

purchase of the electrochemical apparatus and glovebox. B.N.D. also acknowledges the assistance of A. R. Moorer in the early stages of this work.

Supplementary Material Available: Listings of final positional and thermal parameters, bond distances and angles, anisotropic thermal parameters, and hydrogen atom coordinates (5 pages); a listing of final observed and calculated structure factors (17 pages). Ordering information is given on any current masthead page.

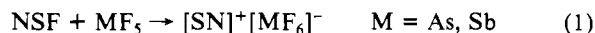
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Convenient Synthesis of Thiazyl Hexafluoroarsenate(V), $[\text{SN}]^+[\text{AsF}_6]^-$, and Small Quantities of Thiazyl Fluoride, NSF

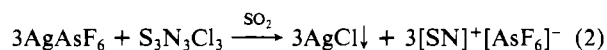
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The simplest, stable sulfur-nitrogen species is the cation $[\text{SN}]^+$. This has been known to have considerable potential as a building block in the synthesis of a wide range of sulfur-nitrogen-containing compounds.²⁻⁴ $[\text{SN}]^+[\text{MF}_6]^-$ (M = As, Sb) were first prepared by the reaction of NSF and MF_5 according to eq 1.⁵ It has also

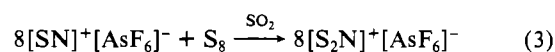


been prepared as one of the products of thermal decomposition of $[\text{S}_3\text{N}_3\text{F}_2]^+[\text{AsF}_6]^-$ ⁶ and the reaction of excess AsF_5 and $\text{S}_3\text{N}_3\text{F}_3$. $[\text{SN}]^+[\text{SbCl}_6]^-$ has also been prepared from a gas-phase reaction of SbCl_5 and NSCl .⁷ None of these reactions give a high-yield synthesis of an $[\text{SN}]^+$ -containing salt from an easily obtained starting material. Recently Herberhold and Haumaier published the preparation of a solution of $[\text{SN}]^+[\text{PF}_6]^-$ in nitromethane by a reaction of $\text{S}_3\text{N}_3\text{Cl}_3$ and AgPF_6 .⁸ The solution of $[\text{SN}]^+[\text{PF}_6]^-$ was used in situ and not isolated. This source of $[\text{SN}]^+$ has utility as a synthetic reagent but its potential would be expanded if a salt was readily prepared as a pure solid, but we were unable to separate the related $[\text{SN}]^+[\text{AsF}_6]^-$ from nitromethane. We report below a convenient, simple synthesis of solid, pure $[\text{SN}]^+[\text{AsF}_6]^-$ in approximately 75% yield by the reaction of $\text{S}_3\text{N}_3\text{Cl}_3$ and an excess of AgAsF_6 in sulfur dioxide solvent according to eq 2. Full details are reported below.



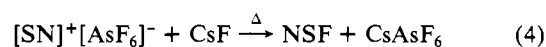
Mews has reported the reaction of $[\text{SN}]^+[\text{AsF}_6]^-$ and S_8 leading to $[\text{S}_2\text{N}]^+[\text{AsF}_6]^-$.⁹ We previously reported a convenient high-yield synthesis of $[\text{S}_2\text{N}]^+[\text{AsF}_6]^-$ and have shown its chemistry to be extensive and diverse.^{10,11} The $[\text{S}_2\text{N}]^+$ cation was first made as the SbCl_6^- salt in unspecified yield.¹² The AlCl_4^- salt has also

been reported in unspecified yield.¹³ In order to compare our previously reported synthesis of $[\text{S}_2\text{N}]^+[\text{AsF}_6]^-$ with that reported by Mews, we repeated the reaction and found that it proceeded in about 50% recovered yield of highly crystalline product according to eq 3. Full details are reported below.



The reactive gas thiazyl fluoride, NSF, is a versatile starting material and of central importance in the field of sulfur-nitrogen-fluorine chemistry.^{14,15} The most important synthetic routes to it are summarized in ref 14. However, these methods suffer either from the formation of mixtures or from lengthy and expensive preparation of starting materials.¹⁴

We report below a convenient, small-scale method for the synthesis of NSF in good yield according to eq 4. We also describe an unoptimized, scaled-up preparation that demonstrates the potential of this method as a route to gram quantities of NSF.



Experimental Section

General Considerations. Except where stated, apparatus and chemicals have been previously described.¹⁶⁻¹⁹ AgAsF_6 was prepared in quantitative yield by the reaction of powdered silver metal and a slight excess of arsenic pentafluoride (AgAsF_6 is also commercially available from Pfaltz and Bauer, Inc.) in sulfur dioxide solution by the addition of aliquots of AsF_5 to the silver in SO_2 at -196°C and slow warming of the mixture to room temperature before the addition of the next aliquot. $\text{S}_3\text{N}_3\text{Cl}_3$ was prepared according to ref 20. Metal apparatus was pre-fluorinated with fluorine and SF_4 until minimal OSF_2 was detected (IR) in the SF_4 . Solids were manipulated in a Vacuum Atmospheres drybox (Type 493), under dry nitrogen.

Preparation of $[\text{SN}]^+[\text{AsF}_6]^-$. In a typical reaction, a large excess of AgAsF_6 (6.94 g, 23.48 mmol), relative to eq 1, and $\text{S}_3\text{N}_3\text{Cl}_3$ (0.865 g, 3.45 mmol) were loaded into a Pyrex, two-bulbed (ca. 25-cm³) vessel incorporating a coarse-glass frit and a J. Young Teflon-in-glass valve. Sulfur dioxide (5.218 g, 81.53 mmol) was condensed onto this mixture at -196°C . At room temperature a reaction occurred, giving a white solid and an opaque, greenish brown solution. After 20 h of stirring the solution was clear yellow over a white solid. The soluble products were washed through the frit into the second bulb, and the white insoluble solid was washed several times with solvent. The volatile products were slowly (approximately 3 h) condensed into a Pyrex U-tube fitted with two Teflon-stemmed Roto-flo valves, held at -196°C in a closed system. A hard yellow solid and a fine white powder remained on the sides of the vessel that had contained the soluble and insoluble products. The vessel was broken open in the drybox and the soluble material (5.684 g, ground to a fine powder and loaded into a sublimation vessel through a side arm. The sublimation vessel was a Pyrex tube (40-cm length, 3-cm o.d.) fitted with a 1 cm o.d. side arm approximately 5 cm from the top of the tube and a J. Young Teflon-in-glass valve and made with a constriction (diameter 1.5 cm) 10 cm from the bottom of the tube. The end of the side arm was temporarily covered with Teflon tape in the drybox and then quickly sealed off and the vessel evacuated (10^{-3} torr). The valve and a short section of the glass tubing connecting it to the sublimation vessel was sealed off and removed. The side arm was sealed off, the vessel evacuated (10^{-3} Torr), and the valve sealed off and removed. The lower half of the sublimation tube was then heated to 120°C . After 3 days a substantial amount of $[\text{SN}]^+[\text{AsF}_6]^-$ had sublimed onto the walls of the sublimation tube as a white film studded with large white crystals. The tube was scored at the constriction and broken open in the drybox. The unsublimed residue that remained consisted of unreacted AgAsF_6 and some of the slightly soluble AgCl originally precipitated from the

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reaction. The sublimed white solid was identified as $[\text{SN}]^+[\text{AsF}_6]^-$ (1.88 g, 8.00 mmol; 75% yield based on $\text{S}_3\text{N}_3\text{Cl}_3$ and eq 2), from its infrared and Raman spectra.⁵ Anal. Calcd for $[\text{SN}]^+[\text{AsF}_6]^-$: S, 13.64; N, 5.96; As, 31.88; F, 48.5. Found: S, 13.52; N, 6.03; As, 31.68; F, 48.70. A negligible amount of $[\text{SN}]^+[\text{AsF}_6]^-$ was carried into the volatile trap with the solvent.

Lower yields were obtained from reactions in which greater amounts of SO_2 or lesser amounts of AgAsF_6 were used and in reactions done in a one-tube vessel followed by sublimation of $[\text{SN}]^+[\text{AsF}_6]^-$ from a mixture of $[\text{SN}]^+[\text{AsF}_6]^-$, AgAsF_6 , and AgCl . Attempts at subliming the $[\text{SN}]^+[\text{AsF}_6]^-$ at lower temperatures under a dynamic vacuum led to substantial (10–20%) amounts of $[\text{SN}]^+[\text{AsF}_6]^-$ condensing out into the U-tube trap, cooled at -196°C .

Preparation of $[\text{S}_2\text{N}]^+[\text{AsF}_6]^-$. In a typical reaction, a large excess of S_8 (1.18 g, 36.91 mmol), relative to eq 3, and $[\text{SN}]^+[\text{AsF}_6]^-$ (2.24 g, 9.51 mmol) was loaded into a reaction vessel as described above. Sulfur dioxide (4.19 g, 65.4 mmol) was condensed onto this mixture. At room temperature, a reaction occurred, giving an opaque, deep red solution over a yellow insoluble solid. The soluble products were washed through the frit with several washings of the solvent. The solvent was slowly condensed from the bulb containing the soluble materials by cooling the bulb with flowing cold water (12°C), until a minimal amount of solvent remained. This small amount of solvent was then washed back through the frit leaving behind large yellow crystals, which were similarly recrystallized several times. The solvent was then removed and the yellow, crystalline $[\text{S}_2\text{N}]^+[\text{AsF}_6]^-$ recovered (1.26 g, 4.74 mmol; 50% yield based on $[\text{SN}]^+[\text{AsF}_6]^-$ and eq 3) and identified by its infrared and Raman spectra.¹⁰ Anal. Calcd for $[\text{S}_2\text{N}]^+[\text{AsF}_6]^-$: S, 24.01; N, 5.24. Found: S, 24.67; N, 5.26. The brown residue (0.96 g), produced by solvent removal from the material washed into the second bulb, was shown by infrared spectroscopy to be almost entirely $[\text{S}_2\text{N}]^+[\text{AsF}_6]^-$.

Small-Scale Preparation of NSF. In a typical reaction, a right-angled, closed tube (o.d. $1/4$ in., length approximately 25 cm) was coupled via a Teflon Swagelok compression fitting and Whitey valve, to a stainless-steel gas infrared cell, fitted with AgCl windows (volume 125 cm^3). A ground mixture of $[\text{SN}]^+[\text{AsF}_6]^-$ (0.123 g, 0.52 mmol) and CsF (0.237 g, 1.56 mmol) was loaded into the side arm. The cell was evacuated and the side arm heated to 65°C at a rate of $14^\circ\text{C min}^{-1}$. The steady evolution of NSF between 40 and 50°C ceased after approximately 3 min, monitored by observing the 655-cm^{-1} S–F peak in the gas-phase infrared spectrum.²¹ The infrared spectrum showed only the presence of NSF (40 Torr) and OSF_2 (2 Torr), pressures estimated by comparison with published spectra.^{21,22} Thus 0.027 ± 0.002 g of NSF was produced, ca. 80% yield based on $[\text{SN}]^+[\text{AsF}_6]^-$ and eq 4.

Larger Scale Preparation of NSF. Cesium fluoride (7.0 g, 46.1 mmol) and $[\text{SN}]^+[\text{AsF}_6]^-$ (3.6 g, 15.3 mmol) was intimately ground and added to a Monel vessel equipped with a removable lid (volume 34.5 cm^3). A further charge of CsF (2.94 g, 19.35 mmol) was packed onto the top of the mixture. The vessel was evacuated and heated to 110°C ($1.5^\circ\text{C min}^{-1}$) at which point a rapid evolution of gas was observed by an increase in pressure. The volatile products contained NSF (0.54 ± 0.07 g; $80 \pm 10\%$ yield based on $[\text{SN}]^+[\text{AsF}_6]^-$ and eq 3), OSF_2 (0.07 ± 0.03 g; $10 \pm 5\%$ yield), SF_4 (0.07 ± 0.03 g; $10 \pm 5\%$ yield), and N_2 ; relative amounts were estimated from published infrared spectra.^{21–23} The N_2 was removed and the volatiles reacted with an excess of AsF_5 in a separate Monel vessel. The Raman spectra of the solid produced showed only the presence of $[\text{SN}]^+[\text{AsF}_6]^-$ (1.76 g) and corresponds to an initial yield of NSF of 49% if the solid produced was 100% $[\text{SN}]^+[\text{AsF}_6]^-$ (N.B. it is likely that the product contains some undetected $[\text{SF}_3]^+[\text{AsF}_6]^-$).²⁴

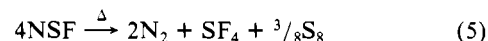
Discussion

$[\text{SN}]^+[\text{AsF}_6]^-$ of high purity can be prepared in 75% yield according to eq 2. $\text{S}_3\text{N}_3\text{Cl}_3$ is easily prepared from S_2Cl_2 and NH_4Cl via $\text{S}_3\text{N}_3\text{Cl}_2$ and chlorine in a well-described, published procedure.²⁰ AgAsF_6 is commercially available or can be easily prepared from silver and AsF_5 .

The utility of $[\text{SN}]^+[\text{AsF}_6]^-$ is illustrated by its reaction with elemental sulfur to give crystalline $[\text{S}_2\text{N}]^+[\text{AsF}_6]^-$ in 50% recovered yield. The advantages of this synthesis of $[\text{S}_2\text{N}]^+[\text{AsF}_6]^-$ are that the starting materials, $\text{S}_3\text{N}_3\text{Cl}_3$, AgAsF_6 , $[\text{SN}]^+[\text{AsF}_6]^-$, and S_8 are easy to handle and nonexplosive. The previously described synthesis of $[\text{S}_2\text{N}]^+[\text{AsF}_6]^-$ ¹⁰ uses potentially explosive S_4N_4 ²⁵ and toxic, corrosive AsF_5 .²⁶ The disadvantages are that

the overall yield of crystalline product is lower (50% based on $\text{S}_3\text{N}_3\text{Cl}_3$ and 78% based on S_4N_4) and the synthesis involves more steps.

The utility of $[\text{SN}]^+[\text{AsF}_6]^-$ is further demonstrated by its reaction with CsF in a solid/solid reaction leading to the versatile reagent, NSF, according to eq 4. The small-scale reaction gave NSF directly in reasonable purity (ca. 95%) in 80% yield, the impurity detected in the infrared spectrum being OSF_2 formed by the hydrolysis of SF_4 . A reaction carried out on a gram quantity scale led to about 50% yield of NSF. The larger scale preparation likely involved less efficient heat transfer to reactants and therefore a higher heating temperature. This led to greater decomposition of NSF according to eq 5.



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Kinetic Study of Ternary Complex Formation between (Terpyridine)nickel and Isomeric (Pyridylazo)naphthol Dyes: Acceleration of a Ring-Closure Step

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It is established that rates of ternary complex formation of some planar aromatic ligands with 1:1 nickel chelates that already contain such a ligand can be unexpectedly high.^{1–4} The accelerations are greater than can be accounted for by inner-sphere water exchange rates and have been ascribed to enhanced outer-sphere association of the chelate and entering ligand.¹ Margerum and his co-workers have attributed the increased association to favorable stacking interactions of the planar aromatic ligands.^{2–4} We have invoked the same interpretation to explain unusually high rates of formation of bis dye–nickel complexes from the 1:1 complexes.^{5–6}

Most examples of accelerated formation of ternary complexes have involved cases where the initial ligation step is rate limiting.⁴ It was anticipated that the advantages of enhanced outer-sphere association would diminish if the rate-determining step (rds) came later in the chelation reaction. To our knowledge there have been no studies of the effect of outer-sphere stacking on rates of complexation where ring closure is rate limiting. We have recently found a case where ring closure appears to be rate limiting in the formation of a 1:1 chelate of Ni^{2+} with a β -PAN dye ligand (2), yet formation of the bis complex from the 1:1 complex is unusually

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