

Fluoride-Ion Acceptor Properties of WSF_4 : Synthesis, Characterization, and Computational Study of the WSF_5^- , and $\text{W}_2\text{S}_2\text{F}_9^-$ Anions, and ^{19}F NMR Spectroscopic Characterization of the W_2OSF_9^- Anion

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Abstract

The new $[\text{N}(\text{CH}_3)_4][\text{WSF}_5]$ salt was synthesized by two preparative methods: (a) by reaction of WSF_4 with $[\text{N}(\text{CH}_3)_4][\text{F}]$ in CH_3CN and (b) directly from WF_6 using the new sulfide transfer reagent $[\text{N}(\text{CH}_3)_4][\text{SSi}(\text{CH}_3)_3]$. The $[\text{N}(\text{CH}_3)_4][\text{WSF}_5]$ salt was characterized by Raman, infrared, and ^{19}F NMR spectroscopy and $[\text{N}(\text{CH}_3)_4][\text{WSF}_5] \cdot \text{CH}_3\text{CN}$ by X-ray crystallography. The reaction of WSF_4 with half an aliquot of $[\text{N}(\text{CH}_3)_4][\text{F}]$ yielded $[\text{N}(\text{CH}_3)_4][\text{W}_2\text{S}_2\text{F}_9]$, which was characterized by Raman and ^{19}F NMR spectroscopy and by X-ray crystallography. The WSF_5^- and $\text{W}_2\text{S}_2\text{F}_9^-$ anions were studied by DFT calculations. The novel $[\text{W}_2\text{OSF}_9]^-$ anion was observed by ^{19}F NMR spectroscopy in CH_3CN solution of WOF_4 and WSF_5^- , as well as CH_3CN solutions of WSF_4 and WOF_5^- .

Introduction

Tungsten sulfide tetrafluoride, WSF_4 , has been known to act as a Lewis acid, as documented by the formation of the $\text{WSF}_4 \cdot \text{CH}_3\text{CN}$ and $\text{WSF}_4 \cdot \text{NC}_5\text{H}_5$ adducts and the fluorine bridging observed in solid WSF_4 .^{1,2} While the fluoride-ion acceptor properties of WSF_4 have not been studied, the anions, WSF_5^- and $\text{W}_2\text{S}_2\text{F}_9^-$, have been observed in acetonitrile solutions by ^{19}F NMR spectroscopy in admixture with other anionic and neutral tungsten species.^{3,4} The synthetic routes to the WSF_5^- and $\text{W}_2\text{S}_2\text{F}_9^-$ anions have utilized fluoride-chloride substitution, starting from WScCl_4 and HF or F^- .³⁻⁵ An X-ray crystal structure of $[\{(\text{C}_6\text{H}_5)_3\text{P}\}_2\text{N}][\text{WSF}_5] \cdot \text{CH}_3\text{CN}$ showed a pseudo-octahedral WSF_5^- anion, which was prepared from WScCl_4 and NaF .⁵ In the present study, the fluoride-ion acceptor properties of WSF_4 are investigated systematically.

Results and Discussion

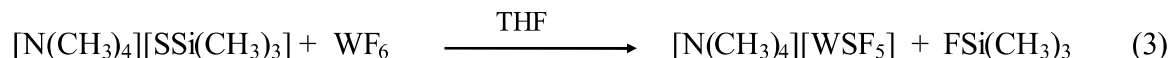
Synthesis of $[\text{N}(\text{CH}_3)_4][\text{WSF}_5]$. The new $[\text{N}(\text{CH}_3)_4][\text{WSF}_5]$ salt was prepared by addition of $[\text{N}(\text{CH}_3)_4][\text{F}]$ to WSF_4 in CH_3CN at -40°C according to eq 1. Upon removal of the solvent under dynamic vacuum, a beige solid was obtained. The solid, $[\text{N}(\text{CH}_3)_4][\text{WSF}_5]$, is stable at ambient temperature under exclusion of moisture and was characterized by Raman and ^{19}F NMR spectroscopy. The WSF_5^- anion was found to be moderately soluble in CH_3CN , producing a bright yellow solution.



Alternatively, the new sulfide transfer agent, $[\text{N}(\text{CH}_3)_4][\text{SSi}(\text{CH}_3)_3]$, can be utilized for the synthesis of $[\text{N}(\text{CH}_3)_4][\text{WSF}_5]$. The $[\text{N}(\text{CH}_3)_4]^+$ salt of the trimethylsilylthiolate anion was prepared from $\text{S}(\text{Si}(\text{CH}_3)_3)_2$ and $[\text{N}(\text{CH}_3)_4][\text{F}]$ in CH_3CN according to eq 2.

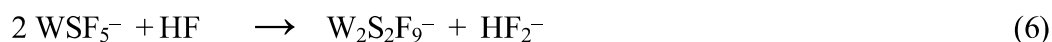
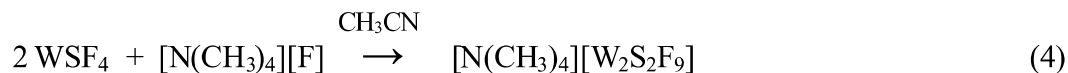


The $[\text{N}(\text{CH}_3)_4][\text{SSi}(\text{CH}_3)_3]$ salt is a white moisture-sensitive solid, that is extremely malodorous when exposed to the atmosphere. It is sparingly soluble in CH_3CN and THF. Reacting $[\text{N}(\text{CH}_3)_4][\text{SSi}(\text{CH}_3)_3]$ directly with WF_6 in THF at -78°C yielded $[\text{N}(\text{CH}_3)_4][\text{WSF}_5]$ according to eq 3.



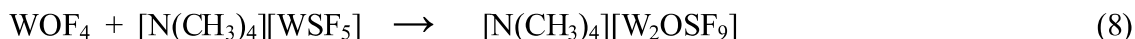
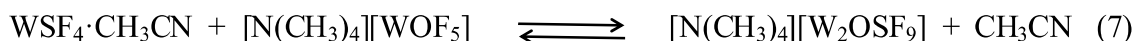
To our knowledge, only the sodium salt of trimethylsilylthiolate has been reported.^{6,7} The $\text{Na}[\text{SSi}(\text{CH}_3)_3]$ salt has been used as a reagent in inorganic oxide/sulfide substitution reactions and in a number of organic reactions.⁷

Synthesis of $[\text{N}(\text{CH}_3)_4][\text{W}_2\text{S}_2\text{F}_9]$ and Formation of the W_2OSF_9^- Anion. The reaction of WSF_4 with $[\text{N}(\text{CH}_3)_4][\text{F}]$ in a 2:1 ratio in CH_3CN yielded brown $[\text{N}(\text{CH}_3)_4][\text{W}_2\text{S}_2\text{F}_9]$ containing the fluorine-bridge dinuclear $\text{W}_2\text{S}_2\text{F}_9^-$ anion (eq 4), which was identified by ^{19}F NMR and Raman spectroscopy. Fluorine-19 NMR spectroscopy (vide infra) of a CH_3CN solution showed the presence of small amounts of WSF_5^- and $\text{WSF}_4 \cdot \text{CH}_3\text{CN}$ besides $\text{W}_2\text{S}_2\text{F}_9^-$ indicating that equilibrium (5) is operative in CH_3CN solvent. In anhydrous HF, the WSF_5^- anion reacts with the solvent to give the $\text{W}_2\text{S}_2\text{F}_9^-$ anion (eq 6).



The presence of small amounts of water in a sample of $[\text{N}(\text{CH}_3)_4][\text{W}_2\text{S}_2\text{F}_9]$ in CH_3CN solvent

resulted in hydrolysis and formation of WOF_5^- , traces of $\text{W}_2\text{O}_2\text{F}_9^-$, as well as the novel W_2OSF_9^- anion. Attempts to prepare CH_3CN solutions containing mainly the W_2OSF_9^- anion utilized reactions of equimolar amounts of WSF_4 and $[\text{N}(\text{CH}_3)_4][\text{WOF}_5]$ (eq. 7), as well as of WOF_4 and $[\text{N}(\text{CH}_3)_4][\text{WSF}_5]$ (eq. 8) in CH_3CN solvent. The resulting solutions, however, contained mixtures of W_2OSF_9^- with the mono- and dinuclear oxide fluoride and sulfide fluoride anions and $\text{WSF}_4 \cdot \text{CH}_3\text{CN}$, confirming equilibria (5) and (7) and the analogous equilibrium between the oxide fluoride anions in CH_3CN solvent. The absence of the ^{19}F resonance attributable to $\text{WOF}_4 \cdot \text{CH}_3\text{CN}$, indicate the higher Lewis acidity of WOF_4 towards F^- compared to WSF_4 .



Vibrational Spectroscopy.

The salts, $[\text{N}(\text{CH}_3)_4][\text{WSF}_5]$, $[\text{N}(\text{CH}_3)_4][\text{W}_2\text{S}_2\text{F}_9]$, and $[\text{N}(\text{CH}_3)_4][\text{SSi}(\text{CH}_3)_3]$ were characterized by infrared and Raman spectroscopy. The assignments for the $\text{N}(\text{CH}_3)_4^+$ cation follow those previously given for other $\text{N}(\text{CH}_3)_4^+$ salts.^{8,9} The infrared and Raman spectra of $[\text{N}(\text{CH}_3)_4][\text{SSi}(\text{CH}_3)_3]$ are shown in Figure S2 and the vibrational frequencies are listed in Table S2. The most intense band in the Raman spectrum $[\text{N}(\text{CH}_3)_4][\text{SSi}(\text{CH}_3)_3]$ at 509 cm^{-1} , together with its strong infrared counterpart at 508 cm^{-1} , corresponds to the Si–S stretching mode. This band appears at substantially higher frequency than the symmetric and asymmetric stretching bands of the $\text{S}(\text{Si}(\text{CH}_3)_3)_2$ precursor (484 and 437 cm^{-1}), reflecting stronger Si–S bonding in the thiolate anion.¹⁰

(a) $[\text{N}(\text{CH}_3)_4][\text{WSF}_5]$. The vibrational spectra of $[\text{N}(\text{CH}_3)_4][\text{WSF}_5]$ at room temperature are

depicted in Figure 1 and the experimental and calculated vibrational frequencies for the WSF_5^- anion are listed in Table 1, together with their assignments. Overall, the calculated vibrational frequencies at the B3LYP and PBE1PBE levels of theory are in good agreement with the experimental values. The assignment of the Raman and infrared bands is based on the calculated vibrational frequencies and the calculated signal intensities.

The most intense band in the Raman spectrum of $[\text{N}(\text{CH}_3)_4][\text{WSF}_5]$ appears at 520 cm^{-1} and can be attributed to the W=S stretching mode. This frequency is in close agreement with the previously reported W=S stretching frequency for $[\text{Na}(15\text{-crown-5})][\text{WSF}_5]$ (525 cm^{-1}).⁵ It is significantly lower than that for monomeric WSF_4 in HF solvent (563 cm^{-1}) and of solid polymeric WSF_4 (578 cm^{-1}), suggesting a weakened W=S bond in the anion, and even lower than that of the $\text{WSF}_4\cdot\text{NC}_5\text{H}_5$ adduct (539 cm^{-1}), reflecting the stronger Lewis basicity of the ‘naked’ fluoride ion compared to pyridine. The medium intensity Raman band at 664 cm^{-1} , with its infrared counterpart at 662 cm^{-1} , can be assigned to the symmetric WF_5 stretching mode. This W–F stretching band is shifted to lower frequency compared to that of monomeric WSF_4 in HF solvent (690 cm^{-1}) and $\text{WSF}_4\cdot\text{NC}_5\text{H}_5$ (674 cm^{-1}), agreeing with more ionic W–F bonding in the anion. The very strong infrared bands at 598 and 532 cm^{-1} correspond to the W–F stretching modes, $\nu_8(\text{E})$ and $\nu_2(\text{A}_1)$, respectively. The vibrational frequencies and the large infrared and very small Raman intensities that were calculated for these modes are in excellent agreement with the observation of these modes only by infrared spectroscopy. The medium intensity bands observed at 292 cm^{-1} is assigned to the S–W–F bending mode and appears at higher frequency than that for monomeric WSF_4 (241 cm^{-1}). The assignments of the Raman bands at 220 and 131 cm^{-1} to the WF_4 scissoring vibration and the S–W–F_{ax} rocking mode are based on their calculated relative Raman intensity. Significantly higher and lower calculated frequencies for the WF_4 scissoring vibration and the S–W–F_{ax} rocking mode, respectively, have also been observed for monomeric WSF_4 .

(b) $[\text{N}(\text{CH}_3)_4][\text{W}_2\text{S}_2\text{F}_9]$. The infrared and Raman spectra of $[\text{N}(\text{CH}_3)_4][\text{W}_2\text{S}_2\text{F}_9]$ are depicted in

Figure 2 and the experimental and calculated vibrational frequencies for the $W_2S_2F_9^-$ anion are given in Table 2, together with their assignments. The calculated vibrational frequencies are in good agreement with the experimental values and the assignment of the Raman and infrared bands is based on the calculated vibrational frequencies and the calculated signal intensities.

The small number of bands associated with the $W_2S_2F_9^-$ anion and observed by Raman and infrared spectroscopy is in accordance with the very few modes, which are predicted to have sufficiently large intensities to be observable in the recorded frequency ranges. The bands at 560 and 556 cm^{-1} in the Raman spectrum and at 578 and 553 cm^{-1} in the infrared spectrum are attributed to the in-phase and out-of-phase phase combinations of the two W–S stretching vibrations, respectively, and are closer to the stretching frequency of monomeric WSF_4 than that of the WSF_5^- anion, reflecting the lower overall charge density and more covalent W=S bonding in the dinuclear anion compared to the mononuclear anion. The calculated values predict similar frequencies for the in-phase (541 cm^{-1}) and the out-of-phase (535 cm^{-1}) $\nu(W-S)$ stretching modes, which is likely a consequence of the overestimated W–F_{br} distance in the calculations, resulting in weaker vibrational coupling between the two WSF_4 moieties. The most intense W–F stretching bands in the Raman spectrum appear at 672 and 678 cm^{-1} and are assigned to the in-phase combination of the two $\nu_s(WF_4)$ vibrations. The intense, high-frequency W–F stretching band in the infrared spectrum at 688 cm^{-1} is assigned to the out-of-phase combination of the two $\nu_s(WF_4)$ vibrations. Both are significantly higher than $\nu_s(WF_5)$ of the WSF_5^- anion at 664 cm^{-1} , reflecting less ionic bonding in the dinuclear anion compared to the mononuclear anion. The calculated values (B3LYP: in-phase: 686 and out-of-phase: 688 cm^{-1}) are in very good agreement with the observed values. The most intense infrared band at 625 cm^{-1} is assigned to the two in-phase combinations of the two $\nu_{as}(WF_4)$ vibrations, which are calculated to be degenerate in the linear geometry. The corresponding $\nu_{as}(WF_4)$ mode of the WSF_5^- anion (598 cm^{-1}) also appears at a lower frequency than observed for the dinuclear anion. The strong band observed at 434 cm^{-1} in

the infrared spectrum is associated with the W–F_b stretching modes and appears at slightly higher frequency than the calculated frequency (403 cm⁻¹). All deformation modes are calculated to have frequencies below 306 cm⁻¹ and therefore none of them was observed in the infrared spectrum. However, the two bending modes that are predicted to be strong enough to be observed in the Raman spectrum were observed at 243 and 298 cm⁻¹, in agreement with the calculated values, 237 and 241 cm⁻¹. The bending mode at 243 cm⁻¹ is assigned to the out-of-phase combination of the umbrella motions of the two WF₄ groups, whereas the band at 298 cm⁻¹ is attributed to a S–W–F bending mode.

NMR Spectroscopy.

The tetramethylammonium salts of WSF₅⁻ and W₂S₂F₉⁻ were studied in CH₃CN solvent by ¹⁹F NMR spectroscopy. In a sample of [N(CH₃)₄][W₂S₂F₉] in CH₃CN, the W₂OSF₉⁻ anion was observed for the first time by ¹⁹F NMR spectroscopy. The ¹⁹F NMR parameters for these anions are given in Table 3.

As expected, the equatorial and axial fluorine environments in the WSF₅⁻ anion give rise to a doublet and a quintet with ¹⁸³W satellites at 77.2 and –111.4 ppm, respectively. These chemical shift values differ from some of the previously reported values for the axial⁵ and equatorial^{3,4} fluorine environments observed in the same, except deuterated, solvent. The absolute value of the ¹J(¹⁹F_{eq}–¹⁸³W) coupling constant is found to be significantly smaller than |¹J(¹⁹F_{ax}–¹⁸³W)|, although the W–F_{eq} bond is stronger, less ionic than the W–F_{ax} bond. This counter intuitive finding can be explained by assuming that the two *J*-values have different signs based on the previous determination of opposite signs of axial and equatorial ¹J(¹⁹F–¹⁸³W) coupling constants for the related WOF₅⁻ anion by homonuclear ¹⁹F tickling experiments.¹¹ The opposite signs of the axial and equatorial *J* values in WOF₅⁻ and WSF₅⁻ can only be the result of dramatically different contributions of at least two different scalar coupling mechanisms of opposite sign. As a

consequence, a simple correlation between the bond length and the absolute values of the J coupling constants can not be made.

The present ^{19}F NMR data for the $\text{W}_2\text{S}_2\text{F}_9^-$ anion in CH_3CN solvent (doublet: $\delta(^{19}\text{F}_{\text{term}}) = 85.6$ ppm; nonet: $\delta(^{19}\text{F}_{\text{br}}) = -156.5$ ppm) (Figure 3) are in excellent agreement with those reported in the literature.^{3,4} In addition, the present NMR study could resolve the $^1J(^{19}\text{F}-^{183}\text{W})$ coupling constants for the first time for the terminal (31.3 Hz) and bridging (83.9 Hz) fluorine environments. The larger $|^1J(^{19}\text{F}-^{183}\text{W})|$ coupling constant for the weaker, more ionic $\text{W}---\text{F}_{\text{br}}$ bond compared to that of the terminal $\text{W}-\text{F}$ bond is unexpected, but can also be explained by assuming different contributions of at least two different J -coupling mechanisms of opposite sign, resulting in opposite signs of the terminal and bridging J -coupling values. As for the axial and equatorial fluorine environments in WOF_5^- anion, the $^1J(^{19}\text{F}_{\text{term}}-^{183}\text{W})$ and $^1J(^{19}\text{F}_{\text{br}}-^{183}\text{W})$ values for the $\text{W}_2\text{O}_2\text{F}_9^-$ anions have been shown to have opposite signs by homonuclear ^{19}F tickling experiments..¹¹

In the ^{19}F NMR spectra of $[\text{N}(\text{CH}_3)_4][\text{W}_2\text{S}_2\text{F}_9]$, additional signals were observed that could not be attributed to known compounds. The new signals, i.e., two doublets and a quintet of quintets, can be assigned to the novel W_2OSF_9^- anion (Figure 3), which had formed as a result of accidental hydrolysis and which was subsequently generated in admixture with sulfide fluoride and oxide fluoride species (vide supra) by deliberate synthetic routes. The doublet at 86.0 ppm can be assigned to the terminal fluorine environments of the WSF_4 moiety, since its chemical shift is only slightly higher than that of the terminal fluorines in $\text{W}_2\text{S}_2\text{F}_9^-$. The lower frequency doublet at 60.8 ppm arises from the terminal fluorine environments of the WOF_4 moiety, which is similar to the chemical shift of the terminal fluorine environment of $\text{W}_2\text{O}_2\text{F}_9^-$ (61.8 ppm). The bridging fluorine appears, as expected, at low frequency between those of the $\text{W}_2\text{O}_2\text{F}_9^-$ and $\text{W}_2\text{S}_2\text{F}_9^-$ anions. The coupling of the bridging fluorine to the two non-equivalent terminal fluorine environments results in a quintet of quintets with two different $^2J(^{19}\text{F}-^{19}\text{F})$ coupling values that are in the characteristic ranges for tungsten(VI) oxide fluorides and sulfide fluorides. The anion is the first anion with

bridged oxide fluoride and sulfide fluoride moieties. Attempts to isolate a pure salt of this mixed oxide sulfide anion have been unsuccessful so far, because of equilibria operative between this dinuclear anion and the mononuclear species.

Crystal Structures of $[\text{N}(\text{CH}_3)_4][\text{WSF}_5] \cdot \text{CH}_3\text{CN}$ and $[\text{N}(\text{CH}_3)_4][\text{W}_2\text{S}_2\text{F}_9]$. Details of the data collection parameters and other crystallographic information for $[\text{N}(\text{CH}_3)_4][\text{WSF}_5] \cdot \text{CH}_3\text{CN}$ and $[\text{N}(\text{CH}_3)_4][\text{W}_2\text{S}_2\text{F}_9]$ are given in Table 4, while important bond lengths and bond angles are listed in Tables 5 and 6, respectively.

$[\text{N}(\text{CH}_3)_4][\text{WSF}_5] \cdot \text{CH}_3\text{CN}$. The $[\text{N}(\text{CH}_3)_4][\text{WSF}_5] \cdot \text{CH}_3\text{CN}$ salt crystallizes from a solution of $[\text{N}(\text{CH}_3)_4][\text{WSF}_5]$ in CH_3CN in the monoclinic space group $P2_1/c$ with one crystallographically independent formula unit in the unit cell. The crystal structure contains well separated $\text{N}(\text{CH}_3)_4^+$ cations, WSF_5^- anions, and CH_3CN solvent molecules. Interestingly, one CH_3CN solvent molecule cocrystallizes with the $[\text{N}(\text{CH}_3)_4][\text{WSF}_5]$ salt, as observed in the crystal structure of $[\{(\text{C}_6\text{H}_5)_3\text{P}\}_2\text{N}][\text{WSF}_5] \cdot \text{CH}_3\text{CN}$,⁵ although no significant interactions between CH_3CN and the anions or cations are found in both cases. The packing of $[\text{N}(\text{CH}_3)_4][\text{WSF}_5] \cdot \text{CH}_3\text{CN}$ is comprised of layers of $\text{N}(\text{CH}_3)_4^+$ cations in the *ac*-plane, separating layers of $\text{WSF}_5^-/\text{CH}_3\text{CN}$ (Figure S3).

The WSF_5^- anion (Figure 4) adopts a pseudo-octahedral geometry similar to that observed in $[\{(\text{C}_6\text{H}_5)_3\text{P}\}_2\text{N}][\text{WSF}_5] \cdot \text{CH}_3\text{CN}$. In the $\text{N}(\text{CH}_3)_4^+$ salt, the $\text{W}-\text{F}_{\text{eq}}$ bonds *cis* to the $\text{W}=\text{S}$ bond range from 1.870(5) to 1.884(4) Å and are significantly shorter than the $\text{W}-\text{F}_{\text{ax}}$ bond *trans* to $\text{W}=\text{S}$ (1.998(5) Å), as a consequence of the *trans*-influence of the $\text{W}=\text{S}$ bond. The $\text{W}=\text{S}$ bond length in $[\text{N}(\text{CH}_3)_4][\text{WSF}_5] \cdot \text{CH}_3\text{CN}$ (2.114(2) Å) is somewhat shorter than that observed for $[\{(\text{C}_6\text{H}_5)_3\text{P}\}_2\text{N}][\text{WSF}_5] \cdot \text{CH}_3\text{CN}$ (2.123(1) Å), and as a result, the $\text{W}-\text{F}_{\text{ax}}$ bond in the $\text{N}(\text{CH}_3)_4^+$ salt is elongated compared to that in the $\{(\text{C}_6\text{H}_5)_3\text{P}\}_2\text{N}^+$ salt. In both crystal structures, the $\text{S}-\text{W}-\text{F}_{\text{ax}}$ moiety is essentially linear and the $\text{S}-\text{W}-\text{F}_{\text{eq}}$ angles in both salts are comparable.

$[\text{N}(\text{CH}_3)_4][\text{W}_2\text{S}_2\text{F}_9]$. The $[\text{N}(\text{CH}_3)_4][\text{W}_2\text{S}_2\text{F}_9]$ salt crystallized from a solution of $[\text{N}(\text{CH}_3)_4][\text{WSF}_5]$

in aHF in the orthorhombic space group *Pnma*. The crystal structure contains well separated dinuclear fluorine-bridged $W_2S_2F_9^-$ anions and $N(CH_3)_4^+$ cations.

The W–S (2.0981(6) and 2.0955(7) Å) and terminal W–F bond lengths (1.8482(15) to 1.8649(11) Å) in the $W_2S_2F_9^-$ anion (Figure 5) are significantly shorter than those observed for the WSF_5^- anion, reflecting the lower charge density and the more covalent bonding in the dinuclear anion. This finding is corroborating the higher W=S and W–F stretching frequencies observed for the dinuclear anion compared to those of the mononuclear anion. The bridging fluorine is close to being symmetric with W–F_{br} distances of 2.1324(13) and 2.1246(13) Å. These distances are significantly longer than the W–F_{eq} bonds in the WSF_5^- anion. The W–F_{br}–W angle is bent (151.56(7)°). The two WF_4 moieties adopt a staggered conformation and the S–W–F_{br} angles deviate slightly from linearity. The W–F_{br}–W angle is expected to be somewhat flexible and dependent on the packing in the crystal lattice. Within experimental error, the W–F_{br}–W angle is slightly larger than that observed in the related $W_2O_2F_9^-$ anion in the crystal structure of $[H_3O][W_2O_2F_9]$ (144(2)°). Similarly to the $W_2S_2F_9^-$ anion, the two WOF_4 moieties are staggered with respect to each other. The calculated W–F_{br}–W angle of the gas-phase geometry is somewhat larger (159.3°) than the experimental value.

Computational Results.

The electronic structures of the WSF_5^- and $W_2S_2F_9^-$ anions in the gas phase were optimized at the B3LYP level and resulted in stationary points with all frequencies real, except for the staggered/bent and linear/eclipsed geometries of the $W_2S_2F_9^-$ anion which resulted in local minima with one negative frequency. The optimized geometries of the WSF_5^- and $W_2S_2F_9^-$ anions are depicted in Figures 4 and 5 and the calculated metric parameters are listed in Tables 5 and 6, respectively. The same level of theory has previously been employed for WSF_4 and its nitrogen-base adducts and produced excellent agreement with experimental findings.^{1,2} Attempts to optimize

the geometry of the novel $W_2SOF_9^-$ anion did not yield an energy minimum.

(a) Calculated Geometries.

The geometry optimization of WSF_5^- in the gas phase resulted in a C_{4v} geometry with the calculated $W=S$ and $W-F_{eq}$ bond lengths being somewhat longer than the experimental ones. The calculated $W-F_{ax}$ bond length (1.964 Å), on the other hand, is underestimated comparing to the experimental value (1.998(5) Å).

The three conformations of the $W_2S_2F_9^-$ anion that gave local minima have very similar energies, with the bent/staggered geometry (also the experimental geometry) being more stable than the linear/eclipsed and linear/staggered conformations by only 1.88 and 3.97 kJ mol⁻¹. These results confirm that the geometry of the anion will easily be affected by packing effects in the solid state. In the optimized bent/staggered geometry, all $W=S$ and $W-F$ bond lengths are somewhat larger compared to the experimental values, which is expected since ion-pairing is not taken into account in the calculated gas-phase geometry. Ion-pairing in the solid state will reduce the negative charge of the anion, resulting in less polar $W=S$ and $W-F$ bonds.

(b) Vibrational Frequencies.

The calculated vibrational frequencies for the WSF_5^- and $W_2S_2F_9^-$ anions are listed in Tables 1 and 2. The experimental and calculated vibrational frequencies for WSF_5^- are in good agreement. Overall the frequencies for the bent and linear staggered geometries of the $W_2S_2F_9^-$ anion are comparable, with those associated with the linear conformation coming at slightly lower frequency. As expected, the largest difference occurs for $\delta(W-F_{br}-W')$ which occur at 15 and 44 cm⁻¹ for the linear and bent configuration, respectively.

(c) Charges, Valencies, and Bond Orders. Natural bond order analyses were carried out at the B3LYP level of theory for the WSF_5^- , the bent $W_2S_2F_9^-$ and the linear $W_2S_2F_9^-$ anions. The natural population analysis (NPA) charges, the valencies, and bond orders are listed in Table 7. The axial fluorine in WSF_5^- , and more so, the bridging fluorine $W_2S_2F_9^-$ bear the largest negative charge,

reflecting the more ionic W–F_{ax} and W–F_{br} bonding compared to the bonding to the equatorial and terminal fluorine atoms. The W=S bond order in these anions is more than double than the W–F_{eq} and F_{term} bond orders, while the bonds to the axial and bridging fluorines are significantly weaker than those to the equatorial and terminal fluorines in WSF₅[–] and W₂S₂F₉[–], respectively.

Conclusions

The fluoride-ion acceptor properties of WSF₄ have been studied. While one aliquot of F[–] yields the WSF₅[–] anion, half an aliquot produces the dinuclear W₂S₂F₉[–] anion. Tetramethylammonium salts of these anions were isolated and characterized by Raman and infrared spectroscopy in the solid state and ¹⁹F NMR spectroscopy in solution. Metric parameters were obtained for both anions from crystals structures. The fluoride-ion addition to WSF₄ represents a new synthetic route to salts of these anions, and the W₂S₂F₉[–] anion was characterized in the solid state for the first time. The [N(CH₃)₄][SSi(CH₃)₃] reagent was prepared and its utility as a sulfide transfer agent was shown in the reaction with WF₆ providing an alternative route to [N(CH₃)₄][WSF₅]. Fluorine-19 NMR spectroscopic characterization of W₂SOF₉[–] in solution provided evidence for the first fluorine-bridged tungsten oxide fluoride and sulfide fluoride species.

Experimental

Materials and Apparatus. All volatile materials were handled on a Pyrex vacuum line equipped with glass/Teflon J. Young valves. Nonvolatile materials were handled in the dry nitrogen atmosphere of a dry box (Omni Lab, Vacuum Atmospheres).

Acetonitrile solvent (Baker, HPLC Grade) was purified according to the standard literature method.¹² The synthesis of WSF₄,¹ anhydrous [N(CH₃)₄]⁺F[–],⁸ and WOF₄¹³ have been described previously.

Elemental analyses were performed out using an Elementar Vario Microcube

instrument.

Preparation of $[\text{N}(\text{CH}_3)_4][\text{SSi}(\text{CH}_3)_3]$. Inside the dry box, 0.099 g (1.1 mmol) of anhydrous $[\text{N}(\text{CH}_3)_4]\text{F}$ was loaded into the sidearm of a two-armed glass vessel equipped with a J. Young stopcock. Excess $\text{S}(\text{Si}(\text{CH}_3)_3)_2$ (0.280 g, 1.57 mmol) was vacuum distilled into the straight arm of the glass vessel, followed by vacuum distillation of approximately 1 mL of CH_3CN into both arms. The solutions were combined at $-35\text{ }^\circ\text{C}$, instantaneously yielding a white precipitate. After agitation for ca. 15 min at $-30\text{ }^\circ\text{C}$, volatiles were removed under dynamic vacuum, first at low-temperature, following by pumping at ambient temperatures, yielding a finely divided white solid (collected yield: 0.153 g, 8.53 mmol). Decomposition at $191\text{ }^\circ\text{C}$. ^1H NMR (CH_3CN , unlocked, 300.13 MHz, δ [ppm]): 3.35 (s, $\text{N}(\text{CH}_3)_4^+$), 0.16 (s, $(\text{CH}_3)_3\text{SiS}^-$). $^{13}\text{C}\{^1\text{H}\}$ NMR (CH_3CN , unlocked, 100.61 MHz, δ [ppm]): 55.73 (t, $^1J(^{14}\text{N}-^{13}\text{C}) = 4.1\text{ Hz}$, $\text{N}(\text{CH}_3)_4^+$), 8.44 (s, $(\text{CH}_3)_3\text{SiS}^-$). Anal. Found: C, 46.69; H, 11.95; N, 8.12. Anal Calcd. For $\text{C}_7\text{H}_{21}\text{NSSi}$: C, 46.90; H, 11.82; N, 7.82.

Preparation of $[\text{N}(\text{CH}_3)_4][\text{WSF}_5]$. (a) Inside the dry box, 0.136 g (0.466 mmol) WSF_4 and 0.042 g (0.45 mmol) of $[\text{N}(\text{CH}_3)_4][\text{F}]$ were loaded into a $\frac{1}{4}$ -in. o.d. FEP reactor equipped with a Kel-F valve. After vacuum-distillation of 0.5 mL of CH_3CN onto the solid, agitation at $-35\text{ }^\circ\text{C}$ resulted in a yellow solution above dark brown solid. Removal of volatiles yielded 0.178 g of beige $[\text{N}(\text{CH}_3)_4][\text{WSF}_5]$. Decomposition at $133\text{ }^\circ\text{C}$. Anal. Found: C, 12.48; H, 2.84; N, 3.99. Anal Calcd. For $\text{C}_4\text{H}_{12}\text{F}_5\text{NSW}$: C, 11.48; H, 3.14; N, 3.64.

(b) Inside the dry box, 0.026 g (0.15 mmol) of $[\text{N}(\text{CH}_3)_4][\text{SSi}(\text{CH}_3)_3]$ and a small Teflon coated magnetic stir bar were added to a $\frac{3}{4}$ -in. o.d. FEP reactor equipped with a stainless steel valve. Subsequently, 6.219 g (86.23 mmol) of THF was vacuum distilled onto the solid at $-196\text{ }^\circ\text{C}$. The reaction mixture was then stirred at $20\text{ }^\circ\text{C}$ to achieve maximum dissolution of $[\text{N}(\text{CH}_3)_4][\text{SSi}(\text{CH}_3)_3]$, which formed a clear colorless solution. Some 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 $-196\text{ }^\circ\text{C}$ was followed by warming the mixture to $-78\text{ }^\circ\text{C}$ and stirring for ca. one hour as the solution went from yellow to pale pink. The solvent THF was removed under dynamic vacuum overnight at $-78\text{ }^\circ\text{C}$ and then for 30 minutes at room temperature into a FEP U-tube at $-196\text{ }^\circ\text{C}$ that was connected to the glass vacuum line. The reaction vessel was holding 0.060 g of a homogeneous pale pink colored powder. The amount of solid recovered corresponded to 0.15 mmol of $[\text{N}(\text{CH}_3)_4][\text{WSF}_5]$ indicating the presence of a small amount of $\text{C}_4\text{H}_8\text{O}$ in the final product. The ^1H NMR spectrum revealed a very small peak at 12.39 ppm and a broad feature at *ca.* 4.9 ppm which likely correspond to an aldehyde and an aliphatic chain resulting from the ring opening of THF.

Preparation of $[\text{N}(\text{CH}_3)_4][\text{W}_2\text{S}_2\text{F}_9]$. Inside the dry box, 0.087 g (0.30 mmol) of WSF_4 and 0.013 g (0.014 mmol) of $[\text{N}(\text{CH}_3)_4][\text{F}]$ were loaded into a 1/4-in. o.d. FEP tube equipped with a Kel-F valve. Approximately 0.75 mL CH_3CN was vacuum distilled on to the solid. The solvent was allowed to melt at $-37\text{ }^\circ\text{C}$, resulting in a deep brown suspension. Warming to ambient temperature and agitating the reaction mixture allowed for complete reaction. The solvent was removed under dynamic vacuum, yielding 0.096 g (0.14 mmol) of brown $[\text{N}(\text{CH}_3)_4][\text{W}_2\text{S}_2\text{F}_9]$. Decomposition at $184\text{ }^\circ\text{C}$ Anal. Found: C, 6.72; H, 1.40; N, 2.42. Anal Calcd. For $\text{C}_4\text{H}_{12}\text{F}_9\text{NS}_2\text{W}_2$: C, 7.10; H, 1.79; N, 2.07.

Vibrational Spectroscopy. The Raman spectra of $[\text{N}(\text{CH}_3)_4][\text{WSF}_5]$ and $[\text{N}(\text{CH}_3)_4][\text{W}_2\text{S}_2\text{F}_9]$ were recorded on a Bruker RFS 100 FT Raman spectrometer with a quartz beam splitter, a liquid-nitrogen-cooled Ge detector, and a low-temperature accessory. The backscattered (180°) radiation was sampled. The actual usable Stokes range was 50 to 3500 cm^{-1} with a spectral resolution of 2 cm^{-1} . The 1064-nm line of an Nd:YAG laser was used for excitation of the sample. The room-temperature and low-temperature ($-100\text{ }^\circ\text{C}$) Raman spectra of $[\text{N}(\text{CH}_3)_4][\text{WSF}_5]$ and $[\text{N}(\text{CH}_3)_4][\text{W}_2\text{S}_2\text{F}_9]$ were recorded on powdered samples in sealed melting point capillaries using a laser power of 200 and 150 mW, respectively. The FT-infrared spectrum

of $[\text{N}(\text{CH}_3)_4][\text{WSF}_5]$ was recorded on a Nicolet Avatar 360 FTIR spectrometer at ambient temperature as a KBr pellet. The FT-infrared spectrum of $[\text{N}(\text{CH}_3)_4][\text{W}_2\text{S}_2\text{F}_9]$ was recorded at ambient temperature on Bruker Tensor FTIR spectrometer as a KBr pellet. The KBr pellet was formed in a Wilks minipress inside the dry box by sandwiching the sample between two layers of KBr. The infrared spectra were acquired in 64 scans at a resolution of 2 cm^{-1} .

Nuclear Magnetic Resonance Spectroscopy. All NMR spectra were recorded unlocked on a 300 MHz Bruker Avance II NMR spectrometer equipped with a 5-mm broad-band probe. All NMR spectra were externally referenced to neat CFCl_3 (^{19}F) and neat $\text{Si}(\text{CH}_3)_4$ (^1H and ^{13}C) at 25°C . The ^{19}F NMR spectra were typically acquired in 128 K memory with spectral settings of 34 kHz, yielding an acquisition time of 1.9 s and a data point resolution of 0.26 Hz/data point. The number of transients accumulated was between 200 and 600 using a pulse width of $10.3\text{ }\mu\text{s}$. The ^1H / ^{13}C NMR spectra were typically acquired in 64/64 K memory with spectral settings of 6/18 kHz, yielding an acquisition times of 5.3/1.8 s and data point resolutions of 0.09/0.27 Hz/data point. The numbers of transients accumulated were 68/9200 using pulse widths of $12.4/7.6\text{ }\mu\text{s}$.

X-ray Crystal Structure Determination

(a) Crystal Growth. $[\text{N}(\text{CH}_3)_4][\text{WSF}_5]\cdot\text{CH}_3\text{CN}$. A solution of about 0.100 g of $[\text{N}(\text{CH}_3)_4][\text{WSF}_5]$ in 1.0 ml of CH_3CN inside a 9-mm o.d. FEP tube equipped with a stainless steel valve was cooled to -20°C . About 3/4 of the solvent was slowly removed under dynamic vacuum at this temperature over a period of approximately 3 hours and orange prismatic crystals were formed. Under an atmosphere of dry nitrogen, the remaining solution was decanted off and clear orange prismatic crystals of $[\text{N}(\text{CH}_3)_4][\text{WSF}_5]\cdot\text{CH}_3\text{CN}$ were isolated. $[\text{N}(\text{CH}_3)_4][\text{W}_2\text{S}_2\text{F}_9]$. A solution of about 0.050 g of $[\text{N}(\text{CH}_3)_4][\text{W}_2\text{S}_2\text{F}_9]$ in 0.5 ml of anhydrous HF inside a 9-mm o.d. FEP tube equipped with a stainless steel valve was cooled to 0°C . The solvent was slowly removed under dynamic vacuum at this temperature over a period of 6 hours and clear yellow prismatic crystals of $[\text{N}(\text{CH}_3)_4][\text{W}_2\text{S}_2\text{F}_9]$ were obtained.

(b) Crystal Mounting, Collection and Reduction of X-ray Data. Inside the dry box, several crystals were selected and dropped into a small dish containing some Krytox GPL107 oil. The dish was taken out of the dry box and the crystal trapped in a Nylon Cryoloop. The single crystal diffraction data were collected on a Bruker SMART 3-circle platform diffractometer,¹⁴ equipped with an APEX CCD detector with the χ -axis fixed at 54.74° , and using Mo K α radiation ($\lambda = 0.71073 \text{ \AA}$) from a fine-focus tube. This diffractometer was equipped with a CRYO Industries LT-3 low-temperature apparatus using controlled nitrogen boil off. Cell constants were determined from 90 10-s frames at -155°C ($[\text{N}(\text{CH}_3)_4][\text{WSF}_5]\cdot\text{CH}_3\text{CN}$) and -130°C $[\text{N}(\text{CH}_3)_4][\text{W}_2\text{S}_2\text{F}_9]$. A complete hemisphere of data was collected, using 1271 frames at 10s/frame at a detector resolution of 512×512 pixels, including 50 frames that were collected at the beginning and end of the data collection to determine crystal decay. The frames were processed on a PC running Windows XP software by using the SAINT software.¹⁵ The absorption correction was applied using the SADABS program.¹⁶

(c) Solution and Refinement of Structures. The structures were solved by the Patterson method, using the SHELXS program, and refined by the least-squares method on F^2 with SHELXL incorporated in SHELXTL V2011.4-0.¹⁷ All atoms were refined anisotropically.

Crystallographic data have been deposited with the Cambridge Crystallographic Data Center, CCDC Nos 855350 and 855351. Copies of the data can be obtained free of charge from CCDC via <http://www.ccdc.cam.ac.uk>.

Computational Methods. The optimized geometries and frequencies of WSF_5^- and $\text{W}_2\text{S}_2\text{F}_9^-$ were calculated at the density functional theory (DFT) level by use of the B3LYP¹⁸ method. The Stuttgart basis set augmented by one f-type polarization function ($\alpha_f \text{W } 0.823$)¹⁹ for tungsten and aug-cc-pVTZ basis sets for fluorine, nitrogen, carbon and hydrogen was used. Pseudo-potentials were used for tungsten. Quantum-chemical calculations were carried out using the programs Gaussian 03.¹⁸ The geometries were fully optimized using analytical

gradient methods. The vibrational frequencies were calculated at the B3LYP level using the appropriate minimized structure, and the vibrational mode descriptions were assigned with the aid of Gaussview.²⁰

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Supporting Information Available: Table with vibrational spectroscopy data of $[\text{N}(\text{CH}_3)_4][\text{SSi}(\text{CH}_3)_3]$ (Table S1); Raman and infrared spectra of $[\text{N}(\text{CH}_3)_4][\text{SSi}(\text{CH}_3)_3]$ (Figure S1); thermal ellipsoid plot of the asymmetric unit of $[\text{N}(\text{CH}_3)_4][\text{WSF}_5] \cdot \text{CH}_3\text{CN}$ (Figure S2); and view of packing of $[\text{N}(\text{CH}_3)_4][\text{WSF}_5] \cdot \text{CH}_3\text{CN}$ (Figure S3).

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Figure Captions

- Figure 1.** Vibrational spectra of $[\text{N}(\text{CH}_3)_4][\text{WSF}_5]$: infrared spectrum (upper trace) recorded at room temperature as a KBr pellet and Raman spectrum (lower trace) recorded at $-100\text{ }^\circ\text{C}$ using 1064-nm excitation. Asterisks (*) and dagger (†) denote $\text{N}(\text{CH}_3)_4^+$ cation bands and bands arising from an $\text{W}_2\text{S}_2\text{F}_9^-$ impurity, respectively.
- Figure 2.** Vibrational spectra of $[\text{N}(\text{CH}_3)_4][\text{W}_2\text{S}_2\text{F}_9]$: infrared spectrum (upper trace) recorded at room temperature as a KBr pellet and Raman spectrum recorded at $-100\text{ }^\circ\text{C}$ using 1064-nm excitation. Asterisks (*) denote $\text{N}(\text{CH}_3)_4^+$ cation bands.
- Figure 3.** Fluorine-19 NMR spectrum of $[\text{N}(\text{CH}_3)_4][\text{W}_2\text{S}_2\text{F}_9]$ in CH_3CN solvent at ambient temperature, including the $[\text{N}(\text{CH}_3)_4][\text{W}_2\text{OSF}_9]$ impurity. (a) terminal fluorine environments of $\text{W}_2\text{S}_2\text{F}_9^-$ and the WSF_4 moiety of W_2OSF_9^- , (b) terminal fluorine environment of WOF_4 moiety of W_2OSF_9^- , (c) bridging fluorine environment of W_2OSF_9^- , $^2J(^{19}\text{F}_\text{t}-^{19}\text{F}_\text{br})$ couplings are indicated, and (d) bridging fluorine environment of $\text{W}_2\text{S}_2\text{F}_9^-$.
- Figure 4.** View of the WSF_5^- anion; (a) thermal ellipsoid plot of the WSF_5^- anion in the crystal structure of $[\text{N}(\text{CH}_3)_4][\text{WSF}_5]\cdot\text{CH}_3\text{CN}$; thermal ellipsoids are drawn at the 50% probability level; and (b) optimized geometry of WSF_5^- in the gas phase.
- Figure 5.** View of the $\text{W}_2\text{S}_2\text{F}_9^-$ anion; (a) thermal ellipsoid plot of the $\text{W}_2\text{S}_2\text{F}_9^-$ anion in the crystal structure of $[\text{N}(\text{CH}_3)_4][\text{W}_2\text{S}_2\text{F}_9]$; thermal ellipsoids are drawn at the 50% probability level; and (b) optimized geometry of $\text{W}_2\text{S}_2\text{F}_9^-$ in the gas phase.

Table 1. Observed and Calculated Vibrational Frequencies for WSF_5^- and Their Assignments in the C_{4v} Point Group.

| frequencies, cm^{-1} | | | |
|--|-----------------------|-----------------------|--|
| WSF_5^- | | | |
| Raman ^b | expt ^{a,b} | | calcd ^c |
| | infrared ^c | infrared ^d | |
| 664(28) | 662 m 598 vs | 662 s 607 vs,b | B3LYP 653(14)[92] 608(<1)[264] |
| 527sh | 532 vs | 526 s | 572(4)[0] 513(2)[215] |
| 520(100) | | | 498(44)[75] |
| 292(38) | 490m | 472 s,br | 292(3)[8] 281(<1)[19] 281(2)[0] 217(<1)[22] 201(<1)[0] 117(1)[<1] |
| 220(13) | | | |
| 131(19) | | | |
| 97sh | | | |
| 71(32) | | | |
| 59(44) | | | |
| lattice modes | | | |
| assignment (C_{4v}) | | | |
| $\nu_1(A_1), \nu_s(\text{WF}_5)$ | | | |
| $\nu_8(E), \nu_{as}(\text{WF}_{4,\text{eq}})$ | | | |
| $\nu_5(B_1), \nu_{as}(\text{WF}_{4,\text{eq}})$ | | | |
| $\nu_2(A_1), \nu(\text{WF}_{5,\text{ax}})$ | | | |
| $\nu_3(A_1), \nu(\text{WS})$ | | | |
| combination mode | | | |
| $\nu_9(E), \delta(\text{WF1F4F5}) + \delta(\text{WF2F3S})$ | | | |
| $\nu_4(A_1), \delta_{\text{umbrella}}(\text{WF}_{4,\text{eq}})$ | | | |
| $\nu_6(B_2), \delta_{\text{scissoring}}(\text{WF}_{4,\text{eq}})$ | | | |
| $\nu_{10}(E), \delta(\text{F2WF1}) - \delta(\text{F4WF3}) + \delta(\text{SWF5})$ | | | |
| $\nu_7(B_1), \delta_{\text{out-of-plane}}(\text{WF}_{4,\text{eq}})$ | | | |
| $\nu_{11}(E), \delta(\text{F2WF1}) - \delta(\text{F4WF3}) + \rho(\text{SWF5})$ | | | |

^a Abbreviations denote shoulder (sh), very strong (vs), strong (s), medium (m), and broad (br). ^b Relative intensities are given in parentheses. The $\text{N}(\text{CH}_3)_4^+$ cation modes were observed in the Raman spectrum at 458(8), $\nu_{19}(\text{T}_2)$; 740sh, 753(31), $\nu_3(A_1)$; 948(22), 983(4), $\nu_{18}(\text{T}_2)$; 1420(8), $\nu_{16}(\text{T}_2)$; 1461 (24), $\nu_2(A_1)$, $\nu_6(E)$; 2820(12), 2927(24), 2960(28), 2986(40), 3040(36) cm^{-1} , $\nu(\text{CH}_3)$ and binary bands; bands for an impurity of the $\text{W}_2\text{S}_2\text{F}_9^-$ anion were observed at 679(8), 556(22), and 241(14) cm^{-1} , a laser line was observed at 84 cm^{-1} . ^c The $\text{N}(\text{CH}_3)_4^+$ cation modes were observed in the infrared spectrum at 457w, $\nu_{19}(\text{T}_2)$; 949vs, 957vs, $\nu_{18}(\text{T}_2)$; 1252 w, $\nu_{17}(\text{T}_2)$; 1488vs, 1497vs, $\nu_{15}(\text{T}_2)$; 2921w, 2962w, 3034s cm^{-1} , ν_{CH_3} and binary bands. ^d Values are from reference 5. ^e Unscaled Raman intensities, in $\text{\AA}^4 \text{u}^{-1}$ are given in parentheses, infrared intensities in km mol^{-1} are given in square brackets.

Table 2. Observed and Calculated Vibrational Frequencies for $W_2S_2F_6^-$ and Their Assignments

| exptl ^a | | calcd ^b | | assgnt (C_1) |
|--------------------|-----------------------|--------------------|-----------------|--|
| Raman ^c | Infrared ^c | bent | linear | |
| | 688 s | 688(<1)[172] | 679(<0.1)[184] | $\nu(WF_{1-4}) - \nu(W'F_{1-4})$ |
| 678(13) | | 686(31)[<1] | 676(32)[<0.1] | $\nu(WF_{1-4}) + \nu(W'F_{1-4})$ |
| 672(13) | 625 vs | 664(<1)[407] | 650(<0.1)[425] | $[\nu(WF_1) - \nu(WF_3)] + [\nu(W'F_1') - \nu(W'F_3')]$ |
| | | 659(<0.1)[400] | 650(<0.1)[425] | $[\nu(WF_2) - \nu(WF_4)] + [\nu(W'F_2') - \nu(W'F_4')]$ |
| | | 646(<1)[44] | 634(<1)[<0.1] | $[\nu(WF_1) - \nu(WF_3)] + [\nu(W'F_3') - \nu(W'F_1')]$ |
| | | 641(<1)[5] | 634(<1)[<0.1] | $[\nu(WF_2) - \nu(WF_4)] + [\nu(W'F_4') - \nu(W'F_2')]$ |
| | | 609(3)[<1] | 601(3)[<0.1] | $([\nu(WF_1) + \nu(WF_3)] - [\nu(WF_2) + \nu(WF_4)]) +$ $([\nu(W'F_2') + \nu(W'F_4')] - [\nu(W'F_1') + \nu(W'F_3')])_{small}$ |
| | | 609(3)[1] | 600(3)[<0.1] | $([\nu(WF_1) + \nu(WF_3)] - [\nu(WF_2) + \nu(WF_4)])_{small} +$ $([\nu(W'F_2') + \nu(W'F_4')] - [\nu(W'F_1') + \nu(W'F_3')])$ |
| 560(100) | 578 m | 541(120)[6] | 539(124)[<0.1] | $\nu(WS) + \nu(W'S')$ |
| 556 sh | 553 m | 535(2)[174] | 533(<0.1)[167] | $[\nu(WS) - \nu(W'S')] + [\nu(WF_{br}) - \nu(W'F_{br})]_{small}$ |
| | 434 s | 403(1)[457] | 410(<0.1)[503] | $\nu(WF_{br}) - \nu(W'F_{br})$ |
| | | 306(<1)[7] | 297(2)[<0.1] | $[\delta(F_1WF_4) + \delta(F_2WF_3)] + [\delta(F_1'W'F_4') + \delta(F_2'W'F_3')]$ |
| | | 301(1)[<1] | 296(1)[<0.1] | $[\delta(F_1WF_4) + \delta(F_2WF_3)] - [\delta(F_1'W'F_4') + \delta(F_2'W'F_3')]$ |
| | | 301(1)[<0.1] | 294(<0.1)[6] | $[\rho_w(F_1WF_2) - \rho_w(F_3WF_4)] + [\delta(F_1'W'F_{br}) - \delta(F_3'W'F_{br})]$ |
| | | 292(<0.1)[6] | 294(<0.1)[6] | $[\rho_w(F_2WF_3) - \rho_w(F_1WF_4)] + [\delta(F_2'W'F_{br}) - \delta(F_4'W'F_{br})]$ |
| | | 277(<1)[<1] | 274(1)[<0.1] | $\delta(WF_{1-4})_{umb} + \delta(W'F_{1-4}')_{umb}$ |
| 298(10) | | 241(5)[48] | 237(8)[<0.1] | $\delta(SWF_3) - \delta(S'W'F_3')$ |
| | | 238(1)[182] | 234(<0.1)[245] | $[\delta(SWF_2) - \delta(SWF_4)] + [\delta(S'W'F_4') - \delta(S'W'F_2')]$ |
| 243(40) | | 237(8)[<1] | 237(8)[<0.1] | $\delta(WF_{1-4})_{umb} - \delta(W'F_{1-4}')_{umb}$ |
| | | 229(<1)[22] | 224(<0.1)[24] | $[\delta(WSF_1F_2) - \delta(F_3WF_4)] + [\delta(W'S'F_3'F_4') - \delta(F_1'W'F_2')]$ |
| | | 227(<0.1)[28] | 224(<0.1)[24] | $\delta(WSF_2F_4) - \delta(W'S'F_2'F_4')$ |
| | | 217(<1)[<0.1] | 211(<0.1)[<0.1] | $\rho_w(F_1WF_3) - \rho_w(F_1'W'F_3')$ |
| | | 215(<0.1)[<1] | 211(<0.1)[<0.1] | $\rho_w(F_2WF_4) - \rho_w(F_2'W'F_4')$ |
| | | 189(<1)[<0.1] | 187(<1)[<0.1] | $\rho_w(F_1WF_3) - \rho_w(F_2W'F_4')$ |
| | | 189(<1)[3] | 187(<1)[<0.1] | $\rho_w(F_1'W'F_3') - \rho_w(F_2'W'F_4')$ |
| | | 173(<1)[1] | 156(1)[<0.1] | $[\delta(SWF_{br}) - \delta(F_2WF_4)] + [\delta(F_{br}W'S') - \delta(F_2'W'F_4')]$ |
| | | 157(<1)[<1] | 156(1)[<0.1] | $[\delta(SWF_{br}) - \delta(F_1WF_3)] + [\delta(F_{br}W'S') - \delta(F_1'W'F_3')]$ |
| | | 95(<1)[<0.1] | 96(<1)[<0.1] | $\rho_w(SWF_{1-4}) + \rho_w(S'W'F_{1-4}')$ |
| | | 89(5)[<1] | 85(5)[0] | $\rho_r(SWF_1F_3) + \rho_r(S'W'F_1'F_3')$ |
| | | 86(5)[<0.1] | 85(5)[0] | $\rho_r(SWF_2F_4) + \rho_r(S'W'F_2'F_4')$ |
| | | 47(<1)[<1] | 16(0)[<1] | $\rho_r(WF_{1-4}) - \rho_r(W'F_{1-4}')$ |
| | | 44(<0.1)[<0.1] | 15(0)[<1] | $\delta(WF_{br}W')$ |
| | | -21(<0.1)[<1] | 11(0)[<0.1] | $\rho_t(WSF_2F_4) - \rho_t(W'S'F_2'F_4')$ |

^a Abbreviations denote shoulder (sh), very strong (vs), strong (s), medium (m), weak (w), and very weak (vw). ^b B3LYP level of theory. Infrared intensities, in km mol^{-1} , are given in parentheses, Raman intensities, in $\text{\AA}^4 \text{u}^{-1}$, are given in square brackets. ^c The $N(\text{CH}_3)_4^+$ cation modes were observed in the Raman spectrum (-100°C) at 457(4), $\nu_{19}(\text{T}_2)$; 751(11), $\nu_3(\text{A}_1)$; 947, $\nu_{18}(\text{T}_2)$; 1454(13), $\nu_2(\text{A}_1)$; 2924(9), 2990(18), 3043(12) cm^{-1} , ν_{CH_3} and binary bands. ^c The $N(\text{CH}_3)_4^+$ cation modes were observed in the infrared spectrum at 949s, 988w, $\nu_{18}(\text{T}_2)$; 1265 w, $\nu_{17}(\text{T}_2)$; 1420 w, $\nu_{16}(\text{T}_2)$; 1486vs, $\nu_{15}(\text{T}_2)$; 2929w, 2971w, 3052w cm^{-1} , ν_{CH_3} and binary bands. An impurity of WOF_5^- was observed at 1022 cm^{-1} (small), $\nu(\text{WO})$.

Table 3. Fluorine-19 NMR Spectroscopic Data for the $\text{N}(\text{CH}_3)_4^+$ Salts of WSF_5^- , $\text{W}_2\text{S}_2\text{F}_9^-$, W_2OSF_9^- in CH_3CN solvent at room temperature.

| | $\delta(^{19}\text{F})$, ppm ^a | $^1J(^{183}\text{W}-^{19}\text{F})$, Hz | $^2J(^{19}\text{F}-^{19}\text{F})$, Hz |
|---|--|--|---|
| WSF_5^- | 77.2 (d) (F_{eq}) | 28.3 | 75.5 |
| | −111.4 (qn) (F_{ax}) | 68.6 | |
| $\text{W}_2\text{S}_2\text{F}_9^-$ ^b | 85.6 (d) (F_{term}) | 31.3 | 70.0 |
| | −156.5 (n) (F_{br}) | 83.9 | |
| W_2OSF_9^- ^b | 86.0 (d) ($\text{F}_{\text{term, W=S}}$) | 16-19 ^c | 70 |
| | 60.8 (d) ($\text{F}_{\text{term, W=O}}$) | 71.0 | 56.7 |
| | −148.1 (qn/qn) (F_{br}) | not obs. | |

^a Abbreviations denote doublet (d), quintet (qn), nonet (n), and quintet of quintets (qn/qn). ^b Signals were observed for $\text{WSF}_4 \cdot \text{CH}_3\text{CN}$ (singlet at 85.4 ppm, satellites: $^1J(^{183}\text{W}-^{19}\text{F})$ 33.4 Hz), WOF_5^- (doublet at 48.4 ppm, $^2J(^{19}\text{F}-^{19}\text{F}) = 51.9$ Hz, quintet at −83.5 ppm), and WSF_5^- . ^c Uncertainty arises from overlap with ^{19}F resonance for $\text{W}_2\text{S}_2\text{F}_9^-$.

Table 4. Crystallographic Data for $[\text{N}(\text{CH}_3)_4][\text{WSF}_5] \cdot \text{CH}_3\text{CN}$ and $[\text{N}(\text{CH}_3)_4][\text{W}_2\text{S}_2\text{F}_9]$

| chem formula | $\text{C}_6\text{H}_{15}\text{F}_5\text{N}_2\text{SW}$ | $\text{C}_4\text{H}_{12}\text{F}_9\text{NS}_2\text{W}_2$ |
|--------------------------------------|--|--|
| space group | $P2_1/c$ | $Pnma$ |
| a (Å) | 7.7095(11) | 13.122(2) |
| b (Å) | 19.815(3) | 7.8937(12) |
| c (Å) | 8.1597(12) | 14.072(2) |
| β (°) | 90.562(2) | 90 |
| molecules/unit cell | 4 | 4 |
| mol wt (g mol^{-1}) | 426.11 | 676.97 |
| calcd density (g cm^{-3}) | 2.271 | 3.085 |
| T (°C) | −155 | −130 |
| μ (mm^{-1}) | 9.469 | 16.136 |
| R_1^a | 0.0415 | 0.0244 |
| wR_2^b | 0.1089 | 0.0581 |

^a R_1 is defined as $\Sigma||F_o| - |F_c||/\Sigma|F_o|$ for $I > 2\sigma(I)$. ^b wR_2 is defined as $[\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma w(F_o^2)^2]^{1/2}$ for $I > 2\sigma(I)$.

Table 5. Experimental and Calculated Metric Parameters for the WSF_5^- Anion

| | exptl | calcd |
|--------------------|------------|-------|
| Bond lengths (Å) | | |
| W–S | 2.114(2) | 2.184 |
| W–F(1) | 1.871(5) | 1.894 |
| W–F(2) | 1.870(5) | 1.894 |
| W–F(3) | 1.884(4) | 1.894 |
| W–F(4) | 1.880(4) | 1.894 |
| W–F(5) | 1.998(5) | 1.964 |
| Bond angles (deg.) | | |
| S–W–F(1) | 97.70(16) | 96.2 |
| S–W–F(2) | 96.82(15) | 96.2 |
| S–W–F(3) | 96.80(17) | 96.2 |
| S–W–F(4) | 97.32(17) | 96.2 |
| S–W–F(5) | 179.72(14) | 180.0 |
| F(1)–W–F(2) | 89.4(3) | 89.3 |
| F(1)–W–F(3) | 165.5(2) | 167.6 |
| F(1)–W–F(4) | 89.7(2) | 89.3 |
| F(1)–W–F(5) | 82.50(19) | 83.8 |
| F(2)–W–F(3) | 89.5(2) | 89.3 |
| F(2)–W–F(4) | 165.8(2) | 167.6 |
| F(2)–W–F(5) | 82.99(19) | 83.8 |
| F(3)–W(2)–F(4) | 88.0(2) | 89.3 |
| F(3)–W(2)–F(5) | 83.0(2) | 83.8 |
| F(4)–W(2)–F(5) | 82.9(2) | 83.8 |

Table 6. Experimental and Calculated Metric Parameters for the Staggered $W_2S_2F_9^-$ Anion

| exptl | | calcd | |
|-------------------|------------|--------------------------------------|-------|
| Bond lengths (Å) | | | |
| W(2)–S(2) | 2.0981(6) | W–S | 2.146 |
| W(2)–F(6) | 1.8525(14) | W–F ₃ | 1.874 |
| W(2)–F(7A) | 1.8568(13) | W–F ₄ | 1.875 |
| W(2)–F(8) | 1.8482(15) | W–F ₁ | 1.876 |
| W(2)–F(7) | 1.8569(13) | W–F ₂ | 1.877 |
| W(2)–F(5) | 2.1324(13) | W–F _b | 2.157 |
| W(1)–S(1) | 2.0955(7) | W'–S' | 2.146 |
| W(1)–F(1A) | 1.8649(11) | W'–F ₂ ' | 1.874 |
| W(1)–F(1) | 1.8649(11) | W'–F ₃ ' | 1.874 |
| W(1)–F(3A) | 1.8589(10) | W'–F ₄ ' | 1.877 |
| W(1)–F(3) | 1.8589(10) | W'–F ₁ ' | 1.877 |
| W(1)–F(5) | 2.1246(13) | W'–F _b | 2.157 |
| Bond angle (deg.) | | | |
| S(2)–W(2)–F(6) | 100.22(5) | S–W–F ₃ | 99.0 |
| S(2)–W(2)–F(7A) | 99.65(4) | S–W–F ₄ | 98.8 |
| S(2)–W(2)–F(8) | 98.74(6) | S–W–F ₁ | 99.0 |
| S(2)–W(2)–F(7) | 99.65(4) | S–W–F ₂ | 98.8 |
| S(2)–W(2)–F(5) | 177.36(4) | S–W–F _b | 179.6 |
| F(6)–W(2)–F(7A) | 87.06(4) | F ₃ –W–F ₄ | 88.9 |
| F(6)–W(2)–F(8) | 161.05(7) | F ₃ –W–F ₁ | 162.0 |
| F(6)–W(2)–F(7) | 87.06(4) | F ₃ –W–F ₂ | 88.4 |
| F(6)–W(2)–F(5) | 82.42(6) | F ₃ –W–F _b | 81.1 |
| F(7A)–W(2)–F(6) | 87.06(4) | F ₄ –W–F ₁ | 88.7 |
| F(7A)–W(2)–F(7) | 160.54(8) | F ₄ –W–F ₂ | 162.3 |
| F(7A)–W(2)–F(5) | 80.42(4) | F ₄ –W–F _b | 80.7 |
| F(8)–W(2)–F(7A) | 89.78(4) | F ₁ –W–F ₂ | 88.4 |
| F(8)–W(2)–F(5) | 78.63(6) | F ₁ –W–F _b | 80.9 |
| F(7)–W(2)–F(5) | 80.42(4) | F ₂ –W–F _b | 81.6 |
| S(1)–W(1)–F(5) | 177.99(4) | S'–W'–F _b | 179.6 |
| S(1)–W(1)–F(1) | 99.18(4) | S'–W'–F ₃ ' | 99.0 |
| S(1)–W(1)–F(3A) | 98.56(3) | S'–W'–F ₄ ' | 98.8 |
| S(1)–W(1)–F(3) | 98.56(3) | S'–W'–F ₁ ' | 99.0 |
| S(1)–W(1)–F(1A) | 99.18(4) | S'–W'–F ₂ ' | 98.9 |
| F(1)–W(1)–F(5) | 82.26(4) | F ₃ '–W'–F _b | 81.1 |
| F(1)–W(1)–F(3A) | 88.79(5) | F ₃ '–W'–F ₄ ' | 88.4 |
| F(1)–W(1)–F(3) | 162.22(5) | F ₃ '–W'–F ₁ ' | 162.0 |
| F(1A)–W(1)–F(1) | 87.18(7) | F ₂ '–W'–F ₃ ' | 88.9 |
| F(3A)–W(1)–F(5) | 80.04(4) | F ₄ '–W'–F _b | 81.6 |
| F(3A)–W(1)–F(3) | 89.79(5) | F ₄ '–W'–F ₁ ' | 88.4 |
| F(1A)–W(1)–F(3A) | 162.22(5) | F ₂ '–W'–F ₄ ' | 162.3 |
| F(3)–W(1)–F(5) | 80.04(4) | F ₁ '–W'–F _b | 80.9 |
| F(1A)–W(1)–F(3) | 88.79(5) | F ₂ '–W'–F ₁ ' | 88.7 |
| F(1A)–W(1)–F(5) | 82.26(4) | F ₂ '–W'–F _b | 80.7 |
| W(1)–F(5)–W(2) | 151.56(7) | W–F _b –W' | 159.3 |

Table 7. Natural Bond Order (NBO) Valencies, Bond Orders and Natural Population Analysis (NPA) Charges for WSF_5^- and $\text{W}_2\text{S}_2\text{F}_9^-$ (Bent and Linear Geometries)

| | WSF_5^- | | $\text{W}_2\text{S}_2\text{F}_9^-$ (bent) | | $\text{W}_2\text{S}_2\text{F}_9^-$ (linear) | |
|------------------|------------------|----------|---|----------|---|----------|
| | charges | valences | charges | valences | charges | valences |
| W | 2.129 | 3.717 | 2.099 | 3.617 | 2.100 | 3.617 |
| S | -0.372 | 1.112 | -0.237 | 1.182 | -0.236 | 1.180 |
| F ₁ | -0.535 | 0.544 | -0.510 | 0.563 | -0.508 | 0.565 |
| F ₂ | -0.535 | 0.544 | -0.510 | 0.562 | -0.508 | 0.565 |
| F ₃ | -0.535 | 0.544 | -0.504 | 0.570 | -0.508 | 0.564 |
| F ₄ | -0.535 | 0.544 | -0.506 | 0.567 | -0.508 | 0.564 |
| F ₅ | -0.617 | 0.432 | -0.664 | 0.481 | -0.665 | 0.483 |
| bond orders | | | | | | |
| W-S | 1.129 | | 1.183 | | 1.181 | |
| W-F ₁ | 0.539 | | 0.551 | | 0.552 | |
| W-F ₂ | 0.539 | | 0.550 | | 0.552 | |
| W-F ₃ | 0.539 | | 0.554 | | 0.552 | |
| W-F ₄ | 0.539 | | 0.553 | | 0.552 | |
| W-F ₅ | 0.431 | | 0.230 | | 0.231 | |

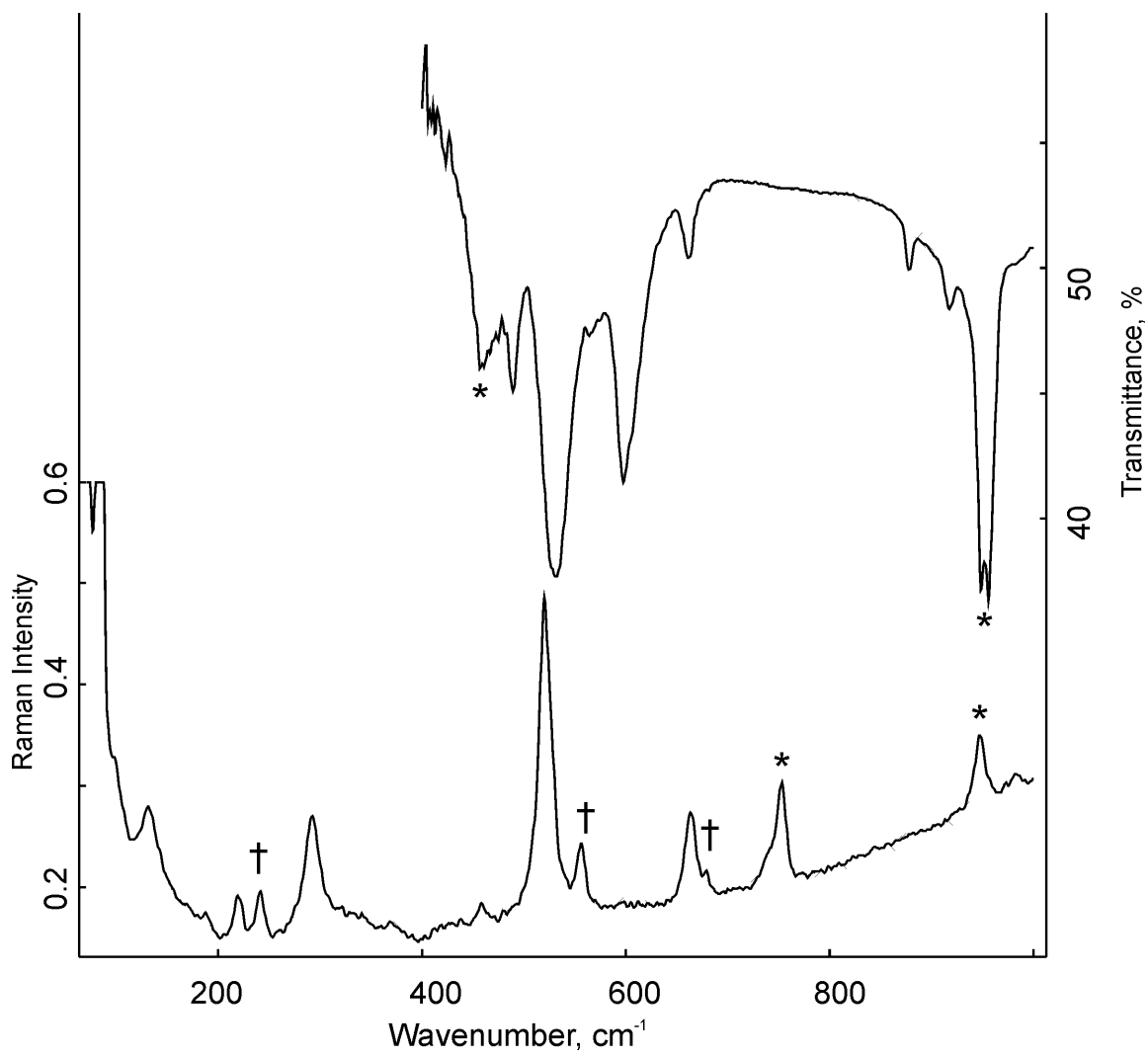


Figure 1

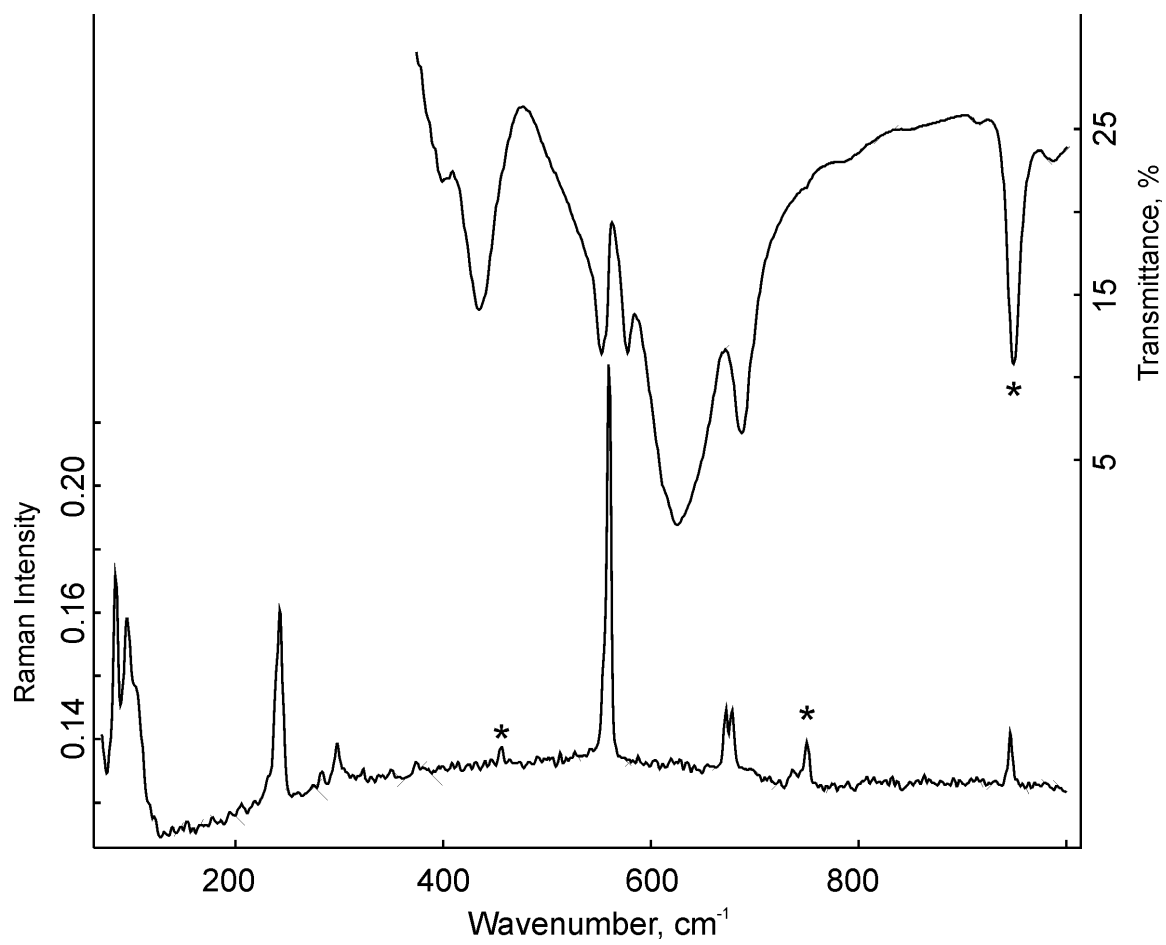
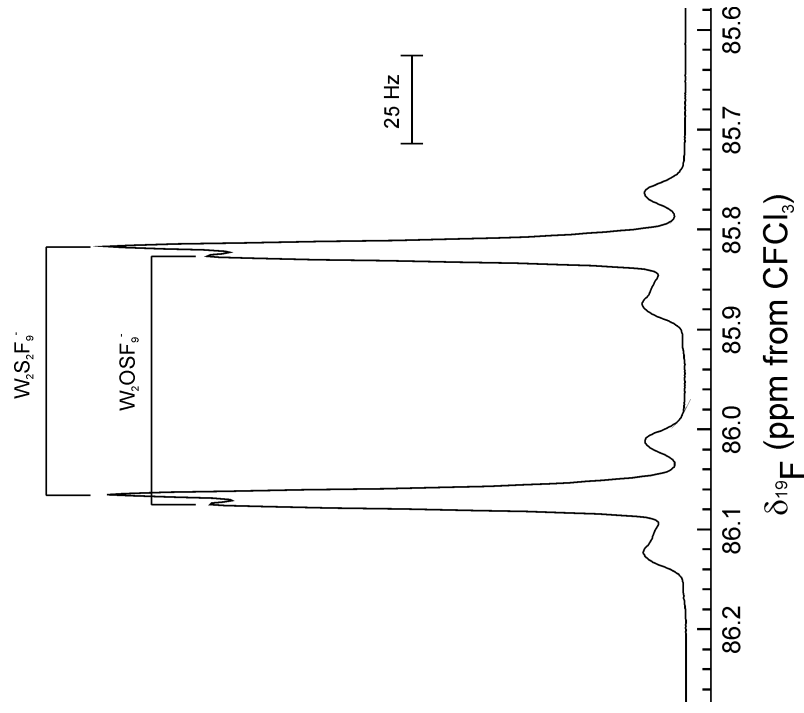
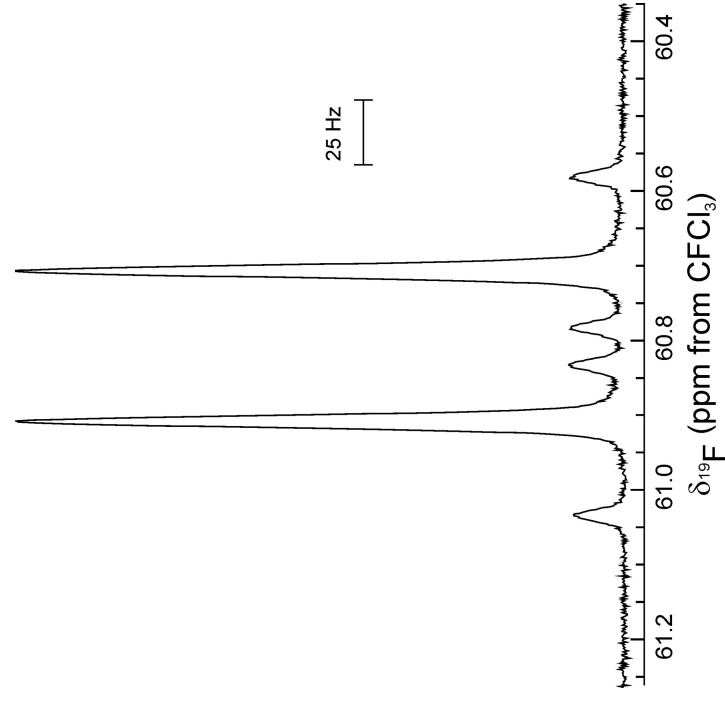


Figure 2

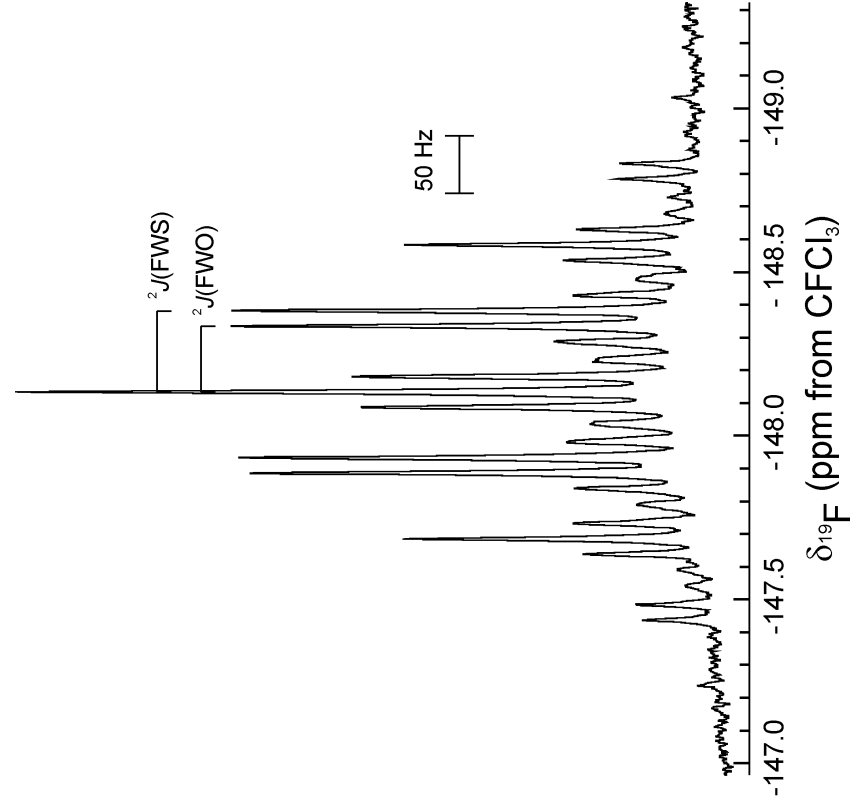
(a)



(b)



(c)



(d)

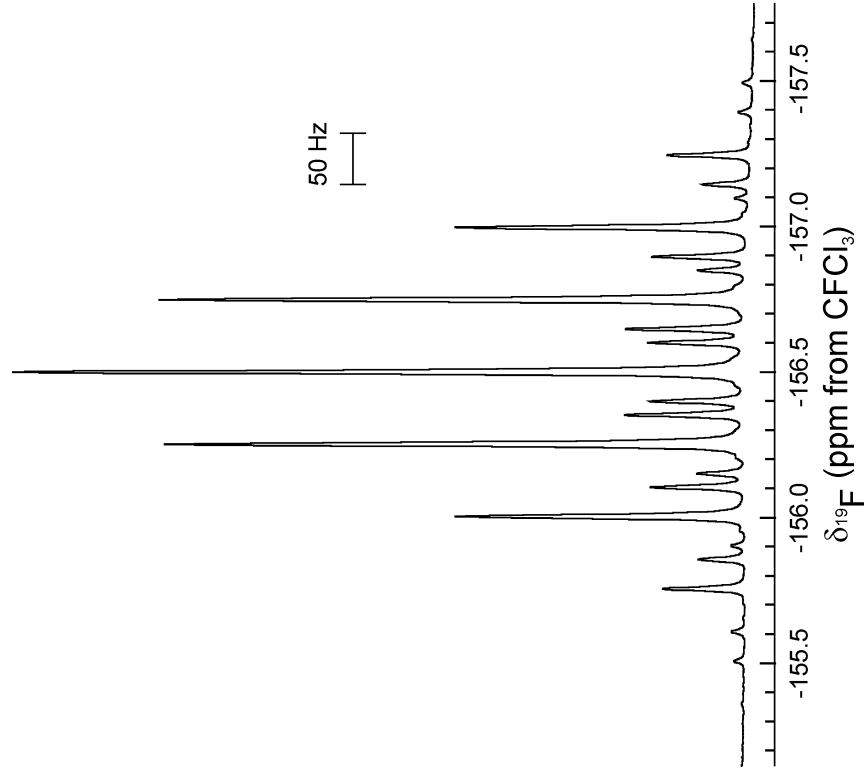


Figure 3

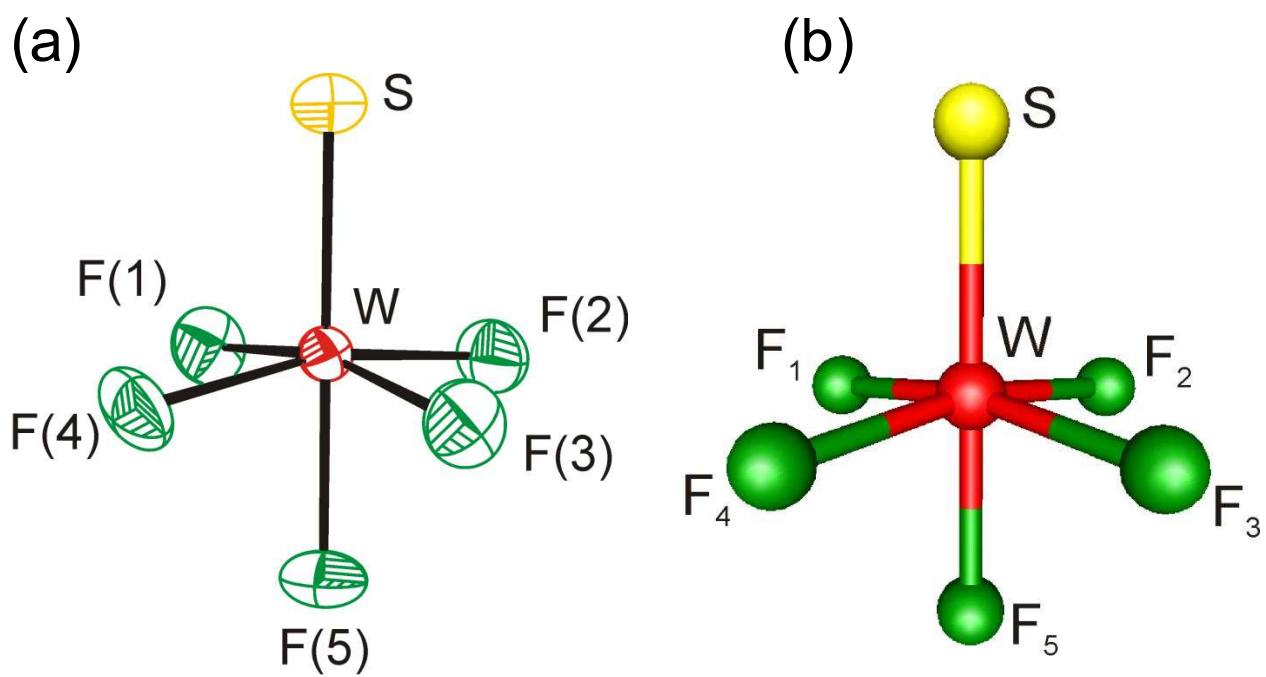


Figure 4

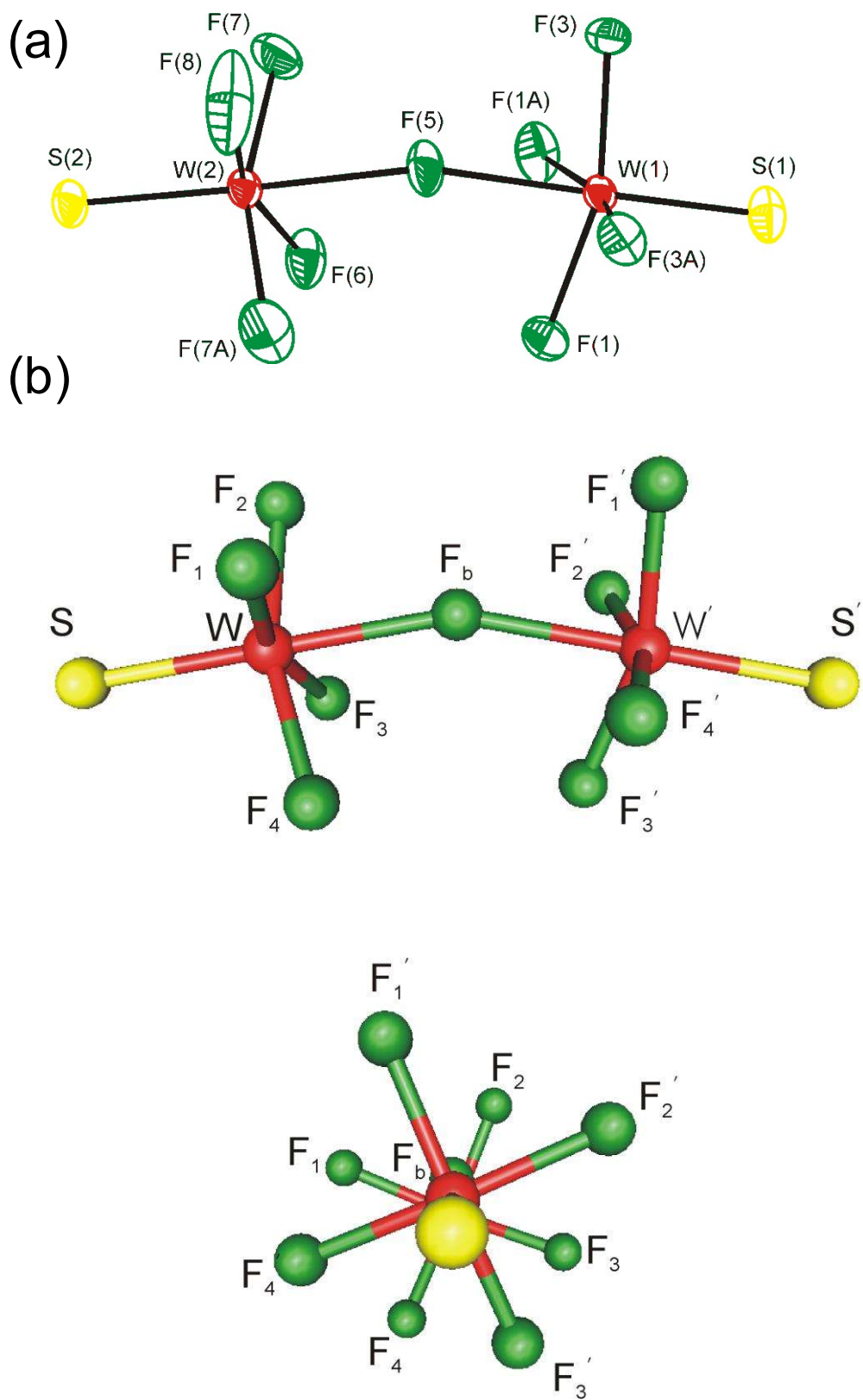


Figure 5

Table of Contents Graphic and Caption

The $[\text{N}(\text{CH}_3)_4][\text{WSF}_5]$ and $[\text{N}(\text{CH}_3)_4][\text{W}_2\text{S}_2\text{F}_9]$ salts were prepared by addition of $[\text{N}(\text{CH}_3)_4][\text{F}]$ to WSF_4 and were characterized by infrared, Raman, and ^{19}F NMR spectroscopy. Alternatively, $[\text{N}(\text{CH}_3)_4][\text{WSF}_5]$ was prepared by reaction of WF_6 with $[\text{N}(\text{CH}_3)_4][\text{SSi}(\text{CH}_3)_3]$. The X-ray crystal structures of $[\text{N}(\text{CH}_3)_4][\text{WSF}_5] \cdot \text{CH}_3\text{CN}$ and $[\text{N}(\text{CH}_3)_4][\text{W}_2\text{S}_2\text{F}_9]$ show pseudooctahedral WSF_5^- and fluorine-bridged $\text{W}_2\text{S}_2\text{F}_9^-$ anions. These tungsten sulfide fluoride anions were studied computationally at the DFT level of theory. In this study, the novel fluorine-bridged W_2OSF_9^- was observed in solution by ^{19}F NMR spectroscopy.

