Supplemental Material

to

A convenient preparation and full characterization of a synthetically useful salt of the
dithianitronium cation, SNSSbF₆, from readily available starting materials

by

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Contents

Large scale preparation and purification of SNSSbF ₆	S3
NMR parameters.....	S4
Scheme S1: Predicted route of sulfur insertion ¹ into the S-Cl bond of S ₃ N ₂ Cl ₂	S5
Modified condenser for a large scale preparation of S ₃ N ₂ Cl ₂	S6
Calculation of the heat of formation of SNSSbF ₆	S7
Table S1: Bond angles and distances for SNSSbF ₆ and symmetry operations.....	S8
Figure S1: The almost octahedral anion SbF ₆ ⁻	S9
Table S2: Reactions of S ₃ N ₂ Cl ₂ + AgSbF ₆ + 1/8 S ₈	S10
Table S3: Purification of crude material collected from preparations S ₃ N ₂ Cl ₂ + AgSbF ₆ + 1/8 S ₈	S11
Figure S2: Raman spectrum of SNSSbF ₆	S12
Figure S3: ¹⁴ N-NMR of reaction of S ₃ N ₂ Cl ₂ with AsF ₅ (excess) in SO ₂ at 298 K.....	S13
Figure S4: ¹⁴ N-NMR of reaction of S ₃ N ₂ Cl ₂ with AsF ₅ (excess) in SO ₂ at 298 K after 4 weeks in solution.....	S14
Figure S5: ¹⁴ N-NMR of reaction of S ₃ N ₂ Cl ₂ with AsF ₅ in SO ₂ at 298 K.....	S15
Figure S6: ⁷⁵ As-NMR of reaction of S ₃ N ₂ Cl ₂ with AsF ₅ in SO ₂ at 298 K.....	S16
Figure S7: ¹⁴ N-NMR <i>in situ</i> of reaction of S ₃ N ₂ Cl ₂ with excess AgSbF ₆ (1:2 stoichiometric ratio, respectively) in SO ₂ at 298 K.....	S17
Figure S8: ¹⁴ N-NMR <i>in situ</i> of reaction of S ₃ N ₃ Cl ₃ with S ₈ and AgSbF ₆ in SO ₂ at 298 K.....	S18
Figure S9: ¹⁴ N-NMR <i>in situ</i> of reaction of S ₃ N ₂ Cl ₂ with S ₈ and AgSbF ₆ according to Equation S7 in SO ₂ at 298 K.....	S19
References.....	S20

Large scale preparation and purification of S_2NSbF_6

Although 25.12 g (87 % yield) of $SNSAsF_6$ can be prepared according to Equation S1 by published procedures, large amounts of expensive and toxic AsF_5 and potentially explosive S_4N_4 are required. The need for large quantities of a soluble (c.f. SO_2) SNS^+ salt, preparable in a short time period, from readily available starting materials led us to develop a large scale preparation of $SNSSbF_6$ from the relatively inexpensive $AgSbF_6$ and the easily prepared $S_3N_2Cl_2$, according to equation S7.

The reaction was carried out in a carefully dried, leak tight, evacuated and pre-weighed vessel incorporating two 100 ml bulbs and a 20 mm o.d. fine frit (replacing a 10 mm o.d. medium frit) and Teflon coated magnetic stir bar. In the largest scale reaction, SO_2 (28.71 g), $AgSbF_6$ (23.04 g, 9.2 % excess relative to Equation S7) and S_8 (2.46 g, 40 % excess relative to Equation S7) were loaded into bulb 1. A red solution, which formed on warming slowly to r.t., over a white precipitate, became a dark brown solution over a white solid and unreacted S_8 were allowed to stir for 48 hours. Stirring was stopped and $AgCl$ and unreacted S_8 were allowed to aggregate for 12 hours. This was then separated from the soluble product by filtration into bulb 2 leaving unreacted S_8 and $AgCl$ in bulb 1. The contents of bulb 1 are washed several time with the entire volume of SO_2 and filtered to bulb 2 (soluble fraction). The amount of SO_2 was reduced to 5.10 g and then $CFCl_3$ (2.07 g, ~1: 3 ratio) was added until a dark brown solution (mainly S_x^{2+} , x=16-22) formed over a yellow solid when cooled to $-78^\circ C$. The cold solution was swirled and then gently filtered to bulb 1. The solvent was recondensed onto the solid and the process repeated until the solid turned bright yellow and the more soluble impurities filtered to bulb 1. The solvent was removed leaving crystalline $SNSSbF_6$ [16.15 g, 51.5 mmol, 78 % recovered yield based on $S_3N_2Cl_2$ used in Equation S7) in bulb 2. Recovering $SNSSbF_6$ from the less pure fraction (including $S_8/AgCl$) can increase the yield to > 80 %.

Notes:

- 1) Modification of the above procedure has not been found to greatly affect the isolated yields (See tables S1-4). A stepwise approach (Equation S7) requires a three-bulb vessel (more difficult to get leak tight and dry) or two two-bulb vessels (greater handling of hydrolytic materials and more glassblowing) is more labour intensive and therefore not recommended. Typically, one vessel (as described above) is preferred, however, it is reasonable to isolate the entire soluble fraction after washing and filtering to bulb 2. The soluble fraction can then be collected and loaded into a second vessel for purification as described above. The moisture sensitive nature of SNS^+ salts suggests that fewer vessels and less handling are sensible to avoid excessive hydrolysis.
- 2) The use of two 100 ml bulbs accommodates more material and reduces the total pressure in the vessel.
- 3) The use of a 20 mm o.d. fine frit, allowed the filtering to proceed faster and removed the fine solids from the filtered solutions.

- 4) The purification was faster with the use of CFCl_3 (CH_2Cl_2 can be substituted for CFCl_3 ; continuous extraction in a sealed extractor with CH_2Cl_2 has previously been shown to be an effective purification method and CH_2Cl_2 is a more 'green' alternative to CFCl_3). It has been noted that the impurities (mainly S_x^{2+} , $x=16-22$) have a greater solubility in CH_2Cl_2 than CFCl_3 .
- 5) AgCl has some solubility in SO_2 (~ 20 mmol / 1000 g SO_2) and excessive washing should be avoided.
- 6) Scaling up the reaction requires large volumes of SO_2 (larger vessels to deal with greater safety hazards) and produces more AgCl which requires more washing and subsequently AgCl is washed into the soluble fraction more readily.

NMR parameters:

The ^{14}N (298 K, 228 K) and ^{75}As (298 K) were recorded at 28.091 MHz and 68.481 MHz, respectively, on a Varian UNITY 400 spectrometer and obtained unlocked. Chemical shift values are reported on the δ scale and externally referenced at 298 K (high-frequency direction positive) to neat nitromethane (^{14}N) and $\text{D}_2\text{O} / \text{LiAsF}_6$ (^{75}As). ^{14}N spectra were obtained with a minimum of 500 scans (approx. 15 min.), a pulse width of 25 μs and spectral width of 50 kHz. A standard line broadening routine of 4-100 Hz was applied to improve signal-to-noise ratio. ^{75}As spectra were obtained with a minimum of 2000 scans (approx. 30 min.), a pulse width of 17.5 μs and spectral width of 81.9675 kHz. A standard line broadening routine of 50 was applied, providing better signal-to-noise ratio.

Scheme S1: Predicted route of sulfur insertion¹ into the S-Cl bond of $\text{S}_3\text{N}_2\text{Cl}_2$

Modified condenser for a large scale preparation of $\text{S}_3\text{N}_2\text{Cl}_2$

Note: This type of condenser has been used by German groups (ie. Rudger Mews) previously and was suggested by Dr. Carsten Knapp.

The modification of the condenser apparatus allowed for more efficient cooling and more rapid crystal growth, hence overall reaction time was reduced (~ 3 hr). The use of this apparatus was found to provide more consistent results and yields, which typically exceed 20 g per preparation according to the literature procedure.

The NH_4Cl used was of reagent grade and used without further purification.

Calculation of the heat of formation of SNSSbF₆

$$U_{\text{POT}} = \left| z_+ \right| \left| z_- \right| v \left((\alpha / V^{-1/3}) + \beta \right) = \sum n_k z_k \left((\alpha / V^{-1/3}) + \beta \right) \text{ KJ mol}^{-1}$$

The error was based on the correlation coefficient for MX 1:1 salts²; $\alpha = 117.3 \text{ KJ mol}^{-1} \text{ nm}$ and $\beta = 51.9 \text{ KJ mol}^{-1}$.

$$U_{\text{POT}} (\text{SNSAsF}_6)_{(\text{s})} = 530 \pm 32 \text{ KJ mol}^{-1}$$

$$U_{\text{POT}} (\text{SNSSbF}_6)_{(\text{s})} = 525 \pm 32 \text{ KJ mol}^{-1}$$

$$\Delta_f H (\text{SNSAsF}_6)_{(\text{s})}^3 = -1414 \pm 2 \text{ KJ mol}^{-1}$$

$$\Delta_f H (\text{AsF}_6)_{(\text{g})}^4 = -1907 \pm 22 \text{ KJ mol}^{-1}$$

$$\Delta_f H (\text{SbF}_6)_{(\text{g})}^{12} = -2064 \pm 18 \text{ KJ mol}^{-1} *$$

Therefore,

$$\Delta_f H (\text{SNSSbF}_6)_{(\text{s})} = U_{\text{POT}} (\text{SNSSbF}_6)_{(\text{s})} + \Delta_f H (\text{SbF}_6)_{(\text{g})} - \Delta_f H (\text{AsF}_6)_{(\text{g})} - U_{\text{POT}} (\text{SNSAsF}_6)_{(\text{s})} + \Delta_f H (\text{SNSAsF}_6)_{(\text{s})} = -1566 \pm 24 \text{ KJ mol}^{-1}$$

This allows us to estimate the heat of formation of SNS⁺ in the gas phase by two routes,

$$[1] \Delta_f H (\text{SNS}^+)_{(\text{g})} = \Delta_f H (\text{SNSAsF}_6)_{(\text{s})} - \Delta_f H (\text{AsF}_6^-)_{(\text{g})} + U_{\text{POT}} (\text{SNSAsF}_6)_{(\text{s})} = 1023 \pm 39 \text{ KJ mol}^{-1}$$

$$[2] \Delta_f H (\text{SNS}^+)_{(\text{g})} = \Delta_f H (\text{SNSSbF}_6)_{(\text{s})} - \Delta_f H (\text{SbF}_6^-)_{(\text{g})} + U_{\text{POT}} (\text{SNSSbF}_6)_{(\text{s})} = 1025 \pm 61 \text{ KJ mol}^{-1}$$

X-ray Crystallography Section

Table S1. Bond distances and angles for SNSSbF₆ according to X-ray data.

Bond	Distance, Å	Atoms	Angle (°)
Sb(1)-F(2)	1.866(2)	F(2)-Sb(1)-F(2)'	180.0
Sb(1)-F(1)	1.8710(17)	F(2)-Sb(1)-F(1)	90.05(8)
S – N	1.4871(10)	F(2)-Sb(1)-F(1)'	89.95(8)
		F(2)-Sb(1)-F(1) †	90.05(8)
		F(1)-Sb(1)-F(1)''	90.48(13)
		F(2)'-Sb(1)-F(1) †	89.95(8)
		F(1)-Sb(1)-F(1)†	89.52(13)
		F(1)-Sb(1)-F(1)'*	180.0

‘ -x, -y, -z

“ -x, y, -z

† x, -y, z

- Also F(1)''-Sb(1)-F(1) †

Figure S1: The almost octahedral anion SbF_6^- . Atoms drawn at the 30% probability

Table S7: Reactions of $S_3N_2Cl_2 + 2 AgSbF_6 + 1/8 S_8$ Equation S7: $S_3N_2Cl_2 + 2 AgSbF_6 + 1/8 S_8 \rightarrow 2 S_2NSbF_6 + 2 AgCl$

Entry	$S_3N_2Cl_2$ g, (mmol)	S_8 g, (mmol)	$AgSbF_6$ g, (mmol)	SO_2 g	Color Changes	Reaction Time.	Solubles ^f g, (calc. g)	Insolubles ^h g (calc. g) ⁱ
1 ^a	5.990 (30.7)	2.463 (9.60)	23.04 (67.04)	28.71	Red ↓ golden -brown	48	9.38 (19.26)	22.10 (12.23)
2 ^b	3.90 (19.99)	0.64 (2.49)	13.76 (40.04)	60.09	Red ↓ golden -brown	39	7.78 (12.54)	10.11 (5.76)
3	3.66 (18.76)	0.60 (2.34)	12.90 (37.53)	53.21	Red ↓ golden -brown	15	5.50 (11.77)	11.65 (5.39)
4 ^c	3.97 (20.35)	0.65 (2.53)	14.04 (65.23)	35.60	Greenish-brown ↓ golden -brown	24	14.72 (12.77)	3.47 (2.92)
5 ^d	5.31 (27.21)	1.04 (4.05)	22.42 (65.23)	71.09	Red ↓ golden -brown	24	21.26 (17.074)	7.31 (11.70)
6 ^e	0.975 (4.99)	0.16 (0.62)	3.44 (10.01)	40.95	Greenish-brown ↓ golden -brown	17	2.76 (3.13)	1.82 (2.76)
7	0.195 (0.99)	0.003 (0.01)	0.688 (2.00)	11.27	Greenish-brown ↓ red ↓ golden-brown	60	0.510 (0.610)	0.287 (0.284)

^a See Entry 1 in Table S8; ^b See Entry 2 in Table S8; ^c See Entry 3 in Table S8; ^d See Entry 4 in Table S8; ^e See Entry 2 in Table S8;^f Solubles consist mostly of $SNSSbF_6$, however, the soluble NH_4SbF_6 and S_x^{2+} ($x = 16-22$) are expected to be present as more soluble impurities- See Sxx^g Insolubles refer to precipitated $AgCl$ and unreacted S_8 and may contain some solubles such as $SNSSbF_6$, S_x^{2+} ($x=16-22$) and NH_4SbF_6 when only one vessel is used (Entries 3 and 7);^h Purification of the initially obtained soluble^f product by discarding the more soluble fraction leads to a greater mass of insolubles^g – See Large Scale Preparation of $SNSSbF_6$ (S12).

Table S8: Purification of crude material collected from preparations $S_3N_2Cl_2 + AgSbF_6 + 1/8 S_8$

Entry	Crude g	SO ₂ ^b g	CF ₃ Cl g	SNSSbF ₆ ^c (g)	% Yield ^d	Insolubles ^e (g)
1	20.316	1.709	1.567	5.77		14.37
2	12.74	4.19	2.43	4.37		8.30
3	14.72	3.20	4.47	8.76		5.13
4	21.26	1.05	5.05	11.05		1.05 ^f
5	1.82	1.36	0.51	0.510		0.910

^a Crude material refers to the insolubles (see above-Table S7) collected from the initial reaction according to Equation S7 and further purification carried out in a separate vessel.

^b A greater mass of SO₂ was used to wash the solubles (SNSSbF₆, S_x²⁺ (x = 16-22) and NH₄SbF₆) from the insoluble (AgCl and unreacted S₈) and then reduced to the mass indicated above for the purification - See Large Scale Preparation of SNSSbF₆ (S3).

^c Further SNSSbF₆ was obtained from the discard less pure fraction contain in the insolubles (Table S7, and footnote g, above).

^d The percentage yield is the overall recovered yield with respect to S₃N₂Cl₂ from Equation S7, including the isolated solubles from Table S7.

^e Insolubles are mainly AgCl and unreacted S₈, however the more soluble impurities (S_x²⁺ (x = 16-22) and NH₄SbF₆) are discarded with the insolubles upon purification - See Large Scale Preparation of SNSSbF₆ (S3).

^f Additional 1.0 g of S₈ added to insolubles prior to purification, to presumably form S_x²⁺ (x = 16-22) from higher oxidation state sulfur homopolyatomic cations.

Figure S3: ^{14}N -NMR of reaction of $\text{S}_3\text{N}_2\text{Cl}_2$ with AsF_5 (excess) in SO_2 at 298 K

* assigned to the m.p. sample tube (Pyrex), plus cut-off effects.

Figure S4: ^{14}N -NMR of reaction of $\text{S}_3\text{N}_2\text{Cl}_2$ with AsF_5 (excess) in SO_2 at 298 K after 4 weeks in solution

Figure S5: ^{14}N -NMR of reaction of $\text{S}_3\text{N}_2\text{Cl}_2$ with AsF_5 in SO_2 at 298 K

Figure S6: ^{75}As -NMR of reaction of $\text{S}_3\text{N}_2\text{Cl}_2$ with AsF_5 in SO_2 at 298 K

Figure S7: ^{14}N -NMR *in situ* of reaction of $\text{S}_3\text{N}_2\text{Cl}_2$ with excess AgSbF_6 (1:2 stoichiometric ratio, respectively) in SO_2 at 298 K

Figure S8: ^{14}N -NMR *in situ* of reaction of $\text{S}_3\text{N}_3\text{Cl}_3$ with S_8 and AgSbF_6 in SO_2 at 298 K

Figure S9: ^{14}N -NMR *in situ* of reaction of $\text{S}_3\text{N}_2\text{Cl}_2$ with S_8 and AgSbF_6 according to Equation S7 in SO_2 at 298 K

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