

Convenient Preparation and Full Characterization of a Synthetically Useful Salt of the Dithianitronium Cation, SNSSbF₆, from Readily Available Starting Materials

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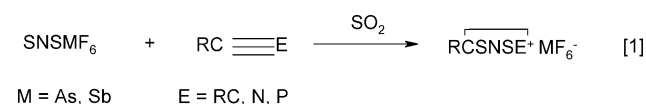
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The synthetically useful SNSSbF₆ is prepared, in good yield, from the reactions of S₃N₂Cl₂ or S₃N₃Cl₃ with stoichiometric amounts of AgSbF₆ and S₈ in liquid SO₂. SNSSbF₆ crystallizes monoclinic in space group C2/m (*a* = 9.740(2) Å, *b* = 6.644(2) Å, *c* = 5.334(1) Å, β = 90.58(2)°, *Z* = 2). The crystal structure was determined by standard methods and refined to *R*¹ = 0.019 and *wR*² = 0.048. The structure consists of discrete linear centrosymmetric SNS⁺ cations [S–N = 1.4871(10) Å] and almost octahedral SbF₆[−] anions, with weak cation–anion interactions. The lattice energy of SNSSbF₆ was determined from the volume-based method as 525 ± 32 kJ mol^{−1} and the heat of formation of SNSSbF_{6(s)} has been estimated as −1566 ± 24 kJ mol^{−1}. The FT-IR, Raman, and ¹⁴N NMR spectra are reported, as well as an in situ study of the reaction of S₃N₂Cl₂ with AsF₅ in SO₂ solution.

Introduction

The simple SNS⁺ cation is of interest as a linear 16 valence electron triatomic species (cf. OCO, ONO⁺, NNN[−], NNO, SCS), and as a unique reagent in sulfur nitrogen chemistry.¹ Of particular note is its extensive quantitative, general, symmetry allowed cycloaddition reactions with unsaturated centers (cf. nitriles, alkynes, olefins, thiazyl halides, phosphoacetylene, and quinones) to give SNS⁺ containing heterocyclic cations, e.g., 1.^{1,2}



The 6π RCSNSE⁺ cations shown in eq 1 are of special interest because they can be reduced to the corresponding 7π radicals,^{2a–c,3} many of which have novel physical properties.⁴ A large number of cycloadducts of SNS⁺ and corresponding radicals can be envisaged.

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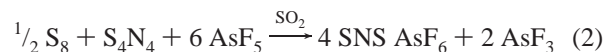
Critical to the efficient exploration of the chemistry of SNS⁺ is the availability of a salt which is soluble in a solvent (e.g., SO₂), in which it undergoes the quantitative cycloaddition reactions described above. The SbCl₆[−], AlCl₄[−], FeCl₄[−], and CF₃SO₃[−] salts of SNS⁺ have been synthesized from readily available starting materials,^{5,6} but they are of low solubility in SO₂ and do not undergo clean cycloaddition

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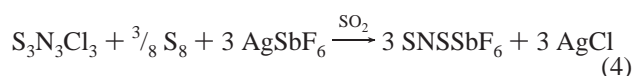
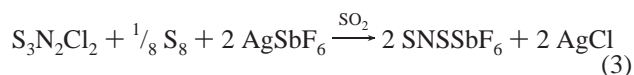
Preparation of Salt of the Dithianitronium Cation, SNSSbF₆

reactions. SNSSbF₆ has previously been prepared on a small scale (~0.25 g, 75% yield) by the reduction of ClNSClSbF₆ with SnCl₂ and characterized by IR and nitrogen analysis.⁵

We have developed a large scale (25 g) synthesis of the synthetically useful SNSAsF₆ in ca. 85% yield, according to eq 2.⁷ However, this requires the use of potentially explosive S₄N₄⁸ and the very toxic and costly AsF₅.^{9,11b}



We report below convenient preparations and full characterization of SNSSbF₆ from S₃N₂Cl₂ and S₃N₃Cl₃ according to eqs 3 and 4.



Experimental Section

Materials. AgSbF₆ (SynQuest Labs, Inc., 99%) was additionally purified by dissolving it in liquid SO₂ and filtering through a fine frit in the absence of light, so that the reagent was snow-white. Sulfur (BDH Inc., precipitated) was vacuum-dried before use. S₃N₂Cl₂ (with traces of S₃N₃Cl₃, IR) and S₃N₃Cl₃ were prepared according to the published procedure.¹⁰ SO₂ (Liquid Air, 99.999%) was stored over CaH₂ for at least 24 h and freshly distilled prior to use.

Methods. Reactions were performed in Pyrex two-bulb vessels (50 mL, unless otherwise stated) incorporating a fine sintered glass

frit and closed by Teflon in glass valves (Rotoflo HP 6K), using techniques that have been previously described.¹¹ All in situ NMR studies were performed in Pyrex 10-mm o.d. NMR tubes equipped with J.Young O-ringette valves. Solid reagents and crystals were manipulated in Vacuum Atmospheres Dri-Labs. The ¹⁴N (28.091 MHz) and ⁷⁵As (68.481 MHz) spectra were recorded on a Varian XL-400 spectrometer at regular intervals and referenced to neat nitromethane (¹⁴N) and D₂O/LiAsF₆ (⁷⁵As) at 298 K (details are given in the Supporting Information). The abbreviations for the NMR peaks are s for singlet, br for broad, t for triplet, and p for pentet. FT-IR spectra of Nujol mulls between CsI plates were recorded on a Thermo Nicolet FT IR 470 spectrometer (32 scans, resolution 2.0 cm⁻¹). FT-Raman spectra were recorded at 172 K on a Bruker IFS 66 FT-IR equipped with a Bruker FRA106 FT-Raman accessory using a Nd:YAG laser (emission wavelength, 1064 nm; maximum laser power, 173 mW; 10 000 scans and resolution 2 cm⁻¹). Samples were sealed in melting point capillaries, and data were collected in the backscattering mode (180° excitation). Chemical analysis was carried out by the Laboratory of Micro-analysis, Novosibirsk Institute of Organic Chemistry, Russia. Actual spectra and supporting information for additional reactions can be found in the Supporting Information

Theoretical Calculations. The geometry of SNS⁺ was optimized, using the Gaussian98W suite of programs,^{12a} at the MPW1PW91^{12b} and B3LYP^{12c} levels of theory employing the 6-311+G (2df) and 6-311+G (d) basis sets, respectively. For comparison, analogous calculations were obtained for SCS and the results are compiled in Table 3. The optimized geometries were minima as indicated by the absence of imaginary frequencies in the vibrational analysis. NBO charges were calculated (MPW1PW91/6-31G(d)) from the optimized geometry at the MPW1PW91/6-311+G (2df) level of theory.

Oxidation of S₃N₂Cl₂ with AsF₅. AsF₅ (1.899 g, 11.17 mmol) and SO₂ (6.90 g) were condensed onto S₃N₂Cl₂ (0.301 g, 1.54 mmol) in bulb 1 of a two-bulb vessel incorporating a 10-mm NMR tube. After stirring for 15 min at -70 °C, the green-yellow solution was warmed to r.t. and stirred for a further 12 h. The solution was cooled to -70 °C and the more soluble fraction was filtered to bulb 2, leaving ~0.3 g of a white insoluble material in bulb 1. Approximately 5 mL of the solution was poured into an NMR tube and ¹⁴N and ⁷⁵As NMR spectra were acquired. ¹⁴N NMR (SO₂, rt) δ 197 [br, SN⁺, 53.9%], 13 [br, (SCl)₂N⁺, 19.8%], -92 [s, SNS⁺, 26.3%]; all ¹⁴N NMR chemical shifts have previously been determined; see ref 23. ⁷⁵As NMR (SO₂, rt), δ 442

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[br, AsCl_4^+].¹³ After four weeks: ^{14}N NMR (SO_2 , rt), δ 199 [br, SN^+ , 45.7%], 17 [br, $(\text{SbCl}_2\text{N}^+$, 35.7%] and -95 [s, SNS^+ , 18.6%].

In situ ^{14}N NMR Studies of the Reaction of $\text{S}_3\text{N}_2\text{Cl}_2 + \text{AgSbF}_6$ in 1:2 Ratio. A 5–6 mL portion of SO_2 was condensed onto $\text{S}_3\text{N}_2\text{Cl}_2$ (0.097 g, 0.50 mmol) and AgSbF_6 (0.344 g, 1.00 mmol) in a NMR tube. The mixture was rigorously shaken to give a brown solution over a white precipitate. ^{14}N NMR (SO_2 , rt), δ 200 [br, SN^+ , 4.5%], 11 [br, $(\text{SbCl}_2\text{N}^+$, 2.1%], -95 [s, SNS^+ , 4.5%], -45 [br, $\text{S}_3\text{N}_2\text{Cl}^+$, 44.9%], -177 [br, $\text{S}_3\text{N}_2\text{Cl}^+$, 44.0%].

In situ ^{14}N NMR Studies of the Reaction of $\text{S}_3\text{N}_2\text{Cl}_2 + 2 \text{AgSbF}_6 + 1/8 \text{S}_8$. A 5–6 mL portion of SO_2 was condensed onto $\text{S}_3\text{N}_2\text{Cl}_2$ (0.097 g, 0.50 mmol) and AgSbF_6 (0.344 g, 1.00 mmol) and S_8 (0.016 g, 0.06 mmol) at -78°C giving a brown-orange solution. After 0.5 h, ^{14}N NMR (SO_2 , -60°C) δ -45 [br, $\text{S}_3\text{N}_2\text{Cl}^+$, 4.2%], -95 [s, SNS^+ , 92%], -178 [br, $\text{S}_3\text{N}_2\text{Cl}^+$, 3.8%]; after 2 h, -95 [s, SNS^+ , 100%]; and after 17 h, -95 [s, SNS^+ , 100%], and minor signals due to hydrolysis products: δ -154 [t, $-\text{NH}_2$], -366 [p, NH_4^+].

Synthesis of SNSSbF_6 from $\text{S}_3\text{N}_2\text{Cl}_2 + 2 \text{AgSbF}_6 + 1/8 \text{S}_8$. The reaction was carried out in a two-bulb vessel incorporating two 100-mL bulbs and 20-mm o.d. fine frit. SO_2 (28.71 g) was condensed onto a mixture of $\text{S}_3\text{N}_2\text{Cl}_2$ (5.99 g, 30.7 mmol) and AgSbF_6 (23.04 g, 67.0 mmol) and S_8 (2.46 g, 9.6 mmol) contained in bulb 1 at -196°C . A red solution formed on warming to ambient temperature, over a large amount of white precipitate (AgCl). The mixture was stirred for 48 h, stirring was stopped, and AgCl and unreacted S_8 were allowed to aggregate for 12 h. The dark brown solution was filtered to the second bulb, and the contents of bulb 1 were washed several times and filtered into bulb 2. The amount of SO_2 was reduced to 5 g, and 2 g of CF_3Cl (Freon-11) was added. A dark brown solution (mainly S_x^{2+} , $x = 16-22$)^{7b} formed over a yellow solid upon cooling to -78°C . The cold solution, containing the more soluble impurities, was carefully filtered back to bulb 1. Washing was continued until the solid was yellow and the more soluble impurities filtered to bulb 1. A total of 9.38 g (29.9 mmol, 48% yield based on $\text{S}_3\text{N}_2\text{Cl}_2$) of SNSSbF_6 was collected. In a separate vessel, an additional 5.77 g (18.4 mmol) of purified SNSSbF_6 was extracted²² from the crude material (most soluble impurities, unreacted S_8 and AgCl) increasing the overall yield to 78% (see Supporting Information).

Elemental analysis for SNSSbF_6 , obsd (calcd): S 19.96 (20.43), N 4.48 (4.46), F 36.38 (36.32). IR, cm^{-1} , (assignment): 1498s

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($\nu_3 \text{SNS}^+$), 660vs, br ($\nu_3 \text{SbF}_6^-$),¹⁴ 374 s ($\nu_2 \text{SNS}^+$). Raman, cm^{-1} , (assignment): 791w (2 $\nu_2 \text{ }^{32}\text{SN}^{34}\text{S}^+$), 699s ($\nu_1 \text{SNS}^+$), 692w ($\nu_1 \text{ }^{32}\text{SN}^{34}\text{S}^+$), 647s ($\nu_1 \text{SbF}_6^-$), 572w ($\nu_2 \text{SbF}_6^-$), 287w, 278w ($\nu_5 \text{SbF}_6^-$). Assignments for SNS^+ were made by comparison with literature values³¹ and with vibrations of SCS (see footnote b, Table 3). Actual spectra have been deposited in the Supporting Information.

Synthesis of SNSSbF_6 from $\text{S}_3\text{N}_3\text{Cl}_3 + 3 \text{AgSbF}_6 + 3/8 \text{S}_8$. SO_2 (22.53 g) was condensed onto a mixture of $\text{S}_3\text{N}_3\text{Cl}_3$ (1.18 g, 4.8 mmol), AgSbF_6 (4.98 g, 14.5 mmol), and S_8 (0.50 g, 1.9 mmol) in bulb 1 (100 mL) at -78°C . A green solution over a white precipitate was immediately given at r.t. A large amount of a white precipitate under a yellow-orange solution was observed after stirring for 48 h. The volume of SO_2 was reduced to one-half and the AgCl and unreacted S_8 were allowed to aggregate (no stirring). The soluble fraction was filtered into bulb 2 (100 mL) and the insoluble product in bulb 1 was washed five times. The crude SNSSbF_6 in bulb 2 was purified by cooling to -78°C and filtering the more soluble impurities to bulb 1. Further purification was performed according to published procedure,⁷ yielding 2.68 g (60% yield based on $\text{S}_3\text{N}_3\text{Cl}_3$) of pure SNSSbF_6 .

X-ray Crystal Structure Determination. Light-yellow single crystals were grown from liquid SO_2 by slow evaporation of the solvent with a temperature gradient of 5°C ($+5^\circ - 0^\circ\text{C}$). A crystal of SNSSbF_6 having approximate dimensions $0.30 \times 0.33 \times 0.10$ mm was mounted on a glass fiber. All measurements were made on a Rigaku AFC5R diffractometer with graphite monochromated $\text{Mo K}\alpha$ radiation (0.71069 \AA). In total 576 reflections were collected; 546 were unique ($R_{\text{int}} = 0.018$). The structure was solved by direct methods¹⁵ and expanded using Fourier techniques.¹⁶ All atoms were refined anisotropically. Full-matrix least-squares refinement on F^2 gave $R^1 = 0.019$ and $wR^2 = 0.048$. All calculations were performed using the teXsan crystallographic software package,¹⁷ except for refinement, which was performed using SHELXL-97. Crystal data are given in Table 1.

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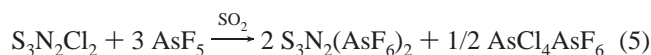
Table 1. Crystallographic Data for SNS⁺SbF₆⁻

empirical formula	SNSSbF ₆
formula weight	313.87
a (Å)	9.740(2)
b (Å)	6.644(2)
c (Å)	5.334(1)
β (deg)	90.58(2)
V (Å ³)	345.2(1)
Z	2
space group	C2/m (No. 12)
T (°C)	-90.0
λ (Å)	0.71069
D _{calc} (g/cm ³)	3.019
μ (Mo Kα) (cm ⁻¹)	46.36
R ¹	0.019 ^a
wR ²	0.048 ^b

$${}^a R^1 = \sum ||F_o| - |F_c|| / \sum |F_o| \quad {}^b wR^2 = [\sum(w(F_o^2 - F_c^2)^2) / \sum w(F_o^2)]^{1/2}.$$

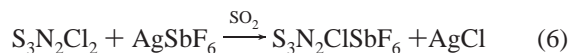
Results and Discussion

This work was initiated by an attempt to prepare a solution of SNSAsF₆ and SNAsF₆ (S₃N₂(AsF₆)₂ in the solid state) by reaction of S₃N₂Cl₂ with an excess of AsF₅ in liquid SO₂ (cf. synthesis of S₃N₂(AsF₆)₂ from S₃N₂FAsF₆ and AsF₅)¹⁸ according to eq 5.



The reaction proceeded as predicted; however the SNS⁺ in solution was slowly chlorinated to ClSNSCl⁺ by AsCl₄AsF₆ which is in equilibrium with AsF₃ and Cl₂ (SO₂Cl₂ in SO₂ solution).¹⁹

We therefore attempted the removal of all chlorine by reaction of S₃N₂Cl₂ (S₃N₂Cl⁺Cl⁻)²⁰ with greater than two equivalents of AgSbF₆; however, only the more anionic chloride was removed as AgCl (eq 6).²¹

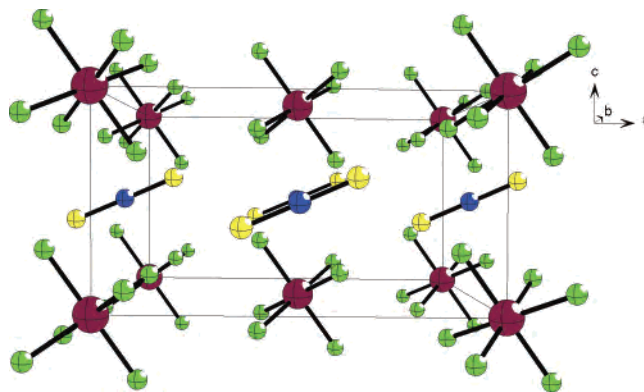
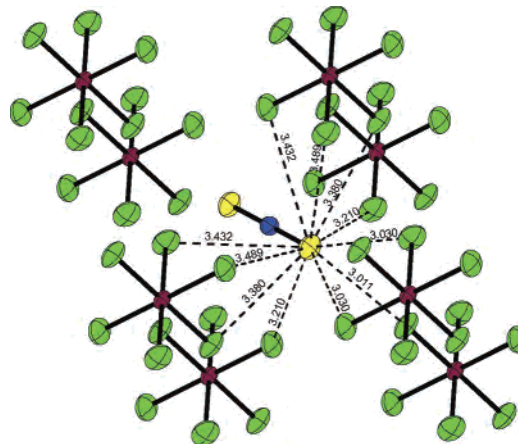


Reaction of S₃N₂Cl₂ with a slight excess (~10%) of elemental sulfur and AgSbF₆ according to eq 3 removed both chlorine and led to pure SNSSbF₆ in recovered yields²² of ~80% on a 15-g scale. The ¹⁴N NMR yields are almost quantitative.

The reaction of S₃N₃Cl₃ with an excess of AgMF₆ (M = As, Sb) in liquid SO₂ leads to a complex mixture that likely contains sulfur–nitrogen–chlorine cations, and not SNMF₆.²³ However, with the addition of sulfur the reaction proceeds almost quantitatively (¹⁴N NMR) according to eq 4 (2.68 g, 60% isolated yield).⁶

Elemental sulfur adds across the S–Cl bond in SCl₃⁺ (MF₆⁻ salts) to give ClSSSCl₂⁺ quantitatively²⁴ and similar results were observed with S₃N₃Cl₃ (see Supporting Information). It is likely that the reactions (eqs 3 and 4) also proceed by addition of sulfur to the S–Cl bond of the generated sulfur–nitrogen–chlorine cation (eg., S₃N₂Cl⁺ or S₃N₃Cl₂⁺).²⁵ S₃N₂Cl₂ is easily prepared in sufficient quantities and purity, and it affords the more efficient route to SNSSbF₆ with greater overall yield.

X-ray Crystal Structure. SNSSbF₆ is isomorphous to SNSAsF₆. Both have ions packed in a CsCl type array (Figure 1), consistent with the relative size of the ions.²⁶ The

**Figure 1.** Unit cell of SNSSbF₆.**Figure 2.** S–F contact distances (in Å) between SNS⁺ and SbF₆⁻.**Table 2.** Compilation of the S–F Contacts and Corresponding Valence Units

contact	value, Å	v.u. (ref 29)	N–S–F angle
S(1)–F(1) ^a	3.030(21)	0.078	153.8
S(1)–F(2)	3.011(28)	0.080	120.5
S(1)–F(1) ^b	3.489(5)	0.046	104.3
S(1)–F(2) ^e	3.380(1)	0.052	89.1
S(1)–F(1) ^c	3.210(5)	0.063	67.3
S(1)–F(1) ^d	3.432(19)	0.049	59.6

Symmetry operators: *a* = *x*, *y*, *z*; *b* = 0.5 – *x*, 0.5 + *y*, –*z*; *c* = 0.5 – *x*, 0.5 + *y*, 1 – *z*; *d* = 0.5 + *x*, 0.5 – *y*, *z*; *e* = 0.5 + *x*, 0.5 + *y*, *z*.

SbF₆⁻ anion is almost octahedral (Sb–F 4 × 1.871(17) and 2 × 1.866(2) Å, F–Sb–F, 89.52(13)–90.48(13)°) consistent with the vibrational spectrum which shows an octahedral SbF₆⁻. The centrosymmetric SNS⁺ has an S–N bond distance of 1.4871(10) Å at 183 K similar to previously determined values. Correction for vibrational motion will increase the bond length. Consequently, the experimental bond length of the S–N bond 1.49 Å, compared in Table 3, for the simple binary SNS⁺ [MF₆⁻, M=As, Sb] is a reasonable bench mark for a sulfur–nitrogen double bond and bond-order of 2. The calculated (gas phase) distances are in good agreement with those found in the solid state, when empirically corrected, giving values of 1.491 (MPW1PW91/6-311G+ (2df)) and 1.495 Å (B3LYP/6-311++G (dp)).²⁷ The vibrational frequencies for different salts are also very similar, implying that the expected greater donation of electron density into the SNS⁺ LUMO by more basic anions has no observable effect on the SNS⁺ geometry.

Table 3. S–N Bond Distances and Fundamental Vibrational Frequencies of Various SNS⁺ Salts and the Calculated Gas Phase Values

salt	<i>T</i> (K)	S–N distance (Å)	ν_1 (Raman)	ν_2 (IR)	ν_3 (IR)
SNSAsF ₆ ^{1,30}	193	1.480(3)	696	374	1494
SNSSbF ₆ ^a	183	1.4874(10)	698	374	1498
SNSSbCl ₆ ³¹	296	1.463(4)	688	374	1498
SNSSbCl ₆ ⁶			692	375	1498
SNSAlCl ₄ ³²	192	1.472(5)		380	1494
SNS ⁺ (MPW1PW91/6-311G+(2df)) ^c	0	1.491 ^e	711	401	1509
SNS ⁺ (B3LYP/6-311+G(d)) ^d	0	1.495 ^e	712	388	1500

^a This work. ^b The experimental vibrational frequencies for carbon disulfide (SCS)³⁰ are ν_1 (R) 657 (SCS), ν_1 (R) 648 (³²S C³⁴S), ν_1 (IR) 397 (³²S C³⁴S), $2\nu_2$ (R) 796 (³²S C³⁴S) and ν_3 (IR) 1523 (SCS). ^c The reported calculated vibrational frequencies equal calculated value multiplied by 0.95. ^d Correction factor 0.98. ^e Previously calculated values 1.482 (HF/STO-3G*),³³ 1.474 (HF/6-31G*)^{32a} and 1.478 (HF/3-21G*)^{32b}

Each sulfur atom makes 11 weak contacts with the surrounding fluorine atoms, illustrated in Figure 2 and compiled in Table 2. The shorter contacts are along the SNS⁺ axis, while the longer contacts are perpendicular to this axis. This is consistent with Nyberg's²⁸ anisotropic van der Waals radius of the sulfur atom in C=S groups: 2.03 Å at 90° to the C=S axis, and 1.60 Å along the axis.

The sum of the valence units (0.66 v.u.) of the S–F contacts to each of the sulfur atoms is consistent with the calculated (MPW1PW91/6-31G(d)) NBO charge of 0.86 on the sulfur atoms. There are no contacts with nitrogen less than the sums of the major anisotropic van der Waals radii of N and F (2.98 Å, respectively)²⁸ consistent with the calculated NBO charge of –0.72 on nitrogen. We note that the calculated charge is contradictory to the full positive charge given by the simple valence bond structure for SNS⁺. A complete description of the total electron charge density and bonding in the simple SNS⁺ warrants further investigation.

Estimated Lattice Potential and Standard Heats of Formation for SNSSbF_{6(s)}. The high quality structure of SNSSbF₆ allows us to derive valuable thermodynamic estimates for the prediction of the energetics of further reactions, using simple Born–Fajan–Haber cycles and the relationship between lattice potential and molecular volume according to the equation

$$U_{\text{pot}} = \sum n_k z_k ((\alpha/V^{-1/3}) + \beta) \text{ KJ mol}^{-1}$$

where α and β for 1:1 salts are 117.3 KJ mol^{–1} nm and 51.9 KJ mol^{–1}, respectively, n_k is the number of ions of charge z_k in the formula unit, and V (nm³) is the molecular (formula unit) volume of the salt.³⁴ This leads to the lattice potential of SNSSbF_{6(s)} (525 ± 32 KJ mol^{–1}) as determined

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from the experimental volume (Table 1). The heat of formation of SNS⁺_(g) is –1023 ± 39 KJ mol^{–1}, derived from the heat of formation of SNSAsF_{6(s)} (–1414 ± 2 KJ mol^{–1}),³⁵ lattice potential (530 ± 32 KJ mol^{–1}), and heat of formation of AsF₆[–]_(g) (–1907 ± 22 KJ mol^{–1}). Therefore, given the heat of formation of SbF₆[–]_(g) (–2070 ± 6 KJ mol^{–1})³⁶ we can estimate the heat of formation of SNSSbF_{6(s)} as –1566 ± 24 kJ/mol. This value will aid in predicting the feasibility of future reactions of SNSSbF₆.

Conclusion

We have shown that SNS⁺, as its synthetically useful SbF₆[–] salt, can be prepared on a 15-g scale, in good yield, by a simple route from S₃N₂Cl₂, 2 AgSbF₆, and S₈ according to eq 3, replacing the previous method that required the use of toxic and not readily available AsF₅ and potentially explosive S₄N₄. Thus, this preparative route makes the very versatile reagent SNS⁺ accessible to a much wider group of researchers than hitherto, and lays the foundation for an expanded exploration of its chemistry.

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Supporting Information Available: Experimental details, additional results, and NMR data (pdf), and crystallographic information (cif). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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