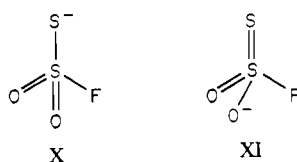


distances in the present anion and that in $(\text{CH}_3\text{C}(\text{OH})_2(\text{S}-\text{O}_3\text{F}))^{51}$

The anion in the structure of $\text{S}_6\text{N}_4(\text{S}_2\text{O}_2\text{F})_2$ is the previously unknown thiofluorosulfate anion $\text{S}_2\text{O}_2\text{F}^-$. During the crystallographic refinement it became clear that the anion has rotational disorder around the S-S bond. Hence the atoms X in Table II were considered to occupy sites which are 67% oxygen and 33% fluorine. Since however two of the S-X distances were then found to be significantly shorter (1.411 (5) Å) than the third (1.438 (5) Å), it would appear that the disorder is not complete. In view of the uncertainty concerning the disorder these bond lengths must be viewed with some caution. We note that the two shorter distances are comparable with the SO distances in the fluorosulfate ion while the longer distance is appreciably shorter than the SF distance in SO_3F^- .

The sulfur-sulfur bond length of 2.071 Å in the $\text{S}_2\text{O}_2\text{F}^-$ ion when compared to that of the S-S bond length of 2.048 Å in S_8^{27} indicates that this bond should be regarded as a single bond as in X and not a double bond as in XI.



As angles involving multiple bonds are invariably found to

be larger than angles on the same atom involving single bonds, the fact that the S(5)-S(4)-X bond angles (103-104°) are substantially smaller than the X-S(4)-X angles (114-117°) is also consistent with the S-S bond being essentially a single bond and the S-X bonds having considerable double-bond character. This conclusion, which appears to be inconsistent with the greater electronegativity of oxygen than sulfur, can perhaps be accounted for on the grounds that the oxygen atom, because of its crowded valence shell, has a much greater tendency to delocalize its electron pairs into vacant orbitals on the central S atom than does the ligand S atom. In other words S=O is preferred to S-O⁻ whereas S-S⁻ is preferred to S=S because oxygen has a strong tendency to relieve the crowding of electron pairs in its valence shell by sharing as many of them as possible.

Acknowledgment. We thank the Natural Sciences and Engineering Research Council of Canada for financial support of this work and Dr. A. J. Banister for kindly supplying atomic coordinates for the structure of $(\text{S}_6\text{N}_4)(\text{S}_2\text{O}_6\text{Cl})$ for comparison with the present data.

Registry No. $\text{S}_6\text{N}_4(\text{S}_2\text{O}_2\text{F})_2$, 78198-88-6; $\text{S}_6\text{N}_4(\text{SO}_3\text{F})_2$, 78198-89-7; $\text{S}_6\text{N}_4(\text{AsF}_6)_2$, 58080-67-4; S_4N_4 , 28950-34-7; HSO_3F , 7789-21-1; AsF_5 , 7784-36-3; $\text{S}_8(\text{AsF}_6)_2$, 33248-05-4; $\text{Te}_6(\text{AsF}_6)_4$, 12536-36-6.

Supplementary Material Available: A listing of structure factor amplitudes (29 pages). Ordering information is given on any current masthead page.

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Reactions of S_4N_4 with SbCl_5 , SbF_5 , AsF_5 , PF_5 , and HSO_3F . Preparation and Crystal Structures of Salts of the $\text{S}_4\text{N}_4^{2+}$ Cation: $(\text{S}_4\text{N}_4)(\text{Sb}_3\text{F}_{14})(\text{SbF}_6)$, $(\text{S}_4\text{N}_4)(\text{SO}_3\text{F})_2$, $(\text{S}_4\text{N}_4)(\text{AsF}_6)_2 \cdot \text{SO}_2$, $(\text{S}_4\text{N}_4)(\text{AlCl}_4)_2$, and $(\text{S}_4\text{N}_4)(\text{SbCl}_6)_2$

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The reactions of S_4N_4 with the Lewis acids SbCl_5 , AlCl_3 , PCl_5 , PF_5 , AsF_5 , and SbF_5 with principally SO_2 as the solvent are reported. It is shown that PF_5 and PCl_5 are not strong enough oxidants to produce any sulfur-nitrogen cationic species but instead give a simple adduct and a mixture of chlorosulfanes and chlorophosphazenes, respectively. However, SbCl_5 , AsF_5 , and SbF_5 in a 3:1 or larger mole ratio oxidize S_4N_4 to the dicationic species $\text{S}_4\text{N}_4^{2+}$, and the compounds $(\text{S}_4\text{N}_4)(\text{SbCl}_6)_2$, $(\text{S}_4\text{N}_4)(\text{Sb}_3\text{F}_{14})(\text{SbF}_6)$, and $(\text{S}_4\text{N}_4)(\text{AsF}_6)_2(\text{SO}_2)$ have been prepared and their crystal structures determined. In addition, the compound $(\text{S}_4\text{N}_4)(\text{AlCl}_4)_2$ has been prepared by oxidizing the $\text{S}_4\text{N}_4 \cdot \text{AlCl}_3$ adduct with chlorine in the presence of a stoichiometric amount of AlCl_3 , and the $(\text{S}_4\text{N}_4)(\text{SO}_3\text{F})_2$ salt has been obtained from the reaction of S_4N_4 with fluorosulfuric acid. Crystal structures of both of these latter two compounds are reported. It is shown from these crystals that the $\text{S}_4\text{N}_4^{2+}$ cation usually has the form of a planar ring with D_{4h} symmetry and equal bond lengths, although a nonplanar boat-shaped structure has been found for the $\text{S}_4\text{N}_4^{2+}$ cation in the $(\text{S}_4\text{N}_4)(\text{SbCl}_6)_2$ salt. The nature of the bonding in the $\text{S}_4\text{N}_4^{2+}$ cation and the strong interionic contacts involving the novel mixed $\text{Sb}^{\text{III}}-\text{Sb}^{\text{V}}$ anion, $\text{Sb}_3\text{F}_{14}^-$, are discussed.

Introduction

Tetrasulfur tetranitride has been known for some time to form adducts with a variety of Lewis acids.¹⁻⁴ The majority of these compounds have a 1:1 stoichiometry, and X-ray crystallographic structures of the 1:1 adducts with BF_3 , SbCl_5 , AsF_5 , SO_3 , and FSO_3NCO show that in each case the Lewis acid is coordinated to a nitrogen atom and the S_4N_4 cage opens up to a saddle-shaped ring with all the sulfur atoms in a plane.

The reported examples of 2:1 adducts, i.e., $(\text{S}_4\text{N}_4)_2\text{SnCl}_4$ and $(\text{S}_4\text{N}_4)_2\text{TiCl}_4$, are probably simple adducts involving six-coordinated tin and titanium.

In addition to these relatively simple 1:1 and 2:1 adducts, others have been reported with different compositions including $\text{S}_4\text{N}_4 \cdot 2\text{BCl}_3$,⁵ $\text{S}_4\text{N}_4 \cdot 2\text{SbCl}_5$,⁵ $\text{S}_4\text{N}_4 \cdot 4\text{SbF}_5$,⁵⁻⁷ $\text{S}_4\text{N}_4 \cdot 2\text{SO}_3$,⁸ and $\text{S}_4\text{N}_4 \cdot 4\text{SO}_3$ ⁸ as well as a number of mixed complexes such as $\text{S}_4\text{N}_4 \cdot \text{BCl}_3 \cdot \text{SbCl}_5$,⁵ $\text{S}_4\text{N}_4 \cdot \text{AlCl}_3 \cdot \text{SbCl}_5$,⁹ $\text{S}_4\text{N}_4 \cdot \text{BCl}_3 \cdot \text{SO}_3$, and

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$S_4N_4 \cdot TeCl_4 \cdot SO_3$.⁶ Infrared evidence has been presented in support of ionic structures for these mixed compounds, e.g., $(S_4N_4BCl_2^+)(SbCl_6^-)$ and $(S_4N_4TeCl_3^+)(SO_3Cl^-)$,^{5,6} and Paul and co-workers⁶ have suggested that the $S_4N_4 \cdot 4SbF_5$ complex may have an analogous structure, i.e., $(S_4N_4SbF_4^+)(Sb_3F_{16}^-)$.

Recently it has been shown that sulfur-nitrogen cations may be formed in the reactions of Lewis acids with S_4N_4 particularly if the solvent is highly polar or if the mole ratio of Lewis acid to S_4N_4 is increased to 3:1 or larger. For example, Bannister et al.¹⁰ have isolated the salt $S_3N_5^+AlCl_4^-$ from the reaction of S_4N_4 with an equimolar amount of $AlCl_3$ in thionyl chloride as solvent whereas the simple 1:1 adduct was obtained in 1,2-dichloromethane as solvent. It has also been reported¹¹ that if AsF_5 is reacted with S_4N_4 in a 3:1 mole ratio the product is the hexafluoroarsenate salt of the $S_3N_2^+$ cation and not the $S_4N_4 \cdot AsF_5$ adduct. It has subsequently been shown that this compound should in fact be formulated as the hexafluoroarsenate salt of the dimeric $S_6N_4^{2+}$ cation.¹²

As it seemed from this earlier work that reaction of S_4N_4 with Lewis acids having oxidizing properties might be a route to new sulfur-nitrogen cations, a systematic study of the reactions of S_4N_4 with the Lewis acids $SbCl_5$, $AlCl_3$, PCl_5 , PF_5 , AsF_5 , SbF_5 , and related compounds was undertaken using principally SO_2 as solvent. In the present paper we report the preparation and crystal structures of the compounds $(S_4N_4)(Sb_3F_{14})(SbF_6)$, $(S_4N_4)(AsF_6)_2(SO_2)$, $(S_4N_4)(AlCl_4)_2$, and $(S_4N_4)(SbCl_6)_2$ and the characteristic vibrational frequencies of the $S_4N_4^{2+}$ cation. In the course of a study of the reaction of S_4N_4 with HSO_3F , crystals of the compound $(S_4N_4)(SO_3F)_2$ were obtained among several other products. This reaction and its products are discussed in detail in another paper,¹² but the structure of $(S_4N_4)(SO_3F)_2$ is reported here. It is shown that all five structures contain the dipositive cation $S_4N_4^{2+}$, which is a planar ring with equal SN bond lengths except in the salt $(S_4N_4)(SbCl_6)_2$ in which the ring appears to have a nonplanar boat conformation. A preliminary report of the structures of two of these compounds has appeared.¹³

Experimental Section

All reactions were carried out under vacuum in flame-sealed double-arm ampules fitted with medium glass frits. Tetrasulfur tetranitride was prepared as previously described.¹² Sulfur dioxide (Matheson) was repeatedly distilled from, and stored over, phosphoric oxide. Arsenic pentafluoride, phosphorus pentachloride, and phosphorus pentafluoride (Ozark Mahoning Co.) were used directly from the cylinder and were measured on a calibrated Pyrex vacuum line. Antimony pentafluoride (Ozark Mahoning Co.), doubly distilled in a Pyrex glass still before use, was stored in dry Pyrex bottles in a drybox. Antimony pentachloride (Baker Analyzed Reagent) was used directly. All manipulations involving air-sensitive reactants and products were performed in a drybox under an atmosphere of nitrogen. IR spectra were recorded on a Perkin-Elmer grating infrared spectrometer Type 283 or a Nicolet FT-IR spectrometer. Powdered samples were prepared in Nujol dried over sodium wire. Spectra were recorded in the 4000–200-cm⁻¹ range with use of CsI windows. Raman spectra were recorded on a Spex Industries Model 1400 ^{3/4}-m Czerny-Turner double monochromator using a Spectra Physics Model 164 argon ion laser (5145 Å) or a Spectra Physics Model 125 He-Ne laser (6328 Å). Fluorine NMR spectra were obtained at room temperature with the use of either a Varian DA-60 spectrometer (56.4 MHz) or a Varian HA-100 spectrometer (96.4 MHz). Samples were prepared in 5-mm o.d. medium-precision polished glass NMR tubes (Wilmad Glass Co.). Phosphorus NMR spectra were recorded on a Bruker WH90 NMR spectrometer (36.43 Hz). The spectrometer

was internally locked to the deuterium signal of CD_2Cl_2 in the sample solution, and all shifts are reported with the use of 85% phosphoric acid as a reference.

Analyses were by Schwarzkopf Microanalytical Laboratory and Pascher Microanalytisches Laboratorium.

Reaction of S_4N_4 with $SbCl_5$. For a reaction with a large excess of $SbCl_5$, 250 mg (1.35 mmol) of S_4N_4 was added to one side of the reaction vessel and 4.06 g (13.5 mmol) of $SbCl_5$ was added to the other bulb of the reaction vessel. Sulfur dioxide (10 mL) was condensed at -196 °C into each bulb, and both ends were flame sealed. Upon warming to room temperature, the $SbCl_5$ completely dissolved but some S_4N_4 remained undissolved. The $SbCl_5$ solution was poured onto the S_4N_4 solution which immediately became deep red. After 24 h of stirring, a yellow orange solution was obtained containing some bright yellow solid. The latter was filtered off, and on heating it gave a sublimate which was shown from its Raman spectrum to be $SbCl_5$. On slow removal of the solvent from the solution, small yellow needlelike crystals were obtained.

The same reaction was carried out with the use of a 1:3 mole ratio, i.e., 250 mg (1.35 mmol) of S_4N_4 and 1.22 g (4.07 mmol) of $SbCl_5$. The reaction proceeded as above, and the Raman spectrum of the yellow crystals was the same as that given by the product from the reaction above. A crystal of this material was identified by X-ray analysis as the compound $(S_4N_4)(SbCl_6)_2$. The same reaction was also carried out in CH_2Cl_2 as solvent and gave the same product. Anal. Calcd for $S_2N_2SbCl_6$: S, 15.03; N, 6.54; Sb, 28.54; Cl, 49.86. Found: S, 14.18, 14.81; N, 6.54, 6.74; Sb, 28.83, 30.77; Cl, 46.82, 48.74.

When the reaction was carried out with a 1:2 molar ratio, i.e., 250 mg (1.35 mmol) of S_4N_4 and 810 mg (2.71 mmol) of $SbCl_5$, the product was an orange solid which did not appear to be very stable. Good crystals could not be obtained, and when crystallization was carried out slowly the product always contained both the $S_4N_4 \cdot SbCl_5$ adduct and the $(S_4N_4)(SbCl_6)_2$ salt. When this mixture was reacted with an additional mole of $SbCl_5$, only $(S_4N_4)(SbCl_6)_2$ was obtained.

When S_4N_4 and $SbCl_5$ were reacted in a 1:1 molar ratio, i.e., 250 mg (1.35 mmol) of S_4N_4 and 404 mg (1.35 mmol) of $SbCl_5$, a solid red material was obtained. This material had an infrared spectrum that was identical with that of a product obtained from methylene chloride solution, previously identified as the 1:1 adduct by Jolly and co-workers.⁵ On reacting this material with a further 2 mol of $SbCl_5$, only $S_4N_4(SbCl_6)_2$ was obtained.

Reaction of S_4N_4 with PF_5 . Tetrasulfur tetranitride (250 mg, 1.35 mmol) was placed in one arm of the reaction vessel, and 490 mg (3.89 mmol) of PF_5 was condensed on at -196 °C followed by 20 mL of SO_2 . The vessel was flame sealed and allowed to warm to room temperature. A deep red solution was obtained immediately, and after several days of stirring, what appeared to be a small amount of unreacted S_4N_4 was filtered off. On slow removal of solvent from the solution a bright red crystalline material was obtained. The reaction was repeated with the use of a $S_4N_4:PF_5$ ratio of 1:1, and the product was found to be identical with that obtained above. The product was identified as the adduct $S_4N_4 \cdot PF_5$ by means of its ¹⁹F and ³¹P NMR spectra. The infrared spectrum had the following bands: 1069 (s), 1010 (sh), 969 (ms), 902 (m), 877 (sh), 842 (m), 803 (sh), 785 (m), 720 (sh), 680 (mw), 623 (w), 610 (sh), 598 (w), 570 (w), 519 (s), 455 (s), 389 (m), 369 (s), 311 (m), and 239 (w) cm⁻¹.

Reaction of S_4N_4 with PCl_5 . These reactions were carried out in CH_2Cl_2 because of the solvolysis of PCl_5 by SO_2 . Phosphorus pentachloride (113 mg, 0.54 mmol) and S_4N_4 (100 mg, 0.54 mmol) were placed in the same bulb of the reaction vessel, and 20 mL of CH_2Cl_2 was distilled on at -196 °C. On warming to room temperature, a bright orange solid was formed which within 0.5 h changed to a black-green solid in an orange solution. The ³¹P NMR spectrum of the solution showed the presence of a number of phosphorus-containing species which were not identified with certainty. Removal of the solvent produced a viscous oil which had the odor of chlorosulfanes and had Raman bands at 512 and 210 cm⁻¹ which can be attributed to SCl_2 . When the reaction was carried out with a 1:3 mole ratio of S_4N_4 to PCl_5 , the reaction appeared to be similar although the ³¹P spectrum of the solution differed somewhat from that obtained in the above reaction.

Reaction of S_4N_4 with SbF_5 . Antimony pentafluoride (938 mg, 4.38 mmol) and S_4N_4 (199 mg, 1.08 mmol) were placed in separate bulbs of the reaction vessel, and 10 mL of SO_2 was condensed into both sides of the apparatus at -196 °C. The vessel was allowed to warm to room temperature, and the SbF_5 solution was then poured

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onto the S_4N_4 solution. An immediate red color was formed which became purple within a few minutes and then within 0.5 h turned green. After several days without stirring, some white solid precipitated which was filtered off. Slow removal of the solvent gave golden yellow crystals which had the composition $SNSbF_5$. Anal. Calcd for $SNSbF_5$: S, 12.20; N, 5.33; Sb, 46.33; F, 36.10. Found: S, 11.16; N, 4.54; Sb, 47.87; F, 37.10. An X-ray study of one of the crystals showed it to be $(S_4N_4)(Sb_3F_{14})(SbF_6)$. The white precipitate was identified as $SbF_3 \cdot SbF_5$ by means of its Raman spectrum.¹⁴

With use of a 1:3 molar ratio of reactants and constant stirring, the insoluble white material which formed was identified as SbF_3 by Raman spectroscopy.¹⁵ The yellow crystalline material which was finally obtained was identified as $(S_4N_4)(SbF_6)_2 \cdot xSO_2$ by means of its Raman and infrared spectra. In order to obtain crystalline samples of this salt, it was necessary to flame seal the vessel containing the final product at $-78^\circ C$ in order to prevent too rapid a loss of the solvent which gave a pale yellow powder rather than the desired crystalline material.

Reaction of S_4N_4 with AsF_5 . In a typical reaction, S_4N_4 (250 mg, 1.35 mmol) was reacted with AsF_5 (692 mg, 4.0 mmol) in SO_2 solution. The color of the solution became red as it warmed to room temperature and then green after about 1 h, and finally brownish green over a period of 24 h. No further color change was observed even after 1 week. The solution was allowed to stand and, if necessary, the solvent slowly removed until yellow cubic-shaped crystals were obtained. These crystals were shown by infrared and Raman spectroscopy to be $(S_4N_4)(AsF_6)_2 \cdot xSO_2$. The same product was obtained when a molar ratio of reactants of 1:6 was used.

Reaction of S_4N_4 with $AlCl_3$ and Chlorine. S_4N_4 (250 mg, 1.35 mmol) and $AlCl_3$ (362 mg, 2.71 mmol) were added to one side of a double-bulb reaction vessel. The vessel was evacuated, and chlorine (192 mg, 2.71 mmol) and sulfur dioxide (10 mL) were condensed at $-196^\circ C$ onto the solid reactants. When the vessel was warmed to room temperature, the solution turned a cherry red color which remained on stirring for 24 h. The solution was filtered, and after the solvent had been slowly removed for 24 h large yellow prismatic crystals were formed. After the crystals were washed with sulfur dioxide, they were isolated and one crystal was identified as the $(S_4N_4)(AlCl_4)_2$ salt by crystallographic examination.

An alternate method may be used to obtain the above salt from trithiazyl trichloride and $AlCl_3$. In a typical reaction, 250 mg (1.02 mmol) of $S_3N_3Cl_3$ and 273 mg (2.04 mmol) of $AlCl_3$ were added to one side of the reaction vessel. Sulfur dioxide was condensed onto the solid reactants, and the vessel was flame sealed. When the reaction mixture was warmed to room temperature, a reddish green color developed. After 24 h of stirring, the solution became orange. No further color changes were noted in the next 24-h period. The solvent was slowly removed giving yellow prismatic crystals. The product gave an identical Raman spectrum with that obtained from the compound $S_4N_4(AlCl_4)_2$ identified above.

X-ray Crystallography

X-ray Intensity Measurements. (1) $S_4N_4Sb_3F_{14}SbF_6$. Crystalline samples of $(S_4N_4)(Sb_3F_{14})(SbF_6)$ and $(S_4N_4)(SbF_6)_2 \cdot xSO_2$ are both yellow in the presence of SO_2 . However, in the case of $(S_4N_4)(SbF_6)_2 \cdot xSO_2$, the SO_2 is very easily lost from the lattice, producing a pale yellow powder which turns black on exposure to traces of moisture. From the block-shaped crystals of $(S_4N_4)(Sb_3F_{14})(SbF_6)$, it was possible to cut and shape several crystals into approximate spheres before sealing them in Lindemann capillaries under a dry-air atmosphere in a specially designed drybox equipped with a microscope. All other crystals were also handled and mounted in Lindemann capillaries with the use of the same drybox.

(2) $(S_4N_4)(SO_3F)_2$. The crystal of this compound, an approximately rectangular block, was obtained as one of several products of the reaction of S_4N_4 with fluorosulfuric acid. The crystal used was red and not colorless or yellow like the crystals of the other $S_4N_4^{2+}$ salts studied. As there was a significant interval of time between mounting this crystal and its final examination, the red color may be a surface effect due perhaps to the production of some radical species. The

diffraction photographs appear to be unaffected by any possible surface reactions.

(3) $(S_4N_4)(AsF_6)_2SO_2$. Freshly prepared crystals occur as clear colorless blocks sometimes coated with a second unidentified straw colored material. Although crystals were selected and sealed in Lindemann capillaries in the drybox with only trace amounts of moisture present and in a minimum of time, the mounted crystals eventually became black on their surface. However, the crystals did not show any marked loss in crystallinity and gave good diffraction photographs even after several months in the Lindemann capillaries.

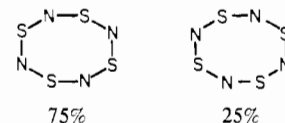
(4) $(S_4N_4)(SbCl_6)_2$. Freshly prepared crystals are thin yellow needles which on exposure to even trace amounts of moisture gradually became deep red. Despite this color change, the crystals gave good diffraction patterns. The preliminary precession photographs on this compound appeared to indicate that the crystals were tetragonal (needle axis c as rotation axis). Least-squares refinement of 2θ , ω , and χ for 15 high-angle ($25 < 2\theta < 29^\circ$) reflections on a Syntex P2₁ diffractometer also gave a pseudotetragonal cell $17.904(5) \times 17.897(5) \times 13.551(4) \text{ \AA}$. However, the γ angle for this cell was only 89° , and the correct orthorhombic cell was given by taking the diagonals $1/2(\bar{a} + \bar{b})$ and $1/2(\bar{a} - \bar{b})$ of the "tetragonal" cell as a_{orth} and b_{orth} .

(5) $(S_4N_4)(AlCl_4)_2$. Crystals of this compound occur as large well-defined yellow blocks and rhombuses. The crystal used in the data collection was, however, a trapezoidal-shaped plate obtained by cleaving a large crystal into smaller fragments. Some darkening of the surface was again observed.

All further work on each crystal was performed on a Syntex P2₁ diffractometer using graphite-monochromatized $Mo K\alpha$ radiation ($\lambda = 0.71069 \text{ \AA}$). Unit cell dimensions were obtained in each case by a least-squares fit of 2θ , ω , and χ for 15 high-angle reflections normally in the 2θ range $25 < 2\theta < 30^\circ$. The resulting crystal data and other details of the data collection options used for each crystal are included in Table I.

For all five data sets, Lorentz and polarization corrections were applied to all reflections. Absorption corrections were applied as indicated (Table I). After equivalent data were averaged and reflections which either were systematically extinct or have observed structure amplitudes equal to 0, were excluded the final numbers of nonzero data in each data set were as given in Table I.

Structure Solutions. (1) $(S_4N_4)(Sb_3F_{14})(SbF_6)$. The structure of this compound was solved with the use of direct methods (XRAY 71¹⁶). Subsequent Fourier maps gave the positions of the remaining atoms in the structure. Least-squares refinement of the positional and anisotropic thermal parameters of all atoms in the structure using 3688 observed reflections converged to give the residual $R_1 = 0.036$.¹⁷ At this point it was noted that the geometry of the two independent $S_4N_4^{2+}$ cations in the structure were different. While the $S_4N_4^{2+}$ ring at (0, 0, 0) appeared to be planar with equal S-N bond lengths, that at $(1/2, 0, 1/2)$, although also planar, had some alternation in the S-N distances around the ring. However, it had been noted earlier that the isotropic temperature factors for the atoms N(3) and N(4) were significantly lower than those for N(1) and N(2), although the corresponding temperature factors for the four sulfur atoms were very similar. One explanation for these temperature factor differences was to assume that the second ring was disordered, and it was found that a significant lowering in the residual to $R_1 = 0.033$ could be obtained on refining the population parameters for the atoms in this second cation. The population parameters resulting from this last refinement indicated that there were 13.25 and 9.25 $e/\text{\AA}^3$ at the sites assumed to be sulfur and nitrogen, respectively. This is consistent with a disordered model in which the cation at $(1/2, 0, 1/2)$ exists 75% in one orientation and 25% in the orientation obtained by rotating the cation by 180° about an axis bisecting an opposite pair of bonds. This superimposed sulfur on nitrogen and nitrogen on sulfur.



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(17) $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$. $R_2 = [\sum w|F_o| - |F_c|]^2 / \sum wF_o^2$ ^{1/2}.

Table I

	(S ₄ N ₄)(Sb ₃ F ₁₄)(SbF ₆)	(S ₄ N ₄)(SO ₃ F) ₂	(S ₄ N ₄)(AsF ₆) ₂ ·SO ₂	(S ₄ N ₄)(AlCl ₄) ₂	(S ₄ N ₄)(SbCl ₆) ₂
Crystal Data					
system	monoclinic	monoclinic	monoclinic	monoclinic	orthorhombic
<i>a</i> , Å	16.292 (3)	6.121 (2)	13.404 (2)	6.908 (2)	12.775 (3)
<i>b</i> , Å	16.162 (4)	13.540 (4)	7.958 (1)	16.117 (3)	12.543 (3)
<i>c</i> , Å	8.446 (1)	7.005 (2)	15.341 (3)	9.005 (2)	13.550 (3)
β, deg	109.52 (1)	108.89 (2)	100.05 (1)	122.24 (2)	
<i>U</i> , Å ³	2096.2 (7)	549.3 (3)	1611.4 (5)	848.1 (3)	2171.1 (9)
<i>D</i> _{calcd} , g cm ⁻³	3.33	2.31	2.58	2.04	2.61
<i>Z</i>	4	2	4	2	4
fw	1051.1	382.4	610.2	521.8	853.1
<i>F</i> (000)	1904	380	1192	508	1592
μ(Mo Kα)	60.2	12.6	51.4	18.7	44.8
space group	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>c</i>	<i>C</i> 2/ <i>c</i> (or <i>Cc</i>)	<i>P</i> 2 ₁ / <i>n</i>	<i>Pbcn</i>
Data Collections					
mode		θ:2θ			
wavelength		Mo Kα radiation (λ = 0.710 69 Å)			
stds	3/67	3/47	3/37	3/37	3/37
no./interval ^a	(0, 5, 2), (7, 0, 1), and (5, 2, 3)	(2, 1, 1), (1, 4, 3), and (3, 4, 4)	(1, 1, 3), (2, 2, 3), and (2, 4, 6)	(2, 2, 3), (2, 0, 0), and (3, 1, 4)	(3, 0, 2), (2, 3, 4), and (1, 2, 7)
scan range, deg	Kα ₁ - 0.8 to Kα ₂ + 0.8	Kα ₁ - 1.0 to Kα ₂ + 1.0	Kα ₁ + 0.75 to Kα ₂ + 0.75	Kα ₁ - 0.85 to Kα ₂ + 0.85	Kα ₁ - 0.9 to Kα ₂ + 0.9
scan speeds, ^b deg/min	2.5-29.3	3.0-29.3	2.5-29.3	2.2-29.3	2.0-29.3
max 2θ, deg	55	55	50	55	50
bkgds	stationary crystal-stationary counter at each end of scan, each for one-quarter of scan time				
Details of Refinements					
abs	spherical	none	absorb	absorb	absorb
cor	μ _R = 0.75 (<i>R</i> = 0.013 cm) <i>A</i> *: 2.84-2.95		{1,1,1}: 0.0125 {1,0,0}: 0.0100 {0,0,1}: 0.0075 8 × 6 × 10 grid <i>A</i> *: 2.098-2.498	{0,1,0}: 0.0050 {1,0,0}: 0.0105 (1,0,4): 0.0125 (1,0,2): 0.0045 7 × 11 × 7 grid <i>A</i> *: 1.184-1.404	{1,0,0}: 0.00325 {0,1,0}: 0.00325 {0,0,1}: 0.02850 6 × 6 × 12 grid <i>A</i> *: 1.306-1.371
no. of nonzero data	4596	1226	1598	1759	1679
no. of data with <i>F</i> ≥ 2.0σ(<i>F</i>)	4312	1125 (<i>F</i> > 1.0σ(<i>F</i>))	1180	1594	1551
no. of data with <i>F</i> ≥ 6.0σ(<i>F</i>)	3673	936	905	1191	1225
<i>R</i> factors					
2σ: <i>R</i> ₁	0.040	0.034	0.063	0.057	0.051
<i>R</i> ₂	0.038	0.038	0.057	0.048	0.042
6σ: <i>R</i> ₁	0.031	0.027	0.045	0.038	0.033
<i>R</i> ₂	0.033	0.033	0.048	0.038	0.033
max shift/error	0.09	0.03	0.20	0.11	0.28
weighting scheme ^c					
<i>w</i> = <i>x</i> * <i>y</i> <i>A</i>	48.0	6.5	30.0	16.0	60.0
<i>B</i>	105.0	14.0	100.0	35.0	145.0
<i>C</i>	0.28	0.32	0.23	0.21	0.18
<i>D</i>	0.40	0.45	1.00	0.33	0.33

^a No systematic trends in the intensities of the standards were observed. ^b Dependent on prescan. ^c In the weighting scheme *w* = *x***y*: (1) *x* = *F*/*A* if *F* < *A* or *x* = *B*/*F* if *F* > *B*, otherwise *x* = 1.0, and (2) *y* = (sin θ)/*C* if sin θ < *C*, or *y* = *D*/sin θ if sin θ > *D*, otherwise *y* = 1.0. In each case the final comparison of the average *w*||*F*_o|| - ||*F*_c||² as a function of *F*_o and sin θ after the use of these schemes showed no systematic trends.

With use of this disordered model, the least-squares refinement converged to the final residuals shown in Table I. A final difference Fourier contained a maximum residual peak of 3.0 e/Å³ close to Sb(2). However, no other peaks in the map were greater than 1.5 e/Å³.

(2) (S₄N₄)(SO₃F)₂. The structure of this compound was solved with the use of the direct-methods routines of the program SHELX¹⁸ after rescaling the normalized structure factors of reflections (*hkl*) with *k* = 2*n* + 1 so that they were comparable in magnitude to those reflections (*hkl*) with *k* = 2*n* and would thus interact much more strongly in the sign-determining process. The best *E* map gave the positions of virtually all the atoms in the structure, and missing atoms were located in a following Fourier map. Atomic assignments in the anion were made on the basis of isotropic temperature factors and bond lengths.

Least-squares refinement of an ordered model gave a residual *R*₁ = 0.029 for 936 observed data (all atoms with anisotropic temperature factors). At this point it was observed that the sulfur-fluorine bond in the fluorosulfate anion was too short and one of the sulfur-oxygen

distances too long for the anion to be ordered. Refinement of the population parameters for these two atoms confirmed that this anion was disordered with *C*_{2v} symmetry compared with the expected *C*_{3v} symmetry. This is common for the fluorosulfate anion.^{12,19} An average scattering factor *f*_x = 1/2(*f*_O + *f*_F) was introduced for these two atoms. The least squares then converged to the final agreement indices in Table I. A final difference Fourier was featureless with no peak greater than +0.33 e/Å³ or trough greater than -0.61 e/Å³.

(3) (S₄N₄)(AsF₆)₂(SO₂). The systematic absences for this compound are consistent with the space groups *C*2/*c* (centric) and *Cc* (acentric). The centric space group *C*2/*c* was initially assumed. This space group imposes crystallographic symmetry on the S₄N₄²⁺ ring since *Z* = 4. The positional coordinates for one arsenic atom was readily obtained from a Patterson map and a subsequent Fourier map indicated likely positions for the S₄N₄²⁺ cation and six fluorine atoms in the AsF₆⁻ anion. A subsequent difference Fourier then revealed the presence of an SO₂ solvent molecule on a special position (symmetry 2). When the occupancies of the atoms in this solvent molecule

(18) Sheldrick, G. M. SHELX Program for Crystal Structure Determination, University of Cambridge, England, 1976.

(19) O'Sullivan, K.; Thompson, R. C.; Trotter, J. J. *Chem. Soc. A* 1970, 1814.

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

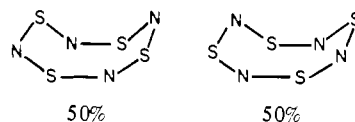
atom	x	y	z	atom	x	y	z
(a) $(S_4N_4)(Sb_3F_{14})(SbF_6)$ (1)				(c) $(S_4N_4)(AsF_6)_2(SO_2)$ (3)			
Sb(1)	-2054.2 (3)	4772.4 (3)	1845.1 (6)	As(1)	1412.1 (7)	1058.1 (12)	1272.0 (6)
Sb(2)	-3205.7 (3)	2150.8 (3)	1549.6 (5)	F(1)	862 (5)	2317 (8)	445 (4)
Sb(3)	-299.8 (3)	1674.5 (3)	3417.3 (5)	F(2)	1236 (7)	2608 (9)	1977 (5)
Sb(4)	2558.9 (3)	2447.8 (3)	1973.6 (5)	F(3)	1587 (5)	-509 (8)	555 (4)
S(1)	1378 (1)	-68 (1)	920 (3)	F(4)	1949 (8)	-228 (11)	2099 (5)
S(2)	-78 (1)	-1102 (1)	1299 (3)	F(5)	2555 (5)	1829 (11)	1174 (7)
S(3) ^a	701 (1)	4876 (1)	2576 (2)	F(6)	266 (5)	267 (9)	1332 (6)
S(4) ^a	69 (1)	3709 (1)	-335 (3)	SN(1) ^d	1248 (2)	6988 (5)	9043 (2)
N(1)	921 (4)	648 (4)	-265 (8)	SN(2) ^d	2976 (3)	9303 (4)	9193 (2)
N(2)	-803 (4)	714 (4)	-1369 (8)	NS(1) ^d	1951 (4)	8417 (7)	8808 (3)
N(3) ^b	4577 (3)	763 (2)	3009 (5)	NS(2) ^d	3713 (3)	9048 (6)	10097 (4)
N(4) ^b	4512 (3)	-952 (3)	3555 (5)	S(1)	5000	7985 (6)	7500
F(1)	-3045 (4)	4869 (3)	-12 (9)	O(1)	4874 (7)	8807 (12)	8246 (7)
F(2)	-2641 (6)	4782 (5)	3366 (12)	(d) $(S_4N_4)(SbCl_6)_2$ (4)			
F(3)	-2039 (4)	5967 (3)	1952 (6)	Sb(1)	2042.9 (4)	1462.6 (4)	-583.9 (4)
F(4)	-1005 (4)	4767 (4)	3620 (7)	Cl(1)	3686 (2)	509 (2)	-741 (2)
F(5)	-1386 (3)	4855 (3)	437 (6)	Cl(2)	463 (2)	2412 (2)	-408 (2)
F(6)	-2079 (5)	3636 (3)	1730 (9)	Cl(3)	2713 (2)	2273 (2)	851 (2)
F(7)	-3801 (4)	1399 (3)	-154 (6)	Cl(4)	1466 (2)	683 (2)	-2059 (2)
F(8)	-4138 (3)	2200 (4)	2408 (6)	Cl(5)	1411 (2)	58 (2)	358 (2)
F(9)	-1438 (3)	1387 (4)	2146 (7)	Cl(6)	2767 (2)	2886 (2)	-1498 (2)
F(10)	-283 (5)	990 (5)	5175 (8)	SN(1) ^e	4496 (3)	-1152 (3)	7281 (3)
F(11)	-233 (3)	2342 (4)	1693 (7)	SN(2) ^e	3727 (4)	-156 (4)	6778 (3)
F(12)	903 (3)	1935 (3)	4679 (6)	SN(3) ^e	3838 (3)	933 (4)	6567 (3)
F(13)	-657 (4)	2549 (5)	4418 (9)	SN(4) ^e	4617 (3)	1936 (3)	7134 (3)
F(14)	111 (3)	812 (3)	2422 (7)	(e) $(S_4N_4)(AlCl_4)_2$ (5)			
F(15)	2563 (3)	2374 (4)	-233 (5)	S(1)	7199 (2)	9432.6 (8)	7467 (2)
F(16)	1354 (3)	2335 (3)	1156 (6)	S(2)	2700 (2)	8976.7 (7)	4249 (2)
F(17)	2425 (3)	3593 (3)	1771 (7)	N(1)	4941 (6)	8998 (2)	6103 (5)
F(18)	2679 (3)	1305 (3)	2200 (7)	N(2)	7816 (6)	10283 (2)	7002 (5)
F(19)	3775 (3)	2542 (3)	2781 (6)	Al	5431 (2)	8479.7 (8)	1416 (2)
F(20)	2537 (4)	2544 (4)	4156 (6)	Cl(1)	7560 (2)	9218.5 (7)	3735 (2)
(b) $(S_4N_4)(SO_3F)_2$ (2)				Cl(2)	3912 (3)	7558.3 (8)	2151 (2)
S(1)	2207 (1)	8895.0 (5)	-574 (1)	Cl(3)	2815 (2)	9258.6 (9)	-527 (2)
S(2)	-92 (1)	9207.7 (5)	2575 (1)	Cl(4)	7552 (3)	8021.1 (9)	561 (2)
S(3)	6026 (1)	6496.8 (5)	1446 (1)				
OF(1) ^c	6307 (4)	5922 (2)	-315 (3)				
OF(2) ^c	7694 (6)	7305 (2)	1733 (4)				
O(1)	3701 (4)	6845 (2)	840 (4)				
O(2)	6634 (4)	5861 (2)	3159 (3)				
N(1)	1330 (4)	8817 (2)	1270 (3)				
N(2)	-1449 (4)	10191 (2)	1990 (3)				

^a Population parameters of these atoms fixed at 0.83. ^b Population parameters of these atoms fixed at 1.32. ^c These atoms have the complex scattering factor $f_{OF} = 1/2(f_O + f_F)$. ^d These atoms have the complex scattering factors $f_{SN} = 1/3f_S + 1/3f_N$ and $f_{NS} = 1/3f_S + 1/3f_N$. ^e Atoms on disordered positions have the complex scattering factor $f_{SN} = 1/2(f_S + f_N)$.

were initially fixed at 0.5, the isotropic temperature factors of the two independent atoms in the molecule appeared to be reasonably small, although the resulting S-O bond length was clearly too short. Similarly, there was also a considerable difference in the temperature factors of the S and N atoms in the $S_4N_4^{2+}$ cation. Further least-squares refinement varying the population parameters of the atoms in the cation and the SO_2 solvent molecule improved the crystallographic residual and indicated that there was a complete molecule of SO_2 in the lattice and that the cation was disordered. The best model for the disorder which was consistent with the number of electrons at each site in the cation was one in which the molecule has the two orientations described above for the $(S_4N_4)(Sb_3F_{14})(SbF_6)$ salt but now in the ratio 67%:33% (cf. 75%:25% above). With use of this disordered model with the complex scattering curves $f_{SN} = 2/3f_S + 1/3f_N$ and $f_{NS} = 1/3f_S + 2/3f_N$ for the alternate sites around the cation, further cycles of least-squares refinement converged to give the final agreement indices in Table I. A final difference Fourier was featureless with no residual peaks greater than $\pm 0.5 e/\text{\AA}^3$.

(4) $(S_4N_4)(SbCl_6)_2$. This structure was solved with the use of the Patterson function to locate the heavy atom. Subsequent least-squares and Fourier calculations gave the positions of the remaining atoms. In this case, the $S_4N_4^{2+}$ ring was found to be nonplanar with crystallographic symmetry 2 and was disordered with the two arrangements shown below, of equal probability. Least-squares refinement with each atom in the cation having the scattering curve $f_{NS} = 1/2(f_S +$

$f_N)$ converged to the final agreement indices in Table I (all atoms with anisotropic thermal parameters).



A final difference Fourier contained a major residual peak of ca. 3.0 $e/\text{\AA}^3$ close to the antimony. However, no other peaks in the map were greater than 1.0 $e/\text{\AA}^3$.

(5) $(S_4N_4)(AlCl_4)_2$. The value of $Z = 2$ in the space group $P2_1/n$ requires the $S_4N_4^{2+}$ cation in this structure to have crystallographic symmetry $\bar{1}$. The positions of all but one nitrogen atom in this compound were readily located by direct methods.¹⁸ Least-squares refinement and a subsequent difference Fourier located the missing atom. From a consideration of the isotropic temperature factors, it was apparent that the $S_4N_4^{2+}$ cation in this compound was ordered. Least-squares refinement with all atoms having anisotropic thermal parameters converged to the final agreement indices in Table I. A final difference Fourier was featureless with no residual peaks greater than $\pm 0.47 e/\text{\AA}^3$.

For all structures neutral atom scattering curves were taken from ref 20. All computing was on a CDC 6400 computer using the series

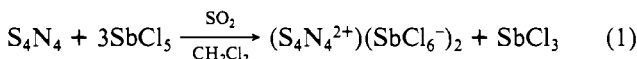
of programs in the XRAY¹⁶ and SHELX¹⁸ systems along with some local programs. The final atomic parameters for all structures are given in Table II. Tabulations of anisotropic thermal parameters and observed and calculated structure factors for each compound are available as supplementary material.²¹

Results and Discussion

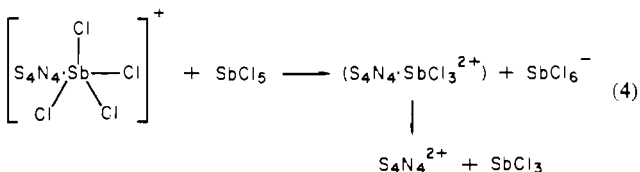
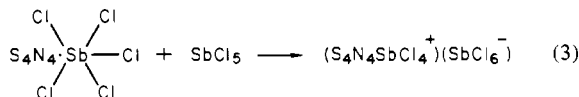
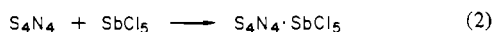
Reactions of S₄N₄ with SbCl₅. When the reaction was carried out in SO₂ with equimolar amounts of reactants, the simple adduct S₄N₄·SbCl₅ was obtained as reported previously. A 2:1 molar ratio or addition of a further mole of SbCl₅ to S₄N₄·SbCl₅ gave the orange compound S₄N₄·2SbCl₅. It has been proposed previously^{5,6} that this compound has the structure (S₄N₄·SbCl₄⁺)(SbCl₆⁻) on the basis of infrared evidence for SbCl₆⁻. We have confirmed the presence of the SbCl₆⁻ anion from both Raman and infrared data. We also found the Mössbauer spectrum to consist of a single broad line. While indicating that SbCl₃ was not present, this did not provide any evidence for the two distinct antimony sites in the proposed structure, although the broad signal could possibly arise from two overlapping signals.

When a 3:1 or larger excess of SbCl₅ was used, the deep red 1:1 adduct was initially formed but the final product was the yellow crystalline salt (S₄N₄)(SbCl₆)₂. The same product was also obtained from the reaction of S₄N₄·SbCl₅ with 2 mol of SbCl₅ or by the reaction of S₄N₄·2SbCl₅ with 1 mol of SbCl₅.

The overall reaction may be represented by eq 1. It appears



that the reaction takes place via the successive formation of the 1:1 and 1:2 compounds: eq 2-4. However, there is at



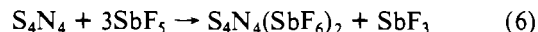
present no certain experimental evidence for either of these intermediates although Wynn and Jolly⁵ have noted that S₄N₄·BCl₂⁺·SbCl₆⁻ obtained during the reaction of S₄N₄·BCl₃ and SbCl₅ does not undergo any further reaction with SbCl₅. This is consistent with the above mechanism as (S₄N₄)BCl₂⁺ would not be expected to give S₄N₄²⁺ by loss of Cl⁻ and BCl whereas (S₄N₄)SbCl₄⁺ can lose Cl⁻ and SbCl₃. Even when a tenfold molar excess of SbCl₅ was used, the only products of the reaction were (S₄N₄)(SbCl₆)₂ and SbCl₃ and no further oxidation or cleavage of the ring was observed.

Reaction of S₄N₄ with PCl₅ in Methylene Chloride. Using S₄N₄:PCl₅ ratios of 1:1 and 1:3 gave yellow-orange oils after 24 h. There was no evidence for the formation of any S₄N₄²⁺ salts or for the formation of a S₄N₄·PCl₅ adduct. The ³¹P spectrum of the orange oil showed the presence of a large number of phosphorus species which may be chlorophosphazenes but this was not verified. SCl₂ was identified in the product by Raman spectroscopy. The reaction was not further investigated.

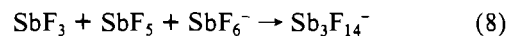
Reaction of S₄N₄ with SbF₅. The product of the reaction of S₄N₄ with SbF₅ in a 1:4 mole ratio was a green solution which deposited golden yellow crystals. These were shown by X-ray crystallography to have the composition (S₄N₄)(Sb₃F₁₄)(SbF₆) and to contain the previously unreported Sb₃F₁₄⁻ anion. The overall reaction may be written as eq 5. This



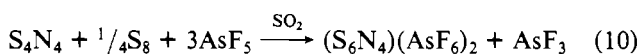
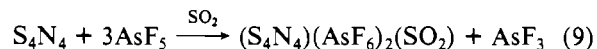
compound is presumably the same as that described previously as S₄N₄·4SbF₅⁷ and formulated by Paul and co-workers⁶ as (S₄N₄)SbF₄⁺·Sb₃F₁₆⁻. With a 1:6 mole ratio, the same product was obtained. However, with a 1:3 mole ratio, SbF₃ was precipitated and the resulting yellow solution on evaporation yielded a yellow material which was shown by its infrared and Raman spectra to be (S₄N₄)(SbF₆)₂·xSO₂. The overall reaction is eq 6. In the reaction using a 1:4 ratio of SbF₅, a



small amount of insoluble SbF₃·SbF₅ material was identified by means of its Raman spectrum.¹⁴ It seems that SbF₃, formed in the above reaction, reacts with a further mole of SbF₅ in two different ways (eq 7 and 8). The second of these reactions predominates so that the major product is (S₄N₄)(Sb₃F₁₄)(SbF₆).



Reaction of S₄N₄ with AsF₅. It was previously reported¹¹ that the reaction of S₄N₄ with AsF₅ in a 1:3 mole ratio gave (S₃N₂⁺)(AsF₆⁻) which was characterized by X-ray crystallography. However, it has been shown recently that this compound should be formulated as (S₆N₄)(AsF₆)₂ containing the dimeric cation S₆N₄²⁺.¹² Moreover, when the same reaction was repeated a number of times during the present work, (S₆N₄²⁺)(AsF₆)₂ was not obtained but the reaction gave (S₄N₄)(AsF₆)₂·SO₂ which was characterized by X-ray crystallography. The same product was also obtained when a S₄N₄:AsF₆ ratio of 1:6 was used. We have shown elsewhere that a more efficient preparation of (S₆N₄)(AsF₆)₂ is by the oxidation of S₄N₄ with S₈(AsF₆)₂.¹² It therefore seems that oxidation of S₄N₄ with AsF₅ gives only the S₄N₄²⁺ cation. If, however, the S₄N₄ is contaminated by small amounts of sulfur, as appears to have been the case in the original preparation of the S₆N₄²⁺ cation, then reaction 10 is favored over reaction 9 due to the initial preferential formation of the S₈²⁺ cation which then reacts with the S₄N₄.



The reaction of S₄N₄ with HSO₃F, although very complex, gives both S₄N₄²⁺ and S₆N₄²⁺, but in this case the yields of S₆N₄²⁺ are much greater than those of S₄N₄²⁺.¹²

No evidence was obtained in the present work for the formation of the S₄N₄·AsF₅ adduct which has previously been prepared in CCl₄.³ It seems that in the presence of excess AsF₅ it reacts very quickly to give the S₄N₄²⁺ cation, presumably by the same mechanism as proposed above for the SbCl₅ reaction. Somewhat surprisingly the adduct S₄N₄·AsF₅ was isolated from reactions of S₄N₄ with Se₈(AsF₆)₂ in methylene chloride and with Te₄(AsF₆)₂ in SO₂ at room temperature.⁴

Reaction of S₄N₄ with PF₅. A 1:1 and a 1:3 S₄N₄:PF₅ mole ratio gave the same red crystalline product. The 94.1-MHz ¹⁹F NMR spectrum of a solution of the red crystalline product in SO₂ (Figure 1) consists of two doublets and two apparent quintets which, under higher resolution, split into the nine lines expected for an AB₄ spectrum (see inset). The second-order splitting of the doublets is not observed because of the width

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

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Table III. ^{19}F NMR Data for Molecular Adducts of PF_5^a

	$S_4N_4 \cdot PF_5$	$(CH_3)_3O \cdot PF_5^b$	$(C_2H_5)_2O \cdot PF_5^c$	$CH_3CN \cdot PF_5^b$
$J_{P-F_{eq}}$, Hz	755.8	777	745	747
$J_{P-F_{ax}}$, Hz	789.7	820	790	848
$J_{F_{ax}-F_{eq}}$, Hz	57.3	65	62	55
δF_{eq}	65.4	69.6	66.3	71.1
δF_{ax}	82.8	88.8	86.0	83.6

^a Chemical shifts are measured with respect to external $CFCl_3$ (positive chemical shifts are to high field). ^b Muetterties, E. L.; Bither, T. A.; et al. *J. Inorg. Nucl. Chem.* 1960, 16, 52. ^c Gibson, J. A.; Ibbot, P. G.; et al. *Can. J. Chem.* 1973, 51, 3203.

of the lines. The observation of two essentially identical and overlapping AB_4 spectra is attributed to coupling with the ^{31}P nucleus, i.e., the spectrum is the AB_4X part of the AB_4X spectrum. Thus the ^{19}F spectrum is in accord with the presence of a simple $S_4N_4 \cdot PF_5$ adduct in the SO_2 solution in which the PF_5 has the expected square-pyramidal geometry. The chemical shifts and coupling constants are compared with those of other PF_5 adducts in Table III. The ^{31}P spectrum (Figure 1) is the X part of the AB_4X spectrum, and because $J_{AX} \approx J_{BX}$ ($J_{F(eq)-P} = 789.7$ Hz, $J_{F(ax)-P} = 755.8$ Hz), it consists of two closely overlapping quintets which give approximately the six-line spectrum expected if $J_{AX} = J_{BX}$. It appears that PF_5 is not a sufficiently strong oxidizing agent to oxidize S_4N_4 to $S_4N_4^{2+}$.

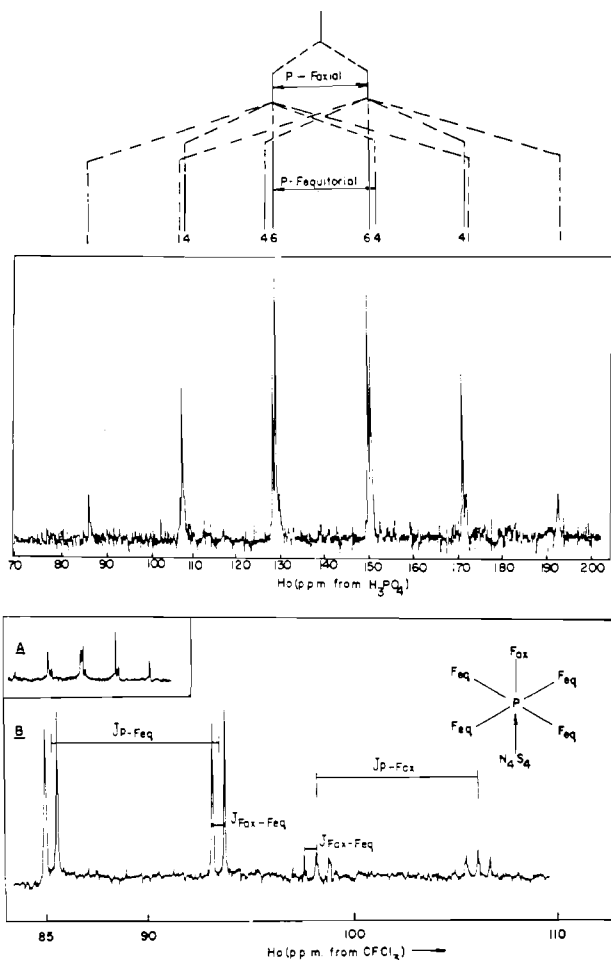
Infrared and Raman Spectra. Infrared and Raman spectra were recorded for all the $S_4N_4^{2+}$ salts described. No attempt is made to assign all the observed bands and to discuss the spectra in detail. Table IV lists only the infrared and Raman bands that can clearly be assigned to the $S_4N_4^{2+}$ ion in each of the compounds. There are six such bands in the Raman spectra some of which are sometimes observed as doublets and one band in the infrared which was either a doublet or a triplet. The spectra of all six compounds are very similar, and one must conclude that the $S_4N_4^{2+}$ cation has a very similar if not identical structure in each of the compounds. The absence of coincidences between the Raman and infrared spectra is fully consistent with the planar D_{4h} structure found in the X-ray crystallographic studies.

Discussion of Crystal Structures

(1) $(S_4N_4)(SO_3F)_2$. The structure of $(S_4N_4)(SO_3F)_2$ can be considered to consist of discrete $S_4N_4^{2+}$ cations and fluoro-sulfate anions (Figures 2 and 3). The cation, which has crystallographic inversion symmetry, is a completely planar ring with approximate D_{4h} symmetry and alternating S and N atoms. The SN bond lengths in the ring are essentially equal (average 1.553 (3) Å), and the average NSN and SNS bond angles are 118.8 and 151.2°, respectively. The fluoro-sulfate anion in this structure was found to be disordered as is common for this anion.^{12,19}

Table IV. Characteristic Vibrational Frequencies (cm^{-1}) of the $S_4N_4^{2+}$ Cation

$(S_4N_4)(AsF_6)_2 \cdot SO_2$		$(S_4N_4)(SbF_6)_2 \cdot SO_2$		$(S_4N_4)(Sb_3F_{14})(SbF_6)$		$(S_4N_4)(SbCl_6)_2$		$(S_4N_4)(AlCl_4)_2$		$(S_4N_4)(SO_3F)_2$
Raman	IR	Raman	IR	Raman	IR	Raman	IR	Raman	IR	Raman
1218 (55)				1217 (60)						
1210 (42)		1210 (96)		1205 (80)		1197 (100)		1189 (100)		1205 (96)
	1054 (s)		1085 (s)		1062 (m)		1056 (m)		1091 (m)	
	1040 (s)				1021 (m)		1011 (m)		1020 (m)	
	1015 (s)		995 (s)						974 (s)	
503 (100)		501 (100)		501 (66)		501 (74)		489 (38)		501 (83)
230 (87)		234 (67)		230 (100)		225 (48)		219 (26)		223 (100)
		223 (51)		221 (35)						
				152 (13)						
165 (17)				145 (12)		145 (6)		143 (10)		156 (13)
160 (16)		145 (23)		111 (16)		121 (10)		104 (29)		118 (26)
102 (49)		104 (48)		81 (56)		83 (54)		86 (21)		88 (40)
81 (35)		96 (45)								

Figure 1. $S_4N_4 \cdot PF_5$ spectrum.

(2) $(S_4N_4)(AlCl_4)_2$. This structure consists of $S_4N_4^{2+}$ cations and tetrachloroaluminate anions. The $S_4N_4^{2+}$ cation which has crystallographic inversion symmetry is a planar ring with approximate D_{4h} symmetry, alternating S and N atoms, essentially equal SN bond lengths (average 1.552 (4) Å), and average NSN and SNS bond angles of 118.8 and 151.2°, respectively (Figure 2). These dimensions are exactly the same as for the cation in the fluoro-sulfate salt. The slight deviations from these average values may be due to some of the short $S \cdots Cl$ contacts discussed below.

The tetrachloroaluminate anion in the structure is a slightly flattened tetrahedron with one Al-Cl bond [2.160 (3) Å] significantly longer than the remaining three bonds (2.118–2.128 Å). When a riding correction to the bond lengths is applied, the difference is decreased but is still significant (Table VI) so that this lengthening is not due to thermal effects

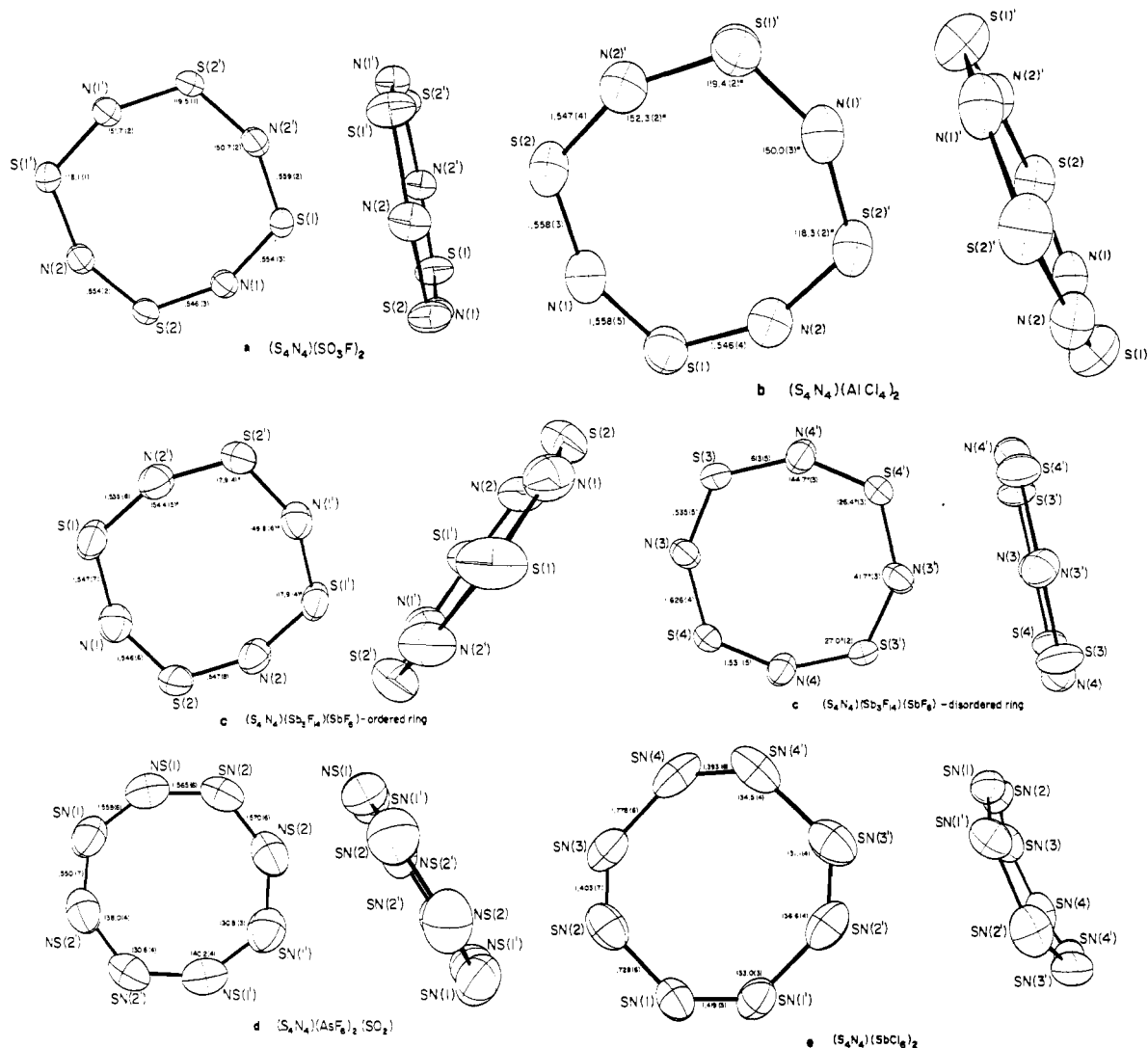


Figure 2. Molecular view and principal dimensions of the $S_4N_4^{2+}$ cations: (a) $(S_4N_4)(SO_3F)_2$; (b) $(S_4N_4)(AlCl_4)_2$; (c) $(S_4N_4)(Sb_3F_{14})(SbF_6)_2$ (ordered and disordered rings); (d) $(S_4N_4)(AsF_6)_2(SO_2)_2$; (e) $(S_4N_4)(SbCl_6)_2$.

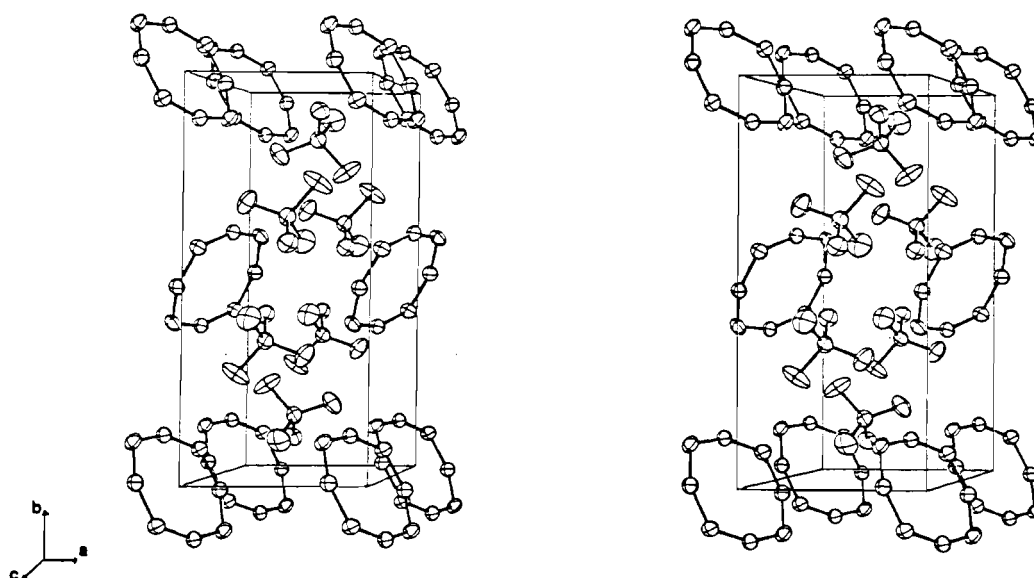


Figure 3. Stereoscopic view of the packing in $(S_4N_4)(SO_3F)_2$ as viewed down c .

but may be related to the significantly larger number of short $S \cdots Cl$ contacts involving the Cl atom forming this longer bond. A similar effect is also observed in the structure of $(S_4N_4)(SbCl_6)_2$. Consistent with the lengthening of the Al-Cl(1)

bond, it may be noted that the Cl-Al-Cl angles involving this atom are slightly smaller than the tetrahedral value. In general, the dimensions of the $AlCl_4^-$ anion are very similar to those observed in several other structures.²¹

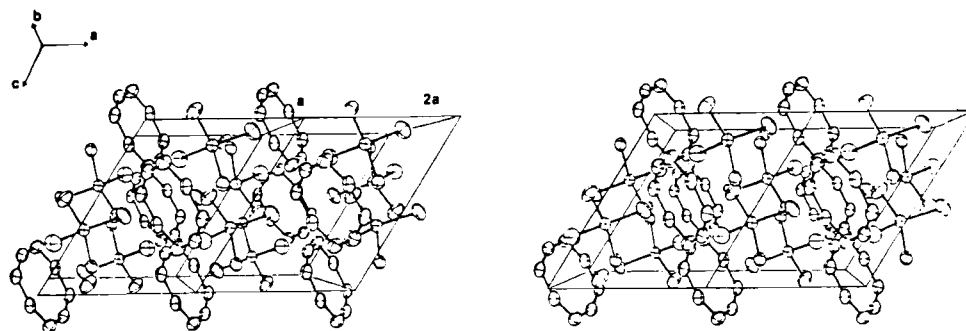


Figure 4. Stereoscopic view of the packing in $(S_4N_4)(AlCl_4)_2$ as viewed down b .

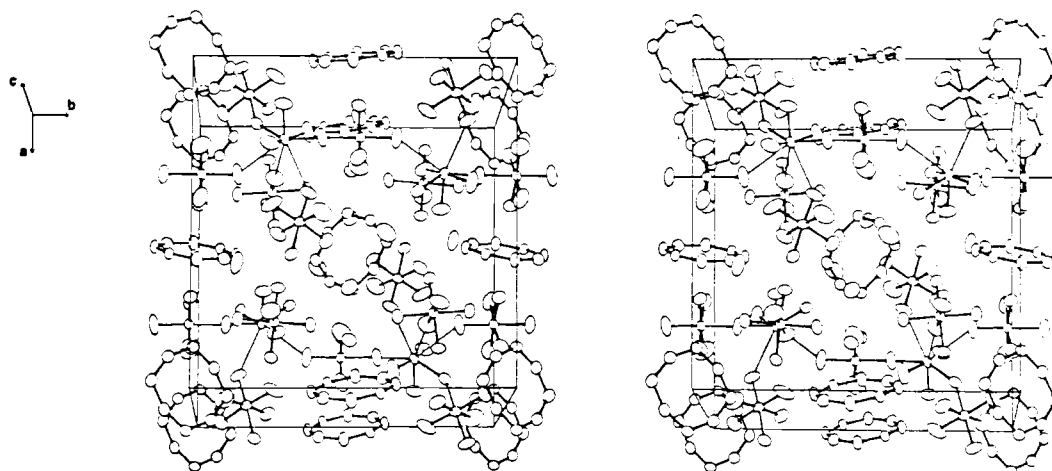


Figure 5. Stereoscopic view of the packing in $(S_4N_4)(Sb_3F_{14})(SbF_6)$ as viewed down b .

Table V. Bond Distances (Å) and Bond Angles (Deg) in the Tetrathiazyl Cation, $S_4N_4^{2+}$

compd	$(S_4N_4)(Sb_3F_{14})(SbF_6)$		$(S_4N_4)(SO_3F)_2$	$(S_4N_4)(AsF_6)_2(SO_2)$	$(S_4N_4)(AlCl_4)_2$	$(S_4N_4)(SbCl_6)_2$
	ring 1	ring 2				
$S_4N_4^{2+}$ cation	ordered	disordered (3:1)	ordered	disordered (2:1)	ordered	disordered (1:1)
cryst symmetry	planar $\bar{1}$	planar $\bar{1}$	planar $\bar{1}$	planar $\bar{1}$	planar $\bar{1}$	boat 2
S(1)-N(2')	1.534 (7)	1.613 (5)	1.559 (2)	1.550 (7)	1.546 (4)	1.419 (5)
S(1)-N(1)	1.548 (6)	1.535 (5)	1.555 (3)	1.558 (6)	1.558 (5)	1.728 (6)
S(2)-N(1)	1.545 (6)	1.606 (4)	1.545 (3)	1.565 (6)	1.558 (3)	1.403 (7)
S(2)-N(2)	1.548 (6)	1.531 (5)	1.553 (2)	1.570 (6)	1.547 (4)	1.778 (6)
N(2')-S(1)-N(1)	117.9 (3)	127.0 (2)	118.1 (1)	130.8 (3)	119.4 (2)	133.0 (3)
N(1)-S(2)-N(2)	117.9 (4)	126.4 (3)	119.5 (1)	130.6 (4)	118.3 (2)	136.6 (4)
S(1)-N(1)-S(2)	149.8 (5)	141.7 (3)	151.7 (2)	140.2 (4)	150.0 (3)	131.1 (4)
S(2)-N(2)-S(1')	154.3 (4)	144.7 (3)	150.7 (2)	138.0 (4)	152.3 (2)	134.5 (4)

A view of the crystal packing in this compound is given in Figure 4 where it may be noted that there are alternating layers of anions and cations parallel to the $(\bar{1}01)$ plane. These layers are held together by several $S \cdots Cl$ contacts shorter than the van der Waals distance of 3.65 Å (see below).

(3) $(S_4N_4)(Sb_3F_{14})(SbF_6)$. Although there are some relatively strong $Sb^{III} \cdots F$ interactions between the anions, the structure may be considered to consist of the ions $S_4N_4^{2+}$, $Sb_3F_{14}^-$, and SbF_6^- (Figure 5) with two nonequivalent $S_4N_4^{2+}$ cations in the asymmetric unit. At the origin, the $S_4N_4^{2+}$ cation is a centrosymmetric ordered ring with equal bond lengths (average 1.541 (7) Å) and NSN and SNS bond angles of 117.9 (4) and 152.0 (5)°, respectively (Figure 2). However, the second $S_4N_4^{2+}$ cation at the center of symmetry at $(0, 1/2, 0)$ was found to be disordered. The disorder may be described by applying to 25% of the cations in this position either a 180° rotation about an axis bisecting two opposite bonds of the ring or a 45° rotation about the C_4 axis perpendicular to the ring so that sulfur is superimposed on nitrogen and vice versa. This model of the disorder assumes that both the major and minor orientations of the ring are planar, have equal bond lengths

and the same center. The disorder would be expected to average the NSN and SNS bond angles, and indeed the observed values agree well with those expected for the 75%/25% disorder model of ca. 126 and 142°, respectively (Table V). The observation of unequal bond lengths is unexpected, and it seems reasonable to suppose that these observed differences are not real but are a consequence of the disorder. Because of the very different NSN and SNS bond angles, the N and S atoms are not superimposed in the two orientations and this could be responsible for the apparent differences in bond lengths.

As described above, the vibrational spectra are also consistent with the supposition that the cations have essentially the same structure in all the compounds studied and in particular have rings with equal bond lengths. The existence of a form of $S_4N_4^{2+}$ with unequal bond lengths could only be deduced with certainty from a completely ordered structure.

This structure also provided the first well-characterized example of the fluorine-bridged anion $[Sb_3F_{14}]^-$ containing both Sb(III) and Sb(V). This anion may be described as consisting of an angular SbF_2^+ cation linked by two trans

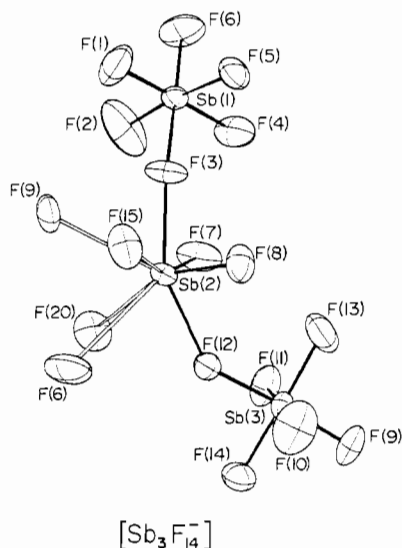


Figure 6. ORTEP view of the $\text{Sb}_3\text{F}_{14}^-$ anion in the compound $(\text{S}_4\text{N}_4)(\text{Sb}_3\text{F}_{14})(\text{SbF}_6)$ showing the four strong $\text{Sb}^{\text{III}}\cdots\text{F}$ interionic bonds (unfilled).

asymmetric fluorine bridges [$\text{Sb}^{\text{III}}\text{-F}_{\text{bridge}} = 2.254(3), 2.293(4) \text{ \AA}$; $\text{Sb}^{\text{V}}\text{-F}_{\text{bridge}} = 1.933(4), 1.939(4) \text{ \AA}$] to two SbF_6^- anions, giving the Sb^{III} atom a trigonal-bipyramidal AX_4E configuration [$\text{F}_{\text{bridge}}\text{-Sb}^{\text{III}}\text{-F}_{\text{bridge}} = 152.4(3)^\circ$; $\text{Sb}^{\text{III}}\text{-F-Sb}^{\text{V}} = 144.1(3), 150.6(2)^\circ$]. In addition this Sb^{III} atom forms four longer contacts of lengths 2.696(4), 2.725(6), 2.995(6), and 3.017(5) \AA to fluorine atoms in other SbF_6^- and $\text{Sb}_3\text{F}_{14}^-$ anions which are somewhat shorter than the van der Waals limit of ca. 3.55 \AA for neutral atoms. These four contacts surround the lone pair on the Sb^{III} which is in an equatorial position of the AX_4E trigonal-bipyramidal description of the primary geometry so that overall there is approximately a distorted capped square antiprism $\text{AX}_4\text{Y}_4\text{E}$ coordination (Figure 6). It is noteworthy that the strongest of the $\text{Sb}^{\text{III}}\text{-F}$ longer contacts are to the two fluorine atoms trans to the bridging fluorine atoms F(3) and F(12) in two different $\text{Sb}_3\text{F}_{14}^-$ anions. These additional $\text{Sb}^{\text{III}}\cdots\text{F}$ contacts are a common feature of the solid-state packing of fluoride complexes containing Sb^{III} and will be discussed in greater detail in a following paper.²² Similar overall coordination geometries are also observed for the iodine atom in the compound $\text{IF}_4^+\text{-Sb}_2\text{F}_{11}^-$ and several other compounds particularly those containing other examples of this anion.^{23,24} A more detailed comparison of the geometries of the known $\text{Sb}_3\text{F}_{14}^-$ anions is given elsewhere.²⁴

The lengths of the $\text{Sb}^{\text{III}}\text{-F}$ bond lengths in the SbF_2^+ ion of the $\text{Sb}_3\text{F}_{14}^-$ anion are 1.885(5) and 1.890(6) \AA . These bonds are comparable in length to those observed for the four SbF_2^+ ions in the complex cation $\text{Sb}_6\text{F}_{13}^{5+}$ described by Edwards and Slim.²⁵ These $\text{Sb}^{\text{III}}\text{-F}$ bonds are marginally longer than the $\text{Sb}^{\text{V}}\text{-F}$ bond lengths in the $\text{Sb}_3\text{F}_{14}^-$ and SbF_6^- anions due to the difference in the oxidation state, or in other words, the repulsive effect of the lone pair on Sb^{III} . In the SbF_6^- anion, the Sb-F bond lengths of 1.860(5)–1.874(4) \AA are significantly shorter than the $\text{Sb}^{\text{V}}\text{-F}_{\text{bridge}}$ distances and are comparable to the distances observed for the remaining $\text{Sb}^{\text{V}}\text{-F}$ distances in the $\text{Sb}_3\text{F}_{14}^-$ anion and those in the structure of

K^+SbF_6^- .²⁶ Bond angles in the SbF_6^- anion are all within 1.7° of the expected values of 90 and 180° . In the $\text{Sb}_3\text{F}_{14}^-$ anion, the lengthening of the $\text{Sb}(1)\text{-F}(3)$ and $\text{Sb}(3)\text{-F}(12)$ bonds results in a decrease in the $\text{F}_{\text{bridge}}\text{-Sb}^{\text{V}}\text{-F}_{\text{eq}}$ angles by up to 3° and corresponding distortions in some of the other angles around each Sb^{V} .

(4) $(\text{S}_4\text{N}_4)(\text{AsF}_6)_2(\text{SO}_2)$. The $\text{S}_4\text{N}_4^{2+}$ cation in this compound was found to be disordered with ca. 67% of the rings having one orientation and ca. 33% having an orientation related to the first by a 180° rotation about a twofold axis in the plane of the cation that superimposes S on N and N on S.

Because of the disorder, there is considerable averaging of the NSN and SNS bond angles and the bond angles calculated on the basis of the disordered model, 129 and 139° , respectively, agree well with the observed bond angles. Differences in the bond lengths around the ring can again be attributed to the disorder. The average of these apparently different bond lengths (1.561(6) \AA) is in good agreement with the bond lengths observed in the ordered rings above (Figures 2 and 7; Table V).

The hexafluoroarsenate anion was found to be approximately octahedral with As-F distances of 1.678(8)–1.706(6) \AA and cis and trans angles within 3° of the expected values of 90 and 180° . There is, however, significant anisotropy in the thermal ellipsoids of the fluorine positions in the anions (Figure 7 and Table B (supplementary material)) which may indicate some slight orientational disorder. The lengths of the As-F bonds in this anion are however comparable to that observed in K^+AsF_6^- of 1.719(3) \AA .²⁷

The atoms in the SO_2 molecule were also found to have large anisotropic temperature factors. The S-O bond length (1.35(1) \AA) and OSO bond angle ($122.2(7)^\circ$) are, however, similar to those observed for crystalline SO_2 .²⁸ Crystals of the $(\text{S}_4\text{N}_4)(\text{SbF}_6)_2$ salt which were also isolated in the reaction between S_4N_4 and SbF_5 also contain SO_2 in the lattice which is even more weakly held and is readily lost at room temperature.

(5) $(\text{S}_4\text{N}_4)(\text{SbCl}_6)_2$. The structure of this compound consists of discrete $\text{S}_4\text{N}_4^{2+}$ cations and SbCl_6^- anions with, notably, a significantly different conformation for the $\text{S}_4\text{N}_4^{2+}$ cation than that found in the structures described above. This cation, which has crystallographic twofold symmetry, was found to be a nonplanar tub-shaped ring which deviates from planarity by ca. 10° (Table C in the supplementary material) and has approximate S_4 symmetry. Each site of the cation consists of an equal mixture of nitrogen and sulfur atoms. The disorder can be described as arising from a random occupation of the molecular sites by two orientations of the cations which are related by mirror planes through opposite (eclipsed) pairs of SN bonds. As expected, the bond angles around the ring are averaged to the same value of 133.8° . The positions of the N and S atoms in the two orientations are not coincident, and this is reflected in the considerable anisotropy of the thermal ellipsoids at each average atom. The apparent bond lengths show a very considerable alternation around the ring (1.45 and 1.71 \AA). The vibrational bands that may be attributed to $\text{S}_4\text{N}_4^{2+}$ in this compound are not significantly different from those observed in the other compounds which contain a planar $\text{S}_4\text{N}_4^{2+}$ ring with equal bond lengths (Table IV). The stretching frequencies of bonds of lengths 1.45 and 1.71 \AA would be expected to be markedly different from the stretching frequency corresponding to a bond length of 1.54 \AA . The apparent differences in bond lengths must therefore be at-

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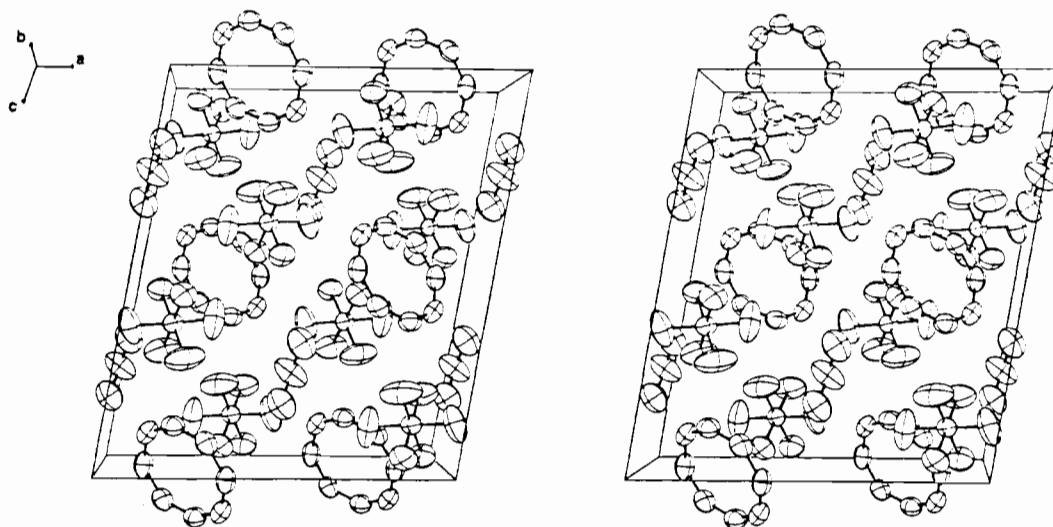


Figure 7. Stereoscopic view of the packing in $(S_4N_4)(AsF_6)_2(SO_2)$ as viewed down b . (Note the large thermal ellipsoids for virtually all atoms in the structure.)

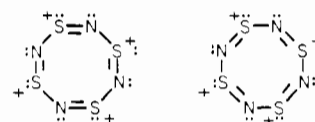
tributed to the disorder. Although the $S_4N_4^{2+}$ cation in this compound apparently deviates significantly from planarity, this does not appear to have any observable effect on the vibrational spectrum.

A notable feature of the hexachloroantimonate anion in this structure is a significant distortion of the anion from octahedral toward C_{2v} symmetry. In particular, one Sb-Cl bond is somewhat longer (2.425 (2) Å) than the others (2.320 (3)–2.361 (2) Å) and, as a result of the lengthening of this bond, the equatorial chlorine atoms bend by a small amount (up to 1.5°) toward Cl(1) (Table VI). The lengthening of this bond is not attributed to thermal effects but may be related to the larger number of short contacts involving Cl(1) compared to the remaining chlorines (see below). This longer bond is also significantly long when compared with the Sb-Cl bond lengths in several other hexachloroantimonate(V) structures which are normally within the range 2.33–2.39 Å.^{29–34}

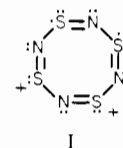
The $S_4N_4^{2+}$ Cation. Despite the disorder in some of the structures, the $S_4N_4^{2+}$ cation appears to have two well-defined isomeric forms: a planar form and a non-planar form. The planar form has equal bond lengths, and the nonplanar form is presumed to also have equal bond lengths although because of the disorder this cannot be concluded with certainty from the X-ray crystallographic data. Our earlier conclusions¹³ that the nonplanar form has unequal bond lengths and that there is a third planar form also with unequal bond lengths must now be regarded as incorrect.

On adduct formation with Lewis acids, electron density is withdrawn, and the S_4N_4 cage opens up to a rather flat saddle structure. This flattening of the molecule is completed with the removal of two electrons in the formation of $S_4N_4^{2+}$. The planar form of $S_4N_4^{2+}$ closely resembles the planar $S_4N_3^+$ and $S_5N_5^+$ cations which have nearly equal SN bond lengths in the range 1.55–1.60 Å.^{12,35,37–39} The $S_4N_4^{2+}$ cation has the

magic number of 10 electrons corresponding to a Hückel-type aromatic system if 16 electrons are allocated to 8 σ bonds and another 16 to a lone pair on each atom.⁴⁰ The cations $S_4N_3^+$ and $S_5N_5^+$ similarly have 10 and 14 π electrons, respectively. However, one cannot be certain that in the heteronuclear SN systems these magic numbers of electrons confer any extra stability on the molecule. Direct application of simple ideas taken from carbon chemistry may indeed obscure fundamental differences between the SN systems and carbon aromatic systems. Although it is recognized that valence-bond formulations and resonance structures have their limitations, an examination of such structures does appear to throw some light on the characteristic features of SN systems. Let us first consider the unknown planar $S_4N_4^{4+}$ cation. Two resonance structures with alternating single and double bonds can be written for this cation corresponding to a regular planar octagonal structure with equal bond lengths.



If we make the reasonable assumption that we can exceed the octet for sulfur but not for nitrogen, we can only place two additional electrons to form $S_4N_4^{2+}$ on two of the four sulfur atoms as in I. The S-S distance between adjacent S atoms



in $S_4N_4^{2+}$ is only 3.0 Å which is well below the van der Waals intermolecular contact distance of 3.7 Å and is almost the same as Glidewells intramolecular contact distance of 2.9 Å which is the closest distance to which two nonbonded sulfur atoms bonded to the same atom, in an SXS system, appear to be able to approach each other.⁴¹ Thus it is not unreasonable to

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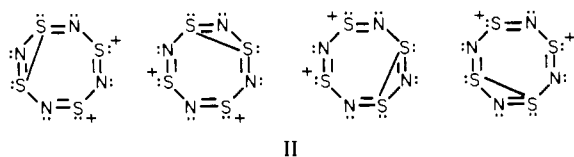
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Table VI. Bond Lengths (Å) and Bond Angles (Deg), with Estimated Standard Deviations in Parentheses, in the Anions^a

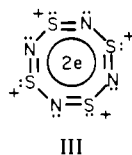
(a) (S ₄ N ₄)(Sb ₃ F ₁₄)(SbF ₆)								
Lengths								
Sb(1)-F(1)	1.843 (5)	[1.880]	Sb(2)-F(12)	2.293 (4)	[2.303]	Sb(3)-F(13)	1.838 (8)	[1.886]
Sb(1)-F(2)	1.840 (12)	[1.911]	Sb(2)-F(6)	2.995 (6)		Sb(3)-F(14)	1.865 (6)	[1.886]
Sb(1)-F(3)	1.933 (4)	[1.949]	Sb(2)-F(9)	3.017 (5)		Sb(4)-F(15)	1.869 (5)	[1.898]
Sb(1)-F(4)	1.859 (5)	[1.889]	Sb(2)-F(15)	2.696 (4)		Sb(4)-F(16)	1.859 (4)	[1.879]
Sb(1)-F(5)	1.867 (6)	[1.882]	Sb(2)-F(20)	2.725 (6)		Sb(4)-F(17)	1.864 (5)	[1.892]
Sb(1)-F(6)	1.838 (5)	[1.878]	Sb(3)-F(9)	1.865 (5)	[1.890]	Sb(4)-F(18)	1.860 (5)	[1.886]
Sb(2)-F(3)	2.254 (4)	[2.273]	Sb(3)-F(10)	1.844 (7)	[1.888]	Sb(4)-F(19)	1.874 (4)	[1.891]
Sb(2)-F(7)	1.885 (5)	[1.905]	Sb(3)-F(11)	1.845 (6)	[1.871]	Sb(4)-F(20)	1.862 (5)	[1.898]
Sb(2)-F(8)	1.890 (6)	[1.913]	Sb(3)-F(12)	1.939 (4)	[1.949]			
Angles								
F(1)-Sb(1)-F(2)	94.7 (4)		F(3)-Sb(2)-F(15)	75.0 (2)		F(15)-Sb(4)-F(16)	88.7 (2)	
F(1)-Sb(1)-F(3)	87.1 (2)		F(3)-Sb(2)-F(20)	122.0 (2)		F(15)-Sb(4)-F(17)	90.7 (3)	
F(1)-Sb(1)-F(4)	173.8 (3)		F(12)-Sb(2)-F(6)	75.8 (2)		F(15)-Sb(4)-F(18)	90.2 (3)	
F(1)-Sb(1)-F(5)	89.0 (3)		F(12)-Sb(2)-F(9)	136.7 (2)		F(15)-Sb(4)-F(19)	90.7 (2)	
F(1)-Sb(1)-F(6)	92.4 (3)		F(12)-Sb(2)-F(15)	119.0 (2)		F(15)-Sb(4)-F(20)	178.6 (3)	
F(2)-Sb(1)-F(3)	87.7 (3)		F(12)-Sb(2)-F(20)	73.0 (2)		F(16)-Sb(4)-F(17)	89.2 (2)	
F(2)-Sb(1)-F(4)	89.4 (3)		F(7)-Sb(2)-F(6)	134.9 (2)		F(16)-Sb(4)-F(18)	90.2 (2)	
F(2)-Sb(1)-F(5)	173.8 (3)		F(7)-Sb(2)-F(9)	94.7 (2)		F(16)-Sb(4)-F(19)	179.0 (2)	
F(2)-Sb(1)-F(6)	92.2 (4)		F(7)-Sb(2)-F(15)	154.2 (2)		F(16)-Sb(4)-F(20)	90.5 (3)	
F(3)-Sb(1)-F(4)	88.5 (2)		F(7)-Sb(2)-F(20)	78.1 (2)		F(17)-Sb(4)-F(18)	178.9 (3)	
F(3)-Sb(1)-F(5)	87.6 (2)		F(12)-Sb(3)-F(9)	177.3 (2)		F(17)-Sb(4)-F(19)	91.7 (2)	
F(3)-Sb(1)-F(6)	179.5 (3)		F(12)-Sb(3)-F(10)	87.0 (3)		F(17)-Sb(4)-F(20)	88.1 (3)	
F(4)-Sb(1)-F(5)	86.5 (3)		F(12)-Sb(3)-F(11)	89.5 (2)		F(18)-Sb(4)-F(19)	88.9 (2)	
F(4)-Sb(1)-F(6)	92.1 (3)		F(12)-Sb(3)-F(13)	89.9 (2)		F(18)-Sb(4)-F(20)	91.0 (3)	
F(5)-Sb(1)-F(6)	92.6 (3)		F(12)-Sb(3)-F(14)	87.7 (2)		F(19)-Sb(4)-F(20)	90.0 (2)	
Sb(1)-F(3)-Sb(2)	150.6 (2)		F(9)-Sb(3)-F(10)	93.3 (3)		F(8)-Sb(2)-F(6)	120.2 (2)	
F(3)-Sb(2)-F(7)	80.3 (2)		F(9)-Sb(3)-F(11)	90.1 (2)		F(8)-Sb(2)-F(9)	142.9 (2)	
F(3)-Sb(2)-F(8)	80.5 (2)		F(9)-Sb(3)-F(13)	92.9 (3)		F(8)-Sb(2)-F(15)	76.3 (2)	
F(3)-Sb(2)-F(12)	152.4 (2)		F(9)-Sb(3)-F(14)	89.5 (2)		F(8)-Sb(2)-F(20)	152.8 (2)	
F(7)-Sb(2)-F(8)	92.6 (3)		F(10)-Sb(3)-F(11)	175.9 (3)		F(6)-Sb(2)-F(9)	77.6 (2)	
F(7)-Sb(2)-F(12)	81.0 (2)		F(10)-Sb(3)-F(13)	90.7 (3)		F(6)-Sb(2)-F(15)	69.5 (2)	
F(8)-Sb(2)-F(12)	80.3 (2)		F(10)-Sb(3)-F(14)	90.2 (3)		F(6)-Sb(2)-F(20)	58.4 (2)	
Sb(2)-F(12)-Sb(3)	144.1 (3)		F(11)-Sb(3)-F(13)	91.4 (3)		F(9)-Sb(2)-F(15)	81.5 (2)	
F(3)-Sb(2)-F(6)	131.4 (2)		F(11)-Sb(3)-F(14)	87.5 (3)		F(9)-Sb(2)-F(20)	64.0 (2)	
F(3)-Sb(2)-F(9)	65.1 (2)		F(13)-Sb(3)-F(14)	177.4 (3)		F(15)-Sb(2)-F(20)	121.6 (2)	
(b) (S ₄ N ₄)(SO ₃ F) ₂								
Lengths								
S(3)-O(1)	1.427 (3)		S(3)-OF(1)	1.515 (3)		S(3)-OF(2)	1.465 (3)	
S(3)-O(2)	1.425 (2)							
Angles								
O(1)-S(3)-O(2)	114.4 (2)		O(1)-S(3)-OF(2)	112.2 (2)		O(2)-S(3)-OF(2)	110.8 (1)	
O(1)-S(3)-OF(1)	107.0 (1)		O(2)-S(3)-OF(1)	108.0 (1)		OF(1)-S(3)-OF(2)	103.7 (2)	
(c) (S ₄ N ₄)(AsF ₆) ₂ (SO ₂)								
Lengths								
As-F(1)	1.683 (6)	[1.713]	As-F(4)	1.690 (8)	[1.773]	As-F(6)	1.678 (8)	[1.735]
As-F(2)	1.684 (8)	[1.748]	As-F(5)	1.681 (8)	[1.763]	S-O(1)	1.354 (11)	
As-F(3)	1.706 (6)	[1.740]						
Angles								
F(1)-As-F(2)	87.5 (3)		F(2)-As-F(4)	92.9 (4)		F(3)-As-F(6)	89.5 (4)	
F(1)-As-F(3)	92.3 (3)		F(2)-As-F(5)	91.2 (5)		F(4)-As-F(5)	90.7 (5)	
F(1)-As-F(4)	179.1 (4)		F(2)-As-F(6)	90.4 (4)		F(4)-As-F(6)	90.3 (4)	
F(1)-As-F(5)	90.1 (4)		F(3)-As-F(4)	87.3 (3)		F(5)-As-F(6)	178.0 (5)	
F(1)-As-F(6)	88.8 (3)		F(3)-As-F(5)	88.8 (4)		O(1)-S-O(1')	122.2 (7)	
F(2)-As-F(3)	179.8 (4)							
(d) (S ₄ N ₄)(SbCl ₆) ₂								
Lengths								
Sb(1)-Cl(1)	2.425 (2)	[2.431]	Sb(1)-Cl(3)	2.356 (2)	[2.364]	Sb(1)-Cl(5)	2.320 (3)	[2.337]
Sb(1)-Cl(2)	2.355 (2)	[2.369]	Sb(1)-Cl(4)	2.344 (3)	[2.363]	Sb(1)-Cl(6)	2.361 (2)	[2.373]
Angles								
Cl(1)-Sb(1)-Cl(2)	178.86 (8)		Cl(2)-Sb(1)-Cl(3)	90.53 (8)		Cl(3)-Sb(1)-Cl(5)	90.05 (9)	
Cl(1)-Sb(1)-Cl(3)	88.36 (8)		Cl(2)-Sb(1)-Cl(4)	91.58 (9)		Cl(3)-Sb(1)-Cl(6)	87.93 (8)	
Cl(1)-Sb(1)-Cl(4)	89.52 (9)		Cl(2)-Sb(1)-Cl(5)	91.74 (9)		Cl(4)-Sb(1)-Cl(5)	92.45 (10)	
Cl(1)-Sb(1)-Cl(5)	88.53 (8)		Cl(2)-Sb(1)-Cl(6)	90.37 (9)		Cl(4)-Sb(1)-Cl(6)	89.49 (9)	
Cl(1)-Sb(1)-Cl(6)	89.32 (8)		Cl(3)-Sb(1)-Cl(4)	176.68 (9)		Cl(5)-Sb(1)-Cl(6)	177.10 (9)	
(e) (S ₄ N ₄)(AlCl ₄) ₂								
Lengths								
Al-Cl(1)	2.160 (2)	[2.165]	Al-Cl(3)	2.128 (2)	[2.147]	Al-Cl(4)	2.118 (3)	[2.138]
Al-Cl(2)	2.118 (3)	[2.136]						
Angles								
Cl(1)-Al-Cl(2)	106.22 (9)		Cl(1)-Al-Cl(4)	107.32 (8)		Cl(2)-Al-Cl(4)	115.02 (9)	
Cl(1)-Al-Cl(3)	108.13 (7)		Cl(2)-Al-Cl(3)	108.99 (9)		Cl(3)-Al-Cl(4)	110.85 (10)	

^a Values in square brackets are thermally corrected bond lengths (riding model) calculated with use of the local program STREP.

suppose that two sulfur atoms at a distance of 3.0 Å can be weakly bonded together. Indeed in the cation $S_6N_4^{2+}$ there is clear evidence of S-S bonding at this distance.¹² Thus we can write the following four resonance structures:

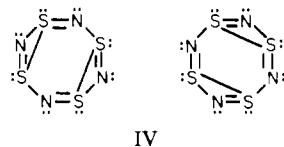


These are equivalent to a pair of electrons in a delocalized orbital concentrated largely inside the σ -bond framework which could be represented by III. Thus in this ion the ten delo-

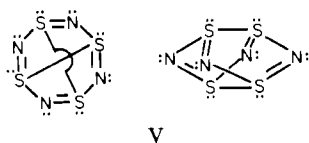


calized electrons split into two groups: eight conventional π -type electrons and two electrons that occupy an orbital associated with the four S atoms. These two electrons can also be described as occupying a π' orbital as postulated for P/N systems.^{42,43}

It is interesting to consider the addition of four electrons to $S_4N_4^{4+}$ to form the S_4N_4 molecule. Starting with an unpaired electron on each sulfur atom, the following different arrangements of SS bonds can be envisaged:



We have not previously considered the possibility of cross-ring bonds between nonadjacent S atoms as in V because the

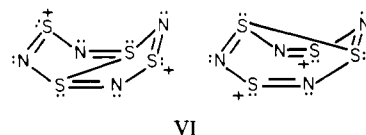


corresponding cross-ring distance of 4.1 Å in the planar structure seems long enough to exclude the possibility of such bonds. Moreover, two such bonds cross each other. However, if the molecule were to distort to a nonplanar form, the SS bonds could be much reduced in length and correspondingly increased in strength. If the buckling of the ring could occur without a great loss in the resonance energy of the single bond-double bond " π " system, then a nonplanar form could become the most stable form. This indeed is what appears to occur in the S_4N_4 molecule which has SS bonds of only 2.5 Å.⁴⁷ Two additional and presumably less important structures (IV) with S-S bonds of ca. 2.7 Å must also be considered. It is a basic assumption of this argument that the planar con-

jugated SN system can be distorted to a nonplanar form without the loss of a substantial amount of resonance energy.⁴⁸

Thus in S_4N_4 the SN bonds are all equivalent and have a length (1.61 Å) that is very slightly longer but quite comparable to the length of the SN bonds in the planar systems $S_4N_4^{2+}$, $S_4N_3^+$, and $S_5N_5^+$ and certainly shorter than the accepted S-N single bond length (e.g., 1.73 Å in $H_3N^+SO_3^-$ ⁴⁹). The SN "ring" in S_4N_4 must be considered as a delocalized system even though it is distinctly nonplanar. Any loss of resonance energy rising from this nonplanarity is apparently more than compensated for by the formation of S-S bonds which although long have an appreciable strength.

In the case of the nonplanar form of the $S_4N_4^{2+}$ cation, there is only one S-S bond and in the planar form this cannot be a cross-ring bond. However, if the molecule distorts to a nonplanar form, then the S-S distances diminish and S-S bonding is strengthened. In the "tub" form of the $S_4N_4^{2+}$ cation, two different structures (VI) with a cross-ring S-S bond



can be envisaged, giving with the structures II a total of six resonance structures equivalent to a delocalized electron pair occupying the interior of the molecule. This presumably gives sufficient additional bond strength to compensate for a slight loss in the resonance energy of the SN conjugated system.

It would appear that in $S_4N_4^{2+}$ the energies of the planar form and the nonplanar form are very finely balanced and that the perturbation caused by the $SbCl_6^-$ anion is sufficient to stabilize the non-planar form. It is reasonable to assume that the $SbCl_6^-$ ion is a slightly stronger donor than the other ions and the additional electron density thus gained by the cation is sufficient to strengthen the cross-ring S-S bonds just enough to cause the ion to distort from its otherwise planar form. In distorting in this way the cation is moving toward the cage structure of S_4N_4 in which two electrons have been added to the initial $S_4N_4^{2+}$ cation. It seems reasonable to predict that if the cation could be prepared in a stable crystalline form with a slightly more basic anion than $SbCl_6^-$ it would be still more distorted toward the S_4N_4 structure.

Anion-Cation Interactions. A tabulation of virtually all interionic contacts less than the van der Waals limits for the present structures is included in Table D in the supplementary material. Although many of these contacts must be treated with some caution due to disorder in the cation and, in the case of $(S_4N_4)(SO_3F)_2$, the fluorosulfate anion, it is clear that the majority of these contacts are to S and not to N and that some of them are appreciably shorter than the van der Waals limits.

Although the geometries of the contacts in the present $S_4N_4^{2+}$ salts are not as precisely defined as those of the contacts in salts of the thiodithiazyl cations $S_3N_2^+$ and $S_6N_4^{2+}$,¹² the contacts in the $S_4N_4^{2+}$ structures are presumably also nucleophilic in character and form in directions toward minima in the bonding and nonbonding electron density around each S atom. If the sulfur atoms are considered to be approximately sp^3 -hybridized, the contacts tend to be either approximately trans to the two primary bonds and hence in the plane of the cation or approximately trans to the two lone pairs on each sulfur atom.^{12,36} In this way, the secondary bonds as far as

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(43) Various different types of MO calculations, however, conflict on the role of transannular interactions in S/N systems such as $S_5N_5^+$,⁴⁴ $S_3N_3^-$,⁴⁵ and S_4N_2 .⁴⁶

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(46) Adkins, R. R.; Turner, A. G. *J. Am. Chem. Soc.* **1978**, *100*, 1383.

(47) Delucia, M. L.; Coppens, P. *Inorg. Chem.* **1978**, *17*, 2336.

(48) Indeed calculations on a series of [n]-paracyclophanes have indicated that quite large deformations of conventional aromatic systems are possible without seriously affecting the C-C bond lengths (Allinger, N. L.; Sprague, J. T. *J. Am. Chem. Soc.* **1973**, *95*, 3893).

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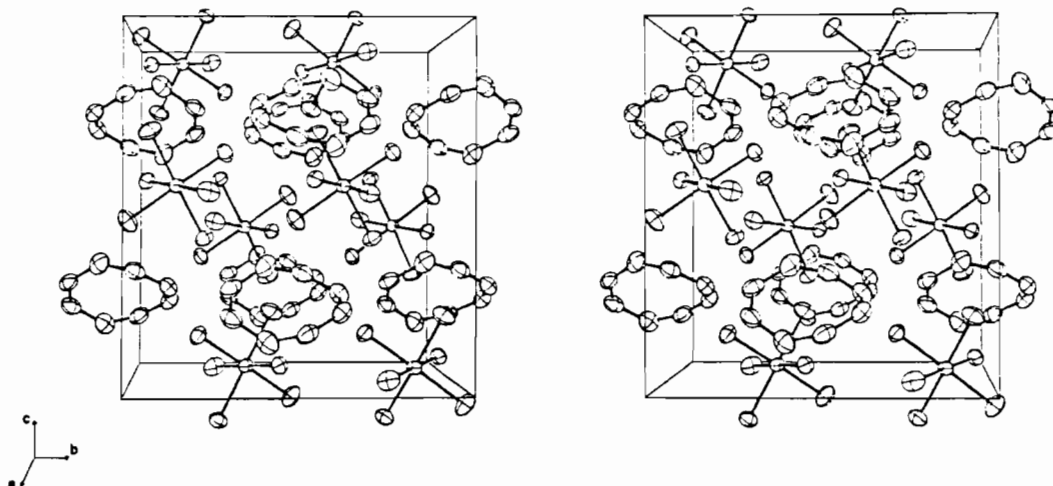


Figure 8. Stereoscopic view of the packing in $(S_4N_4)(SbCl_6)_2$ as viewed down a .

possible avoid the primary bonds and the lone pairs. Some examples are now discussed.

$(S_4N_4)(SO_3F)_2$. The two contacts from S(1) to O(1) and O(1') of 2.990 (3) and 3.104 (3) Å, respectively, are the shortest contacts to this atom, and the atoms O(1) and O(1') are only 0.50 and 0.72 Å out of plane of the cation with N(1)–S(1)⋯O(1') and N(2')–S(1)⋯(1) angles of 157.0 (1) and 160.6 (1)°, respectively. No similar contacts to S(2) exist, and all additional contacts to both S(1) and S(2) lie well out of the plane of the cation (Table C).

$(S_4N_4)(AlCl_4)_2$. With the exception of the contact S(2)⋯Cl(4) which has Cl(4) only 0.57 Å out of the plane of the cation and close to the extension of the N(2)–S(2) bond [N(2)–S(2)⋯Cl(4) = 158.7 (2)°, N(1)–S(2)⋯Cl(4) = 81.1 (2)°], all the S⋯Cl contacts deviate markedly (≥ 1.9 Å) from the plane of the cation. The shortest S⋯Cl (3.304 (2) Å) is ca. 0.35 Å less than the van der Waals limit.

$(S_4N_4)(Sb_3F_{14})(SbF_6)$. For the ordered ring, two contacts S(1)⋯F(17)⁹ and S(2)⋯F(10)⁶ are of note. The former contact is approximately collinear with the N(1)–S(1) bond [N(1)–S(1)⋯F(17)⁹ = 170.7 (3)° and N(2')–S(1)⋯F(17)⁹ = 71.3 (3)°] with the fluorine atom forming the contact 0.04 Å out of the plane of the ring, and the latter contact [of length 2.843 (7) Å] is approximately perpendicular to the plane of the ring at S(2) [N–S⋯F angles are 94 and 113°]. All the other S⋯F contacts to both S(1) and S(2) lie significantly out of the plane of this cation.

The shortest of the contacts to the disordered ring is "S(3)⋯F(7)¹⁴ = 2.746 (5) Å, with the fluorine atom F(7)¹⁴ 0.39 Å out of the plane of the ring with N–S⋯F angles of 155.8 (2) and 75.3 (2)°. There are no other really short contacts to either of the predominantly sulfur atoms (S(3) and S(4)). Of the contacts to the two "nitrogen" atoms, the shortest is N(4)⋯F(7)¹⁴ which is of length 2.809 (6) Å [S(3)–N(4)⋯F(7)¹⁴ = 169.3 (2)°; S(4)–N(3)⋯F(7)¹⁴ = 144.0 (3)°].

$(S_4N_4)(AsF_6)_2(SO_2)$. Due to disorder the contacts are again somewhat unreliable, with the shortest being SN(1)⋯F(6)

[2.969 (8) Å]. A short S⋯F(6') contact to the SO₂ solvent molecule of 3.203 (9) Å is approximately collinear with the S–O bonds (O–S⋯F(6') = 155°).

$(S_4N_4)(SbCl_6)_2$. A feature of the Sb–Cl distances in hexachloroantimonate(V) anions is the marked variance of the observed bond lengths with differences in the environment (packing) of the chlorine atoms.³⁴ In the present structure, Cl(1) is involved in significantly more contacts to the disordered $S_4N_4^{2+}$ cations than the other chlorine atoms (Table D) and forms the longest Sb–Cl bond. Furthermore some of these contacts, and particularly those involving Cl(1), may also have a role in the distortion of the $S_4N_4^{2+}$ cation. Figure 8 shows that the atom Cl(1) appears to project between cations in the a direction so that it is almost centrally above the closer ring with short contacts to the majority of the disordered positions around the ring. Those contacts from Cl(1) to the averaged positions in the base of the overall "tub"-shaped cation are however possibly longer (3.59, 3.69, 3.69, and 3.75 Å) than those to the out-of-plane atoms (3.39, 3.40, 3.46, and 3.55 Å). Several additional contacts involve all of the edges of the cation although the actual contact distances involved vary from 3.207 (6) Å up to the approximate van der Waals limit (ca. 3.75 Å).

Acknowledgment. We thank the Natural Science and Engineering Research Council of Canada for financial support of this work and Stefan Latour for assistance with the preparation of $(S_4N_4)(AlCl_4)_2$.

Registry No. 1, 64006-49-1; 2, 78764-05-3; 3, 78764-07-5; 4, 64095-05-2; 5, 78764-08-6; S_4N_4 PF₆, 78764-11-1; $(S_4N_4)(SbF_6)_2$ SO₂, 78764-10-0; S_4N_4 , 28950-34-7; SbCl₅, 7647-18-9; PF₅, 7647-19-0; PCl₅, 10026-13-8; SbF₅, 7783-70-2; AsF₅, 7784-36-3; AlCl₃, 7446-70-0; S₃N₃Cl₃, 18428-81-4; Cl₂, 7782-50-5; HSO₃F, 7789-21-1.

Supplementary Material Available: Compilations of observed and calculated structure factor amplitudes, anisotropic thermal amplitudes, root-mean-square vibration amplitudes, equations of least-squares mean planes, and interionic contact distances (77 pages). Ordering information is given on any current masthead page.