Contribution from the Department of Chemistry,
McMaster University, Hamilton, Ontario, Canada, L8S 4M1

Reactions of $S_3N_3F_3$ and $S_3N_3Cl_3$ with Lewis Acids. Preparation and Crystal Structure of Pentathiazyl Hexachloroantimonate, $(S_5N_5)(SbCl_6)$

RONALD J. GILLESPIE,* JEFFERY F. SAWYER, DAVID R. SLIM, and J. DAVID TYRER

Received April 17, 1981

The reactions of $S_3N_3Cl_3$ with $SbCl_5$ and the reactions of $S_3N_3F_3$ with AsF_5, SbF_5, and SO_3 have been studied. The reaction of $S_3N_3Cl_3$ with $SbCl_5$ in a 1:2 mole ratio gave $(S_4N_4)(SbCl_6)_2$ as the major product in SO_2, CH_2Cl_2, and $SOCl_2$ as solvents. With a 1:1 mole ratio and CH_2Cl_2 as solvent the products were $(S_5N_5)(SbCl_6)$ and $S_4N_4{\cdot}SbCl_5$. This mixture reacted with additional $SbCl_5$ to give $(S_4N_4)(SbCl_6)_2$. Both $(S_5N_5)(SbCl_6)$ and $S_4N_4{\cdot}SbCl_5$ were characterized by X-ray crystallography. The geometry of the planar pentathiazyl cation $S_5N_5^+$ is intermediate between the "azulene-like" and heart-shaped conformations found previously for other examples of this cation. This is attributed to disorder in part of the cation. The reactions of $S_3N_3F_3$ with AsF_5, SbF_5, and SO_3 in the mole ratios 1:6, 1:6, and 1:3 gave the thiazyl salts $SN(AsF_6)$, $SN(Sb_2F_{11})$, and $SN(SO_3F)$, respectively.

Introduction

Recently there has been considerable interest in the cationic species produced by the reactions of tetrasulfur tetranitride with Lewis acids. In comparison the reactions of $S_3N_3Cl_3$ and $S_3N_3F_3$ with Lewis acids have not been extensively studied. Early work indicated that $SbCl_5$ forms 1:1, 2:1, and 3:1 adducts with $S_3N_3Cl_3$ as well as abstracting a chloride ion to give the salt $(S_3N_3Cl_2)(SbCl_6)$.[1-3] It has also been shown that the reaction of $S_3N_3F_3$ with Lewis acids such as AsF_5 and SbF_5 gives the $S_3N_3F_2^+$ cation.[1] More recently the reaction of $S_3N_3Cl_3$ with $AlCl_3$ and SCl_2 has been shown to give the cation $N(SCl)_2^+$.[4] In the present work the reactions of $S_3N_3Cl_3$ with $SbCl_5$ and those of $S_3N_3F_3$ with the Lewis acids AsF_5, SbF_5, and SO_3 have been studied in various solvents.

Experimental Section

Preparation of $S_3N_3Cl_3$. Trichlorocyclotrithiazene was prepared by chlorinating a stirred solution of S_4N_4 in CCl_4 at room temperature.[5] The $S_3N_3Cl_3$ was crystallized from CCl_4 below 50 °C and stored in a dry evacuable bulbs with a slight pressure of anhydrous chlorine gas. A sample was analyzed by the Schwarzkopf Microanalytical Laboratory. Anal. Calcd for $S_3N_3Cl_3$: S, 39.50; N, 17.28; Cl, 43.12. Found S, 38.87; N, 17.4; Cl, 43.20.

The melting point of $S_3N_3Cl_3$ recrystallized from hot CCl_4 has previously been reported as 142.5 °C.[5] Patton and Jolly,[6] however, have noted that whenever CCl_4 solutions of $S_3N_3Cl_3$ are heated above 60 °C, green solutions are obtained and samples isolated from these solutions have variable and high melting points. They suggested that the melting point of 142.5 °C quoted by Schroder and Glemser[5] corresponds to the melting or decomposition of a solid decomposition product of $S_3N_3Cl_3$. Crystals obtained in this laboratory from solutions that had not been heated above 50 °C melted consistently at 90-91 °C, and this melting point is in agreement with that reported by Patton and Jolly[6] for crystals obtained by a similar procedure.

Preparation of $S_3N_3F_3$. Trifluorocyclotrithiazene was prepared by fluorination of $S_3N_3Cl_3$ with AgF_2 in CCl_4 according to the method of Glemser[7] with the following modifications. The quartz reaction vessel was fitted with a Teflon Rotaflo valve and did not contain a stirring bar. This enabled the flask to be rigorously flame-dried under high vacuum. The AgF_2 was placed in a Monel bomb and subjected to a pressure of fluorine of 1000 lb/in.^{2} at 150 °C for 1 week to ensure complete fluorination. The required amounts of $S_3N_3Cl_3$ and AgF_2 were transferred to the quartz reaction bulb in a drybox, and CCl_4 (40 mL) that had been dried over molecular sieves was distilled onto the $S_3N_3Cl_3/AgF_2$ mixture. The bulb was then placed on a mechanical agitator for 3 days, after which time the solution was yellow rather than colorless as reported.[5] With a procedure identical with that of Schroder and Glemser,[5] the $S_3N_3F_3$ was sublimed into a Kel-F trap that had been previously conditioned with HF and fluorine. The $S_3N_3F_3$ was stored in this trap under 25 lb/in.^{2} of dry argon.

When $S_3N_3F_3$ was sublimed into either Kel-F or glass vessels, an initially colorless crystalline solid was obtained that turned yellow with time. This may be due to some decomposition although the ^{19}F NMR spectrum of the material was consistent with that reported by Richert and Glemser[8] and indicated that no other fluorine-containing species were present.

Other Materials. S_4N_4 was prepared by the method of Becke-Goering with some modifications as has been described previously.[9] Anhydrous sulfur dioxide (Matheson of Canada) was stored as a liquid over P_4O_{10} and was distilled directly before use. Thionyl chloride (J. T. Baker Chemical Co.) was distilled twice from triphenyl phosphate to remove traces of SCl_2, S_2Cl_2, and SO_2Cl_2 and used immediately after purification. Commercial antimony pentachloride (Baker Analyzed reagent) was used directly. Silver difluoride (Bentron Alfa Products) was subjected to 1000 lb/in.^{2} of fluorine at 150 °C for 1 week prior to use.

The Reaction of $S_3N_3Cl_3$ with $SbCl_5$ in SO_2 (1:2 Mole Ratio). $S_3N_3Cl_3$ (250 mg, 1.02 mmol) and $SbCl_5$ (615 mg, 2.05 mmol) were both added in the drybox to separate bulbs of a double-bulb reaction vessel. The vessel was evacuated and SO_2 (5 mL) condensed at −196 °C onto both reactants. On warming to room temperature the $SbCl_5$ completely dissolved in SO_2 while $S_3N_3Cl_3$ was only moderately soluble. The $SbCl_5/SO_2$ solution was then poured onto the $S_3N_3Cl_3/SO_2$ solution and stirred for 24 h. The product was a yellow solid and a green-brown solution. The solution was filtered, and after 24 h yellow needles and a few green needles crystallized out. Continual washing with SO_2 removed the green material, yielding a pure yellow crystalline sample. This was shown to be $S_4N_4(SbCl_6)_2$ by comparison of its Raman spectrum with that of a pure sample.[10]

The above procedure was repeated but instead of filtering the solution the solvent was removed on the vacuum line, yielding a crude solid mixture. The Mössbauer spectrum of this mixture indicated the presence of Sb(V) but no Sb(III). A Raman spectrum of the material has bands due to $S_4N_4(SbCl_6)_2$ and another product, a green crystalline material, that could be extracted from the mixture with methylene chloride. This material had the following Raman spectrum: 44 (19), 66 (14), 74 (17), 83 (13), 102 (9), 126 (6), 130 (7), 149 (9), 167 (18), 171 (19), 175 (13), 184 (17), 192 (8), 280 (11), 329 (64), 336 (49), 351 (10), 360 (10), 376 (22), 1394 (6), 1403 (100) cm^{-1}. The bands at 130, 167, 175, 184, 280, 329, and 336 cm^{-1} are close to those observed for $SbCl_5$ in the adduct $CH_3CN{\cdot}SbCl_5$[11] and suggest that the green compound also contained $SbCl_5$ coordinated to nitrogen. The band at 1403 cm^{-1} could plausibly be attributed to an SN triple bond. The compound was not further identified.

The Reaction of $S_3N_3Cl_3$ with $SbCl_5$ in $SOCl_2$ (1:2 Mole Ratio). $S_3N_3Cl_3$ (250 mg, 1.02 mmol) and $SbCl_5$ (6.5 mg, 2.05 mmol) were

---

(1) Mews, R.; Wagner, D. L.; Glemser, O. *Z. Anorg. Allg. Chem.* **1975**, *412*, 148.
(2) Glemser, O.; Wegener, J. *Inorg. Nucl. Chem. Lett.* **1971**, *7*, 623.
(3) Banister, A. J.; Clarke, H. G. *J. Chem. Soc. A* **1972**, 2661.
(4) Alange, G. G.; Banister, A. J.; Dainty, P. J. *Inorg. Nucl. Chem. Lett.* **1979**, *15*, 175.
(5) Schroder, H.; Glemser, O. *Z. Anorg. Allg. Chem.* **1959**, *298*, 78.
(6) Patton, R. L.; Jolly, W. L. *Inorg. Chem.* **1970**, *9*, 1079.
(7) Glemser, O. *Prep. Inorg. React.* **1964**, *1*, 227.
(8) Richert, W. H.; Glemser, O. *Z. Anorg. Allg. Chem.* **1961**, *307*, 328.
(9) Gillespie, R. J.; Kent, J. P.; Sawyer, J. F. *Inorg. Chem.* **1981**, *20*, 3812. Gillespie, R. J.; Ireland, P. R.; Vekris, J. E. *Can. J. Chem.* **1975**, *53*, 3147.
(10) Gillespie, R. J.; Kent, J. P.; Sawyer, J. F.; Slim, D. R.; Tyrer, J. D. *Inorg. Chem.* **1981**, *20*, 3799.
(11) Byler, D. M.; Shriver, D. F. *Inorg. Chem.* **1974**, *13*, 2697.

0020-1669/82/1321-1296$01.25/0

transferred in a drybox to separate bulbs of a double-bulb reaction vessel. $SOCl_2$ (10 mL) was also transferred to each of the separate bulbs in the drybox. The vessel was then evacuated, and the $SbCl_5/SOCl_2$ solution was poured through the frit onto the $S_3N_3Cl_3/SOCl_2$ solution to give after 24 h a yellow solution together with yellow crystals. The crystals were filtered off and shown to be $S_4N_4(SbCl_6)_2$ by comparison of their Raman spectrum with that of a pure sample.[10]

Reaction of $S_3N_3Cl_3$ with $SbCl_5$ in CH_2Cl_2 (1:2 Mole Ratio). $S_3N_3Cl_3$ (200 mg, 0.823 mmol) in 10 mL of dry CH_2Cl_2 was added to $SbCl_5$ (492 mg, 1.65 mmol). Within $^1/_2$ h, the stirred solution became increasingly orange and finally orange-red to red. After 24 h the solution became bright yellow and deposited a yellow solid, which was shown to be $S_4N_4(SbCl_6)_2$ by its Raman spectrum. Other products from the reaction were not characterized. The green material obtained in SO_2 was not observed.

This reaction was also attempted with a 1:1 mole ratio of reactants. In this case $S_3N_3Cl_3$ (175 mg, 0.720 mmol) and $SbCl_5$ (2.5 mg, 0.720 mmol) reacted in dry CH_2Cl_2 to yield a red solution. After 24 h there was no further change and the CH_2Cl_2 was removed on a vacuum line to give a predominantly black-green residue that also contained some red and yellow material. Sulfur dioxide (20 mL) was then condensed at −196 °C onto the solid, and on warming to room temperature, the solution again became red with some undissolved red solid present. The solution was filtered, and after several days a mixture of at least three different crystalline materials was obtained. Light red and dark red needles were shown to be $S_4N_4{\cdot}SbCl_5$ and $(S_5N_5^+)(SbCl_6^-)$, respectively, by X-ray crystallography. A few yellow crystals were also present, and these were characterized as $S_4N_4(SbCl_6)_2$.[10]

Reaction of $S_3N_3Cl_3$ with $SbCl_5$ in SO_2 (1:1 Mole Ratio). $S_3N_3Cl_3$ (2.50 mg, 1.02 mmol) and $SbCl_5$ (307 mg, 1.02 mmol) were each transferred in a drybox to separate bulbs of a double-bulb reaction vessel. Sulfur dioxide (10 mL) was condensed at −196 °C onto both reactants, and the vessel was allowed to warm to room temperature. The $SbCl_5/SO_2$ solution was poured through the frit onto the $S_3N_3Cl_3/SO_2$ solution. A yellow precipitate which formed immediately was shown by Raman spectroscopy to be a mixture of $(S_3N_3Cl_2)(SbCl_6)$[1] and $S_4N_4(SbCl_6)_2$. After removal of the yellow solid, the solution was set aside for several days when a yellow crystalline solid was formed which was shown to be $(S_4N_4)(SbCl_6)_2$.[10]

Preparation of $(S_3N_3Cl_2)(SbCl_6)$. The compound $(S_3N_3Cl_2)(SbCl_6)$ was prepared by the reaction of $S_3N_3Cl_3$ with $SbCl_5$ in CCl_4 in a 1:1 mole ratio according to the method of Glemser.[7] $S_3N_3Cl_3$ (200 mg, 0.823 mmol) and $SbCl_5$ (246 mg, 0.823 mmol) were added, in a drybox, to separate bulbs of a double-bulb reaction vessel, and CCl_4 (20 mL) was distilled at −196 °C onto both reactants. The vessel was then allowed to warm to room temperature, and the mixture was stirred for 24 h. The product was a yellow solid which had a Raman spectrum identical with that reported by Glemser[7] for $(S_3N_3Cl_2)(SbCl_6)$.

Solutions of $(S_3N_3Cl_2)(SbCl_6)$ in CH_2Cl_2 and SO_2. Methylene chloride was condensed at −196 °C onto the yellow $(S_3N_3Cl_2)(SbCl_6)$ prepared by the above method, and the mixture was allowed to warm to room temperature. Upon reaching room temperature, the solution became orange-red and appeared to be very similar to solutions obtained directly from the reaction of $S_3N_3Cl_3$ with $SbCl_5$ in CH_2Cl_2. A Raman spectrum of the solid obtained on removal of CH_2Cl_2 was identical with that obtained from the crude mixture prepared directly from $S_3N_3Cl_3$ and $SbCl_5$ in CH_2Cl_2. Similar observations were made with liquid SO_2 as solvent.

Preparation of $(S_5N_5)(SbCl_6)$. Cyclotetrathiazyl bis(hexachloroantimonate (V)) was prepared in thionyl chloride by the reaction of trichlorocyclotrithiazene (320 mg, 1.32 mmol) and $SbCl_5$ (1.17 g, 3.94 mmol). After 24 h S_4N_4 (0.727 g, 3.05 mmol) was added to the stirred $SOCl_2$ solution. The solution immediately turned green and after 24 h had a dark red–green dichroic appearance. Filtration yielded a yellow-brown solid. This was washed with thionyl chloride to give a yellow-orange material which had an infrared spectrum identical with that reported by Bannister for $S_5N_5(SbCl_6)$.[12]

Reaction of $S_3N_3F_3$ with SO_3. Under dynamic vacuum, $S_3N_3F_3$ (0.1395 g, 0.715 mmol) was sublimed from a Kel-F storage trap onto one bulb of a double-bulb reaction vessel that had been previously weighed and flame-dried under vacuum for 48 h. SO_3 (0.1716 g, 2.14 mmol) was then sublimed onto the $S_3N_3F_3$ at −196 °C, followed by 10 mL of SO_2. The solution was allowed to warm to room temperature. After 3 h large cream-colored needles appeared in a green solution. After the solution was filtered, the crystals were washed with SO_2 until they were white. The solvent was removed, and the bulb containing the crystalline material was flame-sealed and stored at −196 °C. A Raman spectrum of the white crystalline material showed it to be mainly $SN(SO_3F)$, although there were some additional weak lines in the spectrum that could not be assigned (Table I).

Reaction of $S_3N_3F_3$ with SbF_5. Antimony pentafluoride (6.72 g, 28.6 mmol was added in the drybox to one bulb of a preweighed double-bulb reaction vessel. Under dynamic vacuum, $S_3N_3F_3$ (932 mg, 4.78 mmol) was sublimed from a Kel-F trap into the other bulb at −196 °C. Sulfur dioxide (5 mL) was condensed at −196 °C into both bulbs, and the vessel was allowed to warm to room temperature. $S_3N_3F_3$ and SbF_5 were both completely soluble in SO_2, and the SbF_5/SO_2 solution when reacted with the $S_3N_3F_3$ solution produced a cream-colored suspension from which a pale yellow solid was isolated. The Raman spectrum of this solid was consistent with its formulation as $(SN)(Sb_2F_{11})$.

Reaction of $S_3N_3F_3$ with AsF_5. Into one bulb of a double-bulb reaction vessel at −196 °C was sublimed $S_3N_3F_3$ (52.3 mg, 0.268 mmol) under dynamic vacuum from a Kel-F storage vessel. AsF_5 (0.257 g, 1.61 mmol) and SO_2 (10 mL) were then condensed at −196 °C onto the $S_3N_3F_3$, and the vessel was allowed to warm to room temperature. The $S_3N_3F_3$ reacted quickly to yield a yellow solution from which a yellow solid was isolated. The Raman spectrum of this material showed the presence of $(SN)(AsF_6)$, but there were additional lines in the spectrum that could not be assigned.

X-ray Crystallography. Crystals of the compounds $S_4N_4{\cdot}SbCl_5$ and $(S_5N_5)(SbCl_6)$ were selected from the products of the 1:1 reaction of $S_3N_3Cl_3$ and $SbCl_5$ in CH_2Cl_2 and were sealed in Lindemann capillaries in a specially designed drybox equipped with a microscope. Precession photographs were used to give preliminary symmetry and unit cell data. For the compound $(S_5N_5^+)(SbCl_6^-)$, the crystal had approximate dimensions 0.2 × 0.2 × 0.4 mm and was mounted so that the c axis was approximately coincident with the ϕ axis of the diffractometer. The crystal of $S_4N_4{\cdot}SbCl_5$ had the approximate dimensions 0.25 × 0.18 × 0.21 mm and was mounted with b approximately coincident with the ϕ axis of the diffractometer. Accurate unit cell dimensions were obtained from least-squares fit of 2θ, ω, and χ for 15 well-centered strong reflections from each crystal with a Syntex $P2_1$ diffractometer and graphite-monochromatized Mo $K\bar{\alpha}$ radiation ($\lambda = 0.71069$ Å).

Crystal Data. For $(S_5N_5)(SbCl_6)$: fw = 564.8; orthorhombic; space group $Fdd2$; $a = 18.05$ (1), $b = 56.72$ (1), $c = 7.380$ (3) Å; $V = 6223$ Å^3; $D_c = 2.41$ g cm^{-3} for $Z = 16$; Mo $K\bar{\alpha}$ radiation ($\lambda = 0.71069$ Å); μ(Mo $K\bar{\alpha}$) = 34.4 cm^{-1}. For $S_4N_4{\cdot}SbCl_5$: fw = 483.2; monoclinic; space group $P2/c$; $a = 6.955$ (3), $b = 12.400$ (5), $c = 15.224$ (7) Å; $\beta = 107.09$ (7)°; $V = 1255$ Å^3; $D_c = 2.56$ g cm^{-3} for $Z = 4$; μ(Mo $K\bar{\alpha}$) = 38.0 cm^{-1} (Neubauer and Weiss[13] report the unit cell parameters of $S_4N_4{\cdot}SbCl_5$ as $a = 7.01$ (1) Å, $b = 12.60$ (6) Å, $c = 15.6$ (1) Å, $\beta = 108.7$ (3)°).

Data on each crystal were collected with θ–2θ scans with variable-scan rates dependent on the intensity of a preliminary count so that the weaker reflections were examined more slowly to minimize counting errors. Stationary-background counts with a time equal to half the scan time for each reflection were made at each end of the scan range. For each crystal, standard reflections were regularly checked to monitor the stability of the crystal and its alignment, but in each case no significant variations were observed. For the compound $(S_5N_5)(SbCl_6)$, all reflections in the quadrants (h,k,l) with $2\theta < 50°$ were measured. Lorentz and polarization corrections were applied to all data. After equivalent reflections were averaged and reflections which were systematically absent or had $I < \sigma(I)$ were excluded, a total of 1371 independent reflections were obtained and used in the subsequent refinements.

For the compound $S_4N_4{\cdot}SbCl_5$, 2447 reflections in the quadrants $(h,k,\pm l)$ with $2\theta < 50°$ were measured. Lorentz and polarization corrections were applied. Subsequent averaging and removal of systemically absent data with $I < \sigma(I)$ gave a final data set of 2049 reflections. No absorption corrections were applied for either crystal.

---

(12) Banister, A. J.; Padley, J. S. *J. Chem. Soc. A* **1969**, 286. Banister, A. J.; Clarke, H. G. *Inorg. Synth.* **1977**, *17*, 188.

(13) Neubauer, D.; Weiss, J. *Z. Anorg. Allg. Chem.* **1960**, *303*, 28.

Table I. Raman Frequencies for Thiazyl Salts ($\Delta\nu$, cm^{-1})[a]

(SN)(SO_3F)	KSO_3F[17]	assignt	(SN)(Sb_2F_{11})	$XeF^+Sb_2F_{11}^-$[18]	(SN)(AsF_6)	assignt
52 (26)					64 (28)	
68 (18)					109 (30)	
78 (11)					139 (24)	
85 (9)					176 (10)	
100 (15)					225 (20)	
113 (6)					327 (6)	
119 (9)					360 (14)	$\nu_5(AsF_6^-)$
130 (33)					369 (28)	
139 (11)					407 (8)	
150 (6)			222 (59)	212 (5)	497 (28)	
165 (13)			233 (21)	226 (12)	553 (24)	
178 (7)			271 (5)	269 (11)	558 (18)	
221 (3)			300 (32)	293 (8)	572 (18)	$\nu_2(AsF_6^-)$
405 (6)	405 (3)	ν_6(e)			580 sh	
420 (10)					608 (20)	
499 (4)					680 (88)	$\nu_1(AsF_6^-)$
562 (2)			497 (44)			
572 (2)	571 (2)	ν_3(a)		518 (16)		
581 (3)	587 (2)	ν_5(e)	585 (32)	603 (<1)		
594 (2)				651 (39)		
			647 (94)	669 (9)		
778 (2)	741 (2)	ν_2(a)				
794 (7)	821 (1)		673 sh	678 (8)		
1058 (100)			680 (100)	688 (48)		
	1084 (10)	ν_1(a)				
1063 (55)					1023 (8)	
1210 (7)						
1228 (6)	1285 (1)	ν_4(e)			1190 (20)	
1256 (41)						
1263 (16)						
1425 (4)		$^{34}S\equiv N$ str			1428 (4)	$^{34}S\equiv N$ str
1438 (90)		$S\equiv N$ str	1436 (100)		1438 (100)	$S\equiv N$ str

[a] Key: sh = shoulder; vs = very strong; s = strong; m = medium; w = weak; vw = very weak.

Structure Solutions. (1) (S_5N_5)($SbCl_6$). For the compound (S_5N_5)($SbCl_6$), the position of the antimony atom was located in the Patterson function, and subsequent cycles of least squares and Fourier calculations located all the remaining atoms in the structure. The peaks of some of the atoms in the cation were somewhat low and diffuse, and on refinement with anisotropic thermal parameters, it was noted that there was considerable anisotropy in this portion of the cation. This was attributed to some disorder in the cation. It was not possible to resolve individual peaks due to different arrangements, and the averaged positions were used throughout. Least-squares refinement with all atoms having anisotropic thermal parameters converged to final agreement indices $R_1 = 0.0391$ and $R_2 = 0.0446$ for 1265 observed ($I/\sigma(I) > 3.0$) data ($R_1 = \sum||F_o| - |F_c||/\sum|F_o|$; $R_2 = [\sum w|F_o - F_c|^2/\sum wF_o^2]^{1/2}$). Refinement of the alternative "hand" of the crystal (by reversing the signs of $\Delta f''$ for the anomalous scatters) improved this value slightly, and the least-squares refinement converged (maximum shift/error = 0.04) with the final agreement indices $R_1 = 0.0381$ and $R_2 = 0.0434$ for the 1265 observed reflections. The corresponding weighted R factor for all 1371 independent reflections was $R_2 = 0.0457$. A final difference Fourier contained some residual electron density of 1.4 e/Å^3 close to the antimony and some peaks and troughs of up to 0.5 e/Å^3 in the region of the cation. In the final cycle weights were given by $w^{1/2} = 155 - 1.116F + 0.0032F^2$, and the standard deviation of an observation of unit weight was 0.87.

(2) $S_4N_4 \cdot SbCl_5$. With the positional parameters reported by Neubauer and Weiss,[13] least-squares refinement with all atoms having anisotropic temperature factors converged (maximum shift/error = 0.09) to final agreement indices $R_1 = 0.0391$ ($R_2 = 0.0446$) for 2165 reflections. Weights in the final cycle of refinement were given by the expression $w^{1/2} = 8.8 - 0.105F + 0.002F^2$. A final difference Fourier was featureless.

For both compounds neutral-atom scattering factors were taken from ref[14]. All calculations were performed with the XRAY system[15] and the local program CUDLS. The final atomic parameters and bond lengths and bond angles for the two compounds are given in Table

Table II. Final Atomic Positional ($\times 10^4$) Parameters with Estimated Standard Deviations in Parentheses

atom	x	y	z
	(a) ($S_5N_5^+$)($SbCl_6^-$)		
Sb	1608.7 (4)	613.9 (2)	0 (0)
Cl(1)	3370 (2)	1510 (1)	1381 (6)
Cl(2)	4843 (2)	2260 (1)	3722 (7)
Cl(3)	3030 (2)	2166 (1)	2918 (9)
Cl(4)	3987 (3)	1701 (1)	5451 (6)
Cl(5)	4233 (3)	2082 (1)	−403 (6)
Cl(6)	5185 (2)	1610 (1)	2054 (8)
S(1)	3962 (3)	161 (1)	8557 (7)
S(2)	3476 (2)	367 (1)	5060 (8)
S(3)	3831 (3)	968 (1)	4760 (9)
S(4)	4562 (3)	1094 (1)	8238 (9)
S(5)	4749 (3)	594 (1)	10831 (8)
N(1)	3820 (6)	377 (2)	6993 (18)
N(2)	3531 (7)	667 (3)	4190 (25)
N(3)	4166 (9)	963 (3)	6597 (24)
N(4)	4736 (8)	901 (4)	9674 (23)
N(5)	4393 (8)	317 (4)	10022 (27)
	(b) $S_4N_4 \cdot SbCl_5$		
Sb	1686.5 (1)	2137.5 (1)	972.8 (1)
Cl(1)	516 (5)	2816 (2)	345 (2)
Cl(2)	2576 (5)	1642 (2)	−353 (2)
Cl(3)	902 (5)	2539 (2)	2344 (2)
Cl(4)	4944 (4)	2837 (2)	1600 (2)
Cl(5)	−1492 (4)	1355 (2)	369 (2)
S(1)	1466 (4)	−189 (2)	2044 (2)
S(2)	3692 (6)	675 (3)	3839 (2)
S(3)	7213 (4)	882 (3)	3138 (3)
S(4)	4757 (4)	−2 (2)	1398 (2)
N(1)	2749 (11)	604 (6)	1550 (5)
N(2)	2108 (15)	30 (8)	3106 (8)
N(3)	5505 (16)	1218 (9)	3581 (7)
N(4)	6691 (14)	293 (8)	2212 (8)

---

(14) "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1965.

(15) "XRAY 71 System of Crystallographic Programs", Technical Report TR 192; Computer Science Centre, University of Maryland: College Park, MD, 1972.

Table III. Bond Distances (Å) and Bond Angles (Deg) with Standard Deviations in Parentheses

(a) $(S_5N_5^+)(SbCl_6^-)$

Bond Lengths

Sb–Cl(1)	2.354 (4)	[2.371]	Sb–Cl(4)	2.353 (5)	[2.393]
Sb–Cl(2)	2.372 (4)	[2.309]	Sb–Cl(5)	2.341 (5)	[2.370]
Sb–Cl(3)	2.365 (4)	[2.406]	Sb–Cl(6)	2.356 (4)	[2.380]

S(1)–N(1)	1.556 (13)	S(3)–N(3)	1.484 (18)
S(1)–N(5)	1.518 (18)	S(4)–N(3)	1.533 (18)
S(2)–N(1)	1.557 (14)	S(4)–N(4)	1.429 (19)
S(2)–N(2)	1.548 (15)	S(5)–N(4)	1.664 (19)
S(3)–N(2)	1.565 (14)	S(5)–N(5)	1.566 (18)

Bond Angles

Cl(1)–Sb–Cl(2)	178.2 (2)	Cl(2)–Sb–Cl(6)	89.7 (1)
Cl(1)–Sb–Cl(3)	89.6 (1)	Cl(3)–Sb–Cl(4)	90.3 (2)
Cl(1)–Sb–Cl(4)	89.9 (2)	Cl(3)–Sb–Cl(5)	89.0 (2)
Cl(1)–Sb–Cl(5)	91.4 (2)	Cl(3)–Sb–Cl(6)	179.4 (2)
Cl(1)–Sb–Cl(6)	90.5 (1)	Cl(4)–Sb–Cl(5)	178.5 (2)
Cl(2)–Sb–Cl(3)	90.2 (1)	Cl(4)–Sb–Cl(6)	90.3 (2)
Cl(2)–Sb–Cl(4)	88.3 (2)	Cl(5)–Sb–Cl(6)	90.4 (2)
Cl(2)–Sb–Cl(5)	90.4 (2)		

N(5)–S(1)–N(1)	107.5 (8)	S(1)–N(1)–S(2)	136.5 (8)
N(1)–S(2)–N(2)	109.0 (8)	S(2)–N(2)–S(3)	136.6 (12)
N(2)–S(3)–N(3)	111.8 (9)	S(3)–N(3)–S(4)	154.9 (12)
N(3)–S(4)–N(4)	115.9 (10)	S(4)–N(4)–S(5)	158.1 (13)
N(4)–S(5)–N(5)	120.6 (10)	S(5)–N(5)–S(1)	151.6 (14)

(b) $S_4N_4 \cdot SbCl_5$

Bond Lengths

Sb–Cl(1)	2.334 (3)	Sb–Cl(4)	2.352 (3)
Sb–Cl(2)	2.359 (3)	Sb–Cl(5)	2.342 (3)
Sb–Cl(3)	2.360 (3)	Sb–N(1)	2.134 (7)

S(1)–N(1)	1.651 (9)	S(3)–N(3)	1.585 (13)
S(1)–N(2)	1.569 (12)	S(3)–N(4)	1.533 (12)
S(2)–N(2)	1.541 (10)	S(4)–N(4)	1.581 (9)
S(2)–N(3)	1.580 (13)	S(4)–N(1)	1.662 (9)

Bond Angles

Cl(1)–Sb–Cl(2)	91.7 (1)	Cl(2)–Sb–N(1)	88.5 (3)
Cl(1)–Sb–Cl(3)	91.7 (1)	Cl(3)–Sb–Cl(4)	90.6 (1)
Cl(1)–Sb–Cl(4)	90.9 (1)	Cl(3)–Sb–Cl(5)	89.8 (1)
Cl(1)–Sb–Cl(5)	91.9 (1)	Cl(3)–Sb–N(1)	88.1 (3)
Cl(1)–Sb–N(1)	179.8 (2)	Cl(4)–Sb–Cl(5)	177.2 (1)
Cl(2)–Sb–Cl(3)	176.5 (1)	Cl(4)–Sb–N(1)	89.2 (2)
Cl(2)–Sb–Cl(4)	88.8 (1)	Cl(5)–Sb–N(1)	88.0 (2)
Cl(2)–Sb–Cl(5)	90.7 (1)		

Sb–N(1)–S(1)	123.4 (5)	N(3)–S(3)–N(4)	120.8 (6)
Sb–N(1)–S(4)	123.3 (5)	N(4)–S(4)–N(1)	110.1 (5)
S(1)–N(1)–S(4)	112.6 (5)	S(1)–N(2)–S(2)	139.7 (8)
N(1)–S(1)–N(2)	109.8 (5)	S(2)–N(3)–S(3)	138.4 (8)
N(2)–S(2)–N(3)	119.6 (6)	S(3)–N(4)–S(4)	138.4 (8)

II and III, respectively. Observed and calculated structure factors for each compound are available as supplementary material.

Discussion

Reactions of $S_3N_3Cl_3$. The reaction of $S_3N_3Cl_3$ with $SbCl_5$ was found to give several different products depending on the mole ratio of $SbCl_5$, the concentration of the reactants, and the solvent. The reaction between $S_3N_3Cl_3$ and $SbCl_5$ in a 1:2 molar ratio in sulfur dioxide, thionyl chloride, and methylene chloride all gave a yellow solution that deposited yellow crystals of the hexachloroantimonate salt of the tetrathiazyl cation, $(S_4N_4)(SbCl_6)_2$, which was characterized by comparison of its Raman spectrum with that of a pure sample.[10]

The reaction in thionyl chloride appears to be fastest, giving a yellow solution almost immediately, while in SO_2 and CH_2Cl_2 the reactions are slower and different intermediate colors were observed.

In all three solvents the initial product of the reaction of $SbCl_5$ with $S_3N_3Cl_3$ was a yellow solid. A Raman spectrum of this material was identical with that reported for $(S_3N_3Cl_2)(SbCl_6)$, prepared by Mews et al.,[1] by the action of $SbCl_5$ on $S_3N_3Cl_3$ in carbon tetrachloride. However, in each case this reacted further to give $(S_4N_4)(SbCl_6)_2$. Presumably in CCl_4 this further reaction does not occur.

A green crystalline material was also obtained as a product of the reaction of $S_3N_3Cl_3$ with 2 mol of $SbCl_5$ in SO_2. Comparison of the Raman spectrum with that of $CH_3CN \cdot SbCl_5$[11] suggests that the green material contained $SbCl_5$ coordinated to nitrogen, but it was not otherwise characterized.

No evidence was obtained in the reaction in $SOCl_2$ for the formation of the $S_3N_3Cl_3 \cdot xSbCl_5$ ($x = 1–3$) adducts reported by Bannister[12] as products of the reaction of $S_3N_3Cl_3$ with $SbCl_5$ in a 1:3 molar ratio in thionyl chloride. Reaction of the mixture of products from this reaction with S_4N_4 gave $(S_5N_5)(SbCl_6)$.

In methylene chloride, the reaction mixtures first became orange before yellow $(S_4N_4)(SbCl_6)_2$ was eventually formed. When $S_3N_3Cl_3$ and $SbCl_5$ were reacted in a 1:1 molar ratio in this solvent, the red-orange material could be isolated if the solvent was removed. On recrystallization from SO_2, two crystalline forms were obtained. These were shown by X-ray crystallography to be $(S_5N_5)(SbCl_6)$ and $S_4N_4 \cdot SbCl_5$. When a further mole of $SbCl_5$ was added to the crude red-orange mixture from the 1:1 reaction, the reaction proceeded further and gave yellow $(S_4N_4)(SbCl_6)_2$ within 24 h.

The red material containing $(S_5N_5)(SbCl_6)$ and $S_4N_4 \cdot SbCl_5$ had an ESR spectrum consisting of five lines with a g value of 2.01 and a hyperfine coupling constant of 2.52 G. The latter value suggests that the radical is not $S_3N_2^{+}\cdot$ ($g = 2.01$, $A = 3.15$ G),[9] but the spectrum is nevertheless consistent with that of a sulfur–nitrogen radical containing two equivalent nitrogen atoms. The red color of the material may be due to the presence of this unidentified radical.

When the reaction between 1 mol of $S_3N_3Cl_3$ and 1 mol of $SbCl_5$ was carried out directly in SO_2 as solvent, a yellow-orange solution was obtained after 24 h. A Raman spectrum of the yellow material deposited from solution showed the presence of $(S_4N_4)(SbCl_6)_2$ and $(S_3N_3Cl_2)(SbCl_6)$, but there was no evidence for the $S_5N_5^+$ cation or $S_4N_4 \cdot SbCl_5$.

From the observations described above, it may be concluded that the first step in the reaction of $SbCl_5$ with $S_3N_3Cl_3$ is the formation of $(S_3N_3Cl_2)(SbCl_6)$ whether or not $SbCl_5$ is present in excess. This product although apparently stable in solution in CCl_4 decomposes in solution in SO_2 or CH_2Cl_2 with the formation of the $S_5N_5^+$ cation, $S_4N_4 \cdot SbCl_5$, and probably other products. Addition of a further mole of $SbCl_5$ to the mixture resulting from the 1:1 reaction in SO_2 or CH_2Cl_2 produced the $S_4N_4^{2+}$ cation. It has been found previously that $S_4N_4 \cdot SbCl_5$ is oxidized by further $SbCl_5$ to $S_4N_4^{2+}$.[10] It is surprising that when the products of the reaction of $S_3N_3Cl_3$ with $SbCl_5$ in a 1:1 ratio in methylene chloride were recrystallized from SO_2, $(S_5N_5)(SbCl_6)$ and $S_4N_4 \cdot SbCl_5$ were obtained, but when the reaction was carried out directly in SO_2, neither of these products was observed. Instead some unchanged $(S_3N_3Cl_2)(SbCl_6)$ and $(S_4N_4)(SbCl_6)_2$ were the only products identified.

Reactions of $S_3N_3F_3$. It has been shown by Mews et al.[1] that $S_3N_3F_3$ behaves as a fluoride ion donor with Lewis acids such as AsF_5 or SbF_5 to give the cation $S_3N_3F_2^+$. The purpose of the present study was to determine if $S_3N_3F_3$ could be oxidized to give new cationic species if the $S_3N_3F_3$:Lewis acid ratio was increased above the ratios of 1:1 (SbF_5) and 1:4 (AsF_5) used by Mews et al.[1] Accordingly, $S_3N_3F_3$ was reacted with the Lewis acids AsF_5, SbF_5, and SO_3 in the molar ratios 1:6, 1:6, and 1:3, respectively, with SO_2 as solvent.

The Raman spectra of the products of these reactions (Table I) show that they are $SN^+AsF_6^-$, $SN^+Sb_2F_{11}^-$, and $SN^+SO_3F^-$. In particular a strong band was observed at 1436 cm^{-1} for the SO_3F^- salt and at 1438 cm^{-1} for the AsF_6^- and $Sb_2F_{11}^-$ salts,

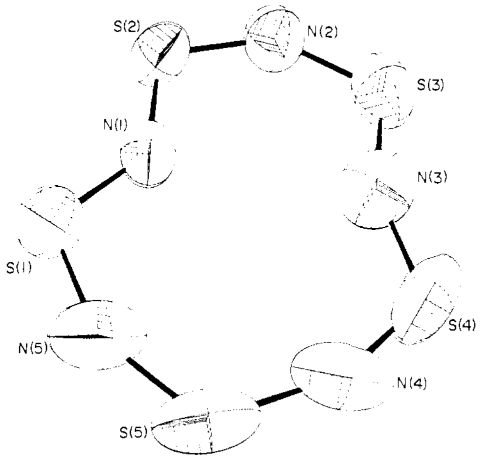


Figure 1. ORTEP view of the pentathiazyl cation in the compound $(S_5N_5)(SbCl_6)$.

which may be attributed to the SN^+ cation. Glemser and Koch have reported a frequency of 1437 cm^{-1} for $SN^+AsF_6^-$.[16] The expected anion frequencies[17,18] were also observed in each case. In addition to low-frequency bands that may be attributed to lattice modes, there were some other unidentified bands that probably indicate that the products were not pure.

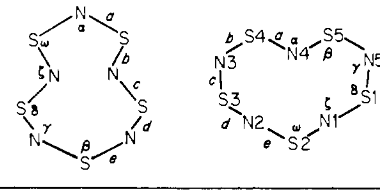
It has been reported previously that $S_3N_3Cl_3$ combines with SO_3 to form the trichlorotrioxocyclotrithiazene $S_3N_3Cl_3O_3$ via the molecular adduct $S_3N_3Cl_3 \cdot 6SO_3$.[19] It appears from our results that the analogous $S_3N_3F_3O_3$ is not produced in the reaction of $S_3N_3F_3$ with SO_3, but rather the $S_3N_3F_3$ ring is depolymerized to produce thiazyl fluorosulfate.

Unlike $S_3N_3Cl_3$, $S_3N_3F_3$ is not oxidized by Lewis acids such as SbF_5 and AsF_5. Instead $S_3N_3F_3$ apparently behaves simply as a fluoride ion donor and successive loss of fluoride ion eventually yields the thiazyl cation although there is no certain evidence for $S_3N_3F^{2+}$ as a stable species.

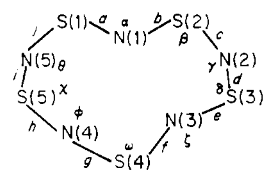
$$S_3N_3F_3 \xrightarrow{MF_5} S_3N_3F_2^+ \xrightarrow{MF_5} S_3N_3F^{2+} \xrightarrow{MF_5} 3SN^+$$

Crystal Structures. The structure determinations show that the crystalline products of the reaction of $S_3N_3Cl_3$ with $SbCl_5$ in a 1:1 mole ratio in CH_2Cl_2 are the known adduct $S_4N_4 \cdot SbCl_5$[13] and the compound $(S_5N_5)(SbCl_6)$ containing the pentathiazyl cation. The $S_5N_5^+$ cation has previously been characterized in the compounds $(S_5N_5)(AlCl_4)$,[20] $(S_5N_5)(S_3N_3O_4)$,[21] and $(S_5N_5)(SnCl_5OPCl_3)$,[22] but it has a different geometry in the present case (Figure 1). It is clear, however, from the anisotropy in the thermal ellipsoids of some of the atoms in the $S_5N_5^+$ cation (Figure 1) that there is very probably some disorder in the present structure. This would explain the differences in the geometry of the present cation when compared with the cations in $(S_5N_5)(S_3N_3O_4)$ and $(S_5N_5)(SnCl_5OPCl_3)$, which are both planar rings with an azulene-like shape and approximately noncrystallographic *mm* symmetry.[21,22] The structure of the cation in $(S_5N_5)(AlCl_4)$ was shown crystallographically[20] to have a heart shape. Subsequently, however, Bannister has suggested that the apparent heart-shaped conformation of this cation arises from a disordering of the "azulene-like" structure.[23] It is presumed that the cations in the structures $(S_5N_5)(S_3N_3O_4)$ and $(S_5N_5)(SnCl_5OPCl_3)$ are ordered as the approximate *mm* symmetry, and equivalent bond lengths are as expected for ordered structures. Although the geometry of the cation in $(S_5N_5)(SbCl_6)$ has neither the azulene or heart-shaped conformations previously observed, it is closest to the azulene structure and probably arises from the superposition (disordering) of two or more azulene-shaped cations which are rotated slightly with respect to each other. All examples of the $S_5N_5^+$ cation including the present salt are planar in the crystal (supplementary Table C).

Table IV. Bond Distances (Å) and Bond Angles (Deg) in the Known Pentathiazyl Cations



(S_5N_5)-$(SnCl_5OPCl_3)$		$(S_5N_5)(S_3N_3O_4)$		$(S_5N_5)(AlCl_4)$	
dist	angle	dist	angle	dist	angle
a 1.58	α 131.5	*a* 1.580	α 133.0	*a* 1.55, 1.56	α 128.9
b 1.52	β 125.0	*b* 1.556	β 124.5	*b* 1.55, 1.54	β 109.1, 110.1
c 1.56	γ 151.0	*c* 1.543	γ 151.0	*c* 1.59, 1.56	γ 137.7, 138.4
d 1.56	δ 111.0	*d* 1.567	δ 109.6	*d* 1.58, 1.47	δ 118.5, 118.6
e 1.56	ζ 141.0	*e* 1.564	ζ 138.3	*e* 1.47, 1.54	ζ 177.1, 177.3
	ω 111.5		ω 108.7		ω 118.4



dist	angle	dist	angle	dist	angle
a 1.56	α 136.5	*d* 1.57	δ 111.8	*g* 1.43	φ 158.1
b 1.56	β 109.0	*e* 1.48	ζ 154.9	*h* 1.66	χ 120.6
c 1.55	γ 136.6	*f* 1.53	ω 115.9	*i* 1.57	θ 151.6
				j 1.52	Σ 107.5

As a result of the disorder in the present cation, the sulfur-nitrogen bond lengths apparently range from 1.43 to 1.66 Å. This may be compared to bond lengths of 1.52–1.58 Å in $(S_5N_5)(S_3N_3O_4)$[21] and 1.54–1.58 Å in $(S_5N_5)(SnCl_5OPCl_3)$.[22] In the disordered $(S_5N_5)(AlCl_4)$ structure, the variation in apparent bond lengths from 1.46 to 1.59 Å is consistent with "thermal" effects on the observed bond lengths due to the disordered model proposed by Bannister[23] (Table IV). In that part of the present cation that appears to be ordered, i.e., where there is almost exact superposition of equivalent positions from the disordered structures (atoms S(1), N(1), S(2), N(2), and S(3)), the bond lengths are 1.54–1.56 Å and are close to the values in the ordered azulene-like structures above. Similarly, in the cation $S_4N_3^+$ the S–N distances are in the range 1.53–1.57 Å,[24-29] and in the ordered planar form of the $S_4N_4^{2+}$ cation the SN distances are 1.546–1.559 Å.[10] It is noteable

---

(16) Glemser, O.; Koch, W. *Angew. Chem., Int. Ed. Engl.* **1971**, *10*, 127.

(17) Goubeau, J.; Milne, J. B. *Can. J. Chem.* **1967**, *45*, 2321.

(18) Gillespie, R. J.; Landa, B. *Inorg. Chem.* **1973**, *12*, 1383.

(19) Goehring, M.; Malaz, H. *Z. Naturforsch., B: Anorg. Chem., Org. Chem., Biochem., Biophys., Biol.* **1954**, *9B*, 567.

(20) Hazell, A. C.; Hazell, R. G. *Acta Chem. Scand.* **1972**, *26*, 1987.

(21) Roesky, H. W.; Bowing, W. G. *J. Chem. Soc., Chem. Commun.* **1975**, 735.

(22) Banister, A. J.; Durrant, J. A.; Rayment, I.; Shearer, H. M. M. *J. Chem. Soc., Dalton Trans.* **1976**, 929.

(23) Banister, A. J.; Durrant, J. A. *J. Chem. Res., Synop.* **1978**, 152; *J. Chem. Res., Miniprint* **1978**, 1931.

(24) Weidenhammer, K.; Ziegler, M. L. *Z. Anorg. Allg. Chem.* **1977**, *434*, 152.

(25) Guru Row, T. N.; Coppens, P. *Inorg. Chem.* **1978**, *17*, 1670.

(26) Mayerle, J. J; Wolmershauser, G.; Street, G. B. *Inorg. Chem.* **1979**, *18*, 1161.

(27) Ziegler, M. L.; Schlimpler, H. U.; Nuber, B.; Weiss, J.; Ertl, G. *Z. Anorg. Allg. Chem.* **1975**, *415*, 193.

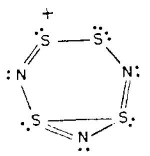
(28) Kruss, B.; Ziegler, M. L. *Z. Naturforsch., B: Anorg. Chem., Org. Chem., Biochem., Biophys., Biol.* **1972**, *27B*, 1282.

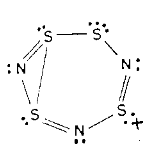
(29) Kruss, B.; Ziegler, M. L. *Z. Anorg. Allg. Chem.* **1972**, *388*, 158.

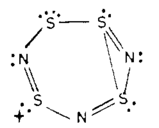
that several examples of the tetrathiazyl cation[10] and the $S_4N_3^+$ cation in $(S_4N_3)[InCl_4(H_2O)_2]$[27] have been found to be disordered.

The cations $S_4N_3^+$, $S_4N_4^{2+}$, and $S_5N_5^+$ have 10, 10, and 14 π electrons, respectively, in excess of the number needed for a σ-bond framework and one lone pair on each atom. It has been suggested[30] that these cations obey the Hückel $4n + 2$ rule and may be considered to be pseudoaromatic SN ring systems with delocalized π bonding. However, it may be inappropriate to extend the σ–π separability and delocalized π MO schemes, which invoke the concepts of aromaticity and Hückel magic number of π electrons in carbon systems, to heteronuclear SN ring systems. Furthermore, these SN cations cannot be described with simple valence-bond structures unless some hypervalence of the sulfur atoms is assumed and transannular bonding interactions are permitted, as have been previously discussed for $S_4N_4^{2+}$.[10] One can then write the resonance structures I–III for $S_4N_3^+$ and similar structures such as IV–VIII for $S_5N_5^+$.

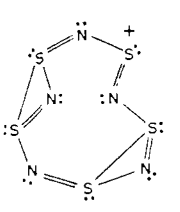
$[S_4N_3^+]$

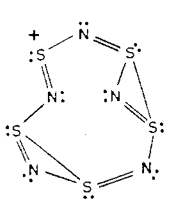

(I)

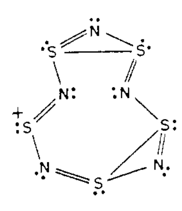

(II)

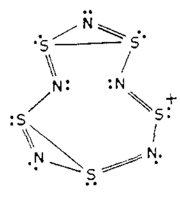

(III)

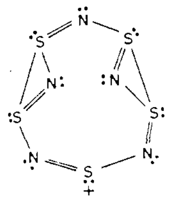
$[S_5N_5^+]$


(IV)

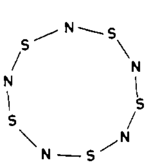

(V)

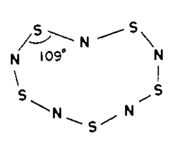

(VI)


(VII)

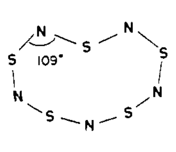

(VIII)

An all-valence electron extended Hückel MO study of various configurations of the $S_5N_5^+$ cation has recently been carried out. The six structural isomers IX–XIV were considered. Initially it was assumed that the SN distances were the same and that all angles at nitrogen and sulfur were equal to 144° with the exception of those indicated. It was found that the reduction of the NSN angles from 144 to 109° reduces the total energy by the same amount that the energy is increased when the corresponding SNS angle is similarly reduced. Thus structures XI and XIV are both destabilized with respect to X and XIII. Furthermore, the predicted total energy differences for these structures, which were primarily a function of the lone-pair combinations in the MO's, were shown to result from either an increase in σ or π-type next-neighbor bonding interactions and an increase or decrease in the bonding or antibonding interactions across the ring. With regard to these transannular interactions it may be noted that the overlap of pσ orbitals is about 5 times smaller for nitrogen compared to sulfur so that structures X and XIII, in which the re-entrant angle(s) are at nitrogen, are stabilized with respect to XI and XIV. Finally it was noted that the total energy of the configuration XIII was lower than that of X and it was suggested that X was only a local minimum.[31]

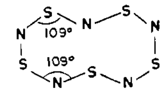

1 (D_{5h}) (IX)



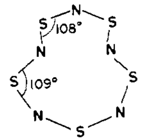
2' (C_{2v}) (X)



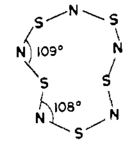
2'' (C_{2v}) (XI)



3' (C_{2v}) (XII)

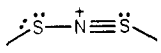


4' (C_{2v}) (XIII)



4'' (C_{2v}) (XIV)

Features of the bond angles in the present cation are the large angles of 155, 158, and 152°, respectively at N(3), N(4), and N(5). Similar large SNS angles are also observed in the azulene and heart-shaped $S_5N_5^+$ cations as well as in the planar $S_4N_4^{2+}$ cation.[10,32] These large angles may be taken to indicate that there are also contributions from having the bond arrangement XV in which the nitrogen "lone pair" also participates in the bonding.


XV

The hexachloroantimonate anion in the present structure is close to octahedral with Sb–Cl bonds of 2.341–2.372 Å (2.370–2.406 Å after applying a riding correction) and cis and trans angles within 2° of the expected values of 90° and 180°. In many hexachloroantimonate(V) structures which have been characterized in the solid state, the Sb–Cl bond lengths are within the range 2.33–2.39 Å. Variations in these bond lengths, and small distortions in the octahedral geometry of the anion, can be correlated with the differences in the environment of each chlorine in the anion.

In the present structure there are several S···Cl anion–cation contacts that are slightly shorter than the van der Waals limit (supplementary Table D), and it may be noted that the longest Sb–Cl bond (2.372 Å) is to the chlorine atom involved in the shortest S···Cl contacts. Also included in this table for comparison are some analogous contacts in the structure of $(S_5N_5)(AlCl_4)$, the only other example of the pentathiazyl cation for which coordinates are available. While the partial disorder in both of these cations means that some of the contact distances need to be viewed with caution, it is apparent that there are some similarities in the contacts to part of each $S_5N_5^+$ ring. In $(S_5N_5)(SbCl_6)$ some of the shortest contacts of lengths (3.468 (7) and 3.309 (7) Å) are from the sulfur atoms S(1) and S(2) to the same chlorine atom Cl(2), which is 0.95 Å out of the plane of the cation. Furthermore, these contacts are close to the projection of the N(5)–S(1) and N(2)–S(2)

---

(30) Banister, A. J. *Nature (London) Phys. Sci.* **1972**, *237*, 92.

(31) Bartetzko, R.; Gleiter, R. *Inorg. Chem.* **1978**, *17*, 995.

(32) One of several correlations between sulfur bond angles and the corresponding sulfur–nitrogen bond distances has been given by Banister in ref 23.

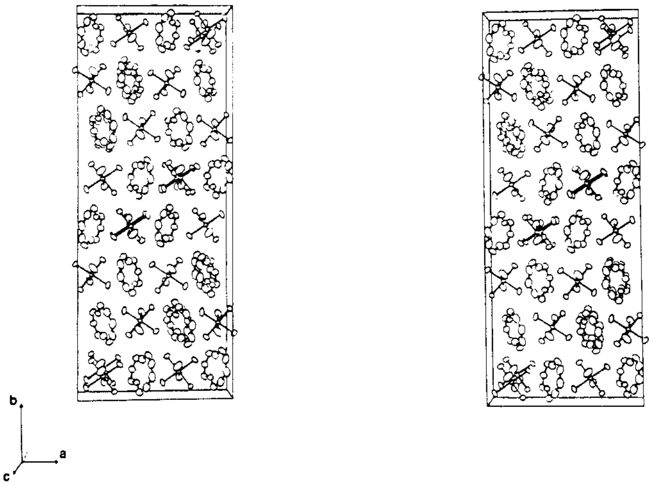


Figure 2. ORTEP view of the crystal packing in $(S_5N_5)(SbCl_6)$ projected down *c*.

bonds [N–S···Cl angles are 164.0 (7) and 156.0 (6)°]. Similarly in the compound $(S_5N_5)(AlCl_4)$ the analogous contacts are S(4)···Cl(4)^{III} and S(5)···Cl(4)^{III}, of lengths 3.493 (3) and 3.495 (3) Å, respectively, with N–S···Cl angles of 158.6 (3) and 158.1 (3)°. In this case the chlorine atom Cl(4) is 0.27 Å out of the plane of the cation. Chlorine atoms which are close to the molecular plane and approximately collinear with the N–S bonds might be considered to be forming weak charge-transfer interactions with the σ^* orbitals of the N–S σ bonds. Similar interactions in $(S_5N_5)(AlCl_4)$ might also involve the chlorine atoms Cl(6)^{I} and Cl(5)^{III}, which are respectively 0.48 and 0.18 Å out of the molecular plane of the cation with N(3)–S(3)···Cl(6)^{I} and N(4)–S(5)···Cl(5)^{III} angles of 160.8 and 150.2°. The lengths of these contacts should be compared to the S···Cl distances of 2.811 (2) Å in the compound $S_4N_5{}^+Cl^-$, which link the anions and cations into polymeric chains,[33] the S···Cl contacts of 3.06–3.12 Å in the structure of 1,7-di-4-tolyltetrasulfurtrinitrogen chloride,[34] and some S···Cl contacts of 2.929–3.288 Å in the structure of $S_3N_2Cl_2$.[35] Thus the interionic contacts involving the present $S_5N_5{}^+$ cation are weak, and there are virtually no contacts to the atoms in the disordered half of the cation. Similarly no contacts were found to be atoms with the highest anisotropic thermal parameters in the cation of $(S_5N_5)(AlCl_4)$, and this anisotropy was attributed to some disorder in this cation.[23] Other examples of compounds containing sulfur–nitrogen cations with strong interactions to anions are discussed elsewhere.[9] A view of the crystal packing in $(S_5N_5)(SbCl_6)$ is given in Figure 2, where it may be noted that there are alternating layers of anions and cations approximately parallel to the (1,2,0) plane.

The second product in the reaction between $S_3N_3Cl_3$ and $SbCl_5$ was identified by its unit cell parameters as the adduct $S_4N_4\cdot SbCl_5$, the crystal structure of which was first determined in 1960 by Neubauer and Weiss.[12] In this original work, the structure was not refined and high accuracy was not claimed. As a consequence, the SN bond lengths and bond angles are not comparable to those reported for the $S_4N_4\cdot BF_3$ adduct.[36] We redetermined the structure in the expectation of obtaining more reliable structural information. Bond distances and bond angles in the redetermined structure are given in Table III and atomic coordinates in Table II. Since the completion of this work several other adducts of S_4N_4 with a variety of Lewis acids have been prepared and characterized,[37] and the crystal structures of the adducts with AsF_5, SO_3, CuCl, and FSO_3-NCO have all been recently published.[38]

The structure of $S_4N_4\cdot SbCl_5$ is comparable to the structures of other S_4N_4 adducts, with the exception of that with CuCl, in that coordination of the Lewis acid is at a nitrogen atom and results in the opening out of the S_4N_4 structure into a saddle conformation with the four sulfur atoms in a plane. The bond lengths and bond angles in the S_4N_4 ring of $S_4N_4\cdot SbCl_5$ do not differ significantly from the distances and angles in the other adducts in which the S_4N_4 is monodentate.[38]

The Sb–N bond in $S_4N_4\cdot SbCl_5$ has a length of 2.134 (7) Å, which is significantly shorter than most other Sb–N bonds, for example, 2.283 (8) Å in $(S_2N_2)(SbCl_5)_2$,[39] 2.179 (14) and 2.193 (15) Å in the bridged complex $[SbCl_4(N_3)]_2$,[40] 2.278 (4) Å in $[SbCl_4NCO]_3$,[41] and 2.340 (6) Å in the compound $[C_4H_7N_2O_2SbCl_4]$,[42] all of which contain six-coordinate antimony. In structures in which the antimony atoms are five-coordinate, the distances tend to be slightly shorter, for example, 2.122, 2.236, and 2.344 Å in the compounds $Ph_3Sb(NCO)_2$, $(Ph_3SbN_3)_2O$, and $(Me_3SbN_3)_2O$.[43–45] From these values it is clear that the $SbCl_5$ is quite strongly coordinated to the S_4N_4 ring.

Acknowledgment. We thank the Natural Science and Engineering Research Council of Canada for financial support of this work.

Registry No. $S_4N_4\cdot SbCl_5$, 12442-70-5; $(S_5N_5)(SbCl_6)$, 39928-97-7; $(SN)(SO_3F)$, 80572-93-6; $(SN)(Sb_2F_{11})$, 77098-60-3; $(SN)(AsF_6)$, 31967-65-4; $S_3N_3Cl_3$, 5964-00-1; $S_3N_3F_3$, 14097-07-5; S_4N_4, 28950-34-7; $SbCl_5$, 7647-18-9; $S_4N_4(SbCl_6)_2$, 64095-05-2; $(S_3N_3Cl_2)(SbCl_6)$, 56174-83-5; SO_3, 7446-11-9; SbF_5, 7783-70-2; AsF_5, 7784-36-3.

Supplementary Material Available: Tables of final thermal parameters (Table A), root-mean-square amplitudes of vibration (Table B), least-squares mean plane (Table C), and some short interionic contacts to the $S_5N_5{}^+$ cations (Table D), and listings of observed and calculated structure factors for $(S_5N_5{}^+)(SbCl_6{}^-)$ and $S_4N_4\cdot SbCl_5$ (24 pages). Ordering information is given on any current masthead page.

---

(33) Chivers, T.; Fielding, L. *J. Chem. Soc., Chem. Commun.* **1978**, 212.

(34) Mayerle, J. J.; Kuyper, J.; Street, G. B. *Inorg. Chem.* **1978**, *17*, 2610.

(35) Zalkin, A.; Hopkins, T. E.; Templeton, D. H. *Inorg. Chem.* **1966**, *5*, 1767.

(36) Heal, H. G.; Nelson, J. *Inorg. Nucl. Chem. Lett.* **1970**, *6*, 429.

(37) Alange, G. G.; Banister, A. J. *Inorg. Nucl. Chem.* **1978**, *40*, 203.

(38) Gillespie, R. J.; Kent, J. P.; Sawyer, J. F. *Acta Crystallogr., Sect. B* **1980**, *B36*, 655 and references therein.

(39) Patton, R. L.; Raymond, K. N. *Inorg. Chem.* **1969**, *8*, 2426.

(40) Muller, U. *Z. Anorg. Allg. Chem.* **1972**, *388*, 207.

(41) Muller, U. *Z. Anorg. Allg. Chem.* **1976**, *422*, 141.

(42) Kruss, B.; Ziegler, M. L. *Z. Anorg. Allg. Chem.* **1973**, *401*, 89.

(43) Ferguson, G.; Goel, R. G.; Ridley, D. R. *J. Chem. Soc., Dalton Trans.* **1975**, 1288.

(44) Ferguson, G.; Ridley, D. R. *Acta Crystallogr., Sect. B* **1973**, *B29*, 2221.

(45) Ferguson, G.; March, F. C.; Ridley, D. R. *Acta Crystallogr., Sect. B* 1975, *B31*, 1260.