6]$ with pyridine in SO_2 solvent. The isolation of pure $[\text{SF}_3(\text{py})][\text{AsF}_6]$ proved difficult as samples were often contaminated with $[\text{SF}_3(\text{py})_2][\text{AsF}_6]$. A more reliable route to the $[\text{SF}_3(\text{py})]^+$ cation is the reaction of an excess of SF_4 (1.5 equivalents) with $[(\text{CH}_3)_3\text{Si}(\text{NC}_5\text{H}_5)][\text{O}_3\text{SCF}_3]$ ($[(\text{CH}_3)_3\text{Si}(\text{py})][\text{OTf}]$) (eq 5.4) where $[(\text{CH}_3)_3\text{Si}(\text{py})][\text{OTf}]$ acts as the source of the pyridine base, as well as the fluoride-ion acceptor, yielding the $[\text{SF}_3(\text{py})][\text{OTf}]$ salt as an off-white powder without any traces of $[\text{SF}_3(\text{py})_2][\text{OTf}]$. The $[\text{SF}_3(\text{py})][\text{OTf}]$ salt is soluble in SO_2 and CH_3CN but was found to be insoluble in CH_2Cl_2 and SO_2ClF . Like salts of the 1:2 pyridine adduct, $[\text{SF}_3(\text{py})][\text{OTf}]$ was found to be thermally unstable at ambient temperature decomposing within minutes into unidentified brown material.



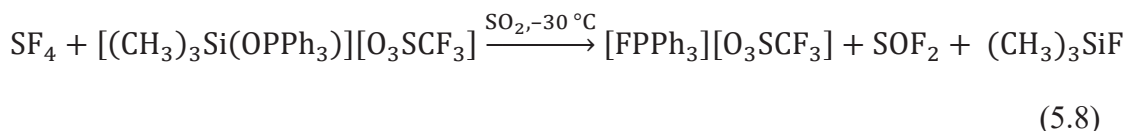
In order to target the DMAP adduct cation, the equivalent reaction between SF_4 and $[(\text{CH}_3)_3\text{Si}(\text{dmap})][\text{OTf}]$ was used (eq 5.5). The major products of this reaction, however, were $[\text{SF}_2(\text{dmap})_2][\text{OTf}]_2$ and SF_4 with only small quantities of $[\text{SF}_3(\text{dmap})][\text{OTf}]$ present based on ^{19}F NMR spectroscopy. It therefore appears that $[\text{SF}_3(\text{dmap})]^+$ is undergoing facile dismutation in solution (eq 5.6). In an attempt to quantitatively form the $[\text{SF}_2(\text{dmap})_2]^{2+}$ dication, SF_4 was reacted in a 1:2 molar ratio with $[(\text{CH}_3)_3\text{Si}(\text{dmap})][\text{OTf}]$; however, small amounts of $[\text{SF}_3(\text{dmap})]^+$ were always present. Further dismutation of

$[\text{SF}_2(\text{dmap})_2]^{2+}$ was found to occur in CH_3CN solutions at $-40\text{ }^\circ\text{C}$ (eq 5.7), resulting in the precipitation of some $[\text{SF}(\text{dmap})_4][\text{OTf}]_3$ as evidenced by X-ray crystallography and Raman spectroscopy.



Similar results were obtained in reactions of $[\text{SF}_3][\text{SbF}_6]$ and DMAP in a 1:1 ratio in CH_3CN solvent at $-35\text{ }^\circ\text{C}$. The resulting intense yellow solid was identified as $[\text{SF}_2(\text{dmap})_2][\text{SbF}_6]_2$ by NMR and Raman spectroscopy, which is soluble in CH_2Cl_2 , CH_3CN , and SO_2 . No evidence for the $[\text{SF}_3(\text{dmap})]^+$ cation was obtained with the $[\text{SbF}_6]^-$ counter anion, even when using a 1:2 molar ratio of $[\text{SF}_3][\text{SbF}_6]$ and DMAP at $-40\text{ }^\circ\text{C}$. Crystals of $[\text{SF}_2(\text{dmap})_2][\text{SbF}_6]_2 \cdot \text{CH}_3\text{CN}$ were characterized by X-ray crystallography that grew from a CH_3CN solution. In addition to those crystals, a few crystals of $[\text{SF}(\text{dmap})_4][\text{SbF}_6]_3 \cdot 2\text{CH}_3\text{CN}$ grew at $-40\text{ }^\circ\text{C}$.

The reaction of an excess of SF_4 (1.5 equivalents) with $[(\text{CH}_3)_3\text{Si}(\text{OPPh}_3)][\text{OTf}]$ resulted in the deoxofluorination of OPPh_3 forming $[\text{FPPh}_3][\text{OTf}]$ and SOF_2 (eq 5.8) based on multinuclear NMR spectroscopy and X-ray crystallographic identification of $[\text{FPPh}_3][\text{OTf}]$. In an attempt to isolate $[\text{SF}_3(\text{OPPh}_3)]^+$ at low temperatures the reaction of $[\text{SF}_3][\text{AsF}_6]$ with OPPh_3 was carried out in SO_2 . However, even at $-60\text{ }^\circ\text{C}$ rapid deoxofluorination occurred with no evidence of adduct formation (eq 5.9).



The facile deoxofluorination with $[\text{SF}_3]^+$ at low temperature is in contrast to the previously reported conditions for deoxofluorination of OPPh_3 by SF_4 in benzene, *i.e.*, 50 to 150 °C for 14 h with a 67% yield.²⁴

5.3.2 Molecular Structures.

The structures of $[\text{SF}_3(\text{py})][\text{OTf}]$, $[\text{SF}_2(\text{dmap})_2][\text{SbF}_6]_2 \cdot \text{CH}_3\text{CN}$, $[\text{SF}(\text{dmap})_4][\text{OTf}]_3 \cdot 2\text{CH}_3\text{CN}$, $[\text{SF}(\text{dmap})_4][\text{SbF}_6]_3 \cdot 2\text{CH}_3\text{CN}$ and $[\text{FPPh}_3][\text{OTf}]$ were elucidated by X-ray crystallography. The $[\text{FPPh}_3]^+$ cation has previously been crystallographically characterized and will not be discussed further.²⁵ Additionally the gas-phase geometries of $[\text{SF}_3(\text{py})]^+$ and $[\text{SF}_2(\text{dmap})_2]^{2+}$ were optimized at the B3LYP-D3(BJ)/def2-TZVPPD level of theory, resulting in strong agreement between the experimental and calculated structures. A stable geometry with no imaginary frequencies could not be obtained at the B3LYP-D3(BJ)/def2-TZVPPD level of theory for $[\text{SF}(\text{dmap})_4]^{3+}$ with the imaginary frequencies corresponding to rotations of the methyl groups; however, a minimum could be found using the MN15/def2-TZVPPD level of theory. The key geometric parameters are given in Tables 5.1 & 5.2 and details of the data processing and crystal structure refinement are given in Appendix D (Tables D.1 & D.2).

Crystals of $[\text{SF}_3(\text{py})][\text{OTf}]$ could be grown from concentrated CH_3CN solutions at $-40\text{ }^\circ\text{C}$ over the course of 16 hours. The salt crystallizes in the monoclinic space group $P2_1/c$ with one formula unit in the asymmetric unit. The cation adopts a seesaw geometry

with one fluoro ligand and the pyridine ring occupying the axial positions with the remaining two fluoro ligands in the equatorial plane. The $[\text{SF}_3(\text{py})]^+$ cation acts as a double chalcogen-bond donor towards two adjacent triflate anions which coordinate via an oxygen atom to the σ -holes *trans* to the equatorial S–F bonds, resulting in a hexacoordinate sulfur center (Figure 5.1). The S---O distances (2.653(2)-2.707(2) Å) are substantially shorter than the sum of the van der Waals radii ($\Sigma_r(\text{vdW}) = 1.89(\text{S}) + 1.50(\text{O}) = 3.39$ Å),²⁶ but notably longer than the axial S–N bond (2.0103(15) Å), highlighting the difference between the weaker chalcogen bonding interactions to the triflate anions and the dative covalent interaction between $[\text{SF}_3]^+$ and py. As a result of significant electron density donation to $[\text{SF}_3]^+$ from py, the S–F bonds lengths (S–F_{ax} = 1.6072(11); S–F_{eq} = 1.5406(11)-1.5477(11) Å) are elongated compared to non-adducted $[\text{SF}_3]^+$ ($[\text{SF}_3][\text{MoO}_2\text{O}_2\text{F}_9] = 1.5102(9)$ - $1.5144(9)$ Å).⁷ A similar degree of elongation of the S–F bond lengths *trans* to the py ring (ca. 0.1 Å) was observed for both the 1:1 and the 1:2 adducts ($[\text{SF}_3(\text{py})_2][\text{SbF}_6] \cdot 0.5\text{py}$ S–F_{eq} = 1.5996(14)-1.6287(15) Å); the remaining S–F bonds are elongated to a greater extent in the 1:2 adduct ($[\text{SF}_3(\text{py})_2][\text{SbF}_6] \cdot 0.5\text{py}$ S–F_{ax} = 1.5605(14) Å). The S–N bond length in $[\text{SF}_3(\text{py})]^+$ is shorter than those in $[\text{SF}_3(\text{py})_2]^+$ ($[\text{SF}_3(\text{py})_2][\text{SbF}_6] \cdot 0.5\text{py}$ S–N = 2.0596(19)-2.1403(18) Å), which is consistent with the smaller coordination number when ignoring the chalcogen-bonding interactions to the triflate anions. The axial and equatorial fluoro ligands are normal to each other (F(1)–S(1)–F(2) = 90.33(7); F(1)–S(1)–F(3) = 90.03(6)), while the presence of a stereochemically active lone pair, as well as the chalcogen-bonds to triflate cause a contraction of the F(2)–S(1)–F(3) bond angle (97.20°) from the ideal 120°. The axial ligands are slightly distorted from the expected linear arrangement (F(1)–S(1)–N(1) = 173.30(6)°).

The calculated gas-phase geometry of $[\text{SF}_3(\text{py})]^+$ reproduces the experimental bond lengths and angles well; the largest deviation between calculated and experimental structure is the overestimation of the dative S–N bond in the calculation (2.035 vs. 2.0103(15) Å) and the smaller F(2)–S(1)–F(3) bond angle (calcd. = 93.36°), even in the absence of the two S–O chalcogen bonding interactions observed in the crystal structure.

Table 5.1. Selected bond lengths (Å) and angles (°) of $[\text{SF}_3(\text{py})]^+$ and $[\text{SF}_2(\text{dmap})_2]^{2+}$

	$[\text{SF}_3(\text{py})]^+$		$[\text{SF}_2(\text{dmap})_2]^{2+}$	
	Exptl.	Calcd. ^[a]	Exptl.	Calcd.
S(1)–F(1)	1.6072(11)	1.594	1.701(4)	1.690
S(1)–F(2)	1.5406(11)	1.551		
S(1)–F(3)	1.5477(11)	1.551		
S(1)–N(1)	2.0103(15)	2.035	1.724(5)	1.751
F(1)–S(1)–F(1')			175.4(3)	173.88
F(1)–S(1)–F(2)	90.33(7)	90.16		
F(1)–S(1)–F(3)	90.03(6)	90.76		
F(2)–S(1)–F(3)	97.20(6)	93.36		
F(1)–S(1)–N(1)	173.30(6)	174.95	100.4(3)	88.45

[a] Calculated using the B3LYP-D3(BJ)/ def2-TZVPPD level of theory.

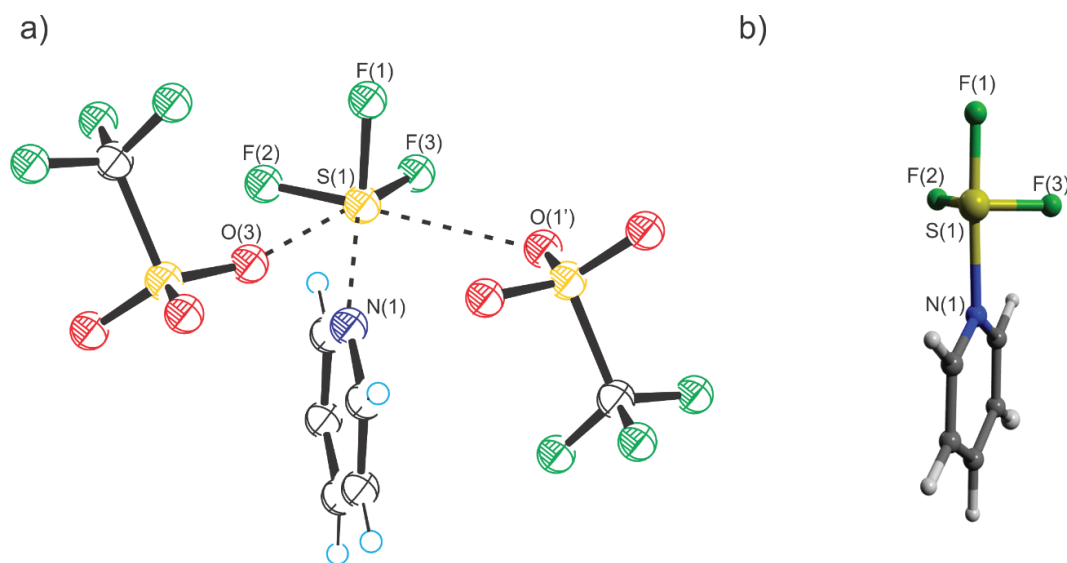


Figure 5.1 (a) Thermal ellipsoid plot (50-% probability level) of [SF₃(NC₅H₅)]⁺ showing the hexacoordination at the sulfur center. (b) Optimized gas-phase geometry of [SF₃(NC₅H₅)]⁺ calculated at the B3LYP-D3(BJ)/ def2-TZVPPD level of theory

Crystals of [SF₂(dmap)₂][SbF₆]₂·CH₃CN were grown from concentrated CH₃CN solutions at −35 °C over the course of ca. 1.5 h. The salt crystallizes in the monoclinic space group *C2/c* with four formula units in the unit cell without any appreciable anion-cation contacts. The [SF₂(dmap)₂]²⁺ dication adopts a seesaw geometry around the sulfur center with the two fluoro ligands in the axial positions and the two DMAP ligands occupying the equatorial positions (Figure 5.2). The sulfur center lies on a crystallographic *C*₂ axis. The symmetry-related S–N bond lengths (1.724(5) Å) are substantially shorter than those found in the N-base adducts of [SF₃]⁺ but do resemble those found in bis(imidazole)sulfur difluorides ((C₃H₃N₂)₂SF₂ 1.700(2) Å and 1.690(3) Å), indicative of highly covalent S–N bonds in the [SF₂(DMAP)₂]²⁺ dication, which is supported by NBO calculations (see 5.3.5. Computational Results).^{27,28} The significant donation of electron density by the DMAP ligands to the sulfur center led to an elongation of the S–F bonds

(1.701(4) Å) compared to free $[\text{SF}_3]^+$ and its N-base adducts, but they are comparable to those found in bis(imidazole)sulfur difluorides ($(\text{C}_3\text{H}_3\text{N}_2)_2\text{SF}_2$ 1.709(2) and 1.693(2) Å). The F(1)–S–F(1') motif adopts a near-linear arrangement (175.4(3)°). The presence of a lone pair on sulfur in the third equatorial position causes a contraction of the N(1)–S–N(1') bond angle (100.4(3)°).

The gas-phase geometry-optimized structure reproduces the experimental structure well with only minor variations of the bond lengths and angles, with the largest variation being the overestimation of the S–N bond length and underestimation of the calculated N(1)–S(1)–N(1') bond angle (88.45 °).

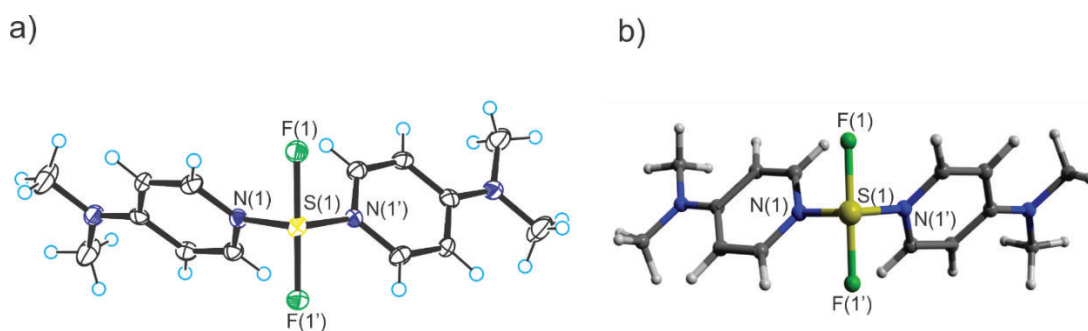


Figure 5.2. (a) Thermal ellipsoid plot (50 % probability level) of $[\text{SF}_2(\text{dmap})_2][\text{SbF}_6]_2$. (b) optimized gas-phase geometry of $[\text{SF}_2(\text{dmap})_2]^{2+}$ calculated at the B3LYP-D3(BJ)/def2-TZVPPD level of theory.

Crystals of $[\text{SF}(\text{dmap})_4][\text{OTf}]_3 \cdot 2\text{CH}_3\text{CN}$ and $[\text{SF}(\text{dmap})_4][\text{SbF}_6]_3 \cdot \text{CH}_3\text{CN}$ were grown from concentrated CH_3CN solutions at -40°C over the course of several hours. The $[\text{OTf}]^-$ and $[\text{SbF}_6]^-$ salts crystallize in the triclinic space group $P\bar{1}$ and in the monoclinic space group $C2/c$, respectively. The $[\text{SF}(\text{dmap})_4]^{3+}$ trication adopts a square pyramidal geometry around the sulfur center where the fluoro ligand occupies the apical position and the four DMAP ligands occupy the basal plane (Figure 5.3). There are no appreciable anion-cation contacts in either salt. In the monoclinic system the F_{ax} atom is disordered

with respect to a crystallographic C_2 axis, and each position is modelled with 50% occupancy. Similarly, the F_{ax} is disordered in the triclinic system over the two apical positions; in this case the occupancies were allowed to freely refine leading to 38% and 62% occupancies. Due to the positional disorder of the F_{ax} atom and the inability to refine separate sulfur positions for the two disorder components in both crystal systems the accurate determination of an S–F bond length is not possible. The crystallographic S–F bond length is expected to be too short, since the lone pair on sulfur will displace the sulfur below the plane of the equatorial nitrogen atoms. The DFT-optimized structure reproduces the S–F bond lengths (1.595 Å) fairly well, suggesting that only a minor truncation of the S–F bond length manifests in the experimental structure. The calculated S–F bond length in $[SF(dmap)_4]^+$ is comparable to the calculated S– F_{ax} bond length of the square pyramidal $[SF_5]^-$ anion (1.604 Å), and considerably shorter than the calculated S–F bond lengths in the $[SF_2(dmap)_2]^{2+}$ dication (1.690 Å). The combination of the Lewis-basic DMAP ligands (BF_3 affinity = 151.55 ± 0.76)²³ and the highly electrophilic $[SF]^{3+}$ moiety results in covalent S–N bonds ($[OTf]^-$ salt S–N = 1.879(5)-1.926(5) Å; $[SbF_6]^-$ salt S–N = 1.878(7)-1.924(7) Å). The S–N bond lengths are elongated in $[SF(dmap)_4]^{3+}$ compared to those found in $[SF_2(dmap)_2]^{2+}$ likely resulting from a mutual *trans*-influence caused by the near linear N–S–N bond angles in $[SF(dmap)_4]^{3+}$. The other bond angles around the sulfur center are mostly unremarkable and lie close to the idealized values for a square pyramidal geometry.

Table 5.2. Selected bond lengths [Å] and angles [°] of [SF(dmap)₄]³⁺.

	[SF(dmap) ₄] ³⁺		
	Exptl. ^[a]	Exptl. ^[b]	Calcd. ^[c]
S(1)–F(1)	1.542(6)	1.567(7)	1.595
S(1)–N(1)	1.904(8)	1.924(7)	1.878
S(1)–N(3)	1.879(5)	1.878(7)	1.878
S(1)–N(5)	1.905(4)	1.924(7)	1.878
S(1)–N(7)	1.926(5)	1.878(7)	1.878
F(1)–S(1)–N(1)	90.0(6)	88.7(4)	85.39
N(1)–S(1)–N(3)	87.7(5)	90.0(3)	89.63
N(1)–S(1)–N(5)	176.8(5)	178.3(3)	170.78

[a] From [SF(dmap)₄][OTf]₃. [b] From [SF(dmap)₄][SbF₆]₃. [c] Calculated using MN15/def2-TZVPPD level of theory

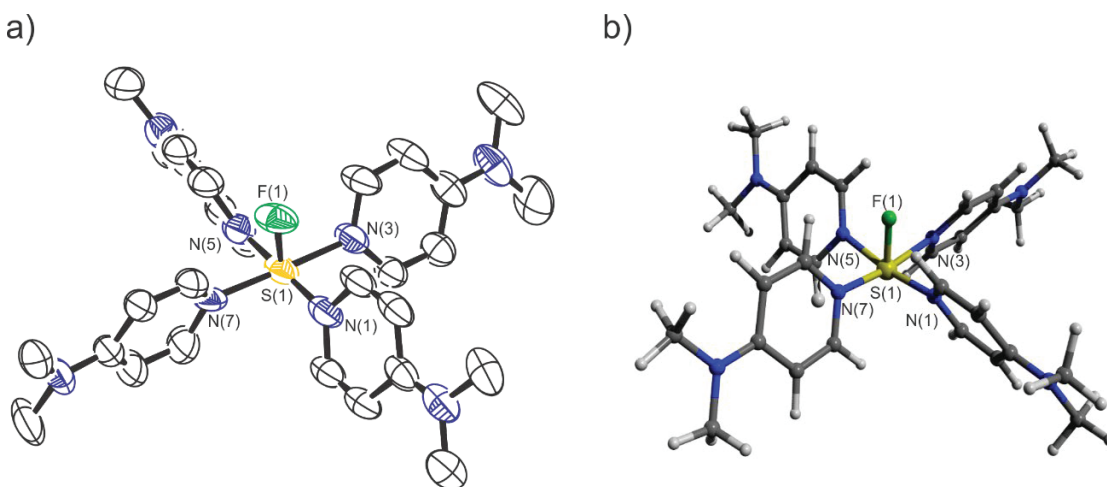


Figure 5.3. (a) Thermal ellipsoid plot (50% probability level) of [SF(dmap)₄]³⁺ from [SF(dmap)₄][OTf]₃. Hydrogen atoms are omitted for clarity. (b) Optimized gas-phase geometry of [SF(dmap)₄]³⁺ calculated at the MN15/def2-TZVPPD level of theory.

5.3.3 NMR Spectroscopy.

The ¹⁹F NMR spectrum of the reaction between SF₄ and [(CH₃)₃Si(py)][OTf] was recorded in SO₂ at –54 °C and the fluorine-on-sulfur region is shown in Figure 5.4. An excess of SF₄ (1.5 equivalents) is used in the synthesis of [SF₃(py)][OTf], resulting in the presence of two triplets in the spectrum at 87.0 ppm and 33.5 ppm [²J_{FF} = 74 Hz] for SF₄; also present is a small amount of SOF₂ (72.8 ppm) which is a contaminant from the SF₄

and which is assumed not to interfere with the current chemistry, due to its poor Lewis acidity and fluoride-ion donor properties. The resonances due to the $[\text{SF}_3(\text{py})]^+$ cation have been assigned to the broad singlets at 62.8 ppm (1F; $\Delta\nu_{1/2} = 181$ Hz) and 10.0 ppm (2F; $\Delta\nu_{1/2} = 123$ Hz) and are attributed to the F_{ax} and F_{eq} environments, respectively, on the basis of their relative integrations. The broadness of the cation resonances in $[\text{SF}_3(\text{py})][\text{OTf}]$ suggests some fluxionality of the cation in solution at the NMR time scale. It is worth noting that samples of $[\text{SF}_3(\text{py})_2][\text{PnF}_6]$ (Pn = As or Sb) recorded in pyridine displayed an even greater degree of fluxionality on the NMR timescale as the F_{ax} and F_{eq} environments were found to coalesce into a single resonance ($\delta = 18.5$ ppm).¹² In contrast, $[\text{SF}_3(\text{phen})]^+$ exhibited a rigid square pyramidal geometry allowing for the resolution of the F_{ax} ($\delta = 56$ ppm) and F_{eq} ($\delta = 23$ ppm) and the J coupling constant ($^2J_{\text{FF}} = 11$ Hz). Such a homonuclear coupling constant is easily obscured by the broadness of the $[\text{SF}_3(\text{py})]^+$ cation resonances. Also present in the spectrum is the triflate resonance at -78.6 (3F) and some residual $(\text{CH}_3)_3\text{SiF}$ at -148.8 ppm.

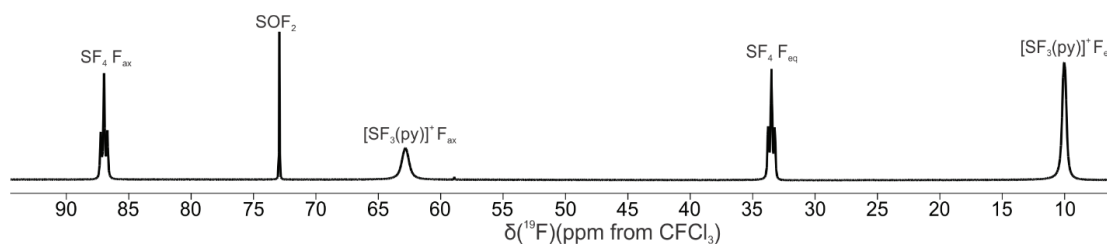


Figure 5.4. The fluorine-on-sulfur region of the ^{19}F NMR spectrum of $[\text{SF}_3(\text{py})][\text{OTf}]$ recorded in SO_2 at -54 °C.

The ^{19}F NMR spectrum of the reaction of excess SF_4 (1.5 equivalents) with $[(\text{CH}_3)_3\text{Si}(\text{dmap})][\text{OTf}]$ was recorded in SO_2 at -54 °C (Figure 5.5). The reaction mixture was warmed to -30 °C for 30 min before the spectrum was acquired. The targeted product $[\text{SF}_3(\text{dmap})]^+$ was present in small quantities, confirmed by the presence of a doublet and

triplet at 76.3 ppm and 3.7 ppm ($^2J_{\text{FF}} = 20$ Hz), respectively, in a 2:1 ratio. The size of the ^2J coupling constant is in excellent agreement with that found for the $[\text{SF}_3(\text{phen})]^+$ cation. The high-frequency resonance, *i.e.*, the axial fluorines, integrates as 2F in the DMAP salt, suggesting that DMAP in $[\text{SF}_3(\text{dmap})]^+$ is binding in an equatorial position, whereas pyridine in $[\text{SF}_3(\text{py})]^+$ binds in an axial position, resulting in its high-frequency resonance integrating as 1F. Quantum chemical calculations of the chemical shifts for the pyridine and DMAP adducts qualitatively support the assignment of the high-frequency and low-frequency resonances to the axial and equatorial fluorine environments, respectively. (See section 5.5.7 NMR Shift Calculations for a more detailed discussion of the chemical shift calculations.) The two triplets of SF_4 are the two most intense signals in the fluorine-on-sulfur region; the next most intense signal is the sharp singlet at 57.7 ppm which has been assigned to the $[\text{SF}_2(\text{dmap})_2]^{2+}$ dication where the sulfur center adopts a seesaw geometry with two equivalent fluorido ligands consistent with the crystallographically observed structure. The SF_4 resonances arise from the excess SF_4 used, as well as the SF_4 formed via the dismutation (eq 5.6). Warming up the sample to -35 °C for another 30 min had no effect on the relative proportions of each species.

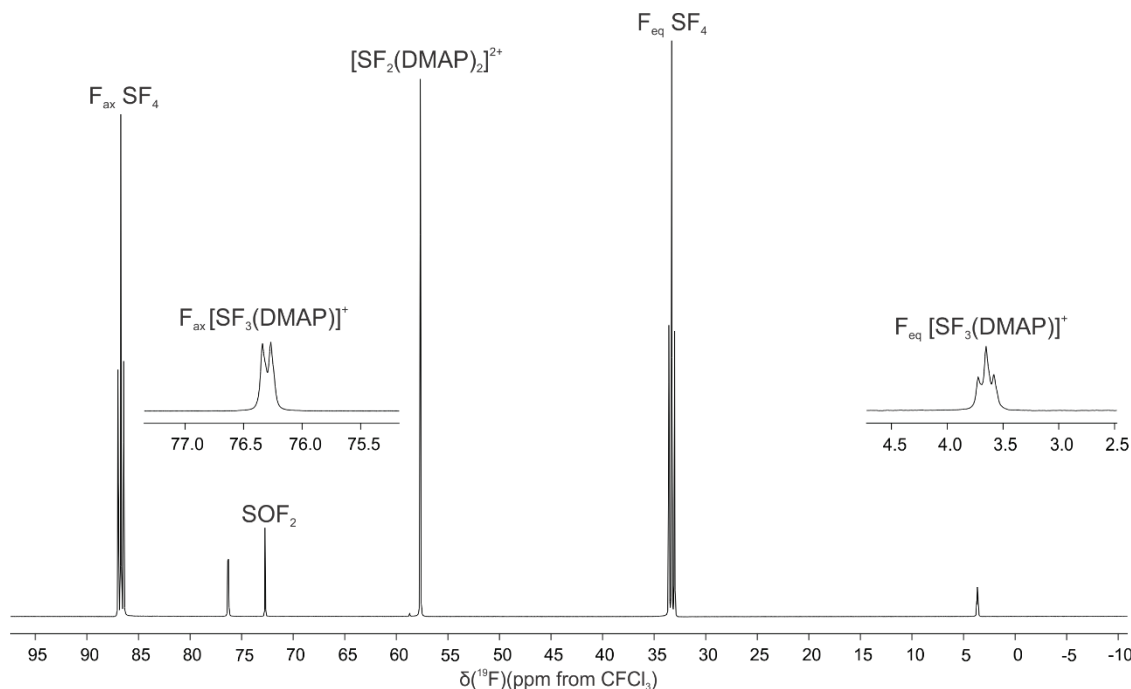


Figure 5.5. The fluorine-on-sulfur region of the ^{19}F NMR spectrum of the reaction between SF_4 and $[(\text{CH}_3)_3\text{Si}(\text{dmap})][\text{OTf}]$ after allowing to react at $-30\text{ }^\circ\text{C}$ for 30 min, recorded in SO_2 at $-54\text{ }^\circ\text{C}$.

In an attempt to quantitatively form the $[\text{SF}_2(\text{dmap})_2]^{2+}$ dication a 1:2 reaction of SF_4 with $[(\text{CH}_3)_3\text{Si}(\text{dmap})][\text{OTf}]$ was performed and studied using ^{19}F NMR spectroscopy. Warming up the sample to $-20\text{ }^\circ\text{C}$ for a total of 6 hours leads to completion of the reaction evidenced by the complete consumption of the $[(\text{CH}_3)_3\text{Si}(\text{dmap})][\text{OTf}]$ starting material, during this time the initially colourless solution slowly turns a pale purple colour. The origin of the purple colour is unknown but is potentially due to the presence of traces of sulfur radicals generated by having the sample at $-20\text{ }^\circ\text{C}$ for a prolonged period of time. Once the reaction is complete the major product is the $[\text{SF}_2(\text{dmap})_2]^{2+}$ dication (57.7 ppm) but small amounts (8 mol%) of the $[\text{SF}_3(\text{dmap})]^+$ cation are still present.

The $[\text{SF}_2(\text{dmap})_2]^{2+}$ dication can also be obtained without the presence of $[\text{SF}_3(\text{dmap})]^+$ by the 1:1 reaction of $[\text{SF}_3][\text{SbF}_6]$ and DMAP. The ^{19}F NMR spectrum of this reaction mixture acquired in CH_3CN at $-30\text{ }^\circ\text{C}$ (Figure 5.6) shows the two triplets of

SF₄ (84.2 ppm and 32.8 ppm) and a sharp singlet at 52.6 ppm from the [SF₂(dmap)₂]²⁺ which all integrate in an approximate 1:1:1 ratio, confirming the disproportionation reaction (eq 5.6). Also present is the [SbF₆][−] multiplet with ¹J(¹²¹Sb–¹⁹F) and ¹J(¹²³Sb–¹⁹F) as 1946 and 930 Hz, respectively, indicating an absence of anion-cation interactions in solution.

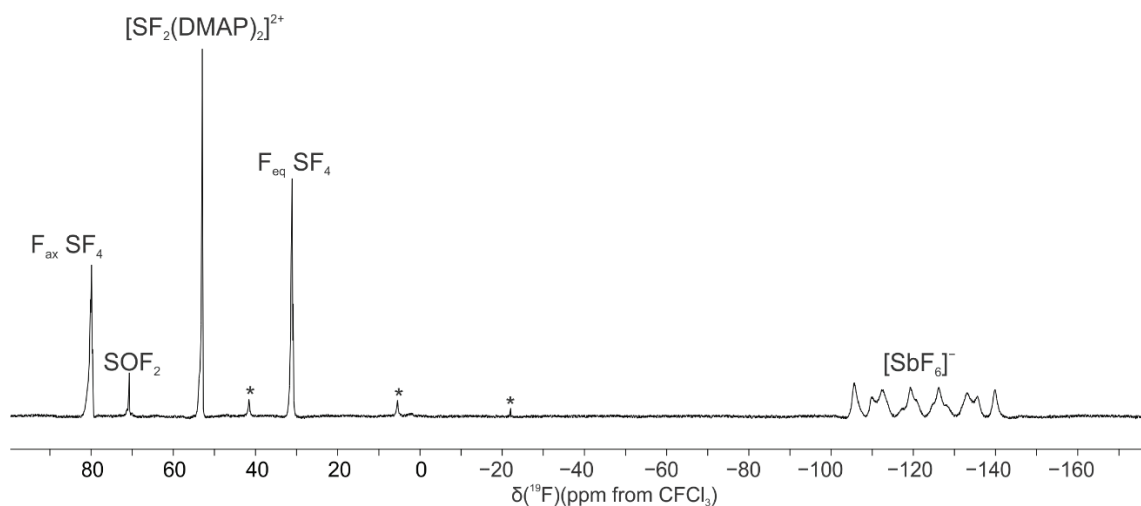


Figure 5.6. ¹⁹F NMR spectrum of [SF₂(dmap)₂][SbF₆]₂ recorded in CH₃CN at −30 °C. Asterisks (*) denotes unknown impurity.

NMR spectra of the equimolar reaction of [SF₃][AsF₆] and OPPh₃ were recorded in SO₂ at −60 °C (Figure 5.7); attempts to run the sample at a lower temperature always resulted in the solution freezing. No evidence of adduct formation is observed in the ¹⁹F NMR spectrum. The negative chemical shift region of the ¹⁹F NMR spectrum shows resonances attributable to [FPPh₃][AsF₆], namely a doublet at −125.7 ppm (¹J_{PF} = 996 Hz) which aligns well with the previously reported data for [FPPh₃][FB(C₆F₅)₃] (¹⁹F in CD₂Cl₂ δ = −128.3 ppm; ¹J_{PF} = 996 Hz).²⁵ The corresponding doublets are also observed in the ³¹P and ³¹P{¹H} spectra (³¹P δ = 97.0 ppm; [FPPh₃][FB(C₆F₅)₃] ³¹P δ = 94.7 ppm). In addition to the doublet, the characteristic equal-intensity quartet of [AsF₆][−] was observed [¹⁹F δ = −56.7 ppm; ¹J(¹⁹F–⁷⁵As) = 934 Hz]. The relative integrations of [FPPh₃]⁺ cation and [AsF₆][−] anion are not in the expected 1:6 ratio but instead in a 1:4.5 ratio suggesting of a greater

proportion of cationic species in solution than is expected. The most intense signal in the fluorine-on-sulfur region of the spectrum is SOF_2 , a by-product of deoxofluorination. This reaction is also generating small quantities of SF_4 . While we are unable to definitively explain the origin of the SF_4 , one potential route to its formation is eq. 5.10, in which a $[\text{SF}_3(\text{OPPh}_3)]^+$ adduct is initially formed which undergoes rapid ligand scrambling yielding $[\text{SF}_2(\text{OPPh}_3)_2]^{2+}$ and SF_4 . The elusive $[\text{SF}_2(\text{OPPh}_3)_2]^{2+}$ dication is potentially the active deoxofluorinating agent. As discussed above similar rearrangement reactions were also observed in the $[\text{SF}_3(\text{dmap})]^+$ system where the $[\text{SF}_2(\text{dmap})_2]^{2+}$ dication was the major product regardless of the starting stoichiometry lending a plausibility to the existence of an intermediate $[\text{SF}_2(\text{OPPh}_3)_2]^{2+}$ dication and its possible involvement in deoxofluorination reactions.

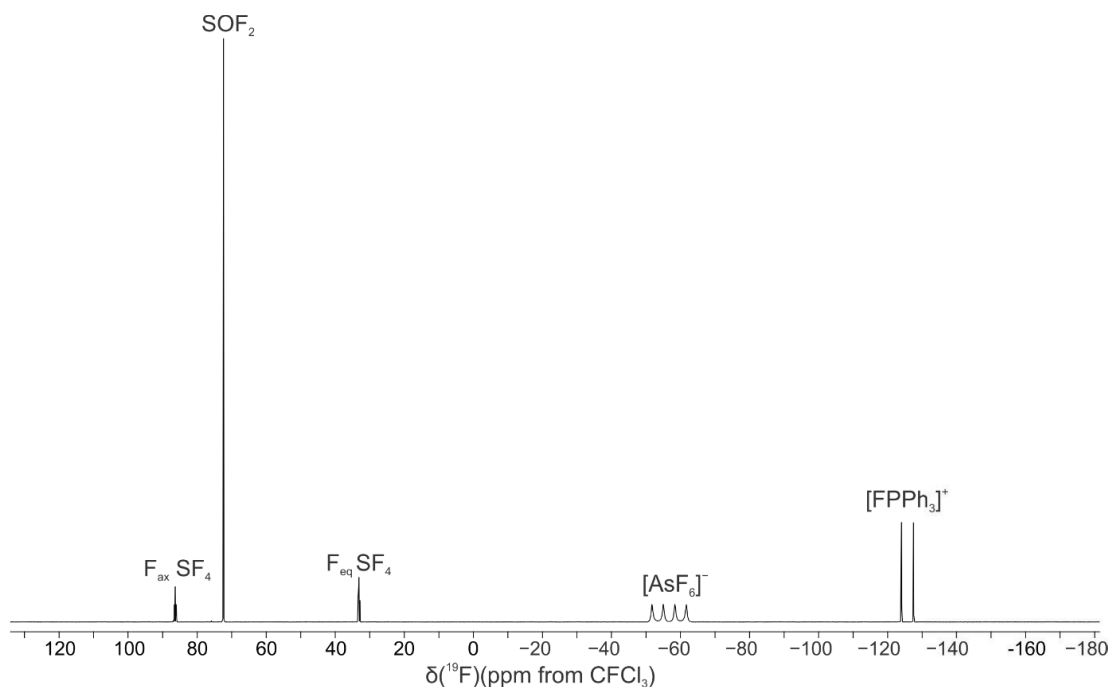


Figure 5.7. The ^{19}F NMR spectrum of the reaction between $[\text{SF}_3][\text{AsF}_6]$ and OPPh_3 , recorded in SO_2 at -60°C .

After warming the sample to ambient temperature for 15 minutes SF₄ is no longer detected and the relative proportion of SOF₂ increases, coupled with the disappearance of the OPPh₃ signal in the ³¹P NMR indicate completion of the deoxofluorination reaction.

5.3.4 Raman Spectroscopy.

The low-temperature Raman spectra of [SF₃(py)][OTf], [SF₂(dmap)₂][SbF₆]₂ and [SF(dmap)₄][OTf]₃·2CH₃CN were acquired at –100 or –110 °C. Additionally quantum chemical calculations were employed to aid in the assignment of the vibrational modes of the cations, resulting in strong agreement between the experimental and calculated spectroscopic data. Table 5.3 contains key modes and assignments; complete lists of vibrational frequencies and assignments are available in Appendix D.

Adduct formation between [SF₃]⁺ and pyridine causes the ν(SF₃) modes to split into distinct ν(SF_{ax}) and ν(SF_{eq}) modes, these modes are red-shifted relative to the parent [SF₃]⁺ cation ([SF₃][SbF₆], 928–955 cm^{–1}; [SF₃(py)]⁺ ν(SF_{ax}) exptl. 714 cm^{–1}, calcd. 752 cm^{–1}; ν_s(SF_{2eq}) exptl. 860 cm^{–1}, calcd. 873 cm^{–1}; ν_{as}(SF_{2eq}) exptl. 848 cm^{–1}, calcd. 872 cm^{–1}).¹⁶ The SF stretching modes for [SF₃(py)]⁺ are not shifted as far as those for the 1:2 adduct where two nitrogen donors are present ([SF₃(py)₂][SbF₆]·CH₃CN, ν(SF_{ax}) 828 cm^{–1}, 808 cm^{–1}; ν(SF_{2eq}) 700 cm^{–1}, 671 cm^{–1}). In both adducts, the ν(SF) mode *trans* to the N-donor is shifted to a greater extent, consistent with the more pronounced elongation of these S–F bond in the solid-state structures.¹²

In the Raman spectrum of the [SF₂(dmap)₂][SbF₆]₂ salt, the ν_s(SF₂) mode (exptl. 538 cm^{–1}, calcd. 510 cm^{–1}) occurs at a substantially lower frequency than those observed in the N-base adducts of [SF₃]⁺, reflective of the longer, weaker S–F bonds found in the dication. Conversely, the ν(SN) modes in the [SF₂(dmap)₂]²⁺ dication (ν_s(SN₂) exptl. 635

cm^{-1} , calcd. 638 cm^{-1} ; $\nu_{\text{as}}(\text{SN}_2)$ exptl. 577 cm^{-1} , 609 cm^{-1}) occur at far higher frequencies than those in the pyridine adducts of $[\text{SF}_3]^+$ ($[\text{SF}_3(\text{py})]^+$ $\nu(\text{SN})$ exptl. 198 cm^{-1} , calcd. 192 cm^{-1} ; $[\text{SF}_3(\text{py})_2]^+$ $\nu_{\text{s}}(\text{SN}_2)$ 192 cm^{-1}) reflective of the change from weak dative S–N bonding in the monocation to strongly covalent S–N bonds in the dication.

The $[\text{SF}(\text{dmap})_4][\text{OTf}]_3 \cdot 2\text{CH}_3\text{CN}$ salt gives rise to very weak Raman bands, the $\nu(\text{SF})$ mode of $[\text{SF}(\text{dmap})_4]^{3+}$ (exptl. 762 cm^{-1} , calcd. 764 cm^{-1}) occurs at a slightly higher frequency than the $\nu(\text{SF}_{\text{ax}})$ of $[\text{SF}_3(\text{py})]^+$ and a considerably higher frequency than the $\nu(\text{SF}_2)$ mode of $[\text{SF}_2(\text{dmap})_2]^{2+}$, but at a lower frequency than the $\nu_{\text{s}}(\text{SF}_{2\text{eq}})$ and $\nu_{\text{as}}(\text{SF}_{2\text{eq}})$ modes of $[\text{SF}_3(\text{py})]^+$. It should be noted that the $\nu(\text{SF})$ mode of the $[\text{SF}(\text{dmap})_4]^{3+}$ overlaps with the $\delta_{\text{s}}(\text{CF}_3)$ mode of the $[\text{OTf}]^-$ anion.

The formation of Lewis acid-base adducts between nitrogen-containing heterocycles and Lewis acidic sites causes a blue shift of the vibrational frequencies of the heterocycle, with stronger interactions leading to greater charge transfer from the nitrogen lone pair to the Lewis acid resulting in the modes being blue shifted to a greater extent.^{29,30} Indicative of the greater acidity of $[\text{SF}_3]^+$ than SF_4 the symmetric ring-breathing mode of pyridine (990 cm^{-1}) shifts to a higher frequency in $[\text{SF}_3(\text{py})]^+$ (exptl. 1017 cm^{-1} , calcd. 1039 cm^{-1}) compared to $\text{SF}_4 \cdot \text{py}$ (1003 cm^{-1}). The shift in frequency of the $\nu_{\text{s}}(\text{NC}_5)$ mode in $[\text{SF}_3(\text{py})]^+$ is comparable to $[\text{SF}_3(\text{py})_2][\text{SbF}_6] \cdot \text{CH}_3\text{CN}$ (1021 cm^{-1}). In free DMAP the symmetric ring-breathing mode occurs at 985 cm^{-1} , this is shifted by a sizable amount in both $[\text{SF}_2(\text{dmap})_2]^{2+}$ (exptl. 1056 cm^{-1} , calcd. 1047 cm^{-1}) and $[\text{SF}(\text{dmap})_4][\text{OTf}]_3$ (exptl. 1054 cm^{-1} , calcd. 1020 cm^{-1}) highlighting the considerable Lewis acidity of the sulfur center in both species.

Table 5.3. Selected vibrational frequencies (cm^{-1}) of $[\text{SF}_3(\text{py})]^+$, $[\text{SF}_2(\text{dmap})_2]^{2+}$, and $[\text{SF}(\text{dmap})_4]^{3+}$

	$[\text{SF}_3(\text{py})]^+$		$[\text{SF}_2(\text{dmap})_2]^{2+}$		$[\text{SF}(\text{dmap})_4]^{3+}$	
	Exptl.	Calcd. ^[a]	Exptl.	Calcd. ^[a]	Exptl.	Calcd. ^[b]
$\nu(\text{SF})$					762(100)	764(35)[8]
$\nu(\text{SF}_{\text{ax}})$	762(26)	752(14)[661]				
$\nu_{\text{s}}(\text{SF}_{2\text{ax}})$			538(16)	510(4)[16]		
$\nu_{\text{s}}(\text{SF}_{2\text{eq}})$	860(73)	873(33)[119]				
$\nu_{\text{as}}(\text{SF}_{2\text{eq}})$	848(31)	872(2)[136]				
$\nu(\text{SN})$	198(18)	192(9)[39]				
$\nu_{\text{s}}(\text{SN}_2)$			635(8)	638(49)[24]		
$\nu_{\text{as}}(\text{SN}_2)$			577(8)	609(4)[166]		
$\nu(\text{NC}_3)$	1017(60)	1039(37)[43]	1056(23)	1047(54)[92]	1054(25)	1020(53)[1]

Normalised Raman intensities given in parenthesis. [a] Calculated using the B3LYP-D3(BJ)/def2-TZVPPD level of theory. [b] Calculated using the MN15/def2-TZVPPD level of theory. Absolute Raman intensities ($\text{\AA}^4 \text{u}^{-1}$) are given in parentheses and IR intensities (km mol^{-1}) given in square brackets.

5.3.5. Computational Results.

The seesaw geometries of the $[\text{SF}_3\text{L}]^+$ L = py, DMAP and $[\text{SF}_2(\text{dmap})_2]^{2+}$ adduct cations allow for different isomers where the N-base can bind in either the axial or equatorial positions. The gas-phase geometries of $[\text{SF}_3\text{L}]^+$, *i.e.*, axial- $[\text{SF}_3\text{L}]^+$ and equatorial- $[\text{SF}_3\text{L}]^+$ with L in the axial and equatorial position, respectively, and of the three possible isomers for $[\text{SF}_2(\text{dmap})_2]^{2+}$ were optimised at the B3LYP-D3(BJ)/def2-TZVPPD level of theory (Figure 5.8). The calculated S–F and S–N bond lengths for the various isomers are given in Table 5.4. As expected, the equatorial S–F and S–N bond lengths are shorter than the corresponding axial bond lengths, highlighting the greater level of covalency in the equatorial bonds as a result of increased orbital overlap. In order to

determine the relative energies of the various isomers, their single-point energies were calculated at the DLPNO-CCSD(T)/def2-TZVPP level of theory. For the pyridine adducts, the axial isomer was of $[\text{SF}_3(\text{py})]^+$ found to be 28 kJ mol^{-1} more stable than the equatorial isomer, which is consistent with the experimental results as only the axial isomer was observed in the solid state and solution. For the DMAP adducts of $[\text{SF}_3]^+$, the equatorial isomer increased in relative stability with the isomers being almost energetically degenerate and the axial isomer predicted to be $<2 \text{ kJ mol}^{-1}$ lower in energy than the equatorial isomer. The increased stability of the equatorial isomer for the stronger base DMAP is consistent with the NMR spectroscopic evidence, but the predicted near degeneracy is in contrast with our results, where only the equatorial isomer was seen without any evidence for the axial isomer or any interconversion between the two isomers on the NMR timescale. Solvation effects may stabilize the equatorial isomer to a greater extent. Chemical shift calculations (section 5.5.7) for the equatorial and axial $[\text{SF}_3(\text{L})]^+$ predict the axial ^{19}F resonances to appear at higher chemical shifts, supporting the assignment of experimentally observed species as axial- $[\text{SF}_3(\text{py})]^+$ and equatorial- $[\text{SF}_3(\text{dmap})]^+$.

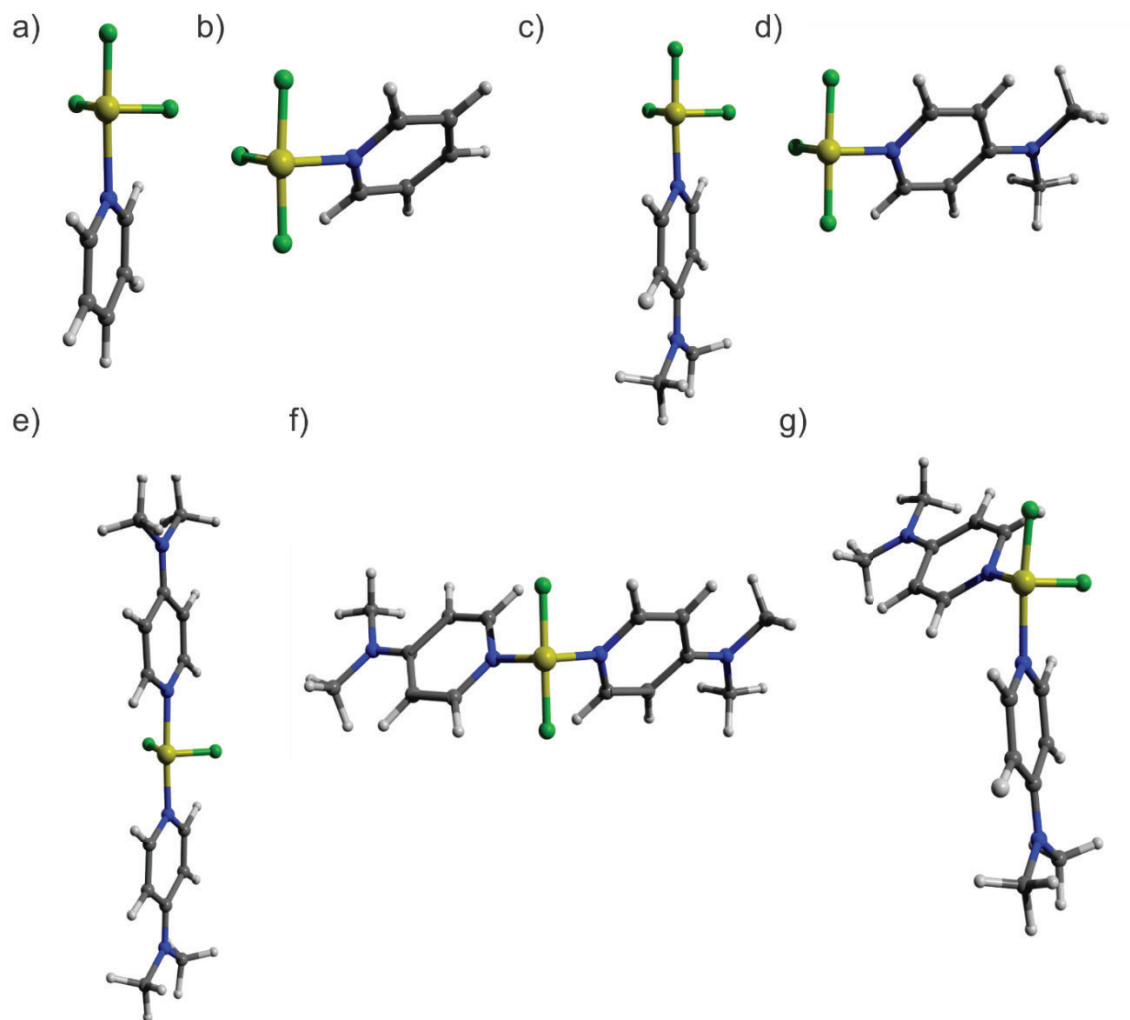


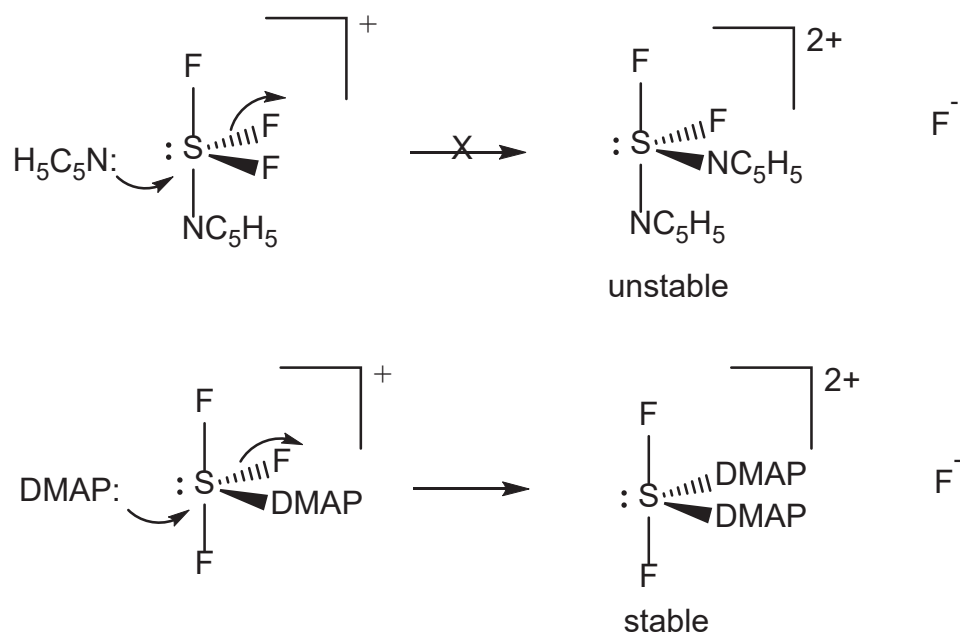
Figure 5.8. Optimised gas-phase geometries of (a) $[\text{SF}_3(\text{py}_{\text{ax}})]^+$ (b) $[\text{SF}_3(\text{py}_{\text{eq}})]^+$ (c) $[\text{SF}_3(\text{dmap}_{\text{ax}})]^+$ (d) $[\text{SF}_3(\text{dmap}_{\text{eq}})]^+$ (e) $[\text{SF}_2(\text{dmap}_{\text{ax}})_2]^{2+}$ (f) $[\text{SF}_2(\text{dmap}_{\text{eq}})_2]^{2+}$ (g) $[\text{SF}_2(\text{dmap}_{\text{cis}})_2]^{2+}$. Calculated at the B3LYP/def2-TZVPPD level of theory.

Table 5.4. Selected bond lengths of $[\text{SF}_3]^+$, $[\text{SF}_3(\text{py})]^+$, $[\text{SF}_3(\text{dmap})]^+$ and $[\text{SF}_2(\text{dmap})]^{2+}$. [a]

	$[\text{SF}_3]^+$	$[\text{SF}_3(\text{py}_{\text{ax}})]^+$	$[\text{SF}_3(\text{py}_{\text{eq}})]^+$	$[\text{SF}_3(\text{dmap}_{\text{ax}})]^+$	$[\text{SF}_3(\text{dmap}_{\text{eq}})]^+$	$[\text{SF}_2(\text{dmap}_{\text{ax}})_2]^{2+}$	$[\text{SF}_2(\text{dmap}_{\text{eq}})_2]^{2+}$	$[\text{SF}_2(\text{dmap}_{\text{cis}})_2]^{2+}$
S-F _{ax}	1.526	1.594	1.660	1.617	1.675		1.690	1.649
S-F _{eq}	1.526	1.551	1.560	1.560	1.568	1.572		1.576
S-N _{ax}		2.035		1.933		1.847		1.903
S-N _{eq}			1.811		1.760		1.751	1.735

[a] Calculated at the B3LYP-D3(BJ)/def2-TZVPPD level of theory.

In the DMAP adducts of $[\text{SF}_2]^{2+}$, the experimentally observed equatorial isomer was found to be 7.9 kJ mol^{-1} lower in energy than the axial isomer and 26 kJ mol^{-1} lower in energy than the mutually *cis* isomer, reflecting the experimental finding. In contrast, the axial isomer of the $[\text{SF}_2(\text{py})_2]^{2+}$ dication is predicted to be the stable isomer, 35 kJ mol^{-1} lower in energy than the equatorial and 41 kJ mol^{-1} lower in energy than the mutually *cis* isomer. The difference in the minimum energy isomer between pyridine and DMAP dication adducts highlights the influence of the significantly stronger Lewis basicity of DMAP on the structure. The formation of the DMAP-containing dication and lack of evidence for the pyridine-containing dication can be rationalized by the different geometries of the monocations (Scheme 5.1). The attack of DMAP towards the σ -hole opposite of the equatorial S–F bond will lead to displacement of the equatorial fluorine by DMAP, yielding the observed dication isomer and a fluoride ion that can displace a DMAP molecule in a separate equatorial- $[\text{SF}_3(\text{dmap})]^+$ cation producing SF_4 . The attack of a pyridine towards one of the σ -hole opposite of the equatorial S–F bonds of the axial- $[\text{SF}_3(\text{py})]^+$ will lead to the strongly disfavoured dication with pyridines *cis* to each other.



Scheme 5.1. Proposed mechanism of ligand exchange reactions for axial-[SF₃(py)]⁺ and equatorial-[SF₃(dmap)]⁺.

The covalent component of the bonding in these adducts was studied using natural bond order (NBO) analysis, the NBO results are summarized in Table 5.5. The NBO results further highlight the greater ionicity of the S–F_{ax} bonds as the F_{ax} atoms have larger natural population analysis (NPA) charges and the S–F_{ax} bonds have lower Wiberg bond indices (WBI) than their equatorial counterparts. The binding of py or DMAP in an equatorial position leads to vastly more covalent S–N bonds than those that bind axially as a result of favourable sterics in the equatorial isomers and greater charge transfer [$\Sigma(L)$] from the ligand to the sulfur centre, resulting in substantially shorter S–N_{eq} bond lengths in the calculated structures. In both [SF₃(dmap)]⁺ and [SF₂(dmap)₂]²⁺ the S–N_{eq} ([SF₃(dmap)]⁺ S–N WBI = 0.81; [SF₂(dmap)₂]²⁺ S–N_{eq} WBI = 0.84) bond shows a greater level of covalency than the S–F bonds ([SF₃(dmap)]⁺ S–F WBI = 0.59-0.77; [SF₂(dmap)₂]²⁺ S–F

WBI = 0.56). In the pyridine adduct there is a comparable level of covalency in the S–N_{eq} (WBI = 0.87) and S–F_{eq} (WBI = 0.89) bonds.

Table 5.5. Selected Natural Population Analysis (NPA) Charges, Wiberg Valences,^[a] and Wiberg Bond Indices of $[\text{SF}_3(\text{py})]^+$, $[\text{SF}_3(\text{dmap})]^+$ and $[\text{SF}_2(\text{dmap})_2]^{2+}$.^[b]

	$[\text{SF}_3(\text{py}_{\text{ax}})]^+$	$[\text{SF}_3(\text{py}_{\text{eq}})]^+$	$[\text{SF}_3(\text{dmap}_{\text{ax}})]^+$	$[\text{SF}_3(\text{dmap}_{\text{eq}})]^+$	$[\text{SF}_2(\text{dmap}_{\text{ax}})_2]^{2+}$	$[\text{SF}_2(\text{dmap}_{\text{eq}})_2]^{2+}$
S	2.11 [2.76]	2.01 [2.81]	2.07 [2.80]	2.00 [2.81]	1.95 [2.89]	1.85 [2.90]
F _{ax}	-0.51 [0.82]	-0.58 [0.72]	-0.53 [0.78]	-0.59 [0.71]		-0.60 [0.69]
F _{eq}	-0.45 [0.88]	-0.44 [0.88]	-0.46 [0.87]	-0.45 [0.87]	-0.47 [0.86]	
N _{ax}	-0.61 [3.27]		-0.68 [3.22]		-0.68 [3.24]	
N _{eq}		-0.55 [3.40]		-0.63 [3.29]		-0.63 [3.27]
$\Sigma(\text{L})^{[c]}$	0.30	0.59	0.39	0.64	0.49	0.72
S-F _{ax}	0.71	0.78	0.67	0.59		0.56
S-F _{eq}	0.79	0.89	0.77	0.77	0.74	
S-N _{ax}	0.44		0.54		0.64	
S-N _{eq}		0.87		0.81		0.84

[a] Number in square brackets. [b] Calculated at the DLPNO-CCSD(T)/def2-TZVPP level of theory. [c] Total NPA charge of the ligands

5.4 Conclusion

In summary a 1:1 adduct between $[\text{SF}_3]^+$ and pyridine can readily be made by the reaction of an excess of SF_4 and $[\text{TMS}(\text{py})][\text{OTf}]$. The resulting cationic adduct $[\text{SF}_3(\text{py})]^+$ adopts a seesaw geometry with two close anion contacts, so each sulfur center is hexacoordinate. The analogous DMAP adduct $[\text{SF}_3(\text{dmap})]^+$ was found to undergo dismutation in solution to form $[\text{SF}_2(\text{dmap})_2]^{2+}$ and SF_4 . No evidence was observed for such a dismutation for $[\text{SF}_3(\text{py})]^+$. The different reactivity of the $[\text{SF}_3(\text{L})]^+$ with $\text{L} = \text{py}$, DMAP can possibly be attributed to two factors. Firstly, the presence of the significantly stronger base DMAP weakens the S–F bonds, possibly facilitating dismutation reactions. Secondly, the change in geometry, evidenced by NMR spectroscopy from the axial ligand position in the seesaw-shaped $[\text{SF}_3(\text{py})]^+$ cation to the equatorial position of the seesaw-shaped $[\text{SF}_3(\text{dmap})]^+$ cation could cause the dismutation to $[\text{SF}_2(\text{dmap})_2]^{2+}$, where the DMAP ligands also occupy the equatorial positions. The $[\text{SF}_2(\text{dmap})_2]^{2+}$ dication can undergo further dismutation to the $[\text{SF}(\text{dmap})_4]^{3+}$ trication. The $[\text{SF}(\text{dmap})_4]^{3+}$ trication has a square pyramidal geometry with no appreciable anion-cation interactions resulting in a square pyramidal sulfur center.

Adducts of $[\text{SF}_3]^+$ with organic oxygen bases are invoked as intermediates in the mechanism for deoxofluorination using SF_4 , yet there are no well characterized examples of such adducts. We reasoned that the use of more Lewis basic phosphine oxides might facilitate the isolation of such an adduct, however, no evidence of adduct formation was found, just the products of deoxofluorination. The facile deoxofluorination under these conditions contrasts with the harsh reported conditions necessary when using SF_4 . The stronger interaction between $[\text{SF}_3]^+$ and oxygen serves to increase the polarization of the

O=P bond making it more susceptible to deoxofluorination. The presence of SF₄ in the LT ¹⁹F NMR spectrum suggests a similar ligand scrambling process to that seen in the [SF₃(dmap)]⁺ system is occurring and hints at the potential involvement of an elusive [SF₂(OPPh₃)]²⁺ dication.

5.5 Experimental

5.5.1 General Methods

***Caution!** Elemental F₂, SF₄, AsF₅ and SbF₅ are highly toxic and corrosive, rapidly evolving HF upon exposure to moisture. Appropriate safety measures should be taken during their handling.*

All reactions were carried out in heat-sealed 1/4" o.d. FEP reactors that were connected to either 316-stainless-steel or Kel-F valves via flared fittings. Sulfur dioxide, acetonitrile and SbF₅ were distilled on a Pyrex vacuum line equipped with high-vacuum PTFE valves (Chemglass). Arsenic pentafluoride and sulfur tetrafluoride were distilled through a nickel/316 stainless-steel vacuum line equipped with 316 stainless-steel valves (Autoclave Engineers) and pre-passivated with F₂. Solid materials were handled in a drybox (Omni Lab, Vacuum Atmospheres) under an atmosphere of dry N₂.

Acetonitrile was distilled from a solvent purification system (M. Braun MB-SPS) onto 3-Å molecular sieves and distilled again onto fresh sieves. Sulfur dioxide (Matheson) was dried over CaH₂. Antimony pentafluoride (Galaxy chemicals) was purified by distillation. Sulfur tetrafluoride (Ozark-Mahoning Co.) was purified by passing the gas through a column of activated charcoal. Traces of thionyl fluoride are present in the sulfur

tetrafluoride, but did not interfere with the chemistry. 4-Dimethylaminopyridine (Sigma-Aldrich), trimethylsilyl trifluoromethanesulfonate (Sigma-Aldrich 99%) and OPPh_3 were used as received. Pyridine was transferred onto 3-Å molecular sieves in a glove bag under an atmosphere of dry N_2 , then distilled onto fresh 3-Å molecular sieves. The $[(\text{CH}_3)_3\text{Si}(\text{L})][\text{OTf}]$ (L = pyridine, DMAP or OPPh_3) reagents³¹, AsF_5 ³² and $[\text{SF}_3][\text{PnF}_6]$ ³³ (Pn = As or Sb) were made as previously described.

5.5.2. Synthesis

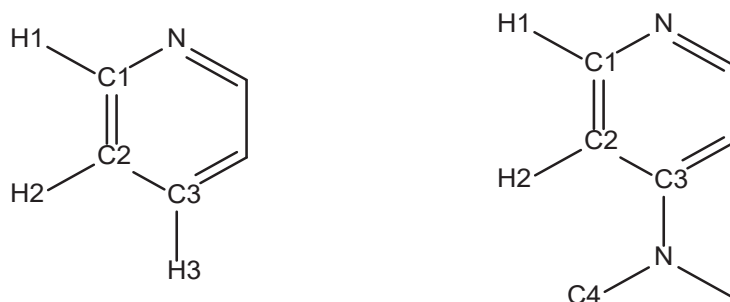


Figure 5.9. Atom Labelling used for py and DMAP.

Synthesis and Crystal Growth of $[\text{SF}_3(\text{py})][\text{OTf}]$

In a typical reaction a 1/4" o.d FEP reactor is loaded with $[(\text{CH}_3)_3\text{Si}(\text{py})][\text{OTf}]$ (0.075 g, 0.25 mmol). Sulfur dioxide (ca. 2 mL) was then distilled into the reactor at -196°C and the mixture was warmed to ambient temperature resulting in a clear and colourless solution. Sulfur tetrafluoride (0.040 g, 0.37 mmol) is then distilled into the reactor at -196°C and the reaction mixture is slowly warmed to -30°C leading to a colourless solution. Volatiles are removed under dynamic vacuum at -60°C yielding $[\text{SF}_3(\text{py})][\text{OTf}]$ (0.070, 0.22 mmol, 92% yield) as an off-white powder. Crystals suitable for single crystal X-ray diffraction could be grown by distilling CH_3CN at -196°C onto $[\text{SF}_3(\text{py})][\text{OTf}]$ and slowly

warming the mixture to $-40\text{ }^{\circ}\text{C}$ forming a pale-yellow solution. Storing the solution at $-40\text{ }^{\circ}\text{C}$ for 16 hours results in colourless blocks of $[\text{SF}_3(\text{py})][\text{OTf}]$.

In a separate NMR-scale reaction $[(\text{CH}_3)_3\text{Si}(\text{py})][\text{OTf}]$ (0.041 g, 0.14 mmol) and SF_4 (0.023 g, 0.21 mmol) were reacted as described above in a 4mm o.d FEP reactor. NMR data in SO_2 at $-54\text{ }^{\circ}\text{C}$ $\delta(^{19}\text{F}, 282\text{ MHz})$: 87.0 (t, $^2J_{\text{FF}} = 74\text{ Hz}$, $\text{SF}_4\text{ F}_{\text{ax}}$), 72.9 (s, SOF_2), 62.8 (s, br, $[\text{SF}_3(\text{py})][\text{OTf}]\text{ F}_{\text{ax}}$), 33.5 (t, $^2J_{\text{FF}} = 74\text{ Hz}$, $\text{SF}_4\text{ F}_{\text{eq}}$), 10.0 (s, br, $[\text{SF}_3(\text{py})][\text{OTf}]\text{ F}_{\text{eq}}$), -78.6 (s, $[\text{OTf}]^-$), -148.8 (s, br, $\text{FSi}(\text{CH}_3)_3$); $\delta(^1\text{H}, 300\text{ MHz})$ 8.94 (s, H1), 8.65 (s, H3), 8.19 (s, H2), 0.31 (s, $\text{FSi}(\text{CH}_3)_3$); $\delta(^{13}\text{C}\{^1\text{H}\}, 75\text{ MHz})$: 147.4 (C1), 141.1 (C3), 128.8 (C2), 120.5 (q, $^1J_{\text{CF}} = 318\text{ Hz}$, $[\text{OTf}]^-$), 0.5 (d, $^2J_{\text{CF}} = 16\text{ Hz}$, $\text{FSi}(\text{CH}_3)_3$).

Atom labelling as shown in Figure 5.9

Attempted synthesis of $[\text{SF}_3(\text{dmap})][\text{OTf}]$

In a typical reaction a 1/4" o.d FEP reactor is loaded with $[(\text{CH}_3)_3\text{Si}(\text{dmap})][\text{OTf}]$ (0.075 g, 0.22 mmol). Sulfur dioxide (ca. 2 mL) is then distilled into the reactor at $-196\text{ }^{\circ}\text{C}$, the mixture is then warmed to ambient temperature forming a colourless solution. Sulfur tetrafluoride (0.036 g, 0.33 mmol) is then distilled into $-30\text{ }^{\circ}\text{C}$ resulting in a yellow solution. Volatiles are removed under dynamic vacuum yielding a mixture of $[\text{SF}_3(\text{dmap})][\text{OTf}]$ and $[\text{SF}_2(\text{dmap})_2][\text{OTf}]_2$ (0.098 g) as observed by Raman spectroscopy as an off-white powder.

In a separate NMR-scale reaction $[(\text{CH}_3)_3\text{Si}(\text{dmap})][\text{OTf}]$ (0.069 g, 0.20 mmol) and SF_4 (0.032 g, 0.30 mmol) were reacted as described above in a 4-mm o.d FEP reactor. NMR data in SO_2 $-54\text{ }^{\circ}\text{C}$ $\delta(^{19}\text{F}, 282\text{ MHz})$: 87.0 (t, $^2J_{\text{FF}} = 77$, $\text{SF}_4\text{ F}_{\text{ax}}$), 76.3 (d, $^2J_{\text{FF}} = 20\text{ Hz}$, $[\text{SF}_3(\text{dmap})]^+\text{ F}_{\text{ax}}$), 72.7 (s, SOF_2), 57.7 (s, $[\text{SF}_2(\text{dmap})_2]^{2+}$), 33.3 (t, $^2J_{\text{FF}} = 77$, $\text{SF}_4\text{ F}_{\text{eq}}$), 3.7

(t, $^2J_{\text{FF}} = 20$ Hz, $[\text{SF}_3(\text{dmap})]^+ \text{F}_{\text{eq}}$), -78.1 (s, $[\text{OTf}]^-$), -149.0 (dec, $^3J_{\text{FH}} = 7$ Hz, $\text{FSi}(\text{CH}_3)_3$); $\delta(^1\text{H}, 300 \text{ MHz})$ 8.42 (d, $^3J_{\text{HH}} = 7.9$ Hz, $[\text{SF}_2(\text{dmap})_2]^{2+} \text{H1}$), 8.12 (s, br, $[\text{SF}_3(\text{dmap})]^+ \text{H1}$), 7.23 (d, $^3J_{\text{HH}} = 7.9$ Hz, $[\text{SF}_2(\text{dmap})_2]^{2+} \text{H2}$), 7.03 (s, br, $[\text{SF}_3(\text{dmap})]^+ \text{H2}$), 3.61 (s, $[\text{SF}_2(\text{DMAP})_2]^{2+} \text{N}(\text{CH}_3)_2$), 3.42 (s, $[\text{SF}_3(\text{dmap})]^+ \text{N}(\text{CH}_3)_2$), 0.36 (d, $^3J_{\text{FH}} = 6.5$, $\text{FSi}(\text{CH}_3)_3$).

Atom labelling as shown in Figure 5.9

Attempted synthesis of $[\text{SF}_2(\text{dmap})_2][\text{OTf}]_2$

In an NMR-scale reaction $[(\text{CH}_3)_3\text{Si}(\text{dmap})][\text{OTf}]$ (0.057 g, 0.17 mmol) and SF_4 (0.009 g, 0.09 mmol) were reacted as described above in a 4-mm o.d. FEP reactor. NMR data in SO_2 at -54 °C ($\delta(^{19}\text{F}, 282 \text{ MHz})$): 86.7 (t, $^2J_{\text{FF}} = 73$ Hz, $\text{SF}_4 \text{F}_{\text{ax}}$), 76.4 (d, $^2J_{\text{FF}} = 17$ Hz $[\text{SF}_3(\text{dmap})]^+ \text{F}_{\text{ax}}$), 72.8 (s, SOF_2), 57.7 (s, $[\text{SF}_2(\text{dmap})_2]^{2+}$), 33.4 (t, $^2J_{\text{FF}} = 73$ Hz, $\text{SF}_4 \text{F}_{\text{eq}}$), 3.8 (t, $^2J_{\text{FF}} = 17$ Hz, $[\text{SF}_3(\text{dmap})]^+ \text{F}_{\text{eq}}$), -78.5 (s, $[\text{OTf}]^-$), -148.7 (s, br, $\text{FSi}(\text{CH}_3)_3$); $\delta(^1\text{H}, 300 \text{ MHz})$ 11.13 (s, $[\text{H}-\text{dmap}]^+$), 8.36 (d, $^3J_{\text{HH}} = 7.5$ Hz, $[\text{SF}_2(\text{dmap})_2]^{2+} \text{H1}$), 8.06 (s, br, $[\text{SF}_3(\text{dmap})]^+ \text{H1}$), 7.17 (d, $^3J_{\text{HH}} = 7.5$ Hz, $[\text{SF}_2(\text{dmap})_2]^{2+} \text{H2}$), 6.96 (d, $^3J_{\text{HH}} = 6.5$ Hz, $[\text{SF}_3(\text{dmap})]^+$), 3.55 (s, $[\text{SF}_2(\text{dmap})_2]^{2+} \text{N}(\text{CH}_3)_2$), 3.36 (s, $[\text{SF}_3(\text{dmap})]^+ \text{N}(\text{CH}_3)_2$), 0.29 (d, $^3J_{\text{HF}} = 7.3$ Hz, $\text{FSi}(\text{CH}_3)_3$); $\delta(^{13}\text{C}\{^1\text{H}\}, 75 \text{ MHz})$: 157.8 (C3), 138.2 (C1), 120.5 (q, $^1J_{\text{CF}} = 319$ Hz, $[\text{OTf}]^-$), 109.6 (C2), 42.1 (C4), 0.4 (d, $^2J_{\text{CF}} = 15$ Hz, $\text{FSi}(\text{CH}_3)_3$).

Atom labelling as shown in Figure 5.9.

Synthesis and Crystal Growth of $[\text{SF}_2(\text{dmap})_2][\text{SbF}_6]_2$

In the drybox a 1/4" o.d FEP reactor is loaded with $[\text{SF}_3][\text{SbF}_6]$ (0.012 g, 0.037 mmol) and DMAP (0.046 g, 0.038 mmol). Acetonitrile was then distilled into the reactor at -196°C , the mixture was then slowly warmed to -40°C resulting in a pale-yellow solution. Slow removal of volatile material under dynamic vacuum at -40°C yields yellow needles of $[\text{SF}_2(\text{dmap})_2][\text{SbF}_6]_2$. NMR data in CH_3CN at -30°C $\delta(^{19}\text{F}, 300\text{ MHz})$: 86.5 (s, br, $\text{SF}_4\text{ F}_{\text{ax}}$), 71.9 (s, SOF_2), 52.6 (s, $[\text{SF}_2(\text{dmap})_2]^{2+}$), 32.0 (s, br, $\text{SF}_4\text{ F}_{\text{eq}}$), -122.7 (m, $^1J(^{121}\text{Sb}-^{19}\text{F}) = 1946\text{ Hz}$, $^1J(^{123}\text{Sb}-^{19}\text{F}) = 930\text{ Hz}$).

Attempted synthesis of $[\text{SF}_3(\text{OPPh}_3)][\text{AsF}_6]$

(a) $[(\text{CH}_3)_3\text{Si}(\text{OPPh}_3)][\text{OTf}]$ (0.106 g, 0.212 mmol) was combined with SF_4 (0.0390 g, 0.357 mmol) in SO_2 solvent yielding $[\text{FPPH}_3][\text{OTf}]$ as an off-white powder in a near quantitative yield. Recrystallizing from a conc. CH_3CN solution at -40°C yields colourless blocks of $[\text{FPPH}_3][\text{OTf}]$ after 16 hours.

(b) In the drybox, a 4-mm o.d FEP reactor is loaded with $[\text{SF}_3][\text{AsF}_6]$ (0.0242 g, 0.0871 mmol) and OPPh_3 (0.0236 g, 0.0848 mmol). Sulfur dioxide (ca. 1.5 mL) is distilled into the reactor at -196°C the sample is then slowly warmed to -60°C yielding a colourless solution. Low-temperature NMR spectroscopy was then run on this sample. NMR data in SO_2 at -60°C $\delta(^{19}\text{F}, 282\text{ MHz})$: 86.4 (t, $^2J_{\text{FF}} = 76\text{ Hz}$, $\text{SF}_4\text{ F}_{\text{ax}}$), 72.4 (s, SOF_2), 33.1 (t, $^2J = 76\text{ Hz}$, $\text{SF}_4\text{ F}_{\text{eq}}$), -56.7 (q, $^1J(^{75}\text{As}-^{19}\text{F}) = 935\text{ Hz}$, $[\text{AsF}_6]^-$), -125.7 (d, $^1J_{\text{PF}} = 996\text{ Hz}$, $[\text{FPPH}_3]^+$); $\delta(^{31}\text{P}, 122\text{ MHz})$: 97.0 (d, $^1J_{\text{PF}} = 996\text{ Hz}$, $[\text{FPPH}_3]^+$); $\delta(^1\text{H}, 300\text{ MHz})$ 8.09 (m, 3H), 7.91 (m, 8H), 7.74 (m, 2H), 7.66 (m, 2H); $\delta(^{13}\text{C}\{^1\text{H}\}, 75\text{ MHz})$: 139.8 (dd, $^4J_{\text{CP}} = 3$

Hz, $^5J_{\text{CF}} = 2$ Hz, *p*-Ph), 135.4 (d, $^3J_{\text{CP}} = 13$ Hz, *m*-Ph), 131.6 (d, $^2J_{\text{CP}} = 14$ Hz, *o*-Ph), 117.2 (dd, $^1J_{\text{CP}} = 109$ Hz, $^2J_{\text{CF}} = 15$ Hz, *ipso*-Ph).

5.5.3. X-ray Crystallography.

The reactors containing the crystals were cut on an aluminium trough that was positioned close to the diffractometer and cooled to ca. -80 °C by a stream of cold, dry N_2 . Once the crystals were deposited onto the trough, the selected crystal was affixed to a Nylon cryo-loop submerged in perfluorinated polyether oil (Fomblin Z-25) and transferred to the goniometer using liquid- N_2 -cooled cryo-tongs. All the crystals except $[\text{SF}_2(\text{dmap})_2][\text{SbF}_6]_2 \cdot \text{CH}_3\text{CN}$ and $[\text{SF}(\text{dmap})_4][\text{SbF}_6]_3 \cdot 2\text{CH}_3\text{CN}$ were centred on a Rigaku SuperNova diffractometer equipped with a Dectris Pilatus 3R 200 K-A hybrid-pixel-array detector, a four-circle κ goniometer, an Oxford Cryostream 800 cooling device, and sealed $\text{MoK}\alpha$ and $\text{CuK}\alpha$ X-ray sources. Data were collected using the $\text{CuK}\alpha$ source at -173 °C. Crystals were screened for quality before a pre-experiment was run to determine the unit cell, and a data-collection strategy was calculated based on the determined unit cell and intensity of the preliminary data. This strategy was optimized to collect 5-fold redundant data at a resolution of 0.77 Å. X-ray data for $[\text{SF}_2(\text{dmap})_2][\text{SbF}_6]_2 \cdot \text{CH}_3\text{CN}$ and $[\text{SF}(\text{dmap})_4][\text{SbF}_6]_3 \cdot 2\text{CH}_3\text{CN}$ 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 Kryoflex low-temperature device, and a $\text{Mo K}\alpha$ radiation ($\lambda = 0.71073$ 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. All data was processed using CrysAlisPro,³⁴ which applied necessary Lorentz and polarization corrections to the integrated data and scaled the data. A numerical (Gaussian-grid) absorption correction was

generated based upon the indexed faces of the crystal. Atom positions were determined using the intrinsic phasing method (ShelXT)³⁵ and were refined using least-squares refinement (ShelXL).³⁶ Non-hydrogen atoms were refined anisotropically, and recommended weights for the atoms were determined. Structure solution and refinement were performed with the aid of Olex2 (version 1.5).³⁷

5.5.4. Raman Spectroscopy.

The Raman spectra were recorded using a Bruker RFS-100 Raman spectrometer outfitted with a quartz beam-splitter and liquid-N₂-cooled germanium detector. The 1064-nm line of a Nd:YAG laser was used for excitation of the sample, and backscattered (180°) radiation was sampled. The usable Stokes range of the collected data was 85–3500 cm⁻¹ with a resolution of 2 cm⁻¹. The laser power was typically set for 100 mW. The Raman spectra are shown in Appendix D (Figures D.1–D.4)

5.5.5 NMR spectroscopy.

The ¹⁹F, ³¹P, ¹³C{¹H} and ¹H NMR spectra were recorded in heat-sealed 4-mm o.d. FEP tubes sheathed in a 5-mm o.d. glass insert using a Bruker Avance II 300 MHz spectrometer equipped with a 5-mm broadband probe. Spectra were recorded unlocked in dilute CH₃CN solutions at –40 °C ([SF₂(dmap)₂][SbF₆]₂) and in dilute SO₂ solutions at –54 °C ([SF₃(py)][OTf] and [SF₂(dmap)₂][OTf]₂) or –60 °C ([FPPH₃][OTf]) and referenced externally to CFC₃ (¹⁹F), 85% H₃PO₄ (³¹P), and Si(CH₃)₄ (¹H, ¹³C) at 22 °C. NMR spectra are shown Appendix D (Figures D.5–D.16).

5.5.6 Computational Methods

Calculations were performed at the B3LYP-D3(BJ)/def2-TZVPPD level of theory except those involving the $[\text{SF}(\text{dmap})_4]^{3+}$ trication which used the MN15/def2-TZVPPD level of theory as implemented in Gaussian 16 (revision D.01).^{38,39} The geometries were optimized using analytic-gradient methods, resulting in stationary points with no imaginary frequencies. All subsequent calculations were performed on these optimized geometries without imposing symmetry constraints. The single-point energies and the NBO analyses were calculated at the DLPNO-CCSD(T)/def2-TZVPP level of theory as implemented in ORCA 5.0.⁴⁰ The NBO analysis was performed using NBO (version 7.0),⁴¹ and GaussView (version 6.0)⁴² was used to visualize the vibrational modes and aid in their description.

5.5.7 NMR Chemical Shift Calculations

The geometries of $[\text{SF}_3(\text{dmap}_{\text{ax}})]^+$ and $[\text{SF}_3(\text{dmap}_{\text{eq}})]^+$ (and CFCl_3) were optimized at the B3LYP-D3(BJ)/def2-TZVPPD level of theory in CH_3CN using the SMD solvent model as implemented in Gaussian 16, resulting in stationary points with no imaginary frequencies. The nuclear shielding tensors were calculated using the GIAO method at the $\omega\text{B97X-D}/\text{def2-TZVPPD}$ level of theory in CH_3CN using the SMD solvent model. The equation $\delta = \sigma_{\text{CFCl}_3} - \sigma_{\text{F}}$ was used to determine the chemical shifts from the calculated shielding values of CFCl_3 and the fluorine environment of interest. It is worth noting that the accurate calculation of ^{19}F NMR chemical shift values is not trivial.⁴³ Despite the inaccuracy of the calculated values, they still aid in the qualitative determination of which isomers are present in solution. Table 6 shows calculated chemical shifts for $[\text{SF}_3(\text{dmap}_{\text{ax}})]^+$ and $[\text{SF}_3(\text{dmap}_{\text{eq}})]^+$ and the experimental values for $[\text{SF}_3(\text{dmap})][\text{OTf}]$, together with its

pyridine analogues. The calculated values for $[\text{SF}_3(\text{dmap}_{\text{eq}})]^+$ better align with the experimental values than $[\text{SF}_3(\text{dmap}_{\text{ax}})]^+$ suggesting that it is the $[\text{SF}_3(\text{dmap}_{\text{eq}})]^+$ isomer that is observed in solution. The calculations for the $[\text{SF}_3(\text{py})]^+$ cation also predict the axial fluorine environments to have a significantly higher chemical shift.

Table 5.6. Calculated^[a] and experimental chemical shifts (ppm) for the two possible isomers of $[\text{SF}_3(\text{py})]^+$ and $[\text{SF}_3(\text{dmap})]^+$.

	$[\text{SF}_3(\text{dmap}_{\text{ax}})]^+$	$[\text{SF}_3(\text{dmap}_{\text{eq}})]^+$	$[\text{SF}_3(\text{py}_{\text{ax}})]^+$	$[\text{SF}_3(\text{py}_{\text{eq}})]^+$
Calcd. F_{ax}	101 (1F)	90.4 (2F)	92.4 (1F)	107 (2F)
Calcd. F_{eq}	26.1 (2F)	5.37 (1F)	21.2 (2F)	6.1 (1F)
	$[\text{SF}_3(\text{dmap})][\text{OTf}]$		$[\text{SF}_3(\text{py})][\text{OTf}]$	
Exptl. F_{ax}	76.3 (2F)		62.8 (1F)	
Exptl. F_{eq}	3.7 (1F)		10.0 (2F)	

[a] Calculated at the $\omega\text{B97X-D/def2-TZVPPD}$ level of theory.

5.6. References

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Chapter 6—Conclusions, Preliminary Results and Future Work

6.1 Conclusions

The fluoride-ion donor properties of AsF_5 and SbF_5 were investigated in detail and for the first time SbF_5 was shown to be able to act as a fluoride-ion donor in the presence of a base. Both AsF_5 and SbF_5 were found to autoionise in the presence of the rigid bidentate base phen to form $[\text{PnF}_4(\text{phen})][\text{PnF}_6]$ ($\text{Pn} = \text{As}$ or Sb) salts. In the presence of the more flexible bipy ligand SbF_5 was again found to autoionise; conversely, AsF_5 forms a neutral $(\text{AsF}_5)_2 \cdot \text{bipy}$ adduct. The donor-stabilised cations were found to be surprisingly stable at ambient temperature, especially compared to neutral adducts of AsF_5 or SbF_5 with nitriles which decompose within 30 min at ambient temperature.¹ DFT calculations showed that the $\text{Pn}-\text{N}$ interaction has a high degree of covalency, and the N-bases are donating a considerable amount of electron density to the highly electrophilic pnictogen centres. The use of the tridentate N-donor ligand terpy allowed for the isolation and first structural characterisation of a heptacoordinate fluoro $\text{Sb}(\text{V})$ complex. The $[\text{SbF}_4(\text{terpy})]^+$ cation adopts a heavily distorted pentagonal bipyramidal geometry. The pentagonal bipyramid is the preferred geometry for heptacoordinate main group compounds.

Previous work in the group studied the Lewis acidity of $[\text{SF}_3]^+$ towards two nitrogen donors. The strength of the nitrogen base has a profound effect on the structure of the resulting cationic adduct. When a weak N-base is used, such as CH_3CN , the $\text{S} \cdots \text{N}$ interactions are electrostatic in nature and best described as a chalcogen bonding interaction.² The $[\text{SF}_3]^+$ cation in $[\text{SF}_3(\text{CH}_3\text{CN})_2]^+$ retains its trigonal pyramidal geometry

and displays a third chalcogen bonding interaction to the $[\text{PnF}_6]^-$ (Pn = As or Sb) anion resulting in a hexacoordinate sulfur centre. In contrast, when stronger bases, such as py or phen, are used the S---N interaction has a significant degree of covalency and is best described as a dative bonding interaction, causing a change in the geometry and electronic structure of the cation, resulting in pentacoordinate square pyramidal cations. Chapter 5 extended this work by studying 1:1 adducts of $[\text{SF}_3]^+$ with N-donors as they are more relevant to the intermediates invoked in the deoxofluorination mechanism. A 1:1 adduct between $[\text{SF}_3]^+$ and pyridine can readily be made by the reaction of an excess of SF_4 and $[\text{TMS}(\text{py})][\text{OTf}]$, the resulting cationic adduct $[\text{SF}_3(\text{py})]^+$ adopts a seesaw geometry with py binding in an axial position. The analogous DMAP adduct was found to undergo dismutation in solution to form $[\text{SF}_2(\text{dmap})_2]^{2+}$ and SF_4 . The difference in reactivity could possibly be attributed to two factors. The first possible factor is that upon adduct formation with the much stronger DMAP base the S–F bond weakens to a greater extent than in the py adduct, possibly facilitating dismutation. Secondly, the differences in geometry, in $[\text{SF}_3(\text{dmap})]^+$ the DMAP ligand is found to bind in an equatorial position of the seesaw geometry, whereas py binds in an axial position. The $[\text{SF}_2(\text{dmap})]^{2+}$ dication can undergo further dismutation to the square pyramidal $[\text{SF}(\text{dmap})_4]^{3+}$ trication.

Attempts to isolate a 1:1 adduct of $[\text{SF}_3]^+$ with OPPh_3 resulted in the deoxofluorination of OPPh_3 to form $[\text{FPPH}_3]^+$ salts. The facile deoxofluorination with $[\text{SF}_3]^+$ at low temperature is in contrast to the previous reported conditions for deoxofluorination of OPPh_3 by SF_4 in benzene, *i.e.*, 50 to 150 °C for 14 h with a 67% yield.³ The presence of SF_4 in the low-temperature ^{19}F NMR spectrum suggests that a similar ligand scrambling process to that seen in the $[\text{SF}_3(\text{dmap})]^+$ system is occurring and

hints at the possible involvement of an elusive $[\text{SF}_2(\text{OPPh}_3)]^{2+}$. This implies that it is the $[\text{SF}_2]^{2+}$ dication that is the active species in deoxofluorination reactions. Therefore, the incorporation of $[\text{SF}_2]^{2+}$ motifs into organic scaffolds, or species which can generate $[\text{SF}_2]^{2+}$ *in situ*, could be the basis for the next generation of deoxofluorinating agents.

6.2 Preliminary Results

The strong preference for hexacoordination seen in Sb(V) fluorides, motivated an investigation into the ability to abstract a second fluoride ion from the heptacoordinate $[\text{SbF}_4(\text{terpy})]^+$ cation, in order to achieve the preferred coordination number of six and synthesise a $[\text{SbF}_3(\text{terpy})]^{2+}$ dication. Initial attempts used $(\text{CH}_3)_3\text{SiO}_3\text{SCF}_3$ (TMSOTf) as the fluoride-ion acceptor. The equimolar reaction of $[\text{SbF}_4(\text{terpy})][\text{SbF}_6]$ with TMSOTf is expected to yield $[\text{SbF}_3(\text{terpy})][\text{SbF}_6][\text{OTf}]$. The reaction produced a pale-yellow powder that was found to be soluble in SO_2 and CH_3CN . Solutions in CH_3CN were found to decompose at -40°C over the course of 10 days yielding a brown oil that was not analysed further. The reaction was performed multiple times but ^{19}F NMR studies suggest that the product of these reactions is not consistent. One batch in particular seemed to show extensive fluoride/triflate exchange in the $[\text{SbF}_6]^-$ anion. In order to prevent any unwanted side reactions involving the $[\text{SbF}_6]^-$ and $[\text{OTf}]^-$ anions subsequent attempts to abstract a second fluoride ion from $[\text{SbF}_4(\text{terpy})][\text{SbF}_6]$ used $\text{SbF}_5 \cdot \text{SO}_2$ as the fluoride-ion acceptor instead. The reaction of $[\text{SbF}_4(\text{terpy})][\text{SbF}_6]$ with 3 equivalents of $\text{SbF}_5 \cdot \text{SO}_2$ yielded a golden-brown powder, with the targeted product being $[\text{SbF}_3(\text{terpy})][\text{Sb}_2\text{F}_{11}]_2$. The

resulting product was found to be soluble in SO₂ and stable under an inert atmosphere for at least two months.

The [SbF₃(terpy)]²⁺ dication presumably adopts an octahedral geometry with two fluoro ligands in the axial positions, while the equatorial plane contains the remaining fluoro ligand and the terpy ligand. To test the validity of this assumption the gas-phase geometry of [SbF₃(terpy)]²⁺ (Figure 6.1) was optimised using DFT methods resulting in a stable structure. Upon F⁻ abstraction the calculated Sb–F bond lengths contract ([SbF₃(terpy)]²⁺ Sb–F_{ax} = 1.888 Å, Sb–F_{eq} = 1.867 Å; [SbF₄(terpy)]⁺ Sb–F_{ax} = 1.893/1.894 Å, Sb–F_{eq} = 1.905 Å) in the dication compared to the [SbF₄(terpy)]⁺ cation. A dramatic contraction is seen in the calculated Sb–N bond lengths compared to the monocation ([SbF₃(terpy)]²⁺ Sb–N(1)/N(3) = 2.134 Å, Sb–N(2) = 2.103 Å; [SbF₄(terpy)]⁺ Sb–N(1)/N(2) = 2.329 Å, Sb–N(2) = 2.346 Å), presumably to off-set the extreme electrophilicity of the hypothetical naked [SbF₃]²⁺ cation. As a result of reduced steric crowding in the equatorial plane the N–Sb–N ([SbF₃(terpy)]²⁺ N–Sb–N = 77.1°; [SbF₄(terpy)]⁺ N–Sb–N = 67.9°) and N–Sb–F_{eq} ([SbF₃(terpy)]²⁺ N–Sb–F_{eq} = 103.0°; [SbF₄(terpy)]⁺ N–Sb–F_{eq} = 73.7°) bond angles are widened compared to the heptacoordinate [SbF₄(terpy)]⁺ cation. The F(1)–Sb–F(2) angle (177.85°) is predicted to be essentially linear.

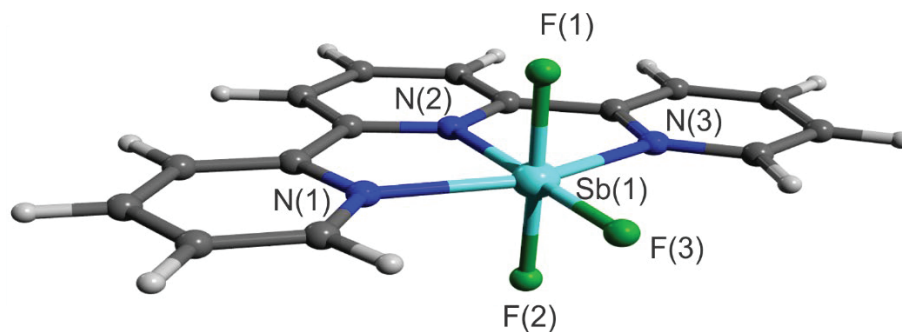


Figure 6.1. Optimised gas-phase geometry of $[\text{SbF}_3(\text{terpy})]^{2+}$ calculated using the B3LYP-D3(BJ) functional using the def2-TZVPPD-PP (Sb) and def2-TZVPPD (C, H, N, F) basis set.

Table 6.1. Selected bond lengths (Å) and angles (°) of $[\text{SbF}_4(\text{terpy})]^+$.

	$[\text{SbF}_4(\text{terpy})]^+$		$[\text{SbF}_3(\text{terpy})]^{2+}$
	Exptl.	Calcd. ^[a]	Calcd. ^[a]
Sb(1)–F(1)	1.8851(10)	1.894	1.888
Sb(1)–F(2)	1.8857(9)	1.893	1.888
Sb(1)–F(3)	1.9181(10)	1.905	1.867
Sb(1)–F(4)	1.9141(10)	1.905	-
Sb(1)–N(1)	2.2563(13)	2.329	2.134
Sb(1)–N(2)	2.2248(12)	2.346	2.103
Sb(1)–N(3)	2.2684(13)	2.329	2.134
F(1)–Sb(1)–F(2)	175.49(5)	167.5	177.9
F(3)–Sb(1)–F(4)	75.97(4)	79.9	-
F(3)–Sb(1)–N(1)	74.67(4)	73.7	103.0
N(1)–Sb(1)–N(2)	70.76(4)	67.9	77.1
N(2)–Sb(1)–N(3)	70.09(5)	67.9	77.1
N(3)–Sb(1)–F(4)	72.61(4)	73.7	103.0

[a] Calculated using the B3LYP-D3(BJ) functional using the def2-TZVPPD-PP (Sb) and def2-TZVPPD (C, H, N, F) basis set.

The ^{19}F NMR spectra of the products from the reactions of $[\text{SbF}_4(\text{terpy})][\text{SbF}_6]$ with either TMSOTf or $\text{SbF}_5 \cdot \text{SO}_2$ were recorded in SO_2 at $-50\text{ }^\circ\text{C}$ or $-60\text{ }^\circ\text{C}$, respectively. Both salts show a broad resonance at -93 ppm which has tentatively been assigned as the F_{ax} environment of the $[\text{SbF}_3(\text{terpy})]^{2+}$ dication. The experimental value aligns well with the calculated value of -84 ppm (calculated in CH_3CN solvent). The F_{eq} environment is calculated to resonate at -132 ppm and, therefore, it is likely that the F_{eq} environment of the dication overlaps with anion signals or the F_{ax} environment of $\text{SbF}_5 \cdot \text{SO}_2$ in both salts. In the supposed $[\text{SbF}_3(\text{terpy})][\text{Sb}_2\text{F}_{11}]_2$ (Figure 6.2) salt the expected integration ratio of the F_{ax} environment of the dication and the bridging F_{b} environment of the anion is 1:1, however, in the experimental spectrum the ratio is 0.5:1, so half as much of the cationic species is present than would be expected, indicating that the expected product is not being synthesised. It is possible that the assignments of F_{ax} and F_{eq} are wrong and the resonance at -93 ppm corresponds to the F_{eq} environment of $[\text{SbF}_3(\text{terpy})]^{2+}$ instead, but if this were the case then the integration value of the overlapping signals (F_{b} of $[\text{Sb}_2\text{F}_{11}]^-$, F_{ax} $[\text{SbF}_3(\text{terpy})]^+$ and F_{ax} $\text{SbF}_5 \cdot \text{SO}_2$) at ca. -132 ppm is too low (expected = 6.9, experimental = 5.7).

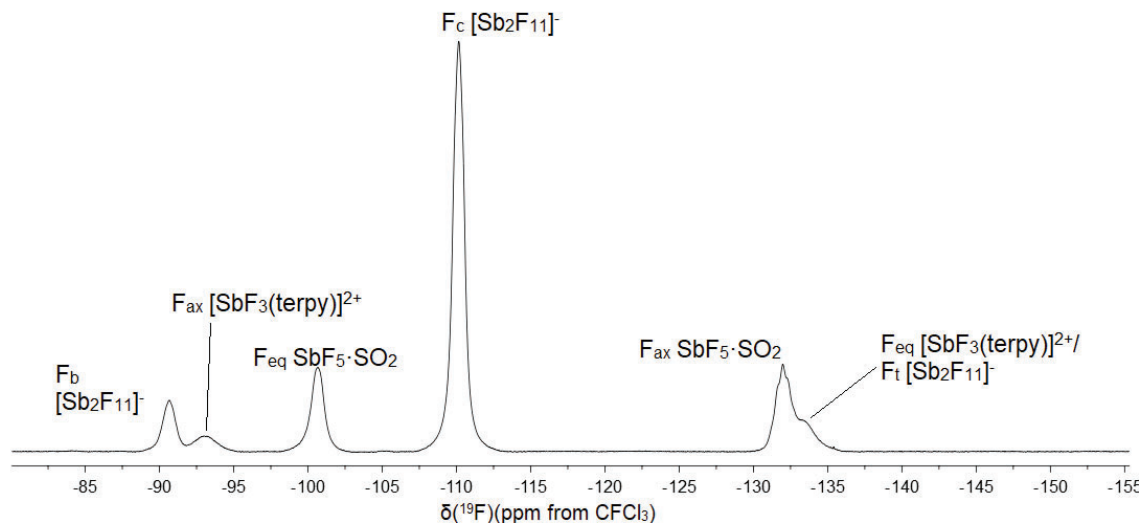
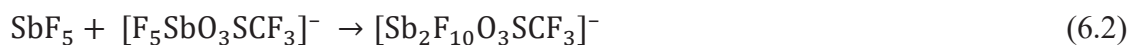


Figure 6.2. ^{19}F NMR spectrum of the product of the reaction of $[\text{SbF}_4(\text{terpy})][\text{SbF}_6]$ and three equivalents of $\text{SbF}_5 \cdot \text{SO}_2$ recorded in SO_2 at -60°C .

The ^{19}F NMR spectra of two different batches of “ $[\text{SbF}_3(\text{terpy})][\text{SbF}_6][\text{OTf}]$ ” are shown in Figures 6.3 and 6.4. Both products were synthesised under similar conditions yet yielded vastly different ^{19}F NMR spectra. In the first batch (Figure 6.3) it appears that the multiplets arising due to $[\text{SbF}_6]^-$ are present but overlapping as only eight of the expected 14 transitions are discernible. The $^1J(^{121}\text{Sb}-^{19}\text{F}) = 1963\text{ Hz}$ is in the typical range for this coupling constant. Also present in the spectrum is $\text{SbF}_5 \cdot \text{SO}_2$ ($F_{\text{ax}} \delta = 100\text{ ppm}$, $F_{\text{eq}} \delta = 134\text{ ppm}$), suggesting that F^- abstraction from $[\text{SbF}_6]^-$ is occurring. Only one major resonance was observed in the triflate region at -78.2 ppm , typical of $[\text{O}_3\text{SCF}_3]^-$, with small minor signals at -76.5 ppm and -76.2 ppm . This is consistent with $[\text{SbF}_6]^-$ and $[\text{O}_3\text{SCF}_3]^-$ being the major anionic species. The unassigned signals at -76.2 , -76.5 , -82.5 and -91.0 ppm likely arise due to fluorine/triflate exchange in the $[\text{SbF}_6]^-$ anion, based on previously reported chemical shift values the signals likely correspond to $[\text{SbF}_5\text{O}_3\text{SCF}_3]^-$ and the *cis* and *trans* isomers of $[\text{F}_4\text{Sb}(\text{O}_3\text{SCF}_3)_2]^-$.⁴

In batch 2 there are two major resonances in the triflate region at -76.8 and -78.4 ppm that integrate in an approximate 1.2:1 ratio, respectively. This suggests that extensive fluorine/triflate exchange is occurring as the major triflate signal no longer corresponds to $[\text{O}_3\text{SCF}_3]^-$. As a result of this exchange the $[\text{SbF}_6]^-$ anion now appears as a quadrupolar collapsed singlet at -121.1 ppm. It appears that the $[\text{Sb}_2\text{F}_{10}\text{O}_3\text{SCF}_3]^-$ and *trans*- $[\text{Sb}_2\text{F}_{10}\text{O}_3\text{SCF}_3]^-$ anions are also present. A potential route to the formation of $[\text{SbF}_5\text{O}_3\text{SCF}_3]^-$, $[\text{Sb}_2\text{F}_{10}\text{O}_3\text{SCF}_3]$ and $[\text{F}_4\text{Sb}(\text{O}_3\text{SCF}_3)_2]^-$ is proposed in eq. 6.1–6.3, the assignments of the fluorine environments in these anions are given in Table 6.2 and Figure 6.5.



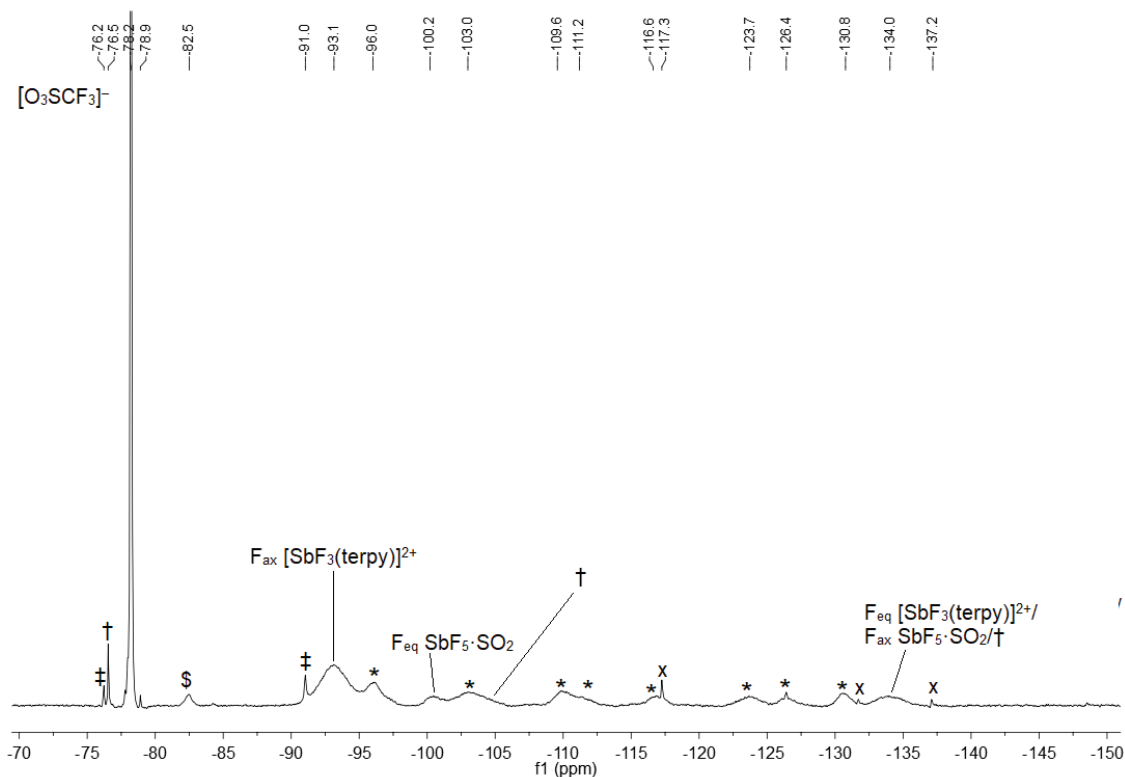


Figure 6.3. ^{19}F NMR spectrum of the product of the reaction of $[\text{SbF}_4(\text{terpy})][\text{SbF}_6]$ and TMSOTf (batch 1). Recorded in SO_2 at -50°C . Asterisks (*), dagger ($\dagger$), double dagger ($\ddagger$), dollar sign (\$) and (x) denote $[\text{SbF}_6]^-$, $[\text{SbF}_5\text{O}_3\text{SCF}_3]^-$, $\text{trans-}[\text{F}_4\text{Sb}(\text{O}_3\text{SCF}_3)_2]^-$, $\text{cis-}[\text{F}_4\text{Sb}(\text{O}_3\text{SCF}_3)_2]$ and an unknown impurity respectively.

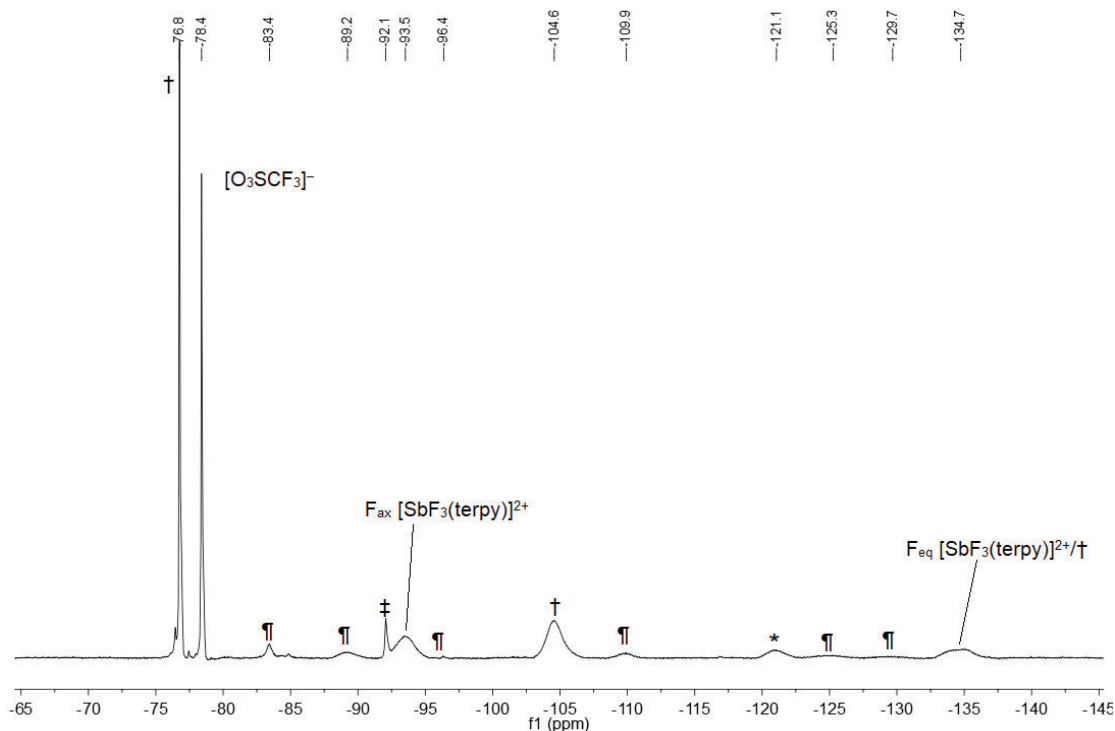


Figure 6.4. ^{19}F NMR spectrum of the product of the reaction of $[\text{SbF}_4(\text{terpy})][\text{SbF}_6]$ and TMSOTf (batch 2). Recorded in SO_2 at $-50\text{ }^\circ\text{C}$. Asterisks (*), dagger (†), double dagger (‡) and pilcrow (¶) denotes $[\text{SbF}_6]^-$, $[\text{SbF}_5\text{O}_3\text{SCF}_3]^-$, $\text{trans}-[\text{F}_4\text{Sb}(\text{O}_3\text{SCF}_3)_2]^-$, and $[\text{Sb}_2\text{F}_{10}\text{O}_3\text{SCF}_3]^-$ respectively.

Table 6.2. The assignments of the fluorine-on-antimony environments for the $[\text{F}_5\text{SbO}_3\text{SCF}_3]^-$, $[\text{Sb}_2\text{F}_{10}\text{O}_3\text{SCF}_3]^-$, $\text{cis}-[\text{F}_4\text{Sb}(\text{O}_3\text{SCF}_3)_2]^-$ and $\text{trans}-[\text{F}_4\text{Sb}(\text{O}_3\text{SCF}_3)_2]^-$ anions.

	F1	F2	F3	F4	F5	F6
$[\text{F}_5\text{SbO}_3\text{SCF}_3]^-$	-135	-105				
$[\text{Sb}_2\text{F}_{10}\text{O}_3\text{SCF}_3]^-$	N.O.	-110	-83	-130	-89	-125
$\text{cis}-[\text{F}_4\text{Sb}(\text{O}_3\text{SCF}_3)_2]^-$	-83	-117				
$\text{trans}-[\text{F}_4\text{Sb}(\text{O}_3\text{SCF}_3)_2]^-$	-92					

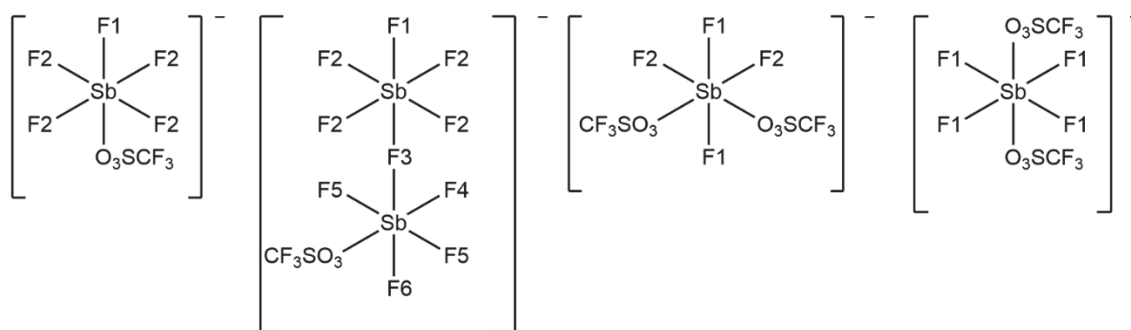


Figure 6.5. Atom labelling scheme used for the $[\text{F}_5\text{SbO}_3\text{SCF}_3]^-$, $[\text{Sb}_2\text{F}_{10}\text{O}_3\text{SCF}_3]^-$, *cis*- $[\text{F}_4\text{Sb}(\text{O}_3\text{SCF}_3)_2]^-$ and *trans*- $[\text{F}_4\text{Sb}(\text{O}_3\text{SCF}_3)_2]^-$ anions.

The Raman spectrum of “[$\text{SbF}_3(\text{terpy})$][SbF_6][OTf]” is shown in Figure 6.6 and key vibrational frequencies are given in Table 6.3. The axial and equatorial Sb–F stretches in $[\text{SbF}_3(\text{terpy})]^{2+}$ are predicted in the typical range for octahedral Sb(V) fluorides of 600–700 cm^{-1} . The splitting of the $\nu(\text{SbF}_{2\text{ax}})$ mode likely results from vibrational coupling in the unit cell.^{5,6} The key vibrational modes of the terpy ligand in $[\text{SbF}_4(\text{terpy})]^+$ are blue shifted relative to the free base, indicative of a Lewis acid-base interaction. This is best demonstrated by the symmetric ring-breathing mode where the three rings are undergoing ring-breathing in-phase with each other. This mode occurs at 1030 cm^{-1} (calcd. 1044 cm^{-1}) in $[\text{SbF}_4(\text{terpy})]^+$ and at 996 cm^{-1} (calcd. 1013 cm^{-1}) in free terpy. This band is shifted even further in the dication to 1051 cm^{-1} (calcd. 1067 cm^{-1}), as a result of increased electron density transfer from terpy to the more electron deficient Sb centre. However, most of the terpy bands in the dication do not experience an additional blue shift relative to the monocation and are found to occur at very similar frequencies as those in the monocation. DFT calculations also predict this trend and is likely an effect of the change in geometry between the mono and dication.

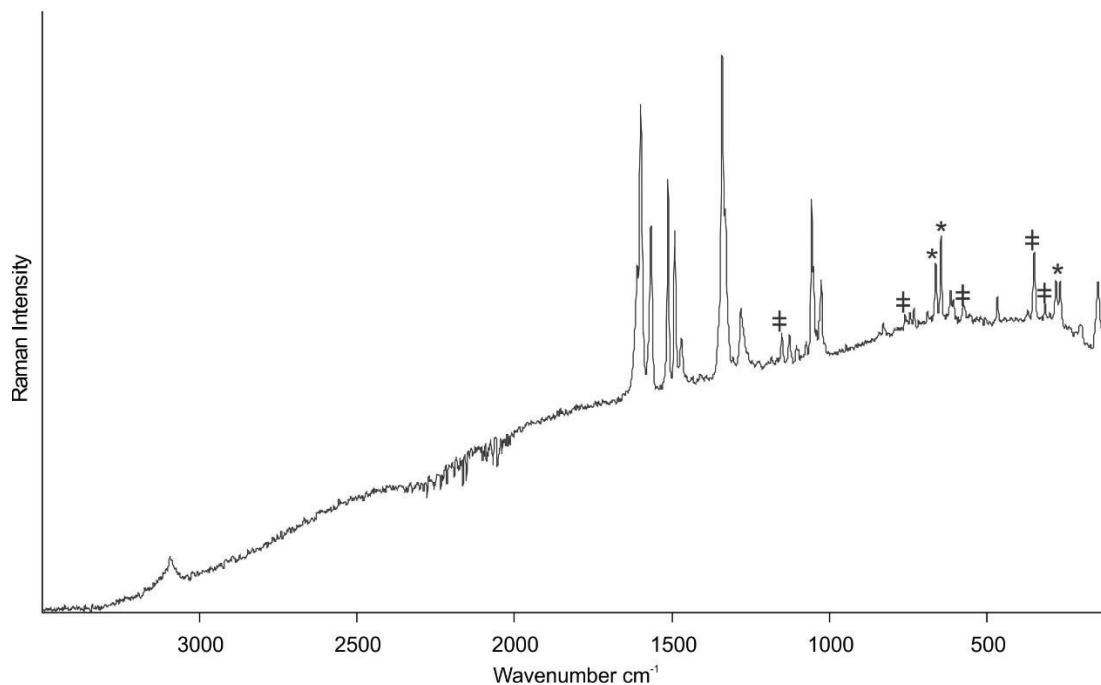


Figure 6.6. Raman spectrum of $[\text{SbF}_3(\text{terpy})][\text{SbF}_6][\text{OTf}]$. Asterisks (*) and double dagger (‡) denotes bands associated with the $[\text{SbF}_6]^-$ anion and $[\text{OTf}]^-$ anion, respectively.

Table 6.3. Selected vibrational frequencies (cm^{-1}) of $[\text{SbF}_3(\text{terpy})]^{2+}$.

	$[\text{SbF}_3(\text{terpy})]^{2+}$	
	Exptl. ^[a]	Calcd. ^[b]
$\nu_{\text{as}}(\text{SbF}_{2\text{ax}})$	-	680(1)[93]
$\nu_{\text{s}}(\text{SbF}_{2\text{ax}})$	615(31)/607(sh)	610(18)[1]
$\nu(\text{SbF}_{\text{eq}})$	688(25)	672(13)[37]
Symmetric ring-breathing mode	1051(sh)	1067(132)[21]

Normalised Raman intensities given in parenthesis. [a] Taken from $[\text{SbF}_3(\text{terpy})][\text{SbF}_6][\text{O}_3\text{SCF}_3]$. [b] Calculated using the B3LYP-D3(BJ) functional using the def2-TZVPPD-PP (Sb) and def2-TZVPPD (C, H, N, F) basis set. Absolute Raman intensities ($\text{\AA}^4 \text{u}^{-1}$) are given in parentheses and IR intensities (km mol^{-1}) given in square brackets.

6.3 Future Work

As PF_5 , AsF_5 and SbF_5 all exhibit fluoride-ion donor abilities in the presence of multidentate ligands, it begs the question whether BiF_5 follows this trend? Similar to the other group 15 pentafluorides, the fluoride-ion acceptor properties of BiF_5 are well known, but its ability to act as a fluoride-ion donor has not been explored. In a reaction similar to the ones used in Chapters 2 and 4 the tendency for BiF_5 to autoionise in the presence of the bidentate nitrogen bases phen and bipy to form $[\text{BiF}_4(\text{L-L})][\text{BiF}_6]$ salts should be investigated. Bismuth pentafluoride is a very strong oxidising agent which might make it incompatible with organic bases and prevent the formation of a stable $[\text{BiF}_4(\text{L-L})][\text{BiF}_6]$ salt; therefore, the reactions should be performed at a small scale and using low temperatures (ca. $-40\text{ }^\circ\text{C}$) in a suitably oxidatively resistant solvent, such as SO_2ClF .

The Lewis acidity of AsF_5 and BiF_5 towards a tridentate nitrogen base, such as terpy, should be studied. In the case of SbF_5 a heptacoordinate $[\text{SbF}_4(\text{terpy})]^+$ cation could be isolated. The smaller size of AsF_5 and the flexibility of the terpy ligand will likely prevent the formation of a heptacoordinated $[\text{AsF}_4(\text{terpy})]^+$ cation. Potentially leading to the formation of a neutral adduct similar to $(\text{AsF}_5)_2\cdot\text{bipy}$ or a hexacoordinate $[\text{AsF}_4(\text{terpy})]^+$ cation where the terpy ligand is binding in a κ^2 mode instead of κ^3 , allowing the free N-donor to potentially bond to another AsF_5 molecule. In addition, the formation of the hexacoordinate $[\text{AsF}_3(\text{terpy})]^{2+}$ is conceivable, which would be a very interesting product. This could also be contrasted with the use of a more rigid tridentate base, such as Me_3tacn , to see if reducing conformational flexibility of the ligand favours autoionisation above adduct formation. Bismuth is capable of attaining heptacoordination, therefore, BiF_5 will likely behave in a similar fashion to SbF_5 towards tridentate ligands. As seen from the preliminary

results, it is unclear whether abstraction of a second fluoride-ion from $[\text{SbF}_4(\text{terpy})][\text{SbF}_6]$ to generate a $[\text{SbF}_3(\text{terpy})]^{2+}$ dication is occurring, and therefore, the synthetic procedures need to be improved. Developing synthetic routes to multiply charged donor-stabilised $[\text{PnF}_{5-n}]^{n+}$ (Pn = As, Sb, Bi) cations represents another intriguing avenue of study.

In the deoxofluorination of OPPh_3 with $[\text{SF}_3]^+$ an elusive $[\text{SF}_2(\text{OPPh}_3)]^{2+}$ dication was invoked as the active species but not observed spectroscopically; in contrast, the $[\text{SF}_2(\text{dmap})_2]^{2+}$ cation was isolated and characterised. The $[\text{SF}_2(\text{dmap})_2]^{2+}$ dication can undergo further dismutation to form $[\text{SF}(\text{dmap})_4]^{3+}$, featuring a donor-stabilised $[\text{SF}]^{3+}$ trication. This warrants a thorough investigation of $[\text{SF}_2]^{2+}$ and $[\text{SF}]^{3+}$ cations and their Lewis acidity towards organic bases to see the plausibility of their involvement in deoxofluorination reactions. Reliable synthetic routes to $[\text{SF}_2]^+$ and $[\text{SF}]^{3+}$ cations need to be developed, likely starting from either SF_4 or $[\text{SF}_3(\text{L})]^+$ (L = organic base) adducts and reacting them with an appropriate number of equivalents of $[\text{TMS}(\text{L})][\text{OTf}]$ to form the desired $[\text{SF}_2(\text{L})_2]^{2+}$ or $[\text{SF}(\text{L})_4]^+$ donor-stabilised cations. The temperature sensitivity of the $[\text{SF}_3(\text{L})]^+$ adducts could complicate this synthesis. Finally, is it possible to abstract four F^- from SF_4 to access a donor-stabilised $[\text{S}]^{4+}$ cation, similar to the $[\text{Sb}(\text{bipy})_2][\text{OTf}]_3$ salt which is synthesised by the sequential abstraction of F^- from SbF_3 using TMSOTf and bipy , and features a donor-stabilised $[\text{Sb}]^{3+}$ cation?⁷

6.4 References

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Appendix A – Supporting Information for Chapter 2

Table A.1: Crystallographic Data Collection and Refinement Parameters for [SbF₄(phen)][SbF₆]·3CH₃CN and [SbF₄(phen)][SbF₆]·2SO₂

	[SbF ₄ (phen)][SbF ₆]·3CH ₃ CN	[SbF ₄ (phen)][SbF ₆]·2SO ₂
Chemical formula	C ₁₈ H ₁₇ F ₁₀ N ₅ Sb ₂	C ₁₂ H ₈ F ₁₀ N ₂ O ₄ S ₂ Sb ₂
Formula weight	736.86	741.82
Temperature (°C)	−173	−173
Crystal system	monoclinic	monoclinic
Space group	<i>P</i> 2 ₁ / <i>m</i>	<i>P</i> 2 ₁ / <i>c</i>
<i>a</i> (Å)	9.1707(3)	8.31527(19)
<i>b</i> (Å)	12.6920(5)	8.56180(19)
<i>c</i> (Å)	10.2983(3)	28.9087(7)
β (°)	91.817(3)	97.899(2)
<i>V</i> (Å ³)	1198.06(7)	2038.59(8)
<i>Z</i>	2	4
R ₁ [I ≥ 2σ(I)] ^[a]	0.0186	0.0170
wR ₂ [I ≥ 2σ(I)] ^[b]	0.0444	0.0412
CCDC	2105510	2105524

[a]. $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$. [b]. $wR_2 = [\sum [w(F_o^2 - F_c^2)^2] / \sum w(F_o^4)]^{1/2}$

Table A.2: Experimental bond lengths and angles for [SbF₄(phen)][SbF₆]·3CH₃CN and [SbF₄(phen)][SbF₆]·2SO₂.

	[SbF ₄ (phen)][SbF ₆]·3CH ₃ CN	[SbF ₄ (phen)][SbF ₆]·2SO ₂
Sb(1)–F(1)	1.8763(12)	1.8852(11)
Sb(1)–F(2)	1.8783(17)	1.8772(12)
Sb(1)–F(3)	1.8683(12)	1.8644(11)
Sb(1)–F(4)	1.8683(12)	1.8731(12)
Sb(1)–N(1)	2.1126(16)	2.0986(16)
Sb(1)–N(2)	2.1126(16)	2.1025(16)
N(1)–C(1)	1.338(2)	1.336(3)
C(1)–C(2)	1.397(3)	1.395(3)
C(2)–C(3)	1.381(3)	1.375(3)
C(3)–C(4)	1.415(3)	1.416(3)
C(4)–C(5)	1.432(3)	1.439(3)
C(4)–C(12)	1.397(3)	1.397(3)
C(5)–C(6)	1.362(4)	1.357(3)
C(6)–C(7)	1.432(3)	1.439(3)
C(7)–C(8)	1.415(3)	1.416(3)
C(7)–C(11)	1.397(3)	1.397(3)
C(8)–C(9)	1.381(3)	1.372(3)
C(9)–C(10)	1.397(3)	1.397(3)

C(10)–N(2)	1.338(2)	1.334(2)
N(2)–C(11)	1.361(2)	1.365(2)
N(1)–C(12)	1.361(2)	1.336(3)
F(2)–Sb(1)–F(3)	90.11(5)	91.42(5)
F(2)–Sb(1)–F(4)	90.11(50)	90.54(5)
F(2)–Sb(1)–F(1)	179.12(7)	178.38(5)
F(2)–Sb(1)–N(2)	89.70(6)	89.09(6)
F(2)–Sb(1)–N(1)	89.70(6)	90.35(6)
F(3)–Sb(1)–F(4)	97.61(8)	95.46(5)
F(3)–Sb(1)–F(1)	90.47(6)	89.66(5)
F(3)–Sb(1)–N(2)	170.65(6)	172.17(6)
F(3)–Sb(1)–N(1)	91.73(6)	92.71(6)
F(4)–Sb(1)–F(1)	90.47(6)	90.56(5)
F(4)–Sb(1)–N(2)	91.73(6)	92.34(6)
F(4)–Sb(1)–N(1)	170.65(6)	171.76(6)
F(1)–Sb(1)–N(2)	89.62(6)	89.67(6)
F(1)–Sb(1)–N(1)	89.62(6)	88.40(6)
N(2)–Sb(1)–N(1)	78.93(6)	79.48(6)
Sb(1)–N(2)–C(11)	113.10(12)	112.56(12)
Sb(1)–N(2)–C(10)	126.42(13)	126.51(13)
C(11)–N(2)–C(10)	120.44(17)	120.91(16)
Sb(1)–N(1)–C(12)	113.10(12)	112.90(12)
Sb(1)–N(1)–C(1)	126.42(13)	126.46(14)
C(12)–N(1)–C(1)	120.44(17)	120.62(17)
N(2)–C(11)–C(12)	117.42(10)	117.57(16)
N(2)–C(11)–C(7)	122.24(17)	121.97(17)
C(12)–C(11)–C(7)	120.30(11)	120.46(17)
N(1)–C(12)–C(11)	117.42(10)	117.33(17)
N(1)–C(12)–C(4)	122.24(17)	122.07(17)
C(11)–C(12)–C(4)	120.30(11)	120.59(17)
C(9)–C(8)–C(7)	120.25(18)	120.42(18)
N(2)–C(10)–C(9)	120.66(18)	120.06(18)
N(1)–C(1)–C(2)	120.66(18)	120.20(19)
C(12)–C(4)–C(5)	118.52(52)	118.33(17)
C(12)–C(4)–C(3)	116.77(17)	116.87(18)
C(5)–C(4)–C(3)	124.71(18)	124.79(18)
C(1)–C(2)–C(3)	119.63(19)	120.37(18)
C(8)–C(9)–C(10)	119.63(19)	120.12(18)
C(11)–C(7)–C(8)	116.77(17)	116.51(17)
C(11)–C(7)–C(6)	118.52(52)	118.24(18)
C(8)–C(7)–C(6)	124.71(18)	125.25(18)
C(7)–C(6)–C(5)	121.11(11)	121.36(18)
C(4)–C(5)–C(6)	121.11(11)	121.00(18)
C(4)–C(3)–C(2)	120.25(18)	119.86(18)

Table A.3: Vibrational frequencies (cm^{-1}) of 1,10-phenanthroline (phen) and $[\text{SbF}_4(\text{phen})]^+$

phen		$[\text{SbF}_4(1,10\text{-phen})]^+$		Tentative assignment ^[f]
Exptl ^[a]	Calcd ^[b]	Exptl ^{[a],[c]}	Exptl ^{[d],[e]}	
3092sh	3191(618)[0] 3191(<1)[41]		3170(4)	C-H stretching modes
3063(20)	3176(210)[26]		3127(5)	
3052(12)	3165(165)[1] 3164(27)[13]		3107(7)	
	3157(21)[<1]	3092(6)	3095(8)	
3029(6)	3128(185)[27] 3137(123)[21]		3053(4)	
2992(4)				C-N and C-C stretching modes + in-plane ring deformations
2970(2)				
			1660(2)	
			1644(7)	
1619(6)	1657(27)[9]		1634(15)	
1609(10)	1646(42)[9]		1628(16)	
1590(16)	1632(51)[9]	1629(29)	1621(23)	
1560(11)	1589(32)[15]	1586(22)	1587(7)	
1537(2)				
1503(17)	1536(76)[40] 1534(5)[8]	1527(18)	1534(8)	
	1483(42)[1]		1529(sh)	
1448(30)	1455(5)[47]		1472(4)	
1413(35)	1450(8)[1]			
1406 sh	1412(373)[0]	1455(100)	1457(100)	
1400(100)		1440(67)	1441(51)	
		1423(sh)	1426(sh)	
			1396(2)	
1343(11)	1379(83)[2]	1352(16)	1351(4)	
1314 sh	1337(11)[1]		1338(sh)	
1293(43)	1321(93)	1330(36)	1330(20)	
1268(4)	1297(9)[1]	1255(18)	1261(sh)	
1259 sh			1255(5)	
1251 sh				

1219(2)	1247(5)[1]	1220(16)	1219(5)	1257(2)[10]	C-N and C-C stretching modes + in-plane ring deformations
1204(4)	1229(1)[0]		1209(sh)	1245(1)[1]	
1186(4)	1219(35)[<1]			1237(11)[0]	
1137(5)	1167(2)[1]	1157(11)	1157(3)	1183(1)[3]	
	1162(3)[9]			1182(1)[14]	
1095(7)	1116(18)[11]		1117(1)	1135(5)[19]	
			1109(1)		
	1095(0)[4]			1123(<1)[0]	
1039sh	1058(42)[1]	1077(27)	1077(21)	1088(53)[1]	
1035(19)		1066(18)	1066(13)		
1001(1)	1054(2)[1]		1036(2)	1054(1)[3]	
992(1)	1006(<1)[0]			1041(0)[0]	
	1002(0)[1]			1039(0)[1]	
963(1)	985(<1)[0]			1016(1)[0]	
	969(0)[<1]			1006(<1)[<1]	
	968(1)[0]			999(1)[0]	ring breathing mode (s)
882(2)	898(2)[5]			937(2)[3]	
854(4)	870(3)[5]	883(9)	884(3)	892(2)[23]	
	864(<1)[0]			881(<1)[66]	ring breathing mode (as)
816(1)	862(1)[54]			860(0)[0]	
	817(0)[0]			823(<1)[0]	
	778(0)[20]			801(0)[6]	out-of-plane ring deformations
768(1)	760(<1)[38]	755(44)	757(23)	761(21)[23]	
	742(<1)[4]			740(<1)[21]	
706(41)	715(36)[3]			736(0)[52]	in-plane ring deformation
				680(<1)[27]	
				675(1)[106]	
			666(sh)	664(1)[34]	out-of-plane ring deformations
			670(7)	657(12)[99]	
620(2)	632(1)[7]	668(20)			
607(1)	620(1)[0]				in-plane ring deformation
		607(18)	607(sh)	627(<1)[0]	
		600(7)	600(7)	603(17)[1]	
560 sh	564(1)[0]		566(18)		out-of-plane ring deformation
550(8)	562(6)[0]				
511(4)	521(3)[<1]				
				573(16)[7]	out-of-plane ring deformation
				554(<1)[0]	
				518(<1)[1]	

499(1)	507(1)[<1]	549(3)	521(1)[0]	ring deformations
461(3)	466(2)[<1]	495(7)	496(3)[<1]	
429(2)	442(1)[0]		463(<1)[<1]	
407(21)	414(18)[2]	443(7)	439(27)[8]	
401 sh	412(1)[0]	415(2)	430(1)[0]	
253 sh	241(1)[0]		285(0)[0]	
242(10)	240(3)[4]	331(7)	327(3)[16]	
		256(6)	262(1)[97]	$\delta_{\text{sc}}(\text{SbF}_{2,\text{eq}}) + \delta(\text{SbF}_{2,\text{ax}}) + \text{deformation mode}$
		249(7)	260(1)[23]	$\omega(\text{SbF}_{\text{eq}}) + \rho(\text{SbF}_{\text{ax}})$
		238(4)	240(1)[32]	$\delta(\text{SbF}_{\text{ax}})$
		234(sh)		
	234(<1)[3]		238(1)[0]	Ring deformation
			228(<1)[0]	$\tau(\text{SbF}_{2,\text{ax}}) + \tau(\text{SbF}_{2,\text{eq}})$
			227(<1)[9]	out-of-plane ring deformation
	202(7)	203(6)	193(5)[1]	$\delta_{\text{sc}}(\text{SbF}_{2,\text{eq}})$
			186(1)[5]	$\rho(\text{SbF}_{\text{ax}}) + \text{ring rocking mode}$
			172(0)[0]	out-of-plane ring deformation mode
142(15)			162(<1)[2]	$\delta_{\text{sc}}(\text{SbF}_{2,\text{eq}}) - \delta(\text{SbF}_{2,\text{ax}})$
				twisting modes
120(24)			123(0)[<1]	$\rho(\text{SbF}_{2,\text{eq}})$
100(36)				Twisting and lattice modes

[a] Recorded in flame sealed m.p. capillaries at ambient temperature. Normalised Raman intensities are given in parentheses. Shoulders are denoted sh. [b] Calculated using the B3LYP functional with the aug-cc-pVTZ-PP (Sb) and aug-cc-pVTZ (C, H, N, F) basis sets. Absolute Raman intensities ($\text{\AA}^4 \text{u}^{-1}$) are given in parentheses and IR intensities (km mol^{-1}) are given in square brackets. [c] From $[\text{SbF}_4(\text{phen})][\text{Sb}_2\text{F}_{11}]$. Bands corresponding to $[\text{Sb}_2\text{F}_{11}]^-$ are observed at 679(20), 659(18), 649(33), 566(29), 294(11), 281(15), 245(9). [d] Recorded in a $\frac{1}{4}$ "-o.d. FEP sample tube at -100°C . [e] From $[\text{SbF}_4(\text{phen})][\text{SbF}_6]$. Bands corresponding to $[\text{SbF}_6]^-$ are observed at 681(sh), 660(sh), 645(22), 281(9). [f] Abbreviations denote stretch (ν), bend (δ), rock (ρ), twist (τ), and wag (ω).

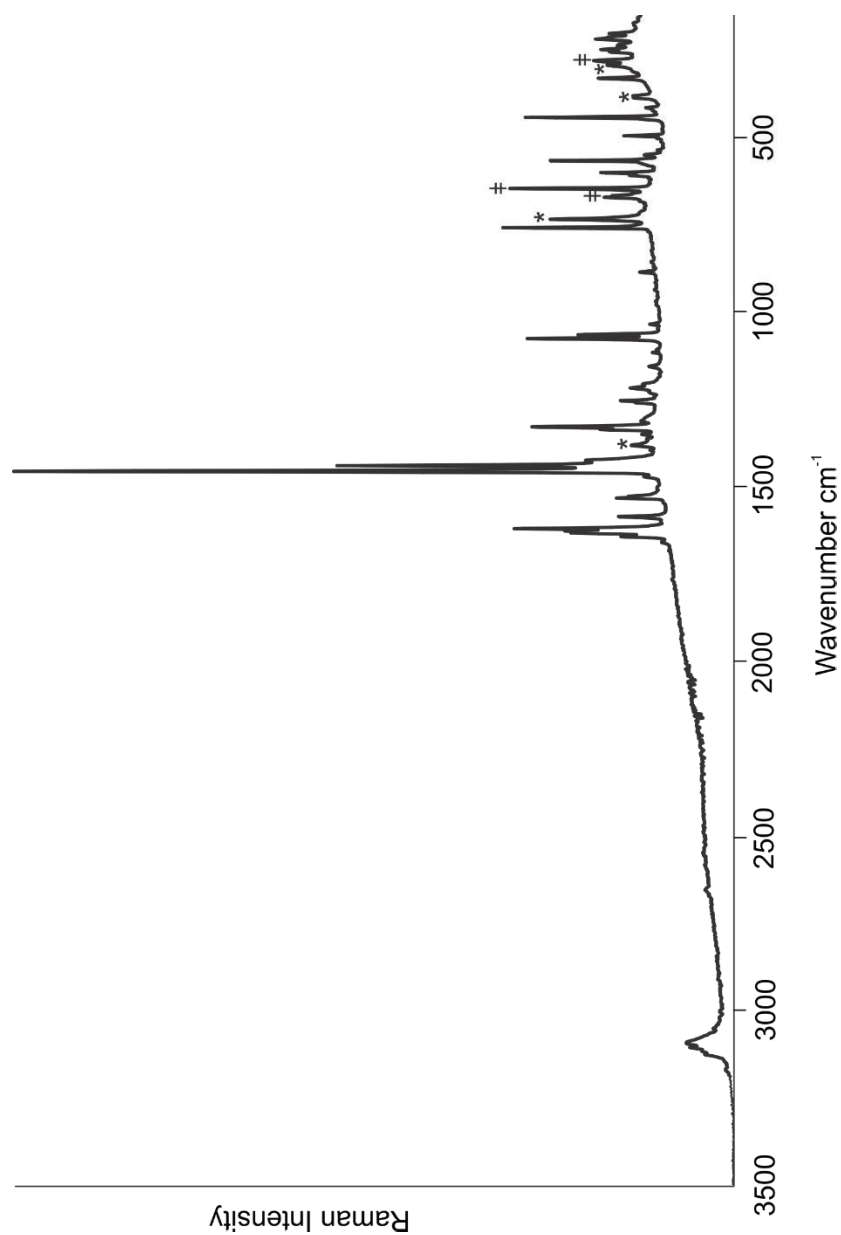


Figure A.1. Raman spectrum of $[\text{SbF}_4(\text{phen})][\text{SbF}_6]$, recorded in a $\frac{1}{4}$ " o.d. FEP sample tube at -100°C . Asterisks (*) denote bands arising from the FEP sample tube and $[\text{SbF}_6]^-$ anion, respectively. Daggers (‡) denote bands arising from the FEP sample tube and $[\text{SbF}_6]^-$ anion, respectively.

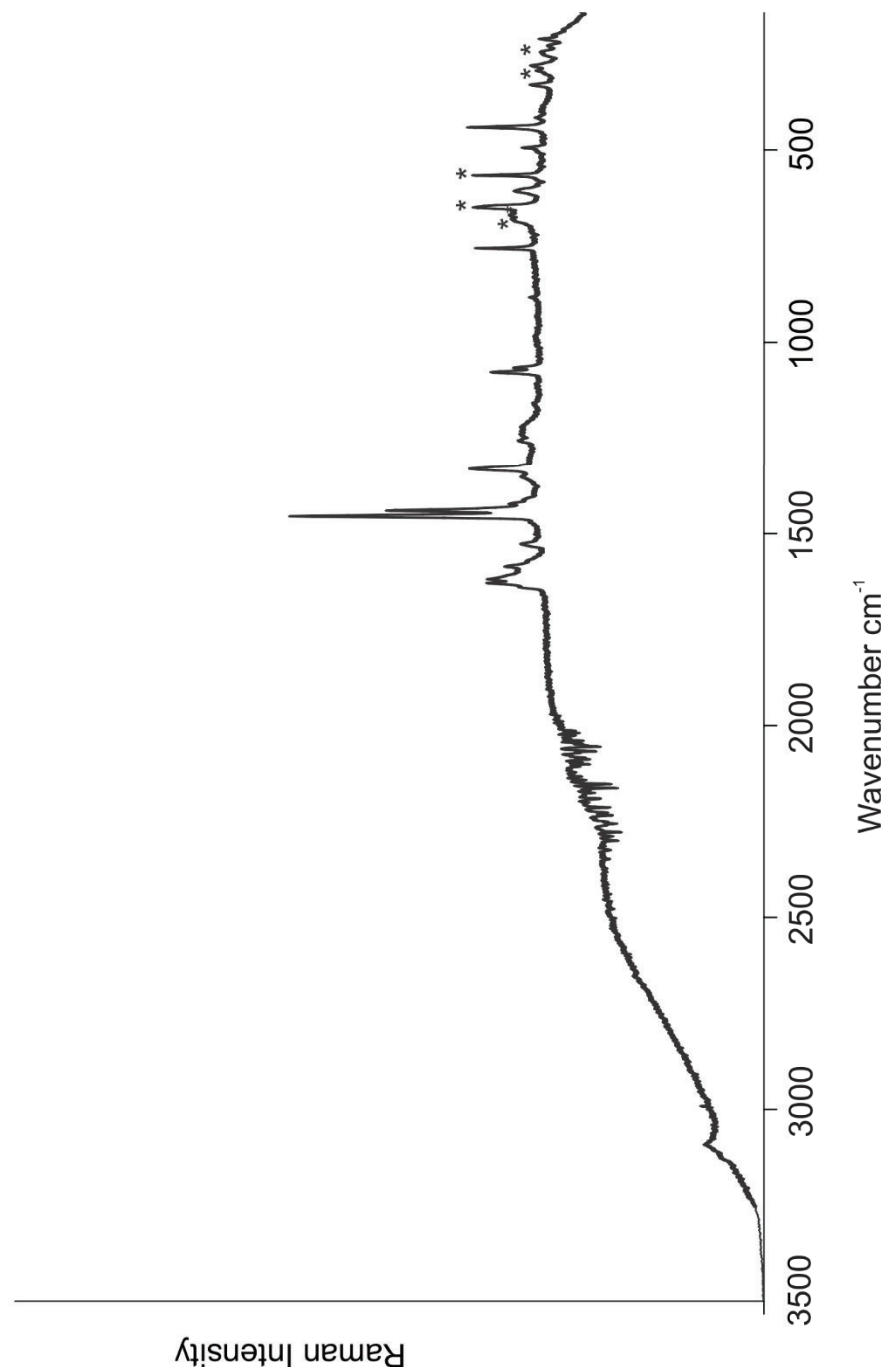


Figure A.2. Raman spectrum of $[\text{SbF}_4(\text{phen})][\text{Sb}_2\text{F}_{11}]$. (*) denotes bands corresponding to the $[\text{Sb}_2\text{F}_{11}]^-$ anions.

Table A.4: Vibrational frequencies (cm^{-1}) of 2,2'-bipyridine (bipy) and $[\text{SbF}_4(\text{bipy})]^+$

bipy			$[\text{SbF}_4(\text{bipy})]^+$		Tentative Assignment ^[f]
Exptl ^[a]	Calcd ^[b]	Exptl ^{[a],[c]}	Exptl ^{[d],[e]}	Calcd ^[b]	
3144(1)					C-H stretching modes, combinations modes, and overtones
3120(2)					
3088 sh					
3076(6)					
3064(10)					
3052(5)					
3046(5)					
3030(1)					
3008(3)					
2957(1)					
2680(1)					
2519(1)					
1759(1)					
1676(1)					
1633(2)					C-N and C-C stretching modes and in-plane deformations
1613(5)					
1590(83)					
1573(85)					C-N and C-C stretching modes and in-plane deformations
1548(1)					
1531(1)					
1483(29)					
1447(49)					C-N and C-C stretching modes and in-plane deformations
1331 sh					C-N and C-C stretching modes and in-plane deformations
1310 sh					
1302(32)					
1294 sh					

		$\delta(\text{C1N1C5} + \text{C2C3C4})$ (as)	
614(12)	641(2)[10] 626(6)[5]	607(33) 601 sh	605(10) 603(14)[<1]
550(1)	570(2)[1] 508(0)[3]		555(<1)[0] 463(<1)[2]
439(3)	420(6)[<1]	480(3)	477(2)[<1]
409(1)	417(<1)[6] 369(<1)[1]		433(0)[12] 431(<1)[0]
333(2)	320(3)[0]	387(32)	378(10)[0]
			ring deformations
224(10)	253(3)[<1]		$\delta(\text{SbF}_{2\text{ax}} + \text{SbF}_{2\text{eq}})$ $\tau(\text{SbF}_{2\text{ax}} + \text{SbF}_{2\text{eq}})$ $\omega(\text{SbF}_{2\text{eq}}) + \tau(\text{SbF}_{2\text{ax}})$ twisting mode
			$\rho(\text{SbF}_{2\text{eq}} + \text{SbF}_{2\text{ax}})$ $\omega(\text{SbF}_{2\text{ax}}) + \tau(\text{SbF}_{2\text{eq}})$ $\tau(\text{SbF}_{2\text{ax}})$ $\tau(\text{SbF}_{2\text{ax}} + \text{SbF}_{2\text{eq}})$ $\rho(\text{SbF}_{2\text{eq}} - \text{SbF}_{2\text{ax}})$ $\rho(\text{SbF}_{2\text{ax}} + \text{SbF}_{2\text{eq}} + \text{N1SbN1}')$ $\delta(\text{SbF}_{2\text{ax}} - \text{SbF}_{2\text{eq}} - \text{N1SbN1}')$ $\rho(\text{SbF}_{2\text{eq}} + \text{SbF}_{2\text{ax}} + \text{ring rocking})$
102(44)	125(3)[2] 92(1)[4] 55(8)[0]	139(6) 122(6)	121(1)[0] 95(0)[2] 62(5)[1]
			twisting and lattice modes

[a] Recorded in flame sealed m.p. capillaries at ambient temperature. Normalised Raman intensities are given in parentheses. Shoulders are denoted sh. [b] Calculated using the B3LYP functional with the aug-cc-pVTZ-PP (Sb) and aug-cc-pVTZ (C, H, N, F) basis sets. Absolute Raman intensities ($\text{\AA}^4 \text{u}^{-1}$) are given in parentheses and IR intensities (km mol^{-1}) are given in square brackets. [c] From $[\text{SbF}_4(\text{bipy})][\text{Sb}_2\text{F}_{11}]$. Bands corresponding to $[\text{Sb}_2\text{F}_{11}]^-$ anion are observed at 694(sh), 685(37), 649(41), 294(18), 281(15). [d] Recorded in a $\frac{1}{4}$ "-o.d. FEP sample tube at -100°C . [e] From $[\text{SbF}_4(\text{bipy})][\text{SbF}_6]$. Bands corresponding to $[\text{SbF}_6]^-$ are observed at 684(6), 646(22), 281(10). [f] Abbreviations denote stretch (ν), bend (δ), rock (ρ), twist (τ), and wag (ω).

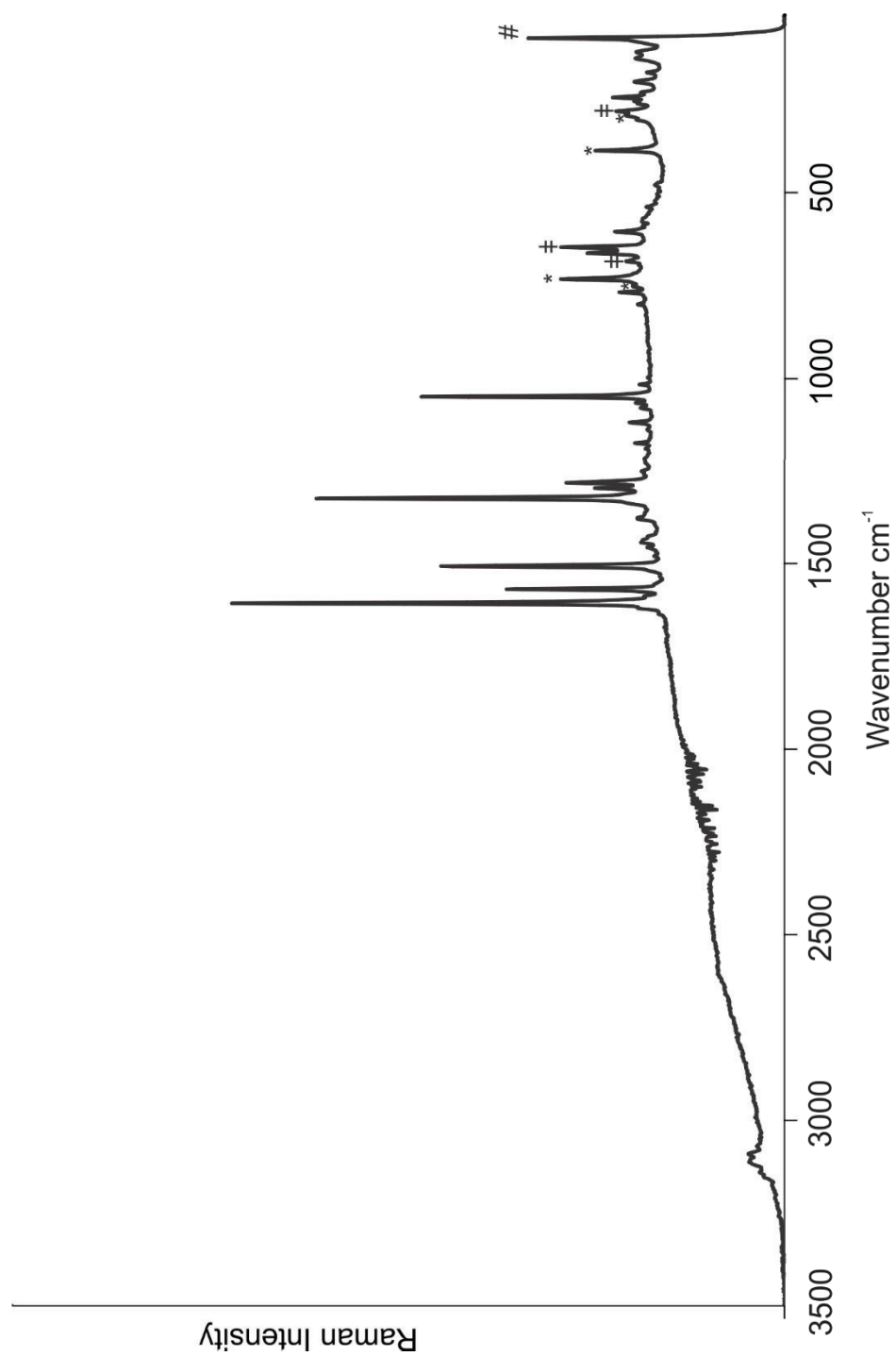


Figure A.3. Raman spectrum of $[\text{SbF}_4(\text{bipy})][\text{SbF}_6]$. (*) and (‡) denote bands corresponding to the FEP sample tube and $[\text{SbF}_6]^-$ anion respectively.

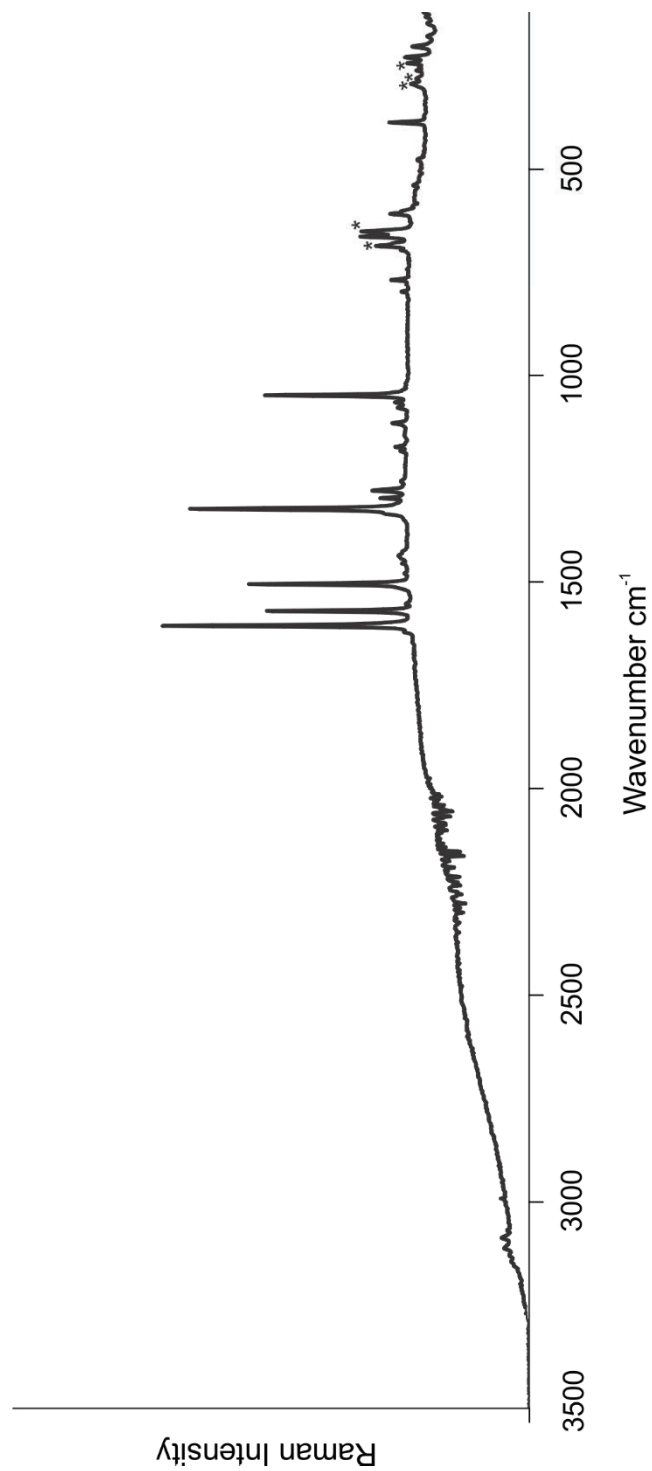


Figure A.4. Raman spectrum of [SbF₄(bipy)][Sb₂F₁₁]. (*) denotes bands corresponding to the [Sb₂F₁₁]⁻ anion.

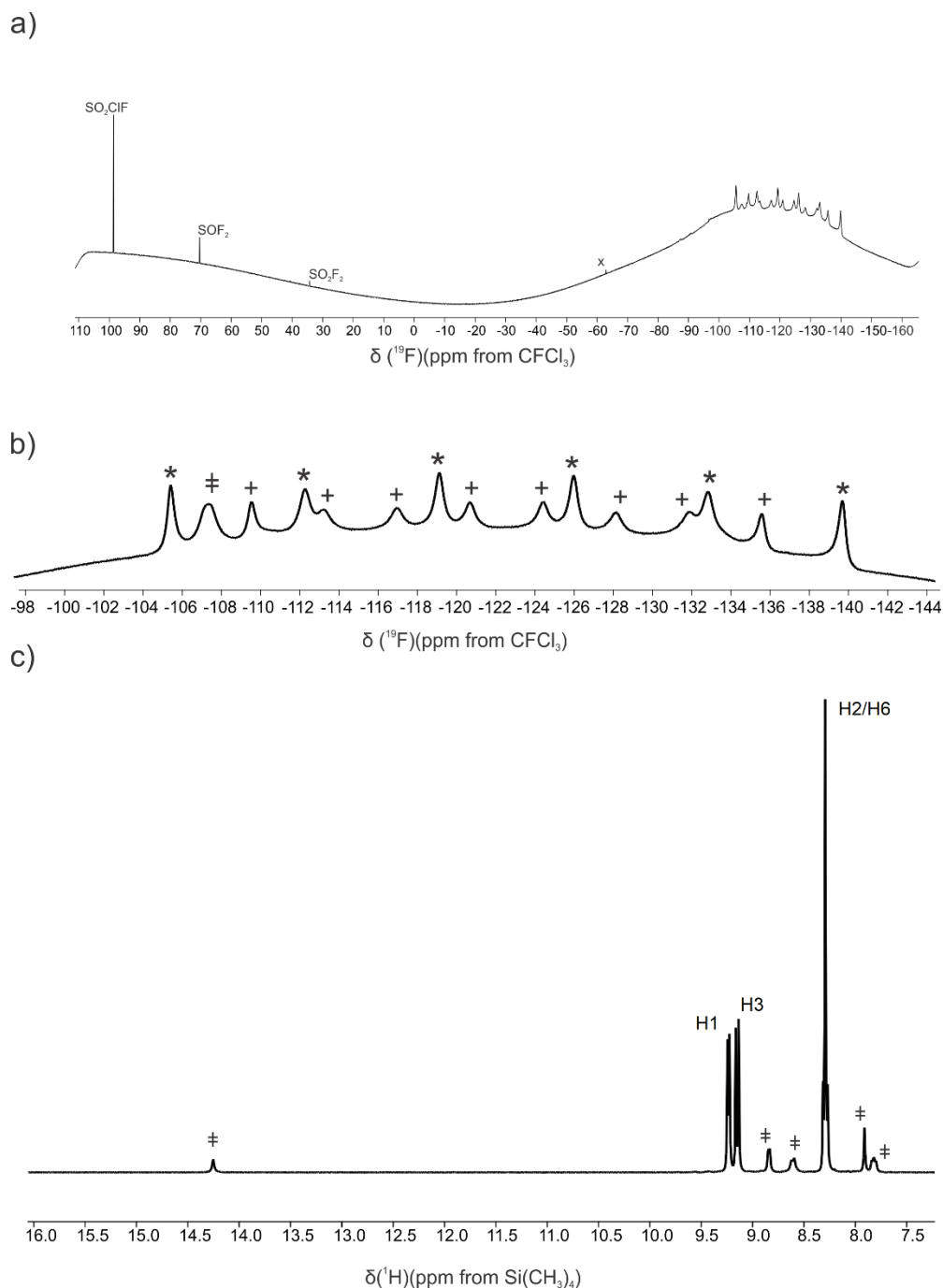


Figure A.5. (a) The full ^{19}F NMR spectrum of $[\text{SbF}_4(\text{phen})][\text{SbF}_6]$ in CH_3CN at -40°C . (x) denotes an unknown impurity. The spectrum is not baseline corrected. The baseline between ca. -80 to -150 ppm contains broad resonances arising from the FEP sample tube. (b) Fluorine-on-antimony region of the ^{19}F NMR spectrum of $[\text{SbF}_4(\text{phen})][\text{SbF}_6]$ in CH_3CN at -40°C . (*), (+) and (‡) denote multiplets arising from $^1\text{J}(^{19}\text{F}-^{121}\text{Sb})$ and $^1\text{J}(^{19}\text{F}-^{123}\text{Sb})$ coupling and the singlet for $[\text{H-phen}][\text{SbF}_6]$ impurity, respectively. c) ^1H NMR spectrum of $[\text{SbF}_4(\text{phen})][\text{SbF}_6]$. (‡) denotes $[\text{H-phen}][\text{SbF}_6]$ impurity.

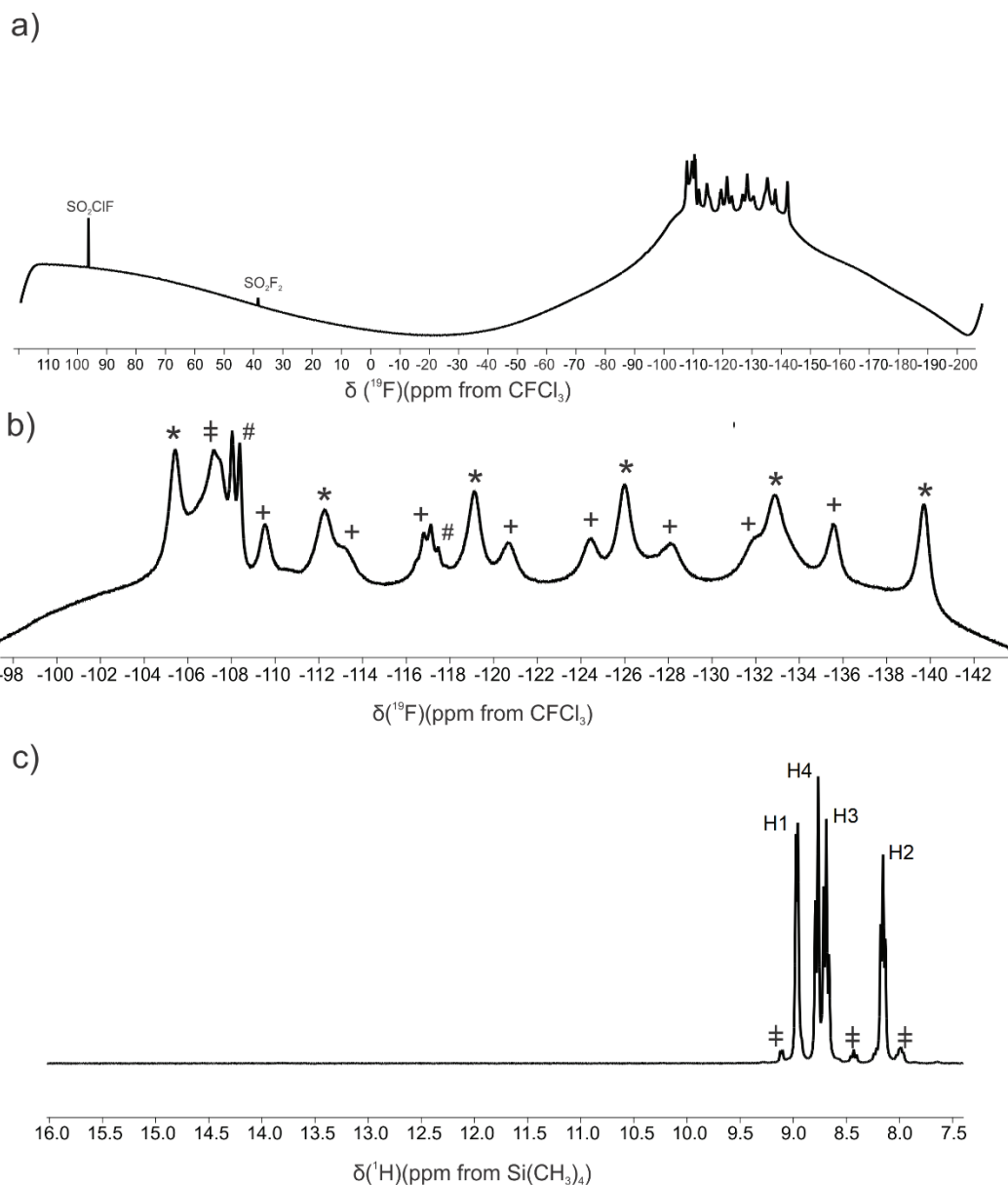


Figure A.6. (a) The full spectrum of $[\text{SbF}_4(\text{bipy})][\text{SbF}_6]$ in CH_3CN at -40°C . The spectrum is not baseline corrected. The baseline between ca. -80 to -150 ppm contains broad resonances arising from the FEP sample tube. (b) Fluorine-on-antimony region of the ^{19}F NMR spectrum of $[\text{SbF}_4(\text{bipy})][\text{SbF}_6]$ in CH_3CN at -40°C . (*), (+) and (‡) denote multiplet arising from $^1\text{J}(^{19}\text{F}-^{121}\text{Sb})$ and $^1\text{J}(^{19}\text{F}-^{123}\text{Sb})$ coupling, and the singlet for $[\text{H-bipy}][\text{SbF}_6]$, respectively. (#) Tentatively assigned to a neutral SbF_5 adduct, possibly $\text{SbF}_5\text{-bipy-SbF}_5$. (c) ^1H NMR spectrum of $[\text{SbF}_4(\text{bipy})][\text{SbF}_6]$. (‡) denotes $[\text{H-bipy}][\text{SbF}_6]$ impurity.

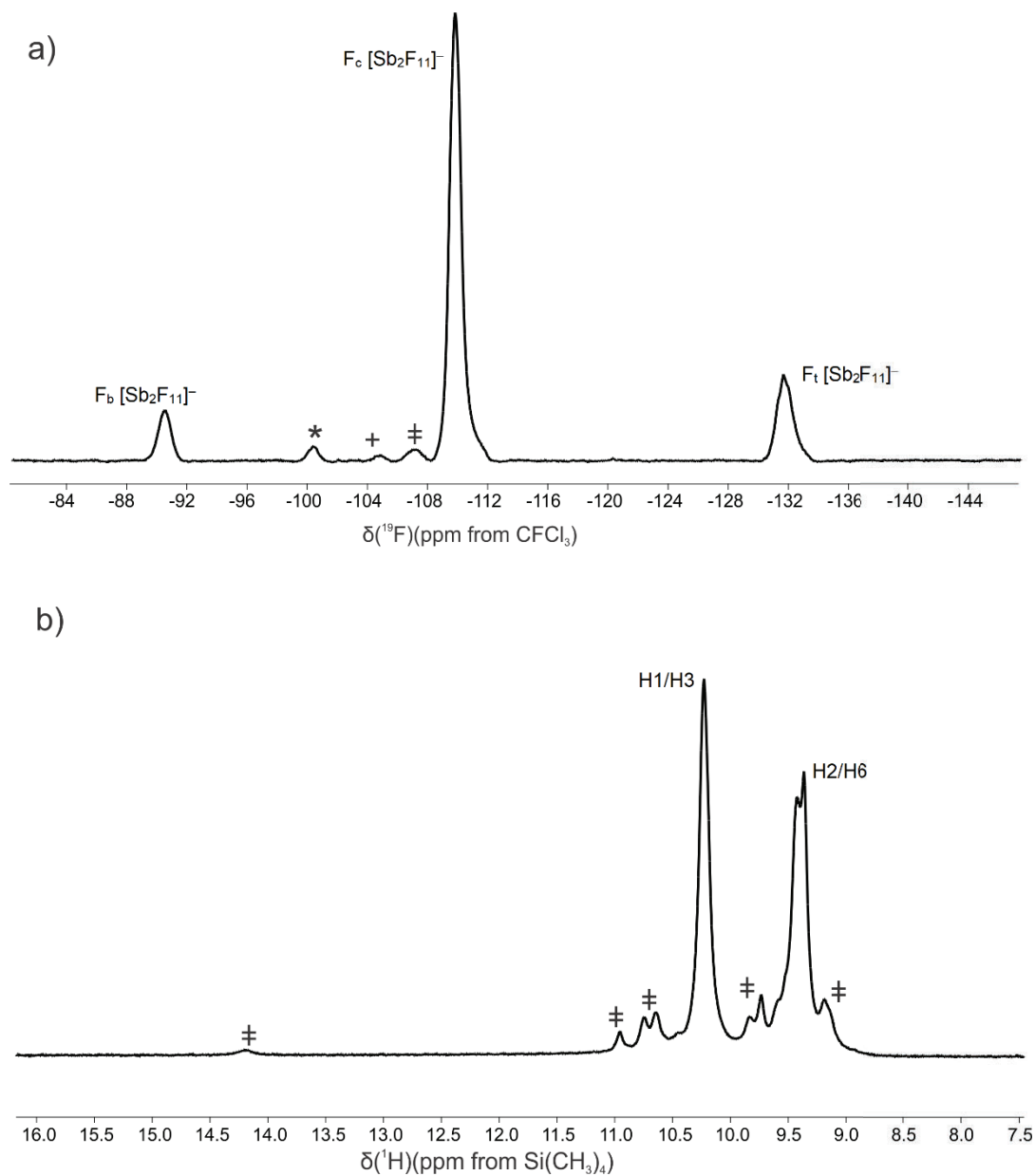


Figure A.7. (a) ^{19}F NMR spectrum of $[\text{SbF}_4(\text{phen})][\text{Sb}_2\text{F}_{11}]$ in SO_2 at $-70\text{ }^\circ\text{C}$. ($*$), ($+$) and ($\ddagger$) denotes $\text{SbF}_5 \cdot \text{SO}_2$, $\text{SbF}_5 \cdot \text{SOF}_2$ and $[\text{H-phen}][\text{SbF}_6]$ respectively. (b) ^1H NMR spectrum of $[\text{SbF}_4(\text{phen})][\text{Sb}_2\text{F}_{11}]$. ($\ddagger$) denotes $[\text{H-phen}][\text{SbF}_6]$ impurity.

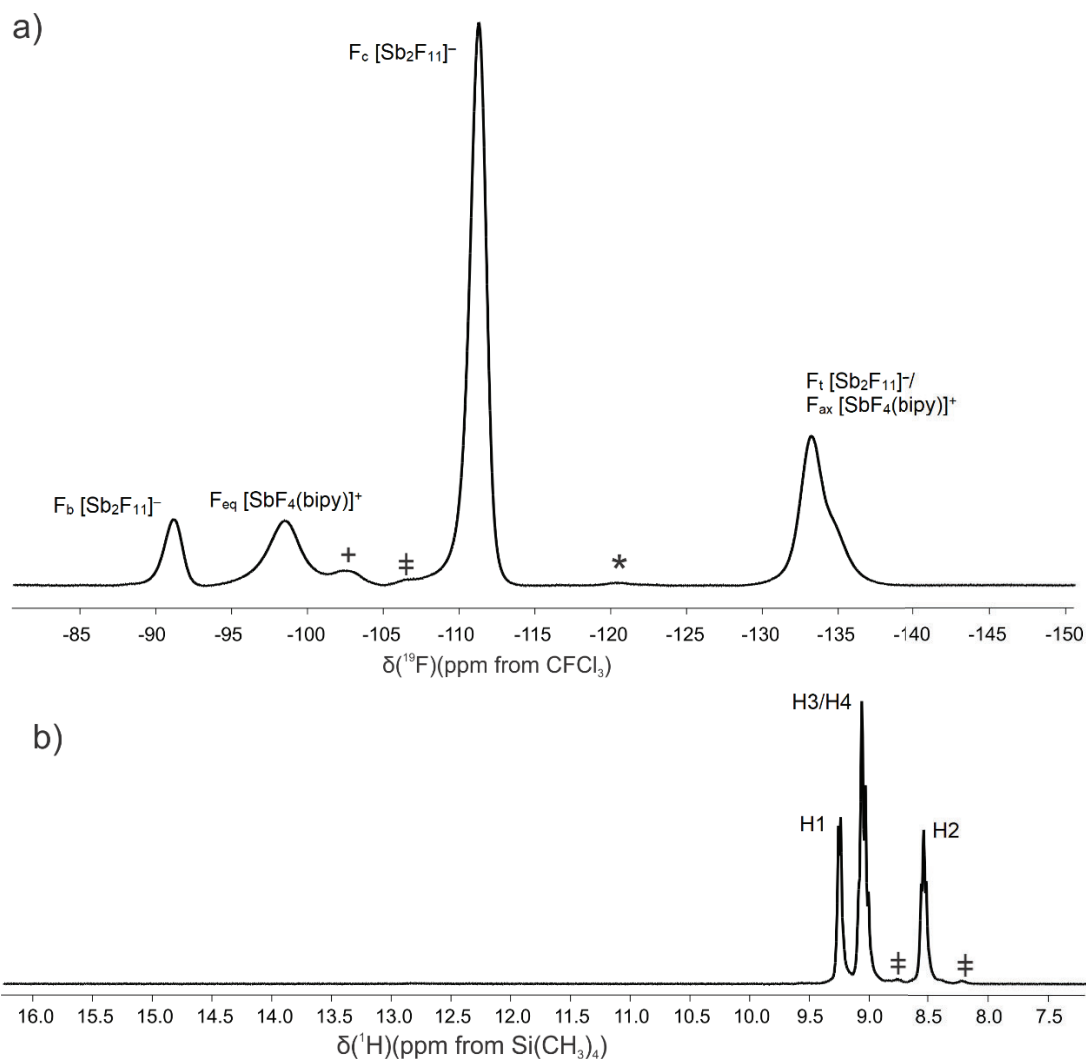


Figure A.8. (a) ^{19}F NMR spectrum of $[\text{SbF}_4(\text{bipy})][\text{Sb}_2\text{F}_{11}]$ in SO_2 at $-70\text{ }^\circ\text{C}$. (+), (‡) and (*) denotes $\text{SbF}_5 \cdot \text{SO}_2$, $[\text{H-bipy}][\text{SbF}_6]$ and an unknown impurity respectively. (b) ^1H NMR spectrum of $[\text{SbF}_4(\text{bipy})][\text{Sb}_2\text{F}_{11}]$. (‡) denotes $[\text{H-bipy}][\text{SbF}_6]$ impurity.

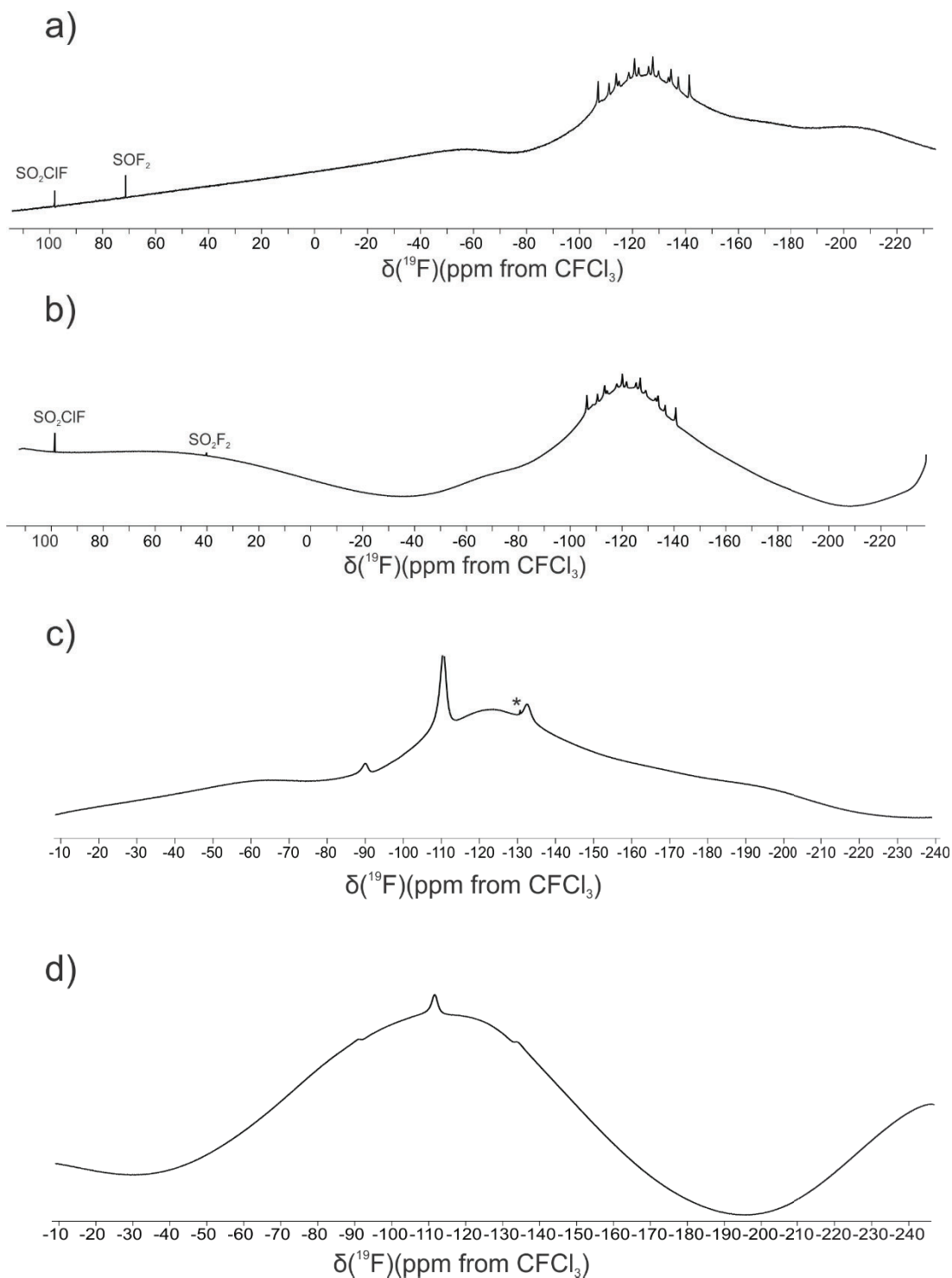


Figure A.9. The ^{19}F NMR spectra recorded at ambient temperature of: (a) $[\text{SbF}_4(\text{phen})][\text{SbF}_6]$, (b) $[\text{SbF}_4(\text{bipy})][\text{SbF}_6]$, (c) $[\text{SbF}_4(\text{bipy})][\text{Sb}_2\text{F}_{11}]$. Asterisks (*) denotes $\text{SbF}_5 \cdot \text{SO}_2$, (d) $[\text{SbF}_4(\text{phen})][\text{Sb}_2\text{F}_{11}]$. Spectra are not baseline corrected. The baseline between ca. -80 to -150 ppm contains broad resonances arising from the FEP sample tube.

Table A.5. Natural population analysis charges and Wiberg valences^[a] for various fluoroantimonic species.^[b]

	SbF ₅	[SbF ₄] ⁺	[SbF ₆] [−]	[SbF ₄ (phen)] ⁺	[SbF ₄ (bipy)] ⁺
Sb	3.04 [2.81]	3.08 [2.71]	3.04[2.84]	2.92 [2.91]	2.92 [2.91]
F(1)	−0.61 [0.67]	−0.52 [0.81]	— 0.67[0.58]	−0.63 [0.66]	−0.63 [0.66]
F(2)	−0.60 [0.69]	−0.52 [0.81]	— 0.67[0.58]	−0.63 [0.66]	−0.63 [0.66]
F(3)	−0.60 [0.69]	−0.52 [0.81]	— 0.67[0.58]	−0.62 [0.67]	−0.62 [0.68]
F(4)	−0.60 [0.69]	−0.52 [0.81]	— 0.67[0.58]	−0.62 [0.67]	−0.62 [0.68]
F(5)	−0.61 [0.67]		— 0.67[0.58]		
F(6)			— 0.67[0.58]		
N(1)				−0.59 [3.31]	−0.59 [3.31]
C(1)				0.13 [3.89]	0.11 [3.89]
C(2)				−0.21 [3.95]	−0.19 [3.95]
C(3)				−0.01 [3.96]	−0.01 [3.94]
C(4)				0.00 [4.03]	−0.21 [3.97]
C(5)				0.25 [4.00]	0.28 [3.98]
C(6)				−0.18 [3.98]	
H(1)				0.25 [0.93]	0.25 [0.94]
H(2)				0.25 [0.94]	0.25 [0.94]
H(3)				0.24 [0.95]	0.24 [0.94]
H(4)					0.24 [0.95]
H(6)				0.24 [0.95]	
Σ(L) ^[c]				0.74	0.74

[a] number in brackets. [b] Calculated using the B3LYP functional with the aug-cc-pVTZ-PP (Sb) and aug-cc-pVTZ (C, H, N, F) basis sets Values are given for one half of bipy and phen ligands as the two halves are symmetry related. Atomic labelling is as seen in figure S1. [c] Total NPA charge for the phen and bipy ligands.

Table A.6. Optimised gas-phase atomic coordinates (Å) for [SbF₄(phen)]⁺

1 1

Sb	-0.000071	-1.571872	-0.000000
F	1.891179	-1.429183	-0.000000
F	-1.891203	-1.427726	-0.000000
F	-0.000789	-2.760574	1.459196
N	0.000593	0.136831	1.353194
C	0.000131	1.330092	0.714141
C	0.000737	0.070640	2.679785
H	0.001502	-0.916041	3.120391
C	0.000324	1.237187	3.450020
H	0.000187	1.153904	4.526387
C	-0.000122	2.545100	1.418858
C	-0.000156	2.465148	2.826866
H	-0.000269	3.374749	3.412500
C	-0.000225	3.770227	0.679265
H	-0.000678	4.703194	1.225469
N	0.000593	0.136831	-1.353194
C	0.000131	1.330092	-0.714141
C	0.000737	0.070640	-2.679785
H	0.001502	-0.916041	-3.120391
C	0.000324	1.237187	-3.450020
H	0.000187	1.153904	-4.526387
C	-0.000122	2.545100	-1.418858
C	-0.000156	2.465148	-2.826866
H	-0.000269	3.374749	-3.412500
C	-0.000225	3.770227	-0.679265
H	-0.000678	4.703194	-1.225469
F	-0.000789	-2.760574	-1.459196

Table A.7. Optimised gas-phase atomic coordinates (Å) for [SbF₄(bipy)]⁺

1 1

Sb	-1.263215	0.000013	0.000000
F	-1.128651	-1.891925	0.000000
F	-1.128344	1.891936	0.000000
F	-2.454339	0.000104	1.457366
N	0.447098	-0.000072	1.337248
C	1.657256	-0.000019	0.740289
C	0.315253	-0.000094	2.670004
H	-0.693994	-0.000140	3.054728
C	1.429501	-0.000049	3.490540
H	1.302591	-0.000059	4.562524

C	2.804454	0.000027	1.519983
C	2.687187	0.000012	2.904973
H	3.576506	0.000061	3.519286
N	0.447098	-0.000072	-1.337248
C	1.657256	-0.000019	-0.740289
C	0.315253	-0.000094	-2.670004
H	-0.693994	-0.000140	-3.054728
C	1.429501	-0.000049	-3.490540
H	1.302591	-0.000059	-4.562524
C	2.804454	0.000027	-1.519983
C	2.687187	0.000012	-2.904973
H	3.576506	0.000061	-3.519286
F	-2.454339	0.000104	-1.457366
H	3.780819	0.000073	-1.062195
H	3.780819	0.000073	1.062195

Table A.8. Optimised gas-phase atomic coordinates (Å) for SbF₅

0 1

Sb	0.000000	0.000000	0.000000
F	0.000000	0.000000	1.882182
F	0.000000	1.874346	-0.000000
F	1.623232	-0.937173	-0.000000
F	-1.623232	-0.937173	-0.000000
F	0.000000	0.000000	-1.882182

Table A.9. Optimised gas-phase atomic coordinates (Å) for [SbF₄]⁺

1 1

Sb	-0.000152	-0.000006	-0.000000
F	-0.612187	-0.866637	1.500372
F	-0.612187	-0.866637	-1.500372
F	-0.612187	1.732332	-0.000000
F	1.837424	0.000978	0.000000

Table A.10. Optimised gas-phase atomic coordinates (Å) for [SbF₆]⁻

-1 1

Sb	0.000000	0.000000	0.000000
F	-0.000000	-0.000000	1.918675
F	-0.000000	1.918675	-0.000000
F	1.918675	-0.000000	0.000000
F	-0.000000	-0.000000	-1.918675
F	-1.918675	-0.000000	-0.000000
F	-0.000000	-1.918675	0.000000

Appendix B – Supporting Information for Chapter 3

Table B.1. Crystallographic Data collection and refinement parameters for [SbF₄(terpy)][SbF₆]·CH₃CN.

	[SbF ₄ (terpy)][SbF ₆]·CH ₃ CN
Chemical formula	C ₁₇ H ₁₄ F ₁₀ N ₄ Sb ₂
Formula weight	707.82
Temperature (°C)	100.0(3)
Crystal system	monoclinic
Space group	<i>P</i> 2 ₁ / <i>c</i>
<i>a</i> (Å)	8.1799(2)
<i>b</i> (Å)	9.7724(2)
<i>c</i> (Å)	26.7678(5)
β (°)	98.724(2)
<i>V</i> (Å ³)	2114.99(8)
<i>Z</i>	4
ρ _{calc} (g cm ⁻³)	2.223
μ (mm ⁻¹)	2.655
F(000)	1344.0
Crystal size (mm ³)	0.27 x 0.21 x 0.18
Radiation	Mo Kα (λ = 0.71073)
Goodness-of-fit on F ²	1.049
Final R indexes [I ≥ 2σ(I)] ^[a]	R ₁ = 0.0223, wR ₂ = 0.0514
Final R indexes [all data]	R ₁ = 0.0270, wR ₂ = 0.0527
Largest diff. peak/hole (e Å ⁻³)	1.55/−0.45
CCDC	2451990

$$^{[a]} R_1 = \sum ||F_o| - |F_c| | / \sum |F_o|. \text{ wR}_2 = [\sum [w(F_o^2 - F_c^2)^2] / \sum w(F_o^4)]^{1/2}$$

Table B.2. Experimental bond lengths and angles for [SbF₄(terpy)][SbF₆]·CH₃CN. Atom labelling is as seen in Figure B.1

	[SbF ₄ (terpy)][SbF ₆]·CH ₃ CN
Sb(1)–F(1)	1.8851(10)
Sb(1)–F(2)	1.8857(9)
Sb(1)–F(3)	1.9181(10)
Sb(1)–F(4)	1.9141(10)
Sb(1)–N(1)	2.2563(13)
Sb(1)–N(2)	2.2248(12)
Sb(1)–N(3)	2.2684(13)
N(1)–C(1)	1.3489(19)
N(1)–C(5)	1.3474(18)
C(1)–C(2)	1.386(2)
C(2)–C(3)	1.389(2)
C(3)–C(4)	1.390(2)
C(4)–C(5)	1.392(2)
C(5)–C(6)	1.468(2)

C(6)–N(2)	1.3461(19)
C(6)–C(7)	1.391(2)
C(7)–C(8)	1.388(2)
C(8)–C(9)	1.387(2)
C(9)–C(10)	1.388(2)
C(10)–N(2)	1.3454(18)
C(10)–C(11)	1.467(2)
C(11)–N(3)	1.3446(19)
C(11)–C(12)	1.394(2)
C(12)–C(13)	1.392(2)
C(13)–C(14)	1.390(2)
C(14)–C(15)	1.384(2)
C(15)–N(3)	1.351(2)
Sb(2)–F(5)	1.8696(11)
Sb(2)–F(6)	1.8799(10)
Sb(2)–F(7)	1.8863(11)
Sb(2)–F(8)	1.8757(11)
Sb(2)–F(9)	1.8870(11)
Sb(2)–F(10)	1.8762(11)
N(4)–C(16)	1.143(2)
C(16)–C(17)	1.451(3)
F(2)–Sb(1)–F(3)	89.38(5)
F(2)–Sb(1)–F(4)	96.94(5)
F(2)–Sb(1)–N(2)	98.10(4)
F(2)–Sb(1)–N(1)	85.71(4)
F(2)–Sb(1)–N(3)	81.95(5)
F(3)–Sb(1)–N(2)	143.87(5)
F(3)–Sb(1)–N(1)	74.67(4)
F(3)–Sb(1)–N(3)	146.02(5)
F(1)–Sb(1)–F(2)	175.49(5)
F(1)–Sb(1)–F(3)	89.76(5)
F(1)–Sb(1)–F(4)	87.15(5)
F(1)–Sb(1)–N(1)	89.79(5)
F(1)–Sb(1)–N(3)	101.16(5)
F(4)–Sb(1)–F(3)	75.97(4)
F(4)–Sb(1)–N(2)	137.09(4)
F(4)–Sb(1)–N(1)	150.48(4)
F(4)–Sb(1)–N(3)	72.61(4)
N(2)–Sb(1)–N(1)	70.76(4)
N(2)–Sb(1)–N(3)	70.09(5)
N(1)–Sb(1)–N(3)	136.60(5)
C(10)–N(2)–Sb(1)	119.84(10)
C(10)–N(2)–C(6)	120.47(12)
C(6)–N(2)–Sb(1)	119.13(9)
C(5)–N(1)–Sb(1)	118.09(9)
C(5)–N(1)–C(1)	119.21(13)
C(1)–N(1)–Sb(1)	122.57(10)

C(15)–N(3)–Sb(1)	121.60(10)
C(11)–N(3)–Sb(1)	118.89(10)
C(11)–N(3)–C(15)	119.39(13)
C(3)–C(4)–C(5)	118.66(14)
C(13)–C(12)–C(11)	118.32(14)
N(2)–C(10)–C(9)	121.11(14)
N(2)–C(10)–C(11)	114.70(12)
C(9)–C(10)–C(11)	124.10(13)
C(2)–C(3)–C(4)	119.09(15)
N(1)–C(5)–C(4)	122.00(13)
N(1)–C(5)–C(6)	114.69(12)
C(4)–C(5)–C(6)	123.21(13)
C(1)–C(2)–C(3)	119.36(14)
N(3)–C(15)–C(14)	121.34(15)
N(1)–C(1)–C(2)	121.58(14)
C(8)–C(9)–C(10)	118.88(14)
N(3)–C(11)–C(12)	122.17(14)
N(3)–C(11)–C(10)	114.15(13)
C(12)–C(11)–C(10)	123.63(13)
N(2)–C(6)–C(5)	114.76(12)
N(2)–C(6)–C(7)	121.03(13)
C(7)–C(6)–C(5)	124.12(13)
C(9)–C(8)–C(7)	119.73(14)
C(8)–C(7)–C(6)	118.74(14)
C(14)–C(13)–C(12)	119.17(15)
C(15)–C(14)–C(13)	119.50(15)
F(7)–Sb(2)–F(9)	89.44(5)
F(6)–Sb(2)–F(7)	89.51(5)
F(6)–Sb(2)–F(9)	89.17(5)
F(8)–Sb(2)–F(7)	178.59(5)
F(8)–Sb(2)–F(9)	89.51(5)
F(8)–Sb(2)–F(6)	89.53(5)
F(8)–Sb(2)–F(10)	90.93(5)
F(10)–Sb(2)–F(7)	90.11(5)
F(10)–Sb(2)–F(9)	179.47(5)
F(10)–Sb(2)–F(6)	90.54(5)
F(5)–Sb(2)–F(7)	89.91(5)
F(5)–Sb(2)–F(9)	89.73(5)
F(5)–Sb(2)–F(6)	178.76(5)
F(5)–Sb(2)–F(8)	91.04(5)
F(5)–Sb(2)–F(10)	90.55(6)
N(4)–C(16)–C(17)	179.6(2)

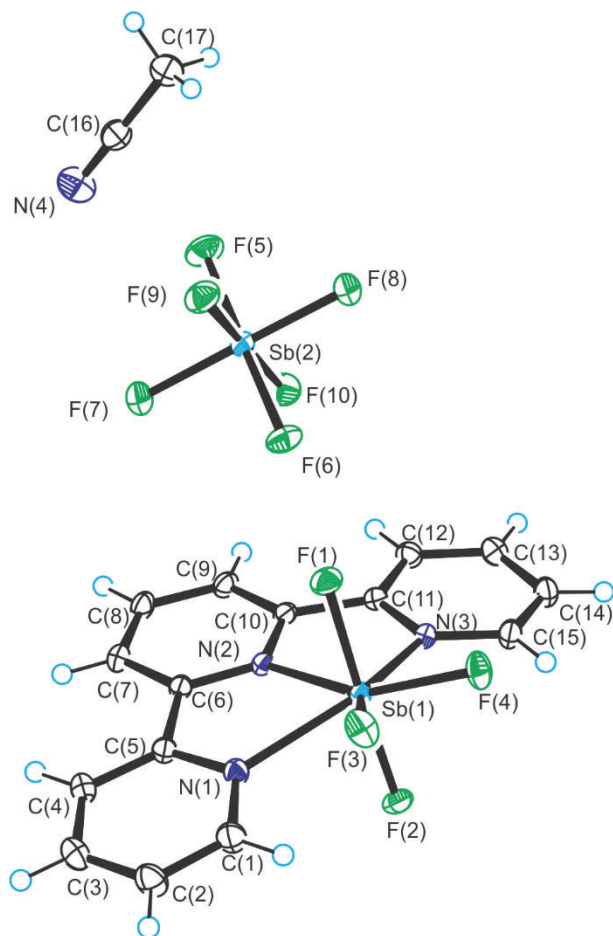


Figure B.1. Thermal ellipsoid plot (50% probability level) of $[\text{SbF}_4(\text{terpy})][\text{SbF}_6] \cdot \text{CH}_3\text{CN}$

Table B.3. Vibrational frequencies (cm^{-1}) of terpy and $[\text{SbF}_4(\text{terpy})]^+$

Terpy		$[\text{SbF}_4(\text{terpy})]^+$		Tentative assignments ^[d]
Exptl. ^[a]	Calcd. ^[b]	Exptl. ^{[a][c]}	Calcd. ^[b]	
3087(5)	3204(439)[7]	3144(4)	3266(142)[21]	ν(C–H)
3073sh	3201(40)[27]		3265(7)[8]	
3061(12)	3201(270)[4]	3140(sh)	3239(264)[1]	
3052(8)	3197(132)[<1]		3238(69)[1]	
	3194(84)[13]		3227(79)[1]	
	3192(24)[21]		3226(16)[2]	
	3178(48)[10]	3100(6)	3222(287)[<1]	
	3177(67)[12]		3222(81)[2]	
3042sh	3176(169)[<1]		3207(116)[0]	
3011(3)	3150(142)[29]		3204(70)[1]	
	3150(81)[16]	3093(sh)	3204(156)[<1]	
1646(2)				C–N and C–C stretching modes + in-plane ring deformations
1620(8)				
1610(9)				
1594(60)	1630(391)[5]		1656(2)[2]	
1580sh	1629(149)[106]		1646(150)[13]	
1575(100)	1621(116)[21]	1608(89)	1638(534)[56]	
1561sh	1624(113)[39]		1629(<1)[91]	
	1613(6)[39]		1619(143)[13]	
	1608(76)[43]	1572(81)	1611(370)[15]	
1478(23)	1515(71)[2]	1513(49)	1540(164)[9]	
1470(35)	1509(64)[22]	1491(31)	1524(103)[51]	
1454(20)	1482(99)[9]	1473(28)	1506(132)[13]	
	1480(23)[82]		1497(13)[119]	
1406(6)	1466(3)[31]		1482(1)[22]	
1439(15)	1437(7)[8]		1448(3)[9]	
1365(2)	1354(296)[2]	1355(100)	1376(554)[2]	
1344(2)		1340(43)		
1321(94)				
1302(3)	1333(6)[3]		1363(1)[48]	
	1293(2)[2]		1342(4)[30]	
1283(10)	1309(177)[<1]	1290(19)	1330(26)[12]	
1248(15)	1291(76)[6]		1316(119)[13]	
1235(10)	1288(4)[1]	1273(13)	1313(103)[10]	
1223(10)	1289(13)[3]		1296(9)[37]	
	1191(3)[15]		1222(<1)[19]	
1154(8)	1178(4)[5]		1200(8)[15]	
	1178(6)[6]		1200(1)[5]	
	1153(1)[14]		1175(<1)[5]	
	1124(2)[1]		1153(4)[<1]	
	1115(<1)[1]		1131(4)[2]	
1097(5)	1120(8)[4]	1104(8)	1130(11)[4]	
1087(2h)	1103(6)[8]	1081(8)	1108(7)[3]	
1064(4)	1072(4)[10]		1091(2)[5]	
1041(19)	1067(44)[<1]	1056(16)	1077(31)[2]	out-of-plane ring deformation
	1023(1)[<1]	1051(sh)	1046(13)[1]	
	1023(<1)[0]		1045(1)[2]	
996(99)	1013(114)[1]	1030(64)	1044(150)[4]	symmetric ring-breathing mode
	1013(11)[6]		1043(13)[33]	
	1016(1)[2]		1038(10)[4]	
	1011(64)[2]		1035(4)[3]	out-of-plane ring deformation
981(2)	990(1)[<1]		1016(<1)[1]	
	990(<1)[<1]		1016(0)[<1]	
	932(5)[<1]		939(0)[0]	
	915(1)[0]		919(0)[0]	
	913(2)[<1]		918(1)[<1]	in-plane ring deformation
832(10)	847(5)[6]		862(9)[2]	
	861(<1)[1]		853(1)[2]	

795(3)	820(5)[10] 794(1)[62] 767(<1)[37] 764(1)[17] 762(1)[11]		809(3)[6] 794(<1)[133] 770(1)[0] 760(1)[5] 753(<1)[6]	} out-of-plane ring deformation
724(19)	743(16)[<1]	731(10)	746(10)[4] 678(4)[17] 672(<1)[27]	
640(4)	656(5)[6]		663(1)[87]	} in-plane ring deformations
656(3)	672(1)[23]		663(1)[9] 655(4)[7]	
			644(1)[1]	} $v_{as}(SbF_{2ax})$
631(2)	636(1)[11]		623(15)[81]	
620(7)	627(7)[1]		589(22)[<1]	} in-plane ring deformations
615(4)	677(1)[5]		586(<1)[55]	
		659(sh)	549(<1)[2]	} $v_s(SbF_{2eq})$
		610(19)	522(1)[6] 469(2)[4] 458(0)[0] 454(2)[1] 440(<1)[<1]	
	563(1)[4] 507(1)[2] 490(2)[2] 419(1)[4] 409(5)[1]		428(1)[10]	} in-plane ring deformation
400(8)	417(6)[2]		377(4)[36]	
		348(14)	375(1)[1]	} $\delta(SbF_{2eq})$
			317(10)[13]	
281(5)	337(0)[<1] 352(2)[1] 279(1)[<1]	324(8) 268(10)	294(4)[1] 292(<1)[14] 270(0)[34]	} in-plane ring deformation
245(8)	272(1)[<1]		250(2)[15] 241(1)[12] 227(<1)[19]	
		230(11)	214(1)[22] 204(<1)[52]	} $\omega(SbF_{2eq}) - \rho(SbF_{2ax})$
			192(3)[0] 170(6)[0] 144(1)[5] 137(3)[1]	
223(16)	223(8)[<1]		113(1)[<1] 92(1)[<1] 70(4)[0] 65(<1)[<1] 35(5)[3] 30(1)[0]	} ring rocking
			193(10) 149(15) 118(27)	
			192(2)	} $\delta(SbF_{2ax})$
			140(1)[1]	
			193(10)	} $\delta(SbF_{2ax})$
			149(15)	
			118(27)	} $\rho(SbF_{2ax}) + \rho(SbF_{2eq})$
			124(12) 102(22)	
	103(4)[<1] 93(4)[4] 59(8)[1] 39(<1)[3] 39(13)[<1]		103(4)[<1] 93(4)[4] 59(8)[1] 39(<1)[3] 39(13)[<1]	} $v_{as}(SbN_3)$
			102(22)	
			113(1)[<1] 92(1)[<1] 70(4)[0] 65(<1)[<1] 35(5)[3] 30(1)[0]	} $v_{as}(SbN_3)$
			102(22)	
			113(1)[<1] 92(1)[<1] 70(4)[0] 65(<1)[<1] 35(5)[3] 30(1)[0]	} $v_s(SbN_3)$
			102(22)	
			113(1)[<1] 92(1)[<1] 70(4)[0] 65(<1)[<1] 35(5)[3] 30(1)[0]	} twisting modes
			102(22)	

[a] Recorded in flame sealed m.p. capillaries at ambient temperature. Normalised Raman intensities are given in parentheses. Shoulders are denoted sh. [b] Calculated using the B3LYP-D3(BJ) functional using the def2-TZVPPD-PP (Sb) and def2-TZVPPD (C, H, N, F) basis set. Absolute Raman intensities ($\text{\AA}^4 \text{u}^{-1}$) are given in parentheses and IR intensities (km mol^{-1}) are given in square brackets. [c] From $[SbF_4(terpy)][SbF_6]$. Bands corresponding to $[SbF_6]^-$ are observed at 662(10), 645(35), and 280(19) cm^{-1} . [d] Abbreviations denote stretch (v), bend (δ), rock (ρ), twist (τ), and wag (ω).

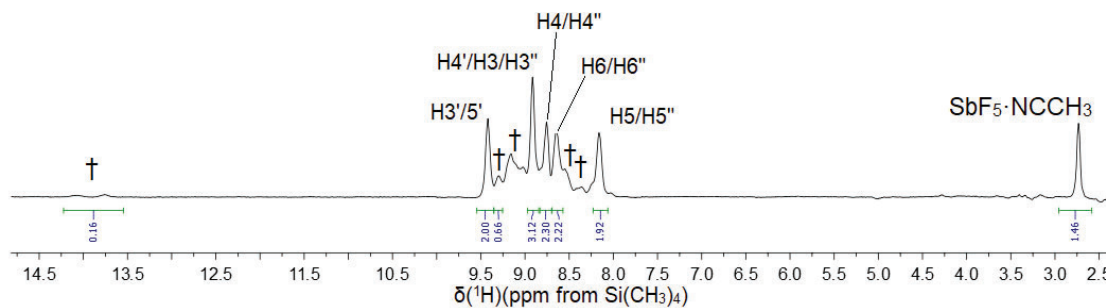


Figure B.2. ^1H NMR spectrum of $[\text{SbF}_4(\text{terpy})][\text{SbF}_6]$ recorded in CH_3CN at $-40\text{ }^\circ\text{C}$. Dagger (†) denotes $[\text{H-terpy}][\text{SbF}_6]$ impurity. Assignments based on Pazderski, L.; Pawlak, T.; Sitkowski, J.; Kozerski, L.; Szlyk, E. *Magn. Reson. Chem.* **2011**, 49, 237–241.

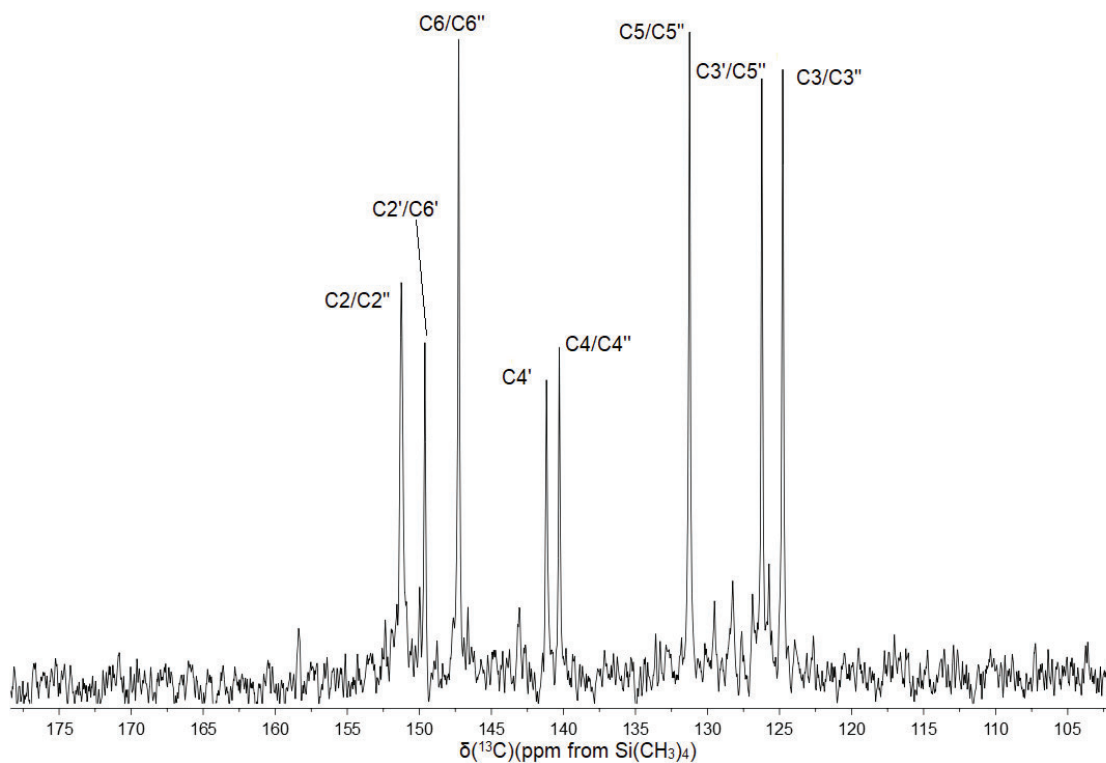


Figure B.3. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of $[\text{SbF}_4(\text{terpy})][\text{SbF}_6]$ recorded in SO_2 at $-30\text{ }^\circ\text{C}$. Assignments based on Pazderski, L.; Pawlak, T.; Sitkowski, J.; Kozerski, L.; Szlyk, E. *Magn. Reson. Chem.* **2011**, 49, 237–241.

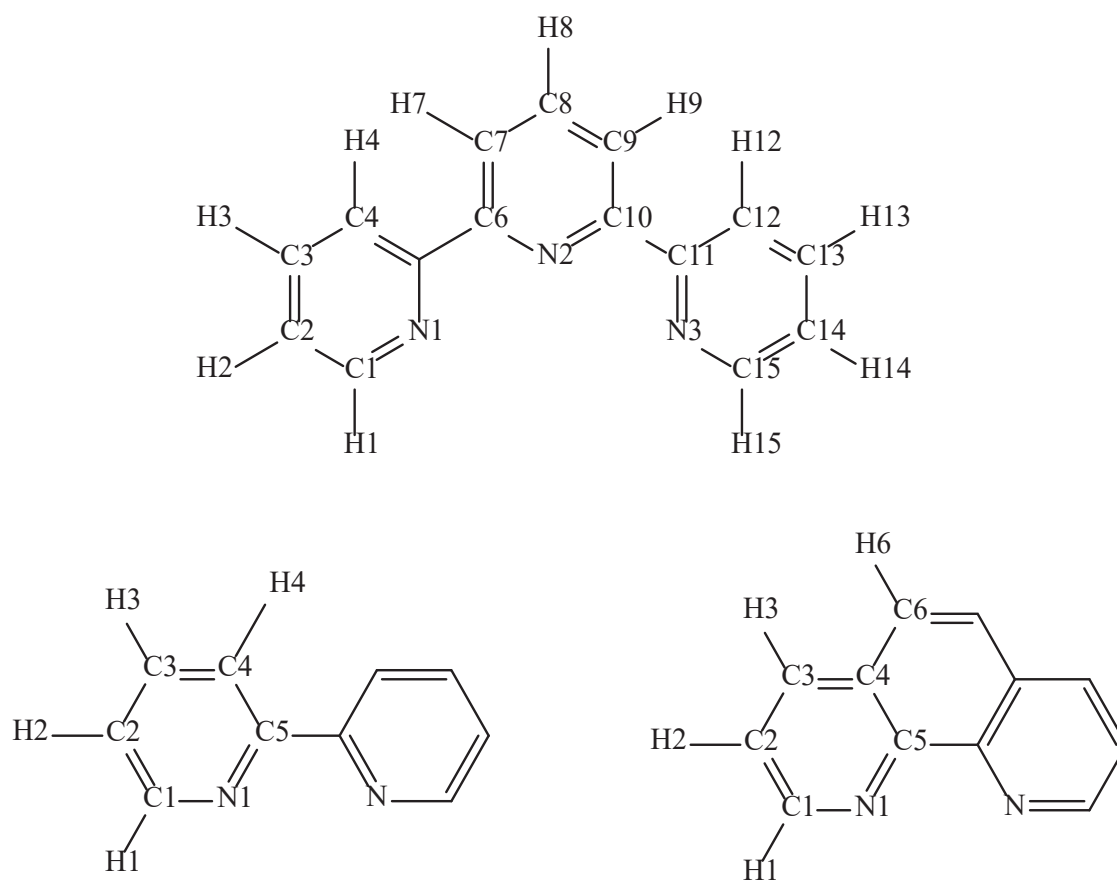


Figure B.4. Atom labelling used for terpy, bipy and phen in the NBO calculations.

Table B.4. Natural population analysis charge and Wiberg valences^[a] for various fluoroantimony species.^[b]

	SbF ₅	[SbF ₄ (phen)] ⁺	[SbF ₄ (bipy)] ⁺	[SbF ₄ (terpy)] ⁺
Sb	3.04 [2.81]	2.92 [2.91]	2.92 [2.91]	2.88 [2.93]
F(1)	−0.61 [0.67]	−0.63 [0.66]	−0.63 [0.66]	−0.63 [0.66]
F(2)	−0.60 [0.69]	−0.63 [0.66]	−0.63 [0.66]	−0.63 [0.66]
F(3)	−0.60 [0.69]	−0.62 [0.67]	−0.62 [0.67]	−0.65 [0.63]
F(4)	−0.60 [0.69]	−0.62 [0.67]	−0.62 [0.67]	−0.65 [0.63]
F(5)	−0.61 [0.67]			
N(1)		−0.59 [3.31]	−0.59 [3.31]	−0.51 [3.29]
N(2)				−0.53 [3.29]
N(3)				−0.54 [3.29]
C(1)		0.13 [3.89]	0.11 [3.89]	0.12 [3.88]
C(2)		−0.21 [3.95]	−0.19 [3.95]	−0.20 [3.95]
C(3)		−0.01 [3.96]	−0.01 [3.94]	−0.11 [3.94]
C(4)		0.00 [4.03]	−0.21 [3.97]	−0.18 [3.96]
C(5)		0.25 [4.00]	0.28 [3.98]	0.14 [4.02]
C(6)		−0.18 [3.98]		0.31 [3.96]
C(7)				−0.22 [3.96]
C(8)				−0.11 [3.94]
C(9)				−0.19 [3.96]
C(10)				0.18 [4.02]
C(11)				0.28 [3.97]
C(12)				−0.21 [3.97]
C(13)				−0.12 [3.95]
C(14)				−0.11 [3.95]
C(15)				−0.20 [3.95]
H(1)		0.25 [0.93]	0.25 [0.94]	0.25 [0.94]
H(2)		0.25 [0.94]	0.25 [0.94]	0.24 [0.94]
H(3)		0.24 [0.95]	0.24 [0.94]	0.24 [0.94]
H(4)			0.24 [0.95]	0.23 [0.95]
H(6)		0.24 [0.95]		
H(7)				0.24 [0.95]
H(8)				0.24 [0.95]
H(9)				0.24 [0.95]
H(12)				0.23 [0.95]
H(13)				0.23 [0.95]
H(14)				0.24 [0.94]
H(15)				0.25 [0.94]
Σ(L) ^[c]		0.74	0.74	0.43

[a] number in brackets. [b] [a] Calculated using the B3LYP-D3(BJ) functional using the def2-TZVPPD-PP (Sb) and def2-TZVPPD (C, H, N, F) basis set. Values are given for one half of bipy and phen ligands as the two halves are symmetry related. Atomic labelling is as seen in figure S5. [c] Total NPA charge for the terpy, phen and bipy ligands.

Table B.5. Energies ($E(2)$, kJ mol^{-1}) of the Sb–N and Sb–F interactions in $[\text{SbF}_4(\text{terpy})]^+$.^[a]

	$\sigma(\text{lp}(\text{N}) \rightarrow \text{lv}(\text{Sb}))$	$\sigma(\text{lp}(\text{F}) \rightarrow \text{lv}(\text{Sb}))$	$\Sigma_{\pi}(\text{lp}(\text{F}) \rightarrow \text{lv}(\text{Sb}))$	$\Sigma_{\text{T}}(\text{lp}(\text{F}) \rightarrow \text{lv}(\text{Sb}))$
	$[\text{SbF}_4(\text{terpy})]^+$			
Sb–N(1)	1992			
Sb–N(2)	1838			
Sb–N(3)	2094			
Sb–F(1)		1303	254	1557
Sb–F(2)		1301	248	1549
Sb–F(3)		1179	223	1402
Sb–F(4)		1184	223	1407

[a] Calculated using the B3LYP-D3(BJ) functional using the def2-TZVPPD-PP (Sb) and def2-TZVPPD (C, H, N, F) basis set. (lp) and (lv) denote lone pair and lone valence, respectively.

Table B.6. Wiberg bond indices of various fluoroantimony compounds

	SbF_5	$[\text{SbF}_4(\text{phen})]^+$	$[\text{SbF}_4(\text{bipy})]^+$	$[\text{SbF}_4(\text{terpy})]^+$
Sb–F(1)	0.67	0.51	0.51	0.49
Sb–F(2)	0.69	0.51	0.51	0.49
Sb–F(3)	0.69	0.54	0.54	0.50
Sb–F(4)	0.69	0.54	0.54	0.50
Sb–F(5)	0.67			
Sb–N(1)		0.37	0.37	0.30
Sb–N(2)				0.27
Sb–N(3)				0.30
N–C		1.23–1.39	1.26–1.34	1.29–1.36
C–C		1.30–1.64	1.40–1.43 (1.05)	1.37–1.44 (1.05)
C–H		0.90–0.91	0.90–0.91	0.90–0.91

[a] Calculated using the B3LYP-D3(BJ) functional using the def2-TZVPPD-PP (Sb) and def2-TZVPPD (C, H, N, F) basis set.

Table B.7. Gas-phase atomic coordinates (Å) of [SbF₄(phen)]⁺

1	1			
	Sb	-0.000071	-1.571872	-0.000000
	F	1.891179	-1.429183	-0.000000
	F	-1.891203	-1.427726	-0.000000
	F	-0.000789	-2.760574	1.459196
	N	0.000593	0.136831	1.353194
	C	0.000131	1.330092	0.714141
	C	0.000737	0.070640	2.679785
	H	0.001502	-0.916041	3.120391
	C	0.000324	1.237187	3.450020
	H	0.000187	1.153904	4.526387
	C	-0.000122	2.545100	1.418858
	C	-0.000156	2.465148	2.826866
	H	-0.000269	3.374749	3.412500
	C	-0.000225	3.770227	0.679265
	H	-0.000678	4.703194	1.225469
	N	0.000593	0.136831	-1.353194
	C	0.000131	1.330092	-0.714141
	C	0.000737	0.070640	-2.679785
	H	0.001502	-0.916041	-3.120391
	C	0.000324	1.237187	-3.450020
	H	0.000187	1.153904	-4.526387
	C	-0.000122	2.545100	-1.418858
	C	-0.000156	2.465148	-2.826866
	H	-0.000269	3.374749	-3.412500
	C	-0.000225	3.770227	-0.679265
	H	-0.000678	4.703194	-1.225469
	F	-0.000789	-2.760574	-1.459196

Table B.8. Gas-phase atomic coordinates (Å) of [SbF₄(bipy)]⁺.

1	1			
	Sb	-1.263215	0.000013	0.000000
	F	-1.128651	-1.891925	0.000000
	F	-1.128344	1.891936	0.000000
	F	-2.454339	0.000104	1.457366
	N	0.447098	-0.000072	1.337248
	C	1.657256	-0.000019	0.740289
	C	0.315253	-0.000094	2.670004
	H	-0.693994	-0.000140	3.054728
	C	1.429501	-0.000049	3.490540

H	1.302591	-0.000059	4.562524
C	2.804454	0.000027	1.519983
C	2.687187	0.000012	2.904973
H	3.576506	0.000061	3.519286
N	0.447098	-0.000072	-1.337248
C	1.657256	-0.000019	-0.740289
C	0.315253	-0.000094	-2.670004
H	-0.693994	-0.000140	-3.054728
C	1.429501	-0.000049	-3.490540
H	1.302591	-0.000059	-4.562524
C	2.804454	0.000027	-1.519983
C	2.687187	0.000012	-2.904973
H	3.576506	0.000061	-3.519286
F	-2.454339	0.000104	-1.457366
H	3.780819	0.000073	-1.062195
H	3.780819	0.000073	1.062195

Table B.9. Gas-phase atomic coordinates (Å) of SbF₅

0 1			
Sb	0.000000	0.000000	0.000000
F	0.000000	0.000000	1.882182
F	0.000000	1.874346	-0.000000
F	1.623232	-0.937173	-0.000000
F	-1.623232	-0.937173	-0.000000
F	0.000000	0.000000	-1.882182

Table B.10. Gas-phase atomic coordinates (Å) of CFC₃

0 1			
C	-0.000155	-0.000055	0.248194
F	-0.000200	-0.000433	1.592352
Cl	0.964582	-1.382075	-0.310295
Cl	-1.679605	-0.143858	-0.310309
Cl	0.715183	1.526181	-0.310004

Appendix C – Supporting Information for Chapter 4

Table C.1. Crystallographic Data collection and refinement parameters for [AsF₄(phen)][AsF₆]·2.5SO₂, [AsF₄(phen)][Sb₂F₁₁], (AsF₅)₂·bipy.

	[AsF ₄ (phen)][AsF ₆]·2.5SO ₂	[AsF ₄ (phen)][Sb ₂ F ₁₁]	(AsF ₅) ₂ ·bipy
Empirical formula	C ₁₂ H ₈ As ₂ F ₁₀ N ₂ O ₅ S _{2.5}	C ₁₂ H ₈ AsF ₁₅ N ₂ Sb ₂	C ₁₀ H ₈ As ₂ F ₁₀ N ₂
Formula weight	680.19	783.62	496.02
T (K)	100.4(9)	100.01(10)	100.01(10)
Crystal system	Triclinic	monoclinic	orthorhombic
Space group	<i>P</i> $\bar{1}$	<i>P</i> 2 ₁ / <i>n</i>	<i>Pbca</i>
a (Å)	8.3360(2)	9.1907(4)	8.4960(3)
b (Å)	11.2826(2)	19.4085(6)	11.4313(4)
c (Å)	11.8094(3)	11.4411(5)	30.3960(4)
α (°)	88.980(2)	90	90
β (°)	81.037(2)	106.835(6)	90
γ (°)	70.837(2)	90	90
V (Å ³)	1035.68(7)	1953.37(14)	2952.07(18)
Z	2	4	8
ρ_{calc} (g cm ⁻³)	2.181	2.665	2.232
μ (mm ⁻¹)	7.519	4.590	4.638
F(000)	660.0	1456.0	1904.0
Crystal size (mm ³)	0.27x0.11x0.07	0.44 × 0.16 × 0.11	0.23 × 0.17 × 0.09
Radiation	Cu K α (λ = 1.54184)	Mo K α (λ = 0.71073)	Mo K α (λ = 0.71073)
Goodness-of-fit on F ²	1.034	1.165	1.024
Final R indexes [I ≥ 2 σ (I)] ^a	R ₁ = 0.0251	R ₁ = 0.0436	R ₁ = 0.0263
	wR ₂ = 0.0617	wR ₂ = 0.0931	wR ₂ = 0.0480
Final R indexes [all data] ^a	R ₁ = 0.0271	R ₁ = 0.0614	R ₁ = 0.0390
	wR ₂ = 0.0627	wR ₂ = 0.1027	wR ₂ = 0.0510
Largest diff. peak/hole (e Å ⁻³)	0.48/−0.49	1.64/−0.95	0.48/−0.37
CCDC	2308827	2308828	2308826

$$^a R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|. \quad wR_2 = [\sum [w(F_o^2 - F_c^2)^2] / \sum w(F_o^4)]^{1/2}$$

Table C.2. Vibrational frequencies (cm^{-1}) of phen and $[\text{AsF}_4(\text{phen})]^+$.

Phen		$[\text{AsF}_4(\text{phen})]^+$		Tentative Assignment ^[e]	
Exptl ^{[a],[c]}	Calcd ^{[b],[c]}	Exptl ^{[a],[d]}	Exptl ^{[a],[e]}	Calcd ^[b]	
3092sh	3191(618)[0] 3191(<1)[41]	3172(2) 3165(2) 3115(6)	3126(3) 3111(5)	3229(244)[26] 3229(37)[10] 3215(286)[5] 3215(11)[4] 3202(212)[<1] 3192(129)[0] 3192(70)[<1] 3188(19)[1]	C-H stretching modes, combination bands and overtones
3063(20)	3176(210)[26]	3094(11)	3085(5)		
3052(12)	3165(165)[1] 3164(27)[13] 3157(21)[<1]	3073(4) 3068(4)	3071(4)		
3029(6)	3128(185)[27] 3137(123)[21]	3047(3)			
2992(4)					
2970(2)					
1619(6)	1657(27)[9]	1651(6)	1650(6)	1659(62)[13] 1648(61)[8] 1623(42)[16] 1618(1)[15]	
1609(10)	1646(42)[9]	1637(26) 1626(20)	1635(19) 1627(19)		
1590(16)	1632(51)[9]	1586(7)	1586(7)		
1560(11)	1589(32)[15]				
1537(2)					C-N and C-C stretching modes + in-plane ring deformations
1503(17)	1536(76)[40] 1534(5)[8]	1528(9)	1528(9)	1556(34)[53]	
1448(30)	1483(42)[1]			1526(0)[20] 1485(109)[0] 1472(2)[76] 1460(271)[20] 1454(11)[5] 1380(4)[4]	
1413(35)	1455(5)[47] 1450(8)[1]	1462(100)	1462(100)		
1406 sh	1412(373)[0]	1438(sh)	1436(sh)		
1400(100)					
1343(11)	1379(83)[2]	1420(11)	1420(10)		
1314 sh	1337(11)[1]		1409(sh)		
1293(43)	1321(93)	1338(16)	1334(18)	1361(5)[10] 1356(54)[5] 1279(11)[<1]	
1268(4)	1297(9)[1]	1253(7)	1251(7)		

499(1)	507(1)[<1]	503(5)	503(9)	519(0)[<1]	in-plane ring deformation
461(3)	466(2)[<1]			507(4)[<1]	
429(2)	442(1)[0]			474(0)[<1]	out-of-plane ring deformation
407(21)	414(18)[2]			444(1)[0]	
401 sh	412(1)[0]	445(19)	444(22)	441(27)[11]	in-plane ring deformation
		435(sh)			
		388(3)		380(1)[104]	$\delta(\text{AsF}_{2,\text{ax}}) + \delta(\text{AsF}_{2,\text{eq}})$
		379(4)			
		370(6)		358(1)[20]	$\rho(\text{AsF}_{2,\text{eq}})$
		342(8)	341(12)	330(4)[25]	
				327(<1)[0]	$\delta(\text{AsF}_{2,\text{ax}}) + \delta(\text{AsN}_2)$
				321(<1)[45]	
253 sh	241(1)[0]	335(sh)			$\tau(\text{AsF}_{2,\text{ax}}) + \tau(\text{AsF}_{2,\text{eq}})$
242(10)	240(3)[4]	284(7)		278(1)[0]	
		269(4)	267(7)	277(1)[4]	ring twisting + $\tau(\text{AsF}_{2,\text{eq}})$
		242(sh)			
		232(6)	231(11)	250(2)[3]	$\delta(\text{AsF}_{2,\text{ax}}) - \delta(\text{AsF}_{2,\text{eq}})$
	234(<1)[3]			234(0)[5]	
		218(7)	217(9)	209(2)[<1]	$\rho(\text{AsF}_{2,\text{ax}}) + \text{ring rocking}$
		203(4)		198(3)[<1]	
				184(<1)[0]	twisting mode
142(15)				170(<1)[<1]	$\rho(\text{AsF}_{2,\text{eq}}) + \text{ring rocking}$
120(24)					
100(36)		114(21)	108(13)	104(0)[3]	lattice and twisting modes
				90(0)[0]	
				60(5)[2]	

[a] Recorded in flame sealed m.p. capillaries at ambient temperature. Normalised Raman intensities are given in parentheses. Shoulders are denoted sh. [b] Calculated using the B3LYP functional with the aug-cc-pVTZ-PP (As) and aug-cc-pVTZ (C, H, N, F) basis sets. Absolute Raman intensities ($\text{\AA}^4 \text{u}^{-1}$) are given in parentheses and IR intensities (km mol^{-1}) are given in square brackets. [c] From reference 1 [d] From $[\text{AsF}_4(\text{phen})][\text{AsF}_6]$. Bands corresponding to $[\text{AsF}_6]^-$ are observed at 680(16), 538(2) [d] From $[\text{AsF}_4(\text{phen})][\text{Sb}_2\text{F}_{11}]$. Bands corresponding to $[\text{Sb}_2\text{F}_{11}]^-$ are observed at 680(17), 649(19), 295(8), 281(9). Band corresponding to $\text{SbF}_5 \cdot \text{SO}_2$ observed at 603(9). [e] Abbreviations denote stretch (ν), bend (δ), rock (ρ), twist (τ), and wag (ω).

Table C.3. Vibrational frequencies (cm^{-1}) of bipy and $(\text{AsF}_5)_2\cdot\text{bipy}$

bipy		$(\text{AsF}_5)_2\cdot\text{bipy}$		Tentative assignments
Exptl. ^{[a],[c]}	Calcd. ^{[b],[c]}	Exptl. ^[a]	Calcd. ^[b]	
3144(1)				C–H stretching modes, combination bands and overtones
3120(2)				
3088 sh	3197(457)[7]	3157(13)	3255(49)[14] 3255(105)[9]	
3076(6)	3195(27)[22]	3152(13)	3230(119)[<1] 3230(42)[1]	
3064(10)	3190(182)[6]	3118(30)	3213(318)[0] 3213(34)[1]	
3052(5)	3187(13)[21]	3100(37) 3086(sh)	3194(99)[1] 3194(76)[2]	
3046(5)	3171(36)[9]			
3030(1)	3170(48)[4]			
3008(3)	3145(146)[21]			
2957(1)	3144(96)[26]			
1759(1)				
1676(1)				
1633(2)				
1613(5)	1628(3)[79]	1644(7)	1652(60)[20]	C–N and C–C stretching modes and in-plane ring deformations
1590(83)	1627(383)[5] 1617(3)[5]	1616(44)	1646(2)[49] 1615(22)[11]	
1573(85)	1607(13)[33]	1580(25) 1572(sh)	1611(4)[25]	
1548(1)				
1531(1)				
1483(29)	1512(87)[6] 1503(0)[29] 1468(2)[54]	1513(11) 1446(18)	1537(6)[4] 1515(<1)[77] 1479(12)[4]	
1447(49)	1459(26)[5]		1468(1)[41]	
1331 sh	1334(4)[4]	1340(16)	1340(7)[2]	
1310 sh				
1302(32)	1335(88)[0]		1333(3)[17]	
1294 sh				
1237(36)	1298(155)[0]	1313(42) 1302(38)	1322(58)[4]	
1217(5)	1285(1)[3]		1272(<1)[<1] 1270(<1)[24]	
1202 sh	1279(2)[<1] 1180(3)[2]	1184(18)	1198(3)[16]	
1147(10)	1176(7)[6] 1131(2)[9]	1179(18)	1194(4)[2] 1149(<1)[3]	ring-breathing mode (s) ring-breathing mode (as) out-of-plane ring deformations
1096(4)	1115(1)[2]	1124(9)	1141(1)[2]	
1092 sh	1101(1)[2]		1114(<1)[18]	
1045(16)	1073(42)[7] 1059(2)[7]	1098(10) 1084(29) 1054(12) 1049(12)	1101(31)[7] 1071(6)[14]	
	1018(2)[<1] 1018(<1)[0]			
995(100)	1010(82)[5] 1009(2)[2] 990(<1)[<1] 987(0)[1]	1039(100) 1025(16) 1019(sh)	1046(43)[10] 1040(2)[9] 1037(4)[<1] 1035(2)[20]	

815(4)	917(3)[<1]		1007(0)[2]	} out-of-plane ring deformations
	912(0)[<1]		1006(<1)[<1]	
	837(3)[5]		922(1)[2]	
			920(0)[1]	
744(1)	781(<1)[48]	767(23)	800(1)[38]	} out-of-plane ring deformations
	766(<1)[44]		794(2)[62]	
	763(2)[7]		786(4)[1]	
764(19)	671(2)[5]		784(<1)[12]	} in-plane ring deformation
	784(12)[0]		775(3)[3]	
		691(63)	715(1)[270]	$v(\text{AsF1}) + v(\text{AsF2}+\text{AsF3}) - v_s(\text{AsF4}+\text{AsF5})$
			713(13)[206]	$v(\text{AsF1})$
			711(1)[58]	$v(\text{AsF1}) - v(\text{AsF2}+\text{AsF3}) - v(\text{AsF4}+\text{AsF5})$
			707(2)[152]	$v(\text{AsF1}) + v(\text{AsF2}+\text{AsF4})$
			706(<1)[17]	$v(\text{AsF1}) + v_s(\text{AsF2}+\text{AsF4}) + v_s(\text{AsF3}+\text{AsF5})$
			703(0)[186]	$v(\text{AsF1}) + v(\text{AsF3}+\text{AsF5}) - v(\text{AsF2}+\text{AsF4})$
614(12)	641(2)[10]	659(87)	669(<1)[2]	} in-plane ring deformation
	626(6)[5]		663(2)[5]	
		648(25)	662(8)[5]	$v_s(\text{AsF}_{4\text{cis}})$
		638(35)	632(1)[1]	
		632(34)	632(40)[8]	
		591(22)	577(1)[4]	
			577(2)[<1]	
550(1)	570(2)[1]		563(1)[3]	} out-of-plane ring deformation
	508(0)[3]		561(1)[3]	
439(3)	420(6)[<1]	409(31)	475(0)[14]	} out-of-plane ring deformation
	409(1)		473(2)[6]	
	417(<1)[6]		394(4)[1]	
			381(0)[56]	$\delta(\text{F2AsF5})$
			378(1)[3]	
			375(1)[73]	
			371(1)[99]	
			364(1)[10]	
			363(1)[19]	
			363(1)[19]	
		382(37)	356(2)[10]	$\omega(\text{F2AsF3})$
		369(sh)	356(1)[141]	$\text{AsF}_{4\text{cis}}$ umbrella mode
			350(<1)[10]	ring deformation
333(2)	369(<1)[1]	348(40)	337(7)[12]	ring deformation
	320(3)[0]		306(<1)[10]	$\tau(\text{F3AsF5}) + \delta(\text{F2AsF4}) +$ ring deformation mode
		308(29)	291(1)[2]	$\tau(\text{F2AsF4}) + \delta(\text{F3AsF5})$
			288(<1)[<1]	$\tau(\text{F3AsF5}) - \delta(\text{F2AsF4}) -$ ring deformation mode
			277(0)[3]	$\tau(\text{F2AsF4}) - \delta(\text{F3AsF5})$
224(10)	253(3)[<1]		240(<1)[6]	ring twisting mode
			229(1)[0]	$\omega(\text{F2AsF4}) + \omega(\text{F3AsF5})$
		257(sh)	226(<1)[2]	$\omega(\text{F2AsF4}) - \omega(\text{F3AsF5})$
		246(44)	217(1)[1]	$\omega(\text{F2AsF4}) + \omega(\text{F3AsF5}) +$ ring rocking
		227(35)	193(1)[7]	$\omega(\text{F2AsF4}) + \omega(\text{F3AsF5}) -$ ring rocking
		197(54)	173(3)[1]	$\rho(\text{F2AsF3}) + \rho(\text{F4AsF5})$
		183(43)	160(1)[5]	$\rho(\text{F2AsF3}) + \rho(\text{F4AsF5}) +$ ring rocking
			160(2)[1]	$\rho(\text{F2AsF3}) + \rho(\text{F4AsF5}) +$ ring rocking

	154(32)	135(1)[1]	$\rho(\text{F2AsF3}) - \rho(\text{F4AsF5})$
	148(32)		
	124(sh)	125(2)[<1]	$\rho(\text{F2AsF3}) - \rho(\text{F4AsF5}) + \text{ring rocking}$
125(3)[2]			} twisting modes
102(44)	108(88)	112(<1)[1]	
		86(5)[1]	
		69(3)[5]	
		61(3)[<1]	
		44(1)[0]	
		40(0)[1]	
		35(1)[3]	

[a] Recorded in flame sealed m.p. capillaries at ambient temperature. Normalised Raman intensities are given in parentheses. Shoulders are denoted sh. [b] Calculated using the B3LYP functional with the aug-cc-pVTZ-PP (As) and aug-cc-pVTZ (C, H, N, F) basis sets. Absolute Raman intensities ($\text{\AA}^4 \text{u}^{-1}$) are given in parentheses and IR intensities (km mol^{-1}) are given in square brackets. [c] From Turnbull, D.; Wetmore, S. D.; Gerken, M. Stabilization of $[\text{WF}_5]^+$ by Bidentate N-Donor Ligands. *Angew. Chem. - Int. Ed.*, **2019**, 58, 13035–13038; *Angew. Chem.*, **2019**, 131, 13169–13172.

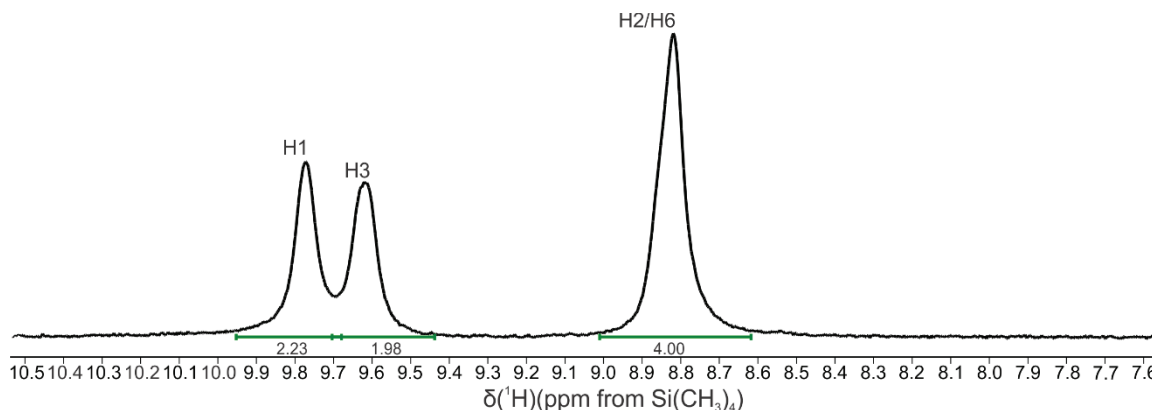


Figure C.1 ^1H NMR spectrum of $[\text{AsF}_4(\text{phen})][\text{AsF}_6]$ recorded in SO_2 at $-60\text{ }^\circ\text{C}$. Atom labelling as shown in Figure 4.9

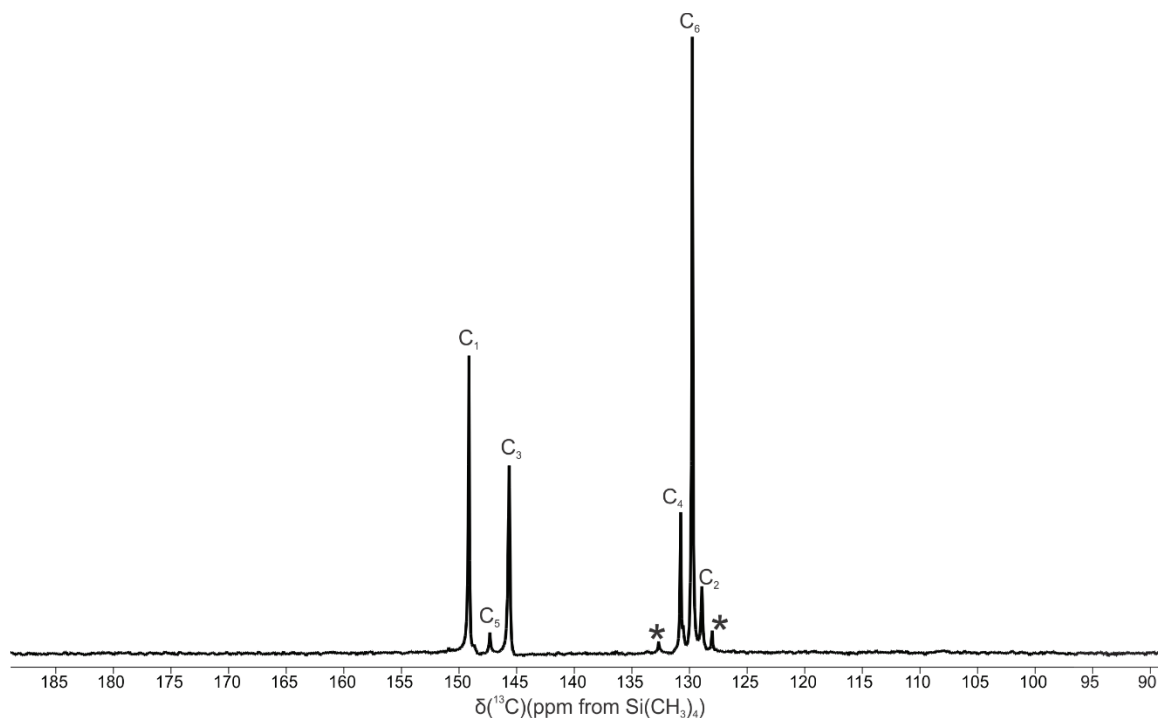


Figure C.2. ^{13}C $\{^1\text{H}\}$ NMR spectrum of $[\text{AsF}_4(\text{phen})][\text{AsF}_6]$ recorded in SO_2 at $-30\text{ }^\circ\text{C}$. (*) denotes unknown impurity. Assignments based on Pazderski, L.; Toušek, J.; Sitkowski, J.; Kozerski, L.; Marek, R.; Szłyk, E. ^1H , ^{13}C and ^{15}N NMR coordination shifts in gold(III), cobalt(III), rhodium(III) chloride complexes with pyridine, 2,2'-bipyridine and 1,10-phenanthroline. *Magn. Reson. Chem.*, **2007**, 45, 24–36. Atom Labelling as shown in Figure 4.9

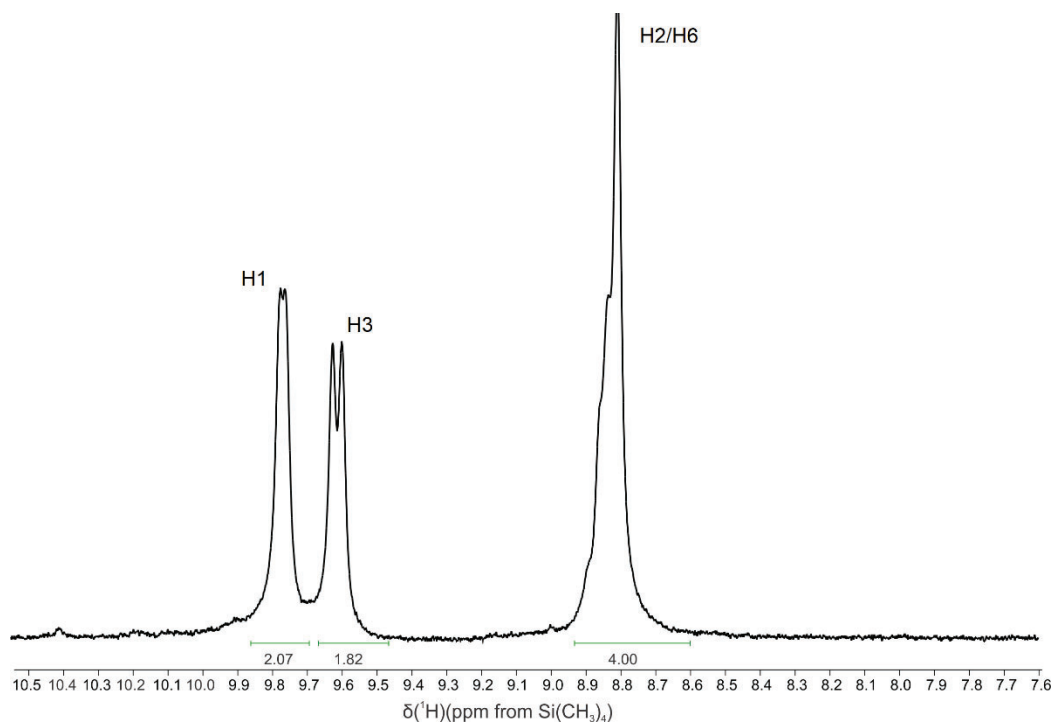


Figure C.3. ^1H NMR spectrum of $[\text{AsF}_4(\text{phen})][\text{Sb}_2\text{F}_{11}]$ recorded in SO_2 at $-65\text{ }^\circ\text{C}$. Atom labelling as shown in Figure 4.9

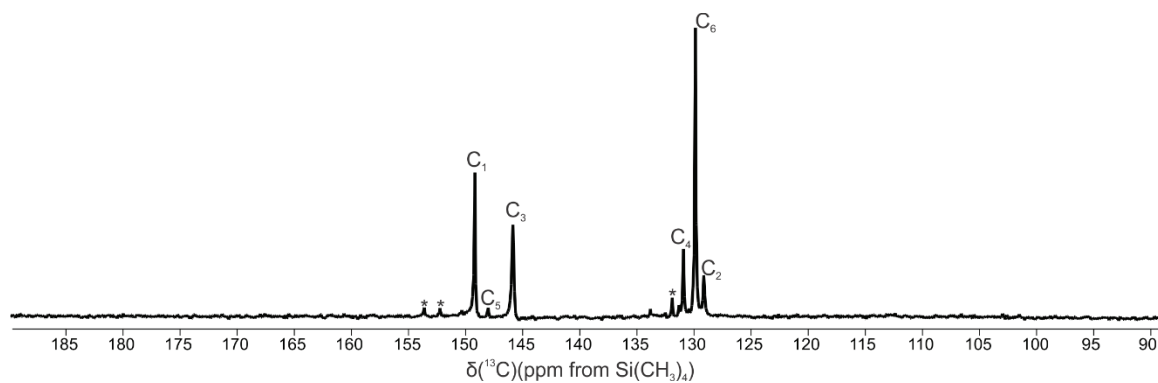


Figure C.4. $^{13}\text{C} \{^1\text{H}\}$ NMR spectrum of $[\text{AsF}_4(\text{phen})][\text{Sb}_2\text{F}_{11}]$ recorded in SO_2 at $-30\text{ }^\circ\text{C}$. (*) denotes unknown impurity. Assignments based on Pazderski, L.; Toušek, J.; Sitkowski, J.; Kozerski, L.; Marek, R.; Szłyk, E. ^1H , ^{13}C and ^{15}N NMR coordination shifts in gold(III), cobalt(III), rhodium(III) chloride complexes with pyridine, 2,2'-bipyridine and 1,10-phenanthroline. *Magn. Reson. Chem.*, **2007**, 45, 24–36. Atom Labelling as shown in Figure 4.9

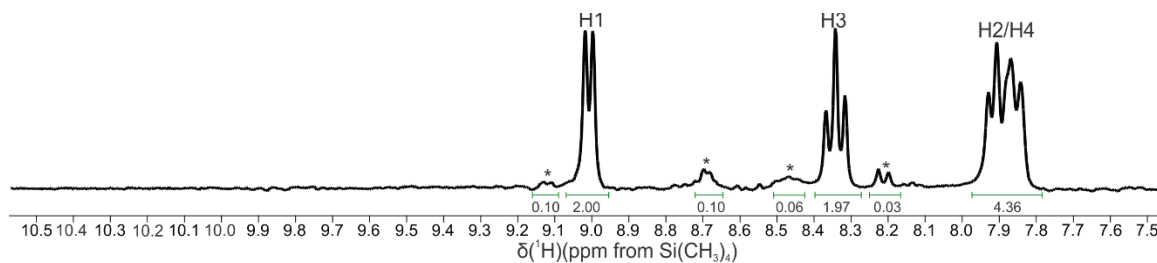


Figure C.5. ^1H NMR spectrum of $(\text{AsF}_5)_2\cdot\text{bipy}$ recorded in CH_3CN at $-40\text{ }^\circ\text{C}$. (*) denotes resonances corresponding to $[\text{H-bipy}][\text{AsF}_6]$ impurity. Atom labelling as shown in Figure 4.9

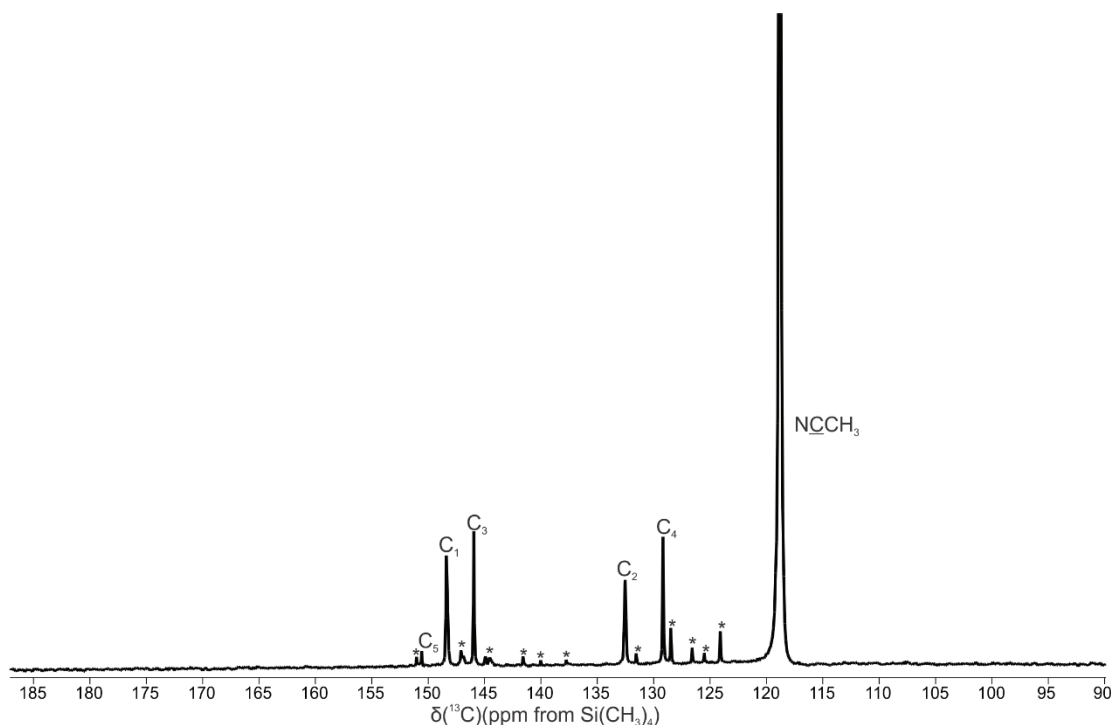


Figure C.6. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of $(\text{AsF}_5)_2\cdot\text{bipy}$ recorded in CH_3CN at $-30\text{ }^\circ\text{C}$. (*) denotes resonances corresponding to $[\text{H-bipy}][\text{AsF}_6]$ and $\text{AsF}_5\cdot\text{CH}_3\text{CN}$ impurities. Assignments based on Pazderski, L.; Toušek, J.; Sitkowski, J.; Kozerski, L.; Marek, R.; Szłyk, E. ^1H , ^{13}C and ^{15}N NMR coordination shifts in gold(III), cobalt(III), rhodium(III) chloride complexes with pyridine, 2,2'-bipyridine and 1,10-phenanthroline. *Magn. Reson. Chem.*, **2007**, 45, 24–36. Atom labelling as shown in Figure 4.9

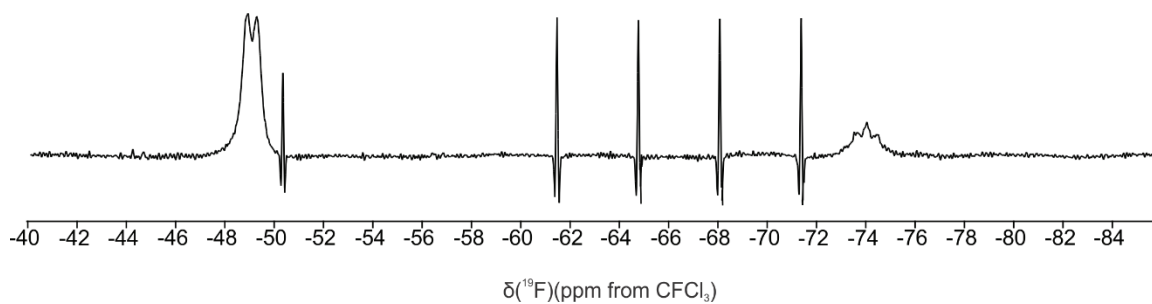


Figure C.7. The ^{19}F NMR spectrum of $(\text{AsF}_5)_2\cdot\text{bipy}$ recorded in CH_3CN at $-40\text{ }^\circ\text{C}$ after Gaussian multiplication (line broadening = -90 Hz , Gaussian broadening = 40 Hz) of the FID.

Table C.4. Natural population analysis charges and Wiberg valences^[a] for various fluoroarsenic species.^[b]

	AsF ₅	[AsF ₄] ⁺	[AsF ₆] [−]	[AsF ₄ (phen)] ⁺	AsF ₅ ·py
As(1)	2.69 [3.19]	2.78 [3.09]	2.65 [3.25]	2.55 [3.30]	2.61 [3.27]
F(1)	−0.55 [0.76]	−0.45 [0.92]	−0.61 [0.67]	−0.56 [0.75]	−0.56 [0.75]
F(2)	−0.53 [0.80]	−0.45 [0.92]	−0.61 [0.67]	−0.56 [0.75]	−0.59 [0.71]
F(3)	−0.53 [0.80]	−0.45 [0.92]	−0.61 [0.67]	−0.55 [0.77]	−0.59 [0.71]
F(4)	−0.53 [0.80]	−0.45 [0.92]	−0.61 [0.67]	−0.55 [0.77]	−0.59 [0.71]
F(5)	−0.55 [0.78]		−0.61 [0.67]		−0.59 [0.71]
F(6)			−0.61 [0.67]		
N(1)				−0.53 [3.39]	−0.50 [3.36]
C(1)				0.13 [3.88]	0.10 [3.90]
C(2)				−0.21 [3.95]	−0.23 [3.96]
C(3)				−0.08 [3.94]	−0.12 [3.95]
C(4)				−0.12 [4.07]	−0.23 [3.96]
C(5)				0.28 [3.97]	0.10 [3.90]
C(6)				−0.09 [3.96]	
H(1)				0.25 [0.94]	0.25 [0.94]
H(2)				0.25 [0.94]	0.23 [0.95]
H(3)				0.24 [0.95]	0.22 [0.95]
H(4)				0.22 [0.97]	0.23 [0.95]
H(5)					0.25 [0.94]
Σ(L) ^[c]				0.68	0.30

[a] number in brackets. [b] Calculated using the B3LYP-D3(BJ) functional using the def2-TZVPPD-PP (Sb) and def2-TZVPPD (C, H, N, F) basis set. Values are given for one half of bipy and phen ligands as the two halves are symmetry related. Atomic labelling is as seen in figure S5. [c] Total NPA charge for the terpy, phen and bipy ligands.

Table C.5. Optimised gas-phase atomic coordinates (Å) for [AsF₄(phen)]⁺

1 1			
F	-1.728428	1.522958	0.000000
F	1.728435	1.522745	0.000000
F	0.000079	2.774095	1.286361
N	-0.000057	0.104265	1.314551
C	-0.000041	-1.100659	0.709528
C	-0.000045	0.200790	2.637877
H	-0.000060	1.194773	3.058918
C	-0.000014	-0.956154	3.425680
H	-0.000009	-0.852079	4.500252
C	-0.000005	-2.305902	1.423933
C	0.000013	-2.199393	2.830104
H	0.000044	-3.094867	3.437035
C	0.000015	-3.530592	0.680327
H	0.000036	-4.465235	1.223660
N	-0.000057	0.104265	-1.314551
C	-0.000041	-1.100659	-0.709528
C	-0.000045	0.200790	-2.637877
H	-0.000060	1.194773	-3.058918
C	-0.000014	-0.956154	-3.425680
H	-0.000009	-0.852079	-4.500252
C	-0.000005	-2.305902	-1.423933
C	0.000013	-2.199393	-2.830104
H	0.000044	-3.094867	-3.437035
C	0.000015	-3.530592	-0.680327
H	0.000036	-4.465235	-1.223660
F	0.000079	2.774095	-1.286361
As	0.000006	1.646454	0.000000

Table C.6. Optimised gas-phase atomic coordinates (Å) for (AsF₅)₂·bipy.

0 1			
As	-2.550726	-0.309030	-0.633922
As	2.550533	0.308730	-0.634052
F	2.740985	1.280012	0.802235
F	-1.083847	-1.151430	-1.009770
F	1.083681	1.151372	-1.009507
F	3.506227	1.354828	-1.592968
F	-3.924869	0.631047	-0.121007
F	3.924804	-0.631459	-0.121605
F	2.265196	-0.818576	-1.915597
F	-2.740449	-1.280171	0.802535
F	-2.265817	0.818325	-1.915460
F	-3.506563	-1.355315	-1.592446
N	-1.384145	1.004058	0.559752
N	1.384394	-1.003828	0.559810
C	-0.285838	0.693547	1.286855
C	1.844314	-2.264993	0.572236
H	2.699487	-2.461237	-0.050723
C	1.272878	-3.257210	1.344770
H	1.683913	-4.254769	1.312102
C	0.286302	-0.692955	1.287083
C	-1.844263	2.265139	0.571957
H	-2.699638	2.461042	-0.050837
C	-0.298600	-1.641093	2.113702
H	-1.160391	-1.362405	2.697505
C	0.299156	1.642017	2.113037
H	1.161091	1.363614	2.696759
C	0.194868	-2.935058	2.149139
H	-0.268978	-3.676649	2.784001
C	-0.194459	2.935932	2.148159
H	0.269463	3.677805	2.782637
C	-1.272770	3.257681	1.344038
H	-1.683958	4.255174	1.311256

Table C.7. Optimised gas-phase atomic coordinates (Å) for AsF₅

0 1			
As	0.000000	0.000000	0.000000
F	0.000000	0.000000	1.702317
F	0.000000	1.680014	-0.000000
F	0.000000	0.000000	-1.702317
F	1.454935	-0.840007	-0.000000
F	-1.454935	-0.840007	-0.000000

Table C.8. Optimised gas-phase atomic coordinates (Å) for $[\text{AsF}_6]^-$

-1	1		
As	0.000000	0.000000	0.000000
F	-0.000000	-0.000000	1.739244
F	-0.000000	1.739244	-0.000000
F	1.739244	-0.000000	0.000000
F	-0.000000	-0.000000	-1.739244
F	-0.000000	-1.739244	0.000000
F	-1.739244	-0.000000	-0.000000

Table C.9. Optimised gas-phase atomic coordinates (Å) for $[\text{Si}(\text{CH}_3)_3]^+$

1	1		
Si	0.000004	-0.000019	-0.000008
C	1.604118	-0.862698	0.000005
H	2.184466	-0.548260	-0.875486
H	2.184574	-0.548053	0.875349
H	1.507046	-1.947717	0.000132
C	-1.549201	-0.957814	0.000002
H	-2.440265	-0.331157	-0.000035
H	-1.567059	-1.617766	-0.875383
H	-1.567078	-1.617676	0.875456
C	-0.054918	1.820530	-0.000002
H	-0.617589	2.165943	-0.875356
H	-0.617425	2.165906	0.875476
H	0.933287	2.278940	-0.000074

Table C.10. Optimised gas-phase atomic coordinates (Å) for $\text{FSi}(\text{CH}_3)_3$

0	1		
Si	-0.000003	0.000009	0.028059
C	-1.567568	0.836453	-0.522750
H	-1.614982	1.863184	-0.153693
H	-1.627353	0.868682	-1.613474
H	-2.446837	0.303837	-0.154183
C	0.059364	-1.775700	-0.522954
H	0.061394	-1.843430	-1.613690
H	0.960223	-2.270942	-0.154417
H	-0.806152	-2.330132	-0.154022
C	1.508169	0.939290	-0.522807
H	1.486740	1.966992	-0.154022
H	2.421046	0.466788	-0.153982
H	1.565823	0.975162	-1.613532
F	0.000039	-0.000059	1.642584

Table C.11. Optimised gas-phase atomic coordinates (Å) for SbF₅

0 1			
Sb	0.000000	0.000000	-0.000002
F	-0.000000	1.849921	0.000006
F	0.000000	0.000000	1.859335
F	1.602079	-0.924961	0.000006
F	-1.602079	-0.924961	0.000006
F	0.000000	0.000000	-1.859343

Table C.12. Optimised gas-phase atomic coordinates (Å) for [SbF₆]⁻

-1 1			
Sb	0.000000	0.000000	0.000000
F	0.000000	-0.000000	1.895568
F	0.000000	1.895568	-0.000000
F	1.895568	-0.000000	0.000000
F	0.000000	-0.000000	-1.895568
F	0.000000	-1.895568	0.000000
F	-1.895568	-0.000000	-0.000000

Appendix D – Supporting Information for Chapter 5

Table D.1. Crystallographic data collection and refinement parameters for [SF₃(py)][OTf], [SF(dmap)₄][OTf]₃·2CH₃CN and [FPPPh₃][OTf]

	[SF ₃ (py)][OTf]	[SF(DMAP) ₄][OTf] ₃ ·2CH ₃ CN	[FPPPh ₃][OTf]
Chemical formula	C ₆ H ₅ F ₆ NO ₃ S ₂	C ₃₄ H ₄₆ F ₇ N ₁₀ O ₆ S ₃	C ₁₉ H ₁₅ F ₄ O ₃ PS
Formula weight	317.23	919.99	430.34
Temperature (°C)	−173.03(14)	−173.03(10)	−173.00(10)
Crystal system	monoclinic	triclinic	monoclinic
Space group	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> $\bar{1}$	<i>P</i> 2 ₁ / <i>n</i>
<i>a</i> (Å)	10.0459(3)	10.9683(4)	11.0808(2)
<i>b</i> (Å)	11.5599(3)	15.2609(6)	8.60930(10)
<i>c</i> (Å)	10.6351(3)	15.3299(3)	19.8802(3)
α (°)	90	89.284(2)	90
β (°)	116.169(4)	89.508(2)	93.7990(10)
γ (°)	90	69.460(3)	90
<i>V</i> (Å ³)	1108.45(6)	2402.67(14)	1892.36(5)
<i>Z</i>	4	2	4
ρ_{calc} (g cm ^{−3})	1.901	1.272	1.510
μ (mm ^{−1})	5.253	2.084	2.848
F(000)	632.0	958.0	880.0
Crystal size (mm ³)	0.3 × 0.19 × 0.15	0.36 × 0.27 × 0.24	0.5 × 0.28 × 0.24
Radiation	Cu K α (λ = 1.54184)	Cu K α (λ = 1.54184)	Cu K α (λ = 1.54184)
Goodness-of-fit on F ²	1.059	1.033	1.062
Final R indexes [<i>I</i> ≥ 2 σ (<i>I</i>)] ^[a]	R ₁ = 0.0304, wR ₂ = 0.0765	R ₁ = 0.0998, wR ₂ = 0.2913	R ₁ = 0.0443, wR ₂ = 0.1109
Final R indexes [all data]	R ₁ = 0.0342, wR ₂ = 0.0789	R ₁ = 0.1135, wR ₂ = 0.3034	R ₁ = 0.0483, wR ₂ = 0.1134
Largest diff. peak/hole (e Å ^{−3})	0.42/−0.43	0.90/−0.53	0.81/−0.43
CCDC	2451985	2451987	2451986

$$R_1 = \sum ||F_o| - |F_c| | / \sum |F_o|, wR_2 = [\sum [w(F_o^2 - F_c^2)^2] / \sum w(F_o^4)]^{1/2}$$

Table D.2. Crystallographic data collection and refinement parameters of $[\text{SF}_2(\text{dmap})_2][\text{SbF}_6]_2 \cdot \text{CH}_3\text{CN}$ and $[\text{SF}(\text{dmap})_4][\text{SbF}_6] \cdot 2\text{CH}_3\text{CN}$.

	$[\text{SF}_2(\text{dmap})_2][\text{SbF}_6]_2 \cdot \text{CH}_3\text{CN}$	$[\text{SF}(\text{dmap})_4][\text{SbF}_6] \cdot 2\text{CH}_3\text{CN}$
Chemical formula	$\text{C}_{15}\text{H}_{23}\text{F}_{14}\text{N}_5\text{SSb}_2$	$\text{C}_{36}\text{H}_{52}\text{F}_{19}\text{N}_{12}\text{SSb}_3$
Formula weight	868.01	1411.20
Temperature ($^\circ\text{C}$)	$-120(3)$	$-120(2)$
Crystal system	Monoclinic	Monoclinic
Space group	$C2/c$	$C2/c$
a ($\text{\AA}$)	12.6807(8)	15.8420(7)
b ($\text{\AA}$)	10.6001(8)	17.1860(7)
c ($\text{\AA}$)	21.8940(14)	19.5841(10)
α ($^\circ$)	90	90
β ($^\circ$)	107.219(7)	107.412(5)
γ ($^\circ$)	90	90
V ($\text{\AA}^3$)	2811.0(3)	5087.7(4)
Z	4	4
ρ_{calc} (g cm^{-3})	2.051	1.842
μ (mm^{-1})	2.111	1.734
$F(000)$	1680	2768.0
Crystal size (mm^3)	$0.21 \times 0.22 \times 0.36$	$0.15 \times 0.19 \times 0.33$
Radiation	Mo $\text{K}\alpha$ ($\lambda = 0.71073$)	Mo $\text{K}\alpha$ ($\lambda = 0.71073$)
Goodness-of-fit on F^2	1.294	1.231
Final R indexes [$I \geq 2\sigma(I)$] ^[a]	$R_1 = 0.0530$, $wR_2 = 0.0962$	$R_1 = 0.0651$, $wR_2 = 0.1048$
Final R indexes [all data]	$R_1 = 0.0574$, $wR_2 = 0.0976$	$R_1 = 0.0824$, $wR_2 = 0.1106$
Largest diff. peak/hole ($\text{e \AA}^{-3}$)	0.75/−1.27	0.95/−0.78
CCDC	2451988	2451989

$R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$. $wR_2 = [\sum [w(F_o^2 - F_c^2)^2] / \sum w(F_o^4)]^{1/2}$

Table D.3. Vibrational frequencies of py and [SF₃(py)]⁺

Pyridine		[SF ₃ (py)] ⁺		Approximate Description ^[e]	Mode
Exptl. ^[a]	Calcd. ^[b]	Exptl. ^{[c][d]}	Calcd. ^[b]		
3173(1)				} combination bands, and overtones	
3145(3)		3162(3)			
3091(5)		3110(6)			
3056(39)	3200(277)[7]	3094(20)	3226(269)[2]	} C–H stretching modes,	
3036 sh	3192(36)[24]		3223(48)[5]		
3025 sh	3177(95)[4]	3079(8)	3210(52)[4]		
2988(5)	3155(88)[4]		3205(48)[<1]		
2955(5)	3152(94)[27]	3022(4)	3182(39)[2]		
2908(1)					
2871(1)					
1597(5)	1627(14)[23]	1608(17)	1646(14)[41]	} C–C/C–N stretching modes and in-plane ring deformations	
1581(9)	1622(9)[10]	1581(9)	1619(9)[3]		
1573(7)		1510(4)			
1482(3)	1519(2)[2]	1487(5)	1524(5)[1]		
	1478(<1)[26]		1498(0)[55]		
	1390(<1)[<1]		1394(0)[5]		
	1287(1)[0]		1323(1)[4]		
1217(8)	1244(8)[4]	1238(11)	1234(5)[4]		
		1203(12)			
1146(2)	1173(2)[3]	1163(7)	1195(2)[3]		
1068(2)	1097(2)[3]		1117(1)[1]	} out-of-plane ring deformation	
	1080(<1)[<1]		1087(<1)[17]		
1030(75)	1055(41)[7]	1044(18)	1063(19)[29]		
	1027(<1)[0]		1055(0)[<1]	} symmetric ring breathing mode	
990(100)	1015(29)[5]	1017(61)	1039(37)[43]		
980(sh)	1012(0)[0]	1010(9)	1015(0)[0]	} out-of-plane ring deformation	
	964(<1)[0]		979(<1)[<1]		
	900(1)[0]		889(<1)[2]		
		860(73)	873(33)[119]	v _s (SF _{2eq})	
		848(31)	872(2)[136]	v _{as} (SF _{2eq})	
	767(0)[7]		783(<1)[37]	out-of-plane ring deformation	
		715(22)	752(14)[661]	v(SF _{ax})	
	719(<1)[64]		705(0)[38]	out-of-plane ring deformation	
652(5)	672(3)[<1]	647(18)	662(4)[8]	in-plane ring deformation	
	619(2)[4]	639(9)	659(4)[<1]	in-plane ring deformation	
603(3)				in-plane ring deformation	
		531(11)	525(1)[54]	δ _s (SF ₃)	
406(1)	421(1)[4]		467(<1)[2]	out-of-plane ring deformation	
			464(1)[47]	δ(SF _{2eq})	
			411(0)[5]	δ(F _{ax} SN) + out-of-plane ring deformation	
	384(0)[0]	318(28)	400(0)[0]	out-of-plane ring deformation	
		280(5)	262(<1)[2]	ring rocking	

213(11)	247(1)[3]	$\delta(\text{SF}_{2\text{eq}})$ + ring rocking
198(18)	192(9)[39]	$\nu(\text{SN})$
186(12)	119(1)[1]	ring rocking mode
152(7)		
133(9)		
97(47)	86(2)[0]	ring rocking mode
	38(3)[0]	twisting mode

[a] From Turnbull, D.; Kostiuk, N.; Wetmore, S. D.; Gerken, M. Synthesis, Characterisation, and Computational Studies of Tungsten Hexafluoride Adducts with Pyridine and its Derivatives. *J. Fluor. Chem.* **2018**, *215*, 1–9. Normalised Raman intensities are given in parentheses. Shoulders are denoted sh. [b] Calculated at the B3LYP/def2-TZVPPD level of theory. Absolute Raman intensities ($\text{\AA}^4 \text{u}^{-1}$) are given in parentheses and IR intensities (km mol^{-1}) are given in square brackets. [c] Recorded in a $\frac{1}{4}$ "-o.d. FEP sample tube at -100°C . Bands corresponding to the FEP sample tube are observed at 1382(12), 1306(7), 1217(7), 751(8), 732(44), 575(sh), 386(11), 381(11), 294(13) cm^{-1} . [d] From $[\text{SF}_3(\text{py})][\text{OTf}]$. Bands corresponding to the $[\text{OTf}]^-$ anion observed at 1282(15), 1229(15), 1180(7), 1034(100), 762(26), 581(14) and 350(28) cm^{-1} . Bands corresponding to residual SO_2 are observed at 1330(17), 1150(80) and 522(sh) cm^{-1} . [e] Abbreviations denote stretch (ν), bend (δ), rock (ρ), twist (τ), and wag (ω).

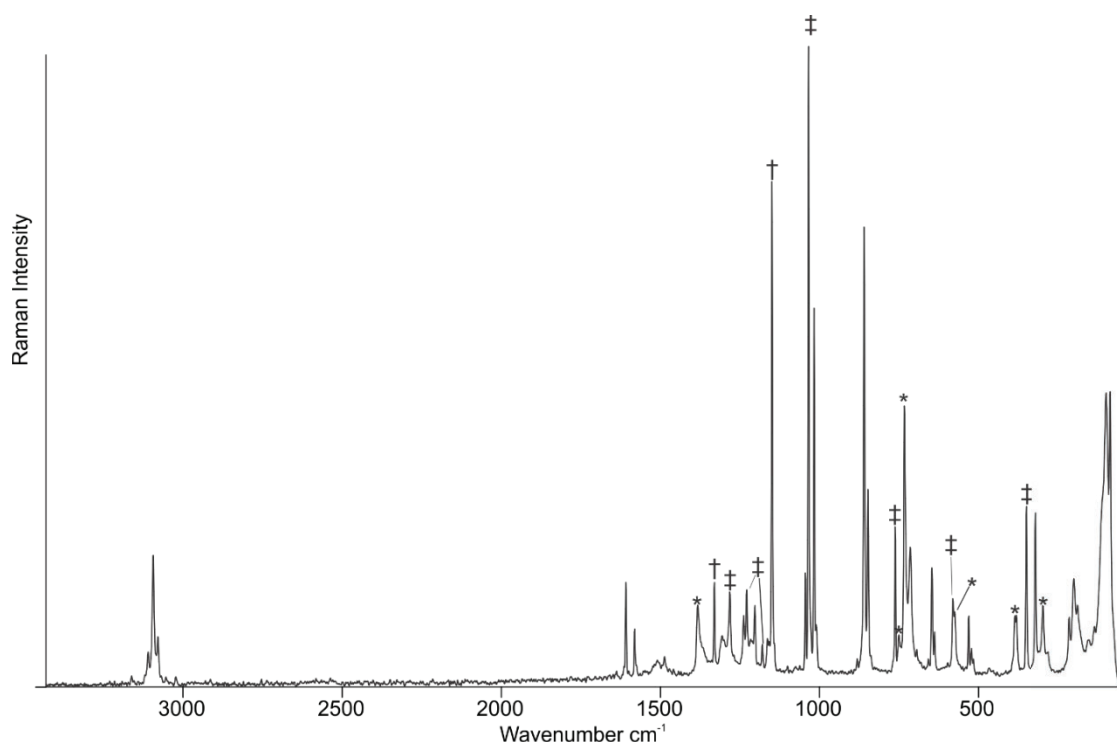


Figure D.1 Raman spectrum of $[\text{SF}_3(\text{py})][\text{OTf}]$. Asterisks (*), daggers (†) and double daggers (‡) denotes bands corresponding to FEP sample tube, SO_2 and $[\text{OTf}]^-$ anion, respectively.

Table D.4. Vibrational frequencies of DMAP and $[\text{SF}_2(\text{dmap})_2]^{2+}$

DMAP			[SF ₂ (dmap) ₂] ²⁺	Approximate Mode Description ^[d]
Exptl. ^[a]	Calcd. ^[b]	Exptl. ^[c] ^[d]	Calcd. ^[b]	
3089(16)	3219(13)[14]	3101(8)	3265(128)[<1]	aromatic C–H stretching modes
			3264(12)[26]	
3077sh	3219(154)[3]		3261(87)[20]	
			3260(34)[27]	
3034(14)	3147(147)[11]	3084(8)	3243(104)[0]	
			3243(7)[10]	
	3145(108)[38]	3034(6)	3242(8)[10]	
			3242(68)[5]	
2999(33)	3137(144)[31]	3001(22)	3187(170)[<1]	
2937sh			3187(123)[1]	
2910(21)	3125(1)[3]		3175(6)[<1]	ν(CH ₃)
			3175(6)[<1]	
2870(41)	3058(74)[46]		3118(52)[3]	
			3118(49)[4]	
2856(18)	3057(108)[13]		3116(100)[1]	
2842sh			3116(21)[2]	
2810(30)	2993(313)[67]	2859(41)	3053(907)[<1]	
			3053(4)[2]	
	2986(68)[73]	2820(6)	3050(113)[5]	
		2809(8)	3050(45)[8]	
1614(8)		1653(29)		in-plane ring and methyl deformations
1590(61)	1642(34)[318]	1642(20)		
		1636(25)		
1524(5)	1550(2)[116]	1592(46)	1688(286)[222]	
			1682(20)[1051]	
	1586(2)[45]	1574(23)	1617(174)[56]	
	1529(7)[14]		1616(70)[238]	
			1579(17)[8]	
			1578(2)[11]	
			1518(14)[<1]	
			1517(15)[8]	

		1037(16)	1036(5)[148]	ring-breathing comb.	antisym.
	1098(8)[0]	1016(25) 943(34)	1031(20)[6] 1010(16)[806]	in-plane ring deformations	
	1004(<1)[0]		994(1)[<1] 994(1)[12]	out-of-plane ring deformation	
949(31)	974(9)[8] 972(7)[9]		988(1)[2] 987(5)[1] 947(19)[0] 946(8)[27]	out-of-plane ring deformation	
810(2)	824(<1)[48]	831(8)	848(2)[54] 848(3)[66]	out-of-plane ring deformation	
827(5)	838(1)[0]	791(14)	810(4)[1] 808(1)[7]	out-of-plane ring deformation	
750(92)	768(18)[9] 755(<1)[1]	762(100) 705(6)	773(3)[<1] 772(57)[0] 723(5)[6] 721(4)[3]	in-plane ring deformation	
			692(<1)[148]	$\nu_{as}(SF_2)$ – in-plane ring deformation	
664(19)	685(3)[<1]	664(8)	666(4)[2] 644(1)[129]	in-plane ring deformation	
			638(49)[24] 609(4)[166]	$\nu_{as}(SF_2)$ + in-plane ring deformation $\nu_s(SN_2)$ $\nu_{as}(SN_2)$	
532(5)	555(<1)[5] 543(2)[15]	571(sh) 546(8)	561(16)[2] 514(<1)[13] 513(1)[19]	$\delta(SN_2)$ out-of-plane ring deformation	
481(12)	483(3)[3]	538(16)	510(4)[16] 497(1)[25]	$\nu_s(SF_2)$ out-of-plane ring deformation	

			483(3)[166]	$\delta(\text{SF}_2)$ + deformation	out-of-plane ring
			482(2)[18]	deformation	ring
	408(0)[0]		447(2)[<1]	out-of-plane ring deformation	
			440(<1)[1]		
402(16)			432(4)[0]	in-plane ring deformation	
	394(6)[<1]		422(<1)[3]	$\omega(\text{SN}_2)$	
			398(2)[55]	$\delta(\text{SF}_2)$	
		353(8)	376(9)[1]	$\rho(\text{SF}_2)$	
263(5)			318(<1)[8]	ring rocking mode	
	270(1)[7]		316(1)[0]		
			303(3)[6]	out-of-plane ring deformation	
			280(1)[<1]	Ring rocking mode	
			270(1)[0]	$\omega(\text{SF}_2)$	
	265(<1)[0]	256(12)	240(24)[2]		
	174(0)[<1]		187(2)[3]		
	142(2)[0]		179(<1)[0]		
153sh			172(3)[1]		
121(18)			164(1)[2]		
			156(2)[0]		
			148(<1)[1]		
			105(3)[1]		
			104(<1)[1]		
			79(1)[<1]		
				twisting and lattice modes	

[a] Recorded in flame sealed m.p. capillaries at ambient temperature. Normalised Raman intensities are given in parentheses. Shoulders are denoted sh. [b] Calculated at the B3LYP/def2-TZVPPD level of theory. Absolute Raman intensities ($\text{\AA}^4 \text{u}^{-1}$) are given in parentheses and IR intensities (kmol^{-1}) are given in square brackets. [c] Recorded in a $\frac{1}{4}$ " -o.d. FEP sample tube at -110°C . Bands corresponding to the sample tube are observed at 1383(22), 1305(10), 1216(10), 750(22), 732(90), 385sh, 382(25), and 294(30) cm^{-1} . [d] From $[\text{SF}_2(\text{dmap})_2][\text{SbF}_6]_2 \cdot \text{CH}_3\text{CN}$. Band corresponding to the $[\text{SbF}_6]^-$ anion observed at 645(75) and 279(31) cm^{-1} . Bands associated with CH_3CN observed at 2945(52), 2936(35), 2256(29), 2248(19), 922(12) and 382(25) {overlap with FEP band} cm^{-1} . [e] Abbreviations denote stretch (ν), bend (δ), rock (ρ), twist (τ), and wag (ω).

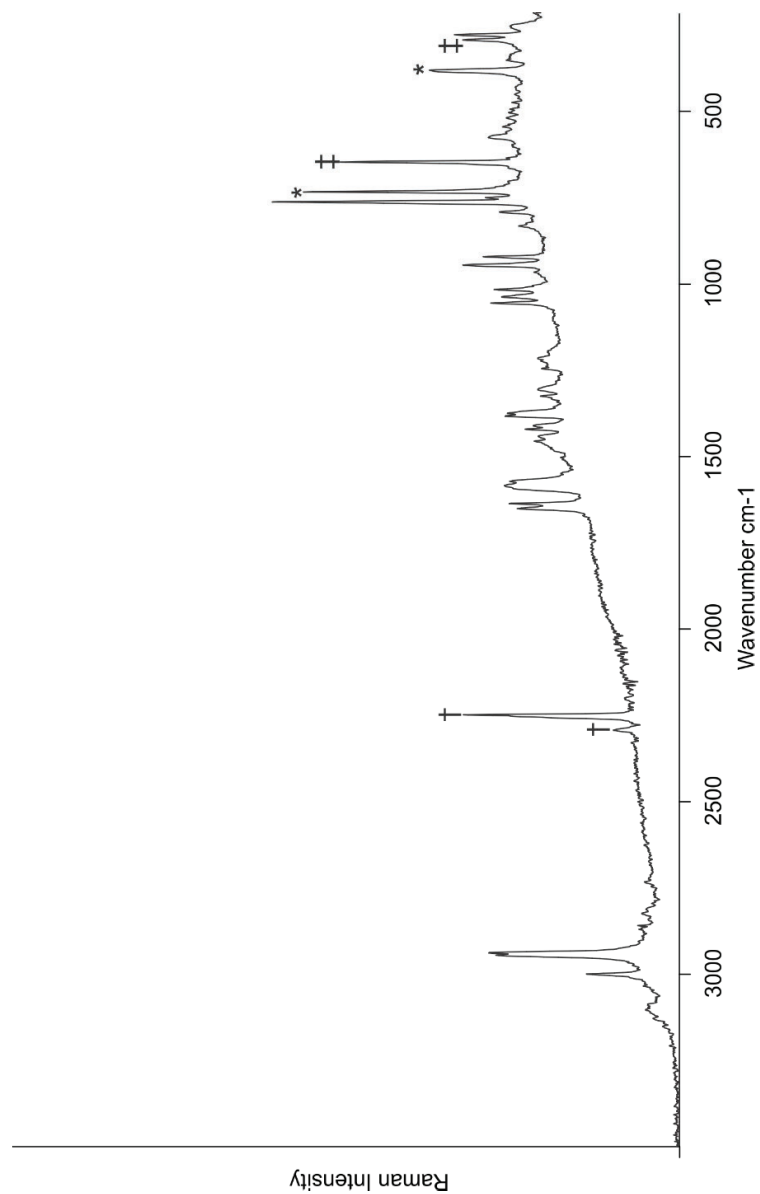


Figure D.2. Raman spectrum of $[\text{SF}_2(\text{dmap})_2][\text{SbF}_6]_2 \cdot \text{CH}_3\text{CN}$. Daggers ($\dagger$), double daggers ($\ddagger$) and asterisks ($*$) denote bands corresponding to CH_3CN , $[\text{SbF}_6]^-$ anion, and FEP sample tube, respectively.

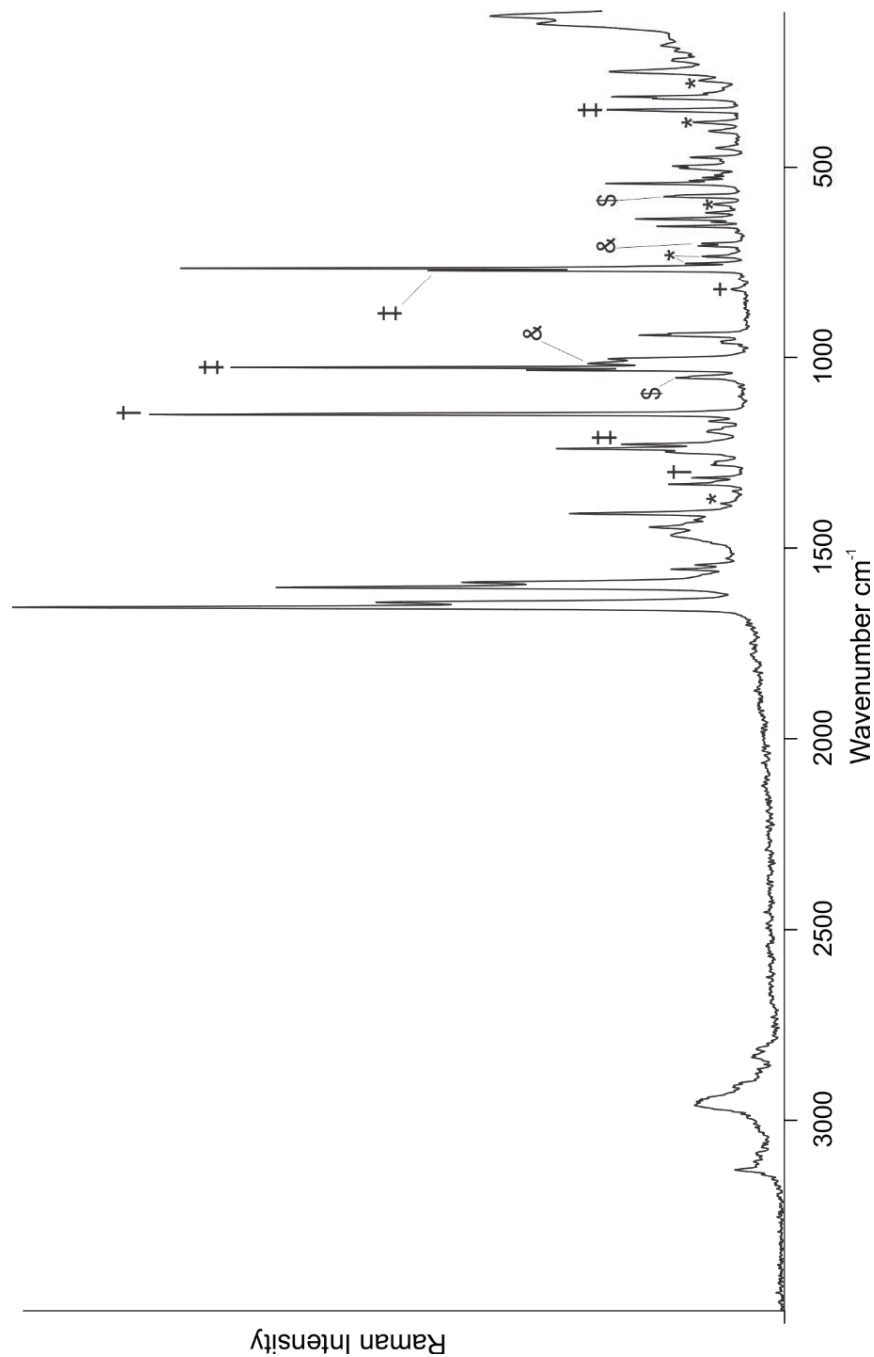


Figure D.3. Raman spectrum of the product of the reaction between SF_4 and $[(\text{CH}_3)_3\text{Si}(\text{dmap})][\text{OTf}]$. Asterisks (*), daggers (†) and double dagger (‡) denote bands corresponding to FEP sample tube, SO_2 and $[\text{OTf}]^-$ anion respectively. The bands denoted dollar sign (\$) correspond to the symmetric ring breathing mode (1054 cm^{-1}) and the $\nu_s(\text{SF}_2)$ (530 cm^{-1}) of the $[\text{SF}_2(\text{dmap})_2]^{2+}$ dication. The bands denoted ampersand (&) correspond to the symmetric ring breathing mode (1015 cm^{-1}), $\nu(\text{SF}_{\text{eq}})$ (821 cm^{-1}) and $\nu_s(\text{SF}_{2\text{ax}})$ ($702/698\text{ cm}^{-1}$) of the $[\text{SF}_3(\text{dmap})]^+$ cation.

2855(18) 2842sh	3038(360)[37]	2938(38)	3076(1607)[<1] 3075(3)[10] 3075(1)[10] 3075(53)[<1] 3072(17)[42] 3072(107)[6] 3072(109)[6] 3072(56)[<1]	v(CH ₃)
2810(30)	3031(31)[94]			
1614(8) 1590(61)	1667(42)[359]	1648(32)	1696(141)[7] 1684(5)[1711] 1684(5)[1711] 1680(1)[0] 1630(187)[2] 1628(1)[488] 1628(1)[488] 1627(200)[0] 1565(0)[64] 1562(<1)[0] 1560(1)[37] 1560(1)[37] 1553(2)[6] 1552(1)[0] 1551(5)[14] 1551(5)[14] 1506(23)[0] 1506(13)[0] 1505(3)[47] 1505(3)[47] 1488(45)[<1] 1488(6)[42] 1488(6)[42] 1488(<1)[23] 1482(1)[0] 1482(1)[<1] 1482(1)[<1] 1482(<1)[0]	C-C/C-N stretching modes and in-plane deformations
1524(5)	1562(3)[172]	1635(29)		v(C-N(CH ₃) ₂)
	1619(2)[55]			C-C/C-N stretching modes and in-plane deformations
	1504(<1)[2]	1574(36)		C-C/C-N stretching modes and in-plane deformations
1479(8)	1517(8)[31]			δ(CH ₃) + ring deformation
1465(11)	1474(10)[14]			δ(CH ₃)
	1473(5)[10]			

	1131(0)[2]	1074(0)[50] 1074(1)[8] 1074(1)[8] 1074(<1)[<1] 1141(0)[<1] 1141(<1)[1] 1141(0)[1] 1141(<1)[0] 1107(1)[0] 1107(<1)[0] 1107(<1)[0] 1107(<1)[0] 1163(1)[1] 1158(0)[0] 1156(<1)[9] 1156(<1)[9] 1083(41)[<1] 1061(60)[0] 1054(<1)[501] 1054(<1)[501] 1000(<1)[<1] 999(4)[<1] 999(<1)[4] 999(<1)[4] 1020(53)[1] 1014(20)[0] 1013(0)[685] 1013(0)[685] 992(4)[<1] 991(1)[8] 991(1)[8] 991(7)[0] 961(46)[<1] 960(20)[0] 960(<1)[15] 960(<1)[15]	C-C/C-N stretching modes and in-plane ring deformations CH ₃ deformations in-plane ring deformation out-of-plane ring deformation ring-breathing modes out-of-plane ring deformation in-plane deformation
1064(30)	1098(11)[1] 1076(<1)[15] 1012(<1)[0]		
985(100)	998(24)[35] 980(<1)[<1] 984(14)[11]	1054(42) 1014(20) 1001(sh) 946(55)	
949(31)			

	408(<1)[0]		440(<1)[0] 438(0)[12] 438(0)[12] 437(<1)[<1] 424(1)[262] 424(1)[262] 416(5)[<1] 414(7)[0] 353(8)[0] 353(0)[4] 353(0)[4] 324(3)[0] 316(2)[3] 307(<1)[12] 307(<1)[12] 271(<1)[44] 271(<1)[44] 264(14)[0] 251(<1)[<1] 203(<1)[65] 203(<1)[65] 201(<1)[0] 200(<1)[0] 199(<1)[35] 199(<1)[35] 188(1)[0] 179(1)[0] 169(3)[0] 169(<1)[1] 169(<1)[1] 169(<1)[1] 151(<1)[12] 151(<1)[12] 149(36)[0] 137(16)[0] 105(2)[0] 101(<1)[<1]	out-of-plane ring deformation out-of-plane ring deformation in-plane deformation $\omega(\text{N}(\text{CH}_3)_2)$ $\rho(\text{N}(\text{CH}_3)_2)$ twisting modes
402(16)	379(6)[<1]	315(58)		
	279(0)[4]			
	249(<1)[<1]	294(38)		
263(5)	223(1)[0]	263(31)		
153 ^{sh} 121(18)	155(1)[<1]	156(22) 139(8)		

86(1)[0] 49(0)[1]	101(<1)[<1] 99(1)[0] 98(2)[<1] 93(<1)[1] 93(<1)[1]	twisting modes
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[a] Recorded in flame sealed m.p. capillaries at ambient temperature. Normalised Raman intensities are given in parentheses. Shoulders are denoted sh. [b] Calculated at the MN15/def2-TZVPPD level of theory. Absolute Raman intensities ($\text{\AA}^4 \text{u}^{-1}$) are given in parentheses and IR intensities (km mol^{-1}) are given in square brackets. [c] Recorded in a $\frac{1}{4}$ ''-o.d. FEP sample tube at -110°C . Bands corresponding to the sample tube are observed at 1382(22), 751(sh), 732(71), 386(51) and 381(51) cm^{-1} . [d] From $[\text{SF(dmap)}_4][\text{OTf}]_3 \cdot 2\text{CH}_3\text{CN}$. Bands corresponding to the $[\text{OTf}]^-$ anion are observed at 1228(35), 1033(64), 762(100) and 350(59) cm^{-1} . Bands corresponding to CH_3CN are observed at 2248(22) and 920(33) cm^{-1} . [e] Abbreviations denote stretch (ν), bend (δ), rock (ρ), twist (τ), and wag (ω). [f] Overlaps with $[\text{OTf}]^-$ band

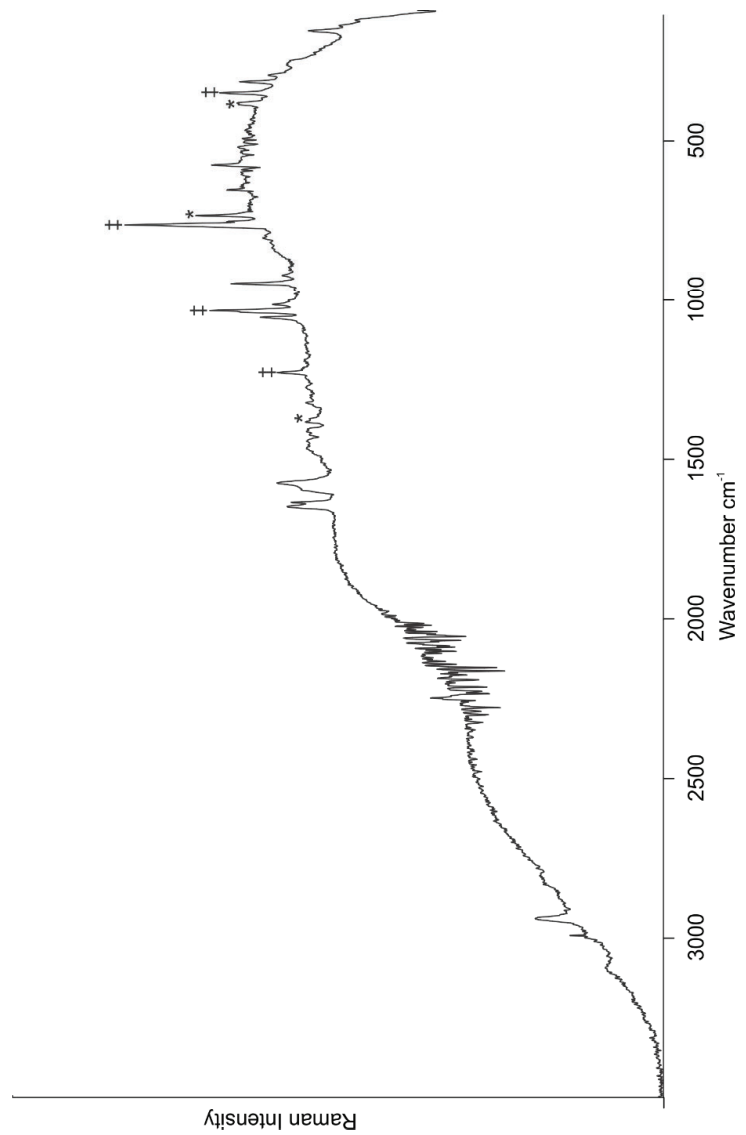


Figure D.4. Raman spectrum of $[\text{SF}(\text{dmap})_4][\text{OTf}]_3 \cdot \text{CH}_3\text{CN}$. Asterisks (*) and double daggers (‡) denote bands corresponding to FEP sample tube and $[\text{OTf}]^-$ anion, respectively.

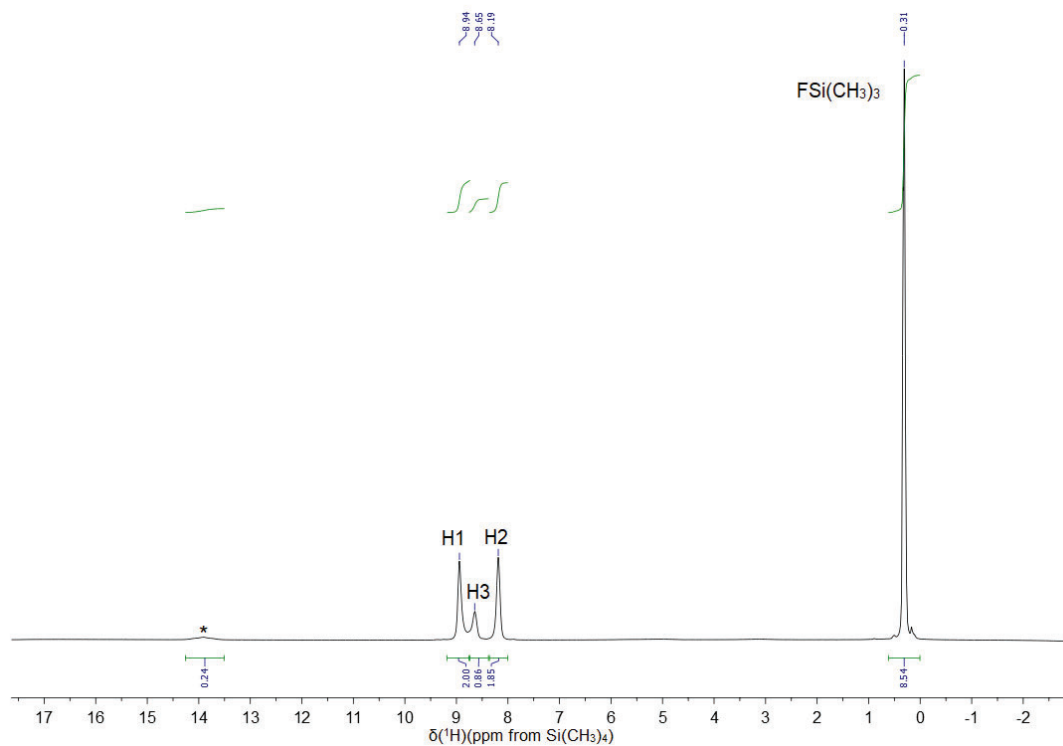


Figure D.5. ^1H NMR spectrum of $[\text{SF}_3(\text{py})][\text{OTf}]$ recorded in SO_2 at -54°C . The asterisk (*) denotes an $[\text{HNC}_5\text{H}_5]^+$ impurity.

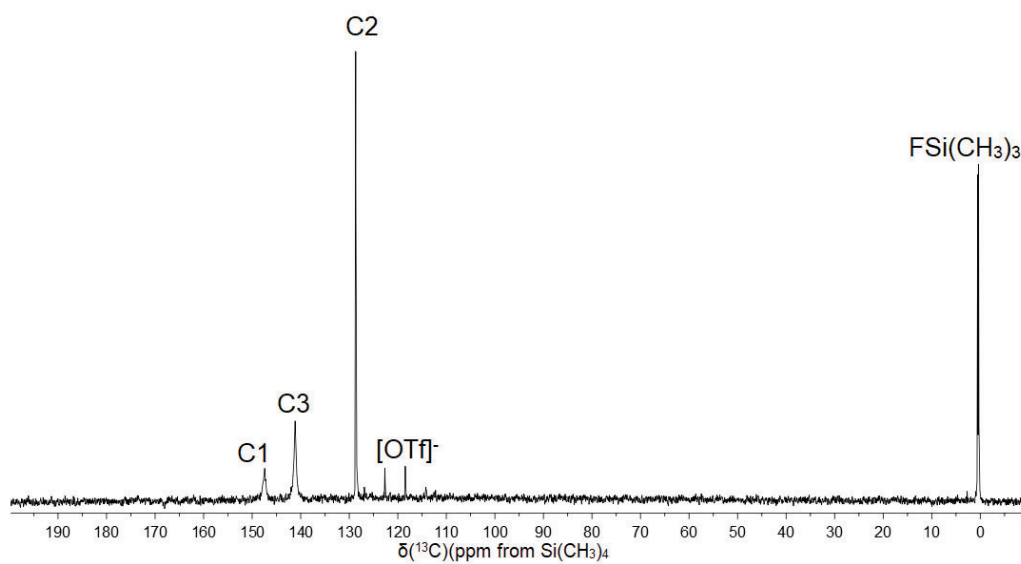


Figure D.6. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of $[\text{SF}_3(\text{py})][\text{OTf}]$ recorded in SO_2 at $-54\text{ }^\circ\text{C}$.

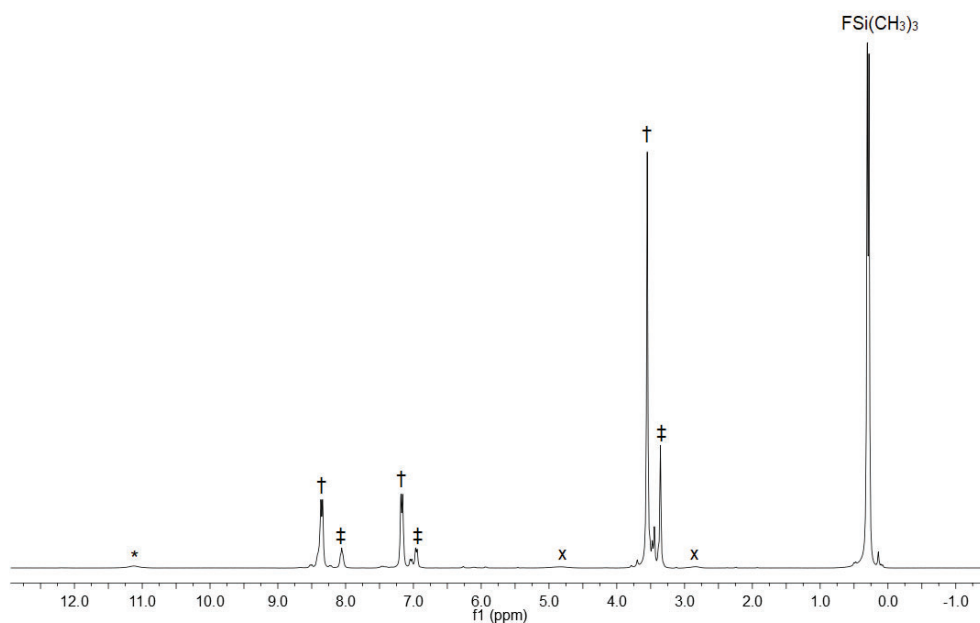


Figure D.7. ^1H NMR spectrum of the 1.5:1 reaction of SF_4 and $[(\text{CH}_3)_3\text{Si}(\text{dmap})][\text{OTf}]$, recorded in SO_2 at $-54\text{ }^\circ\text{C}$. Daggers ($\dagger$), double daggers ($\ddagger$) and asterisks ($*$) denote signals corresponding to $[\text{SF}_2(\text{dmap})_2]^{2+}$, $[\text{SF}_3(\text{dmap})]^+$ and $[\text{H-DMAP}]^+$, respectively.

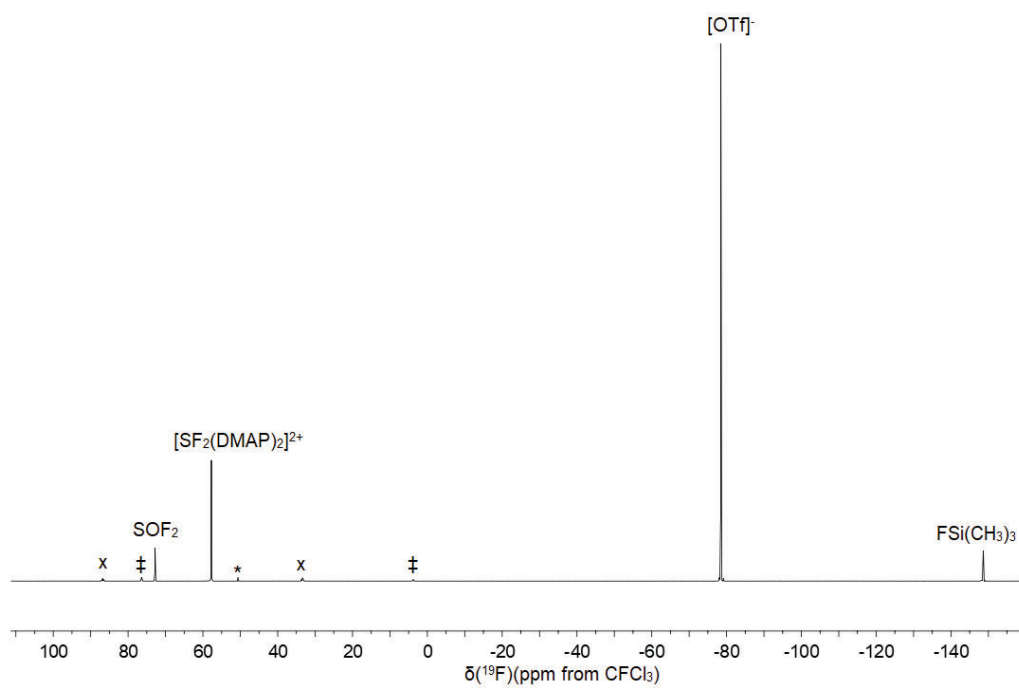


Figure D.8. ^{19}F NMR spectrum of the 1:2 reaction of SF_4 and $[(\text{CH}_3)_3\text{Si}(\text{dmap})][\text{OTf}]$, recorded in SO_2 at $-54\text{ }^\circ\text{C}$ after reacting at $-20\text{ }^\circ\text{C}$ for 6 hours. Double daggers ($\ddagger$), (x) and asterisk (*) denotes $[\text{SF}_3(\text{dmap})]^+$ (8 mol%), SF_4 (8 mol%) and an unknown impurity respectively.

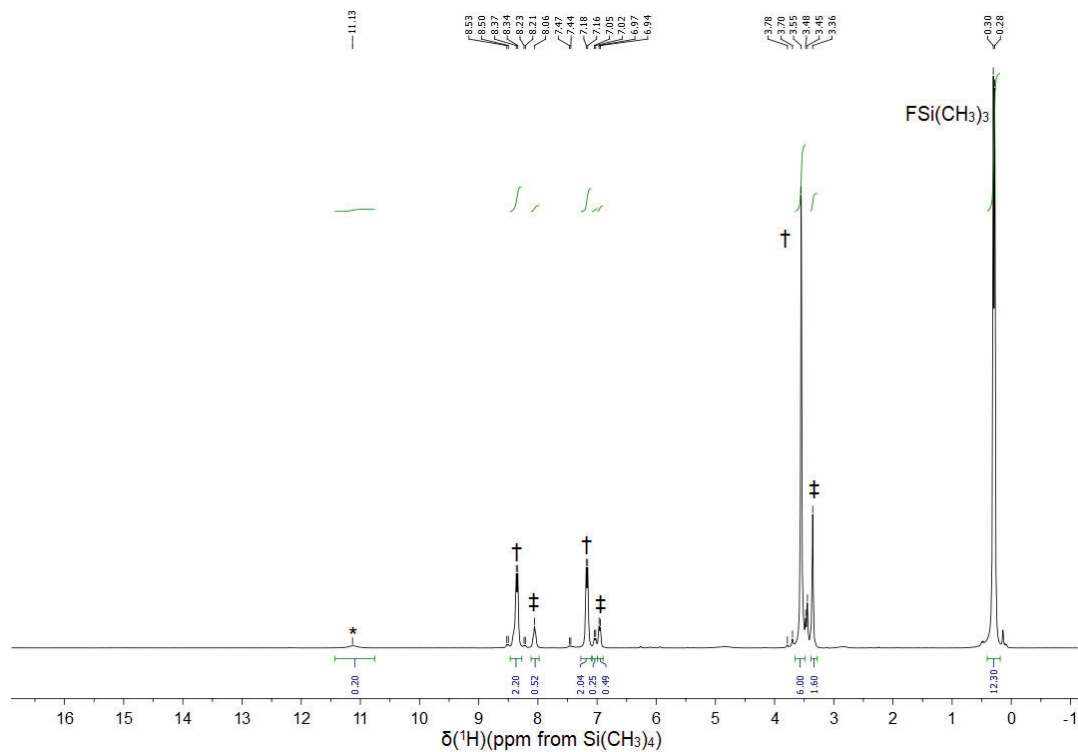


Figure D.9. ^1H NMR spectrum of the 1:2 reaction of SF_4 and $[(\text{CH}_3)_3\text{Si}(\text{dmap})][\text{OTf}]$, recorded in SO_2 at -54°C after reacting at -20°C for 6 hours. Daggers ($\dagger$), double daggers ($\ddagger$) and asterisks ($*$) denote signals corresponding to $[\text{SF}_2(\text{dmap})_2]^{2+}$, $[\text{SF}_3(\text{dmap})]^+$ and $[\text{H-DMAP}]^+$ and respectively.

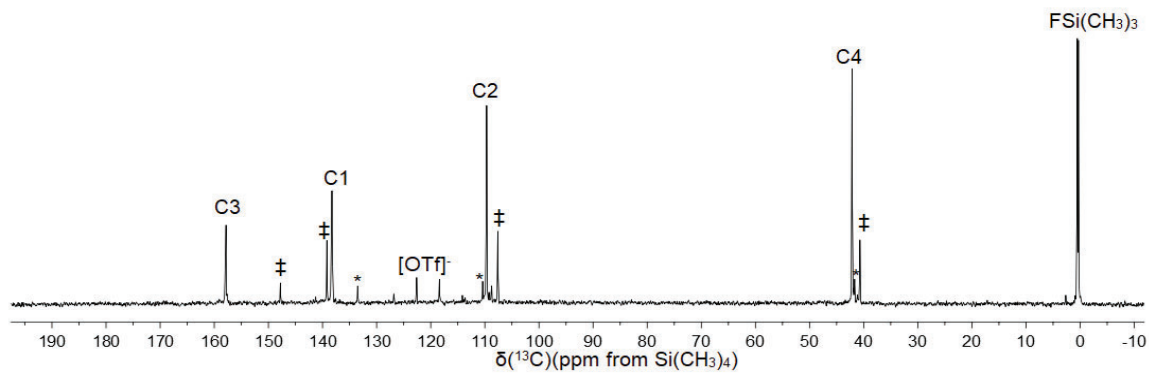


Figure D.10. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of the 1:2 reaction of SF_4 and $[(\text{CH}_3)_3\text{Si}(\text{dmap})][\text{OTf}]$, recorded in SO_2 at $-54\text{ }^\circ\text{C}$ after reacting at $-20\text{ }^\circ\text{C}$ for 6 hours. Double daggers ($\ddagger$) and asterisks (*) denote signals corresponding to $[\text{SF}_3(\text{dmap})]^+$, $[\text{H-DMAP}]^+$.

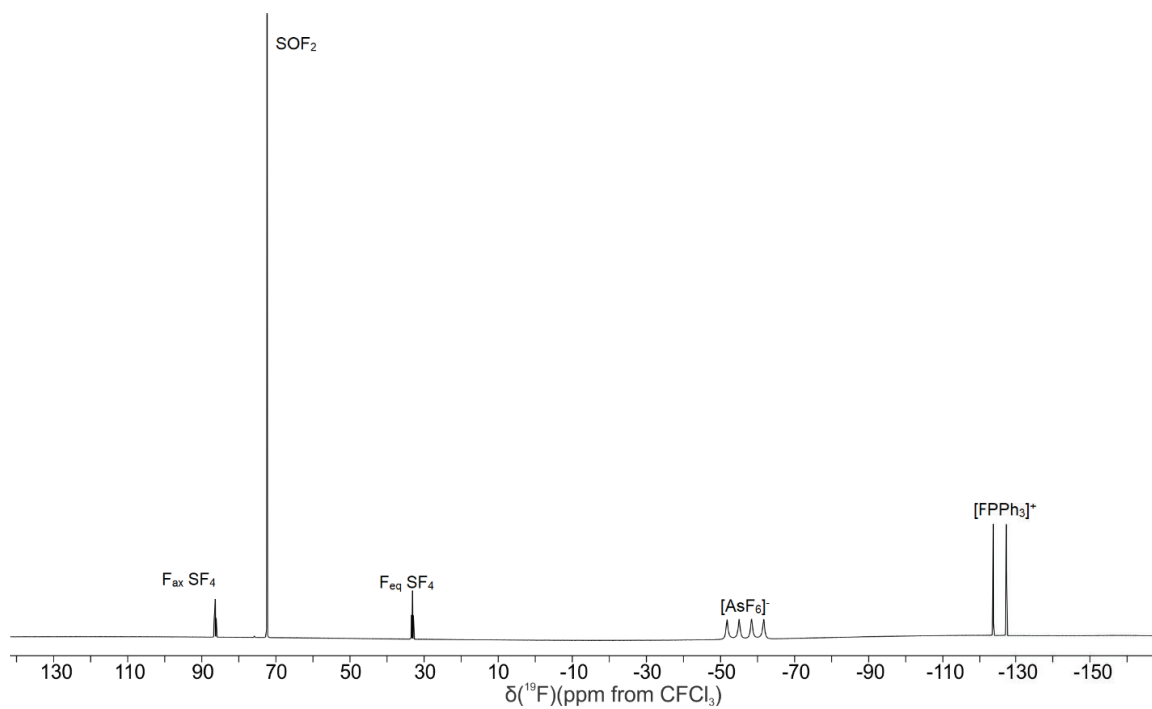


Figure D.11. ^{19}F NMR spectrum of the reaction between $[\text{SF}_3][\text{AsF}_6]$ and OPPh_3 recorded in SO_2 at $-60\text{ }^\circ\text{C}$.

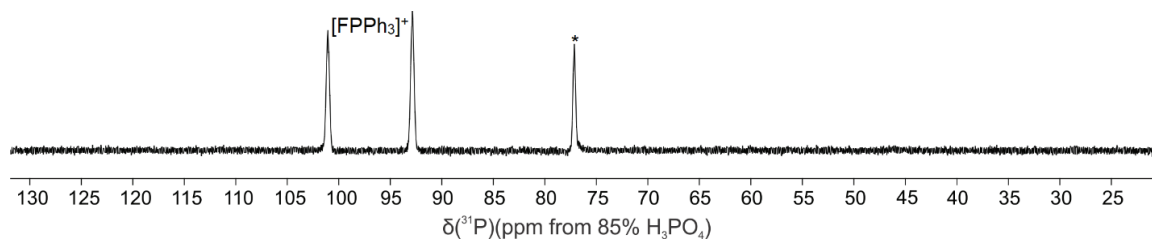


Figure D.12. ^{31}P NMR spectrum of the reaction between $[\text{SF}_3][\text{AsF}_6]$ and OPPh_3 recorded in SO_2 at -60°C . The asterisk (*) denotes an unconfirmed OPPh_3 species, possibly $\text{SF}_4\cdot\text{OPPh}_3$, $\text{AsF}_5\cdot\text{OPPh}_3$ or $[\text{SF}_2(\text{OPPh}_3)_2]^{2+}$.

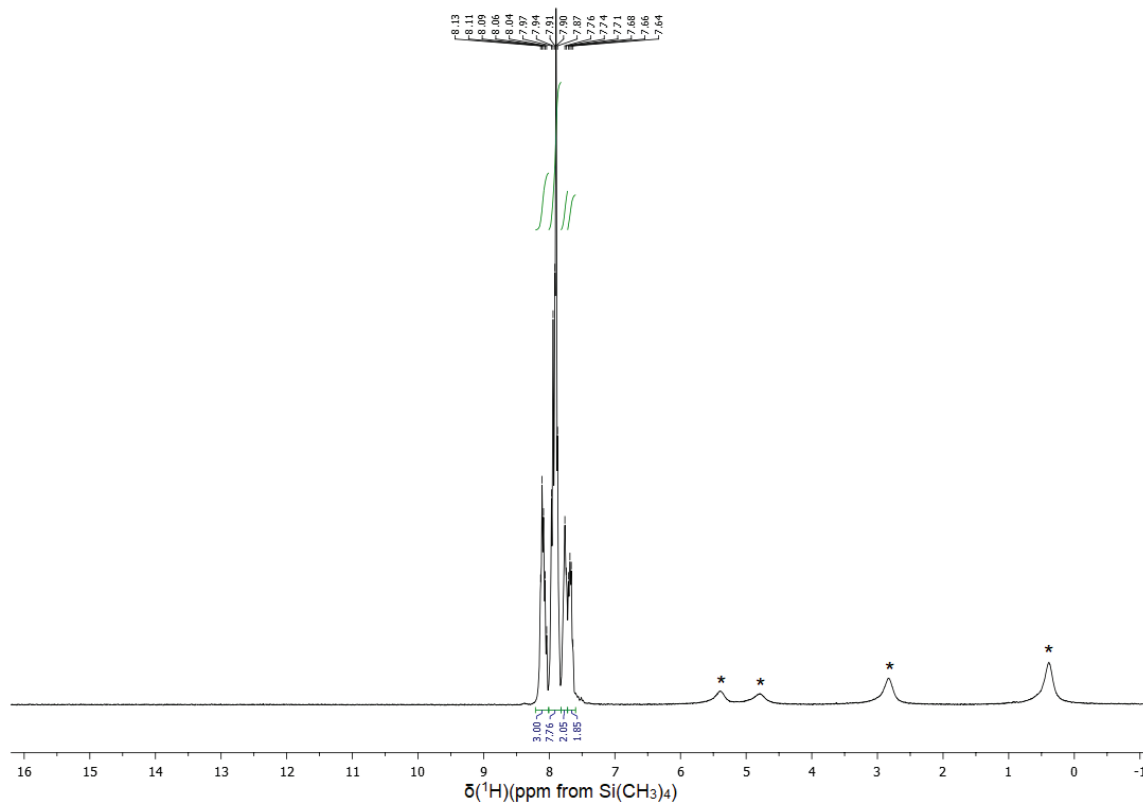


Figure D.13. ^1H NMR spectrum of the reaction between $[\text{SF}_3][\text{AsF}_6]$ and OPPh_3 recorded in SO_2 at -60°C . Asterisks (*) denote water/ethanol coating the outside of the 4-mm FEP sample tube.

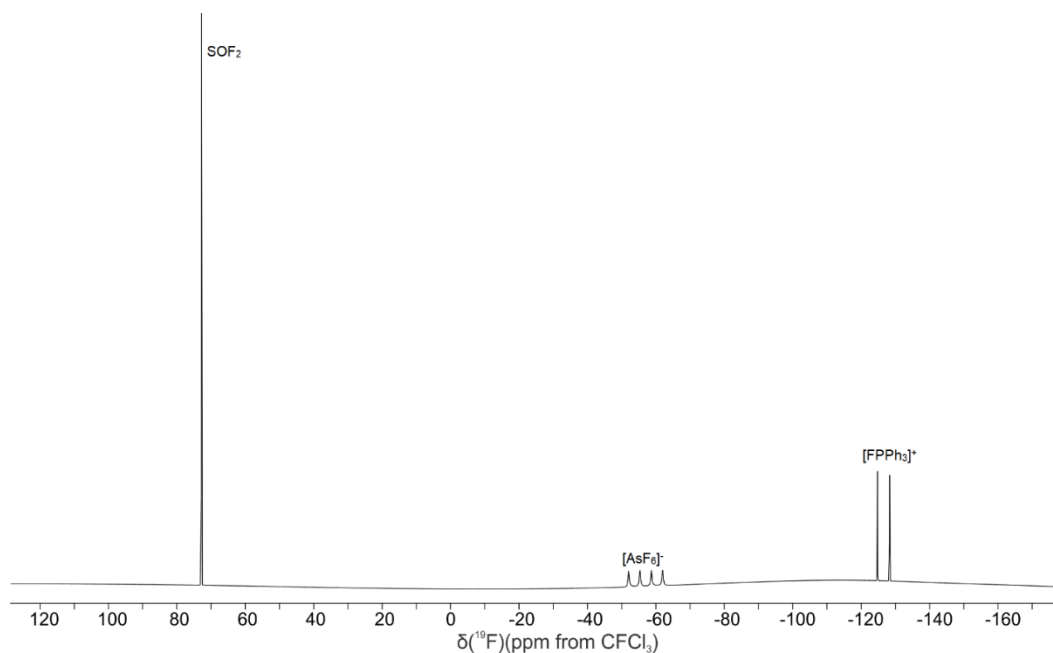


Figure D.14. ^{19}F NMR spectrum of the reaction between $[\text{SF}_3][\text{AsF}_6]$ and OPPh_3 recorded in SO_2 at -60°C after being warmed to RT for 15 min.

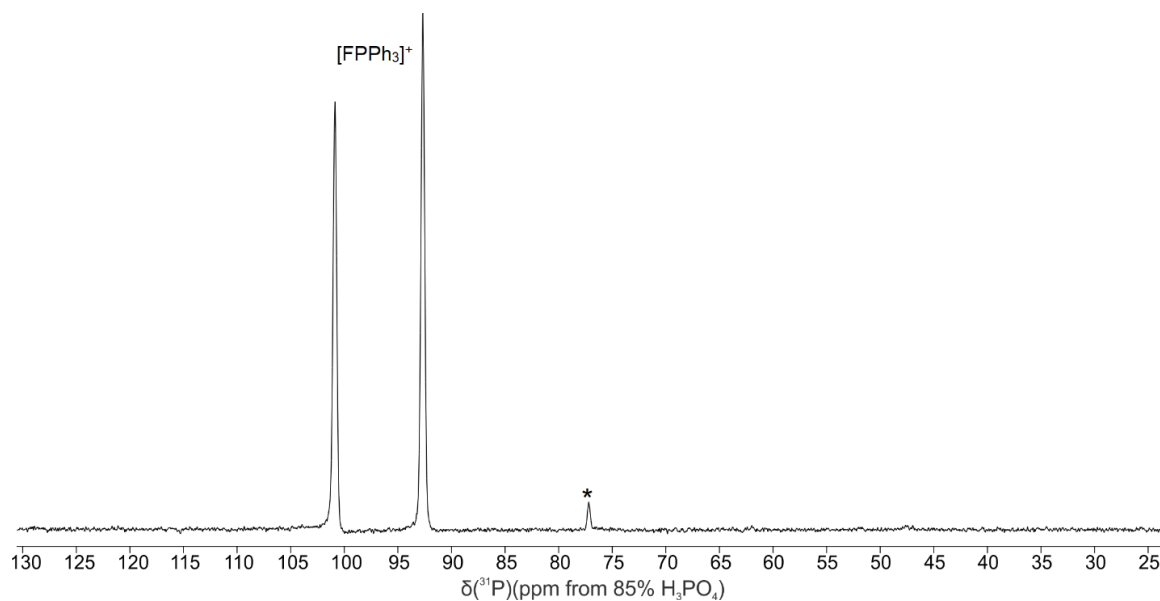


Figure D.15. ^{31}P NMR spectrum of the reaction between $[\text{SF}_3][\text{AsF}_6]$ and OPPh_3 recorded in SO_2 at -60°C after being warmed to RT for 15 minutes. The asterisk (*) denotes an unconfirmed OPPh_3 species, possibly $\text{SF}_4 \cdot \text{OPPh}_3$, $\text{AsF}_5 \cdot \text{OPPh}_3$ or $[\text{SF}_2(\text{OPPh}_3)_2]^{2+}$.

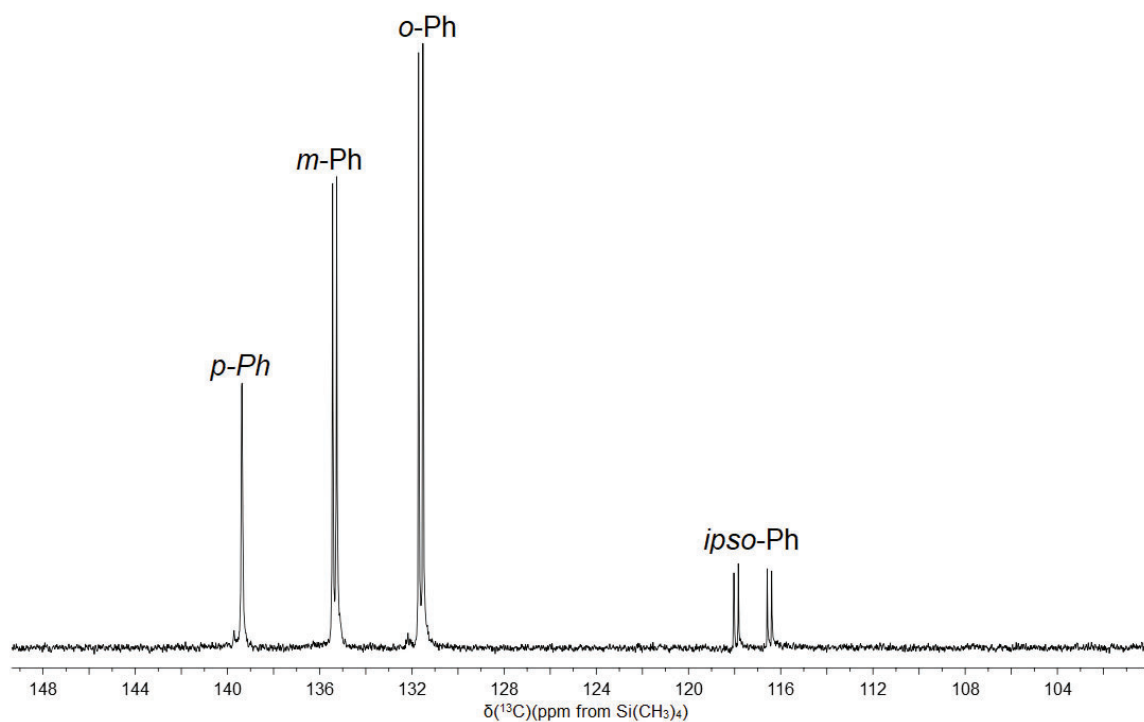


Figure D.16. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of the reaction between $[\text{SF}_3][\text{AsF}_6]$ and OPPh_3 recorded in SO_2 at -54°C after warming to RT for 15 min.

Table D.6. Optimised gas-phase atomic coordinates (Å) for $[\text{SF}_3(\text{py}_{\text{ax}})]^+$

1	1			
S	1.504397	0.358474	-0.000015	
F	3.097472	0.420544	0.000023	
F	1.514391	-0.622737	-1.201291	
F	1.514388	-0.622693	1.201288	
N	-0.512130	0.083409	-0.000001	
C	-1.129445	-1.107581	0.000010	
C	-1.204337	1.229015	-0.000013	
C	-2.507737	-1.180874	0.000015	
H	-0.502576	-1.987803	0.000017	
C	-2.586309	1.222094	-0.000008	
H	-0.630278	2.147283	-0.000023	

C	-3.246269	-0.000774	0.000006
H	-2.990563	-2.146670	0.000025
H	-3.127076	2.156456	-0.000015
H	-4.326625	-0.036023	0.000007

Table D.7. Optimised gas-phase atomic coordinates (Å) for $[\text{SF}_3(\text{py}_{\text{eq}})]^+$

1	1		
S	1.524971	-0.193098	0.316967
F	1.481056	1.317402	1.004539
F	1.410296	-1.622484	-0.525830
F	1.999737	0.485919	-1.005217
N	-0.269511	-0.054587	0.117781
C	-0.810658	1.123982	-0.264732
C	-1.022086	-1.146813	0.384337
C	-2.174846	1.224987	-0.412091
H	-0.133884	1.943602	-0.442032
C	-2.391640	-1.069965	0.274158
C	-0.503191	-2.046854	0.670985
C	-2.978195	0.123158	-0.134229
H	-2.595501	2.164516	-0.737789
H	-2.983425	-1.943783	0.501725
H	-4.052211	0.194566	-0.234907

Table D.8. Optimised gas-phase atomic coordinates (Å) for $[\text{SF}_3(\text{dmap}_{\text{ax}})]^+$

1	1		
S	-2.602318	0.357715	0.000062
F	-4.218857	0.410362	0.000106
F	-2.644718	-0.634390	1.203752
F	-2.644786	-0.634492	-1.203541
N	-0.686230	0.099283	0.000020
C	-0.036972	-1.088839	0.000064

C	0.025719	1.246789	-0.000067
C	1.322371	-1.162377	0.000025
H	-0.650914	-1.977516	0.000130
C	1.388449	1.256636	-0.000111
H	-0.545416	2.166541	-0.000104
C	2.109309	0.027974	-0.000060
H	1.782079	-2.136197	0.000063
H	1.895975	2.206075	-0.000187
N	3.443288	-0.009528	-0.000093
C	4.153545	-1.289271	-0.000079
H	5.220242	-1.098636	-0.000121
H	3.909540	-1.871725	0.888896
H	3.909478	-1.871780	-0.889000
C	4.220989	1.230004	-0.000177
H	4.007739	1.824685	-0.889079
H	4.007666	1.824845	0.888598
H	5.276086	0.983169	-0.000108

Table D.9. Optimised gas-phase atomic coordinates (Å) for $[\text{SF}_3(\text{dmap}_{\text{eq}})]^+$

1	1		
S	-2.615835	0.156937	0.277151
F	-2.580736	-1.359939	0.977250
F	-2.556388	1.598434	-0.574253
F	-3.034666	-0.544625	-1.060675
N	-0.862049	0.083491	0.149591
C	-0.222192	-1.106794	-0.071472
C	-0.130989	1.230833	0.310931
C	1.128113	-1.169737	-0.155033
H	-0.844385	-1.977411	-0.185941

C	1.222543	1.213103	0.260132
H	-0.683921	2.138829	0.479154
C	1.931869	-0.001136	0.014078
H	1.571005	-2.130938	-0.353450
H	1.739749	2.146007	0.406341
N	3.257130	-0.042441	-0.053048
C	4.053307	1.176232	0.125135
C	3.955035	-1.307398	-0.306060
H	3.894439	1.601258	1.116174
H	5.102606	0.927208	0.022969
H	3.799841	1.917953	-0.632084
H	3.667802	-1.721624	-1.272424
H	5.022357	-1.122418	-0.316123
H	3.738292	-2.032655	0.478021

Table D.10. Optimised gas-phase atomic coordinates (Å) for $[\text{SF}_2(\text{dmap}_{\text{ax}})_2]^{2+}$

2	1		
S	-0.000000	-0.032127	-0.000008
N	-1.845775	0.044152	-0.000005
C	-2.454860	-1.174641	-0.000012
C	-2.610516	1.175327	0.000005
C	-3.804905	-1.305992	-0.000010
C	-1.802121	-2.037385	-0.000019
C	-3.964770	1.116442	0.000009
H	-2.084486	2.117677	0.000010
C	-4.642480	-0.146190	0.000002
H	-4.222488	-2.298467	-0.000016
H	-4.513944	2.043040	0.000016
N	1.845776	0.044154	-0.000009
C	2.610517	1.175327	-0.000011
C	2.454859	-1.174639	-0.000006

C	3.964771	1.116442	-0.000006
H	2.084488	2.117678	-0.000016
C	3.804904	-1.305991	-0.000001
H	1.802120	-2.037383	-0.000009
C	4.642480	-0.146190	0.000004
H	4.513946	2.043040	-0.000010
H	4.222487	-2.298468	-0.000004
N	-5.965196	-0.231747	0.000006
C	-6.631477	-1.540154	-0.000005
H	-7.703737	-1.387392	-0.000011
H	-6.364146	-2.109025	-0.890318
H	-6.364158	-2.109033	0.890306
C	-6.798587	0.977749	0.000019
H	-7.841072	0.683905	0.000036
H	-6.609688	1.576855	0.890454
H	-6.609718	1.576854	-0.890422
N	5.965195	-0.231748	0.000014
C	6.798587	0.977748	-0.000003
H	6.609694	1.576873	0.890420
H	7.841072	0.683903	0.000016
H	6.609715	1.576835	-0.890457
C	6.631478	-1.540155	0.000019
H	6.364106	-2.109049	0.890304
H	6.364202	-2.109009	-0.890321
H	7.703738	-1.387390	0.000083
F	0.000001	0.988646	1.195420
F	-0.000002	0.988667	-1.195418

Table D.11. Optimised gas-phase atomic coordinates (Å) for $[\text{SF}_2(\text{dmap}_{\text{eq}})]^{2+}$

2 1

S	0.000001	-1.921022	-0.000005
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N	1.379008	-0.842807	0.040601
F	4.936171	1.248554	-0.114863
N	-1.379008	-0.842809	-0.040604
F	-0.037224	-1.830885	1.687023
C	2.375919	-1.098500	0.959105
H	2.179272	-1.864285	1.689601
N	-4.936171	1.248551	0.114868
C	3.793724	0.586975	-0.056263
C	3.544783	-0.420385	0.930175
H	4.285855	-0.676872	1.668530
C	-1.579916	0.110187	0.929983
H	-0.782517	0.260271	1.636463
C	-3.793725	0.586971	0.056266
C	-2.725673	0.825439	0.982571
H	-2.810481	1.575507	1.750994
C	2.725670	0.825450	-0.982563
H	2.810478	1.575522	-1.750983
C	1.579914	0.110197	-0.929979
H	0.782514	0.260284	-1.636458
C	-3.544781	-0.420381	-0.930179
H	-4.285853	-0.676866	-1.668535
C	-2.375917	-1.098496	-0.959111
H	-2.179269	-1.864278	-1.689611
C	6.011043	0.984021	0.853537
H	5.651801	1.123357	1.872021
H	6.819388	1.682996	0.677517
H	6.394668	-0.029265	0.734926
C	5.176228	2.249252	-1.165003
H	5.074519	1.801011	-2.152498
H	6.186120	2.626941	-1.063073

H	4.482732	3.084190	-1.066905
C	-6.011033	0.984048	-0.853551
H	-5.651759	1.123339	-1.872029
H	-6.819345	1.683069	-0.677569
H	-6.394713	-0.029216	-0.734924
C	-5.176241	2.249223	1.165030
H	-5.074471	1.800973	2.152515
H	-6.186157	2.626857	1.063145
H	-4.482793	3.084199	1.066917
F	0.037226	-1.830873	-1.687032

Table D.12. Optimised gas-phase atomic coordinates (Å) for $[\text{SF}_2(\text{dmap}_{\text{cis}})]^{2+}$

2 1

S	-0.094929	2.109899	0.346511
F	-1.266810	3.269913	0.369675
F	0.189422	2.516650	-1.149550
N	-1.304089	0.889589	0.101075
C	-2.388195	1.146946	-0.710535
C	-1.302176	-0.228672	0.903466
C	-3.436603	0.296687	-0.761169
H	-2.350291	2.047685	-1.300464
C	-2.338942	-1.094735	0.900807
H	-0.439657	-0.372444	1.533386
C	-3.483602	-0.875147	0.063659
H	-4.243374	0.540968	-1.431880
H	-2.278996	-1.950798	1.551630
N	1.291431	0.822546	0.142793
C	1.497872	-0.005110	-0.918281
C	2.256108	0.926890	1.097417
C	2.630254	-0.743413	-1.043660
H	0.718115	-0.038777	-1.664907

C	3.412926	0.217105	1.042049
H	2.056199	1.617414	1.906841
C	3.666771	-0.660790	-0.057385
H	2.734859	-1.377220	-1.908364
H	4.133178	0.349119	1.831670
N	-4.518451	-1.695363	0.058970
C	-4.559922	-2.864264	0.950711
H	-4.463562	-2.556078	1.990940
H	-5.513382	-3.363035	0.828497
H	-3.766127	-3.567439	0.699490
C	-5.674246	-1.449398	-0.818316
H	-6.189248	-0.534133	-0.526955
H	-5.357510	-1.378372	-1.857621
H	-6.363969	-2.279354	-0.727144
N	4.795976	-1.348518	-0.165244
C	5.843550	-1.233051	0.857174
H	5.461865	-1.524931	1.835102
H	6.660821	-1.894948	0.597970
H	6.226217	-0.213460	0.905391
C	5.041580	-2.216102	-1.323708
H	4.296658	-3.009808	-1.378001
H	5.028557	-1.639644	-2.248538
H	6.018674	-2.671660	-1.218869

Table D.13. Optimised gas-phase atomic coordinates (Å) for [SF(dmap)₄]³⁺

3 1

S	-0.000734	-0.000473	0.099883
N	-1.294614	1.374084	-0.072222
N	-4.151876	4.368173	0.111735
N	1.373765	1.293366	-0.072188

N	1.293335	-1.375140	-0.072711
F	-0.000329	-0.000318	-1.544644
N	4.154995	-4.364950	0.112014
C	-2.212330	1.501126	-1.065882
H	-2.150813	0.787990	-1.884924
N	4.367100	4.151352	0.111663
C	-3.237706	3.403141	0.056923
C	-3.170567	2.477203	-1.038005
H	-3.876130	2.529969	-1.862734
C	1.502007	2.209522	-1.067086
H	0.790071	2.146489	-1.887072
C	3.239481	-3.401171	0.056919
C	2.209408	-1.502790	-1.067717
H	2.144998	-0.791631	-1.888276
C	3.402177	3.237063	0.056884
C	2.477791	3.168069	-1.039248
H	2.531465	3.872483	-1.864898
H	-2.260179	3.219071	1.092841
H	-2.235587	3.863076	1.967520
C	-1.336087	2.218008	0.988805
H	-0.584453	2.049200	1.763254
C	2.263596	-3.216468	1.094245
H	2.241670	-3.858631	1.970347
C	3.169205	-2.477350	-1.039597
H	3.873161	-2.530890	-1.865646
C	3.216639	2.261291	1.094187
H	3.859200	2.238402	1.969974
H	1.337941	-2.216841	0.989935
H	0.587738	-2.047367	1.765617
C	2.215971	1.336762	0.990120

H	2.046076	0.586418	1.765587
C	-5.129232	4.525415	-0.965076
H	-4.626068	4.718669	-1.922218
H	-5.776292	5.374486	-0.738929
H	-5.755635	3.627639	-1.057435
C	-4.192387	5.287046	1.248702
H	-4.369479	4.741066	2.185351
H	-5.008552	5.997050	1.105353
H	-3.252935	5.851131	1.327471
C	4.197281	-5.282563	1.249940
H	4.378436	-4.735877	2.185455
H	5.011417	-5.994510	1.104772
H	3.256893	-5.844509	1.332289
C	5.283505	4.194290	1.250537
H	4.735486	4.373454	2.185616
H	5.993934	5.010033	1.106925
H	5.847300	3.254948	1.332584
C	4.525992	5.127126	-0.966332
H	4.718505	4.622433	-1.922789
H	5.376212	5.772961	-0.740972
H	3.629269	5.754941	-1.059545
C	-3.403145	-3.238829	0.057074
C	5.132178	-4.521762	-0.964976
H	4.629161	-4.719770	-1.921243
H	5.782523	-5.367765	-0.736738
H	5.755134	-3.621944	-1.060387
N	-1.375287	-1.294443	-0.072833
C	-2.218609	-1.336674	0.988610
C	-3.219046	-2.261404	1.093107
C	-1.502451	-2.211860	-1.066693

C	-2.477936	-3.170718	-1.038460
H	-3.862445	-2.237527	1.968254
H	-2.049739	-0.585159	1.763186
H	-0.790061	-2.149437	-1.886335
H	-2.531016	-3.875741	-1.863615
N	-4.368008	-4.153496	0.112420
C	-5.287287	-4.193098	1.249065
C	-4.524818	-5.132464	-0.962998
H	-4.721616	-4.630862	-1.920224
H	-3.625480	-5.756392	-1.056559
H	-5.371619	-5.781617	-0.734272
H	-5.849937	-3.252810	1.327830
H	-5.998464	-5.008160	1.105185
H	-4.741842	-4.371278	2.185817

Table D.14. Optimised gas-phase atomic coordinates (Å) for $[\text{SF}_3]^+$

1	1		
S	-0.000132	-0.000254	0.453741
F	1.308074	-0.310678	-0.268840
F	-0.923208	-0.976760	-0.269059
F	-0.384632	1.287890	-0.268753

Table D.15. Optimised gas-phase atomic coordinates (Å) for CFCl_3

0	1		
C	-0.000088	0.000130	0.250014
F	-0.000196	0.000185	1.583573
Cl	0.340889	-1.641124	-0.308768
Cl	1.251148	1.115605	-0.308860
Cl	-1.591901	0.525375	-0.308975

Table D.16 Optimised gas-phase atomic coordinates (Å) for $[\text{SF}_5]^-$

–1	1		
S	-0.000000	-0.000000	0.314363
F	0.000000	0.000000	-1.289541
F	-0.000000	1.749376	0.182668
F	-1.749376	0.000000	0.182668
F	0.000000	-1.749376	0.182668
F	1.749376	-0.000000	0.182668