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The preparation and characterization of tungsten and molybdenum sulfide fluorides

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THE PREPARATION AND CHARACTERIZATION OF TUNGSTEN AND MOLYBDENUM SULFIDE FLUORIDES

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B.Sc., University of Lethbridge, 2005

A Thesis
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Silanethiolate salts of K(18-crown-6)$^+$, N(CH$_3$)$_4$$^+$, Cs$^+$, K$^+$ were synthesized and characterized by vibrational and NMR spectroscopy. The [N(CH$_3$)$_4$][SSi(CH$_3$)$_3$] salt was used to prepare the new [N(CH$_3$)$_4$][WSF$_5$] salt directly from WF$_6$. Alternatively, [N(CH$_3$)$_4$][WSF$_5$] was prepared by the reaction of WSF$_4$ with [N(CH$_3$)$_4$][F].

Pure WSF$_4$ was prepared via a facile new route and was fully characterized by Raman, infrared, and $^{19}$F NMR spectroscopy, and an improved crystal structure. The Lewis-acid properties of WSF$_4$ were studied in reactions with pyridine, yielding the new WSF$_4$·C$_5$H$_5$N adduct, which was studied by Raman and $^{19}$F NMR spectroscopy. A 2:1 stoichiometry of WSF$_4$ and [N(CH$_3$)$_4$][F] yielded W$_2$S$_2$F$_9$ in solution. The novel W$_2$SOF$_9$ anion was characterized in solution by $^{19}$F NMR spectroscopy.

Molybdenum sulfide tetrafluoride was synthesized and unambiguously characterized by Raman, infrared, and $^{19}$F NMR spectroscopy and single-crystal X-ray diffraction.

The experimental characterization of WSF$_4$, MoSF$_4$, WSF$_5$$,^-$, and SSi(CH$_3$)$_3$$^-$ was supplemented by density functional theory calculations.
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LIST OF ABBREVIATIONS

General

ax    axial
eq    equatorial
Kel-F chlorotrifluoroethylene
NMR   Nuclear Magnetic Resonance
DMEU  Dimethylethyl Urea

Nuclear Magnetic Resonance

δ     chemical shift
J     scalar coupling constant in Hertz
ppm   parts per million
TMS   tetramethylsilane

X-ray Crystallography

a, b, c, α, β, γ cell parameters
V     cell volume
λ     wavelength
Z     molecules per unit cell
mol. wt. molecular weight
μ     absorption coefficient
R1    conventional agreement index
wR2   weighted agreement index
GOOF  goodness of fit
Chapter 1
Introduction

1.1 Introduction

It has long been known that electronegative ligands tend to stabilize metal centers in high oxidation states. As such, most metals in their highest oxidation states are surrounded by oxygen or fluorine ligands. The group six metals molybdenum and tungsten are no exception. Therefore, the introduction of the less electronegative sulfur atom to the ligand environment about the metal would be expected to cause a decrease in stability and an increase in reactivity rendering the synthesis of metal sulfide fluorides more challenging. As a result, little is known about tungsten and molybdenum sulfide fluorides in comparison to the oxide fluorides.

In the chemistry of fluorides it has been observed that many compounds form fluorine-bridged oligomeric or polymeric solids of MF$_6$ octahedra, often sharing vertices, sometimes edges but never faces. Similar trends have been observed for the oxide fluorides MoOF$_4$ and WOF$_4$ where polymeric solids contain MOF$_5$ octahedra. In both, the fluorides and oxide fluorides, the strong preference for a hexa-coordinate environment about the metal atom is observed.

1.2 Tungsten and Molybdenum Fluorides

Tungsten and molybdenum fluorides are useful starting materials for oxide fluorides and sulfide fluorides. They are prepared primarily by the combination of the elements in direct fluorination reactions.

\[ M + 3 F_2 \rightarrow MF_6 \quad (M = Mo, W) \]

Tungsten fluorides exist for oxidation states four through six. They are easily identifiable by their respective physical properties. Tungsten hexafluoride is a volatile colourless liquid at temperatures below its boiling point of 17.1 °C. Tungsten pentafluoride is a pale yellow solid at room temperature while WF$_4$ is a red/brown solid at room temperature. Lower fluorides of tungsten have not been observed.
Tungsten pentafluoride is known to crystallize as a fluorine-bridged tetramer.\textsuperscript{2} The arrangement allows for a pseudo-octahedral environment about tungsten with a coordination number of six. The structure of tungsten tetrafluoride is unknown though it is believed to form a fluorine-bridged polymer with coordination number six. X-ray diffraction studies have suggested that WF\textsubscript{4} is an amorphous solid.\textsuperscript{3}

The combination of tungsten metal with a dilute stream of fluorine results in WF\textsubscript{3}. Tungsten pentafluoride is noted for the ease with which it disproportionates to form WF\textsubscript{4} and WF\textsubscript{6}.\textsuperscript{4} Reactions of WF\textsubscript{6} with hot tungsten or nickel filaments have been shown to generate WF\textsubscript{5}.\textsuperscript{3,5,6} Tungsten tetrafluoride has been obtained from reduction of WF\textsubscript{6} with benzene at 110 °C and PF\textsubscript{3} (Equation 1.2.2).\textsuperscript{7,1} It is clear from the ease with which WF\textsubscript{5} disproportionates and the results of reduction reactions with WF\textsubscript{6} that WF\textsubscript{4} is more stable than WF\textsubscript{5}.

\[
\text{WF}_6 + \text{PF}_3 \rightarrow \text{WF}_4 + \text{PF}_5 \quad 1.2.2
\]
\[
2 \text{ MoF}_6 + \text{PF}_3 \rightarrow 2 \text{ MoF}_5 + \text{PF}_5 \quad 1.2.3
\]

Molybdenum fluorides are known for oxidation states three through six. Like the tungsten fluorides, molybdenum fluorides of different oxidation states vary in appearance significantly. Molybdenum hexafluoride, like WF\textsubscript{6}, is a colourless volatile liquid with a freezing point of 17.4 °C, slightly higher than the boiling point of WF\textsubscript{6}. It is well known that MoF\textsubscript{6} is less stable than WF\textsubscript{6} and is considered to be a strong oxidizing agent.

Molybdenum pentafluoride is a yellow solid with a melting point of 64 °C. The reduction of MoF\textsubscript{6} using PF\textsubscript{3} readily yields MoF\textsubscript{5} (Equation 1.2.3), which was attributed to the particularly stable tetrameric structure of MoF\textsubscript{5}.\textsuperscript{1,8} The tetrafluoride, MoF\textsubscript{4}, was formed by the reduction of the hexafluoride with benzene at 110 °C. Mixtures of MoF\textsubscript{5} and MoF\textsubscript{4} have also been obtained from the oxidation of Mo(CO)\textsubscript{6} with F\textsubscript{2}; the significantly higher volatility of MoF\textsubscript{5} allows for their separation.\textsuperscript{9} Unlike tungsten, molybdenum forms the metal trifluoride, MoF\textsubscript{3}, illustrating the trend of heavier group 6 transition metals to form more stable compounds in higher oxidation states. The trifluoride has been reported as both a dark-pink\textsuperscript{10} and a tan-coloured solid.\textsuperscript{11} It was later suggested that the pink solid could have been an oxide fluoride of unknown
composition. Molybdenum fluorides also maintain a coordination number of six about molybdenum throughout all oxidation states.

The reactivity of WF₆ and MoF₆ has been compared in a series of reactions by O’Donnell et al. Reactions between MoF₆ and WF₄ were shown to yield WF₆, showing directly that MoF₆ is a stronger oxidizer than WF₆. Furthermore, quantitative comparisons of the stability of MoF₆ and WF₆ using electrochemistry of their respective MF₆⁻ anions are in agreement with the stronger oxidizing ability of MoF₆. Halogen exchange reactions with a variety of reagents, such as PCl₃, AsCl₃, SbCl₃, CCl₄, and SiCl₄, have shown that MoF₆ readily undergoes reaction to form mixtures of products with Mo₂Cl₃F₆ being produced in all reactions, while WF₆ remains comparatively inert.

The fluoride-ion affinity of WF₆ has been illustrated in reaction with alkali metal fluorides. In addition, the non-alkali metal fluoride CuF₂ was found to react with WF₆ in CH₃CN to produce a blue-coloured solution, which upon removal of solvent produced a moisture-sensitive, blue solid, CuF₂·2WF₆·5CH₃CN according to elemental analysis. Analysis of the infrared spectrum revealed the adduct to be [Cu(NCCH₃)₅][WF₇]⁻. The WF₇⁻ anion has been characterized by ¹⁹F NMR spectroscopy for many salts. The X-ray crystal structures of CsWF₇ as well as that of CsMoF₇ show monocapped octahedral anions. The use of larger cations, such as N(CH₃)₄⁺ and C₁₁H₂₄N⁺, showed that the F⁻ ligands in the MoF₇⁻ anion also assume a monocapped octahedral symmetry about molybdenum, indicating that neither crystal packing nor lattice type have influence over the structure of the anion. Three types of bonds were distinguished: one apical, three equatorial, and three basal bonds having varying lengths with equatorial bonds always shorter. In solution the structure was clearly fluxional as all complexes were observed as singlets by ¹⁹F NMR spectroscopy.

It has been argued that the very existence of WF₇⁻ in CH₃CN might be the result of the poor salvation of F⁻ by CH₃CN, as it has been observed that WF₇⁻ in HF immediately dissociates to form WF₆ and F⁻. It was also shown that Ag[WF₆] and WF₆ react in CH₃CN to produce WF₇⁻.

The presence of [WF₈]²⁻ in solution has never been demonstrated. The MF₈²⁻ (M = Mo, W) anions have been suggested by elemental analysis though there has been controversy over the existence of the MoF₈²⁻ anion as it has never been observed.
Hexavalent K₂WF₈ has been isolated as a white solid that is sensitive to hydrolysis. Raman spectroscopy and single-crystal X-ray diffraction of [NO₂]₂[WF₈], produced in low-temperature reaction of WF₆ and substantial excess NO₂F, have determined WF₈⁻ to be a regular square antiprism.¹⁶

1.3 Tungsten and Molybdenum Oxide Fluorides

Tungsten and molybdenum oxide fluorides in +6 oxidation state have been studied intensively for some time. Tungsten oxide tetrafluoride is a white solid with a melting point of 101 °C. It was first prepared by reaction of WOCl₄ with HF in 1907.¹⁷ The production of WO₂F₂ from WO₂Cl₂ by analogous reaction was also attempted but was unsuccessful according to the mass balance.¹⁷ Since then reactions between WO₃ and F₂,¹⁸ tungsten metal and dilute F₂ with O₂ (3:1 F:O ratio)¹⁹ (5:1 F:O ratio)²⁰ have been shown to generate WOF₄. Small amounts of tungsten oxide tetrafluoride have also been obtained from reactions between CrO₃ and WF₆.²¹ Hydrolysis reactions of WF₆ have been used in attempts to produce WOF₄, however, the single product of this reaction was found to be [H₃O][W₂O₂F₉].³⁸ The reaction of WF₆ with SiO₂ has been used to generate WOF₄ though the presence of anionic side products that were difficult to separate were observed (Equation 1.3.3).²²,²³

\[
\begin{align*}
\text{MO}_3 + \text{F}_2 &\rightarrow \text{MOF}_4 (\text{M} = \text{Mo, W}) + \text{(other products)} \quad 1.3.1 \\
\text{M} + \text{F}_2 + \text{O}_2 &\stackrel{350 - 400 °C}{\rightarrow} \text{MOF}_4 (\text{M} = \text{Mo, W}) + \text{(other products)} \quad 1.3.2 \\
\text{WF}_6 + \text{SiO}_2 &\stackrel{\text{HF}}{\rightarrow} \text{WOF}_4 + (\text{WOF}_5^- + \text{W}_2\text{O}_2\text{F}_9^-) \quad 1.3.3
\end{align*}
\]

Single crystal X-ray diffraction studies show WOF₄ as a fluorine-bridged tetramer that crystallizes in the C2/m space group.²⁴,²⁵ Vibrational spectroscopy had previously suggested a fluorine-bridged network structure.²⁴,²⁵,²⁸-³⁰ Initially, the solid was incorrectly determined to be oxygen-bridged,²⁶ which was later corrected based on the vibrational spectrum. The structure was believed to contain a significant degree of disorder between the fluorine and oxygen atoms, though the suspected disorder may have been due to quality of the X-ray diffraction data and the difficulty distinguishing between oxygen and fluorine atoms by X-ray diffraction.²⁸ Raman spectra of WOF₄ as a solid and
in the melt have been reported. Additional Raman spectroscopy of WOF\textsubscript{4} in the gas phase was also performed indicating a monomeric structure of gaseous WOF\textsubscript{4}. Polarization studies showed significant changes in intensity for bands at 1055, 733 and 248 cm\textsuperscript{-1}, which helped assign their symmetry as A\textsubscript{1}.\textsuperscript{30}

Tungsten dioxide difluoride, WO\textsubscript{2}F\textsubscript{2}, has been generated by the hydrolysis of WOF\textsubscript{4} in HF\textsuperscript{32} and the reaction of K\textsubscript{2}WO\textsubscript{4} with IF\textsubscript{5} yielded a white solid that exhibited peaks attributable to WO\textsubscript{2}F\textsubscript{2} in its infrared spectrum. Electron diffraction was performed on WO\textsubscript{2}F\textsubscript{2} in the vapour phase as it was produced from heating solid W\textsubscript{2}O\textsubscript{4}F to 1043K.\textsuperscript{34}

Tungsten oxide fluoride anions WOF\textsubscript{5}\textsuperscript{-} and W\textsubscript{2}O\textsubscript{2}F\textsubscript{9}\textsuperscript{-} have been observed by \textsuperscript{19}F NMR spectroscopy (Table 1.3.1). These anions have also been observed in the reaction of WOCl\textsubscript{4} with HF.\textsuperscript{35} Solutions of WOF\textsubscript{4} in HF have also produced the W\textsubscript{2}O\textsubscript{2}F\textsubscript{9}\textsuperscript{-} anion.\textsuperscript{31} The direct hydrolysis of WF\textsubscript{6} in HF (Equation 1.3.5) solution was reported to mainly produce [H\textsubscript{3}O][W\textsubscript{2}O\textsubscript{2}F\textsubscript{9}], though production of [H\textsubscript{3}O][WO\textsubscript{F}\textsubscript{5}] by this method was erroneously reported\textsuperscript{36,37} since the vibrational spectra corresponded to [H\textsubscript{3}O][W\textsubscript{2}O\textsubscript{2}F\textsubscript{9}].\textsuperscript{38} The controlled reaction of WF\textsubscript{6} with B(OH\textsubscript{3}) in HF (Equation 1.3.4) was also found to produce exclusively [H\textsubscript{3}O][W\textsubscript{2}O\textsubscript{2}F\textsubscript{9}].\textsuperscript{36} Hydrolysis of WF\textsubscript{6} in aqueous HF (48 %) in the presence of two equivalents of CsF (Equation 1.3.8) resulted in the formation of Cs\textsubscript{2}WO\textsubscript{2}F\textsubscript{4}.\textsuperscript{38}

\[
\begin{align*}
\text{WF}_6 + \text{B(OH)}_3 & \xrightarrow{\text{HF}} [\text{H}_3\text{O}][\text{W}_2\text{O}_2\text{F}_9] + \text{(other products)} \quad 1.3.4 \\
\text{WF}_6 + 2\ \text{H}_2\text{O} & \xrightarrow{\text{HF}} [\text{H}_3\text{O}][\text{WO}\text{F}_5] + \text{HF} \quad 1.3.5 \\
\text{WF}_6 + 2\ \text{CsF} & \xrightarrow{\text{HF} (48 \ %)} \text{Cs}_2\text{WO}_2\text{F}_4 \quad 1.3.6
\end{align*}
\]

The tungsten oxide fluoride anions have been generated as salts of NO\textsuperscript{+}, ClO\textsubscript{2}\textsuperscript{+}, Cs\textsuperscript{+}, and NF\textsubscript{4}\textsuperscript{+}. Their equilibrium reactions in HF have been the subject of considerable interest.\textsuperscript{31,38} Studies involving infrared, Raman, and \textsuperscript{19}F NMR spectroscopy were performed on the NO\textsuperscript{+} salts of WOF\textsubscript{5}\textsuperscript{-} and WOF\textsubscript{6}\textsuperscript{2-};\textsuperscript{31} as well as Cs\textsuperscript{+} and NF\textsubscript{4}\textsuperscript{+} salts of WOF\textsubscript{5}\textsuperscript{-}, WO\textsubscript{2}F\textsubscript{4}\textsuperscript{2-}, and W\textsubscript{2}O\textsubscript{2}F\textsubscript{9}\textsuperscript{-}.\textsuperscript{38,39}

Single-crystal X-ray diffraction studies of [NO][WO\textsubscript{F}_5] have been reported, showing a pseudo-octahedral anion.\textsuperscript{40} Dissolving [NO][WO\textsubscript{F}_5] in anhydrous HF
followed by removal of HF gave a mixture of [NO][WO\textsubscript{5}] and [NO][W\textsubscript{2}O\textsubscript{2}F\textsubscript{9}] based on X-ray powder diffraction.\textsuperscript{31} The observation of a mixture indicates the presence of an equilibrium between the monomeric and dimeric anions in HF solution. Single-crystal X-ray diffraction of the [H\textsubscript{3}O][W\textsubscript{2}O\textsubscript{2}F\textsubscript{9}] salt showed discrete fluorine-bridged W\textsubscript{2}O\textsubscript{2}F\textsubscript{9}\textsuperscript{2\textsuperscript{-}} anions where the fluorine bridge is \textit{trans} to the W=O bond. The complex was found to crystallize in space group P2\textsubscript{1}/c.\textsuperscript{36}

Alkali metal tungsten dioxide fluorides have been prepared from CsF and WO\textsubscript{3} in aqueous HF with dissolved Cs\textsubscript{2}WO\textsubscript{4}. Upon evaporation of the solvent, Cs\textsubscript{2}WO\textsubscript{2}F\textsubscript{4} was obtained in crystalline form. X-ray crystallography studies showed isolated WO\textsubscript{2}F\textsubscript{4}\textsuperscript{2\textsuperscript{-}} octahedra where fluorine and oxygen atoms were completely disordered. Crystals of Na\textsubscript{2}WO\textsubscript{2}F\textsubscript{4} were studied by single-crystal X-ray diffraction, also showing disorder between oxygen and fluorine. The \textit{cis}-dioxo arrangement of the WO\textsubscript{2}F\textsubscript{4}\textsuperscript{2\textsuperscript{-}} anion was deduced from Raman and \textsuperscript{19}F NMR spectroscopy.\textsuperscript{41}

Molybdenum(VI) oxide fluorides, like tungsten(VI) oxide fluorides, generally appear as white solids at room temperature. Molybdenum oxide tetrafluoride, MoOF\textsubscript{4}, was first studied by Ruff and Eisner in 1907.\textsuperscript{42} Molybdenum oxide tetrafluoride has been formed in reactions of MoO\textsubscript{3} with F\textsubscript{2} (Equation 1.3.1),\textsuperscript{18} and CrO\textsubscript{3} with MoF\textsubscript{6}.\textsuperscript{21} Direct hydrolysis of MoF\textsubscript{6} in HF with a deficiency of H\textsubscript{2}O has been found to generate MoOF\textsubscript{4} almost exclusively, unlike hydrolysis of WF\textsubscript{6}.\textsuperscript{37} The formation of the oxide tetrafluoride was attributed to the lower electron affinity of MoF\textsubscript{6} compared to WF\textsubscript{6}.\textsuperscript{36}

MoOF\textsubscript{4} was found to crystallize in polymeric chains of distorted \textit{cis}-fluorine-bridged MoOF\textsubscript{5} octahedra\textsuperscript{43} in the monoclinic space group P2\textsubscript{1}/c\textsuperscript{43} (P2\textsubscript{1}/a\textsuperscript{27}), as opposed to the tungsten analogue.\textsuperscript{27} Raman spectroscopy on solid MoOF\textsubscript{4} was performed with the resulting spectra showing weak bands in the 500 cm\textsuperscript{-1} region indicating fluorine bridging.\textsuperscript{31}

Infrared spectra of MoOF\textsubscript{4} and WOF\textsubscript{4} were later collected in the gas phase as well as in argon and nitrogen matrices.\textsuperscript{18,30} Gas-phase infrared spectroscopy strongly supported \textit{C}_{4v} symmetry for monomeric molecules. It was noticed that the gas-phase spectra observed for MoOF\textsubscript{4} were of poorer quality than for WOF\textsubscript{4}, which was attributed to the seven isotopes of molybdenum between mass numbers 92 and 100. The Raman and
infrared spectra of gaseous and matrix-isolated MoOF\textsubscript{4} and WOF\textsubscript{4} were quite similar indicating related structures.\textsuperscript{30}

The molybdenum dioxide difluoride analogue, MoO\textsubscript{2}F\textsubscript{2}, has been generated in reaction between MoO\textsubscript{2}Cl\textsubscript{2} and HF. A similar reaction with stoichiometric amounts of XeF\textsubscript{2} also formed MoO\textsubscript{2}F\textsubscript{2}, greater amounts of XeF\textsubscript{2} formed MoOF\textsubscript{4}.\textsuperscript{32} Molybdenum dioxide difluoride has been characterized by Raman spectroscopy as both a solid and a melt.\textsuperscript{28,31}

The reagent NOF was shown to react with MoOF\textsubscript{4} in HF yielding [NO][MoOF\textsubscript{5}]. Single-crystal X-ray diffraction studies of [NO][MoOF\textsubscript{5}] have been reported.\textsuperscript{40}

The formation of the dimeric Mo\textsubscript{2}O\textsubscript{2}F\textsubscript{9}\textsuperscript{−} anion in solutions of MoOF\textsubscript{4} in HF has been observed by \textsuperscript{19}F NMR spectroscopy. The H\textsubscript{2}F\textsuperscript{+} cation was suggested as a possible counter ion, but has not been confirmed by its experimental observation. The equilibrium between [NO][MoOF\textsubscript{5}] and [NO][Mo\textsubscript{2}O\textsubscript{2}F\textsubscript{3}] in HF has been studied by powder X-ray diffraction.\textsuperscript{31} Fluorine-19 NMR spectroscopy studies of the reaction of MoOF\textsubscript{4} with acetylacetone in CH\textsubscript{3}CN have also shown the presence of the Mo\textsubscript{2}O\textsubscript{2}F\textsubscript{9}\textsuperscript{−} anion.\textsuperscript{44} The formation of the dimeric anion from HF solutions of MOF\textsubscript{4} (M = Mo, W) tends to be favoured for solutions of WOF\textsubscript{4} in HF indicating stronger acceptance of F\textsuperscript{−} by WOF\textsubscript{4} compared to MoOF\textsubscript{4}.\textsuperscript{31}

Reactions of MoO\textsubscript{3} and W\textsubscript{3} with SeF\textsubscript{4} and IF\textsubscript{5} reportedly produced the [SeF\textsubscript{3}][MoO\textsubscript{2}F\textsubscript{3}], [IF\textsubscript{4}][MoO\textsubscript{2}F\textsubscript{3}] and [SeF\textsubscript{3}][WOF\textsubscript{5}], [SeOF][WOF\textsubscript{5}], [IF\textsubscript{4}][WOF\textsubscript{5}] salts. The nature of the salts were solely deduced by the mass balance of the reaction. Addition of KF to the reaction of SeF\textsubscript{4} and W\textsubscript{3} was said to produce K[WOF\textsubscript{5}].\textsuperscript{45}

The Lewis-acid properties of the tungsten oxide fluorides towards nitrogen bases have been studied by single crystal X-ray diffraction, where possible, and vibrational and NMR spectroscopy. The formation of the tungsten oxide-fluoride adducts with pyridine and bipyridine, WOF\textsubscript{4}·bipy\textsuperscript{46}, WO\textsubscript{2}F\textsubscript{2}·bipy\textsuperscript{46}, WOF\textsubscript{4}·py\textsuperscript{47}, and WOF\textsubscript{4}·2py\textsuperscript{47,48} were studied. The WOF\textsubscript{4}·py adduct was shown to take the form of a distorted octahedron with the oxygen atom trans to the nitrogen ligand of pyridine. The dipyridyl analogue, WOF\textsubscript{4}·2py exhibited a pentagonal bipyramidal geometry about tungsten. Low-temperature \textsuperscript{19}F NMR spectroscopy showed an A\textsubscript{2}MX spin system for WOF\textsubscript{4}·2py.\textsuperscript{48}
temperatures above 0 °C the WOF$_4$·2py adduct was shown to give up a pyridine ligand as only WOF$_4$·py and free pyridine were observed.$^{47}$

When 2-fluoropyridine was introduced as a ligand only the mono F-pyridine, WOF$_4$·Fpy adduct was observed. The adduct was studied by vibrational and NMR spectroscopy along with single-crystal X-ray crystal and powder diffraction showing the tungsten with a distorted octahedral arrangement of ligands with nitrogen of the F-pyridine ligand trans to the oxygen atom.$^{49}$ The XeF$_2$ adducts of MoOF$_4$ and WOF$_4$ were explored by $^{129}$Xe and $^{19}$F NMR spectroscopy.$^{20,50}$ The relative fluoride-acceptor strengths of WOF$_4$ and MoOF$_4$ were deduced from $^{129}$Xe and $^{19}$F chemical shifts indicating WOF$_4$ to be a stronger fluoride acceptor than MoOF$_4$ toward XeF$_2$ and presumably other fluoride donors.$^{20}$

**Table 1.3.1 $^{19}$F NMR Spectroscopic Data of Tungsten and Molybdenum Oxide Fluorides**

<table>
<thead>
<tr>
<th>Compound or Complex</th>
<th>$\delta$ (ppm)$^a$</th>
<th>$^2J$(19F-19F) (Hz)</th>
<th>$^1J$(183W-19F) (Hz)</th>
<th>Solvent$^b$</th>
<th>Multiplicity</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>WOF$_4$</td>
<td>68.5</td>
<td></td>
<td></td>
<td>HF/CH$_3$CN</td>
<td>Singlet</td>
<td>35</td>
</tr>
<tr>
<td>WOF$_4$</td>
<td>65.2</td>
<td>69</td>
<td></td>
<td>PC</td>
<td>Singlet</td>
<td>31</td>
</tr>
<tr>
<td>WOF$_4$</td>
<td>61.9</td>
<td></td>
<td></td>
<td>HF</td>
<td>Singlet</td>
<td>31</td>
</tr>
<tr>
<td>WOF$_5^-$</td>
<td>53.7</td>
<td>55</td>
<td>72</td>
<td>HF/CH$_3$CN</td>
<td>Doublet</td>
<td>35</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>[NO][WOF$_5$]$_c$</td>
<td>54.4</td>
<td></td>
<td>84</td>
<td>HF</td>
<td>Singlet</td>
<td>31</td>
</tr>
<tr>
<td>W$_2$O$_2$F$_9^-$</td>
<td>62.6</td>
<td>59</td>
<td>72</td>
<td>HF/CH$_3$CN</td>
<td>Doublet</td>
<td>35</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Nonet</td>
<td></td>
</tr>
<tr>
<td>MoOF$_4$</td>
<td>142.7</td>
<td></td>
<td></td>
<td>HF</td>
<td>Singlet</td>
<td>31</td>
</tr>
<tr>
<td>MoOF$_4$</td>
<td>145.9</td>
<td></td>
<td></td>
<td>PC</td>
<td>Singlet</td>
<td>31</td>
</tr>
<tr>
<td>[NO][MoOF$_5$]$_c$</td>
<td>134.5</td>
<td></td>
<td></td>
<td>HF</td>
<td>Singlet</td>
<td>31</td>
</tr>
</tbody>
</table>

$^a$ All chemical shifts referenced to CFCl$_3$. $^b$ Propylene Carbonate, C$_4$H$_6$O$_3$ (PC). $^c$ Exists in equilibrium with M$_2$O$_2$F$_9^-$ (M = Mo, W) in HF solvent.

1.4 Tungsten and Molybdenum Sulfide Fluorides

Among all transition-metal sulfide fluorides, WSF$_4$ has attracted the most attention. The first report of WSF$_4$ described the $^{19}$F NMR spectroscopic characterization of the reaction between WSCl$_4$ and HF in CH$_3$CN.$^{51,52}$ It was noticed that with time the $^{19}$F NMR resonance attributed to WSF$_5^-$ increased in intensity and others would decrease.$^{52}$ The substitution of chlorine atoms with fluorine atoms was said to take place
at a very high rate once HF was added. It was also noted that in contrast to the oxide fluorides the $^2J(^{19}\text{F}-^{19}\text{F})$ coupling constant increases with an increasing number of fluorine atoms. Alternatively, chlorine-fluorine substitution could be accomplished using XeF$_2$ according to Equation 1.4.3; the reaction between XeF$_2$ and WSCl$_4$ in CH$_3$CN solvent was described as beginning at ca. 0 °C with a colour change from dark red to pale orange. The reaction products were studied by $^{19}$F NMR spectroscopy. The $^{19}$F NMR spectrum contained eight signals between 90 and -160 ppm, which were dominated by a singlet attributed to WSF$_4$ at 84.3 ppm. The other signals that could be assigned were assigned to WSFCl$_3$, WSF$_2$Cl$_2$, WSF$_3$Cl.$^{51}$

Solid WSF$_4$ was isolated from the reactions of WF$_6$ with B$_2$S$_3$ at 260 °C$^{53}$ and WF$_6$ with Sb$_2$S$_3$ at 300 °C for 3 hours.$^{52}$ Small amounts of WOF$_4$ were common impurities found in the products generated by all methods evidencing the hydrolytic sensitivity of WSF$_4$. It was observed by others that the sublimation of WSF$_4$ occurred readily at 50 °C under vacuum.$^{53}$

$$\text{Sb}_2\text{S}_3 + 3 \text{WF}_6 \quad \xrightarrow{300 \degree \text{C}} \quad 3 \text{WSF}_4 + 2 \text{SbF}_3$$  \hspace{1cm} 1.4.1

$$\text{B}_2\text{S}_3 + 3 \text{WF}_6 \quad \xrightarrow{260 \degree \text{C}} \quad 3 \text{WSF}_4 + 2 \text{BF}_3$$  \hspace{1cm} 1.4.2

$$\text{WSCl}_4 + \text{XeF}_2 \quad \xrightarrow{\text{CH}_3\text{CN}} \quad \text{WSF}_4 + (\text{other products})$$  \hspace{1cm} 1.4.3

$$\text{WSCl}_4 + \text{HF} \quad \xrightarrow{\text{CH}_3\text{CN}} \quad \text{WSF}_4 + (\text{other products})$$  \hspace{1cm} 1.4.4

The most common sulfide transfer agent used for producing WSF$_4$ and other transition-metal thiohalides has been Sb$_2$S$_3$ as it is commercially available (Equation 1.4.1). Yellow and pale brown crystals were isolated from the cooler part of the reactor after the high-temperature reaction of WF$_6$ with Sb$_2$S$_3$. When ground, both types of crystals appeared pale yellow and gave exactly the same vibrational data. Tungsten sulfide tetrafluoride was characterized by infrared spectroscopy with stretching bands for W=S at 577 cm$^{-1}$, terminal W-F at 699, 673, and 634 cm$^{-1}$, and bridging W-F at 534 and 514 cm$^{-1}$. One Raman band for the W=S stretching mode was observed at 580 cm$^{-1}$.\footnote{In a solution synthesis, WSF$_4$ was synthesized at ambient temperature in the reaction of ((CH$_3$)$_3$Si)$_2$S with WF$_6$ in CH$_3$CN. The products contained WSF$_4$ as shown by a singlet at 86.2 ppm with $^{183}$W-satellites showing $^1J(^{19}\text{F}-^{183}\text{W})$ coupling of 33.4 Hz in
the $^{19}$F NMR spectrum. Banger et al. tried various solvents and temperatures and indicated that reactions always generated a brown insoluble byproduct, suggested to be WS$_3$ (Equation 1.4.6). Extended X-ray absorption fine structure (EXAFS) studies were conducted on ca. 0.05 M solutions of WSF$_4$ in CH$_3$CN. The EXAFS spectrum exhibited a single broad peak at ca. 200 pm, and weaker features at ca. 290 and 360 pm. The broad band at 200 pm was attributed to both the four tungsten-fluorine and one tungsten-sulfur bond. The distances of 290 and 360 pm were too long to correspond to tungsten-fluorine bridges, therefore, it was determined that WSF$_4$ was monomeric in CH$_3$CN solution, presumably forming the WSF$_4$·CH$_3$CN adduct.$^{54}$

$$WF_6 + ((CH_3)_3Si)_2S \rightarrow \text{CH}_3\text{CN} \quad \text{WSF}_4 + 2 (CH_3)_3\text{SiF} \quad 1.4.5$$

$$3 \text{WSF}_4 \rightarrow \text{CH}_3\text{CN} \quad \text{WS}_3 + 2 \text{WF}_6 \quad 1.4.6$$

Attempts at generating WS$_2$F$_2$ by increasing the ratio of $((CH_3)_3Si)_2S$ to WF$_6$ were unsuccessful resulting in greater amounts of a brown solid.$^{54}$

The fluorine-bridged structure of solid WSF$_4$, which was suggested by the infrared bands at 534 and 514 cm$^{-1}$ was confirmed by single crystal X-ray diffraction.$^{55}$ This is in line with studies of other tungsten sulfide halides where single-crystal X-ray diffraction studies of the chloride and bromide analogues have shown square pyramidal molecules bridged asymmetrically via the halide to form dimers.$^{56}$

Electron diffraction data were recorded on WSF$_4$ in the gas phase confirming the square pyramidal geometry around tungsten in the monomer. The square pyramidal structure is consistent with all WSX$_4$ (X = F, Cl, Br) in the gas phase. It is interesting to note that W-F bond lengths for WSF$_4$ and WOF$_4$ were the same, a result consistent with the chloride analogues (Table 1.4.1). This result would indicate that W-F stretching bands of oxygen and sulfur analogues should be very similar.$^{53}$
Table 1.4.1 Bond Lengths of Various Tungsten Sulfide and Oxide Halides Using Different Methods

<table>
<thead>
<tr>
<th>Compound</th>
<th>Bond</th>
<th>Electron Diffraction$^{53}$</th>
<th>Crystal Structure</th>
<th>EXAFS$^{54}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>WOF$_4$</td>
<td>W=O</td>
<td>166.6(7)</td>
<td>165$^{46}$</td>
<td>168.6(3)</td>
</tr>
<tr>
<td></td>
<td>W-F</td>
<td>184.7(2)</td>
<td>184$^{26}$</td>
<td>185.2(2)</td>
</tr>
<tr>
<td>WSF$_4$</td>
<td>W=S</td>
<td>210.4(7)</td>
<td>207$^{55}$</td>
<td>202.6(8)</td>
</tr>
<tr>
<td></td>
<td>W-F</td>
<td>184.7(3)</td>
<td>187$^{55}$</td>
<td>186.3(3)</td>
</tr>
<tr>
<td>WOCl$_4$</td>
<td>W=O</td>
<td>168.5(15)</td>
<td>181$^{56}$</td>
<td>169.1(3)</td>
</tr>
<tr>
<td></td>
<td>W-Cl</td>
<td>228.0(3)</td>
<td>228$^{56}$</td>
<td>230.3(1)</td>
</tr>
<tr>
<td>WSCl$_4$</td>
<td>W=S</td>
<td>208.6(6)</td>
<td>209.8$^{56-58}$</td>
<td>NA</td>
</tr>
<tr>
<td></td>
<td>W-Cl</td>
<td>227.7(3)</td>
<td>229.9(11)$^{56-58}$</td>
<td>NA</td>
</tr>
</tbody>
</table>

Table 1.4.2 $^{19}$F NMR Chemical Shifts and Coupling Constants of Tungsten Sulfide Fluorides

<table>
<thead>
<tr>
<th>Material</th>
<th>$\delta$ ($^{19}$F) a (ppm)</th>
<th>$^2J$(F-19F) (Hz)</th>
<th>$^1J$(183W-19F) (Hz)</th>
<th>Solvent</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>WSF$_4$</td>
<td>85.1 (s)</td>
<td>37 ± 2</td>
<td></td>
<td>CH$_3$CN</td>
<td>$^{52}$</td>
</tr>
<tr>
<td>WOF$_4$</td>
<td>66.9 (s)</td>
<td></td>
<td></td>
<td>CH$_3$CN</td>
<td>$^{52}$</td>
</tr>
<tr>
<td>WF$_6$</td>
<td>169.9 (s)</td>
<td></td>
<td></td>
<td>CH$_3$CN</td>
<td>$^{52}$</td>
</tr>
<tr>
<td>W$_2$S$_2$F$_9$</td>
<td>83.7 (d)</td>
<td>70 ± 2</td>
<td></td>
<td>CH$_3$CN</td>
<td>$^{51,52}$</td>
</tr>
<tr>
<td></td>
<td>-159.3 (n)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>WSF$_5$</td>
<td>80 (d)</td>
<td>72 ± 2</td>
<td>32</td>
<td>CH$_3$CN</td>
<td>$^{52}$</td>
</tr>
<tr>
<td></td>
<td>-141.2 (qn)</td>
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</table>

a Abbreviations denote singlet (s), doublet (d), triplet (t), quartet (q), and quintet (qn).

The Lewis-acid/base character of the tungsten oxide fluorides has been studied extensively, while there have been relatively few studies performed on WSF$_4$. The Lewis-acid/base properties of WSF$_4$ are of interest since it remains to be seen what the effect of replacing the oxygen ligand with heavier less electronegative sulfur will have. The WSF$_4$·CH$_3$CN adduct was studied, showcasing the Lewis-acid behaviour of WSF$_4$. The WSF$_4$·SbF$_5$ adduct has been suggested by Holloway, but the adduct was not characterized.$^{55}$

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Molybdenum sulfide trifluoride, MoSF₃, was reportedly generated by reduction of SF₆ with a molybdenum metal filament between 600 and 800 °C.⁵⁹ A liquid film formed on the walls of the reactor at 50 °C that upon cooling to room temperature formed orange crystals of MoSF₃. A melting temperature of 85.6 °C was reported and the solid was characterized by powder X-ray diffraction and infrared spectroscopy. The infrared spectrum contained broad signals, 490 - 525 cm⁻¹ and 660 - 690 cm⁻¹, attributed to Mo-F_bridging and Mo-F_terminal bond stretches, respectively.⁵⁹

Holloway and Puddick claimed the synthesis of MoSF₄ in 1979.⁶⁰ An amber product was produced in reaction between Sb₂S₃ and MoF₆ at 275 °C for six hours (Equation 1.4.7). The product mixture reportedly contained the starting reagents MoF₆ and Sb₂S₃ along with reaction side products MoF₅ and SbF₃, which were removed by sublimation at 40 °C and 130 °C, respectively. The amber-coloured solid MoSF₄ was isolated in unspecified amounts. The product MoSF₄ was reportedly stable for long periods under vacuum at ambient temperature. X-ray powder diffraction studies were performed on MoSF₄ that indicated its structure differed from that of WSF₄. Mass spectrometry of MoSF₄ showed a peak corresponding to MoSF₄⁺ and a much larger peak corresponding to MoSF₃⁺. Infrared spectroscopy of MoSF₄ showed strong bands at 690, 670, and 633 cm⁻¹ attributed to terminal Mo-F stretches and bands at 500 and 458 cm⁻¹ which were attributed to stretches of bridging fluorides. A band at 564 cm⁻¹ attributed to Mo=S stretching was also identified.⁶⁰

\[ 3 \text{ MoF}_6 + \text{Sb}_2\text{S}_3 \xrightarrow{275 \, ^\circ \text{C}, \, 6 \, \text{h}} 3 \text{ MoSF}_4 + 2 \text{ SbF}_3 \]  

The known tungsten and molybdenum sulfide fluorides along with the techniques used to study their structures are listed in Table 1.4.3.
Table 1.4.3 Tungsten and Molybdenum Sulfide Fluorides and Their Methods of Structural Characterization

<table>
<thead>
<tr>
<th>Sulfide fluoride</th>
<th>Characterization</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mo(V) MoSF\textsubscript{3}</td>
<td>powder X-ray diffraction\textsuperscript{59}</td>
</tr>
<tr>
<td>Mo(VI) MoSF\textsubscript{4}</td>
<td>infrared spectroscopy\textsuperscript{60} mass spectrometry\textsuperscript{60}</td>
</tr>
<tr>
<td>W(VI) WSF\textsubscript{4}</td>
<td>infrared spectroscopy\textsuperscript{52} Raman spectroscopy\textsuperscript{52} matrix-isolated infrared spectroscopy\textsuperscript{61} UV/VIS spectroscopy\textsuperscript{61} NMR spectroscopy\textsuperscript{54} single crystal X-ray diffraction\textsuperscript{55} gas-phase electron diffraction\textsuperscript{53} EXAFS\textsuperscript{54}</td>
</tr>
<tr>
<td>WSF\textsubscript{5}\textsuperscript{−}</td>
<td>NMR spectroscopy\textsuperscript{51,52} infrared spectroscopy\textsuperscript{62} Raman spectroscopy\textsuperscript{62} single crystal X-ray diffraction\textsuperscript{62}</td>
</tr>
<tr>
<td>W\textsubscript{2}S\textsubscript{2}F\textsubscript{9}\textsuperscript{−}</td>
<td>NMR spectroscopy\textsuperscript{51,52}</td>
</tr>
</tbody>
</table>

The disproportionation and thermal decomposition of MoSF\textsubscript{3} and MoSF\textsubscript{4} were studied by mass spectral analysis. Studies conducted on MoSF\textsubscript{3} vapour at 308 K suggest that MoSF\textsubscript{3} is susceptible to disproportionation and decomposition as it volatizes forming MoSF\textsubscript{4}, MoF\textsubscript{5} and S\textsubscript{8} molecules that were found in the gas phase. The heat of removal of sulfide from molybdenum sulfides was shown to be much lower than for corresponding tungsten sulfide fluorides, which may help explain the relative instability of MoSF\textsubscript{4}, compared to WSF\textsubscript{4}.\textsuperscript{63}

The heats of formation for MoSF\textsubscript{3} and MoSF\textsubscript{4} were calculated for the gas-phase molecules. Bond lengths for MoSF\textsubscript{3} and MoSF\textsubscript{4} were also estimated at 207 pm for Mo=S and 184 pm for Mo-F bonds.\textsuperscript{63}

Due to their instability and lack of a method for bulk production of MoSF\textsubscript{4}, molybdenum sulfide fluorides have not been studied further and hence have yet to be characterized by NMR and Raman spectroscopy.
1.5 Goal of Present Research

The main hurdle to further studies of tungsten and molybdenum sulfide fluorides is the inability to easily produce them in high purity on a preparative scale. It is hoped that novel, ambient temperature and pressure preparative methods can be developed that will make both, WSF$_4$ and MoSF$_4$, readily accessible. It is also hoped that use of new trimethylsilanethiolate salts as sulfide transfer agents will allow for the facile generation of WSF$_5^-$ and MoSF$_5^-$ anions directly from WF$_6$ and MoF$_6$, respectively. It is the main goal of this research to shed light on the reactivity of these elusive and highly reactive species.
References

(42) Ruff, O.; Eisner, F. *Ber.* 1907, 40, 2931.


Chapter 2
Experimental Section

2.1 Standard Techniques

The compounds used in the course of this work are all moisture and air-sensitive; consequently all manipulations were carried out under rigorously anhydrous inert-atmosphere conditions. Glass and metal vacuum line systems, a dry-nitrogen-filled glove bag, and the oxygen- and moisture-free atmosphere of a Vacuum Atmospheres (Omni Lab) drybox were used. Preparative work inside the dry box requiring low temperatures was carried out in a metal Dewar containing 4.5-mm copper-plated spheres (air rifle BB's) which had been previously cooled in a cryowell by immersion of the cryowell in liquid nitrogen for several hours.

Volatile materials that were non-corrosive towards glass in the absence of water were manipulated on a Pyrex-glass vacuum line equipped with grease-free 6-mm J. Young glass stopcocks equipped with PTFE barrels (Figure 2.1.1). Pressures inside the manifold were monitored using a Heise gauge (model CC, 0–1000 mmHg, beryllium/copper Bourdon tube, Dresser Instruments). The final vacuum was monitored by a Varian thermocouple gauge connected to the vacuum line between the liquid-nitrogen trap and the vacuum pump.

Volatile materials, which attacked glass, were handled on a metal vacuum line constructed from nickel and 316 stainless steel, and equipped with 316 stainless steel valves and fittings (Autoclave Engineers Inc.), PTFE, and FEP (Figure 2.1.2) Pressures were measured at ambient temperature using Baratron capacitance manometers (MKS, Type 626A, effective range 0 – 1000 mmHg) having inert wetted surfaces constructed of Inconel, in conjunction with a digital readout.

Vacuum on the glass (ca. $10^{-5}$ Torr) and metal lines (ca. $10^{-4}$ Torr) was attained by the use of Edwards two stage direct drive RV8 Edwards vacuum pumps. Two vacuum pumps were used on the metal vacuum line; one, a roughing pump, was connected to a fluoride/fluorine trap consisting of a stainless-steel cylinder (75-cm length, 17-cm outer diameter) packed with soda lime absorbent (EMD, 4 mesh). Removal and disposal of volatile reactive fluorinated compounds was accomplished by pumping through, and
Figure 2.1 1 Glass vacuum line system equipped with J. Young PTFE/glass stopcocks and a Heise gauge.
Figure 2.1.2  Metal vacuum system; (A) MKS type 626A capacitance manometer (0-1000 Torr), (B) MKS Model PDR-5B pressure transducers (0-10 Torr), (C) 3/8-in. stainless-steel high-pressure valves (Autoclave Engineers, 30VM6071), (D) 316 stainless-steel cross (Autoclave Engineers, CX6666), (E) 316 stainless-steel L-piece (Autoclave Engineers, CL6600), (F) 316 stainless steel T-piece (Autoclave engineers, CT6660), (G) 3/8-in. o.d., 1/8-in. i.d. nickel connectors, (H) 1/8-in. o.d., 1/8-in. i.d. nickel tube.
entrapment on a bed of soda lime followed by trapping of the volatile reaction products, CO_2 and H_2O, in a glass liquid nitrogen trap. The second vacuum pump provided the high vacuum source for the manifold and was cold trapped with a glass liquid nitrogen trap. All preparative work involving WF_6, MoF_6, and anhydrous HF was carried out in ¾-in, ¼-in., or 4-mm o.d. FEP tubes which were heat-sealed at one end and connected through 45° flares to Kel-F or 37° flares to stainless-steel valves (Swagelok SS-ORM2 and SS-IRF2 valves). The FEP sample tubes were dried under dynamic vacuum overnight on a glass vacuum line prior to transfer onto the metal line where they were checked for leaks, passivated with F_2 at 1 atm for 12 h, re-evacuated and then back filled with dry N_2 before transferring to the dry box. Pyrex-glass reaction vessels were dried under dynamic vacuum overnight periodically flamed out by use of a Bunsen burner.

Nuclear magnetic resonance (NMR) spectra were recorded on samples prepared in 4-mm o.d. FEP tubes. The NMR tubing had one end heat sealed by pushing the end of the FEP tube into the hot end of a thin-walled 5-mm o.d. NMR tube and the other end was fused to a ¼-in. o.d. thick-walled FEP tubing which was heat-flared for direct attachment to a Kel-F valve (Figure 2.1.3(a)). The 4-mm sample tubes used for NMR were heat sealed under dynamic vacuum with a heat gun while the sample was frozen at –196 °C. All heatsealed samples were stored submerged in liquid nitrogen (-196 °C) until they could be spectroscopically characterized. For NMR measurements, the 4-mm FEP tubes were inserted into standard 5-mm precision NMR tubes before insertion into the NMR probe.

Raman spectra of solids that are stable at room temperature and which do not attack glass were recorded on samples in Pyrex-glass melting point capillaries. Before use, the melting point capillaries were heated under dynamic vacuum for 24 h at 200 °C and then stored in the drybox where they were loaded with the appropriate materials. The end of the loaded melting point capillary was temporarily sealed with Kel-F grease before removal from the drybox. The capillaries were then immediately heat-sealed with an oxygen-natural gas torch.

Vessels were attached to vacuum lines through thick-walled FEP tubing and ¼-in. PTFE Swagelok connectors or ¼-in. stainless-steel Ultra-Torr connectors fitted with viton rubber O-rings.
Figure 2.1.3 Common FEP reactors used to conduct experiments: (a) 4-mm o.d. reaction vessel equipped with a Kel-F valve. (b) ¼-in. o.d. FEP T-reactor equipped with Kel-F valve. (c) ¼-in. o.d. FEP T-reactor equipped with a stainless-steel Swagelok-T and a Kel-F valve.
2.2 Preparation and Purification of Starting Materials

2.2.1 Purification of HF, CH₃CN, SO₂ClF, C₅H₅N, THF, Solvents and (Me₃Si)₂S

Anhydrous hydrogen fluoride (Air Products) was stored at room temperature in a nickel storage vessel equipped with a monel (Autoclave Engineers) valve. Hydrogen fluoride was dried over potassium hexafluoronickeolate(VI) in a ¾-in. o.d. FEP vessel (Figure 2.2.1), equipped with a stainless steel valve prior to transfer to reaction vessels by vacuum distillation on the metal vacuum line through connections constructed of FEP.

Acetonitrile (Sigma-Aldrich) was purified according to the literature procedure and was transferred under vacuum using a glass vacuum line and glass Y-piece.

Pyridine (Sigma-Aldrich, 99.8%) was added to CaH₂ in a glass storage bulb inside the glove bag. Then the liquid was vacuum distilled from the original storage bulb and stored over CaH₂ in a glass storage bulb equipped with a Teflon J. Young stopcock.

Tetrahydrofuran was obtained from a dry solvent system and was refluxed over sodium metal with benzophenone indicator and subsequently distilled into a glass storage vessel equipped with PTFE J. Young stopcock over sodium metal.

Hexamethyldisilathiane, (Me₃Si)₂S, (Fluka, purum) was purified by vacuum distillation at room temperature through a glass Y-piece into a glass storage vessel equipped with a Teflon J. Young stopcock.

2.2.2 Purification of MoF₆, WF₆, SbF₃, and SbF₅

Molybdenum hexafluoride (Elf Atochem) and WF₆ (Elf Atochem) were used as provided and were transferred into reaction vessels by vacuum distillation through passivated stainless-steel and fluoroplastic connections.

Antimony trifluoride, SbF₃ (Ozark Fluorine Specialties) was sublimed under vacuum and transferred into a drybox.

Antimony pentafluoride, SbF₅ (Ozark-Mahoning Co) was purified by vacuum distillation in a Teflon and glass apparatus connected with PTFE Swagelok unions and stored in a glass U-tube equipped with PTFE J. Young stopcocks, which was kept in a dessicator. Subsequent transfers of SbF₅ were performed through a glass Y-piece with PTFE Swagelok connections.
Figure 2.2.1 A ¾-in. o.d. FEP vessel equipped with a stainless steel valve and a FEP T-piece connection for distillation of HF to reactors.
2.2.3 Drying of \([\text{N(CH}_3\text{)}_4][\text{F}], \text{CsF}, \text{KF}, \text{Sb}_2\text{S}_3, \text{Sb}_2\text{S}_5\)

Anhydrous tetramethylammonium fluoride, \([\text{N(CH}_3\text{)}_4][\text{F}]\), was prepared from tetramethylammonium fluoride tetrahydrate (Fluka > 98 \%) according to the literature method.  

Cesium fluoride, CsF (Sigma-Aldrich, 99.99\%) was dried by fusion in a platinum crucible, followed by the transfer of the red hot clinker to the dry box port where it was immediately evacuated. Upon transferring to the dry nitrogen atmosphere of the glove box, the sample was ground to a fine powder and stored in the dry box until use.

Potassium fluoride was dried under dynamic vacuum at temperatures of 160° C for six hours prior to being transferred in the dry box.

Antimony (III) sulfide, \(\text{Sb}_2\text{S}_3\) (Alpha Aesar, 100\%) was ground to a fine powder followed by drying under dynamic vacuum at 160 °C for ca. six hours prior to being brought into the dry box.

Antimony (V) sulfide, (Sigma-Aldrich) was heated to 80°C for 16 h under dynamic vacuum prior to being brought into the dry box.

2.3 Synthesis of Silanethiolate Salts

2.3.1 Preparation of \([\text{N(CH}_3\text{)}_4][\text{SSi(CH}_3\text{)}_3]\)

Inside the dry box, 0.273 g (2.93 mmol) of \(\text{N(CH}_3\text{)}_4\text{F}\) was transferred into a glass reactor equipped with J. Young Teflon stopcock and a PTFE-coated stirring bar. The sealed reactor was connected to the glass vacuum line where 4.490 g of \(\text{CH}_3\text{CN}\) and 0.530 g (2.96 mmol) of \((\text{CH}_3)_2\text{Si})_2\text{S}\) were vacuum distilled on top of the powder. The \(\text{CH}_3\text{CN}\) solvent was allowed to melt at -35 °C using an ethanol bath, followed by stirring of the reaction mixture. The clear colourless solution turned milky white for a few moments before a white solid settled from the reaction mixture. The volatiles were removed under dynamic vacuum at -35 °C yielding a white solid aggregate. The solid was further heated to 50 °C under dynamic vacuum to completely remove \(\text{CH}_3\text{CN}\) solvent. Inside the dry box, the aggregate was ground and 0.458 g (2.55 mmol) \([\text{N(CH}_3\text{)}_4][\text{SSi(CH}_3\text{)}_3]\) was collected. Typical yields for the reaction were 87.1 \%.  

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2.3.2 Preparation of [K(18-crown-6)][SSi(CH₃)₃]

Inside the dry box, 0.042 g (0.72 mmol) of KF and 1.950 g (0.73 mmol) of 18-crown-6 were transferred into a glass reactor equipped with a J. Young PTFE/glass stopcock and a PTFE-coated stirring bar. The sealed reactor was connected to the glass vacuum line where 4.883 g CH₃CN was vacuum distilled on top of the powders. The reaction vessel was warmed to -38 °C and the reaction mixture was stirred. The solution was cooled to -196 °C and 0.192 g (1.08 mmol) of ((CH₃)₃Si)₂S was vacuum distilled on top of the frozen solution. The solution was allowed to warm to -38 °C using a cold-ethanol bath followed by stirring. The clear colourless solution turned milky white for a few moments before a white solid settled from the reaction mixture. The volatiles were removed under dynamic vacuum at -40 °C leaving white solid on the sides of the reactor. Inside the drybox, 0.259 g (0.634 mmol) of solid [K(18-crown-6)][SSi(CH₃)₃] was collected and stored inside the dry box for further analysis and future use. Typical yields for reaction were 87.7%.

2.3.3 Preparation of Cs[SSi(CH₃)₃]

Inside the dry box, 0.238 g (1.57 mmol) CsF powder was transferred to one side of a glass H-reactor equipped with J. Young Teflon stopcocks (Figure 2.3.1). The sealed reaction vessel was connected to the glass vacuum line where 3.202 g of CH₃CN and 0.376 g (2.11 mmol) of ((CH₃)₃Si)₂S were vacuum distilled on top of the powder. The reaction vessel was warmed to 0 °C and agitated using an ultrasonic bath. The solution turned milky white, but significantly less intensely than the reaction with N(CH₃)₄F, for several minutes before a white solid settled from the reaction mixture. The volatiles were removed under dynamic vacuum at 0 °C yielding white solid on the sides of the reactor and on the bottom of the reactor indicating solubility in CH₃CN. A further purification step was employed by decanting the CH₃CN to the other side of the H-reactor and washing the solid by vacuum distilling the CH₃CN solvent back to the original side, followed by decantation of the solution until all solid soluble in CH₃CN was transferred. After removal of the solvent, the solid that was soluble in CH₃CN was brought inside the drybox and stored in glass vials in the dry box for further analysis and future use. Typical yields were 71.8 % for the reaction.
2.3.4 Preparation of K[SSi(CH₃)₃]

Inside the dry box 0.118g (2.03 mmol) KF powder was transferred to a glass reactor equipped with a J. Young PTFE/glass stopcock. The sealed reaction vessel was taken from the dry box to the glass vacuum line where 3.262 g of CH₃CN and 0.551 g (3.09 mmol) ((CH₃)₃Si)₂S were vacuum distilled on top of the powder. The reaction vessel was warmed to room temperature and agitated with sonication for several minutes. The solution turned milky white, but significantly less intensely than the reaction with N(CH₃)₄F, before a white solid settled from the reaction mixture. The contents were repeatedly sonicated as KF is insoluble in CH₃CN and decomposition of the solvent from nucleophilic F⁻ attack was not a concern. The volatiles were removed under dynamic vacuum yielding a white solid. Solid K[SSi(CH₃)₃] (0.189 g, 1.31 mmol) was collected and stored in glass vials in the dry box for further analysis and future use. Typical yield for reaction was 64.5 %.
Figure 2.3.1  Glass H-reactor equipped with J. Young PTFE/glass stopcocks and PTFE-coated stir bar.
2.4 Synthesis and Reactions of WSF₄

2.4.1 Synthesis of WSF₄ in HF

Inside the drybox, dried Sb₂S₃ (0.136 g 0.400 mmol) was added to a ¼-in. o.d. thin wall FEP T-reactor equipped with a Kel-F valve (Figure 2.1.3(b)). The reactor was taken from the dry box and 1.76 g of anhydrous HF was vacuum distilled on top of the powder at –196 °C. Tungsten hexafluoride (0.326 g 1.09 mmol) was vacuum transferred on top of the frozen reaction mixture at –196 °C. The reactor was backfilled with dry N₂(g) and allowed to warm to room temperature. The reactor mixture was agitated to dissolve frozen WF₆ as the solution warmed to room temperature. The reaction progressed as the solution above the insoluble dark-grey Sb₂S₃ slowly changed from colourless to deep yellow over the course of 16 hours. The reaction mixture was agitated intermittently as the reaction progressed in order to maximize the contact between reactants. The deep yellow solution was decanted over to side arm of FEP T-reactor at which time the solution was cooled to ca. –78 °C. Yellow solid precipitated out of the solution, allowing for colourless HF solvent to be decanted back to original side. The reaction mixture was washed with the HF and the resulting yellow solution was re-decanted to the side-arm of the reaction vessel. The washing procedure was performed 2-3 times. Anhydrous HF was removed under vacuum at –78 °C, over several hours, yielding yellow crystalline material. Pumping was continued for an additional 10 min at room temperature to guarantee complete removal of HF and unreacted WF₆. The amount of recovered WSF₄ was 0.258 g (0.867 mmol) with a yield of 79.3 %. The highest yield obtained using this method was 82 %.

2.4.2 Reaction of WF₆ with H₂S in CFCl₃

Approximately 1.8 mL (1.496 g) of CFCl₃ was distilled into a ¼-in. o.d. FEP reactor equipped with a Kel-F valve at -196 °C. Hydrogen sulfide (0.043g, 1.3 mmol) was condensed into the reactor at -196 °C. Upon warming to room temperature the solution was clear and colourless. Tungsten hexafluoride (0.228 g, 0.766 mmol) was vacuum distilled into the reactor forming a pale yellow solution. The pale colour of the solution persisted for several hours. Raman spectroscopy of the solution showed strong bands corresponding to WF₆ and H₂S respectively. Both reactants were observed to
coexist in solution at the same time. Above the solution reactions in the gas phase slowly resulted in a red/brown deposit on the sides of the reactor. When the solution was placed in the Raman spectrometer at room temperature the laser light caused the immediate formation of brown solid throughout the solution. At temperatures of -20 °C no brown solid was observed. Volatiles were removed under dynamic vacuum at room temperature yielding a red/brown solid. The order of addition of reagents and amounts always gave the same results. This method was abandoned due to an inability to prevent gas-phase reactions from occurring above the solution level.

2.5 Lewis Acid Chemistry of WSF₄

2.5.1 Reaction of WSF₄ with Pyridine

Inside the dry box, 0.039 g (0.13 mmol) of WSF₄ was transferred to a ¼-in o.d. FEP vessel equipped with a Kel-F valve. On the glass line, 0.566 g (7.15 mmol) of pyridine was vacuum distilled on top of brown WSF₄ powder at -196°C. The powder dissolved completely generating a deep orange solution. Excess C₅H₅N was removed under dynamic vacuum at room temperature yielding 0.051g (0.14 mmol) of dark solid WSF₄·C₅H₅N. The ratio WSF₄ to pyridine was found to be 1:1.1.

Inside the dry box, 0.10 g (0.034 mmol) of WSF₄ was loaded into a 4-mm FEP reactor with Kel-F valve. Pyridine (0.494 g 6.24 mmol) was vacuum transferred to the reactor through a glass Y-piece on the glass vacuum line, generating an orange solution. Approximately 93.1 % of the C₅H₅N was removed at temperatures from –40 to –5 °C over 2 h leaving a intense orange-coloured concentrated solution. Acetonitrile was vacuum transferred into the reaction vessel giving an orange solution. The sample tube was heat-sealed under dynamic vacuum at –196 °C and the sample was stored at -196 °C for analysis by NMR spectroscopy.

2.5.2 Production of [N(CH₃)₄][WSF₅]

Inside the dry box, 0.026 g (0.15 mmol) of [N(CH₃)₄][SSi(CH₃)₃] and a small Teflon coated magnetic stir bar were added to a ¾-in. o.d. FEP reactor equipped with a stainless steel valve. Subsequently 6.219 g (86.23 mmol) THF was vacuum distilled onto the solid at -196 °C. The reaction mixture was then stirred at 20 °C to achieve maximum
dissolution of \([\text{N(CH}_3\text{)}_4][\text{SSi(CH}_3\text{)}_3]\), which formed a clear colourless solution. White solid was still visible at the bottom of the reaction vessel as not all dissolved. Vacuum distillation of 0.040 g (0.13 mmol) of WF\(_6\) at –196 °C was followed by warming the mixture to –78 °C and stirring for ca. one hour as the solution went from yellow to pink. The solvent THF was removed under dynamic vacuum overnight at –78 °C and then for 30 minutes at room temperature into a FEP U-tube at –196 °C that was connected to the glass vacuum line. The reaction vessel contained 0.060 g of a homogeneous pink coloured powder. The amount of solid recovered corresponded to 0.15 mmol of \([\text{N(CH}_3\text{)}_4][\text{WSF}_5]\) indicating the presence of a small amount of \(\text{C}_4\text{H}_8\text{O}\) in the final product. The \(^1\text{H}\) NMR spectrum shows a very small peak at 12.39 ppm and a broad feature at ca. 4.9 ppm, which likely correspond to carboxylic acids and aliphatic chains, respectively, resulting from the ring-opening step in the polymerization of THF.

### 2.5.3 Production of \([\text{N(CH}_3\text{)}_4][\text{WSF}_5]\) from WSF\(_4\)

Direct combination of 0.0070 g (0.024 mmol) WSF\(_4\) and 0.0023 g (0.024 mmol) of \(\text{N(CH}_3\text{)}_4\text{F}\) in CH\(_3\text{CN}\) resulted in the formation of \([\text{N(CH}_3\text{)}_4][\text{WSF}_5]\) in high purity. The powders were added to a 4-mm o.d. FEP reactor equipped with a Kel-F valve in the dry box. Approximately 0.45 mL of CH\(_3\text{CN}\) solvent was distilled on top of the solids at –196 °C and the contents were warmed to –35 °C and agitated yielding a bright yellow solution. After the contents were mixed thoroughly, the reactor contents were frozen and heat-sealed under dynamic vacuum. The NMR sample was warmed to room temperature and the sample was studied by \(^1\text{H}\) and \(^{19}\text{F}\) NMR spectroscopy.

### 2.6 Preparation of MoSF\(_4\)

#### 2.6.1 Synthesis of MoSF\(_4\)

On the glass vacuum line, 5.388 g of CFCl\(_3\) was vacuum distilled into a ¼-in o.d. FEP reactor with stainless steel valve containing a small Teflon-coated stir bar. Subsequently, 0.306 g (1.71 mmol) of ((CH\(_3\))\(_3\text{Si})_2\text{S}\) was vacuum distilled on top of the frozen CFCl\(_3\) at –196 °C and the resulting solution was stirred for one minute at 20 °C to mix the ((CH\(_3\))\(_3\text{Si})_2\text{S}\) into solution well. A slight excess of MoF\(_6\), 0.410 g (1.95 mmol) was transferred into the reaction vessel at -196 °C. The reaction vessel was allowed to
warm towards room temperature very slowly with constant agitation and quenching in liquid N\textsubscript{2} to prevent side-reactions. The reaction mixture changed from colourless to yellow/brown even as solvent was still solid at temperatures below –120 °C. As the reaction progressed the reaction mixture changed to a homogeneous dark purple colour which persisted even at room temperature. The dark purple solid settled from the solvent, which was slowly removed into a ¾-in. o.d. FEP U-tube at –196 °C with other volatile byproducts, yielding 0.300 g (1.47 mmol) yellow-brown MoSF\textsubscript{4} in a 86 % yield.

2.6.2 Attempted Preparation of MoSF\textsubscript{4} from MoF\textsubscript{6} with (CH\textsubscript{3})\textsubscript{3}SiS in CH\textsubscript{3}CN

Acetonitrile (0.410 g) was vacuum distilled into a ¼-in. o.d. FEP T-reactor at equipped with a stainless-steel Swagelok T-connection at –196 °C (Figure 2.1.3(c)). Then, 0.014 g (0.078 mmol) of ((CH\textsubscript{3})\textsubscript{3}Si)\textsubscript{2}S was vacuum distilled on top of the frozen CH\textsubscript{3}CN on the glass line. The reaction vessel was connected to the metal line and 0.10 mmol of MoF\textsubscript{6} was transferred to the frozen reaction mixture. When the solvent melted the reaction mixture began to darken significantly. Upon warming to room temperature the dark red/brown solution was decanted to the other arm of the T-reactor and the solvent was removed under dynamic vacuum into a U-tube at –196 °C leaving a dark solid in the side arm of the reactor. After solvent removal was complete the reactor was backfilled and brought into the dry box where the straight arm of the T-reactor was disconnected from the Swagelok T-connector and exchanged for a 4-mm o.d. FEP tube. Outside the drybox, acetonitrile was vacuum-distilled on top of the recovered solid. The CH\textsubscript{3}CN solution was decanted into the 4-mm FEP NMR tube where the contents were frozen and the tube was heat-sealed under dynamic vacuum.

2.6.3 Attempted Preparation of MoSF\textsubscript{4} from MoF\textsubscript{6} and H\textsubscript{2}S in CFCl\textsubscript{3}

Approximately 1.8 mL of CFCl\textsubscript{3} was distilled into a ¼-in. o.d. FEP reactor equipped with a Kel-F valve at -196 °C. Hydrogen sulfide was condensed into the reactor, which upon warming to room temperature, formed a clear and colourless solution in CFCl\textsubscript{3}. Molybdenum hexafluoride was vacuum distilled into the reactor at -110 °C. Yellow and brown solid immediately appeared on the side walls of the reactor above the solution. Everything that came into contact with solution was dark brown/black a
possible sign of MoS₃ production. The reaction was very difficult to control. The solid product was characterized by vibrational and NMR spectroscopy.

### 2.6.4 Synthesis of MoF₅

Inside the dry box 0.155g Sb₂S₃ (0.456 mmol) was transferred into a bent ¼-in. o.d. FEP reaction vessel. A large excess of MoF₆ (0.494 g, 2.35 mmol) was vacuum distilled on top of the Sb₂S₃ at -196 °C and the contents were warmed to room temperature. The contents were agitated once the reactor was at room temperature. The MoF₆ began to turn yellow until ca. 1h later the MoF₆ solution was dark yellow. The solution was decanted and the MoF₆ was removed under vacuum at room temperature. A yellow crystalline solid was left behind. The reactor was brought into the glove box where crystals were collected and Raman and infrared samples were prepared. The yellow solid readily dissolved in CH₃CN forming a clear and colourless solution which upon freezing appeared bright yellow.

### 2.6.5 Reaction of MoF₅ with [N(CH₃)₄][SSi(CH₃)₃]

Inside the dry box, 0.007 g (0.04 mmol) of MoF₅ and 0.007 g (0.04 mmol) of [N(CH₃)₄][SSi(CH₃)₃] were added to a 4-mm o.d. FEP reactor equipped with a Kel-F valve. Approximately 0.005 mL of CH₃CN was vacuum distilled into the reaction vessel at -196 °C. The reactor was heat-sealed under dymanic vacuum and allowed to warm to room temperature. The solution immediately turned a brown colour with light brown precipitate. Fluorine-19 NMR spectroscopy on the sample did not show any signals.

### 2.7 Attempted Preparation of MoSF₅

#### 2.7.1 Reaction of MoF₆ with [N(CH₃)₄][SSi(CH₃)₃]

Inside the dry box, 0.004 g (0.02 mmol) of [N(CH₃)₄][SSi(CH₃)₃] was added to a 4-mm o.d. FEP reactor. Acetonitrile (0.308 g) and MoF₆ were distilled on top of the solution at -196 °C. The reactor was heat sealed under dynamic vacuum and the solution was warmed to room temperature and agitated to encourage mixing. The solution turned a yellow colour. The sample was characterized by ¹⁹F NMR spectroscopy. An extended period at room temperature caused the sample to turn a deep brown.
2.7.2 Reaction of MoSF₄ with [N(CH₃)₄][F]

Inside the dry box, 0.0020 g (0.0098 mmol) of MoSF₄ and 0.0016 g (0.017 mmol) of N(CH₃)₄F were added to a 4-mm o.d. FEP reactor equipped with a Kel-F valve. Approximately 0.005 mL of CH₃CN was vacuum distilled into the reactor at -196 °C. The reactor was heat sealed and allowed to warm to room temperature. The sample was agitated to encourage mixing. Dark precipitate formed at the bottom of the reactor indicating a reaction took place. Fluorine-19 NMR spectroscopy showed one peak at -22.1 ppm most likely a result of excess N(CH₃)₄F.

2.8 NMR Spectroscopy

All NMR spectra were recorded on a 300 MHz Bruker Advance II NMR spectrometer. Samples were contained in sealed 4-mm FEP reaction vessels. All samples were collected unlocked and were externally referenced. Fluorine-19 NMR spectra were externally referenced to neat CFCl₃ while ¹H and ¹³C NMR spectra were referenced to neat TMS at room temperature.

2.9 Raman Spectroscopy

All Raman Spectra were recorded on a Bruker RFS 100 FT Raman spectrometer with a quartz beam splitter, a liquid-nitrogen cooled Ge detector, and low temperature accessory. The backscattered (180°) radiation was sampled. The useable Stokes range was 50-3500 cm⁻¹ with a spectral resolution of 2 cm⁻¹. A Nd:Yag laser with a 1064-nm line was used for excitation of the sample. Spectra were recorded on powdered samples in sealed mp capillaries and solution samples in either 4-mm or ½-in. o.d. FEP using powers between 40 and 300 mW. Samples were collected at temperatures between -100 and 20 °C.

2.10 Infrared Spectroscopy

All infrared spectra were recorded on a Nicolet Avatar 360 FTIR spectrometer at ambient temperature. The IR spectra were collected as KBr pellets formed inside the dry box using a Wilks minipress. The spectra were aquired in 16 scans at a resolution of 2 cm⁻¹.
2.11 Single Crystal X-ray Diffraction

2.11.1 Crystal Growth

Powdered MoSF₄ (0.015 g, 0.074 mmol) was added to a ¼-in. o.d. FEP T-reactor (Figure 2.1.3(b)) inside the dry box. Anhydrous hydrogen fluoride (ca. 1.2 mL) was vacuum distilled on top of the powder at -196 °C. The orange solution was agitated and left to settle for ca. 1 h before the solution was decanted to the side arm of the T-reactor.

Crystals of MoSF₄ were grown using a vacuum jacketed low-temperature Raman sample holder and the low-temperature liquid-nitrogen boil-off apparatus and controller that are part of the low-temperature Raman accessory. The temperature of the solution was slowly decreased from -65 to -72 °C on the controller (-53 to -59 actual) over a period of 6 hours. After completed crystal growth the solvent was decanted to the other sidearm of the T-reactor and subsequently removed by roughing vacuum. The crystals were kept cold at -78 °C while under dynamic vacuum.

Crystals of WSF₄ were formed directly from the reaction mixture by the slow removal of solvent HF at -78 °C under dynamic vacuum.

Crystals of MoF₅ were prepared by the removal of solvent MoF₆ from the decanted yellow solution under dynamic vacuum at 20 °C.

2.11.2 Low-Temperature Crystal Mounting

A low temperature crystal mounting technique was utilized for thermally unstable and/or moisture sensitive crystals. Each FEP reactor containing crystals was cut open below the KelF valve under a flow of dry nitrogen. The crystals were then quickly dumped from the chilled tube into an aluminum trough cooled by passing a flow of dry nitrogen through a 5-L Dewar of liquid nitrogen (Figure 2.11.1). The temperature of the trough had been previously adjusted to approximately -85 °C and had been measured with a copper-constantan thermocouple inserted midway into the stream ca. 2-mm above the trough. Each crystal was selected under a microscope and mounted on a glass fibre using an inert perfluorinated polyether, Fomblin Z-25 (Ausimont Inc.). The glass fibre had previously been attached using an epoxy to a metallic pin that was, in turn magnetically mounted on a wand. The polyether selected for crystal mounting was sufficiently viscous to adhere to the crystal, engulf it, and freeze quickly thereafter. The
attached crystal was quickly (<30 s) transferred to the goniometer head of the X-ray instrument using cryotongs which had been chilled by liquid nitrogen prior to use, and attached via a magnetic interface.

### 2.11.3 Collection and Reduction of X-ray data

Crystal structures were collected at temperatures from -100 to -120 °C on a Bruker AXS X-ray diffractometer equipped with an Apex II 4K charge-coupled device (CCD) area detector utilizing Mo Kα radiation (λ = 0.71073 Å) with a graphite monochromator. The crystal-to-detector distance was 6.000 cm. A hemisphere of data was collected with 30 s exposure times. Cell reduction was carried out using the Program SAINT which applied Lorentz and polarization corrections to three dimensionally integrated diffraction spots.

### 2.11.4 Solution and Refinement of Structures

Calculations were performed using the Shelxtl v.614 plus package for structure determination, refinement and molecular graphics. The Xprep program was used to confirm the unit cell dimensions and the crystal lattice. Solutions were obtained using direct methods. Successive difference Fourier syntheses revealed all light atoms. The structures were minimized by least squares refinement based on the square of the structure factors, $F^2$. Atom positions were refined anisotropically. Extinction coefficients were calculated for each crystal structure. Both residual values, $R_1$ based on $F$ and the weighted residual values $wR_2$ based on $F^2$, are available in the structure refinement tables along with the goodness of fit $GooF$. They represent the following equations:

\[
R_1 = \frac{\sum |F_0| - |F_c|}{\sum |F_0|} \quad \text{The conventional R-factor based upon the structure factor.}
\]

\[
wR_2 = \sqrt{\frac{\sum [w(F_0^2 - F_c^2)^2]}{\sum [w(F_0^2)^2]}} \quad \text{The Weighted R-Factor based upon intensity.}
\]

\[
GooF = \sqrt{\frac{\sum [w(F_0^2 - F_c^2)]}{(n - p)}} \quad \text{The GooF is based upon intensity where } n \text{ is the number of reflections, } p \text{ is the number of parameters refined.}
\]
Figure 2.11.1  Crystal mounting apparatus consisting of a five-litre liquid nitrogen Dewar equipped with a rubber stopper, a glass dry nitrogen inlet and a silvered-glass cold nitrogen outlet with aluminium cold trough.
2.12 Computational Results

All calculations were performed in Gaussian 98\textsuperscript{5} and viewed in Gaussview 03. Density functional theory calculations were performed at the B3LYP level of theory using the 6-31G(D) basis set for the trimethylsilanethiolate anion and the LANL2DZ basis set for MoSF\textsubscript{4}, WSF\textsubscript{4}, and WSF\textsubscript{5}.\textsuperscript{−}
References


Chapter 3
Synthesis and Characterization of Silanethiolate Salts

3.1 Introduction

Several sulfide transfer agents have been used in the past. Alkali metal or silver sulfides are common reagents, though these reagents have not been the preferred reactants for synthetic chemistry involving high-valent tungsten and molybdenum fluorides. For such syntheses antimony (III) sulfide and boron (III) sulfide have been the principal sulfide sources for high-temperature reactions. Observation and isolation of pure products unstable at high-temperature are untenable with such methods. It has been shown directly by Blackman et al.\textsuperscript{1} that trimethylsilyl-sulfide reagents have great potential as sulfide transfer agents for group six metal fluorides in room temperature syntheses.

The very useful and commercially available hexamethyldisilathiane, ((CH\(_3\))\(_3\)Si)$_2$S, was first synthesized by Eaborn in 1950. Since then, the chemistry of ((CH\(_3\))\(_3\)Si)$_2$S has become quite diverse as it has been used as a reagent in both organic and inorganic synthesis reactions especially in cases where disulfide bridges are a desired product.\textsuperscript{2} Sodium trimethylsilanethiolate, has been prepared by at least two methods (Equations 3.1.1-2).\textsuperscript{3-5} It has found utility in organic chemistry in cyclizations,\textsuperscript{6} demethylations of aromatic methyl ethers,\textsuperscript{3,7,8} conversion of nitriles to thioamides\textsuperscript{3,9}, and conversion of aromatic nitro to amine groups.\textsuperscript{3,4} It has been shown for cyclization reactions that fluorine is the preferred nucleophile for successful heterocycle generation.\textsuperscript{6} Sodium trimethylsilanethiolate has also been used successfully in inorganic chemistry for generation of transition-metal silanethiolate complexes\textsuperscript{10,11} and sulfido ligand substitution reactions.\textsuperscript{5}

\[
\text{((CH}_3\text{)}_3\text{Si})_2\text{S} + \text{NaOCH}_3 \xrightarrow{\text{DMEU}} \text{NaSSi(CH}_3\text{)}_3 + (\text{CH}_3\text{)}_2\text{SiOCH}_3 \quad 3.1.1
\]

\[
(\text{CH}_3\text{)}_3\text{SiCl} + \text{Na}_2\text{S} \xrightarrow{\text{DMEU}} \text{EtOH} \quad \text{NaSSi(CH}_3\text{)}_3 + \text{NaCl} \quad 3.1.2
\]
The strong silicon-oxygen bond (444 kJ/mol) relative to silicon-sulfur bond (292 kJ/mol) provides the significant driving force that has been employed in the conversion of carbonyls to thiocarbonyls at moderate temperatures\(^2\). The even stronger silicon-fluorine bond (594 kJ/mol) provides a much greater driving force, making silanethiolate salts prospective agents for efficient fluoride-sulfide substitution reactions.

3.2 Results and Discussion

3.2.1 Preparation of Trimethylsilanethiolate Salts

Four trimethylsilanethiolate salts were prepared by reactions of \(((\text{CH}_3)_3\text{Si})_2\text{S}\) and \([\text{N}((\text{CH}_3)_4)]\text{F}, [\text{K}(18\text{-crown-6})]\text{F}, \text{CsF}, \text{and KF salts}\) (Equation 3.2.1) at low temperature in \(\text{CH}_3\text{CN}\). Temperatures below -35 °C proved necessary for synthesis of \([\text{N}((\text{CH}_3)_4)]\text{SSi(CH}_3)_3\) and \([\text{K}(18\text{-crown-6})]\text{SSi(CH}_3)_3\) salts because the starting materials, anhydrous \([\text{N}((\text{CH}_3)_4)]\text{F}\) and \([\text{K}(18\text{-crown-6})]\text{F}\) contained “naked fluoride,” which attacks \(\text{CH}_3\text{CN}\) at temperatures higher than -35 °C. Temperatures of 0°C were used for reactions involving \(\text{CsF}\) and \(\text{KF}\). The volatile \((\text{CH}_3)_3\text{SiF}\) byproduct was easily removed under vacuum.

\[
\text{CH}_3\text{CN} \quad \text{MF} + ((\text{CH}_3)_3\text{Si})_2\text{S} \rightarrow \text{MSSi(CH}_3)_3 + (\text{CH}_3)_3\text{SiF} \quad (\text{M} = \text{N}((\text{CH}_3)_4), \text{K}(18\text{-crown-6}), \text{Cs}, \text{K})
\]

Reaction 3.2.1 was most successful for production of \([\text{N}((\text{CH}_3)_4)]\text{SSi(CH}_3)_3\) and \([\text{K}(18\text{-crown-6})]\text{SSi(CH}_3)_3\) salts with yields of 87.1 and 87.7 %, respectively. Production of \([\text{Cs}]\text{SSi(CH}_3)_3\) and \([\text{K}]\text{SSi(CH}_3)_3\) had lower yields of 71.8 and 64.5 %, respectively. The \([\text{N}((\text{CH}_3)_4)]\text{SSi(CH}_3)_3\) salt was produced successfully in high purity as verified by Raman and infrared spectroscopy. The trimethylsilanethiolate salts were all white flocculent solids that decomposed rapidly in contact with moisture generating volatile malodorous products.

Slow decomposition of the salts was observed in \(\text{CH}_3\text{CN}\) which resulted in fluorescence in the Raman spectra. Salts of \([\text{N}((\text{CH}_3)_4)]^+\) and \([\text{K}(18\text{-crown-6})]^+\) were observed to readily react with \(\text{CH}_2\text{Cl}_2\) upon dissolution while the \([\text{Cs}]^+\) salt seemed inert towards \(\text{CH}_2\text{Cl}_2\).
The \([\text{N(CH}_3\text{)}_4][\text{SSi(CH}_3\text{)}_3]\) salt decomposed slowly at 167 °C without melting, decomposition became rapid at temperatures above 189 °C generating a colourless gas. The \(\text{Cs}^+\) salt began to decompose slowly at 337 °C, liquidified at 340 °C and boiled by 343 °C leaving a small amount of unidentified white solid. The \(\text{K}^+\) salt was stable to temperatures of 400 °C. The \([\text{K(18-crown-6)})]\text{}\^+\) salt decomposed at 50 °C.

Crystal growth of \([\text{N(CH}_3\text{)}_4][\text{SSi(CH}_3\text{)}_3]\) was attempted from acetonitrile and THF by slow removal of solvent at low temperature and room temperature. Sublimation was also attempted, but the solid only decomposed into a colourless gas and a clear colourless unidentified substance. All attempts for crystal growth were unsuccessful.

The \(\text{Cs}[\text{SSi(CH}_3\text{)}_3]\) salt formed solids with a small degree of crystallinity when \text{CH}_3\text{CN} was removed at -40 °C. A unit cell could not be obtained due to the poor quality of X-ray diffraction data.

### 3.2.2 Vibrational Spectroscopy of Trimethylsilanethiolate Salts

Raman and infrared spectra were recorded of \([\text{N(CH}_3\text{)}_4][\text{SSi(CH}_3\text{)}_3]\), \([\text{K(18-crown-6)})][\text{SSi(CH}_3\text{)}_3]\), \(\text{Cs}[\text{SSi(CH}_3\text{)}_3]\) and \(\text{K}[\text{SSi(CH}_3\text{)}_3]\) (Figures 3.2.1-4). Vibrational frequencies together with their assignments are found in Tables 3.2.1-4. Raman frequencies of \(\text{SSi(CH}_3\text{)}_3\) are compared in Table 3.2.5. Strong bands in the Raman spectra at \(\text{ca.}\ 500\ \text{cm}^{-1}\) attributable to the Si-S (\(\text{A}_1\)) stretching mode are compared in Table 3.2.6.

Vibrational spectroscopy of alkali metal silanethiolate salts, \(\text{K}^+\) and \(\text{Cs}^+\), show only bands that are directly attributable to the stretching and bending modes of the \([\text{SSi(CH}_3\text{)}_3]\)\^− anion (Tables 3.2.1-2). The assignment of these bands is based upon calculated frequencies and infrared intensities which are compared in Table 3.2.1. It is quite apparent that the infrared spectrum of \(\text{CsSSi(CH}_3\text{)}_3\) contained more weak signals above 3000 cm\(^{-1}\), than were found for the \(\text{K}^+\) salt, which were likely the result of small amounts of hydrolysis while collecting infrared data.

Vibrational spectra of the \([\text{K(18-Crown-6)})][\text{SSi(CH}_3\text{)}_3]\) salt are dominated by the 18-crown-6 constituent of the complex (Figure 3.2.4). Infrared and Raman data for neat 18-crown-6 were collected and are shown for comparison in Table 3.2.4.
Good agreement was found for the relative intensities and frequencies of the Raman bands attributed to the trimethylsilanethiolate anion (Table 3.2.5) of all salts.

From Table 3.2.6 it is quickly observed that the Si-S bond becomes stronger with larger, less coordinating cations. This trend continues to the covalently bonded, $\text{H}^+$, found in ($\text{CH}_3)_3\text{SiSH}$ with an Si-S stretch at 454 cm$^{-1}$.$^{12,13}$ This effect could be due to an increase in the ionic character of the S-Si bond as a result of stronger ion pairing from smaller more coordinating Cs$^+$ and K$^+$ cations resulting in lower stretching frequencies for the S-Si bond. With large, sterically hindered cations a higher degree of S-Si backbonding results from the effectively more negatively charged sulfur of trimethylsilanethiolate salts. Hyperconjugation would serve to increase Si-S bond strength upon donating electrons into the $\sigma^*$ antibonding molecular orbital of SiC$_3$, subsequently elongating the Si-C bonds and decreasing their frequency of vibration. This trend is observed in Table 3.2.5 with the slight decrease in the SiC$_3$ asymmetric stretch for salts with larger cations.

According to theory, non-linear molecules have 3N-6 normal modes of vibration, where N denotes the number of atoms in the molecule. The trimethylsilanethiolate anion should have 36 vibrational modes, as are found in table 3.2.8. The symmetry of the vibrational modes in the $C_{3v}$ point group are represented by $\Gamma_{\text{vib}} = 8 A_1 + 4 A_2 + 12 E$. Vibrations of $A_1$ and $E$ symmetry can be observed in the Raman and infrared spectra while $A_2$ vibrations are Raman and infrared inactive. The observed vibrations therefore span the $8 A_1 + 12 E$ symmetry. Ignoring C-H vibrations and approximating CH$_3$ groups to spheres, the vibrations are simplified greatly to $\Gamma_{\text{vib}} = 3 A_1 + 3 E$ describing four stretching modes and five bending modes. The symmetry assignment of the vibrational bands is given in Table 3.2.5.
Table 3.2.1 Vibrational Spectroscopy Data from K[SSi(CH$_3$)$_3$]  

<table>
<thead>
<tr>
<th>Raman$^b$</th>
<th>Infrared$^c$</th>
<th>Calculated$^d$</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>2948 (47)</td>
<td>2945 vs</td>
<td>3007 [94]</td>
<td>$\nu$(CH$_3$) and combination</td>
</tr>
<tr>
<td>2887 (41)</td>
<td>2887 s</td>
<td>3000 [23]</td>
<td></td>
</tr>
<tr>
<td>2810 (4)</td>
<td>2810 sh</td>
<td>3000 [23]</td>
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</tr>
<tr>
<td>1434 (3)</td>
<td>1435 m</td>
<td>1486-1499</td>
<td></td>
</tr>
<tr>
<td>1417 (sh)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1403 (9)</td>
<td>1390 m</td>
<td>1287-1298</td>
<td>$\delta$(CH$_3$) deformations</td>
</tr>
<tr>
<td>1246 (6)</td>
<td>1246 vs</td>
<td>1287-1298</td>
<td></td>
</tr>
<tr>
<td>1239 (sh)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>849 (2)</td>
<td>852 vs</td>
<td>892 [224]</td>
<td></td>
</tr>
<tr>
<td>820 (5)</td>
<td>821 vs</td>
<td>855 [74]</td>
<td>$\delta$(Si-CH$_3$ rocking)</td>
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<tr>
<td>746 (3)</td>
<td>745 s</td>
<td>762 [20]</td>
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</tr>
<tr>
<td>736 (4)</td>
<td>730 s</td>
<td>761 [20]</td>
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</tr>
<tr>
<td>673 (17)</td>
<td>672 s</td>
<td>675 [0]</td>
<td>$\nu_{as}$SiC$_3$, E</td>
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<tr>
<td>667 (sh)</td>
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<td></td>
</tr>
<tr>
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<td>$\nu$, SiC$_3$, A$_1$</td>
</tr>
<tr>
<td></td>
<td>550 vw</td>
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<td></td>
</tr>
<tr>
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<td></td>
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<td>177 [0.7]</td>
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</table>

$^a$ Abbreviations denote shoulder (sh), very strong (vs), strong (s), medium (m), weak (w), and very weak (vw). $^b$ Neat solid in melting point capillary at room temperature. $^c$ KBr pellet at room temperature. $^d$ Calculations performed at B3LYP/6-31G(D) level of theory, calculated infrared intensities in square brackets; units of km/mol.
Table 3.2.2  Vibrational Spectroscopy Data from Cs[SSi(CH₃)₃]

<table>
<thead>
<tr>
<th>Frequency, cm⁻¹</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>Raman</td>
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</tr>
<tr>
<td>3752 vw</td>
<td>v(CH₃) and combination</td>
</tr>
<tr>
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</tr>
<tr>
<td>3612 vw</td>
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</tr>
<tr>
<td>3184 w</td>
<td></td>
</tr>
<tr>
<td>2808 (sh)</td>
<td>3133 br w</td>
</tr>
<tr>
<td>2790 (sh)</td>
<td>3040 sh</td>
</tr>
<tr>
<td>2943 (32)</td>
<td>2942 sh</td>
</tr>
<tr>
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<td>2931 vs</td>
</tr>
<tr>
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<tr>
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<td></td>
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<tr>
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<tr>
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<td>746 vs</td>
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<tr>
<td>669 (32)</td>
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</tr>
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<td>505 vs</td>
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<td>δ₅ SiC₃, A₁</td>
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<tr>
<td>206 (31)</td>
<td>δ₆ SiC₃, E</td>
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</table>

*Abbreviations denote shoulder (sh), very strong (vs), strong (s), medium (m), weak (w), and very weak (vw).*  
*Neat solid in melting point capillary at room temperature.*  
*KBr pellet at room temperature.*
Table 3.2.3 Vibrational Spectroscopy Data of [N(CH₃)₄][SSi(CH₃)₃]

<table>
<thead>
<tr>
<th>Frequency, a cm⁻¹</th>
<th>Assignment b</th>
<th>Raman b</th>
<th>Infrared c</th>
</tr>
</thead>
<tbody>
<tr>
<td>3024 (13)</td>
<td>v(CH₃) and combination</td>
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Abbreviations denote shoulder (sh), very strong (vs), strong (s), medium (m), weak (w), and very weak (vw). b Neat solid in melting point capillary at room temperature. c KBr pellet at room temperature.
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Abbreviations denote shoulder (sh), very strong (vs), strong (s), medium (m), weak (w), very weak (vw). Neat solid in melting point capillary at room temperature. KBr pellet at room temperature. [SSi(CH₃)₃] bands that overlap with those of 18-crown-6.
Table 3.2.5 Comparison of Raman Vibrational Data for Trimethylsilanethiolate Salts

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<td>500 (100) 505 (100) 509 (100) 511 (33) [100]</td>
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<td>641 (25) 640 (12) 641 (8) 642 (3) [9]</td>
<td>ν(_s) SiC(_3), A(_1)</td>
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<td>673 (17) 669 (32) 665 (18) 662 (5) [15]</td>
<td>ν(_{as}) SiC(_3), E</td>
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\(^{a}\) Values in square brackets show relative intensity compared to ν\(_s\) Si-S, A\(_1\) for direct comparison to other silanethiolate salts.

Table 3.2.6 Si-S Stretching Modes Found in Raman Spectra of Silanethiolate Salts

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<td>[K][SSi(CH(_3))(_3)]</td>
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<td>[Cs][SSi(CH(_3))(_3)]</td>
<td>505 (100)</td>
</tr>
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<td>[N(CH(_3))(_4)][SSi(CH(_3))(_3)]</td>
<td>509 (100)</td>
</tr>
<tr>
<td>[K(18-crown-6)][SSi(CH(_3))(_3)]</td>
<td>511 (33)</td>
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</table>
Figure 3.2.1  The vibrational spectra of K[SSi(CH₃)₃] were collected at room temperature. The Raman spectrum (lower trace) was recorded on the neat solid in a glass melting point capillary. The infrared spectrum (upper trace) was collected as a KBr pellet.
Figure 3.2.2  The vibrational spectra of Cs[SSi(CH₃)₃] were collected at room temperature. The Raman spectrum (lower trace) was recorded on the neat solid in a glass melting point capillary. The infrared spectrum (upper trace) was collected as a KBr pellet.
Figure 3.2.3  The vibrational spectra of [N(CH₃)₄][SSi(CH₃)₃] were collected at room temperature. The Raman spectrum (lower trace) was recorded on the neat solid in a melting point capillary. The infrared spectrum (upper trace) was collected as a KBr pellet.
Figure 3.2.4  The vibrational spectra of $[\text{K}(18\text{-crown-6})][\text{SSi(CH}_3)_3]$ were collected at room temperature. The Raman spectrum (lower trace) was recorded on neat solid in a glass melting-point capillary. The infrared spectrum (upper trace) was collected as a KBr pellet.
3.2.3 Density Functional Theory Calculations of Silanethiolate Salts

Density Functional Theory Calculations were performed on the [SSi(CH\(_3\))]\(^{-}\) anion at the B3LYP/6-31G(D) level of theory. Geometry optimization and frequency calculations were performed in separate steps. Calculated vibrations were viewed using Gaussview 3.09.

The [SSi(CH\(_3\))]\(^{-}\) anion ideally assumes \(C_{3v}\) point symmetry, this geometry is confirmed by DFT calculations (Figure 3.2.5) (Table 3.2.7). Bond lengths and angles are given and compared to calculated bond lengths and angles for (CH\(_3\))\(_3\)SiSH in Table 3.2.7. Comparison of the calculated values for (CH\(_3\))\(_3\)SiS\(^{-}\) and (CH\(_3\))\(_3\)SiSH indicate that the anion has a significantly shorter Si-S bond and longer Si-C bonds which is confirmed by experimental spectroscopic evidence. This in turn supports the argument that the higher frequency for the Si-S stretch of larger cation salts is a result of hyperconjugation.

The calculated frequencies, Raman scattering activities, and infrared intensities are shown in Table 3.2.8 along with vibrational descriptions and symmetry assignments. The Si-S stretching mode (Table 3.2.2) was calculated to appear at 505 cm\(^{-1}\) which is in the midst of experimental data for the silanethiolate salts prepared. The good agreement along with identical calculations performed on the (CH\(_3\))\(_3\)SiSH molecule that calculated the Si-S stretch for that molecule at 451 cm\(^{-1}\), (literature 454 cm\(^{-1}\) Table 3.2.6) indicate that DFT calculations at the B3LYP level of theory using the 6-31G(D) basis set are good at describing these systems.

The calculated vibrational intensities (Table 3.2.8) have been shown to be much closer to experiment in predicting infrared intensity than for predicting Raman scattering activity. For this reason only calculated infrared intensity is given in comparison of experiment to calculation in Table 3.2.1.

The strong agreement between the number of signals and their positions expected from theory and calculation indicate that the anions do not conform to lower site symmetry which would cause splittings of the predicted vibrational bands.
Figure 3.2.5  The geometry-optimized trimethylsilanethiolate anion shows approximate \( C_{3v} \) symmetry. Density functional theory calculations were performed at the B3LYP/6-31G(D) level of theory.

Table 3.2.7  Calculated Geometries of \((\text{CH}_3)_3\text{SiS}^-\) Anion and \((\text{CH}_3)_3\text{SiSH}\) Molecule at the B3LYP/6-31G(D) Level of Theory.

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<th>((\text{CH}_3)_3\text{SiSH})</th>
<th>Bond Angle, °</th>
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<tr>
<td>S-Si-C</td>
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<td>104°, 110°, 110°</td>
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<td>C-Si-C</td>
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<td>111°</td>
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Table 3.2.8 Calculated Intensity of Raman and Infrared Vibrational Modes for the SSi(CH₃)₃⁻ Anion and their Assignments within the C₃v Point Group

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<th>Assignment</th>
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<td>23.6</td>
<td>νₐₛ(C-H), E</td>
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<td>11</td>
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<td>νₐₛ(SiC₃), E</td>
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<td>νₛ(S-Si), A₁</td>
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<td>4.3</td>
<td>δₐₛ(SiC₃), E</td>
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<td>δₛ(SiC₃), A₁</td>
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<tr>
<td>177</td>
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<td>δₐₛ(SiC₃), E</td>
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<td>0.1</td>
<td>(CH₃) rotation, A₂</td>
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<tr>
<td>135</td>
<td>0</td>
<td>0</td>
<td>(CH₃) rotation, A₂</td>
</tr>
</tbody>
</table>

ᵃ Calculated Raman scattering activity is in units of a⁴/u. ᵇ Calculated infrared intensity is in units km/mol.
3.2.4 NMR Spectroscopy of Silanethiolate Salts

Nuclear magnetic resonance (NMR) spectroscopy was used to check the solubility and purity of the trimethylsilanethiolate salts in CH$_3$CN. The $^1$H NMR chemical shifts of the anion for various salts are compared in Table 3.2.9.

The $^{13}$C and $^1$H NMR spectra showed that the [N(CH$_3$)$_4$]$^+$ salt was moderately soluble in CH$_3$CN. Chemical shifts of +3.35 and +0.16 ppm for [N(CH$_3$)$_4$]$^+$ and [SSi(CH$_3$)$_3$]$^-$ were observed, respectively, in the $^1$H NMR spectrum. The chemical shift of the [SSi(CH$_3$)$_3$]$^-$ anion was close to the standard TMS. Two separate chemical shifts were recorded for [N(CH$_3$)$_4$][SSi(CH$_3$)$_3$] in the $^1$H-decoupled $^{13}$C NMR spectrum. The cation [N(CH$_3$)$_4$]$^+$ was a 1:1:1 triplet at +55.7 ppm with a $^1$J$(^{13}$C-$^{14}$N) coupling of 4.05 Hz while [SSi(CH$_3$)$_3$]$^-$ was a singlet at +8.43 ppm.

The $^1$H NMR spectrum of [N(CH$_3$)$_4$][SSi(CH$_3$)$_3$] in THF (C$_4$H$_8$O) showed a small singlet for [SSi(CH$_3$)$_3$]$^-$ at +0.12 ppm with $^{13}$C-satellites with $^1$J$(^1$H-$^{13}$C) coupling of 180 Hz. The 1H resonance for [N(CH$_3$)$_4$]$^+$ was obscured by the solvent signal. The difference in the chemical shift compared to [N(CH$_3$)$_4$][SSi(CH$_3$)$_3$] in CH$_3$CN is an indication that an interaction may occur between the SSi(CH$_3$)$_3$$^-$ anion and the solvent THF.

In HF [N(CH$_3$)$_4$][SSi(CH$_3$)$_3$] broke down to form (CH$_3$)$_3$SiF which is easily recognized by $^3$J$(^1$H-$^{19}$F) coupling of ca 8 Hz showing as a doublet at +0.44 ppm in the $^1$H NMR spectrum and a decet at -157 ppm in the $^{19}$F NMR spectrum. Signals at +3.25 ppm in the $^1$H NMR spectrum and +29.9 and +34.1 ppm in the $^{19}$F NMR spectrum were also observed.

The $^1$H NMR spectrum of [K(18-crown-6)][SSi(CH$_3$)$_3$] in CH$_3$CN contained a singlet at +3.67 ppm with complex $^{13}$C satellite pattern showing coupling to several different carbons (ca. $^1$J$(^{13}$C-$^1$H) = 148 to 132 Hz) corresponding to [K(18-crown-6)]$^+$. The satellites were comprised of at least five different components separated by 0.006 ppm (1.8 Hz). Magnetic inequivalence of the hydrogen environments is likely the cause of this complexity. The [SSi(CH$_3$)$_3$]$^-$ anion signal was found to be at +0.16 ppm, very close to the result for the [N(CH$_3$)$_4$]$^+$ salt. Carbon-13 satellites were barely discernable about the singlet. The $^1$H-decoupled $^{13}$C NMR spectrum showed one singlet at +70.95 ppm corresponding to the [K(18-crown-6)]$^+$ no signal for the anion could be detected.
The $^1$H NMR spectrum of KSSi(CH$_3$)$_3$ showed a singlet from the anion at +0.17 ppm while the $^1$H-decoupled $^{13}$C NMR spectrum showed one small singlet at +8.43 ppm; both attributable to the [SSi(CH$_3$)$_3$]$^-$ anion. The $^{13}$C NMR signal of the anion is corroborated by the $^{13}$C NMR signal from [SSi(CH$_3$)$_3$]$^-$ at +8.43 ppm for the [N(CH$_3$)$_4$]$^+$ salt.

The $^1$H NMR spectrum of CsSSi(CH$_3$)$_3$ gave a singlet at +0.17 ppm with $^{13}$C satellites from $^1J$($^1$H-$^1$C) coupling of 117 Hz corresponding to [SSi(CH$_3$)$_3$]$^-$. Also present was a doublet at +0.36 ppm corresponding to (CH$_3$)$_3$SiF with the characteristic $^3J$($^1$H-$^19$F) coupling of ca 8 Hz. The $^1$H decoupled $^{13}$C NMR spectrum showed one singlet at +8.32 ppm corresponding to the [SSi(CH$_3$)$_3$]$^-$ anion differing only slightly from $^{13}$C NMR shifts for K$^+$ and [N(CH$_3$)$_4$]$^+$ salts. A $^{19}$F NMR spectrum contained a small signal at ca. -155 ppm from (CH$_3$)$_3$SiF in agreement with $^1$H NMR data indicating that a very small amount of starting material CsF may have been present in the CsSSi(CH$_3$)$_3$ product.

In Table 3.2.9 the chemical shift of the SSi(CH$_3$)$_3$ anion is relatively constant for all salts dissolved in CH$_3$CN, indicating the choice of cation has little to do with the anion-solution interaction (besides solubility). There is a relatively large discrepancy between the chemical shift of the anion in THF compared to CH$_3$CN, which is also coupled with a large change in the $^1J$($^1$H-$^1$C) observed, indicating that an interaction with the donor solvent likely occurs.

Attempts were made to collect $^{29}$Si NMR signals for all salts though none were detected. It is likely that the signals were not observed due to slow spin-lattice relaxation.
Table 3.2.9 $^1$H NMR Spectroscopy Data of SSi(CH$_3$)$_3^-$ Anion in Solution at Room Temperature.

<table>
<thead>
<tr>
<th>Salt</th>
<th>Solvent</th>
<th>Chemical Shift (ppm)</th>
<th>$^1J(^1$H-$^1$3C) (Hz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[K(18-crown-6)][SSi(CH$_3$)$_3$]</td>
<td>CH$_3$CN</td>
<td>+0.16</td>
<td></td>
</tr>
<tr>
<td>[N(CH$_3$)$_4$][SSi(CH$_3$)$_3$]</td>
<td>CH$_3$CN</td>
<td>+0.16</td>
<td>+0.12      180</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cs[SSi(CH$_3$)$_3$]</td>
<td>CH$_3$CN</td>
<td>+0.17</td>
<td>117</td>
</tr>
<tr>
<td>K[SSi(CH$_3$)$_3$]</td>
<td>CH$_3$CN</td>
<td>+0.17</td>
<td></td>
</tr>
</tbody>
</table>

3.3 Summary

Hexamethyldisilathiane is a useful reagent for the preparation of ionic trimethylsilanethiolate salts. Novel salts of N(CH$_3$)$_4^+$, K(18-crown-6)$^+$, Cs$^+$, and K$^+$ were successfully prepared with excess amounts of ((CH$_3$)$_3$Si)$_2$S in CH$_3$CN solvent. Their vibrational spectra were collected and compared, to each other and density functional theory calculations showing many similarities and general trends based upon the size of the cation that accompanied SSi(CH$_3$)$_3^-$. The lack of extra vibrational bands indicates that lower site symmetry is not imposed on the anion in the solid state. Solutions of each salt in CH$_3$CN showed very similar chemical shifts for the anion indicating the cation did not seem to have a large effect on their interaction with solution.
References


4.1 Introduction

Tungsten sulfide tetrafluoride, WSF₄, is the transition-metal sulfide fluoride that has been studied most extensively. Prior syntheses of WSF₄ involved the reaction of WF₆ with B₂S₃ or Sb₂S₃ at high temperatures¹,² or with ((CH₃)₃Si)₂S in CH₃CN and CH₂Cl₂ solvents at ambient temperature.³ The production of significant amounts of the WS₃ byproduct which formed via side reactions made it of interest to find a simpler and more reliable synthetic route to WSF₄. Little is known about the reactivity of WSF₄ especially in comparison to the oxygen analogue. A reliable preparative method for pure WSF₄ is necessary for the extensive study of its chemistry.

4.2 Results and Discussion

4.2.1 Syntheses of WSF₄

The best synthesis for pure WSF₄ in 300-mg quantities was found to be the reaction of WF₆ and Sb₂S₃ in anhydrous HF at ambient temperature (Equation 4.2.1).

\[ \text{Sb}_2\text{S}_3 + 3 \text{WF}_6 \rightarrow \text{aHF} \rightarrow 3 \text{WSF}_4 + 2 \text{SbF}_3 \] 4.2.1

The reaction is slow, and it took more than one hour before a colour change was observed at room temperature. The slow approach seemed to have the significant advantage that only WSF₄ was produced with no signs of side reactions. The yellow colour of the solution became more intense with time. It was quite evident that larger amounts of anhydrous HF solvent increased the yield of yellow WSF₄ solid at the end of reaction. Deficiencies or a large excess of WF₆ had no effect on the product. Raman spectroscopy conducted on the reaction solution showed strong signals corresponding to WF₆ after 24 hours even when the solution was deep yellow and Sb₂S₃ was still visibly present. The
deep yellow HF solution was decanted to a side-arm of the reactor where the solvent HF was removed by vacuum at −78 °C giving a yellow solid that was isolated in an 82 % yield. Tungsten sulfide tetrafluoride was fully characterized by vibrational and \(^{19}\)F NMR spectroscopy and X-ray crystallography.

It was necessary to remove all HF from the reaction mixture at −78 °C to maintain the yellow colour of the product. Any unreacted WF\(_6\) was removed under dynamic vacuum at room temperature after complete removal of HF. Removal of HF at room temperature resulted in a large amount of dark material among the yellow product. It was observed that the yellow WSF\(_4\) turned brown over \(ca.\) 48 hours at room temperature in the dry box and proceeded to get darker over longer periods. At low temperatures the solid maintained the original yellow colour.

Freshly generated WSF\(_4\) quickly lost its solubility in HF. At first glance this seemed puzzling, as WSF\(_4\) was highly soluble in HF during production. The solubility is only lost when the original solvating HF has been removed to generate the yellow solid product. Presumably solvated WSF\(_4\) monomers are formed in HF solution; after removal of HF infinite chains of WSF\(_5\) octahedra are formed, as found in the X-ray crystal structure of WSF\(_4\). From that point on HF is not a strong enough Lewis base to entice a large amount of WSF\(_4\) to dissolve. This remains the case, as the yellow product turns brown, as solutions in HF only ever achieve a very slight yellow colour.

The tendency of yellow WSF\(_4\) to turn brown was a concern at first as it was important to know whether or not it was the result of particle size or decomposition. It can now be stated with certainty that the brown colouration of the yellow solid is the result of increased particle size. It is evident that the longer WSF\(_4\) has been stored in the dry box the less electrostatic it becomes; freshly produced WSF\(_4\) adheres to sides of reaction vessels much more persistently than dark brown WSF\(_4\) that has been stored at room temperature for weeks. Solutions of WSF\(_4\) in HF have the same pale yellow colour whether they are made with freshly prepared WSF\(_4\) or older WSF\(_4\). The bands of the Raman spectrum remain the same, as only fluorescence increases as the solid darkens. The addition of Lewis bases, like pyridine, causes the solubility of WSF\(_4\) to increase significantly in anhydrous HF solvent, regardless of the coloration of WSF\(_4\). Fluorine-19
NMR spectroscopy of WSF₄·C₅H₅N did not show other species in solution, besides small amounts of hydrolysis products.

Prior to the successful method presented above, other methods were attempted to prepare WSF₄. The ambient-temperature reaction of WF₆ with ((CH₃)₃Si)₂S in CH₃CN (Equation 4.2.2) has been reported by Brisdon et al.³ The repetition of this reaction at various temperatures resulted in solutions of WSF₄ and significant amounts of insoluble brown solid. The large amount of brown solid was attributed to uncharacterized side reactions that have been observed in the literature.³ Solutions of WSF₄ in CH₃CN by themselves were observed to undergo a solvent-assisted dismutation to form WS₃ and WF₆ (Equation 4.2.3). Conducting the reaction at temperatures below –35 °C still resulted in large amounts of brown solid indicating that temperature was insufficient to prevent side reactions from occurring.

$$\text{WF}_6 + ((\text{CH}_3)_3\text{Si})_2\text{S} \rightarrow \text{CH}_3\text{CN} \rightarrow \text{WSF}_4 + 2 \text{FSi(CH}_3)_3$$

(4.2.2)

$$3 \text{WSF}_4 \rightarrow \text{CH}_3\text{CN} \rightarrow \text{WS}_3 + 2 \text{WF}_6$$

(4.2.3)

The reaction of H₂S with WF₆ in CFCl₃ (Equation 4.2.4) was attempted on several occasions, as it was a potential method for producing WSF₄ with only volatile by-products that could easily be removed under dynamic vacuum. The reaction between WF₆ and H₂S

$$\text{WF}_6 + \text{H}_2\text{S} \rightarrow \text{CFCl}_3 \rightarrow \text{WSF}_4 + 2 \text{HF}$$

(4.2.4)

was very difficult to control. At room temperature the reactants formed a slightly yellow solution immediately upon addition of both reactants, which did not seem to get appreciably stronger coloured with time. Above the solution, however, the reaction vessel slowly became coated with a thin layer of dark solid that could not be removed. The solid layer was very thin and could not be studied but it was presumably WS₃ or WS₅. The partial pressure of H₂S above the CFCl₃ solution would have presumably been much larger than that of WF₆ making the excess H₂S required for production of WS₃ or WS₅ readily accessible. Any warming of the solution above room temperature resulted in
instantaneous formation of dark brown/black solid; in fact exposure to the Raman laser at room temperature was enough to turn the entire reaction mixture dark brown/black. When a reaction vessel was left in the dry box for several days it was noticed that white crystals formed. The crystalline material was studied by single-crystal X-ray diffraction and was shown to be tetrameric WF₅. Crystal-structure information for WF₅ is available in the Appendix.

4.2.2 X-ray Crystal structure of WSF₄

Crystals of WSF₄ were obtained from the slow removal of anhydrous HF solvent from the reaction mixture of Sb₂S₃ and WF₆ at -78°C (Equation 4.2.1). Crystallographic parameters are listed in Table 4.2.1. Bond lengths and bond angles are given in Table 4.2.2. The tables of isotropic and anisotropic displacement parameters can be found in the Appendix.

Tungsten sulfide tetrafluoride crystallizes in the orthorhombic space group Pca₂₁ with eight molecules per unit cell with cell dimensions of a = 1693.1(3) pm, b = 539.01(8) pm, c = 946.93(1) pm. The unit cell parameters obtained were in agreement with those obtained previously by Holloway et al. on crystals grown by sublimation.² The previous crystal structure collected by Holloway et al. retained a significantly higher residual value of 0.072 while the present structure could be refined to an R₁ value of 0.022 and represents a much improved structure of WSF₄ with significantly lower standard deviations in the bond lengths and angles.

It was confirmed that WSF₄ forms an infinite polymeric chain of cis-linked WSF₅ octahedra (Figure 4.2.1) which propagate along the c-axis of the unit cell. Three significantly different sets of tungsten-fluorine bond distances were found, (a) terminal W-F bonds ranging from 183.5(5)-185.2(4) pm, (b) W-F bonds that were cis to the W=S bonds form bridges to adjacent WSF₄ moieties (193.2(5)-194.7(5) pm), and (c) long bridging W─F bonds trans to the W=S bonds (230.8(5)-232.3(4) pm). Characteristic of tungsten fluorides and oxide fluorides the tungsten in WSF₄ molecule retains hexacoordination through fluorine bridging trans- to the sulfur atom in the solid phase. As expected the fluorine atom bonded trans- to the sulfur atom had a much longer W─F bond.
The tungsten atom is raised above the plane of four equatorial fluorine atoms toward the doubly bonded sulfur atom. The equatorial fluorine atoms are likely pushed downward by the W=S bond domain with S=W-F_{eq} bond angles ranging from 99.48(16) to 102.59(19)°. The F_{bridge}-W=S angle, however, is slightly smaller than the F_{terminal}-W=S bond angles because of decreased repulsion caused by the elongated W-F_{bridge} bond. The smaller W-F_{bridge} domain is also reflected by the F_{trans}-W=S angle of 177.90(4)°.

The structure of WSF₄ contrasts significantly with the crystal structure of WOF₄. Unlike WSF₄, WOF₄ crystallizes as a tetramer in the space group C2/m. The similar sized unit cell $a = 965(1)$, $b = 1442(2)$, $c = 515(1)$ pm also contains eight molecules. The terminal W-F bonds of WOF₄ are similar to WSF₄ ranging from 183(4) to 186(4) pm. The bridging W-F bond lengths in the WOF₄ crystal structure range from 210(4) to 212(4) pm. This contrasts with the crystal structure of WSF₄ where the W-F--W bridge forms a long bond \textit{trans} to the sulfur, ranging from 230.8(5) to 232.3(4) pm, and a shorter bond \textit{cis} to the sulfur, ranging from 193.2(5) to 194.7(5) pm. The WOF₄ crystal structure was considered to be disordered with respect to oxygen and fluorine atoms, though a \textit{cis}-fluorine-bridged structure was preferred upon vibrational analysis. The WOF₄ crystal structure was refined to a large residual value of 12.8 % as a result of poor data quality.
Figure 4.2.1 A view of the chain structure of WSF₄ with thermal ellipsoids shown at the 50 % probability level.
Table 4.2.1. Crystal Structure Refinement Data for WSF$_4$

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<tr>
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<th>Value</th>
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</thead>
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<tr>
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<td>Wavelength, pm</td>
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</tr>
<tr>
<td>Space group</td>
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<td>Unit cell dimensions, pm</td>
<td>$a = 1693.1(3)$, $b = 539.01(8)$, $c = 946.93(15)$</td>
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<td>R indices (all data)</td>
<td>$R_1 = 0.0258$, $wR_2 = 0.0413$</td>
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<td>Absolute structure parameter</td>
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<td>Extinction coefficient</td>
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<td>Largest diff. peak and hole, e $10^6$ pm$^3$</td>
<td>1.188 and -1.173</td>
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Table 4.2.2 Experimental Bond Lengths and Bond Angles of WSF₄.

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<th>Bond Length, pm</th>
<th>Bond Angle, °</th>
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<tr>
<td>W(1)-F(1)</td>
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<tr>
<td>W(1)-F(3)</td>
<td>184.4(5)</td>
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<tr>
<td>W(1)-F(2)</td>
<td>185.0(5)</td>
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<tr>
<td>W(1)-F(4)</td>
<td>194.7(5)</td>
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<td>W(1)-S(1)</td>
<td>208.4(2)</td>
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<td>W(1)-F(8)#1</td>
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<td>W(2)-F(6)</td>
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</tr>
<tr>
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<td>184.5(5)</td>
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<tr>
<td>W(2)-F(7)</td>
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<td>193.2(5)</td>
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<td>W(2)-S(2)</td>
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</table>
4.2.3  NMR Spectroscopy of WSF₄.

Fluorine-19 NMR spectra of WSF₄ in HF, CH₃CN, and C₄H₈O solvents were collected at ambient temperature. The chemical shifts and \( ^{1}J(^{19}\text{F}-^{183}\text{W}) \) coupling constants are listed in Table 4.2.3.

The equivalency of the fluorine environments in WSF₄ was confirmed by \(^{19}\text{F}\) NMR spectroscopy. The only signal in CH₃CN was a singlet at +85.3 ppm with \(^{183}\text{W}\)-satellites separated by 33.3 Hz (Table 4.2.3). It has been reported that CH₃CN acts as a Lewis base coordinating to WSF₄ forming the WSF₄·CH₃CN adduct with the nitrogen atom trans to the sulfur.\(^2\) The chemical shift at +85.3 ppm is in the same range as those found in the literature.\(^1,3\) A small amount of the hydrolysis product WOF₄ was observed in the spectrum also at +66.7 ppm with a \( ^{1}J(^{19}\text{F}-^{183}\text{W}) \) coupling of 68 Hz illustrating the marked difference between the \( ^{1}J(^{19}\text{F}-^{183}\text{W}) \) coupling constants for sulfur and oxygen containing tungsten fluorides noted in the literature.\(^7\) The large difference in \( ^{1}J(^{19}\text{F}-^{183}\text{W}) \) coupling aids distinguishing the respective species by \(^{19}\text{F}\) NMR spectroscopy.

Over an extended period of time the yellow solution of WSF₄ in CH₃CN turned brown in colour, which may have been from the solvent assisted dismutation that WSF₄ is known to undergo in CH₃CN (Equation 4.2.3). A small unexplained doublet at +72.3 ppm with a \( J \)-coupling of 36 Hz was observed in the \(^{19}\text{F}\) NMR spectrum.

Fluorine-19 NMR spectroscopy of a yellow solution in HF at room temperature showed a singlet at +77.42 ppm with a \( ^{1}J(^{19}\text{F}-^{183}\text{W}) \) coupling constant of 42.1 Hz corresponding to a solvated WSF₄ monomer. The spectrum contained a small amount of WOF₄ (from hydrolysis) indicated by a small singlet at +60.8 ppm.

The chemical shifts and coupling constants in Table 4.2.3 illustrate a trend with respect to the donor strength of the coordinating ligand. It is apparent that C₅H₅N, a strong electron donor, donor number (D.N) of 33.1, decreases the chemical shift of WSF₄ more than C₄H₈O (D.N = 20.0).\(^8\) Donor numbers are a qualitative measure of Lewis basicity and are defined by the negative enthalpy of formation of a 1:1 adduct between the Lewis base and the standard Lewis acid SbCl₅. The trend continues with CH₃CN the weakest electron donor of the three organic ligands. The same trend is observed with regard to the \( ^{1}J(^{19}\text{F}-^{183}\text{W}) \) coupling of the WSF₄ adducts.
Table 4.2.3  $^{19}$F NMR Spectroscopy of WSF$_4$

<table>
<thead>
<tr>
<th>Chemical shift (ppm)</th>
<th>Solvent</th>
<th>$^{1}J(^{19}$F-$^{183}$W) (Hz)</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>77.4</td>
<td>HF</td>
<td>42.1</td>
<td>WSF$_4$</td>
</tr>
<tr>
<td>85.3</td>
<td>CH$_3$CN</td>
<td>33.3</td>
<td>WSF$_4$·CH$_3$CN</td>
</tr>
<tr>
<td>85.0</td>
<td>THF</td>
<td>28.5</td>
<td>WSF$_4$·THF</td>
</tr>
<tr>
<td>82.7</td>
<td>CH$_3$CN</td>
<td>29</td>
<td>WSF$_4$·THF</td>
</tr>
<tr>
<td>81.8</td>
<td>CH$_3$CN</td>
<td>26.8</td>
<td>WSF$_4$·C$_5$H$_5$N</td>
</tr>
</tbody>
</table>

4.2.4 Vibrational Spectroscopy of WSF$_4$

The Raman spectrum of freshly produced WSF$_4$ as a yellow solid was collected at room temperature and at −100 °C in a sealed melting point capillary. The vibrational frequencies together with tentative assignments are presented in Table 4.2.4. The vibrational bands were dominated by the intense W=S stretching and bending modes. Many smaller signals attributable to W-F stretching and bending vibrations were apparent in the spectrum. The vibrational spectrum is complicated by the presence of different W-F bonds and by vibrational coupling of fluorine-bridged WSF$_4$ moieties which makes a full vibrational assignment of the vibrational bands for solid WSF$_4$ difficult.

The stretching modes observed in the Raman spectrum of solid WOF$_4$ for W-F terminal stretching at 744 w, 728 m, and 705 vvw cm$^{-1}$ are at slightly higher frequency than the analogous bands of WSF$_4$ at 717, 709, and 697 cm$^{-1}$. This trend is a result of the greater electron-withdrawing capability of the oxygen atom compared to the sulfur atom. The bands from the bridging W-F stretching modes follow the same trend at 663 vvw, 563 vvw, and 523 vvw for WOF$_4$.$^9$

The infrared spectrum of the solid shows very intense bands that overlap in the terminal W-F stretching region and bridging W-F stretching regions, which is typical of the solid tungsten and molybdenum fluorides. The spectrum also contained a strong band from the W=S stretching mode at 576 cm$^{-1}$ between the terminal and bridging W-F stretching modes. Overlap of W-F stretching bands made fine details indiscernible in the infrared spectrum.
Figure 4.2.2  The vibrational spectra of solid WSF$_4$. The Raman spectrum (lower trace) was recorded of the neat solid in a m.p. capillary at -100 °C. The infrared spectrum (upper trace) was recorded at room temperature as a KBr pellet.
Table 4.2.4 Vibrational Spectroscopy Data Collected for WSF$_4$

<table>
<thead>
<tr>
<th>Frequency, $^a$ cm$^{-1}$</th>
<th>Raman$^b$</th>
<th>Infrared$^c$</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solid (-100 °C) Solid Literature $^1$ Assignment</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>717 (9)</td>
<td>717</td>
<td>697 (16)</td>
<td></td>
</tr>
<tr>
<td>707 (9)</td>
<td>707</td>
<td>697 (16)</td>
<td></td>
</tr>
<tr>
<td>697 (16)</td>
<td>697</td>
<td>697 (16)</td>
<td></td>
</tr>
<tr>
<td>681 (4)</td>
<td>681</td>
<td>695 s</td>
<td></td>
</tr>
<tr>
<td>672 (7)</td>
<td>672</td>
<td>673 s</td>
<td>$\nu$$<em>s$(WF$</em>\text{term}$)</td>
</tr>
<tr>
<td>659 (2)</td>
<td>659</td>
<td>673 s</td>
<td></td>
</tr>
<tr>
<td>654 (3)</td>
<td>654</td>
<td>673 s</td>
<td></td>
</tr>
<tr>
<td>642 (5)</td>
<td>642</td>
<td>673 s</td>
<td></td>
</tr>
<tr>
<td>634 (4)</td>
<td>634</td>
<td>673 s</td>
<td></td>
</tr>
<tr>
<td>583 (36)</td>
<td>583</td>
<td>673 s</td>
<td></td>
</tr>
<tr>
<td>577 (100)</td>
<td>577</td>
<td>673 s</td>
<td>$\nu$(WS)</td>
</tr>
<tr>
<td>557 (7)</td>
<td>557</td>
<td>556 vs</td>
<td></td>
</tr>
<tr>
<td>553 (7)</td>
<td>553</td>
<td>556 vs</td>
<td></td>
</tr>
<tr>
<td>534 (13)</td>
<td>534</td>
<td>556 vs</td>
<td>$\nu$$<em>s$(W-F$</em>\text{bridge}$)</td>
</tr>
<tr>
<td>513 (16)</td>
<td>513</td>
<td>556 vs</td>
<td>$\nu$(WS)</td>
</tr>
<tr>
<td>463 vs</td>
<td>463</td>
<td></td>
<td></td>
</tr>
<tr>
<td>309 (5)</td>
<td>309</td>
<td></td>
<td></td>
</tr>
<tr>
<td>291 (3)</td>
<td>291</td>
<td></td>
<td></td>
</tr>
<tr>
<td>262 (9)</td>
<td>262</td>
<td></td>
<td></td>
</tr>
<tr>
<td>247 (13)</td>
<td>247</td>
<td></td>
<td></td>
</tr>
<tr>
<td>235 (13)</td>
<td>235</td>
<td></td>
<td></td>
</tr>
<tr>
<td>224 (38)</td>
<td>224</td>
<td></td>
<td>Bending Modes</td>
</tr>
<tr>
<td>216 (16)</td>
<td>216</td>
<td></td>
<td></td>
</tr>
<tr>
<td>208 (9)</td>
<td>208</td>
<td></td>
<td></td>
</tr>
<tr>
<td>196 (7)</td>
<td>196</td>
<td></td>
<td></td>
</tr>
<tr>
<td>188 (5)</td>
<td>188</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$^a$ Abbreviations denote shoulder (sh), very strong (vs), strong (s), medium (m), weak (w), and very weak (vw).  $^b$ Neat solid in melting point capillary at -100 °C.  $^c$ KBr pellet at room temperature.
4.2.5 Density Functional Theory Calculations of WSF\textsubscript{4}

Calculations were performed with Gaussian 98\textsuperscript{10} at the B3LYP/LANL2DZ level of theory. The geometry was optimized using calculations to find the minimum energy before frequency calculations were performed. The geometry was not exactly $C_{4v}$ symmetry but was very close; therefore $C_{4v}$ symmetry was assumed for the assignment of the calculated vibrational bands. Tungsten sulfide tetrafluoride is known to exhibit $C_{4v}$ symmetry in the gas phase based on electron-diffraction studies.\textsuperscript{11}

The calculated structure for the molecule is shown in Figure 4.2.3 with bond lengths and angles and comparisons to electron diffraction data from the literature\textsuperscript{11} listed in Table 4.2.6. The calculated vibrational frequencies with their calculated Raman scattering activities and infrared intensities can be found in Table 4.2.6. The values are compared to the gas phase infrared literature values.\textsuperscript{12}

Analysis of Table 4.2.5 indicates that the bond lengths and angles of the calculated monomeric WSF\textsubscript{4} are quite close to those observed for electron diffraction in the gas phase and in the crystal structure of solid polymeric WSF\textsubscript{4} when effects of the bridging fluorine atom are ignored. The W-F bond lengths (Table 4.2.5) are slightly shorter in the crystal structure at with an average terminal W-F bond length of 184.4(6) pm compared to the calculated values of 188.1 and 188.2 pm. The calculated W=S bond distance at 214 pm is also longer than the experimental value 208.8(5) pm as are the calculated S=W-F bond angles. All of these discrepancies can easily be explained by the effects of fluorine bridging in the crystal structure.

It is important to remember that the calculations are representative of the monomeric molecule in the gas phase, hence, a direct comparison between the solid form of WSF\textsubscript{4} and the calculations is difficult. The calculated frequency of the W=S stretching mode is very close at 544 cm\textsuperscript{-1} compared to the observed frequency of 577 cm\textsuperscript{-1}. The terminal tungsten-fluorine bond stretching modes were also quite close indicating the model is a good fit with experiment. The one shortcoming of the above model is its inability to describe or account for the W-F--W bridging modes. The calculations also provide an invaluable tool for visualizing vibrational modes.
Figure 4.2.3  The calculated geometry of WSF₄ using density functional theory at the B3LYP/LANL2DZ level of theory.

Table 4.2.5 Calculated Bond Distances and Angles for WSF₄ using the B3LYP/LANL2DZ Level of Theory.

<table>
<thead>
<tr>
<th>Bond Distance, pm</th>
<th>Bond Angle, °</th>
<th>Calculated</th>
<th>Electron diffraction¹¹</th>
<th>Calculated</th>
<th>Electron diffraction¹¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>W – F(1)</td>
<td>188.1</td>
<td></td>
<td></td>
<td>S – W – F(1)</td>
<td>104.25</td>
</tr>
<tr>
<td>W – F(2)</td>
<td>188.2</td>
<td></td>
<td>184.7(3)</td>
<td>S – W – F(2)</td>
<td>103.89</td>
</tr>
<tr>
<td>W – F(3)</td>
<td>188.1</td>
<td></td>
<td></td>
<td>S – W – F(3)</td>
<td>104.23</td>
</tr>
<tr>
<td>W – F(4)</td>
<td>188.2</td>
<td></td>
<td></td>
<td>S – W – F(4)</td>
<td>103.86</td>
</tr>
<tr>
<td>W = S</td>
<td>214</td>
<td>210.4(7)</td>
<td></td>
<td>F(1) – W – F(2)</td>
<td>86.67</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>F(2) – W – F(3)</td>
<td>86.54</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>F(3) – W – F(4)</td>
<td>86.63</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>F(4) – W – F(1)</td>
<td>86.64</td>
</tr>
</tbody>
</table>
Table 4.2.6 The Calculated Vibrational Frequencies of WSF₄ using the B3LYP/LANL2DZ Level of Theory Compared to Gas-Phase Infrared Data.

<table>
<thead>
<tr>
<th>Calc. Frequency, cm⁻¹</th>
<th>Raman Activity a</th>
<th>Infrared Intensity a</th>
<th>Frequency, cm⁻¹</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Gas-Phase Infrared¹²</td>
<td></td>
</tr>
<tr>
<td>692</td>
<td>15</td>
<td>58</td>
<td>707</td>
<td>ν₅(WF₄)</td>
</tr>
<tr>
<td>686</td>
<td>1.2</td>
<td>161</td>
<td>671</td>
<td>ν₃₆(WF₄)</td>
</tr>
<tr>
<td>614</td>
<td>5</td>
<td>0</td>
<td></td>
<td>ν(WF₄)</td>
</tr>
<tr>
<td>544</td>
<td>21</td>
<td>23</td>
<td>577</td>
<td>ν(WS)</td>
</tr>
<tr>
<td>322</td>
<td>2.6</td>
<td>0</td>
<td></td>
<td>δ</td>
</tr>
<tr>
<td>234</td>
<td>1</td>
<td>8</td>
<td></td>
<td>δ</td>
</tr>
<tr>
<td>231</td>
<td>0</td>
<td>21</td>
<td></td>
<td>δ(SWF)</td>
</tr>
<tr>
<td>201</td>
<td>6</td>
<td>0</td>
<td></td>
<td>δ</td>
</tr>
<tr>
<td>123</td>
<td>0</td>
<td>0</td>
<td></td>
<td>δ</td>
</tr>
</tbody>
</table>

aIntensities are in units cm⁻¹/amu and km/mole for Raman scattering activity and infrared intensity, respectively.

4.3 Summary

The compound WSF₄ was successfully generated in high purity by an easier and more direct method than was previously known. An improved crystal structure was determined that confirmed the fluorine-bridged chain structure of WSF₄. Tungsten sulfide tetrafluoride was characterized by Raman, infrared, and ¹⁹F NMR spectroscopy. Density functional theory calculations for geometry optimization and frequency were performed and compared to the structure obtained from the X-ray crystal structure of WSF₄.
References


Chapter 5

Lewis-Acid Chemistry of WSF₄

5.1 Introduction

The fluoride-ion affinity of WF₆ and WOF₄ has been studied extensively. Tungsten sulfide tetrafluoride has received relatively little attention in that regard. The thiotetrafluorotungstate (VI), WSF₅⁻, anion has been observed by ¹⁹F NMR, as side products of reactions to produce WSF₄ in solution¹,² and by X-ray crystallography.⁴ Solution-state reactions have also tended to produce the larger W₂S₂F₉⁻ anion in addition to WSF₄ and WSF₅⁻ as observed by ¹⁹F NMR spectroscopy. This behaviour is analogous to reactions of the tungsten oxide fluorides. For reactions in CH₃CN it was postulated that the formation of anions might be a result of its poor solvating ability toward the F⁻ anion.³

5.2 Results and Discussion

5.2.1 Synthesis of [N(CH₃)₄][WSF₅] and Generation of W₂S₂F₉⁻ and W₂OSF₉⁻ Anions

Reaction between WF₆ and [N(CH₃)₄][SSi(CH₃)₃] in tetrahydrofuran (THF) solvent (Equation 5.2.1) yielded the new [N(CH₃)₄][WSF₅] salt with minor impurities as a homogeneous pink powder. The sample was characterized by ¹⁹F NMR spectroscopy in CH₃CN solvent and vibrational spectroscopy in the solid state.

\[
[N(CH₃)₄][SSi(CH₃)₃] + WF₆ \xrightarrow{THF, -78°C} [N(CH₃)₄][WSF₅] + (CH₃)₃SiF \quad 5.2.1
\]

Upon mixing of the reactants the solution immediately became yellow. With continued agitation the solution eventually turned red. The red solution was stable at room temperature with no signs of decomposition and could be kept for weeks reliably in FEP outside of the dry box at room temperature. Fluorine-19 NMR spectroscopy of an orange-coloured solution, harvested in mid-reaction, showed a mixture of WSF₄ and
WSF₅⁻. Therefore, it was postulated that WSF₄ was generated quickly, present as the WSF₄·THF adduct in yellow solutions which slowly formed WSF₅⁻ as the THF ligand was replaced by F⁻ on WSF₄. Larger-scale reactions in a ¾" FEP reactor indicated that excess WF₆ needed to be avoided since [N(CH₃)₄][WF₇] was readily formed. Excess amounts of WF₆ were also thought to cause polymerization of THF. Cooling the reaction mixture to -78 °C seemed to prevent polymerization of the solvent.

Re-crystallization of pink [N(CH₃)₄][WSF₅] was attempted from CH₂Cl₂. Slow removal of the CH₂Cl₂ resulted in a white/pale yellow powder. The powder was characterized by Raman spectroscopy as [N(CH₃)₄][WSF₅] with less fluorescence than found for the pink, impure [N(CH₃)₄][WSF₅] (Table 5.2.2). Hence, dissolution of [N(CH₃)₄][WSF₅] in CH₂Cl₂ followed by removal of volatiles serves as a method of purification.

The ability to produce WSF₄ on a preparative scale allowed for the alternative synthesis of [N(CH₃)₄][WSF₅] by stoichiometric combination of [N(CH₃)₄][F] and WSF₄ in CH₃CN solvent (Equation 5.2.2). The reaction resulted in a yellow solution with a white solid; the white solid was presumed to be [N(CH₃)₄][WSF₅] that was unable to dissolve in the solvent as saturation had been reached. Fluorine-19 NMR spectroscopy of the solution showed the presence of the WSF₅⁻ anion, as the only product.

\[
[N(CH₃)₄][F] + WSF₄ \xrightarrow{CH₃CN} [N(CH₃)₄][WSF₅]
\] 5.2.2

The difference in appearance of [N(CH₃)₄][WSF₅] from two different syntheses indicated that the red colour was likely from the presence of a small amount of organic impurities that formed upon oxidative decomposition of THF solvent. This was confirmed by the presence of a very small resonance in the ¹H NMR spectrum of the pink solid dissolved in CH₃CN at 12.4 ppm corresponding to the formation of a carboxylic acid.

Initially, the reaction between WF₆ and [N(CH₃)₄][SSi(CH₃)₃] in CH₃CN solvent to prepare pure [N(CH₃)₄][WSF₅] was attempted, but resulted in red/yellow/brown mixtures of WSF₄, WSF₅⁻, W₂S₂F₉⁻ and large amounts of insoluble brown solids. Lower concentrations and temperatures of −35 °C did not prevent the side reactions from
occurring. Another aprotic, polar solvent with a lower freezing point than CH$_3$CN in which the products were soluble, such as THF, was necessary to control the reactions.

The formation of W$_2$S$_2$F$_9^-$ anions was the result of the combination of WSF$_4$ and WSF$_5^-$ in CH$_3$CN (Equation 5.2.4)

$$\text{WSF}_4 + \text{WSF}_5^- \overset{\text{CH}_3\text{CN}}{\rightleftharpoons} \text{W}_2\text{S}_2\text{F}_9^- \quad 5.2.3$$

Reaction of [N(CH$_3$)$_4$][F] and WSF$_4$ in a 1:2 ratio forms primarily W$_2$S$_2$F$_9^-$ in CH$_3$CN. The W$_2$S$_2$F$_9^-$ anion was in equilibrium with WSF$_4$ and WSF$_5^-$, as both WSF$_4$ and WSF$_5^-$ were present in the $^{19}$F NMR spectrum though the equilibrium clearly lies to the right for Equation 5.2.3.

Tungsten sulfide fluorides are extremely sensitive toward moisture resulting in hydrolysis of the sulfide group on tungsten. A small amount of hydrolysis occurred in the NMR sample generating WOF$_4$ and WOF$_5^-$. The W$_2$O$_2$F$_9^-$ anion was gave rise to a very small $^{19}$F resonance while the novel mixed oxo-sulfido anion W$_2$OSF$_9^-$ was readily observed (Table 5.2.1). It is evident that WOF$_4$ is a stronger Lewis acid than WSF$_4$ as no WOF$_4$ was detected in solution by $^{19}$F NMR spectroscopy. Like the reaction between WSF$_5^-$ and WSF$_4$ the mixed W$_2$OSF$_9^-$ anion is formed in equilibrium with WOF$_5^-$ and WSF$_4$ (Equation 5.2.4).

$$\text{WOF}_5^- + \text{WSF}_4 \overset{\text{CH}_3\text{CN}}{\rightleftharpoons} \text{W}_2\text{OSF}_9^- \quad 5.2.4$$

Analogous reactions with [Cs][SSi(CH$_3$)$_3$] and WF$_6$ in THF were attempted. A yellow solution which turned red/brown in colour upon agitation was observed. Polymerization of THF occurred, even at –78 °C, indicating the solution was not stable. When THF solvent was removed quickly to prevent polymerization, the $^{19}$F NMR spectrum of the resulting brown powder dissolved in CH$_3$CN showed WF$_7^-$ and WSF$_5^-$. The poor solubility of the Cs[SSi(CH$_3$)$_3$] salt in THF meant that excess WF$_6$ was present in solution to participate in Equation 5.2.5 to form the WF$_7^-$ anion as well as catalyze THF polymer formation.
\[ 2 \text{WF}_6 + \text{[SSi(CH}_3\text{)]}_3^{-} \rightarrow \text{[WF}_7\text{]}^{-} + \text{WSF}_4 + \text{(CH}_3\text{)_3SiF} \]

Tetrahydrofuran has been observed to polymerized via a cationic mechanism where the propagating species is an oxonium ion.\(^7\) In this case, however, no cations were available to initiate the reaction. It could be that the strong Lewis-acidic character of \text{WF}_6 was instead sufficiently electron-withdrawing to cause pseudo-oxonium ion propagation leading to polymer formation.

### 5.2.2 NMR Spectroscopy

The \([\text{N(CH}_3\text{)}_4][\text{WSF}_5]\) salt was characterized by \(^{19}\text{F}\) NMR spectroscopy in \text{CH}_3\text{CN} and THF solvents. The NMR parameters are listed in Table 5.2.1.

Fluorine-19 NMR spectroscopy of \([\text{N(CH}_3\text{)}_4][\text{WSF}_5]\) (Figure 5.2.1-2) dissolved in \text{CH}_3\text{CN} showed a doublet attributed to \text{WSF}_5^{-} at +77.2 ppm with 2\(\text{J}^{(19\text{F}-19\text{F})}\) coupling of 75.5 Hz and 1\(\text{J}^{(19\text{F}-183\text{W})}\) satellites (28.34 Hz). The corresponding quintet with the same 2\(\text{J}^{(19\text{F}-19\text{F})}\) coupling was centered at –111.3 ppm. Small 183\text{W}-satellites were visible with 1\(\text{J}^{(19\text{F}-183\text{W})}\) = 68.6 Hz. The hydrolysis product \text{WOF}_5^{-} was observed as a doublet with 183\text{W}-satellites at +47.2 ppm(2\(\text{J}^{(19\text{F}-19\text{F})}\) = 52.5 Hz and 1\(\text{J}^{(19\text{F}-183\text{W})}\) = 71.0 Hz) and a quintet at –82.7 ppm.

The 1\(\text{H}\) NMR spectrum of \([\text{N(CH}_3\text{)}_4][\text{WSF}_5]\) dissolved in \text{CH}_3\text{CN} showed a singlet at +3.25 ppm attributable to \([\text{N(CH}_3\text{)}_4]^{+}\). The 19\text{F} NMR spectrum of \([\text{Cs}][\text{WSF}_5]\) in \text{CH}_3\text{CN} was very similar to that of \([\text{N(CH}_3\text{)}_4][\text{WSF}_5]\) with a doublet and quintet at chemical shifts of +77.9 and –111.7 ppm, respectively. Tungsten-183 satellites were observed with 1\(\text{J}^{(19\text{F}-183\text{W})}\) coupling constants of 28.6 and 59.3 Hz for \text{F}\text{eq} and \text{F}\text{ax}, respectively. The 19\text{F} NMR signal at +143.5 ppm also indicated that significant amounts of \text{WF}_7^{-} were present in the sample.

In the literature conflicting reports can be found about the 19\text{F} chemical shifts of \text{WSF}_5^{-}.\(^{1,2,4}\) Buslaev \textit{et al.}\(^1\) assigned a doublet at +80.0 ppm and a quintet at -141.5 ppm in the 19\text{F} NMR spectrum to \text{WSF}_5^{-} in solution. Their assignment of the quintet to -141.5 ppm is in contrast with our observation (-111.35 ppm). The 19\text{F} NMR spectrum of \([\text{Na}(15\text{-crown-5})][\text{WSF}_5]\) was reported as the doublet at -62.8 ppm and the quintet at -116.2 ppm in CD\text{3}CN solvent.\(^4\) The chemical shift for the doublet is in disagreement

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with the chemical shifts observed in this work and in other literature previously mentioned. The $^2J(^{19}\text{F}-^{19}\text{F})$ coupling constants reported for WSF$_5^-$ by Buslaev et al.$^1$ and Hilbers et al.$^4$ were 74 and 75.6 Hz, respectively, in accordance with our value of 75.5 Hz.

Fluorine-19 NMR spectroscopy of [N(CH$_3$)$_4$][W$_2$S$_2$F$_9$] showed a doublet centered at +85.6 ppm and a nonet centered at −156.5 ppm (Figures 5.2.3, 5.2.5). Tungsten-183 satellites for F$_{\text{terminal}}$ and F$_{\text{bridging}}$ atoms were resolved on both signals with coupling constants of 31.3 and 83.9 Hz, respectively. The chemical shifts and $^2J(^{19}\text{F}-^{19}\text{F})$ coupling constant of 70.0 Hz are in accordance with those previously reported in the literature.$^{1,2}$

A complex multiplet (Figure 5.2.6), derived from a quintet split into quintets by secondary coupling, with $^{183}\text{W}$ satellites, was centered at -148.1 ppm. The multiplet is attributed to the new W$_2$OSF$_9^-$ anion. The bridging fluorine atom in W$_2$OSF$_9^-$ is coupled to two sets of four fluorine atoms generating an A$_4$B$_4$X spin system. The $^2J(^{19}\text{F}-^{19}\text{F})$ couplings 57 and 70 Hz are assigned to the WOF$_4$ and WSF$_4$ moieties, respectively. The $^2J(^{19}\text{F}-^{19}\text{F})$ couplings to each set of fluorine atoms was the same or very close to those observed for W$_2$O$_2$F$_9^-$ and W$_2$S$_2$F$_9^-$ anions. The same couplings were observed in a doublet centered at +86.0 ppm (Figure 5.2.3) and a doublet centered at +60.8 ppm (Figure 5.2.4). Tungsten-183 satellites were resolved about the doublet at +60.8 ppm giving a $^1J(^{19}\text{F} = ^{183}\text{W})$ coupling of 71.0 Hz in good agreement with $^1J(^{19}\text{F}-^{183}\text{W})$ observed in the oxide fluorides. Other tungsten satellites for the doublet at +86.0 ppm and the multiplet could not be resolved fully due to overlap with the doublet arising from the terminal fluorine environment in W$_2$S$_2$F$_9^-$, though $^1J(^{19}\text{F}=^{183}\text{W})$ coupling could be estimated at between 16 and 19 Hz.

Fluorine-19 NMR spectroscopy of reactions of [N(CH$_3$)$_4$][SSi(CH$_3$)$_3$] with excess WF$_6$ (Equation 5.2.3) dissolved in CH$_3$CN revealed that WF$_7^-$ is stable with respect to WSF$_4$·CH$_3$CN in solution and does not donate a fluoride to WSF$_4$ indicating WF$_6$ is a stronger Lewis acid than WSF$_4$.

Combinations of [N(CH$_3$)$_4$][WSF$_5$] and pyridine showed no sign of Lewis adduct formation by Raman or $^{19}$F NMR spectroscopy, even at −40°C, indicating that WSF$_5^-$ does not possess significant Lewis-acid character.
Figure 5.2.1 The $^{19}$F NMR spectrum of equatorial fluorine atoms of the WSF$_5^-$ anion in CH$_3$CN at room temperature.

Figure 5.2.2 The $^{19}$F NMR spectrum of the axial fluorine atom of the WSF$_5^-$ anion in CH$_3$CN at room temperature.
Figure 5.2.3 The $^{19}$F NMR spectrum of the terminal-fluorine atoms of W$_2$S$_2$F$_9^-$ and the W=S portion of W$_2$SOF$_9^-$ anions overlapped.

Figure 5.2.4 The $^{19}$F NMR spectrum of the terminal-fluorine atoms of the W=O portion of the W$_2$SOF$_9^-$ anion in CH$_3$CN at room temperature.
Figure 5.2.5 The $^{19}\text{F}$ NMR spectrum of the bridging-fluorine atom in the $\text{W}_2\text{S}_2\text{F}_9^-$ anion in CH$_3$CN at room temperature.

Figure 5.2.6 The $^{19}\text{F}$ NMR spectrum of the bridging-fluorine atom of the $\text{W}_2\text{SOF}_9^-$ anion in CH$_3$CN at room temperature.
### Table 5.2.1 $^{19}$F NMR Spectroscopy Data for WSF$_5^-$, W$_2$S$_2$F$_9^-$ and W$_2$OSF$_9^-$ Anions

<table>
<thead>
<tr>
<th>Chemical shift $^a$, (ppm)</th>
<th>Solvent</th>
<th>$^1J(^{19}$F-$^{183}$W) (Hz)</th>
<th>$^2J(^{19}$F-$^{19}$F) (Hz)</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>77.15 (d)</td>
<td>CH$_3$CN</td>
<td>28.3 (F$_{eq}$)</td>
<td>75.5</td>
<td>WSF$_5^-$</td>
</tr>
<tr>
<td>-111.35 (qn)</td>
<td>CH$_3$CN</td>
<td>68.6 (F$_{ax}$)</td>
<td>52.2</td>
<td>WOF$_5^-$</td>
</tr>
<tr>
<td>47.2 (d)</td>
<td>CH$_3$CN</td>
<td>71.0 (F$_{eq}$)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>-82.7 (qn)</td>
<td>THF</td>
<td>62 (F$_{ax}$)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>79.0 (d)</td>
<td>THF</td>
<td>28.2 (F$_{eq}$)</td>
<td>76.0</td>
<td>WSF$_5^-$</td>
</tr>
<tr>
<td>-111.8 (qn)</td>
<td>CH$_3$CN</td>
<td>68.6 (F$_{ax}$)</td>
<td></td>
<td>W$_2$S$_2$F$_9^-$</td>
</tr>
<tr>
<td>85.6 (d)</td>
<td>CH$_3$CN</td>
<td>31.3 (F$_{eq}$)</td>
<td>70.0</td>
<td></td>
</tr>
<tr>
<td>-156.5 (n)</td>
<td>CH$_3$CN</td>
<td>83.9 (F$_{bridge}$)</td>
<td>58.4</td>
<td>W$_2$O$_2$F$_9^-$</td>
</tr>
<tr>
<td>61.8 (d)</td>
<td>CH$_3$CN</td>
<td>16-19 (F$_{eq}$, WS)</td>
<td>70 (WS)</td>
<td>W$_2$OSF$_9^-$</td>
</tr>
<tr>
<td>86.0 (d)</td>
<td>CH$_3$CN</td>
<td>60.8 (d)</td>
<td>56.7 (WO)</td>
<td></td>
</tr>
</tbody>
</table>

$^a$ Abbreviations denote doublet (d), quintet (qn), nonet (n), and quintet of quintets (qn/qn).

### 5.2.3 Vibrational Spectroscopy of [N(CH$_3$)$_4$][WSF$_5$]

Raman and infrared spectra of [N(CH$_3$)$_4$][WSF$_5$] were recorded. The vibrational frequencies together with their assignments are listed in Table 5.2.2.

The WSF$_5^-$ anion was expected to exhibit $C_4v$ symmetry according to calculations (Section 5.2.4) like monomeric WSF$_4$ (see Chapter 4) and MoSF$_4$ (see Chapter 6). Under group theoretical treatment all vibrations span the reducible representation $\Gamma_{vib} = 4 A_1 + 2 B_1 + B_2 + 4 E$. The stretching modes form a basis for $\Gamma_{stretch} = 3 A_1 + B_1 + E$ leaving the bending modes to $\Gamma_{bend} = A_1 + B_1 + B_2 + 3 E$. All vibrational modes are Raman active while only $A_1$ and $E$ are infrared active. The calculated vibrations (Section 5.2.4) and actual experimental vibrations in Table 5.2.2 were described by the applied symmetry. Vibrational bands of the solid phase may be split by crystallographic symmetry requirements causing direct correlation of data to be difficult.
The Raman spectrum collected on the pink solid, $\text{[N(CH}_3\text{)]}_4\text{[WSF}_5\text{]}$, corresponds reasonably well to the calculated values with the exception of several smaller bands that could have been the result of crystallographic symmetry requirements.

Some small bands disappeared from the Raman spectrum when $\text{[N(CH}_3\text{)]}_4\text{[WSF}_5\text{]}$ was dissolved in CH$_2$Cl$_2$ though the major bands remained. A significant drop in the intensity of the W-F$_\text{ax}$ stretching band at 473 cm$^{-1}$ coupled with the lack of any new bands indicates that CH$_2$Cl$_2$ did not react with WSF$_5^-$, instead it separated the anion from THF polymer impurities.

The $\nu_s$(WF$_4$) and $\nu$(W=S) bands observed in the Raman spectrum and the $\nu_s$(WF$_4$), $\nu_{as}$(WF$_4$), $\nu$(W=S) and $\nu$(W-F$_\text{ax}$) observed in the infrared spectrum of $\text{[Na(15-crown-5)]}[\text{WSF}_5]^-$ (Table 5.2.2) agree well with the strong bands observed in the Raman spectrum of $\text{[N(CH}_3\text{)]}_4\text{[WSF}_5\text{]}$ (Figure 5.2.7). The splitting of the W=S stretch into two bands indicates that distortion of the WSF$_5^-$ anion reduces the symmetry to less than $C_{4v}$ symmetry in solid $\text{[N(CH}_3\text{)]}_4\text{[WSF}_5\text{]}$. 


Figure 5.2.7  Vibrational spectroscopy of solid [N(CH₃)₄][WSF₅] collected at room temperature. The Raman spectrum (lower trace) was recorded on the neat powder in glass melting point capillary. The infrared spectrum (upper trace) was collected as a KBr pellet. Asterisks (*) denote bands attributable to [N(CH₃)₄]⁺.
Table 5.2.2 Vibrational Spectroscopy of Solid \([\text{N(CH}_3\text{)}_4][\text{WSF}_5]\) Compared to Calculations and Values for \([\text{Na(15-crown-5)}][\text{WSF}_5]\)

<table>
<thead>
<tr>
<th>Frequency, (\text{cm}^{-1})</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>([\text{N(CH}_3\text{)}_4][\text{WSF}_5])</td>
<td>([\text{Na(15-crown-5)}][\text{WSF}_5])</td>
</tr>
<tr>
<td>([\text{WSF}_5]^\text{–})</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Raman b,c</th>
<th>Raman b</th>
<th>Infrared d</th>
<th>Raman</th>
<th>Infrared</th>
<th>Calc. c</th>
</tr>
</thead>
<tbody>
<tr>
<td>pink solid from reaction in THF</td>
<td>white solid recrystallized from CH(_2)Cl(_2)</td>
<td>pink solid</td>
<td>662 m</td>
<td>662 s</td>
<td>643 [78]</td>
</tr>
<tr>
<td>658 (38)</td>
<td>657 (28)</td>
<td>662 s</td>
<td>662 m</td>
<td>662 s</td>
<td>643 [78]</td>
</tr>
<tr>
<td>597 (10)</td>
<td>597 vs</td>
<td>607 vs</td>
<td>628 [218]</td>
<td>(\nu_{as}(\text{WF}_4), \text{E})</td>
<td></td>
</tr>
<tr>
<td>567 (3)</td>
<td>566 w</td>
<td>566 [0]</td>
<td>(\nu(\text{WF}_4), \text{B}_1)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>530 (86)</td>
<td>531 sh</td>
<td>529 s</td>
<td>542 [133]</td>
<td>(\nu(\text{WF}_4), \text{B}_1)</td>
<td></td>
</tr>
<tr>
<td>524 (100)</td>
<td>524 (100)</td>
<td>525 vs</td>
<td>526 s</td>
<td>471 [39]</td>
<td>(\nu(\text{W=S}), \text{A}_1)</td>
</tr>
<tr>
<td>491 (21)</td>
<td>474 (72)</td>
<td>473 (41)</td>
<td>473 m</td>
<td>472 s</td>
<td>(\nu(\text{SWF}_ax), \text{A}_1)</td>
</tr>
<tr>
<td>456 (21)</td>
<td>456 (18)</td>
<td>458 m</td>
<td>472 s</td>
<td>(\nu(\text{SWF}_ax), \text{A}_1)</td>
<td></td>
</tr>
<tr>
<td>440 (7)</td>
<td></td>
<td></td>
<td></td>
<td>Impurity</td>
<td></td>
</tr>
<tr>
<td>377 (7)</td>
<td>378 (4)</td>
<td></td>
<td></td>
<td>Impurity</td>
<td></td>
</tr>
<tr>
<td>292 (41)</td>
<td>292 (40)</td>
<td>285 [5.5]</td>
<td>(\delta_{\text{cis}}(\text{WSF}_3)\text{E})</td>
<td></td>
<td></td>
</tr>
<tr>
<td>246 (7)</td>
<td></td>
<td>279 [17]</td>
<td>Impurity</td>
<td></td>
<td></td>
</tr>
<tr>
<td>219 (83)</td>
<td>221 (79)</td>
<td>272 [0]</td>
<td>(\delta_{\text{cis}}(\text{WF}_4), \text{B}_2)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>182 (14)</td>
<td>177 (22)</td>
<td>207 [29]</td>
<td>(\delta, \text{E})</td>
<td></td>
<td></td>
</tr>
<tr>
<td>155 (34)</td>
<td>153 (59)</td>
<td>202 [0]</td>
<td>(\delta_{\text{out-of-plane}})</td>
<td></td>
<td></td>
</tr>
<tr>
<td>137 (21)</td>
<td>134 (22)</td>
<td>109 [0.2]</td>
<td>(\delta_{\text{wag}}(\text{WSF}_3), \text{E})</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\(a\) Abbreviations denote shoulder (sh), very strong (vs), strong (s), medium (m), weak (w), very weak (vw), \(b\) Neat solid in melting point capillary at room temperature. \(c\) Vibrations attributable to \([\text{N(CH}_3\text{)}_4]^\text{+}\) not shown were at 3033 (27), 2981 (16), 2962 (20), 2930 (21), 2831 (7), 2819 (7), 1476 (19), 1465 (22), 1460 (25), 1417 (6), 1176 (6), 950 (34), 917 (7), 752 (34) \(\text{cm}^{-1}\). \(d\) KBr pellet at room temperature. \(e\) Calculated infrared intensities were included.
5.2.4 Density Functional Theory Calculations for WSF$_5^-$

Geometry optimization was performed using the B3LYP/LANL2DZ level of theory to optimize the molecular geometry and calculate the vibrational frequencies of WSF$_5^-$. The bond lengths of the geometry optimized anion (Table 5.2.3) are longer than those observed for WSF$_4$ as expected due to the increased electron density about the tungsten from the addition of a fluoride. The fluoride coordinates trans to the sulfur atom with the W–F$_{ax}$ bond distance, greater than the W-F$_{eq}$ distance because of the trans-effect. The calculated difference is just under 5.5 pm, which is a reasonably small amount that is reflected in the close proximity of the calculated W–F$_{eq}$ and W–F$_{ax}$ stretching bands. When the calculated bond lengths and angles are compared to literature values it is found that the W=S bond is calculated to be much longer than the observed bond length of 212.3(1) pm. The calculated W-F$_{eq}$ and W-F$_{ax}$ bond lengths are quite close to the experimental values for W-F$_{ax}$ (196.3(3) pm) and W-F$_{eq}$ (ranging from 185.4(3) to 188.9(3) pm).

The calculated W=S bond length is 7 pm longer than that calculated for WSF$_4$. As a result, the calculated W=S stretching vibration for WSF$_5^-$ (Table 5.2.3) was significantly lower than the calculated value for WSF$_4$ (544 cm$^{-1}$). The addition of the fluoride trans to the sulfur atom would be expected to weaken the W=S bond in accordance with the decreased frequency provided from the calculations. Stretching bands close to the calculated value of 471 cm$^{-1}$ for W=S stretching were observed in the vibrational spectrum of the solid (Table 5.2.2). This is not in line with calculated Raman activities, as the strongest band in the Raman spectrum is at 524 cm$^{-1}$ not 473 cm$^{-1}$ and the W=S stretch would be the most polarizable bond in the system generating the strongest signals in the Raman spectrum. The observed vibrational bands contained many similar frequencies to the calculated bands but the assignment of strong bands was different.

The equatorial fluorine atoms still form a plane below the tungsten atom, though not as pronounced as for the calculated WSF$_4$ molecule. The addition of the fluoride changed the S=W–F$_{eq}$ angle from ca. 104 $^\circ$ to 95.7 $^\circ$. The presence of the fluoride also increased the energy of the calculated out-of-plane WF$_4$ (B$_1$) bending mode quite
considerably from ca. 120 to 202 cm\(^{-1}\) while the calculated in-plane WF\(_4\) (B\(_2\)) bending mode dropped in energy considerably from 322 to 272 cm\(^{-1}\). The WF\(_4\) (A\(_1\)) bending mode increased in energy while the WF\(_4\) (A\(_1\)) stretching modes decreased in energy. The WF\(_4\) (E) bending modes maintained similar energies while the WF\(_4\) (E) stretching mode decreased in energy somewhat.

In Table 5.2.3 the calculated data is shown to fit the observed X-ray data very closely. All calculated angles and bond lengths are either slightly larger than or matching to what was observed by Hilbers et al.\(^4\)

![Image of WSF\(_5^-\) anion](image)

Figure 5.2.8 The calculated geometry of the WSF\(_5^-\) anion using density functional theory at the B3LYP/LANL2DZ level of theory.
Table 5.2.3 Calculated Bond Lengths and Angles for the WSF$_5^-$ Anion Compared to Values from the X-ray Crystal Structure.

<table>
<thead>
<tr>
<th>Bond Lengths, pm</th>
<th>Bond Angles, °</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Calc</td>
</tr>
<tr>
<td>W–F(1)</td>
<td>191.47</td>
</tr>
<tr>
<td>W–F(2)</td>
<td>191.48</td>
</tr>
<tr>
<td>W–F(3)</td>
<td>196.93</td>
</tr>
<tr>
<td>W–F(4)</td>
<td>191.47</td>
</tr>
<tr>
<td>W–F(5)</td>
<td>191.48</td>
</tr>
</tbody>
</table>

Table 5.2.4 Calculated Vibrations for WSF$_5^-$ Anion using Density Functional Theory at the B3LYP/LANL2DZ Level of Theory

<table>
<thead>
<tr>
<th>Frequency, cm$^{-1}$</th>
<th>Raman Activity$^a$</th>
<th>Infrared Intensity</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>643</td>
<td>19</td>
<td>78</td>
<td>$\nu_5$(WF$_{4eq}$) $\nu_3$(A$_1$)</td>
</tr>
<tr>
<td>628</td>
<td>0</td>
<td>218</td>
<td>$\nu_8$(WF$_{4eq}$) $\nu_8$(E)</td>
</tr>
<tr>
<td>566</td>
<td>5</td>
<td>0</td>
<td>$\nu$(WF$_{4eq}$) $\nu_5$(B$_1$)</td>
</tr>
<tr>
<td>542</td>
<td>1</td>
<td>133</td>
<td>$\nu$(WF$_{ax}$), $\nu_2$(A$_1$)</td>
</tr>
<tr>
<td>471</td>
<td>27</td>
<td>39</td>
<td>$\nu$(WS), $\nu_1$(A$_1$)</td>
</tr>
<tr>
<td>285</td>
<td>5</td>
<td>5.5</td>
<td>$\delta$(FWS) $\nu_9$(E)</td>
</tr>
<tr>
<td>279</td>
<td>1</td>
<td>17</td>
<td>$\delta$(WF$_{4}$) $\nu_4$(A$_1$)</td>
</tr>
<tr>
<td>272</td>
<td>3</td>
<td>0</td>
<td>$\delta$in-plane $\nu_7$(B$_2$)</td>
</tr>
<tr>
<td>207</td>
<td>1</td>
<td>29</td>
<td>$\delta$ $\nu_{11}$(E)</td>
</tr>
<tr>
<td>202</td>
<td>0</td>
<td>0</td>
<td>$\delta$out-of-plane $\nu_6$(B$_1$)</td>
</tr>
<tr>
<td>109</td>
<td>1.3</td>
<td>0</td>
<td>$\delta$ $\nu_{10}$(E)</td>
</tr>
</tbody>
</table>

$^a$Raman Intensity is in units a$^4$/u and Infrared intensity is in km/mole
5.3 The WSF$_4$$\cdot$C$_5$H$_5$N Lewis Adduct

5.3.1 Synthesis of WSF$_4$$\cdot$C$_5$H$_5$N

Brown WSF$_4$ dissolved in pyridine resulting in a distinctly orange solution upon formation of the WSF$_4$$\cdot$C$_5$H$_5$N adduct (Equation 5.3.1). A Raman spectrum was collected of both, dilute and very concentrated solutions.

\[
\text{WSF}_4 + \text{C}_5\text{H}_5\text{N} \rightarrow \text{WSF}_4$$\cdot$\text{C}_5\text{H}_5\text{N} \quad 5.3.1
\]

The WSF$_4$$\cdot$C$_5$H$_5$N adduct was soluble in CH$_3$CN yielding an orange solution, which was studied by $^{19}$F NMR spectroscopy. The WSF$_4$$\cdot$C$_5$H$_5$N adduct also formed in anhydrous HF solvent as evidenced by the deep orange colour of the solution. Pyridine was vacuum transferred onto a pale yellow HF solution with brown insoluble WSF$_4$ at the bottom. Upon warming to $-80^\circ$C the HF solution instantly became a much deeper yellow. Melting of C$_5$H$_5$N at $-42^\circ$C resulted in two separate layers with C$_5$H$_5$N above HF. With agitation the C$_5$H$_5$N became orange/yellow while the HF remained yellow. With more vigorous agitation the C$_5$H$_5$N mixed with HF and large amounts of heat were given off indicating reaction between HF and C$_5$H$_5$N. The solution was frozen at $-30^\circ$C well above the freezing points of HF or C$_5$H$_5$N at -83°C and -42°C, respectively. and the solvent could not be removed under dynamic vacuum indicating a significant change to the solvent had occurred. The addition of HF likely protonated the C$_5$H$_5$N resulting in the formation of an ionic liquid [C$_5$H$_5$NH][HF$_2$].

5.3.2 $^{19}$F NMR Spectroscopy of WSF$_4$$\cdot$C$_5$H$_5$N

The pyridine adduct of WSF$_4$ was characterized by $^{19}$F NMR spectroscopy in CH$_3$CN solvent. The chemical shift of 81.8 ppm and $^{1}J(^{19}$F-$^{183}$W) of 26.8 Hz are in line with the NMR values observed for WSF$_4$ in the donor solvents THF and CH$_3$CN. In the case of WOF$_4$ it was noted by $^1$H and $^{19}$F NMR spectroscopy that WOF$_4$$\cdot$C$_5$H$_5$N would coordinate with another C$_5$H$_5$N to become WOF$_4$$\cdot$2C$_5$H$_5$N at temperatures below 0 °C. Upon addition of a second C$_5$H$_5$N ligand, the fluorine atoms were no longer equivalent instead becoming an A$_2$MX spin-system. Fluorine-$19$ NMR spectra were collected of
WSF$_4$C$_5$H$_5$N with excess pyridine in CH$_3$CN. Spectra were collected at –20, -30 and –40 °C and all showed signals for WSF$_4$ as a singlet, indicating that WSF$_4$ was either unable to coordinate two pyridine ligands or the ligands were still fluxional at this temperature. Considering that the A$_2$MX spin-system of WOF$_4$·2C$_5$H$_5$N was observable at 0 °C and -40 °C is close to both the freezing points of C$_5$H$_5$N and CH$_3$CN, it is likely that either a second C$_5$H$_5$N does not coordinate to WSF$_4$ or that the WSF$_4$·2C$_5$H$_5$N adduct is fluxional.

5.3.3 Raman Spectroscopy of WSF$_4$·C$_5$H$_5$N

The pyridine adduct of WSF$_4$ was studied by Raman spectroscopy. The observed Raman bands in concentrated pyridine solution and as a solid are listed in Table 5.3.1 together with the Raman bands of neat pyridine and the tentative vibrational assignments.

The Raman spectra of the concentrated solution and the solid showed bands at 673 and 539 cm$^{-1}$ attributable to terminal W-F and W=S stretching modes, respectively. The emergence of a vibrational band at 1015 cm$^{-1}$ was observed in the Raman spectrum of the concentrated solution. The Raman spectrum of solid (Figure 5.3.1) WSF$_4$·C$_5$H$_5$N was also observed to contain this band except in this case it was the second strongest band in the spectrum. Based on the Raman spectrum of WOF$_4$·C$_5$H$_5$N from the literature the band at 1015 cm$^{-1}$ is assigned to the in-plane ring deformation which appears at 1030 cm$^{-1}$ in free pyridine. The electron-withdrawing effect of the Lewis acid WSF$_4$ on a strong pyridine deformation peak clearly indicates that the WSF$_4$·C$_5$H$_5$N adduct was formed. In WOF$_4$·C$_5$H$_5$N the band was reported at 1020 cm$^{-1}$.

The W=S stretch was shifted to 539 cm$^{-1}$ compared to 577 cm$^{-1}$ in solid WSF$_4$. An even lower frequency was observed for the WSF$_5^-$ anion (524 cm$^{-1}$). The W=O stretch of WOF$_4$·C$_5$H$_5$N was shifted to 996 cm$^{-1}$ from 1053 cm$^{-1}$ in WOF$_4$.

Terminal W-F stretches are found at 673 cm$^{-1}$ in the Raman spectrum of the solid (Figure 5.3.1) compared to ca. 700 cm$^{-1}$ in WSF$_4$. Only one strong band for the W-F symmetric stretch is observed which is different from the multiple bands observed in WSF$_4$. This band compares with 694 cm$^{-1}$ reported for WOF$_4$·C$_5$H$_5$N. The small band at 525 cm$^{-1}$ could easily be a result of $^{34}$S-isotope instead of the more common $^{32}$S.
Figure 5.3.1 The Raman spectrum of solid WSF$_4$C$_5$H$_5$N
Table 5.3.1 Comparison of Raman Spectroscopy of WSF₄·C₅H₅N Adduct as Solid and in Solution with Free Pyridine

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<thead>
<tr>
<th>Frequency, cm⁻¹</th>
<th>WSF₄·C₅H₅N in Pyridine</th>
<th>WSF₄·C₅H₅N Dark Solid</th>
<th>Pyridine</th>
<th>Assignment</th>
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<td>3056 (39)</td>
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<td>96 (22)</td>
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*a Only Bands corresponding to WSF₄·C₅H₅N Tabulated for Free Pyridine  
*b Assignments from comparison with WOF₄·C₅H₅N in Literature
5.5 Summary

The new \([\text{N}(\text{CH}_3)_4][\text{WSF}_5]\) salt was prepared by two methods, through the addition of \([\text{N}(\text{CH}_3)_4][\text{F}]\) to \(\text{WSF}_4\) and directly from \(\text{WF}_6\) and \([\text{N}(\text{CH}_3)_4][\text{SSi}(\text{CH}_3)_3]\). Experiments to produce \(\text{Cs}[\text{WSF}_5]\) suffered from the lack of solubility of \(\text{Cs}[\text{SSi}(\text{CH}_3)_3]\) in \(\text{THF}\). Raman and infrared spectroscopy were used to study the \(\text{WSF}_5^-\) anion, which show a significant decrease in the frequency of the W=S stretching mode compared to \(\text{WSF}_4\). It was also shown conclusively that the \(\text{W}_2\text{S}_2\text{F}_9^-\) anion forms in an equilibrium reaction by combination of \(\text{WSF}_4\) with \(\text{WSF}_5^-\) by \(^{19}\text{F}\) NMR spectroscopy. The new mixed \(\text{W}_2\text{OSF}_9^-\) anion was observed in solution for the first time. Density functional theory calculations were performed on the \(\text{WSF}_5^-\) anion and compared to the calculations performed on \(\text{WSF}_4\), and values from literature. The calculated geometry of \(\text{WSF}_5^-\) was in close agreement with literature values from X-ray diffraction. The new Lewis acid/base adduct \(\text{WSF}_4\cdot\text{C}_5\text{H}_5\text{N}\) was prepared and characterized by Raman and \(^{19}\text{F}\) NMR spectroscopy.
References


Chapter 6

Preparation and Characterization of MoSF₄

6.1  Introduction

Molybdenum sulfide fluorides have been the subject of very little reported research. Few reports have mentioned their formation or characterization.¹,² The synthesis of small amounts of MoSF₄ was reported in one publication.¹ The product was poorly characterized by a few infrared bands and mass spectrometry that showed significant amounts of hydrolysis products. No reliable preparation has been reported that produces pure MoSF₄ on a preparative scale. Methods of preparing MoSF₄ in reasonable quantities were investigated to aid in its unambiguous characterization.

6.2  Results and Discussion

6.2.1  Synthesis of MoSF₄

Molybdenum sulfide tetrafluoride was prepared most efficiently by reaction of MoF₆ with ((CH₃)₃Si)₂S in CFCl₃ at low temperature according to Equation 6.2.1. The reaction mixture began to turn yellow/brown even before the solvent had melted at ca. –120 °C and had to be quenched several times to prevent the reaction from going out of control. The reaction was stirred once the solvent had melted at ca. –110 °C and slowly allowed to warm to room temperature. The solvent CFCl₃ was chosen as it has a low melting point allowing for the mixing reagents at low temperatures thus preventing localized heating which could lead to unwanted side reactions. Trichlorofluoromethane is oxidatively resistant compared to other solvents that would form miscible solutions with ((CH₃)₃Si)₂S.

\[
\text{MoF}_6 + ((\text{CH}_3)_3\text{Si})_2\text{S} \rightarrow \text{CFCl}_3 \rightarrow \text{MoSF}_4 + 2 \text{(CH}_3)_3\text{SiF} \quad 6.2.1
\]

The reaction produced a purple solid that settled from solution and was insoluble in CFCl₃. The sample was slowly warmed to room temperature where no further changes were observed. After removal of the CFCl₃ solvent at room temperature yellow/brown
MoSF₄ was isolated and characterized by X-ray crystallography, and Raman, infrared, and ¹⁹F NMR spectroscopy.

Like WSF₄, MoSF₄ also seemed to undergo a colour change to a darker shade of brown after long periods at room temperature. Decomposition and increase in particle size are considered to be possible causes of the change in colour.

Prior to the successful method described (Equation 6.2.1) efforts were made to synthesize MoSF₄ using methods similar to those used for WSF₄. Reactions between MoF₆ and ((CH₃)₃Si)₂S in CH₃CN, however, yielded mainly MoF₅ and another undetermined product. The coloured solution slowly turned dark brown at room temperature.

When MoF₆ was reacted with Sb₂S₃ in HF a brown-coloured product was isolated. The products were a mixture containing mainly MoF₅ and some MoSF₄ according to ¹⁹F NMR spectroscopy of the product dissolved in CH₃CN. The formation of MoSF₄ was believed to occur by Equation 6.2.2. The by-product of the reduction of Mo⁶⁺ to Mo⁵⁺ has not been identified.

\[
3 \text{MoF}_6 + \text{Sb}_2\text{S}_3 \xrightarrow{\text{HF}} 3 \text{MoSF}_4 + 2 \text{SbF}_3 \quad 6.2.2
\]

Conducting the reaction between MoF₆ and Sb₂S₃ in neat MoF₆ without solvent (Equation 6.2.3) resulted in a yellow solution at room temperature. After decanting the yellow solution and removing excess MoF₆ under dynamic vacuum at room temperature a yellow solid was isolated. The yellow solid was characterized by Raman and ¹⁹F NMR spectroscopy in CH₃CN and single crystal X-ray diffraction. The product was found to be pure MoF₅. This reaction serves as a new preparative route for MoF₅.

\[
\text{MoF}_6 + \text{Sb}_2\text{S}_3 \rightarrow \text{MoF}_5 + (\text{other products}) \quad 6.2.3
\]

Similar reactions between MoF₆ and Sb₂S₅ in HF (Equation 6.2.4) were also attempted as it was thought that Sb³⁺ may have been involved in the reduction of MoF₆ experienced previously in reactions with Sb₂S₃. Upon removal of HF solvent the walls of the reaction vessel were coated with a yellow/orange powder. Fluorine-19 NMR
spectroscopy, in CH$_3$CN, showed that MoF$_5$ with a small amount of MoSF$_4$ had been produced.

$$5 \text{ MoF}_6 + \text{Sb}_2\text{S}_5 \rightarrow \text{aHF} \quad 5 \text{ MoSF}_4 + 2 \text{SbF}_5$$

5.2.4

Unlike reactions of WF$_6$ with H$_2$S, reactions involving MoF$_6$ and H$_2$S (Equation 6.2.5) were very exothermic and occurred instantaneously upon mixing even at -100 °C. A yellow/brown powder was isolated from the reaction at -110 °C. Fluorine-19 NMR spectroscopy indicated that moderate amounts of MoSF$_4$ were produced by this method along with MoF$_5$. The Raman spectrum of the sample did contain a band at 580 cm$^{-1}$ indicative of Mo=S stretching of MoSF$_4$.

$$\text{MoF}_6 + \text{H}_2\text{S} \rightarrow \text{MoSF}_4 + 2 \text{HF}$$

6.2.5

The Mo=S bond was shown to be cleaved quite easily. Since at least some MoSF$_4$ was produced in most of the reactions proposed it is likely that MoSF$_4$ acted as an intermediate to production of MoF$_5$. In products containing small amounts of MoSF$_4$ the Mo=S bond may have cleaved to form MoF$_5$. One possible driving force may have been a more favourable lattice energy for MoF$_5$ compared to MoSF$_4$.

6.2.2  X-ray Crystal Structure of MoSF$_4$

Crystals of MoSF$_4$ were grown in anhydrous HF solvent at a temperature slowly varied from -53 to -59 °C. The X-ray crystal structure of MoSF$_4$ was collected at -120 °C (Figure 6.2.1). The least squares refinement on $F^2$ resulted in an $R_I$ value of 2.24 % when data with intensity over 2$\sigma$ was considered and 2.60 % when all of the data was considered. Information on collection and refinement is available in Table 6.2.1. The bond lengths and bond angles are listed in Table 6.2.2. All other information pertaining to the crystal structure is available in the Appendix.

Molybdenum sulfide tetrafluoride crystallizes in the orthorhombic space group $Pca2_1$ with the cell dimensions $a = 1099.21(8)$, $b = 829.57(6)$, $c = 2777.4(2)$ pm. The structure contained six molecules per asymmetric unit giving 24 molecules per unit cell. Molybdenum sulfide tetrafluoride crystallizes in polymeric chains of cis-fluorine-bridged MoSF$_5$ octahedra with chain propagation along the $a$-axis of the unit cell. In comparison,
MoOF4 crystallizes in the monoclinic $P2_1/c$ space group with unit cell dimensions $a = 550(1)$, $b = 1698(2)$, $c = 784(1)$ pm. The much smaller unit cell contains only 8 molecules. The crystal structures of MoSF4 and MoOF4, however, are very similar. Molybdenum oxide tetrafluoride, also forms a cis-fluorine bridged polymeric chain structure of MoOF5 octahedra, analogous to MoSF4. The terminal Mo-F bond lengths are also similar as they range from 182(1) – 184(1) pm in MoOF4 and from 181.1(3) – 184.8(3) pm in MoSF4. The bridging fluorine bonds are also quite similar at 193(1) – 196(1) pm and 192.6(3) – 194.8(2) pm for MoOF4 and MoSF4, respectively. The Mo--F bond distances for fluorine atoms trans to the sulfur ranges from 225.4(2) – 229.5(2) pm, similar to the range for MoOF4 of 227 – 231 pm. As expected the bond length of Mo-S in MoSF4 is much longer than the Mo-O bond in MoOF4. The bond angles in the two structures are also in agreement.3

It was found that MoSF4 is isostructural with ReSF4 which also has six molecular units in the asymmetric unit with unit cell edge lengths of $a = 1089.3(10)$, $b = 827.8(11)$, $c = 2766.3(5)$ pm.4 Both structures were cis-fluorine bridged polymeric chain structures of MSF5 octahdra (where M = Mo, Re), similar to WSF4.

It is apparent upon analysis of the bonds about each molybdenum centre (Table 6.2.3) that the environments are similar about the six crystallographically independent molybdenum atoms; because of this only the angles about three molybdenum centers were given in Table 6.2.3. The Ranges in bond length for particular bonds are given in Table 6.2.2. A complete listing of bond angles is available in the Appendix.

The thermal ellipsoids of some terminal fluorine atoms are elongated perpendicular to the bonding axis. The ellipsoid elongation of the terminal F(3) and F(4) atoms are particularly significant, indicating residual motion in the crystal structure.
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<th>Table 6.2.1 Crystal Data and Structure Refinement for MoSF₄</th>
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<td>b = 829.57(6)</td>
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<td>c = 2777.4(2)</td>
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Figure 6.2.1  The X-ray crystal structure showing the chain structure of MoSF₄. The data was collected at -120 °C with thermal ellipsoids drawn at 50 % probability.

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<tr>
<td>Mo--Fbridge trans to Mo=S</td>
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<tr>
<td>Mo=S</td>
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Table 6.2.3  Bond Lengths and Bond Angles from X-ray Crystal Structure of MoSF₄

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<td>184.1(2)</td>
<td>F(6)-Mo(2)-F(5)</td>
<td>86.17(12)</td>
<td></td>
</tr>
<tr>
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<td>85.91(14)</td>
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<td>S=Mo–F</td>
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<tr>
<td>Mo(4)-F(17)</td>
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<td>F(6)-Mo(2)-S(2)</td>
<td>100.53(9)</td>
<td></td>
</tr>
<tr>
<td>Mo(5)-F(20)</td>
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<td>F(7)-Mo(2)-S(2)</td>
<td>100.14(9)</td>
<td></td>
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<tr>
<td>Mo(5)-F(19)</td>
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<td>F(8)-Mo(2)-S(2)</td>
<td>100.19(11)</td>
<td></td>
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<tr>
<td>Mo(5)-F(18)</td>
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<td>F(5)-Mo(2)-S(2)</td>
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<tr>
<td>Mo(5)-F(17)</td>
<td>193.0(3)</td>
<td>S(2)-Mo(2)-F(9)</td>
<td>178.46(8)</td>
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</tr>
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<td>Mo(5)-S(5)</td>
<td>206.49(12)</td>
<td>F&lt;sub&gt;sym&lt;/sub&gt;-Mo–F&lt;sub&gt;sym&lt;/sub&gt;</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mo(5)-F(21)</td>
<td>225.7(3)</td>
<td>F(6)-Mo(2)-F(9)</td>
<td>79.76(10)</td>
<td></td>
</tr>
<tr>
<td>Mo(6)-F(23)</td>
<td>183.1(3)</td>
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<td>81.36(11)</td>
<td></td>
</tr>
<tr>
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<td>79.40(12)</td>
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<td>193.0(3)</td>
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<td></td>
<td></td>
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<tr>
<td>Mo(6)-S(6)</td>
<td>205.89(11)</td>
<td>F&lt;sub&gt;sym&lt;/sub&gt;-Mo–F&lt;sub&gt;sym&lt;/sub&gt;</td>
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<td></td>
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<tr>
<td>Mo(6)-F(13)#4</td>
<td>229.0(2)</td>
<td>F(11)-Mo(3)-F(10)</td>
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</tr>
<tr>
<td>F(13)-Mo(6)#5</td>
<td>229.0(2)</td>
<td>F(11)-Mo(3)-F(12)</td>
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</tr>
<tr>
<td>F(1)-Mo(5)#2</td>
<td>225.6(3)</td>
<td>F(10)-Mo(3)-F(9)</td>
<td>86.31(13)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>F(12)-Mo(3)-F(9)</td>
<td>83.12(11)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>S=Mo–F</td>
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<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>F(11)-Mo(3)-S(3)</td>
<td>101.60(12)</td>
<td></td>
</tr>
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<td></td>
<td></td>
<td>F(10)-Mo(3)-S(3)</td>
<td>100.14(10)</td>
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<tr>
<td></td>
<td></td>
<td>F(12)-Mo(3)-S(3)</td>
<td>101.66(9)</td>
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</tr>
<tr>
<td></td>
<td></td>
<td>F(9)-Mo(3)-S(3)</td>
<td>96.69(9)</td>
<td></td>
</tr>
</tbody>
</table>

* Only bond angles for three molybdenum centres are shown.
6.2.3 X-ray Crystal Structure of MoF$_5$

Reaction between neat MoF$_6$ and Sb$_2$S$_3$ at room temperature resulted in crystals of MoF$_5$ (Figure 6.2.2) which were studied by X-ray crystallography. The structure was anisotropically refined, resolved with a residual R$_1$ value of 1.47 %. Complete crystallographic information for MoF$_5$ can be found in the Appendix.

Molybdenum pentafluoride crystallizes in the monoclinic C2/m space group. The unit cell dimensions of our improved crystal structure are $a = 951.4(1)$, $b = 1417.4(2)$, $c = 512.66(6)$ pm with angle $\beta = 95.6620(10)^\circ$. The literature unit cell dimensions of MoF$_5$ are $a = 961(1)$, $b = 1422(2)$, $c = 516(1)$ pm where the structure was refined with a much larger residual value of 12 %.5

Molybdenum pentafluoride crystallizes as a fluorine-bridged tetramer. Mo(2) and the terminal fluorine atoms F(4) and F(6) are located on a crystallographic mirror plane. The second molybdenum atom, Mo(1), is located on a crystallographic two-fold rotational axis. The MoF$_5$ tetramer displays symmetric Mo—F—Mo bridging unlike MoSF$_4$. The Mo-F$_\text{terminal}$ bonds $\text{trans}$ to bridging Mo-F bonds range from 181.49(13) to 182.10(13) pm in length while the Mo-F$_\text{terminal}$ bonds $\text{cis}$ to bridging Mo-F bonds are shorter ranging from 179.86(13) to 179.96(19) pm. The Mo-F$_\text{bridge}$ bond lengths are significantly larger than the Mo-F$_\text{terminal}$ bond lengths, ranging from 204.46(12) to 204.95(12) pm.

The ligand environment about molybdenum is pseudo-octahedral with $\text{trans}$-bond angles F(3)-Mo(1)-F(2) of 177.87(6)$^\circ$ and $\text{cis}$-bond angles F(3)-Mo(1)-F(1) of 83.93$^\circ$. The bond angles between terminal Mo-F bonds range from 95.79(7) $^\circ$ to 96.37(6)$^\circ$, while the bond angles between terminal and bridging Mo-F bonds are much smaller ranging from 83.13(6) to 83.93 $^\circ$.5
6.2.4 NMR Spectroscopy of MoSF$_4$ and MoF$_5$

Fluorine-19 NMR spectroscopy was performed on solutions of MoSF$_4$ (Figure 6.2.4) and MoF$_5$ (Figure 6.2.5) in CH$_3$CN at room temperature. The chemical shifts and available coupling constants are listed in Table 6.2.4.

A solution of MoSF$_4$ in CH$_3$CN gave rise to a singlet at 155.0 ppm in the $^{19}$F NMR spectrum. This chemical shift is significantly higher than the chemical shift of MoOF$_4$ at +145.9 but much lower than MoF$_6$ which had been reported at +278 ppm. This is similar to WSF$_4$ as WOF$_4$ has a smaller chemical shift and WF$_6$ has a much larger chemical shift than WSF$_4$, though the difference in chemical shifts between sulfide and oxide-containing species is much less.$^6$ No satellites from $^1J(^{95}$Mo-$^{19}$F) could be observed for MoSF$_4$ as $^{95}$Mo is quadrupolar and expected to undergo rapid relaxation in the asymmetric environment.

Molybdenum pentafluoride dissolved in CH$_3$CN resulted in a $^{19}$F NMR signal at +149.2 ppm with poorly resolved $^{95}$Mo-satellites at its base (Figure 6.2.5). The paramagnetic nature of MoF$_5$ would be expected to broaden the $^{19}$F NMR signals to the
point where it would not be observable; furthermore, a paramagnetic centre at molybdenum would erase all $J$-coupling information. Raman spectroscopy (vide infra) and single crystal X-ray crystallography verified the purity of the MoF$_5$. A possible explanation for the observation of the signal at +149.2 ppm in the $^{19}$F NMR spectrum is the formation of a diamagnetic MoF$_5$ dimer containing a Mo-Mo bond (Figure 6.2.3). The fluorine atoms are expected to be in the fast-exchange regime on the NMR time scale, rendering all fluorine environments equivalent. The symmetry about the molybdenum atoms would be close to octahedral allowing for relatively slow quadrupolar relaxation and the observation of $^{95}$Mo satellites in the $^{19}$F NMR spectrum.

![Figure 6.2.3 A possible structure of the MoF$_5$ dimer in CH$_3$CN solution](image)

![Figure 6.2.4 The $^{19}$F NMR spectrum of MoSF$_4$ in CH$_3$CN at room temperature.](image)
Table 6.2.4  $^{19}$F NMR Spectroscopy Data of MoSF$_4$ and Related Species in Various Solvents at Room Temperature.

<table>
<thead>
<tr>
<th>Chemical Shift (ppm)</th>
<th>Solvent</th>
<th>$^{1}J(^{19}$F-$^{95}$Mo) (Hz)</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>155.0 s</td>
<td>CH$_3$CN</td>
<td></td>
<td>MoSF$_4$·CH$_3$CN</td>
</tr>
<tr>
<td>283.7 s</td>
<td>MoF$_6$</td>
<td>48.0</td>
<td>MoF$_6$</td>
</tr>
</tbody>
</table>

* Abbreviation denotes, singlet (s)
6.2.5 Vibrational Spectroscopy

The Raman spectrum of MoSF$_4$ was collected (Figure 6.2.6) on freshly produced MoSF$_4$ in a melting point capillary at room temperature. The infrared spectrum of MoSF$_4$ was collected as a KBr pellet formed inside the dry box. The vibrational bands are listed in Table 6.2.5 together with the tentative assignments. The Raman spectrum of MoF$_5$ was also collected (Figure 6.2.7) at room temperature as a test of the purity for the yellow solid obtained with the values listed in Table 6.2.6.

The infrared spectrum of MoSF$_4$ contained bands at 671 and 648 cm$^{-1}$ corresponding to terminal Mo-F stretching modes. Holloway et al. reported strong bands in the same area at 690, 670, and 633 cm$^{-1}$. A band at 562 cm$^{-1}$ corresponding to Mo=S stretching was observed, comparing closely to the literature value of 564 cm$^{-1}$. Bridging Mo-F stretching modes were observed at 518 and 511 cm$^{-1}$, while the literature reported bridging Mo-F stretching bands significantly lower at 500 and 458 cm$^{-1}$.

The Raman spectrum (Figure 6.2.6) of MoSF$_4$ was very similar to that of WSF$_4$. The same level of resolution could not be achieved which was most likely a result of the large number of molybdenum isotopes with masses between 92 and 100 u. The Raman spectrum displayed several terminal Mo-F stretching bands in the range 608 – 724 cm$^{-1}$, Mo=S stretching bands were displayed at 580 and 563 cm$^{-1}$, while bridging Mo-F and trans Mo---F bond stretching were observed from 492 - 536 cm$^{-1}$ and 450 to 488 cm$^{-1}$, respectively.

The similarity in frequencies for stretching bands of MoSF$_4$ and WSF$_4$ was unexpected considering that molybdenum is approximately half the mass of tungsten. This same trend is observed for WOF$_4$ and MoOF$_4$. Spectroscopic data on the oxide fluorides, WOF$_4$ and MoOF$_4$, show very similar metal-oxygen stretches of 1056 and 1049 cm$^{-1}$, respectively. This similarity in stretching frequency can only be attributed to weaker bond strengths for the molybdenum (VI) compounds. The Mo=S bond was found to be easily cleaved yielding MoF$_5$.

Comparison of the crystal structures of MoOF$_4$ and MoSF$_4$ shows very similar bond lengths for the Mo-F bonds. It could therefore be reasonably expected that the Mo-F stretching modes would have similar stretching frequencies. This is observed in that
terminal Mo-F stretches are found around 700 cm\(^{-1}\) and bridging stretches are found around 500 cm\(^{-1}\) for both compounds.\(^3\)

The Raman spectrum of MoF\(_5\) (Figure 6.2.7) was basically identical to the Raman spectra of solid MoF\(_5\) reported in the literature.\(^8,9\) The differences in the collected spectrum versus the literature spectra were small differences in the relative intensities of bands; in addition the lower signal-to-noise ratio did not allow for the observation of weak signals that were reported in the literature (Table 6.2.6). The methods used to produce MoF\(_5\) in the literature involved the reduction of MoF\(_6\) with molybdenum metal followed by sublimation in a Pyrex apparatus \(^9\) and material sublimed on the sides of a quartz reaction vessel during a one-stage reaction to generate MoF\(_3\).\(^8\) It is not unreasonable to assume that the MoF\(_5\) generated by reaction of neat MoF\(_6\) with Sb\(_2\)S\(_3\) is of greater purity than the MoF\(_5\) used in the Raman vibrational studies of MoF\(_5\) found in the literature.

![Vibrational spectroscopy of Solid MoSF\(_4\) at room temperature. The Raman spectrum (lower trace) was recorded on the neat solid in a glass melting point capillary. The infrared spectrum (upper trace) was recorded as a KBr pellet.](image)

Figure 6.2.6

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Table 6.2.5 Vibrational Spectroscopy Data of MoSF₄

<table>
<thead>
<tr>
<th>Frequency, a cm⁻¹</th>
<th>Raman ⁶</th>
<th>Infrared ⁷</th>
<th>Literature ⁸</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>724 (3)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>717 (4)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>709 (5)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>693 (7)</td>
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<td></td>
<td></td>
<td>ν(Mo–F_{terminal})</td>
</tr>
<tr>
<td>678 (17)</td>
<td></td>
<td></td>
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<td></td>
</tr>
<tr>
<td>668 (14)</td>
<td>671 sh</td>
<td>670 s</td>
<td></td>
<td></td>
</tr>
<tr>
<td>633 (6)</td>
<td>648 vs br</td>
<td>633 s</td>
<td></td>
<td></td>
</tr>
<tr>
<td>620 (6)</td>
<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>608 (1)</td>
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<td></td>
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<tr>
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<td></td>
<td></td>
<td>ν(Mo=S)</td>
</tr>
<tr>
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<td>562 s</td>
<td>564</td>
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</tr>
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<td>533 (3)</td>
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</tr>
<tr>
<td>518 (8)</td>
<td>519 sh</td>
<td></td>
<td></td>
<td>ν(Mo–F_{bridge})</td>
</tr>
<tr>
<td>514 (8)</td>
<td>511 vs</td>
<td></td>
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</tr>
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<td>500</td>
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<td></td>
<td>ν(Mo---F)</td>
</tr>
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<tr>
<td>472 (sh)</td>
<td>458</td>
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<tr>
<td>310 (sh)</td>
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<td></td>
<td>δ(Mo=S)</td>
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<td>242 (32)</td>
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<td>222 (67)</td>
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<td>δ(Mo=S)</td>
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<td>206 (sh)</td>
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<td>191 (11)</td>
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<td>187 (11)</td>
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<td>152 (6)</td>
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<tr>
<td>132 (4)</td>
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</tr>
<tr>
<td>121 (sh)</td>
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<td>112 (13)</td>
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<tr>
<td>107 (13)</td>
<td></td>
<td></td>
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<td></td>
</tr>
</tbody>
</table>

⁶ Abbreviations denote shoulder (sh), broad (br), very strong (vs), and strong (s). ⁷ Neat solid in melting point capillary at room temperature. ⁸ KBr pellet at room temperature.
Figure 6.2.7 The Raman spectrum of crystalline MoF$_5$ recorded at room temperature in a glass melting point capillary.

Table 6.2.6 Raman Spectroscopy Data Recorded for MoF$_5$ at Room Temperature in a Glass Melting Point Capillary.

<table>
<thead>
<tr>
<th>Frequency, cm$^{-1}$</th>
<th>MoF$_5$ Yellow Solid</th>
<th>Literature$^a$ (Crystal)</th>
<th>Assignment$^a$ ($C_{2h}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>757 (100)</td>
<td>759 s</td>
<td>$v_1$ ($A_1'$)</td>
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</tr>
<tr>
<td>744 (36)</td>
<td>747 m</td>
<td>$v_3$ (E')</td>
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</tr>
<tr>
<td>736 (86)</td>
<td>738 s</td>
<td>$v_1$ ($A_1'$)</td>
<td></td>
</tr>
<tr>
<td>704 (25)</td>
<td>706 m</td>
<td>$v_2$ ($A_1'$)</td>
<td></td>
</tr>
<tr>
<td>695 (24)</td>
<td>696 m</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>684 w</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>494 vw</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>436 w</td>
<td></td>
<td></td>
</tr>
<tr>
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<td>402</td>
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<td></td>
</tr>
<tr>
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<td>332</td>
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<td></td>
</tr>
<tr>
<td></td>
<td>282</td>
<td></td>
<td></td>
</tr>
<tr>
<td>250 (25)</td>
<td>252 m</td>
<td></td>
<td></td>
</tr>
<tr>
<td>244 (sh)</td>
<td></td>
<td>$v_6$ (E')</td>
<td></td>
</tr>
<tr>
<td>238 (39)</td>
<td>239 m</td>
<td></td>
<td></td>
</tr>
<tr>
<td>197 (26)</td>
<td>199 m</td>
<td>$v_7$ (E')</td>
<td></td>
</tr>
<tr>
<td></td>
<td>181 w</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$^a$ Abbreviations denote, strong (s), medium (m), weak (w), weak (w), very weak (vw)
6.2.6 Density Functional Theory Calculations

Calculations were performed on the MoSF$_4$ monomer (Figure 6.2.8) in the gas phase with Gaussian 98 at the B3LYP/LANL2DZ level of theory.

The calculated molecular geometry was of $C_4v$ point group symmetry. The bond lengths and angles of the calculated molecule are listed in Table 6.2.7 and compare well with those of the solid shown in the X-ray crystal structure. Like the case of WSF$_4$ the calculated bond lengths are slightly larger than those observed. The bridging fluorine present in the actual structure could explain this, as it would withdraw significant electron density. The S=Mo–F angle at 104 ° for the calculated molecule is slightly larger than the ca. 100 ° found in the crystal structure while the F$_{\text{term}}$–Mo–F$_{\text{term}}$ angle is slightly less than the ca. 91 ° found in the solid. The structures are quite close and deviations are attributable to fluorine bridging.

Calculated bond vibrations are shown in Table 6.2.8. Many of the frequencies compare well to within a few wavenumbers with the experimental values. The calculated Mo=S stretching mode at 568 cm$^{-1}$ was close to those observed at 580 and 562 cm$^{-1}$ in the Raman and infrared spectra, respectively. The close correlation of the Mo=S stretch indicates that the bridging does not have a large effect on the stretching frequency of the Mo=S bond. The calculated Mo-F bond stretching frequencies show surprising similarity to the Mo-F$_{\text{term}}$ stretching frequencies found in the solid indicating that the bonds are not greatly affected by the bridging fluorine atoms.

Like WSF$_4$, monomeric MoSF$_4$ was expected to be found in a square pyramidal geometry with $C_4v$ point group symmetry. Therefore the group theory applied in Chapter 4 to WSF$_4$ would be identical. Therefore the stretching vibrations have symmetry, $\Gamma_{\text{stretch}} = 2\ A_1 + B_1 + E$ and bending vibrations, $\Gamma_{\text{bend}} = A_1 + B_1 + B_2 + 2\ E$.

When the calculated vibrational frequencies for MoSF$_4$ are compared to those for WSF$_4$ (see Chapter 4), it is interesting to note that the $v_s$(Mo–F)$_{\text{a}}$ ($A_1$) band at 680 cm$^{-1}$ appears below the $v_{\text{as}}$(Mo–F), (E) band at 704 cm$^{-1}$, while for WSF$_4$ the reverse sequence is found.

Comparison of the calculations to actual vibrational data for MoSF$_4$ vapour is not possible as such studies have not been performed.
Figure 6.2.8  The calculated geometry of MoSF₄ in $C_4v$ symmetry using density functional theory at the B3LYP/LANL2DZ level of theory.

Table 6.2.7  Calculated Bond Lengths and Angles for MoSF₄ using Density Functional Theory at the B3LYP/LANL2DZ Level of Theory.

<table>
<thead>
<tr>
<th>Bond Length, pm</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>188.7</td>
<td>Mo–F</td>
</tr>
<tr>
<td>212.6</td>
<td>Mo=Si</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Bond Angles, °</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>104.3</td>
<td>S=Mo–F</td>
</tr>
<tr>
<td>86.5</td>
<td>F–Mo–F</td>
</tr>
</tbody>
</table>
Table 6.2.8 Calculated Vibrational Frequencies for MoSF₄ using Density Functional Theory at the B3LYP/LANL2DZ Level of Theory.

<table>
<thead>
<tr>
<th>Frequency, cm⁻¹</th>
<th>Raman Activity</th>
<th>Infrared Intensity</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>704</td>
<td>1.9</td>
<td>184</td>
<td>νₘ₅(MoF₄)</td>
</tr>
<tr>
<td>680</td>
<td>15</td>
<td>76</td>
<td>ν₆(MoF₄) ν₂(A₁)</td>
</tr>
<tr>
<td>587</td>
<td>6.7</td>
<td>0</td>
<td>ν(MoF₄) ν₄(B₁)</td>
</tr>
<tr>
<td>568</td>
<td>25</td>
<td>18</td>
<td>ν(MoS) ν₁(A₁)</td>
</tr>
<tr>
<td>301</td>
<td>2.9</td>
<td>0</td>
<td>δ ν₆(B₂)</td>
</tr>
<tr>
<td>239</td>
<td>2.4</td>
<td>6</td>
<td>δ ν₅(A₁)</td>
</tr>
<tr>
<td>207</td>
<td>0</td>
<td>18</td>
<td>δ(SMoF) ν₈(E)</td>
</tr>
<tr>
<td>195</td>
<td>6.8</td>
<td>0.8</td>
<td>δ ν₉(E)</td>
</tr>
<tr>
<td>113</td>
<td>0.4</td>
<td>0</td>
<td>δ ν₅(B₁)</td>
</tr>
</tbody>
</table>

6.3 Summary

Molybdenum sulfide tetrafluoride was prepared in large amounts by a facile process at low temperature. Raman, infrared, and ¹⁹F NMR spectroscopy were used to characterize the resulting yellow/brown solid. The previously unknown crystal structure of MoSF₄ was successfully solved and refined from the X-ray diffraction data showing a cis-fluorine-bridged polymeric chain structure of MoSF₅ octahedra very similar to structures observed for MoOF₄ and ReSF₄. Calculations on monomeric MoSF₄ bond stretching frequencies showed a reasonable agreement with the vibrational frequencies observed in the vibrational spectra of the solid.

A new reliable room temperature synthesis of MoF₅ was also discovered. Molybdenum pentafluoride was studied by ¹⁹F NMR spectroscopy in CH₃CN and an improved crystal structure was obtained.
References


Chapter 7

Conclusions and Future Work

I have shown that trimethylsilanethiolate salts are useful sulfur-transfer agent for inorganic fluorine chemistry. The \([\text{N(CH}_3\text{)}_4][\text{SSi(CH}_3\text{)}_3]\) reagent was used for the preparation of \([\text{N(CH}_3\text{)}_4][\text{WSF}_5]\) salt. Their ability to generate sulfide fluoride anions directly from metal fluorides is expected to be extended to other metals in high oxidation states. The commercial availability of \(((\text{CH}_3)_3\text{Si})\text{Se}\) and \(((\text{CH}_3)_3\text{Si})\text{Te}\) raises the possibility to synthesize the new trimethylsilylselenide and telluride reagents \([\text{N(CH}_3\text{)}_4][\text{SeSi(CH}_3\text{)}_3]\) and \([\text{N(CH}_3\text{)}_4][\text{TeSi(CH}_3\text{)}_3]\), respectively. These salts could serve as reagents for the generation of the \(\text{WSeF}_5^-\) and \(\text{WTeF}_5^-\) anions.

The facile method described in this thesis for production of bulk quantities of pure \(\text{WSF}_4\) allows for the detailed study of its reaction behavior. The pyridine adduct, \(\text{WSF}_4\cdot\text{C}_5\text{H}_5\text{N}\), was produced and characterized in this work, showcasing the Lewis acidity of \(\text{WSF}_4\). Other organic donor molecules could be used to form a wide variety of adducts. The Lewis basicity of \(\text{WSF}_4\) has been investigated with \(\text{SbF}_5\) in preliminary experiments and require the unambiguous characterization of the reaction products.

The novel \(\text{W}_2\text{OSF}_9^-\) anion was observed by \(^{19}\text{F}\) NMR spectroscopy in a mixture with \(\text{W}_2\text{S}_2\text{F}_9^-\) in \(\text{CH}_3\text{CN}\). The production of \(\text{W}_2\text{OSF}_9^-\) from \(\text{WO}_4\) and \(\text{WSF}_5^-\) in solution would allow for the isolation of its salts and the full characterization of this mixed anion.

The successful bulk production and full characterization of \(\text{MoSF}_4\) demonstrates that such reactive compounds can be generated and stored for an extended period of time. Very little is known about molybdenum sulfide fluorides. The ability to generate \(\text{MoSF}_4\) reliably on a preparative scale makes possible the study of its fluoride-ion donor and acceptor properties. The information provided by such research could expand our knowledge of the chemistry of elements in group six.
Appendix
<table>
<thead>
<tr>
<th>Empirical formula</th>
<th>WF₅</th>
</tr>
</thead>
<tbody>
<tr>
<td>Formula weight, g mol⁻¹</td>
<td>278.85</td>
</tr>
<tr>
<td>Temperature, K</td>
<td>293(2)</td>
</tr>
<tr>
<td>Wavelength, pm</td>
<td>71.073</td>
</tr>
<tr>
<td>Crystal system</td>
<td>Monoclinic</td>
</tr>
<tr>
<td>Space group</td>
<td>C₂/m</td>
</tr>
<tr>
<td>Unit cell dimensions, pm</td>
<td>a = 956.5(10) b = 1437.0(15) c = 506.0(5) β = 96.494(10)°.</td>
</tr>
<tr>
<td>Volume, 10⁶ pm³</td>
<td>0.6910(12)</td>
</tr>
<tr>
<td>Z</td>
<td>8</td>
</tr>
<tr>
<td>Density (calculated), mg mm⁻³</td>
<td>5.361</td>
</tr>
<tr>
<td>Absorption coefficient, mm⁻¹</td>
<td>33.410 mm⁻¹</td>
</tr>
<tr>
<td>F(000)</td>
<td>952</td>
</tr>
<tr>
<td>Theta range for data collection</td>
<td>2.57 to 28.68°.</td>
</tr>
<tr>
<td>Index ranges</td>
<td>-12≤h≤12, -18≤k≤19, -6≤l≤6</td>
</tr>
<tr>
<td>Reflections collected</td>
<td>4013</td>
</tr>
<tr>
<td>Independent reflections</td>
<td>889 [R(int) = 0.0175]</td>
</tr>
<tr>
<td>Completeness to theta = 28.68°, %</td>
<td>95.6 %</td>
</tr>
<tr>
<td>Refinement method</td>
<td>Full-matrix least-squares on F²</td>
</tr>
<tr>
<td>Data / restraints / parameters</td>
<td>889 / 0 / 61</td>
</tr>
<tr>
<td>Goodness-of-fit on F²</td>
<td>1.272</td>
</tr>
<tr>
<td>Final R indices [I&gt;2sigma(I)]</td>
<td>R₁ = 0.0221, wR₂ = 0.0665</td>
</tr>
<tr>
<td>R indices (all data)</td>
<td>R₁ = 0.0236, wR₂ = 0.0671</td>
</tr>
<tr>
<td>Extinction coefficient</td>
<td>0.00021(10)</td>
</tr>
<tr>
<td>Largest diff. peak and hole, e 10⁶ pm³</td>
<td>1.757 and -1.465</td>
</tr>
</tbody>
</table>
Table A.1.2. Atomic coordinates ($x \times 10^4$) and equivalent isotropic displacement parameters ($\text{pm}^2 \times 10^{-1}$) for WF$_5$. $U(\text{eq})$ is defined as one third of the trace of the orthogonalized $U^\parallel$ tensor.

<table>
<thead>
<tr>
<th></th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>$U(\text{eq})$</th>
</tr>
</thead>
<tbody>
<tr>
<td>W(1)</td>
<td>0</td>
<td>2932(1)</td>
<td>5000</td>
<td>18(1)</td>
</tr>
<tr>
<td>W(2)</td>
<td>2640(1)</td>
<td>5000</td>
<td>2341(1)</td>
<td>19(1)</td>
</tr>
<tr>
<td>F(5)</td>
<td>3618(4)</td>
<td>4068(3)</td>
<td>1412(8)</td>
<td>18(1)</td>
</tr>
<tr>
<td>F(6)</td>
<td>3395(5)</td>
<td>5000</td>
<td>5845(10)</td>
<td>10(1)</td>
</tr>
<tr>
<td>F(1)</td>
<td>1077(4)</td>
<td>3148(3)</td>
<td>8173(7)</td>
<td>8(1)</td>
</tr>
<tr>
<td>F(3)</td>
<td>1201(4)</td>
<td>4058(2)</td>
<td>3756(7)</td>
<td>10(1)</td>
</tr>
<tr>
<td>F(4)</td>
<td>1337(5)</td>
<td>5000</td>
<td>-585(10)</td>
<td>8(1)</td>
</tr>
<tr>
<td>F(2)</td>
<td>1167(5)</td>
<td>2167(3)</td>
<td>3756(9)</td>
<td>16(1)</td>
</tr>
</tbody>
</table>
Table A.1.3. Bond Lengths [pm] and Angles [°] for WF₅.

<table>
<thead>
<tr>
<th>Bond</th>
<th>Length [pm]</th>
</tr>
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<tbody>
<tr>
<td>W(1)-F(2)</td>
<td>173.4(4)</td>
</tr>
<tr>
<td>W(1)-F(2)#1</td>
<td>173.4(4)</td>
</tr>
<tr>
<td>W(1)-F(1)</td>
<td>183.3(4)</td>
</tr>
<tr>
<td>W(1)-F(1)#1</td>
<td>183.3(4)</td>
</tr>
<tr>
<td>W(1)-F(3)#1</td>
<td>212.1(4)</td>
</tr>
<tr>
<td>W(1)-F(3)</td>
<td>212.1(4)</td>
</tr>
<tr>
<td>W(2)-F(5)#2</td>
<td>172.8(4)</td>
</tr>
<tr>
<td>W(2)-F(5)</td>
<td>172.8(4)</td>
</tr>
<tr>
<td>W(2)-F(4)</td>
<td>182.4(5)</td>
</tr>
<tr>
<td>W(2)-F(6)</td>
<td>183.7(5)</td>
</tr>
<tr>
<td>W(2)-F(3)#2</td>
<td>211.3(4)</td>
</tr>
<tr>
<td>W(2)-F(3)</td>
<td>211.3(4)</td>
</tr>
<tr>
<td>F(2)-W(1)-F(2)#1</td>
<td>101.4(3)</td>
</tr>
<tr>
<td>F(2)-W(1)-F(1)</td>
<td>95.98(19)</td>
</tr>
<tr>
<td>F(2)#1-W(1)-F(1)</td>
<td>96.3(2)</td>
</tr>
<tr>
<td>F(2)-W(1)-F(1)#1</td>
<td>96.3(2)</td>
</tr>
<tr>
<td>F(2)#1-W(1)-F(3)#1</td>
<td>96.0(2)</td>
</tr>
<tr>
<td>F(1)-W(1)-F(1)#1</td>
<td>160.5(2)</td>
</tr>
<tr>
<td>F(2)-W(1)-F(3)#1</td>
<td>169.58(18)</td>
</tr>
<tr>
<td>F(2)#1-W(1)-F(3)#1</td>
<td>89.05(18)</td>
</tr>
<tr>
<td>F(1)-W(1)-F(3)#1</td>
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</tr>
<tr>
<td>F(2)-W(1)-F(3)</td>
<td>82.01(16)</td>
</tr>
<tr>
<td>F(2)#1-W(1)-F(3)</td>
<td>89.05(18)</td>
</tr>
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<td>F(1)-W(1)-F(3)</td>
<td>82.01(16)</td>
</tr>
<tr>
<td>F(1)#1-W(1)-F(3)</td>
<td>83.14(16)</td>
</tr>
<tr>
<td>F(3)#1-W(1)-F(3)</td>
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</tr>
<tr>
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</tr>
<tr>
<td>F(5)#2-W(2)-F(4)</td>
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<tr>
<td>F(5)#2-W(2)-F(6)</td>
<td>95.56(17)</td>
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<td>95.56(17)</td>
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</tr>
<tr>
<td>F(5)#2-W(2)-F(3)#2</td>
<td>89.35(18)</td>
</tr>
<tr>
<td>F(5)-W(2)-F(3)#2</td>
<td>169.05(17)</td>
</tr>
<tr>
<td>F(4)-W(2)-F(3)#2</td>
<td>82.15(17)</td>
</tr>
<tr>
<td>F(6)-W(2)-F(3)#2</td>
<td>82.68(16)</td>
</tr>
<tr>
<td>F(5)#2-W(2)-F(3)</td>
<td>169.05(17)</td>
</tr>
<tr>
<td>F(5)-W(2)-F(3)</td>
<td>89.35(18)</td>
</tr>
<tr>
<td>F(4)-W(2)-F(3)</td>
<td>82.15(17)</td>
</tr>
<tr>
<td>F(6)-W(2)-F(3)</td>
<td>82.68(16)</td>
</tr>
<tr>
<td>F(3)#2-W(2)-F(3)</td>
<td>79.7(2)</td>
</tr>
<tr>
<td>W(2)-F(3)-W(1)</td>
<td>170.09(19)</td>
</tr>
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</table>

Symmetry transformations used to generate equivalent atoms:
#1 -x,y,-z+1    #2 x,-y+1,z
Table A.1.4. Anisotropic displacement parameters (pm$^2 \times 10^{-1}$) for WF$_5$. The anisotropic displacement factor exponent takes the form: $-2\pi^2 \left[ h^2 a^{*2} U^{11} + \ldots + 2hk a^{*} b^{*} U^{12} \right]$

<table>
<thead>
<tr>
<th></th>
<th>$U^{11}$</th>
<th>$U^{22}$</th>
<th>$U^{33}$</th>
<th>$U^{23}$</th>
<th>$U^{13}$</th>
<th>$U^{12}$</th>
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<tbody>
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<td>-8(1)</td>
<td>0</td>
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<tr>
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<td>10(1)</td>
<td>35(1)</td>
<td>13(1)</td>
<td>0</td>
<td>3(1)</td>
<td>0</td>
</tr>
<tr>
<td>F(5)</td>
<td>17(2)</td>
<td>17(2)</td>
<td>20(2)</td>
<td>-2(2)</td>
<td>5(2)</td>
<td>9(2)</td>
</tr>
<tr>
<td>F(6)</td>
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<td>3(2)</td>
<td>0</td>
<td>1(2)</td>
<td>0</td>
</tr>
<tr>
<td>F(1)</td>
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<td>4(2)</td>
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<td>-1(1)</td>
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<tr>
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<td>1(1)</td>
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<tr>
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<td>7(2)</td>
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<td>-2(2)</td>
<td>0</td>
</tr>
<tr>
<td>F(2)</td>
<td>13(2)</td>
<td>16(2)</td>
<td>19(2)</td>
<td>-2(2)</td>
<td>6(2)</td>
<td>5(2)</td>
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Table A.2.1. Crystal Data and Structure Refinement for MoF₅

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Empirical formula</td>
<td>MoF₅</td>
</tr>
<tr>
<td>Formula weight</td>
<td>190.94</td>
</tr>
<tr>
<td>Temperature, K</td>
<td>296(2)</td>
</tr>
<tr>
<td>Wavelength, pm</td>
<td>71.073</td>
</tr>
<tr>
<td>Crystal system</td>
<td>Monoclinic</td>
</tr>
<tr>
<td>Space group</td>
<td>C2/m</td>
</tr>
<tr>
<td>Unit cell dimensions, pm</td>
<td>(a = 951.45(11)) (b = 1417.42(16)) (c = 512.66(6)) (\beta = 95.6620(10)^\circ)</td>
</tr>
<tr>
<td>Volume, (10^6) pm³</td>
<td>0.68800(14)</td>
</tr>
<tr>
<td>(Z)</td>
<td>8</td>
</tr>
<tr>
<td>Density (calculated), mg mm³</td>
<td>3.939</td>
</tr>
<tr>
<td>Absorption coefficient, mm⁻¹</td>
<td>4.346</td>
</tr>
<tr>
<td>(F(000))</td>
<td>752</td>
</tr>
<tr>
<td>Theta range for data collection</td>
<td>2.59 to 28.65°</td>
</tr>
<tr>
<td>Index ranges</td>
<td>(-12 \leq h \leq 12, -18 \leq k \leq 18, -6 \leq l \leq 6)</td>
</tr>
<tr>
<td>Reflections collected</td>
<td>3931</td>
</tr>
<tr>
<td>Independent reflections</td>
<td>864 ([R(int) = 0.0148])</td>
</tr>
<tr>
<td>Completeness to theta = 28.65°, %</td>
<td>93.8</td>
</tr>
<tr>
<td>Refinement method</td>
<td>Full-matrix least-squares on (F^2)</td>
</tr>
<tr>
<td>Data / restraints / parameters</td>
<td>864 / 0 / 61</td>
</tr>
<tr>
<td>Goodness-of-fit on (F^2)</td>
<td>1.220</td>
</tr>
<tr>
<td>Final R indices ([I &gt; 2\sigma(I)])</td>
<td>(R_1 = 0.0147, wR_2 = 0.0365)</td>
</tr>
<tr>
<td>R indices (all data)</td>
<td>(R_1 = 0.0151, wR_2 = 0.0367)</td>
</tr>
<tr>
<td>Extinction coefficient</td>
<td>0.00102(15)</td>
</tr>
<tr>
<td>Largest diff. peak and hole, e (10^6) pm⁻³</td>
<td>0.688 and -0.561</td>
</tr>
</tbody>
</table>
Table A.2.2. Atomic coordinates ($x \times 10^4$) and equivalent isotropic displacement parameters ($pm^2 x 10^{-1}$) for MoF$_5$. $U$($eq$) is defined as one third of the trace of the orthogonalized $U^{ij}$ tensor.

<table>
<thead>
<tr>
<th></th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>$U$($eq$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mo(1)</td>
<td>0</td>
<td>2040(1)</td>
<td>10000</td>
<td>12(1)</td>
</tr>
<tr>
<td>Mo(2)</td>
<td>2592(1)</td>
<td>0</td>
<td>7473(1)</td>
<td>12(1)</td>
</tr>
<tr>
<td>F(3)</td>
<td>1266(1)</td>
<td>1010(1)</td>
<td>8710(3)</td>
<td>21(1)</td>
</tr>
<tr>
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<td>1845(1)</td>
<td>13083(3)</td>
<td>21(1)</td>
</tr>
<tr>
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<td>8779(3)</td>
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<tr>
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<td>926(1)</td>
<td>6396(3)</td>
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<td>F(6)</td>
<td>1351(2)</td>
<td>0</td>
<td>4586(4)</td>
<td>20(1)</td>
</tr>
</tbody>
</table>
Table A.2.3. Bond Lengths [pm] and Angles [°] for MoF₅

<table>
<thead>
<tr>
<th>Bond</th>
<th>Length [pm]</th>
</tr>
</thead>
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<tr>
<td>Mo(1)-F(1)#1</td>
<td>179.86(13)</td>
</tr>
<tr>
<td>Mo(1)-F(1)</td>
<td>179.86(13)</td>
</tr>
<tr>
<td>Mo(1)-F(2)#1</td>
<td>182.10(13)</td>
</tr>
<tr>
<td>Mo(1)-F(2)</td>
<td>182.10(13)</td>
</tr>
<tr>
<td>Mo(1)-F(3)#1</td>
<td>204.46(12)</td>
</tr>
<tr>
<td>Mo(1)-F(3)</td>
<td>204.46(12)</td>
</tr>
<tr>
<td>Mo(2)-F(4)</td>
<td>179.90(19)</td>
</tr>
<tr>
<td>Mo(2)-F(6)</td>
<td>179.96(19)</td>
</tr>
<tr>
<td>Mo(2)-F(5)</td>
<td>181.49(13)</td>
</tr>
<tr>
<td>Mo(2)-F(5)#2</td>
<td>181.49(13)</td>
</tr>
<tr>
<td>Mo(2)-F(3)#2</td>
<td>204.95(12)</td>
</tr>
<tr>
<td>Mo(2)-F(3)</td>
<td>204.95(12)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
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<th>Value [°]</th>
</tr>
</thead>
<tbody>
<tr>
<td>F(1)#1-Mo(1)-F(1)</td>
<td>162.31(9)</td>
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<tr>
<td>F(1)#1-Mo(1)-F(2)#1</td>
<td>95.38(6)</td>
</tr>
<tr>
<td>F(1)-Mo(1)-F(2)#1</td>
<td>95.79(7)</td>
</tr>
<tr>
<td>F(1)-Mo(1)-F(2)</td>
<td>96.38(6)</td>
</tr>
<tr>
<td>F(2)#1-Mo(1)-F(2)</td>
<td>92.90(9)</td>
</tr>
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Symmetry transformations used to generate equivalent atoms:
#1 -x,y,-z+2  #2 x,-y,z
Table A.2.4. Anisotropic displacement parameters (pm$^2$x 10$^{-1}$) for MoF$_5$. The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2a^*2U_{11} + ... + 2hk a^* b^* U_{12}]$

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Table A.3.1. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters (pm$^2\times 10^{-1}$) for MoSF$_4$. $U(eq)$ is defined as one third of the trace of the orthogonalized $U^{ii}$ tensor.

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Symmetry transformations used to generate equivalent atoms:

#1 x-1/2,-y+1,z  #2 x-1/2,-y+2,z  #3 x+1/2,-y+2,z  #4 x+1/2,-y+1,z
Table A.3.3. Anisotropic displacement parameters (pm\(^2\times 10^{-3}\)) for MoSF\(_4\). The anisotropic displacement factor exponent takes the form: \(-2\pi^2 [ h^2 a^* U^{11} + \ldots + 2 h k a^* b^* U^{12} ] \)

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Table A.4.1. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (pm^2x 10^{-1}) for WSF_4. U(eq) is defined as one third of the trace of the orthogonalized U^ij tensor.

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Table A.4.2. Anisotropic displacement parameters (pm$^2 \times 10^{-1}$) for WSF$_4$. The anisotropic displacement factor exponent takes the form: 
\[-2\pi^2 [ h^2 a^2 U_{11} + \ldots + 2 h k a^* b^* U_{12} ] \]

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