

Table I. Extended Hückel Parameters

orbital	$H_{ii}$	exponents <sup>a</sup>	
		$\xi_1$	$\xi_2$
Fe 4s	-8.39	1.90	
4p	-4.74	1.90	
3d	-11.46	5.35 (0.5366)	1.80 (0.6678)
Co 4s	-9.29	2.00	
4p	-5.35	2.00	
3d	-13.31	5.55 (0.5679)	2.10 (0.6059)
Ni 4s	-9.18	2.10	
4p	-5.15	2.10	
3d	-13.49	5.75 (0.5798)	2.3 (0.5782)
Rh 5s	-8.09	2.135	
5p	-4.57	2.100	
4d	-12.50	4.29 (0.5807)	1.97 (0.5685)
Re 6s	-9.22	2.398	
6p	-4.45	2.372	
5d	-11.29	5.343 (0.6359)	2.277 (0.5677)
H 1s	-13.60	1.30	
C 2s	-21.40	1.625	
2p	-11.40	1.625	
N 2s	-26.00	1.950	
2p	-13.40	1.950	
O 2s	-32.30	2.275	
2p	-14.80	2.275	

<sup>a</sup> Two Slater exponents are listed for the d functions. Each is followed in parentheses by the coefficient in the double- $\xi$  expression.

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#### Appendix

All the calculations were of the extended Hückel type.<sup>53</sup>

The  $H_{ii}$ 's for Fe, Co, Ni, and Re were obtained from a charge iterative calculation on  $\text{Fe}(\text{NH}_2)_4^{2-}$  ( $d^6$ ),  $\text{Co}(\text{NH}_2)_4^-$  ( $d^6$ ),  $\text{Ni}(\text{NH}_2)_4^{2-}$  ( $d^8$ ), and  $\text{Re}(\text{CO})_5(\text{CH}_3)$  ( $d^6$ ). The  $(\text{NH}_2)_4$  unit is a planar model porphyrin (see the text). The A, B, and C parameters for the quadratic charge dependence of Re were assumed to be the same as those of Tc. Parameters used previously<sup>53</sup> for H, C, N, and O were kept fixed during the iteration procedures. The orbital exponents for Fe 3d, Co 3d, and Ni 3d are those given by Richardson et al.<sup>54</sup> while those for the 4s and 4p atomic orbitals are taken from previous work.<sup>55</sup> The Basch and Gray orbitals are used for the Rh and Re functions.<sup>56</sup> These extended Hückel parameters are listed in Table I.

**Note Added in Proof.** More examples of  $d^n$  ( $n < 4$ ) oxometalloporphyrins have appeared:  $\text{O}=\text{Mo}-\text{TPP}$  and  $\text{O}=\text{Mo}-(\text{tetra-}p\text{-tolylporphyrin})$ ,<sup>57a</sup>  $d^2$ ;  $\text{O}=\text{V}-\text{phthalocyanine}$ ,<sup>57b</sup>  $d^1$ ;  $\text{O}=\text{Mn}-\text{TPP}$ ,<sup>57c</sup>  $d^3$ ;  $(\text{O}=\text{Mo}-\text{TPP})(\text{OR})$  ( $\text{R} = \text{H}, \text{CH}_3, \text{Et}, i\text{-Pr}, t\text{-Bu}$ ),<sup>57d</sup>  $d^1$ .

Iron porphyrins with an oxene inserted into an iron-nitrogen bond (structure 48) have recently been proposed by two groups.<sup>58</sup>

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## Monomeric and Dimeric Thiodithiazyl Cations, $\text{S}_3\text{N}_2^+$ and $\text{S}_6\text{N}_4^{2+}$ . Preparation and Crystal Structures of $(\text{S}_3\text{N}_2)(\text{AsF}_6)$ , $(\text{S}_6\text{N}_4)(\text{S}_2\text{O}_2\text{F})_2$ , and $(\text{S}_6\text{N}_4)(\text{SO}_3\text{F})_2$

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The preparation and characterization by X-ray crystallography of two new examples of compounds containing the bis-(thiodithiazyl) cation,  $\text{S}_6\text{N}_4^{2+}$ , obtained from the reaction of  $\text{S}_4\text{N}_4$  with fluorosulfuric acid are reported. Crystals of the compound  $(\text{S}_6\text{N}_4)(\text{SO}_3\text{F})_2$  are monoclinic, of space group  $P2_1/c$  with  $a = 6.099$  (2) Å,  $b = 11.714$  (2) Å,  $c = 9.765$  (2) Å,  $\beta = 102.44$  (2)°,  $V = 681.3$  (3) Å<sup>3</sup>, and  $D_c = 2.18$  g cm<sup>-3</sup> for  $Z = 2$ . The structure was solved by direct methods and refined to final agreement indices  $R_1 = 0.029$  ( $R_2 = 0.039$ ) for 1239 observed reflections ( $I/\sigma(I) > 3.0$ ). Crystals of the compound  $(\text{S}_6\text{N}_4)(\text{S}_2\text{O}_2\text{F})_2$  are monoclinic, of space group  $C2/c$  with  $a = 12.108$  (4) Å,  $b = 10.350$  (3) Å,  $c = 12.045$  (3) Å,  $\beta = 104.82$  (3)°,  $V = 1459.2$  (8) Å<sup>3</sup>, and  $D_c = 2.18$  g cm<sup>-3</sup> for  $Z = 4$ . The structure was solved by direct methods and refined to final agreement indices  $R_1 = 0.036$  ( $R_2 = 0.041$ ) for 1089 observed reflections. It is noteworthy that, apart from the cation  $\text{S}_6\text{N}_4^{2+}$ , the latter compound also contains the previously unknown thiofluorosulfate anion, which shows rotational disorder about the sulfur-sulfur bond. It is shown that the cation in the compound reported to be  $(\text{S}_3\text{N}_2)(\text{AsF}_6)$  should also be formulated as a salt of the dimeric  $\text{S}_6\text{N}_4^{2+}$  ion, and an improved synthetic route to the compound  $(\text{S}_6\text{N}_4)(\text{AsF}_6)_2$  using the oxidation of  $\text{S}_4\text{N}_4$  with  $\text{S}_8(\text{AsF}_6)_2$  is also reported and discussed. Furthermore, it is shown by X-ray crystallography that the analogous oxidation of  $\text{S}_4\text{N}_4$  using the compound  $\text{Te}_6(\text{AsF}_6)_4$  gives, among other products, the first well-characterized example of a monomeric thiodithiazyl radical cation  $\text{S}_3\text{N}_2^+$ , again with hexafluoroarsenate as the counterion. Crystals of this compound are triclinic, of space group  $P\bar{1}$  with  $a = 9.471$  (4) Å,  $b = 5.645$  (2) Å,  $c = 7.843$  (3) Å,  $\alpha = 74.78$  (3)°,  $\beta = 90.53$  (3)°,  $\gamma = 97.99$  (3)°,  $V = 400.5$  (3) Å<sup>3</sup>, and  $D_c = 2.60$  g cm<sup>-3</sup> for  $Z = 2$ . The structure was solved by the heavy-atom method and refined to final agreement indices  $R_1 = 0.064$  ( $R_2 = 0.076$ ) for 1190 observed reflections. The significance of the strong cation-cation and anion-cation interactions in these salts of the monomeric and dimeric thiodithiazyl cations is discussed in terms of charge-transfer models.

#### Introduction

During the past few years the cyclic sulfur-nitrogen cations  $\text{S}_5\text{N}_5^+$ ,<sup>1-3</sup>  $\text{S}_4\text{N}_3^+$ ,<sup>4-9</sup> and  $\text{S}_4\text{N}_4^{2+}$ <sup>10</sup> have been prepared and

characterized by X-ray crystallography and other physical methods. There is however some confusion in the literature

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regarding the formulation of a fourth cationic species which has been variously reported as either a monomeric radical cation  $S_3N_2^+$  or as a dimer  $S_6N_4^{2+}$ . When Banister and co-workers<sup>11</sup> reacted  $S_3N_2Cl$  with a large excess of chlorosulfuric acid, they obtained a very low yield (~1%) of deep green, virtually black crystals in addition to an unidentified yellow powder. The former compound was identified by an X-ray crystallographic study as  $(S_6N_4^{2+})(S_2O_6Cl^-)_2$ . The cation in this compound has a novel type of structure consisting of two identical, planar  $S_3N_2^+$  cations linked to each other in a pronounced chair conformation by two long bonds between pairs of sulfur atoms.<sup>11</sup> Paul and co-workers carried out the same reactions and obtained a product which they formulated as  $S_3N_2^+SO_3Cl^-$  on the basis of infrared spectroscopic evidence.<sup>12a</sup> It is not clear whether their compound was in fact identical with that prepared by Bannister et al.<sup>11</sup>

Subsequently Roesky and Hamza obtained a compound which they formulated as  $S_3N_2^+CF_3SO_3^-$  as one of the products of the reaction of  $S_4N_4$  with trifluoromethanesulfonic acid in methylene chloride. This black-brown compound gave a five-line ESR spectrum in solution with a  $g$  factor of 2.011 and a hyperfine coupling constant ( $a_N$ ) of 3.15 G. The spectrum is due to the coupling of the odd electron with two equivalent nitrogen atoms and is therefore consistent with the formulation of the compound as containing the monomeric radical cation  $S_3N_2^+$ .<sup>13</sup> Very recently Roesky et al. have shown by an X-ray crystallographic study that this compound is dimeric in the solid state and contains the same  $S_6N_4^{2+}$  ion as that in the  $S_2O_6Cl^-$  salt.<sup>12b</sup>

Independently, Gillespie and co-workers found that  $S_4N_4$  was oxidized by  $AsF_5$  in liquid sulfur dioxide to give a deep red-brown crystalline solid. An X-ray crystallographic determination of the structure of this compound was interpreted as showing that the compound was the hexafluoroarsenate salt of the monomeric radical cation  $S_3N_2^+$ .<sup>14</sup> The ESR spectrum of a solution of this compound in methylene chloride gave a  $g$  value and a hyperfine coupling constant essentially identical with those reported by Roesky and Hamza.<sup>13</sup>

In the light of the reported structures of the  $S_6N_4^{2+}$  cation<sup>11,12b</sup> and further work in this laboratory, we have reexamined the original crystallographic data on the compound formulated as  $(S_3N_2^+)(AsF_6^-)$  and find that, in fact, there are long S-S bonds between two adjacent  $S_3N_2^+$  ions giving a dimeric structure with exactly the same conformation as that observed by Bannister et al.<sup>11</sup> Unexpectedly, attempts to reprepare this compound by the original method have led almost invariably to the formation of the compound  $S_4N_4(AsF_6)_2SO_2$ <sup>10</sup> and very little, if any, of the compound originally formulated as  $S_3N_2^+AsF_6^-$ , which should now be written as the dimer  $S_6N_4^{2+}(AsF_6^-)_2$ . This curious result is discussed later.

The object of the present work was to attempt the preparation of both the monomeric and dimeric forms of the  $S_3N_2^+$  cation and to obtain structural information on the monomer and additional data on its dimer. We now report the preparation of the compounds  $(S_6N_4^{2+})(S_2O_2F^-)_2$  and  $(S_6N_4^{2+})(SO_3F^-)_2$  by the reaction of  $S_4N_4$  with fluorosulfuric acid and a reliable synthesis of  $(S_6N_4^{2+})(AsF_6^-)_2$  by the oxidation of  $S_4N_4$  with  $S_8^{2+}$ . This latter reaction is rather novel in sulfur-nitrogen chemistry, and accordingly the related reactions of  $S_4N_4$  with other group 6 homopolyatomic cations were attempted. In particular the reaction of  $S_4N_4$  with the cations  $Se_8^{2+}$  and  $Se_4^{2+}$  in  $SO_2$  were found to give the new species  $Se_4S_2N_4^{2+}$ , the preparation and structure of which is described in a following paper.<sup>15</sup> Somewhat surprisingly the reaction of  $Te_6^{4+}$  with  $S_4N_4$  did not give an analogous tellurium compound but resulted in the formation of the monomeric compound  $S_3N_2^+AsF_6^-$ . All three compounds,  $(S_6N_4^{2+})(S_2O_2F^-)$ ,  $(S_6N_4^{2+})(SO_3F^-)_2$ , and  $(S_3N_2^+)(AsF_6^-)$  were characterized by X-ray crystallography, and the structures of these compounds along with their infrared spectra are reported and discussed. The compound  $(S_3N_2^+)(AsF_6^-)$  contains the first well-characterized example of the monomeric thiodithiazyl ring.

### Experimental Section

All reactions were carried out under vacuum in flame-sealed double-arm ampules fitted with medium glass frits. Each ampule, prior to addition of reagents, had been flamed several times under vacuum to ensure removal of moisture from all surfaces. Sulfur dioxide (Matheson) was repeatedly distilled from, and stored over, phosphoric oxide before it was used. Methylene chloride (Fisher) was dried over molecular sieves and degassed prior to use. Arsenic pentafluoride (Ozark Mahoning Co.) was used directly from the cylinder and was measured on a calibrated Pyrex vacuum line. Fluorosulfuric acid (technical grade, Baker) was purified by distillation according to the method of Barr<sup>16</sup> and used directly from the collection vessel. All manipulations involving moisture-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). Powdered samples were prepared in Nujol dried over sodium wire. Spectra were recorded in the 4000–200-cm<sup>-1</sup> range with use of CsI windows.

**Preparation of  $S_4N_4$ .** The method of Becke-Goehring<sup>17</sup> with some modifications was used. Anhydrous chlorine was bubbled through a solution of  $S_2Cl_2$  (125 mL) in  $CCl_4$  (2 L) for 2 h in a flask equipped with a mechanical stirrer, a wide-bore (2 cm) condenser, and a gas inlet tube that extended below the surface of the solution. The solution was then cooled to 0 °C, and ammonia was passed in at a rate which was not allowed to exceed 50 L h<sup>-1</sup>. The reaction mixture was stirred constantly throughout the remainder of the preparation. A vigorous reaction ensued, and for the first few hours the reaction flask was cooled to prevent the temperature from rising above 50 °C. The mixture gradually changed from red-brown to gray-green and finally, after 6 h, to salmon red. At this point the ammonia flow was stopped, and the product was filtered, slurried with water (30 min), filtered again, and allowed to dry in the air for 24 h. The crude product remaining was Soxhlet extracted (8 h) with benzene (1 L) and recrystallized twice from benzene containing a pellet of mercury to remove any free sulfur associated with the crystals of  $S_4N_4$  (mp 187 °C, lit. mp 187–189 °C). Typical yields were 25–30 g.

Salts of the  $S_8^{2+}$ ,  $Se_8^{2+}$ ,  $Se_4^{2+}$ , and  $Te_6^{4+}$  cations were prepared according to the methods of Dean, Gillespie, and Ummat<sup>18</sup> with some modifications as given below.

**Preparation of  $S_8(AsF_6)_2$ .** A stoichiometry of 1:4 ( $S_8:AsF_5$ ) was used in order to ensure quantitative reaction since it has been found that the recommended 1:3 stoichiometry results in a mixture of products. In a typical reaction, 3.12 g (16 mmol) of sublimed sulfur (Shawinigan) was used with the appropriate amount of  $AsF_5$ . The

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6.2 g of isolated  $S_8(AsF_6)_2$  (80% yield on the basis of sulfur) was used without further purification. This product and all the other materials that were synthesized were stored under nitrogen in dry storage vessels equipped with Teflon rotflow valves.

**Preparation of  $Te_6(AsF_6)_4$ .** Arsenic pentafluoride (9.34 g, 55 mmol) was condensed onto powdered tellurium (4 g, 31.4 mmol) and 40 mL of frozen sulfur dioxide at  $-196^\circ C$  and the mixture allowed to warm up to room temperature. A deep red solution containing a brown solid was obtained after stirring for several days. The solvent was removed from the precipitate, and the brown solid was washed repeatedly with  $SO_2$  until a yellow-brown solution was obtained. At this point all the solvent was removed by static vacuum distillation (ca. 2–3 h) at liquid-nitrogen temperature. The chocolate brown precipitate which was isolated was used without further purification.

**Reaction of  $S_4N_4$  with  $HSO_3F$ .**  $S_4N_4$  (0.487 g, 2.64 mmol) and  $HSO_3F$  (0.794 g, 7.9 mmol) were each transferred to separate sides of the reaction vessel. The acid was delivered to the ampule arm via a calibrated 0.5-mL BD No. 2002  $1/2$  YT syringe fitted with an 18-gauge  $5 1/2$ -in. filling needle. Quantities delivered were to the nearest 0.01 mL. Both sides of the vessel were evacuated at  $-196^\circ C$ , and  $SO_2$  (ca. 15 mL) was condensed into each arm and then flame-sealed. The vessel was then allowed to warm to room temperature so that the  $HSO_3F$  completely dissolved in  $SO_2$ . This solution was poured onto the  $S_4N_4/SO_2$  solution. Immediately, a red-brown solution formed with an insoluble dark precipitate. Within  $1/2$  h the precipitate had disappeared completely, and on stirring for a further 12 h a bright yellow insoluble precipitate gradually reappeared with subsequent darkening of the solution. No further changes were observed during the next 12-h period. After the solution was filtered at room temperature and solvent was removed over a period of 48 h, five crystalline solids were observed. The predominant product consisted of large cubic dark green crystals identified by crystallographic examination as  $S_6N_4(S_2O_2F)_2$ . The remaining products were a red compound identified as  $S_6N_4(SO_3F)_2$ , two colorless crystalline solids, and long yellow needlelike crystals. From a comparison of the unit cell dimensions of the two colorless crystalline materials with values in the literature it was possible to identify them as ammonium fluorosulfate<sup>19</sup> and sulfamic acid,  $H_2NSO_3H$ .<sup>20</sup> The yellow crystalline product occurred as a widely dispersed surface contaminant on the dark green crystals. Subsequent repetitions of the reaction indicated that the  $S_6N_4(S_2O_2F)_2$  is formed from the yellow product since with extended times of solvent removal (ca. several days to a week) the amount of yellow product was reduced and uncontaminated green crystals could be isolated. On quick removal of solvent in the above procedure (ca. several hours) the predominant product consisted of yellow crystals which slowly turned dark green. Even when the former product was isolated and stored at liquid-nitrogen temperature for a number of weeks, it was again transformed to the dark green color of  $S_6N_4(S_2O_2F)_2$ . As a consequence of these observations, the material used in subsequent characterizations was isolated from reactions carried out in a minimal amount of  $SO_2$  (ca. 5 mL) and after extended periods of solvent removal (ca. 7 days). The initial yellow product isolated in this reaction is currently under investigation. Crystals were selected visually and further checked by microscopic examination to ensure product purity. Both the yellow and green crystals decompose to an orange solid on exposure to air. If the reaction is performed with use of a 1:1 stoichiometry, the  $S_6N_4(SO_3F)_2$  salt is obtained along with some of the red adduct  $S_4N_4SO_3$ . Both of these compounds were identified by their unit cell dimensions.<sup>21</sup>

Infrared spectrum of  $S_6N_4(S_2O_2F)_2$ : 1194 (s), 1118 (m), 1070 (s), 971 (m), 886 (sh), 837 (s), 728 (sh), 720 (vs), 567 (vs), 445 (w), 403

(w), 382 (vw), 372 (sh), 369 (m), 343 (w), 323 (vw), 310 (w), 293 (w), 279 (vw), 253 (w), 243 (w)  $cm^{-1}$ .

**Reaction of  $S_4N_4$  and  $AsF_5$ .**  $S_4N_4$  (0.222 g, 1.2 mmol) was added to one side of the reaction vessel. The vessel was then evacuated, and  $AsF_5$  (3.6 mmol) and  $SO_2$  were both condensed onto the  $S_4N_4$  at  $-196^\circ C$ . Both sides of the apparatus were flame-sealed. On warming to room temperature the solution became red. After 1 h the solution had turned completely green and after a 24-h period was brownish green. No further color changes occurred over the next 24-h period. After filtration of the solution and slow removal of solvent yellow cubic crystals were obtained. These crystals were washed several times with clean  $SO_2$ , and the resulting crystals were colorless. An X-ray diffraction study identified the colorless crystals as  $S_4N_4(AsF_6)_2SO_2$ .<sup>10</sup> Further attempts to obtain the previously reported  $(S_3N_2^+)(AsF_6^-)$  by this method were unsuccessful.

**Reaction of  $S_4N_4$  and  $AsF_5$  with Trace Amounts of Sulfur Present.** The reaction proceeded essentially as described above. After filtration of the solution and removing solvent, however, both yellow and dark green crystals were obtained in approximately equal quantities. Visual comparison of these two crystal types with authentic samples indicated they were probably  $S_6N_4(AsF_6)_2$  and  $S_4N_4(AsF_6)_2SO_2$ .

**Reaction of  $S_4N_4$  with  $S_8(AsF_6)_2$ .**  $S_4N_4$  (0.250 g, 1.36 mmol) and  $S_8(AsF_6)_2$  (0.860 g, 1.36 mmol) were transferred to one side of the reaction vessel. The vessel was then evacuated and sulfur dioxide (ca. 20 mL) condensed at  $-196^\circ C$  onto the solid reactants. Both sides of the apparatus were flame-sealed. The mixture was allowed to warm slowly to room temperature and stirred for 24 h. An initially blue solution quickly turned to green and then reddish brown, with all reactants being completely soluble. Within 0.5 h a solid pale yellow precipitate appeared. The volume of precipitate gradually increased over the next 12-h period. No further changes were observed during a further 24-h period. After filtration at room temperature and removal of the solvent very slowly, large green crystals were obtained in good yield (1.12 mmol, 82% yield on the basis of  $S_4N_4$ ) and were identified by crystallographic examination as the dimeric  $S_6N_4(AsF_6)_2$  salt. The pale yellow insoluble material was identified as elemental sulfur by comparison of its Raman spectrum with that of a sample of crystalline sulfur.

Infrared spectrum of  $S_6N_4(AsF_6)_2$ : 1203 (m), 1164 (m), 1149 (m), 1068 (s), 1035 (m), 1010 (s, sh), 974 (s), 928 (s), 881 (sh), 861 (w), 808 (w), 761 (sh), 728 (sh), 713 (vs), 680 (sh), 655 (sh), 589 (sh), 563 (m), 550 (vw), 531 (m), 510 (sh), 485 (sh), 472 (sh), 445 (m), 437 (m), 382 (s), 350 (w), 230 (w)  $cm^{-1}$ .

**Reaction of  $S_4N_4$  with  $Te_6(AsF_6)_4$ .**  $S_4N_4$  (0.200 g, 1.1 mmol) and  $Te_6(AsF_6)_4$  (1.652 g, 1.1 mmol) were each transferred to one side of the reaction vessel. The vessel was evacuated and sulfur dioxide (ca. 20 mL) condensed at  $-196^\circ C$  onto the solid reactants. Both sides of the ampule were flame-sealed. The reactants on warming immediately gave a red solution which continually darkened until the mixture reached room temperature. The burgundy red solution which resulted contained a deep red precipitate whose volume appeared to increase over the next 48 h of continual stirring. This precipitate was identified as  $Te_4^{2+}(AsF_6^-)_2$  by its characteristic Raman spectrum.<sup>22</sup> No additional color changes were noted during this period. The solution was filtered and solvent removed slowly (ca. 5 days). Dark red crystals were isolated and identified by X-ray diffraction methods as the monomeric  $S_3N_2^+AsF_6^-$  salt.

Infrared spectrum of  $S_3N_2^+AsF_6^-$ : 1203 (m), 1164 (m), 1149 (m), 1119 (vw), 1068 (m), 1035 (vw), 1010 (m), 974 (s), 953 (w), 928 (sh), 918 (sh), 896 (sh), 861 (m), 839 (w), 808 (vw, sh), 761 (sh), 720 (vs), 686 (sh), 655 (sh), 622 (vw, sh), 589 (vw), 558 (vw), 553 (vw), 531 (m), 455 (m), 382 (s), 330 (sh), 271 (sh), 230 (w)  $cm^{-1}$ .

**X-ray Crystallography.** All crystals in the structure determinations were selected and sealed in Lindemann capillaries under a dry nitrogen atmosphere in a specially designed drybox equipped with a microscope. Crystals of the compound  $(S_3N_2)(AsF_6)$  were mainly dark red thin plates and needles. The crystalline material from the  $S_4N_4/HSO_3F$  reaction, however, contained several different products. The principal product was in the form of large well-defined dark green cubic crystals, and crystals for the X-ray studies were obtained by cleaving these into smaller fragments of a more suitable size. Several dark red crystals also isolated from this reaction were found, by crystallography, to be the compounds  $(S_6N_4)(SO_3F)_2$  and  $(S_4N_4)(SO_3F)_2$ .<sup>10</sup> Ammonium

- (19) Cell found: orthorhombic,  $Pnma$ ,  $a = 8.955$  (2) Å,  $b = 5.981$  (1) Å,  $c = 7.519$  (2) Å,  $V = 402.7$  (1) Å<sup>3</sup>. Literature [O'Sullivan, K.; Thompson, R. C.; Trotter, J. *J. Chem. Soc. A* 1970, 1814]: orthorhombic,  $Pnma$ ,  $a = 8.972$  (10) Å,  $b = 5.996$  (10) Å,  $c = 7.542$  (10) Å,  $V = 405.7$  Å<sup>3</sup>.
- (20) Unit cell found: orthorhombic,  $Pbca$ ,  $a = 8.061$  (3) Å,  $b = 8.107$  (5) Å,  $c = 9.209$  (3) Å,  $V = 601.9$  (5) Å<sup>3</sup>. Literature [Bats, J. W.; Coppens, P.; Koetzle, T. F. *Acta Crystallogr., Sect. B* 1977, B33, 37]:  $a = 8.034$  (1) Å,  $b = 8.030$  (1) Å,  $c = 9.236$  (2) Å,  $V = 595.1$  (2) Å<sup>3</sup>.
- (21) Unit cell found:  $S_6N_4(SO_3F)_2$ , monoclinic,  $P2_1/n$ ,  $a = 6.109$  (2) Å,  $b = 11.723$  (3) Å,  $c = 9.775$  (2) Å,  $\beta = 102.48$  (2)°,  $V = 683.6$  (3) Å<sup>3</sup>. Unit cell found:  $S_4N_4SO_3$ , monoclinic,  $P2_1/n$ ,  $a = 7.173$  (2) Å,  $b = 10.451$  (2) Å,  $c = 10.782$  (2) Å,  $\beta = 95.79$  (2)°,  $V = 804.17$  (33) Å<sup>3</sup>. Literature [Gieren, A.; Deberer, B.; Roesky, H. W.; Amin, N.; Petersen, N. Z. *Anorg. Allg. Chem.* 1978, 440, 119]:  $a = 7.175$  (3) Å,  $b = 10.456$  (4) Å,  $c = 10.769$  (4) Å,  $\beta = 95.30$  (4)°,  $V = 804.5$  Å<sup>3</sup>.

- (22) Booth, M.; Morton, M. J.; Gillespie, R. J. *Adv. Raman Spectrosc.* 1972, 1, 364.

Table I. Crystal Data and Intensity Measurements

	$(S_3N_2)(AsF_6)$	$(S_6N_4)(AsF_6)_2^a$	$(S_6N_4)(S_2O_2F)_2$	$(S_6N_4)(SO_3F)_2$
	Crystal Data			
system	triclinic	monoclinic	monoclinic	monoclinic
<i>a</i> , Å	9.471 (4)	8.499 (4)	12.108 (4)	6.099 (2)
<i>b</i> , Å	5.645 (2)	8.298 (4)	10.350 (3)	11.714 (2)
<i>c</i> , Å	7.843 (3)	11.069 (8)	12.045 (3)	9.765 (2)
$\alpha$ , deg	74.78 (3)	90.0	90.0	90.0
$\beta$ , deg	90.53 (3)	94.59 (5)	104.82 (3)	102.44 (2)
$\gamma$ , deg	97.99 (3)	90.0	90.0	90.0
<i>V</i> , Å <sup>3</sup>	400.5 (3)	778	1459.2 (8)	681.3 (3)
fw	313.1	616.2	478.6	446.5
<i>Z</i>	2	2 (dimers)	4 (dimers)	2 (dimers)
<i>D<sub>c</sub></i> , g cm <sup>-3</sup>	2.60	2.67	2.18	2.18
<i>F</i> (000)	298	596	952	444
space group	<i>P</i> $\bar{1}$	<i>P</i> 2 <sub>1</sub> / <i>c</i>	<i>C</i> 2/ <i>c</i>	<i>P</i> 2 <sub>1</sub> / <i>n</i>
$\mu$ (Mo <i>K</i> $\alpha$ ), cm <sup>-1</sup>	52.8	54.4	15	13.1
reflctns used in cell determination, deg	15 (25 < 2 $\theta$ < 30°)		15 (28° < 2 $\theta$ < 32°)	15 (30° < 2 $\theta$ < 35°)
	Intensity Measurements			
cryst dimens, cm	thin plate 0.036 × 0.007 × 0.019 in the <i>a</i> , <i>b</i> , <i>c</i> , directions		irregular, approximately rectangular 0.018 × 0.023 × 0.035	trapezoidal block 0.013 × 0.027 × 0.027
scan width, deg	( <i>K</i> $\alpha_1$ - 1.5) to ( <i>K</i> $\alpha_2$ + 1.5)		( <i>K</i> $\alpha_1$ - 0.75) to ( <i>K</i> $\alpha_2$ + 0.75)	( <i>K</i> $\alpha_1$ - 0.9) to ( <i>K</i> $\alpha_2$ + 0.9)
scan rate, deg/min	4.0-29.3		3.0-29.3	3.0-29.3
std reflctns	3 std every 37 reflctns <sup>b</sup>		3 std every 47 reflctns	3 std every 47 reflctns
max 2 $\theta$ , deg	55		52	55
total reflctns collected <sup>c</sup>	3188 <sup>d</sup>		1849 <sup>e</sup>	3167 <sup>f</sup>
unique nonzero data	1702		1332	1524
obsd data ( <i>I</i> / $\sigma$ ( <i>I</i> ) > 3.0)	1190		1089	1239

<sup>a</sup> Reference 14. <sup>b</sup> A gradual decrease in the intensities of the standard reflections for this crystal was corrected for using the linear equation  $I_{cor} = I_{obsd}(1 + 001172t)$  (*t* = time in h). <sup>c</sup> Total includes all standard reflections collected. <sup>d</sup> Total includes 2127 reflections in the quadrants *h, ±k, ±l* with  $2\theta < 55^\circ$  and a further 1061 reflections in the quadrants  $-h, ±k, ±l$  with  $2\theta < 35^\circ$ . <sup>e</sup> Quadrants *h, k, ±l*. <sup>f</sup> Total includes 1907 reflections in quadrants *h, k, ±l* with  $2\theta < 55^\circ$  and a further 1260 reflections in the quadrants  $-h, -k, ±l$  with  $2\theta < 55^\circ$  (shell incomplete).

fluorosulfate<sup>19</sup> and sulfamic acid<sup>20</sup> were also characterized as products of this reaction.

Precession photographs were used to check crystal quality and to obtain preliminary cell and symmetry information. Further work on each crystal using a Syntex P2<sub>1</sub> diffractometer and graphite-monochromatized Mo *K* $\alpha$  radiation ( $\lambda = 0.71069$  Å) gave the crystal data summarized in Table I. Data on each crystal were collected in a coupled  $\theta$ - $2\theta$  mode under the conditions given in Table I. For each reflection stationary background counts were recorded at each end of the scan, each for one-fourth of the scan time, and several standard reflections were periodically checked for crystal and instrument stability. The total number of reflections collected for each crystal is also given in Table I.

For each data set Lorentz and polarization corrections and in the case of the compound  $(S_3N_2)(AsF_6)$ , a correction for the decay in the intensities of the standard reflections, were applied. Absorption corrections were considered necessary only for the monomer  $(S_3N_2)(AsF_6)$ . These were applied at a later stage of the refinement when the composition of the crystal had been established. The corrections were made with use of the program ABSORB and a  $5 \times 12 \times 8$  grid.<sup>23</sup> *A\** values were found to vary from 1.428 to 2.851. Averaging equivalent data and excluding reflections which are systematically absent or have observed structure amplitudes equal to zero gave the final totals of independent reflections shown in Table I.

**Structure Solutions.**  $(S_3N_2)(AsF_6)$ . Initially, the Patterson function was used to give possible positions in the acentric space group *P* $\bar{1}$  for three heavy atoms, which were assumed to be tellurium. Least-squares refinement of these gave  $R_1 = 0.32$ . Two subsequent Fourier maps were calculated, and as atoms from these maps were added to the initial model, it became clear from temperature factors that the structure did not contain any tellurium but appeared to be the compound  $S_3N_2^+AsF_6^-$ , although not all fluorine atoms had been located. From an inspection of the correlation matrix at this point, it was obvious that the structure had developed a pseudo center of symmetry at (0.45, -0.14, 0.46), and therefore further refinement was in the centric space group *P* $\bar{1}$ . After transformation of all the coordinates

of all the atoms so far located in one of the  $S_3N_2^+AsF_6^-$  groups to conform with this center of symmetry, further least-squares refinement and a subsequent difference Fourier gave the positions of the missing fluorine atoms and established the composition of the compound. At this stage, the data were corrected for absorption effects and refinement of this model, first with isotropic temperature factors and then with all atoms having anisotropic temperature factors, eventually converged to final agreement indices  $R_1 = 0.064$  and  $R_2 = 0.076$  ( $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$ ,  $R_2 = [\sum w||F_o| - |F_c||^2 / \sum w|F_o|^2]^{1/2}$ ) for all 1190 observed reflections and  $R_1 = 0.091$  and  $R_2 = 0.094$  for all 1702 nonzero data (109 parameters). In the final cycle of refinement no parameter shifted more than 15% of its associated standard error, and the weights used were calculated with the expressions  $w = xy$  where (1)  $x = F/10$  if  $F < 10$  or  $x = 19/F$  if  $F > 19$ , otherwise  $x = 1.0$ , and (2)  $y = \sin \theta/0.32$  if  $\sin \theta < 0.32$  or  $y = 0.40/\sin \theta$  if  $\sin \theta > 0.40$ , otherwise  $y = 1.0$ . A final comparison of the average  $w||F_o| - |F_c||^2$  as a function of  $F_o$  or  $\sin \theta$  revealed no systematic trends, and a final difference Fourier was featureless, the maximum peak being  $+1.25 e/\text{Å}^3$  close to the arsenic atom.

$(S_6N_4)(S_2O_2F)_2$ . Since the nature of the compound was unknown at the start of the structure determination, a likely composition for the compound on the basis of volume considerations was used. Normalized structure factors ( $E_{hkl}$ 's) were calculated on the assumption that the unit cell contained 36 sulfur and 50 nitrogen atoms, and the solution of the structure was attempted with use of the direct-method routines in the program SHELX.<sup>24</sup> The best *E* map based on 12 phase permutations and 145 reflections with  $E > 1.4$  contained five peaks in reasonable bonding situations to each other. Least-squares refinement assuming these atoms to be sulfur gave  $R_1 = 0.274$ , and the following Fourier enabled the cation to be identified as the previously known  $S_6N_4^{2+}$ . The counterion in the structure was found to be tetrahedral with two directly bonded sulfur atoms (S-S distance of 2.01 Å), and it was assumed that the anion was the previously unknown thiofluorosulfate anion. Refinement of this model gave  $R_1 = 0.116$  with isotropic temperature factors and  $R_1 = 0.038$  when all atoms were refined with anisotropic temperature factors. At this stage it

(23) X-RAY System of crystallographic programs, Technical Report TR-446; Computer Science Centre: University of Maryland, 1976.

(24) Sheldrick, G. M. "SHELX System of Crystallographic Programs"; University of Cambridge: Cambridge, 1976.

Table II. Final Atomic Positional ( $\times 10^4$ ) and Thermal Parameters<sup>a</sup> ( $\times 10^3$ ) with Standard Deviations in Parentheses

atom	x	y	z	$U_{11}$	$U_{22}$	$U_{33}$	$U_{12}$	$U_{13}$	$U_{23}$
(a) Monomeric ( $S_3N_2$ )(AsF <sub>6</sub> )									
As	2265 (1)	-729 (2)	2311 (1)	36.6 (5)	42.4 (5)	35.1 (5)	6.2 (3)	-4.1 (3)	-5.8 (2)
S(1)	1447 (3)	5236 (6)	7981 (4)	46 (1)	63 (2)	61 (2)	13 (1)	4 (1)	-18 (1)
S(2)	1959 (3)	2674 (5)	6571 (4)	44 (1)	54 (1)	59 (2)	7 (1)	-8 (1)	-18 (1)
S(3)	4321 (3)	5525 (6)	7378 (5)	42 (1)	69 (2)	73 (2)	2 (1)	0 (1)	-31 (1)
N(1)	3064 (11)	6467 (18)	8148 (13)	57 (5)	53 (5)	55 (5)	-2 (4)	5 (4)	-14 (4)
N(2)	3651 (9)	3364 (19)	6570 (13)	33 (4)	68 (6)	63 (6)	11 (4)	-4 (4)	-24 (5)
F(1)	953 (8)	-2750 (19)	3655 (12)	53 (4)	111 (7)	73 (5)	-2 (4)	9 (4)	9 (5)
F(2)	3142 (9)	-3162 (17)	2352 (14)	70 (5)	78 (5)	117 (7)	41 (4)	-11 (5)	-25 (5)
F(3)	1456 (13)	1658 (18)	2313 (15)	131 (8)	75 (6)	113 (7)	54 (6)	-4 (6)	-25 (5)
F(4)	1334 (8)	-1278 (18)	546 (11)	69 (5)	106 (6)	67 (5)	22 (4)	-28 (4)	-39 (4)
F(5)	3532 (10)	1277 (17)	936 (12)	88 (6)	85 (6)	73 (5)	-22 (5)	17 (4)	8 (4)
F(6)	3166 (10)	-250 (21)	4131 (11)	88 (6)	131 (8)	58 (5)	5 (5)	-29 (4)	-38 (5)
(b) $S_6N_4^{2+}(S_2O_2F)_2^-$									
S(1)	1365.8 (9)	1258.2 (9)	-208.3 (8)	43.1 (5)	28.8 (5)	38.8 (5)	-1.9 (4)	16.9 (4)	0.3 (4)
S(2)	1263.0 (9)	3060.0 (9)	-1102.2 (8)	42.4 (5)	33.4 (5)	32.2 (5)	5.0 (4)	16.5 (4)	4.4 (4)
S(3)	-76.5 (9)	2977.8 (12)	407.4 (10)	41.4 (6)	53.6 (6)	47.9 (6)	4.8 (5)	25.3 (5)	-0.4 (5)
S(4)	-2439.4 (9)	3640.2 (10)	2102.2 (8)	52.4 (6)	30.2 (5)	33.3 (5)	5.8 (4)	19.1 (4)	6.1 (4)
S(5)	-2149.8 (12)	1769.2 (10)	1634.9 (11)	80.7 (9)	29.7 (5)	54.0 (7)	4.7 (5)	31.4 (6)	-1.4 (5)
N(1)	478 (3)	1607 (4)	531 (3)	41 (2)	45 (2)	40 (2)	-5 (2)	18 (1)	2 (2)
N(2)	351 (3)	3735 (3)	-524 (3)	45 (2)	37 (2)	43 (2)	11 (2)	17 (2)	2 (1)
X(1) <sup>b</sup>	-1581 (4)	4363 (3)	1783 (4)	140 (4)	42 (2)	107 (3)	-15 (2)	94 (3)	0 (2)
X(2) <sup>b</sup>	-3579 (4)	3884 (4)	1492 (4)	83 (3)	90 (3)	73 (3)	35 (2)	-12 (2)	-20 (2)
X(3) <sup>b</sup>	-2283 (3)	3542 (3)	3324 (2)	65 (2)	50 (2)	39 (1)	4 (1)	21 (1)	6 (1)
(c) $(S_6N_4)(SO_3F)_2$									
S(1)	6690.0 (11)	1316.5 (6)	4968.2 (7)	29.3 (3)	35.3 (3)	41.5 (4)	1.3 (2)	6.6 (3)	2.6 (3)
S(2)	3685.5 (11)	885.1 (6)	3469.4 (7)	36.1 (3)	33.6 (3)	32.0 (3)	1.5 (3)	4.8 (2)	0.1 (3)
S(3)	3154.6 (12)	2719.6 (6)	5118.3 (8)	41.1 (4)	35.7 (3)	44.5 (4)	7.4 (3)	8.4 (3)	-2.5 (3)
N(1)	5689 (4)	2394 (2)	5661 (2)	41 (1)	35 (1)	39 (1)	-2 (1)	3 (1)	-3 (1)
N(2)	2130 (4)	1875 (2)	3906 (2)	32 (1)	37 (1)	41 (1)	5 (1)	3 (1)	4 (1)
S(4)	1830.9 (11)	747.4 (6)	7768.5 (7)	34.5 (3)	35.0 (3)	36.2 (3)	2.6 (3)	8.6 (3)	-1.2 (3)
O(1)	612 (5)	1783 (2)	7538 (3)	81 (2)	63 (2)	60 (2)	38 (1)	10 (1)	-11 (1)
O(2)	2843 (5)	451 (2)	6639 (3)	100 (2)	63 (2)	69 (2)	31 (1)	52 (2)	7 (1)
O(3)	680 (5)	-161 (3)	8261 (3)	76 (2)	82 (2)	76 (2)	-37 (2)	9 (1)	24 (2)
F	3783 (4)	997 (2)	9015 (3)	61 (1)	95 (2)	84 (2)	-13 (1)	-27 (1)	-5 (1)

<sup>a</sup> In the form  $\exp\{-2\pi^2(h^2a^{*2}U_{11} + k^2b^{*2}U_{22} + l^2c^{*2}U_{33} + 2hka^*b^*U_{12} + 2hla^*c^*U_{13} + 2klb^*c^*U_{23})\}$ . <sup>b</sup> Atoms X have the complex scattering factor  $f_X = 1/3(2f_O + f_F)$ .

was noted that, although the sulfur-fluorine distance in the anion was significantly longer than the two sulfur-oxygen distances, the actual distance was still remarkably short. Furthermore, there was considerable anisotropy in the temperature factor ellipsoids for the fluorine and oxygen positions, indicative of oxygen-fluorine rotational disorder in the anion, an effect which has been observed previously in the chlorodifluorooxosulfur(VI) cation  $OSClF_2^+$ .<sup>25</sup> Introduction of a model with use of a weighted average scattering curve ( $1/f_F + 2/3f_O$ ) for the three light atom positions in the anion produced a significant improvement in the crystallographic residual. The final least-squares refinement using this disordered model eventually converged to  $R_1 = 0.036$  and  $R_2 = 0.041$  for the 1089 observed data. The refinement with all 1332 nonzero data gave  $R_1 = 0.046$  and  $R_2 = 0.047$  with a very slight improvement in the standard deviations of individual bond lengths and bond angles, and the results from this refinement are used in the final tables. No extinction corrections were considered necessary. The only reflection which appeared to be suffering from extinction was (2, 0, 2), and this was down-weighted considerably by the weighting scheme used. In the final cycle with all the data no parameter shifted by more than 14% of its associated standard deviation, and a final difference Fourier showed some residual electron density near the disordered oxygen/fluorine positions in the  $S_2O_2F^-$  anion but was nowhere  $>0.65 e/\text{\AA}^3$ . The weighting scheme used in the final cycle was  $w = xy$  where (1)  $x = F/20$  if  $F < 20$  or  $x = 46/F$ , if  $F > 46$ , otherwise  $x = 1.0$ , and (2)  $y = \sin \theta/0.265$  if  $\sin \theta < 0.265$ , otherwise  $y = 1.0$ .

$(S_6N_4)(SO_3F)_2$ . As with the compound  $(S_6N_4)(S_2O_2F)_2$ , the nature of the present compound was again unknown at the start of the structure determination. A solution was however found by using the direct-method routines of the program SHELX and the Patterson

function to check some of the atomic positions indicated in the best  $E$  map. Least-squares refinement gave reasonable  $R$  factors, and the remaining atomic positions were found in subsequent Fourier maps. Atomic assignments in the compound were made on the basis of temperature factors and bond lengths. With all atoms located, least-squares refinement using all the observed data gave  $R_1 = 0.081$  with all atoms having isotropic temperature factors and  $R_1 = 0.031$  when anisotropic temperature factors were introduced for all atoms.

After the introduction of a weighting scheme two further cycles of refinement eventually converged to final agreement indices  $R_1 = 0.029$  ( $R_2 = 0.039$ ) for the 1239 observed data and  $R_1 = 0.035$  ( $R_2 = 0.047$ ) for the 1440 data with  $F > \sigma(F)$ . In the final cycle of refinement no parameter shifted by more than 5% of its standard deviation, and a final difference Fourier was featureless with a residual maximum peak and a minimum trough of  $+0.35$  and  $-0.70 e/\text{\AA}^3$ , respectively. The weighting scheme used in the final cycles gave reflections with  $F > 20$  weights equal to  $(20/F)^2$ , otherwise  $w = 1.0$ . Most reflections were given unit weights. A final comparison of  $w||F_o| - |F_c||^2$  as a function of  $F_o$  and  $\sin \theta$  revealed no systematic trends indicating the suitability of this scheme.

For all three compounds neutral-atom scattering factors in the analytical form were taken from ref 26. All calculations were performed on a CDC 6400 computer using a series of programs in the X-RAY<sup>23</sup> and SHELX<sup>24</sup> systems and some local programs. The final atomic positional and thermal parameters for all three compounds are given in Table II. Interatomic distances and angles in the thiodithiazyl rings along with the dimensions of some related compounds are given in Table III. Information on the least-squares mean planes in the  $S_3N_2^+$  and  $S_6N_4^{2+}$  cations is given in Table IV, and the significant features of the anion-cation interactions in these compounds

(25) Dunphy, R. F.; Lau, C.; Lynton, H.; Passmore, J. J. *Chem. Soc., Dalton Trans.* 1973, 2533.

(26) "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, U.K., 1965.

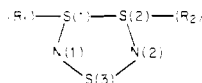
Table III. Bond Distances (Å) and Bond Angles (Deg) in the Known Thiodithiazyl Cations<sup>a</sup> and Related Compounds

Bond Lengths						
compd	S(1)-S(2)	S(1)-N(1)	S(2)-N(2)	S(3)-N(1)	S(3)-N(2)	other
$(S_3N_2)(AsF_6)^b$	2.143 (5)	1.611 (10)	1.595 (9)	1.557 (12)	1.572 (12)	
$(S_6N_4)(AsF_6)_2^c$	2.147 (3)	1.599 (6)	1.610 (6)	1.575 (7)	1.545 (7)	
$(S_6N_4)(S_2O_6F)_2^b$	2.142 (1)	1.603 (4)	1.607 (4)	1.559 (4)	1.560 (4)	
$(S_6N_4)(SO_3F)_2^b$	2.145 (1)	1.613 (3)	1.613 (3)	1.569 (3)	1.566 (2)	
$(S_6N_4)(S_2O_6Cl)_2^d$	2.146 (1)	1.601 (3)	1.609 (4)	1.574 (3)	1.563 (3)	
$(S_6N_4)(SO_3CF_3)_2^e$	2.138 (3)	1.612 (6)	1.617 (5)	1.576 (5)	1.561 (6)	
$S_3N_2 \cdot NCOCF_3^f$	2.206 (1)	1.633 (2)	1.641 (4)	1.551 (2)	1.589 (3)	S-NCOCF <sub>3</sub> 1.600 (2)
$S_3N_2Cl^+Cl^-^g$	2.136 (5)	1.581 (5)	1.615 (5)	1.617 (5)	1.543 (5)	S-Cl 2.168 (5)
$(p\text{-ClC}_6\text{H}_4)_2S_3N_2^h$	3.293 (8)	1.66 (2)	1.66 (2)	1.54 (2)	1.56 (2)	S-C 1.74 (1), 1.75 (1)
$(C_6H_4)_2S_3N_2^i$	3.231 (5)	1.659 (5)	1.659 (5)	1.530 (5)	1.530 (5)	S-C 1.758 (7)

Bond Angles						
compd	N(1)-S(1)-S(2)	S(1)-S(2)-N(2)	N(1)-S(3)-N(2)	S(1)-N(1)-S(3)	S(2)-N(2)-S(3)	other
$(S_3N_2)(AsF_6)$	96.4 (4)	96.9 (5)	107.0 (5)	119.9 (7)	119.7 (7)	
$(S_6N_4)(AsF_6)_2$	96.4 (3)	96.7 (3)	107.2 (3)	119.8 (4)	119.9 (4)	
$(S_6N_4)(S_2O_6F)_2$	97.0 (1)	96.8 (1)	108.1 (2)	119.0 (3)	118.9 (2)	
$(S_6N_4)(SO_3F)_2$	97.2 (1)	96.6 (1)	107.8 (1)	118.9 (1)	119.5 (1)	
$(S_6N_4)(S_2O_6Cl)_2$	97.2 (1)	96.6 (1)	107.6 (2)	119.1 (2)	119.6 (2)	
$(S_6N_4)(SO_3CF_3)_2$	97.0 (2)	97.1 (2)	107.8 (3)	119.0 (4)	119.0 (3)	
$S_3N_2 \cdot NCOCF_3$	97.14 (7)	94.0 (1)	109.2 (2)	118.0 (1)	118.1 (2)	S-S-NCOCF <sub>3</sub> 108.9 (1)
$S_3N_2Cl^+Cl^-$	97.8 (3)	95.5 (3)	106.3 (3)	118.0 (3)	120.7 (3)	S-S-Cl 100.1 (3) N-S-Cl 106.5 (3)
$(p\text{-ClC}_6\text{H}_4)_2S_3N_2$	79.5 (6)	81.4 (6)	124 (1)	129 (1)	126 (2)	C-S-S 172, 176
$(C_6H_4)_2S_3N_2$	81.0 (2)	81.0 (2)	124.8 (3)	126.6 (3)	126.6 (3)	C-S-S 171.6 (2)

<sup>a</sup> The atomic numbering used in some of the original references has been changed to correspond to the arrangement



<sup>b</sup> This work. <sup>c</sup> Reference 14. <sup>d</sup> Reference 11. <sup>e</sup> Reference 12b. <sup>f</sup> Reference 52. <sup>g</sup> Reference 44. <sup>h</sup> Reference 37. <sup>i</sup> Reference 36.

and in structures containing the related sulfur–nitrogen cation  $S_4N_3^+$  are given in Tables V and VI, respectively. Tabulations of the observed and calculated structure factors for each compound are available as supplementary material.

### Discussion

The present work demonstrates that both monomeric and dimeric forms of the cation  $S_3N_2^+$  exist as stable entities and crystalline salts of both forms have been obtained with the same anion  $AsF_6^-$ .<sup>27</sup> The  $AsF_6^-$  salt is indeed the only salt of the monomeric form  $S_3N_2^+$  that has been characterized with certainty. In contrast the dimeric cation  $S_6N_4^{2+}$  is now known in the form of its salts with the  $AsF_6^-$ ,<sup>14</sup>  $SO_3F^-$ ,  $S_2O_6F^-$ , and  $S_2O_6Cl^-$ <sup>11</sup> anions. It is remarkable that the latter two of these anions were previously unknown.

The fact that the  $S_6N_4^{2+}$  cation can be produced rather easily by the reaction of  $S_4N_4$  with  $S_8^{2+}$  provides an explanation for the otherwise puzzling observation that in the first report of the oxidation of  $S_4N_4$  with  $AsF_5$  the only isolated product was  $S_6N_4^{2+}(AsF_6^-)_2$ <sup>14</sup> (actually believed to contain the monomeric ion  $S_3N_2^+$  at that time), while in subsequent repetitions of this reaction the only product isolated was almost invariably  $S_4N_4(AsF_6)_2$ .<sup>10</sup> It seems clear that  $S_4N_4$  contaminated with some sulfur was used in the previous work. This sulfur reacted preferentially with  $AsF_5$  to give  $S_8^{2+}$  which then oxidized the  $S_4N_4$  to  $S_6N_4^{2+}$ . Confirmation of this hypothesis was obtained in an experiment in which a small amount of sulfur was added to  $S_4N_4$  before it was reacted with  $AsF_5$ . In this case both  $(S_6N_4^{2+})(AsF_6^-)_2$  and  $(S_4N_4^{2+})(AsF_6^-)_2$  were obtained as products.

**Discussion of Structures. Monomeric and Dimeric Thiodithiazyl Cations.** The three compounds characterized contain

the thiodithiazyl cation with hexafluoroarsenate, fluorosulfate, and the novel thiofluorosulfate anion as the counterions. The ionic formulation for these compounds is only a first approximation as there are significant anion–cation interactions in all three compounds. Furthermore, in the case of the fluorosulfate and the thiofluorosulfate compounds, pairs of  $S_3N_2^+$  rings are linked across centers of symmetry by long sulfur–sulfur contacts between the disulfide bonds of each ring, of 3.030 (1) and 2.986 (1) Å, respectively. These S...S interactions are 0.67 and 0.71 Å, respectively, shorter than twice the van der Waals radius for sulfur and are considered strong enough to be bonding interactions. Thus both the fluorosulfate and thiofluorosulfate compounds should be formulated as containing the dimeric cation  $S_6N_4^{2+}$  which has been found previously in the  $S_2O_6Cl^-$  and  $CF_3SO_3^-$  salts<sup>11,12b</sup> and, as is shown here, in the previously published hexafluoroarsenate salt.<sup>14</sup> In contrast the monomeric form of this cation  $S_3N_2^+$  in the present hexafluoroarsenate structure has no intermolecular S...S interactions less than 4 Å. It is interesting that the hexafluoroarsenate anion forms stable salts with both the monomeric  $S_3N_2^+$  ion and the dimeric  $S_6N_4^{2+}$  ion.

The characterization of structures containing both the monomeric and dimeric forms of the thiodithiazyl radical cation is of particular importance as there has been some confusion in the three previous reports of the thiodithiazyl ion as to whether it should be formulated as a monomer,  $S_3N_2^+$ , or as the corresponding dimer,  $S_6N_4^{2+}$ . All three of these papers appeared at about the same time, and the first two described compounds formulated as  $(S_3N_2)(AsF_6)$  and  $(S_3N_2)(CF_3SO_3)$  which were produced by the oxidation of  $S_4N_4$  with  $AsF_5$  and trifluoromethanesulfonic anhydride, respectively.<sup>13,14</sup> Consistent with this formulation was the fact that each compound displayed the expected five-line ESR spectrum for a radical ion  $S_3N_2^+$  in solution in methylene chloride. A third report by Bannister et al. however, was the first to suggest

(27) Distinct differences in the magnetic behavior of two forms have been found experimentally: Gillespie, R. J.; Kent, J. P.; Lever, A. B. P., unpublished results.

**Table IV.** Equations of Least-Squares Planes<sup>a</sup> of the Thiodithiazyl Rings in S<sub>3</sub>N<sub>2</sub><sup>+</sup> and S<sub>6</sub>N<sub>4</sub><sup>2+</sup> and Deviations from These Planes (Å)<sup>b</sup>

(i) (S <sub>3</sub> N <sub>2</sub> <sup>+</sup> )(AsF <sub>6</sub> <sup>-</sup> )					
Plane of S <sub>3</sub> N <sub>2</sub> Ring					
0.1444I - 0.6774J + 0.7213K = 3.2759					
S(1)*	0.013	N(1)*	-0.004	F(2) <sup>I</sup>	1.126
S(2)*	-0.020	N(2)*	0.024	F(5) <sup>II</sup>	0.369
S(3)*	-0.012	F(1)	-0.566		
(ii) (S <sub>6</sub> N <sub>4</sub> <sup>2+</sup> )(S <sub>2</sub> O <sub>2</sub> F <sub>2</sub> )					
Plane of S <sub>3</sub> N <sub>2</sub> Ring					
0.5900I + 0.3573J + 0.7241K = 1.2992					
S(1)*	0.004	N(1)*	-0.012	X(1)''	0.735
S(2)*	0.006	N(2)*	-0.014		
S(3)*	0.017	X(3)'	0.072		
Plane of "4c-2e" Sulfur-Sulfur Interaction					
-0.5602I + 0.4378J + 0.7032K = 0.5627					
Angle between Planes = 109.58°					
(iii) (S <sub>6</sub> N <sub>4</sub> <sup>2+</sup> )(AsF <sub>6</sub> ) <sub>2</sub> <sup>c</sup>					
Plane of S <sub>3</sub> N <sub>2</sub> Ring					
-0.2580I + 0.9647J - 0.0525K = 0.9615					
S(1)*	0.004	N(1)*	0.011		
S(2)*	-0.008	N(2)*	0.000		
S(3)*	-0.007	F(2)	-0.022		
Plane of "4c-2e" Sulfur-Sulfur Interaction					
0.6922I + 0.5677J + 0.4456K = 8.0346					
Angle between Planes = 110.23°					
(iv) (S <sub>6</sub> N <sub>4</sub> <sup>2+</sup> )(SO <sub>3</sub> F) <sub>2</sub>					
Plane of S <sub>3</sub> N <sub>2</sub> Ring					
-0.4184I - 0.6148J + 0.6686K = 0.9422					
S(1)*	0.007	N(1)*	-0.002	O(1) <sup>II</sup>	0.536
S(2)*	-0.003	N(2)*	-0.011	O(3) <sup>III</sup>	0.377
S(3)*	0.008	O(2)	-0.005 <sup>I</sup>	O(3) <sup>VI</sup>	-0.640
F <sup>IV</sup>	-0.601	O(2)	2.824		
Plane of "4c-2e" Sulfur-Sulfur Interaction					
-0.6830I + 0.4705J + 0.5587K = 1.2994					
Angle between Planes = 111.72°					

<sup>a</sup> In orthogonal angstrom space the unit vector *I* is parallel to *a*, *K* is perpendicular to *a* in the *ac* plane, and *J* is perpendicular to the *ac* plane. <sup>b</sup> Atoms defining each plane are marked with an asterisk. <sup>c</sup> Calculated from coordinates in ref 14.

an alternative formulation of this ion as the dimer S<sub>6</sub>N<sub>4</sub><sup>2+</sup> on the basis of S...S interactions (3.027 Å) between pairs of S<sub>3</sub>N<sub>2</sub><sup>+</sup> rings across centers of symmetry. The counterion in this case was the previously unknown chlorodisulfate anion, S<sub>2</sub>O<sub>6</sub>Cl<sup>-</sup>.<sup>11</sup> Although not initially formulated as such, the compound first reported as (S<sub>3</sub>N<sub>2</sub>)(AsF<sub>6</sub>)<sup>14</sup> should also be described as a dimer (S<sub>6</sub>N<sub>4</sub>)(AsF<sub>6</sub>)<sub>2</sub> in the solid state since the sulfur-sulfur distances between pairs of rings in this compound, which were not noted in the original paper, have been calculated from the published coordinates to be 2.994 (3) Å. Very recently the CF<sub>3</sub>SO<sub>3</sub><sup>-</sup> salt has also been shown to contain the dimeric S<sub>6</sub>N<sub>4</sub><sup>2+</sup> cation in the solid state. The length of the S...S interactions in this latter case is 2.996 (2) Å.<sup>12b</sup> However it appears that all the dimeric compounds dissociate to the monomer in solution.

It is also worthy of note that the analogous oxidation of S<sub>4</sub>N<sub>4</sub> by the homopolyatomic cations Se<sub>8</sub><sup>2+</sup> and Se<sub>4</sub><sup>2+</sup> in SO<sub>2</sub> results in a mixed sulfur-selenium-nitrogen thiodiselenazyl cation, which also shows appreciable bonding interactions between the diselenide bond in pairs of rings (Se...Se are 3.111 (2) and 3.159 (2) Å) so that this cation may also be formulated as an analogous dimeric cation Se<sub>4</sub>S<sub>2</sub>N<sub>4</sub><sup>2+</sup>.<sup>15</sup>

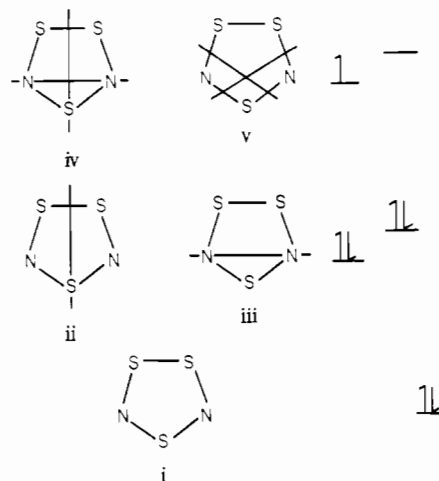
The long cation-cation interactions are not the only important interionic interactions present in these compounds, and some significant anion-cation interactions are also found.

Presumably subtle differences in these additional contacts are responsible for stabilizing the monomeric form of the thiodithiazyl ring compared with the more common dimeric form.

The bond distances and bond angles in the known examples of the thiodithiazyl cations and some related sulfur-nitrogen ring systems are compared in Table III. In the thiodithiazyl structures there are few systematic differences between related bond lengths and bond angles. A significant feature of all the S<sub>3</sub>N<sub>2</sub><sup>+</sup>(S<sub>6</sub>N<sub>4</sub><sup>2+</sup>) structures characterized, however, is the length of the disulfide bond in each ring, which at 2.142–2.147 Å is appreciably longer than a normal sulfur-sulfur single bond (e.g., 2.048 Å in S<sub>8</sub><sup>28</sup>). Similarly, in various structures containing the S<sub>4</sub>N<sub>3</sub><sup>+</sup> ion, the other planar sulfur-nitrogen cation with an S-S bond, the sulfur-sulfur bond lengths range from 2.03–2.11 Å,<sup>4-9</sup> intermediate in length between normal single bond lengths and the S-S bond lengths in the thiodithiazyl rings above. However in the analogous bis(thiodiselenazyl) cation no significant lengthening of the diselenide bond in each ring is observed and the Se-Se bond lengths in this cation (2.335 (3) and 2.351 (3) Å<sup>15</sup>) are very similar to the Se-Se bond lengths in cyclooctaselenium.<sup>29a</sup>

In the thiodithiazyl rings the S-N distances adjacent to the disulfide bond are ca. 0.04 Å longer than both the other SN distances in the rings and the SN bonds adjacent to the disulfide bond in the S<sub>4</sub>N<sub>3</sub><sup>+</sup> structures. In fact these SN distances are among the longest observed in planar pseudo aromatic π-bonded ring systems. However, if a typical SN single bond has a length of ca. 1.73 Å (as for example in sulfamic acid<sup>20</sup>), then it can be seen that all the SN bond lengths in the S<sub>3</sub>N<sub>2</sub><sup>+</sup> ring must have some double-bond character.

In contrast since the SS bond is significantly longer than that in S<sub>8</sub>, it presumably has little if any double-bond character. After allocating 10 electrons to σ bonds and 10 electrons to one unshared pair on each atom, we are left with seven electrons. These may be described either in terms of π-type molecular orbitals or by means of valence-bond structures. Five π molecular orbitals may be constructed from appropriate atomic orbitals on each of the five atoms. They are



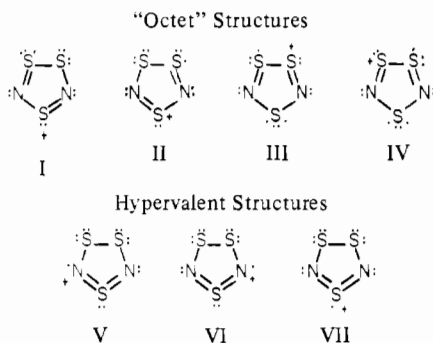
The three lowest are bonding orbitals and are occupied by six of the electrons. The seventh electron must occupy either or both of the two highest antibonding orbitals. These two orbitals are not necessarily degenerate, and it seems reasonable to suppose that iv has the lower energy and the odd electron is concentrated mostly on the atoms of the S-S group. However, the odd electron must also spend some time in v in

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(29) (a) Foss, O.; Janickis, V. *J. Chem. Soc., Chem. Commun.* **1977**, 834. (b) Gleiter, R.; Bartetzko, R.; Hofmann, P. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1980**, *35B*, 1166.

order to account for that fact that the ESR spectrum shows coupling of the odd electron to the two equivalent nitrogen atoms. We might note that orbitals i and iii imply some  $\pi$ -electron density in the S-S bond although this is perhaps effectively reduced by the antibonding character of orbitals ii and iv for the S-S bond.

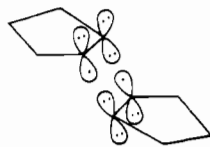
Alternatively if we describe the seven electrons in terms of resonance structures involving double bonds, the most important would appear to be the "octet" structures I-IV. These



also place the odd electron density on the atoms in the S-S group. If we also introduce the probably less important hypervalent structures V-VII, we see that some odd electron density will also be found on the other S and on the two N atoms in accordance with the ESR spectrum. From either the valence-bond or the MO point of view it appears that the majority of the odd electron density is on the two atoms of the S-S group, i.e., on S(1) and S(2).

As mentioned before the length of the S-S bond appears to indicate that it has no double-bond character, and therefore a possible resonance structure involving an S=S double bond has been omitted. The conjugated system is therefore acyclic and not cyclic as in the otherwise analogous cyclopentadienide anion. In this way it is quite analogous to the  $S_4N_3^+$  cation.

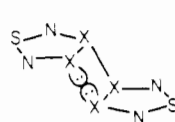
The structure of the dimeric ion is consistent with the majority of the odd electron density being on the two atoms of the S-S group and it suggests that the unshared electron pairs and the odd electron on these S atoms are in approximately tetrahedral "sp<sup>3</sup>" orbitals. [The angle between the plane of the  $S_3N_2$  ring and the plane of the four S atoms is 109–110° in all the dimeric  $S_6N_4^{2+}$  structures characterized (Table IV).] Each sulfur atom can then be imagined as forming a three-electron bond with the opposite S atom in the other half of the dimer.



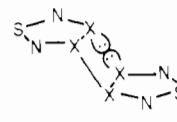
Very recently Gleiter et al.,<sup>29b</sup> on the basis of some semi-empirical and ab initio calculations, have described the bonding between the two  $S_3N_2^+$  rings in the  $S_6N_4^{2+}$  dimer as four-center six-electron bonding. This is essentially equivalent to our description in terms of two three-electron bonds. Their calculations did not, however, take any account of the short anion-cation contacts which are also significantly less than van der Waals distances.

Alternatively, the bonding between the two  $S_3N_2^+$  ions may be described in terms of two resonance structures each of which has one S-S bond between the two rings (see VIII and IX).

In other words, each bond has a bond order of 0.5. This is clearly an over simplified description and implies that no odd electron density remains in the two  $S_3N_2$  rings. This is almost certainly not the case, as, somewhat surprisingly perhaps, there is essentially no change in the geometry of the



VIII



IX

$S_3N_2^+$  ring when it dimerizes. The bond order could therefore well be less than 0.5. Moreover the two long S-S bonds may be described as three-electron bonds which may be weaker than half a single bond. Alternatively, in terms of structures VIII and IX we may say that the overall bonding between the two S-S groups is reduced by the repulsion between the two lone pairs that are directed toward each other and are much closer than the van der Waals contact distance of 3.7 Å.

It might perhaps be objected that the distance between the halves of the dimeric molecule is too long for the interaction to be described as S-S bonding. However, the definite and constant geometry of the dimer in all the structures, despite the considerable variation in the anion, is rather convincing evidence that the interaction between the two S-S groups can be reasonably regarded as having a directed covalent nature. Many other examples of relatively long S-S interactions are known, especially in thiothiophenes where there is delocalized  $\sigma$ -bonding over a row of three, four, or five sulfur atoms with considerable alternation in the S-S distances. In these compounds S...S distances of up to 2.93 Å in length have been considered significant and included in the bonding descriptions.<sup>30</sup> The interring contact distances in the  $S_6N_4^{2+}$  dimers are however significantly longer than the intraring S...S contact distances of ca. 2.7 Å and similar S...S contacts of 2.590 (1) and 2.595 (1) Å in the parent  $S_4N_4$  cage,<sup>31</sup> 2.425 (2) Å in the related neutral molecule  $S_5N_6$ ,<sup>32</sup> 2.482 (2) Å in the  $[S_4N_4O_2(OCH_3)]^-$  anion,<sup>33</sup> and finally 2.777–2.813 (2) Å in the  $S_4N_5^+$  cation.<sup>34</sup> The present S...S interactions are however comparable to the transannular interactions in  $S_8^{2+}$  (2.83–3.10 Å)<sup>35</sup> which have been considered to represent weak bonding interactions. Similarly the compounds  $(PhSN)_2S^{36}$  and  $(p-C_6H_4SN)_2S^{37}$  have the same configurations of the SNSNS chain as in the present cationic ring with weak interactions between two sulfur atoms (S...S at 3.231 (5) and 3.293 (8) Å, respectively), with C-S...S angles close to 180° so that they can perhaps be viewed as being derived from the  $S_3N_2$  ring by populating the  $\sigma^*$  orbital of the S-S bond on formation of the C-S bonds.

Similar interaction between radical centers to give "loose" dimers is, for example, a feature of some compounds containing the nitroxide radical and of nitric oxide itself.<sup>38</sup> The well-known Fremy salt (ammonium or potassium nitrosohydroxylaminesulfonate) in the solid state contains anions linked into dimers by long nitrogen-oxygen "bonds" of 2.84 Å,<sup>39</sup> and the molecule 9-azabicyclo[3.3.1]nonan-3-one-8-oxyl similarly contains interactions between nitroxide groups to give dimers with an N...O separation of 2.28 Å.<sup>40</sup> As with  $S_6N_4^{2+}$ , these interactions involve some spin pairing of the unpaired electron density of each N-O bond (or on each  $S_3N_2$  ring) via weak multicenter bonding.

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Table V. Significant Interionic Contacts in the Thiodithiazyl Cations  $S_6N_4^{2+}$  and  $S_3N_3^+$ <sup>a</sup>

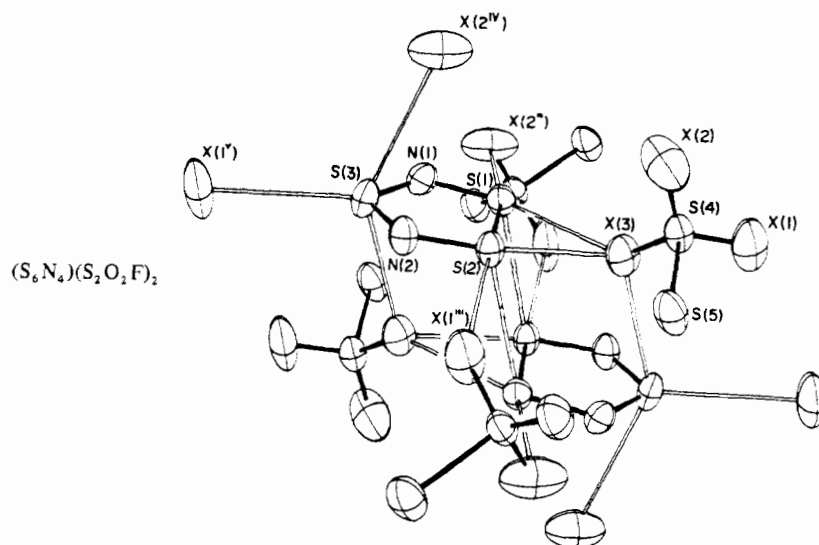
$(S_6N_4)(SO_3F)_2$

$(S_6N_4)(AsF_6)_2$

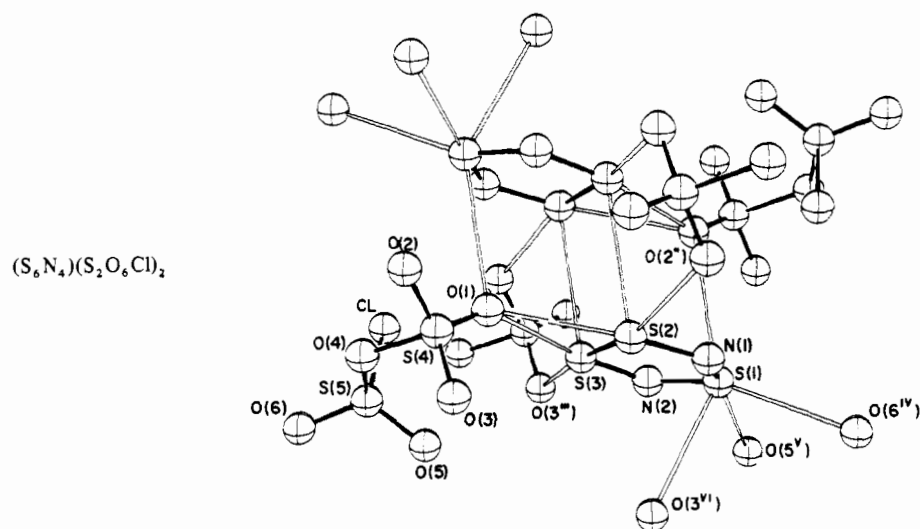
Distances, Å			
S(1)-S(2) <sup>i</sup>	3.030 (1)	S(2)-O(3) <sup>iii</sup>	2.954 (3)
S(1)-O(2) <sup>i</sup>	2.650 (3)	S(3)-O(3) <sup>vi</sup>	2.947 (3)
S(2)-O(2) <sup>i</sup>	2.653 (3)	S(3)-F <sup>iv</sup>	3.048 (3)
Angles, Deg			
S(2)-S(1)-S(2) <sup>i</sup>	89.82 (3)	S(1) <sup>i</sup> -S(2)-O(2) <sup>i</sup>	70.45 (7)
S(1)-S(2)-S(1) <sup>i</sup>	90.18 (3)	S(1)-S(2)-O(3) <sup>iii</sup>	172.05 (7)
N(1)-S(1)-S(2) <sup>i</sup>	112.2 (1)	N(2)-S(2)-O(3) <sup>iii</sup>	81.3 (1)
N(2)-S(2)-S(1) <sup>i</sup>	111.5 (1)	O(2) <sup>i</sup> -S(2)-O(3) <sup>iii</sup>	115.88 (9)
S(2)-S(1)-O(2) <sup>i</sup>	66.22 (7)	S(1) <sup>i</sup> -S(2)-O(3) <sup>iii</sup>	83.53 (6)
S(1)-S(2)-O(2) <sup>i</sup>	66.07 (6)	S(1)-S(2)-O(1) <sup>v</sup>	71.27 (5)
N(1)-S(1)-O(2) <sup>i</sup>	163.4 (1)	N(2)-S(2)-O(1) <sup>v</sup>	74.5 (1)
N(2)-S(2)-O(2) <sup>i</sup>	162.7 (1)	O(2) <sup>i</sup> -S(2)-O(1) <sup>v</sup>	98.52 (9)
S(1)-O(2) <sup>i</sup> -S(2)	47.71 (6)	O(3) <sup>iii</sup> -S(2)-O(1) <sup>v</sup>	115.19 (8)
S(2)-S(1)-O(1) <sup>ii</sup>	169.92 (7)	S(1) <sup>i</sup> -S(2)-O(1) <sup>v</sup>	161.25 (5)
N(1)-S(1)-O(1) <sup>ii</sup>	79.6 (1)	N(1)-S(3)-O(2)	77.6 (1)
O(2) <sup>i</sup> -S(1)-O(1) <sup>ii</sup>	116.84 (8)	N(2)-S(3)-O(2)	76.3 (1)
S(2) <sup>i</sup> -S(1)-O(1) <sup>ii</sup>	82.65 (6)	N(1)-S(3)-O(3) <sup>vi</sup>	85.3 (1)
O(2)-S(3)-O(3) <sup>vi</sup>	120.15 (8)	N(2)-S(3)-O(3) <sup>vi</sup>	161.6 (1)
N(1)-S(3)-F <sup>iv</sup>	164.2 (1)	S(1)-O(2) <sup>i</sup> -S(3) <sup>i</sup>	111.4 (1)
N(2)-S(3)-F <sup>iv</sup>	82.4 (1)	S(2)-O(2) <sup>i</sup> -S(3) <sup>i</sup>	111.0 (1)
O(2)-S(3)-F <sup>iv</sup>	117.22 (8)	S(1)-O(2) <sup>i</sup> -S(4) <sup>i</sup>	140.5 (2)
O(3) <sup>vi</sup> -S(3)-F <sup>iv</sup>	82.28 (8)	S(2)-O(2) <sup>i</sup> -S(4) <sup>i</sup>	131.3 (2)
S(1)-O(1) <sup>ii</sup> -S(4) <sup>ii</sup>	105.3 (1)	S(3)-O(2)-S(4)	104.3 (1)
S(2)-O(1) <sup>v</sup> -S(4) <sup>v</sup>	154.7 (2)	S(3)-O(3) <sup>vi</sup> -S(4) <sup>vi</sup>	137.4 (2)
S(2)-O(3) <sup>iii</sup> -S(4) <sup>iii</sup>	118.2 (2)	S(3)-F <sup>iv</sup> -S(4) <sup>iv</sup>	121.4 (1)
S(2) <sup>i</sup> -S(1)-O(2) <sup>i</sup>	70.28 (7)		

Distances, Å			
S(2)-S(3) <sup>i</sup>	2.994 (2)	S(2)-F(6) <sup>iv</sup>	3.048 (7)
S(2)-F(2) <sup>ii</sup>	2.716 (6)	S(2)-F(6) <sup>iii</sup>	3.106 (6)
Angles, Deg			
S(3) <sup>i</sup> -S(2)-S(3) <sup>i</sup>	90.53 (9)	F(2) <sup>ii</sup> -S(2)-F(6) <sup>iv</sup>	116.6 (2)
S(2)-S(3)-S(2) <sup>i</sup>	89.47 (9)	F(2) <sup>ii</sup> -S(2)-F(6) <sup>iii</sup>	91.0 (1)
N(1)-S(2)-S(3) <sup>i</sup>	110.7 (3)	F(6) <sup>iv</sup> -S(2)-F(6) <sup>iii</sup>	106.1 (2)
N(2)-S(3)-S(2) <sup>i</sup>	110.0 (2)	N(1) <sup>i</sup> -S(1) <sup>i</sup> -F(2)	79.0 (3)
S(3)-S(2)-F(2) <sup>ii</sup>	67.9 (1)	N(2) <sup>i</sup> -S(1) <sup>i</sup> -F(2)	77.9 (2)
S(2)-S(3)-F(2) <sup>ii</sup>	65.9 (1)	N(1)-S(1)-F(4) <sup>iii</sup>	75.7 (3)
N(1)-S(2)-F(2) <sup>ii</sup>	164.2 (3)	N(2)-S(1)-F(4) <sup>iii</sup>	91.4 (3)
N(2)-S(3)-F(2) <sup>ii</sup>	162.6 (3)	F(2) <sup>i</sup> -S(1)-F(4) <sup>iii</sup>	148.2 (2)
S(3) <sup>i</sup> -S(2)-F(2) <sup>ii</sup>	71.1 (1)	S(3) <sup>i</sup> -F(2) <sup>ii</sup>	2.756 (5)
S(2) <sup>i</sup> -S(3)-F(2) <sup>ii</sup>	71.0 (1)	S(1) <sup>i</sup> -F(2)	2.972 (5)
S(3)-F(2) <sup>ii</sup> -S(2)	46.2 (1)	S(1)-F(4) <sup>iii</sup>	3.062 (5)
S(3)-S(2)-F(6) <sup>iv</sup>	154.1 (1)	[S(1)-F(4) <sup>v</sup>	3.203 (7)]
S(3)-S(2)-F(6) <sup>iii</sup>	99.2 (1)	S(2)-F(2) <sup>ii</sup> -S(1) <sup>i</sup>	109.3 (2)
N(1)-S(2)-F(6) <sup>iv</sup>	77.6 (2)	S(3)-F(2) <sup>ii</sup> -S(1) <sup>i</sup>	109.0 (1)
N(1)-S(2)-F(6) <sup>iii</sup>	91.4 (3)	S(1) <sup>i</sup> -F(2)-As(1)	110.3 (2)
		S(2)-F(2)-As(1)	132.1 (2)
		S(3)-F(2) <sup>ii</sup> -As(1) <sup>ii</sup>	135.4 (2)
		S(1)-F(4) <sup>iii</sup> -As(1) <sup>iii</sup>	141.1 (3)
		S(2)-F(6) <sup>iv</sup> -As(1) <sup>iv</sup>	116.5 (3)
		S(2)-F(6) <sup>iii</sup> -As(1) <sup>iii</sup>	117.7 (3)

Table V (Continued)



Distances, Å			
S(1)-S(2) <sup>i</sup>	2.986 (1)	S(1)-X(2) <sup>ii</sup>	3.188 (5)
S(1)-X(3)	2.707 (4)	S(2)-X(1) <sup>iii</sup>	2.846 (4)
S(2)-X(3)	2.635 (4)	S(3)-X(1) <sup>v</sup>	3.108 (5)
S(3) <sup>i</sup> -X(3)	2.934 (3)	S(3)-X(2) <sup>iv</sup>	3.113 (4)
Angles, Deg			
S(2)-S(1)-S(2) <sup>i</sup>	89.11 (5)	N(1)-S(3)-X(3) <sup>i</sup>	78.1 (1)
S(1)-S(2)-S(1) <sup>i</sup>	90.89 (4)	N(2)-S(3)-X(3) <sup>i</sup>	79.4 (1)
N(1)-S(1)-S(2) <sup>i</sup>	110.1 (1)	N(1)-S(3)-X(1) <sup>v</sup>	131.7 (2)
N(2)-S(2)-S(1) <sup>i</sup>	110.0 (1)	N(2)-S(3)-X(1) <sup>v</sup>	119.9 (2)
S(2)-S(1)-X(3)	64.66 (8)	N(1)-S(3)-X(2) <sup>iv</sup>	68.8 (1)
S(1)-S(2)-X(3)	68.12 (8)	N(2)-S(3)-X(2) <sup>iv</sup>	89.4 (2)
N(1)-S(1)-X(3)	161.7 (2)	X(3) <sup>i</sup> -S(3)-X(1) <sup>v</sup>	104.8 (1)
N(2)-S(2)-X(3)	164.9 (2)	X(3) <sup>i</sup> -S(3)-X(2) <sup>iv</sup>	139.7 (1)
S(2) <sup>i</sup> -S(1)-X(3)	70.55 (7)	X(1) <sup>v</sup> -S(3)-X(2) <sup>iv</sup>	114.2 (1)
S(1) <sup>i</sup> -S(2)-X(3)	70.78 (7)	S(1)-X(3)-S(3) <sup>i</sup>	110.2 (1)
S(1)-X(3)-S(2)	47.22 (7)	S(2)-S(1)-X(2) <sup>ii</sup>	169.5 (1)
S(2)-S(1)-X(2) <sup>ii</sup>	169.5 (1)	N(1)-S(1)-X(2) <sup>ii</sup>	74.0 (2)
N(1)-S(1)-X(2) <sup>ii</sup>	74.0 (2)	S(2) <sup>i</sup> -S(1)-X(2) <sup>ii</sup>	89.04 (8)
S(2) <sup>i</sup> -S(1)-X(2) <sup>ii</sup>	89.04 (8)	X(3)-S(1)-X(2) <sup>ii</sup>	124.2 (1)
X(3)-S(1)-X(2) <sup>ii</sup>	124.2 (1)	S(1)-S(2)-X(1) <sup>iii</sup>	165.2 (1)
S(1)-S(2)-X(1) <sup>iii</sup>	165.2 (1)	N(2)-S(2)-X(1) <sup>iii</sup>	82.9 (2)
N(2)-S(2)-X(1) <sup>iii</sup>	82.9 (2)	S(1) <sup>i</sup> -S(2)-X(1) <sup>iii</sup>	75.4 (1)
S(1) <sup>i</sup> -S(2)-X(1) <sup>iii</sup>	75.4 (1)	X(3)-S(2)-X(1) <sup>iii</sup>	111.4 (1)
X(3)-S(2)-X(1) <sup>iii</sup>	111.4 (1)	S(2)-X(3)-S(3) <sup>i</sup>	111.4 (1)
S(1)-X(3)-S(3) <sup>i</sup>	111.4 (1)	S(1)-X(3)-S(4)	136.0 (2)
S(1)-X(3)-S(4)	136.0 (2)	S(2)-X(3)-S(4)	113.0 (2)
S(2)-X(3)-S(4)	113.0 (2)	S(3) <sup>i</sup> -X(3)-S(4)	113.8 (2)
S(3) <sup>i</sup> -X(3)-S(4)	113.8 (2)	S(1)-X(2) <sup>ii</sup> -S(4) <sup>ii</sup>	109.3 (2)
S(1)-X(2) <sup>ii</sup> -S(4) <sup>ii</sup>	109.3 (2)	S(2)-X(1) <sup>iii</sup> -S(4) <sup>iii</sup>	137.6 (3)
S(2)-X(1) <sup>iii</sup> -S(4) <sup>iii</sup>	137.6 (3)	S(3)-X(1) <sup>v</sup> -S(4) <sup>v</sup>	118.3 (2)
S(3)-X(1) <sup>v</sup> -S(4) <sup>v</sup>	118.3 (2)	S(3)-X(2) <sup>iv</sup> -S(4) <sup>iv</sup>	122.0 (3)
S(3)-X(2) <sup>iv</sup> -S(4) <sup>iv</sup>	122.0 (3)		



Distances, Å			
S(2)-S(3) <sup>i</sup>	3.026 (1)	S(3)-O(3) <sup>iii</sup>	3.072 (4)
S(2)-O(1)	2.731 (3)	S(1)-O(6) <sup>iv</sup>	2.917 (3)
S(3)-O(1)	2.680 (3)	S(1)-O(5) <sup>v</sup>	2.996 (4)
S(1) <sup>i</sup> -O(1)	2.980 (3)	S(1)-O(3) <sup>vi</sup>	3.030 (3)
S(2)-O(2) <sup>ii</sup>	3.043 (4)	[S(1)-O(2) <sup>i</sup>	3.250 (3)]
Angles, Deg			
S(3)-S(2)-S(3) <sup>i</sup>	89.62 (4)	N(2)-S(1)-O(6) <sup>iv</sup>	159.3 (2)
S(2)-S(3)-S(2) <sup>i</sup>	90.39 (4)	N(1)-S(1)-O(5) <sup>v</sup>	165.5 (1)
N(1)-S(2)-S(3) <sup>i</sup>	110.0 (1)	N(2)-S(1)-O(5) <sup>v</sup>	80.2 (2)
N(2)-S(3)-S(2) <sup>i</sup>	109.3 (1)	N(1)-S(1)-O(3) <sup>vi</sup>	79.7 (1)
S(3)-S(2)-O(1)	65.39 (8)	N(2)-S(1)-O(3) <sup>vi</sup>	77.7 (1)
S(2)-S(3)-O(1)	67.91 (7)	O(1) <sup>i</sup> -S(1)-O(6) <sup>iv</sup>	118.91 (9)
N(1)-S(2)-O(1)	162.6 (2)	O(1) <sup>i</sup> -S(1)-O(5) <sup>v</sup>	115.57 (8)
N(2)-S(3)-O(1)	164.5 (2)	O(1) <sup>i</sup> -S(1)-O(3) <sup>vi</sup>	141.41 (9)
S(3) <sup>i</sup> -S(2)-O(1)	71.14 (6)	O(6) <sup>iv</sup> -S(1)-O(5) <sup>v</sup>	82.6 (1)
S(2) <sup>i</sup> -S(3)-O(1)	71.09 (6)	O(6) <sup>iv</sup> -S(1)-O(3) <sup>vi</sup>	91.14 (8)
S(2)-O(1)-S(3)	46.71 (6)	O(5) <sup>v</sup> -S(1)-O(3) <sup>vi</sup>	90.27 (9)
S(3)-S(2)-O(2) <sup>ii</sup>	163.79 (6)	S(2)-O(1)-S(1) <sup>i</sup>	109.31 (9)
N(1)-S(2)-O(2) <sup>ii</sup>	85.4 (1)	S(3)-O(1)-S(1) <sup>i</sup>	110.35 (9)
S(3) <sup>i</sup> -S(2)-O(2) <sup>ii</sup>	74.53 (6)	S(1) <sup>i</sup> -O(1)-S(4)	105.0 (1)
O(1)-S(2)-O(2) <sup>ii</sup>	111.2 (1)	S(2)-O(1)-S(4)	122.1 (1)
S(2)-S(3)-O(3) <sup>iii</sup>	170.73 (8)	S(3)-O(1)-S(4)	144.6 (1)
N(2)-S(3)-O(3) <sup>iii</sup>	74.2 (1)	S(2)-O(2) <sup>ii</sup> -S(4) <sup>ii</sup>	127.4 (2)
S(2) <sup>i</sup> -S(3)-O(3) <sup>iii</sup>	92.01 (6)	S(3)-O(3) <sup>iii</sup> -S(4) <sup>iii</sup>	111.3 (2)
O(1)-S(3)-O(3) <sup>iii</sup>	121.31 (9)	S(1)-O(6) <sup>iv</sup> -S(5) <sup>iv</sup>	136.9 (2)
N(1)-S(1)-O(1) <sup>i</sup>	78.4 (1)	S(1)-O(5) <sup>v</sup> -S(5) <sup>v</sup>	124.2 (2)
N(2)-S(1)-O(1) <sup>i</sup>	79.1 (1)	S(1)-O(3) <sup>vi</sup> -S(4) <sup>vi</sup>	138.3 (2)
N(1)-S(1)-O(6) <sup>iv</sup>	87.1 (1)		

Table V (Continued)

		$(S_6N_4)(SO_3CF_3)_2$				$(S_6N_4)(SO_3CF_3)_2$					
		Distances, Å				Distances, Å					
S(1)-S(2) <sup>vii</sup>	2.996 (2)	[S(1)-O(1) <sup>iv</sup>	3.193 (4)]	S(3)-O(3) <sup>iii</sup>	2.989 (4)	S(3)-O(1) <sup>iv</sup>	3.136 (4)				
S(1)-O(3) <sup>vi</sup>	2.600 (5)	S(2)-O(2) <sup>ii</sup>	2.983 (6)	S(1)-O(1) <sup>i</sup>	2.963 (6)	S(3)-F(2) <sup>v</sup>	3.064 (7)				
S(2)-O(3) <sup>vi</sup>	2.624 (5)	[S(3)-O(2) <sup>iii</sup>	3.216 (4)]	[S(1)-O(3) <sup>iii</sup>	3.210 (4)]	[S(2)-O(3) <sup>iii</sup>	3.195 (4)]				
		Angles, Deg				Angles, Deg					
S(2)-S(1)-S(2) <sup>vii</sup>	90.14 (8)	O(3) <sup>vi</sup> -S(2)-O(2) <sup>ii</sup>	118.5 (2)	S(1)-O(3) <sup>vi</sup> -S(2)	48.3 (1)	S(4) <sup>vi</sup> -O(3) <sup>vi</sup> -S(1)	139.8 (3)				
S(1)-S(2)-S(1) <sup>vii</sup>	89.86 (8)	N(1)-S(3)-O(3) <sup>iii</sup>	76.6 (2)	S(2)-S(1)-O(1) <sup>i</sup>	177.9 (1)	S(4) <sup>vi</sup> -O(3) <sup>vi</sup> -S(2)	128.2 (3)				
N(1)-S(1)-S(2) <sup>vii</sup>	111.4 (2)	N(2)-S(3)-O(3) <sup>iii</sup>	76.6 (2)	S(1)-S(2)-O(2) <sup>ii</sup>	161.1 (1)	S(4) <sup>i</sup> -O(1) <sup>i</sup> -S(1)	109.3 (3)				
N(2)-S(2)-S(1) <sup>vii</sup>	112.0 (2)	N(1)-S(3)-O(1) <sup>iv</sup>	71.8 (2)	N(1)-S(1)-O(1) <sup>i</sup>	81.6 (2)	S(4) <sup>ii</sup> -O(2) <sup>ii</sup> -S(2)	119.8 (3)				
S(2)-S(1)-O(3) <sup>vi</sup>	66.4 (1)	N(2)-S(3)-O(1) <sup>iv</sup>	78.2 (2)	S(2) <sup>vii</sup> -S(1)-O(1) <sup>i</sup>	91.9 (1)	S(4) <sup>iv</sup> -O(1) <sup>iv</sup> -S(3)	132.9 (3)				
S(1)-S(2)-O(3) <sup>vi</sup>	65.2 (1)	N(1)-S(3)-F(2) <sup>v</sup>	79.3 (2)	O(3) <sup>vi</sup> -S(1)-O(1) <sup>i</sup>	115.0 (2)	C(1) <sup>v</sup> -F(2) <sup>v</sup> -S(3)	169.1 (4)				
N(1)-S(1)-O(3) <sup>vi</sup>	163.4 (3)	N(2)-S(3)-F(2) <sup>v</sup>	156.1 (2)	S(2) <sup>vii</sup> -S(1)-O(1) <sup>iv</sup>	164.6 (1)	S(4) <sup>iii</sup> -O(3) <sup>iii</sup> -S(3)	103.5 (2)				
N(2)-S(2)-O(3) <sup>vi</sup>	162.3 (3)	O(3) <sup>iii</sup> -S(3)-O(1) <sup>iv</sup>	130.6 (1)	N(2)-S(2)-O(2) <sup>ii</sup>	77.9 (2)	S(1) <sup>vii</sup> -O(3) <sup>vii</sup> -S(3)	113.7 (1)				
S(2) <sup>vii</sup> -S(1)-O(3) <sup>vi</sup>	69.2 (1)	O(3) <sup>iii</sup> -S(3)-F(2) <sup>v</sup>	127.1 (1)	S(1) <sup>vii</sup> -S(2)-O(2) <sup>ii</sup>	75.5 (1)	S(2) <sup>vii</sup> -O(3) <sup>vii</sup> -S(3)	113.2 (1)				
S(1) <sup>vii</sup> -S(2)-O(3) <sup>vi</sup>	69.3 (1)	O(1) <sup>iv</sup> -S(3)-F(2) <sup>v</sup>	82.8 (1)								
		Distances, Å				Distances, Å					
S(1)-F(1) <sup>v</sup>	2.964 (9)	[S(2)-F(1) <sup>vi</sup>	3.218 (9)]	[S(1)-F(4) <sup>ii</sup>	3.214 (8)]	S(3)-F(5) <sup>iii</sup>	3.182 (9)				
S(2)-F(1) <sup>v</sup>	2.768 (8)	S(3)-F(2) <sup>ii</sup>	2.887 (10)	S(2)-F(6)	3.149 (12)						
S(1)-F(4) <sup>i</sup>	3.174 (11)	S(3)-F(5) <sup>iv</sup>	3.055 (10)								
		Angles, Deg				Angles, Deg					
S(1)-S(2)-F(1) <sup>v</sup>	73.0 (3)	N(1)-S(3)-F(2) <sup>ii</sup>	153.8 (5)	F(1) <sup>v</sup> -S(1)-F(4) <sup>i</sup>	128.5 (3)	F(2) <sup>ii</sup> -S(3)-F(5) <sup>iii</sup>	131.2 (3)				
S(2)-S(1)-F(1) <sup>v</sup>	63.2 (2)	N(2)-S(3)-F(2) <sup>ii</sup>	84.7 (4)	S(1)-S(2)-F(6)	168.9 (2)	F(5) <sup>iv</sup> -S(3)-F(5) <sup>iii</sup>	95.0 (3)				
N(1)-S(1)-F(1) <sup>v</sup>	156.2 (5)	N(1)-S(3)-F(5) <sup>iv</sup>	90.5 (5)	N(2)-S(2)-F(6)	74.7 (5)	S(1)-F(1) <sup>v</sup> -As(1) <sup>v</sup>	119.0 (4)				
N(2)-S(2)-F(1) <sup>v</sup>	165.6 (5)	N(2)-S(3)-F(5) <sup>iv</sup>	160.6 (4)	F(1) <sup>v</sup> -S(2)-F(6)	113.8 (3)	S(2)-F(1) <sup>v</sup> -As(1) <sup>v</sup>	126.8 (4)				
S(1)-F(1) <sup>v</sup> -S(2)	43.7 (2)	N(1)-S(3)-F(5) <sup>iii</sup>	78.3 (4)	S(1)-F(4) <sup>i</sup> -As(1) <sup>i</sup>	136.4 (5)	S(3)-F(5) <sup>iv</sup> -As(1) <sup>iv</sup>	116.6 (4)				
S(2)-S(1) <sup>v</sup> -F(4) <sup>i</sup>	166.8 (2)	N(2)-S(3)-F(5) <sup>iii</sup>	80.7 (4)	S(2)-F(6)-As(1)	121.2 (5)	S(3)-F(5) <sup>iii</sup> -As(1) <sup>iii</sup>	149.0 (5)				
N(1)-S(1)-F(4) <sup>i</sup>	73.3 (5)	F(2) <sup>ii</sup> -S(3)-F(5) <sup>iv</sup>	76.0 (3)	S(3)-F(2) <sup>iv</sup> -As(1) <sup>ii</sup>	153.0 (5)						
Symmetry Transformations											
$(S_3N_2)(AsF_6)$			$(S_6N_4)(SO_3F)_2$			$(S_6N_4)(AsF_6)_2$					
i	$x, 1+y, 1+z$		i	$1-x, -y, 1-z$		i	$2-x, -y, 1-z$				
ii	$1-x, -y, 1-z$		ii	$1+x, y, z$		ii	$1+x, 1/2-y, 1/2+z$				
iii	$x, y, 1+z$		iii	$-x, -y, 1-z$		iii	$1-x, 1/2+y, 1/2-z$				
iv	$1-x, 1-y, 1-z$		iv	$-1/2+x, 1/2-y, -1/2+z$		iv	$1+x, y, z$				
v	$-x, -y, 1-z$		v	$1/2+x, 1/2-y, -1/2+z$							
			vi	$-x, -y, 1-z$							
$(S_6N_4)(S_2O_2F)_2$			$(S_6N_4)(S_2O_2Cl)_2$			$(S_6N_4)(SO_3CF_3)_2$					
i	$1/2-x, 1/2-y, -z$		i	$-x, -y, -z$		i	$x, -1+y, z$				
ii	$x, -y, 1/2+z$		ii	$-x, -y, 1-z$		ii	$-x, 1-y, 1-z$				
iii	$1/2-x, 1/2+y, -1/2-z$		iii	$x, y, -1+z$		iii	$-x, 1-y, -z$				
iv	$-x, y, -1/2-z$		iv	$x, 1+y, z$		iv	$1-x, 1-y, 1-z$				
v	$-1/2+x, 1/2-y, 1/2+z$		v	$1-x, -y, -z$		v	$1-x, 1-y, -z$				
			vi	$1-x, -y, 1-z$		vi	$x, -1+y, 1+z$				
						vii	$-x, -y, 1-z$				

<sup>a</sup> Calculated from the atomic coordinates in Table II or from previously published coordinates (see Figure 2 for appropriate references).

Table VI. Three-Center Charge-Transfer Interaction Involving the Disulfide Bonds in Structures Containing the  $S_3N_2^+$ ,  $S_6N_4^{2+}$ , and  $S_4N_3^+$  Cations<sup>a</sup>

compu	$(S_3N_2^+)$ (AsF <sub>6</sub> ) <sup>b</sup>	$(S_6N_4^{2+})$ (AsF <sub>6</sub> ) <sub>2</sub> <sup>c</sup>	$(S_6N_4^{2+})$ (S <sub>2</sub> O <sub>2</sub> F) <sub>2</sub> <sup>b</sup>	$(S_6N_4^{2+})$ (SO <sub>3</sub> F) <sub>2</sub> <sup>b</sup>	$(S_6N_4^{2+})$ (S <sub>2</sub> O <sub>6</sub> Cl) <sub>2</sub> <sup>d</sup>	$(S_6N_4^{2+})$ (SO <sub>3</sub> CF <sub>3</sub> ) <sub>2</sub> <sup>e</sup>	$(S_4N_3^+)$ (NO <sub>3</sub> ) <sup>f</sup>	$(S_4N_3^+)$ (BiCl <sub>4</sub> ) <sup>g</sup>	$(S_4N_3^+)$ (HgCl <sub>4</sub> ) <sup>h</sup>	$(S_4N_3^+)$ (Br <sub>3</sub> ) <sup>i</sup>	$(S_4N_3)_2$ (SbCl <sub>3</sub> ) <sup>j</sup>	$(S_3N_2^+Cl)Cl^k$
S(1)-S(2), Å	2.143 (5)	2.147 (3)	2.142 (1)	2.145 (1)	2.145 (1)	2.138 (3)	2.070 (2)	2.11 (2)	2.037 (13)	2.089 (5)	2.065 (3)	2.136 (4)
S(1)-N(1), Å	1.611 (10)	1.599 (6)	1.603 (4)	1.613 (3)	1.601 (3)	1.612 (6)	1.562 (3)	1.55 (4)	1.58 (3)	1.56 (1)	1.578 (8)	1.581 (5)
S(2)-N(2), Å	1.595 (9)	1.610 (6)	1.607 (4)	1.613 (3)	1.609 (4)	1.617 (5)	1.560 (3)	1.60 (5)	1.48 (2)	1.56 (1)	1.551 (8)	1.615 (5)
X <sup>l</sup>	F <sup>l</sup>	F <sup>l</sup>	O/F <sup>l</sup>	O	O	O	O	Cl	Cl	Br	Cl	Cl
S(1)···X, Å	2.964 (9)	2.716 (6)	2.707 (4)	2.650 (3)	2.731 (3)	2.600 (6)	2.620 (3)	3.11 (2)	3.177 (11)	3.131 (4)	3.005 (4)	3.035 (3)
S(2)···X, Å	2.768 (8)	2.756 (5)	2.635 (4)	2.653 (3)	2.680 (3)	2.624 (5)	2.695 (2)	3.10 (2)	3.191 (14)	3.135 (4)	3.007 (3)	2.929 (3)
N(1)-S(1)-X, deg	156.2 (5)	164.2 (3)	161.7 (2)	163.4 (1)	162.6 (2)	163.4 (3)	178.5 (1)	175 (3)	173 (1)	176.4 (5)	174.1 (4)	161.4 (3)
N(2)-S(2)-X, deg	165.6 (5)	162.6 (3)	164.9 (2)	162.7 (1)	164.5 (1)	162.3 (3)	176.8 (1)	166 (3)	171 (1)	175.9 (5)	175.2 (4)	167.1 (3)
sum of van der Waals radii S + X = B	3.20	3.20	3.20	3.25	3.25	3.25	3.25	3.65	3.65	3.80	3.65	3.65
$\Delta_1 \equiv B - (S(1)\cdots X)$	0.24	0.48	0.49	0.60	0.52	0.65	0.63	0.54	0.47	0.67	0.64	0.61
$\Delta_2 \equiv B - (S(2)\cdots X)$	0.43	0.44	0.56	0.60	0.57	0.63	0.55	0.55	0.46	0.66	0.63	0.72
$1 - \Delta_1/B$	0.925	0.850	0.847	0.815	0.840	0.800	0.806	0.852	0.871	0.824	0.825	0.833
$1 - \Delta_2/B$	0.866	0.863	0.825	0.815	0.825	0.806	0.831	0.849	0.874	0.826	0.827	0.803
dev of atom X from plane of ring, Å	-0.566	-0.022	0.072	-0.005	-0.058	-0.063	-0.078	-0.312	0.144	0.105	0.144	-0.18

<sup>a</sup> The  $S_4N_3^+$  cation in ref 7 was found to be disordered and was not included in this table. <sup>b</sup> This work. <sup>c</sup> Reference 14. <sup>d</sup> Reference 11. <sup>e</sup> Reference 5. <sup>f</sup> Reference 8. <sup>g</sup> Reference 4. <sup>h</sup> Reference 6. <sup>i</sup> Reference 9. <sup>j</sup> Reference 44. <sup>k</sup> Atom forming the three-center interaction. van der Waals radii:  $r_S = 1.85$  Å,  $r_F = 1.35$  Å,  $r_O = 1.40$  Å,  $r_{Cl} = 1.80$  Å, and  $r_{Br} = 1.95$  Å.

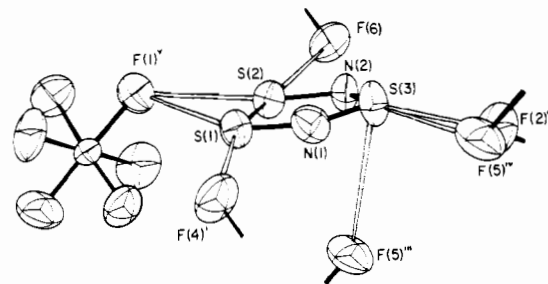


Figure 1. ORTEP view of the anion-cation interactions in the monomeric compound  $(S_3N_2)(AsF_6)$ .

Another striking feature of all the  $S_3N_2^+$  structures is that there is a considerable number of anion-cation contacts significantly shorter than van der Waals distances. The pattern of these contacts is remarkably similar in all the structures despite considerable variation in the nature of the anion. In both monomer and dimer the S(1)-S(2) bond is bridged by an oxygen, fluorine, or disordered oxygen/fluorine atom in the anion, and furthermore in the dimeric structures this same atom also makes a short contact with the atom S(3) in the other half of the dimer. The lengths of the S···F, S···O, or S···X contacts to the disulfide bond vary from 2.63 to 2.96 Å or 0.56 to 0.24 Å less than the appropriate sums of the van der Waals radii. A feature of these contacts is that they deviate by only ca. 20° from being colinear with the sulfur-nitrogen bonds adjacent to the disulfide bond (S-N···O, -F, or -X angles range from 156–166°). Very similar interactions are also a characteristic feature of the solid-state packing of the  $Se_4S_2N_4^{2+15}$  and all the known  $S_4N_3^+$  cations and  $S_3N_2Cl_2$  (Table VI). In these examples the S-N···X angles again approach 180°. This angle is of some significance if these interactions are considered to be examples of charge transfer<sup>41</sup> or secondary bonding<sup>42</sup> interactions.

In all these structures there are also short contacts to be found approximately trans to the S(1)-S(2) bond, and in one case another contact to one of the sulfur atoms at an angle of ca. 80° to the plane of the ring is observed. The actual distances and related angles for this group of contacts are summarized in Table VII. A feature of the contacts trans to the S-S bond is the tendency for one contact to lengthen slightly as the other contact shortens. Thus in  $(S_6N_4)(S_2O_6Cl)_2$  the contacts are virtually the same length, in the compounds  $(S_6N_4)(SO_3F)_2$  and  $(S_6N_4)(S_2O_2F)_2$  there is asymmetry in the contacts, and finally in the compound  $(S_6N_4)(AsF_6)_2$  only one really short contact is observed.

The most significant difference in the anion-cation environments of the monomeric and dimeric rings is in the contacts to the remaining sulfur atom in each ring [S(3)]. In the dimers, the atom bridging the disulfide bond forms another contact of comparable length to the bridging distances. This contact to the atom S(3') in the other half of the dimeric cation deviates by ~10–15° from the perpendicular to the plane of the ring (Figure 2). In the monomeric  $(S_3N_2)(AsF_6)$  the similar contact is to a fluorine atom of another hexafluoroarsenate anion in the structure (Figure 1). In addition it may be noted that this sulfur atom also generally has two or more contacts either approximately trans to the S(3)-N(2) and S(3)-N(1) bonds or approximately perpendicular to the plane of the ring. The geometry of these contacts is summarized in Table V.

It may be noted that the types of interactions observed in the present sulfur-nitrogen rings have also been found in several other ring systems containing disulfide bonds. For example, Hordvik and co-workers<sup>43</sup> have published several

(41) Prout, C. K.; Wright, J. D. *Angew Chem.* **1968**, *7*, 659.

(42) Alcock, N. W. *Adv. Inorg. Chem. Radiochem.* **1973**, *15*, 1.

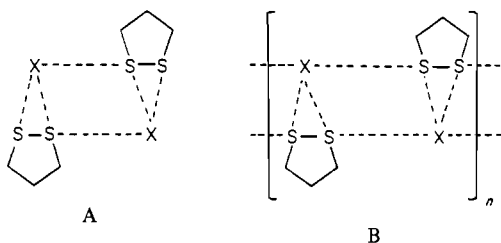
(43) Hordvik, A. Q. *Rep. Sulfur Chem.* **1970**, *5*, 21.

Table VII. Interaction Collinear with the Disulfide Bond in the Thiodithiazyl Rings

compd	Y	S(1)···Y, Å	Z	S(2)···Z, Å	S(2)-S(1)-Y, deg	S(1)-S(2)-Z, deg
(S <sub>3</sub> N <sub>2</sub> )(AsF <sub>6</sub> )	F(4) <sup>i</sup>	3.17 (1)	F(6)	3.15 (1)	166.8 (2)	168.9 (2)
(S <sub>6</sub> N <sub>4</sub> )(AsF <sub>6</sub> ) <sub>2</sub> <sup>a</sup>	F(6) <sup>iv</sup>	3.048 (7)			154.1 (1)	
(S <sub>6</sub> N <sub>4</sub> )(S <sub>2</sub> O <sub>2</sub> F) <sub>2</sub>	X(2) <sup>ii</sup>	3.188 (5)	X(1) <sup>iii</sup>	2.846 (4)	169.5 (1)	165.2 (1)
(S <sub>6</sub> N <sub>4</sub> )(SO <sub>3</sub> F) <sub>2</sub> <sup>b</sup>	O(1) <sup>ii</sup>	3.120 (3)	O(3) <sup>iii</sup>	2.954 (3)	169.9 (1)	172.1 (1)
(S <sub>6</sub> N <sub>4</sub> )(S <sub>2</sub> O <sub>6</sub> Cl) <sub>2</sub> <sup>c</sup>	O(2) <sup>ii</sup>	3.043 (4)	O(3) <sup>iii</sup>	3.072 (4)	163.8 (1)	170.7 (1)
(S <sub>6</sub> N <sub>4</sub> )(SO <sub>3</sub> CF <sub>3</sub> ) <sub>2</sub> <sup>d</sup>	O(1) <sup>i</sup>	2.963 (6)	O(2) <sup>ii</sup>	2.983 (6)	177.9 (1)	161.1 (1)

<sup>a</sup> Reference 14 [NB: S(2)-F(6)<sup>iii</sup> = 3.106 (6) Å; S(3)-S(2)-F(6)<sup>iii</sup> = 99.2 (1)°]. <sup>b</sup> [NB: S(2)-O(1)<sup>v</sup> = 3.183 (3) Å; S(1)-S(2)-O(1)<sup>v</sup> = 71.27 (5)°]. <sup>c</sup> Reference 11. <sup>d</sup> Reference 12b. [NB: S(1)-O(3)<sup>iii</sup> = 3.210 (4) Å; S(2)-O(3)<sup>iii</sup> = 3.195 (4) Å; S(1)-O(1)<sup>iv</sup> = 3.193 (4) Å; S(2)-S(1)-O(1)<sup>iv</sup> = 74.6 (1)°].

structures containing derivatives of the thiuret and 1,2-dithiolium rings and have remarked on the consistency of the two packing arrangements (A and B) in which the halogen



(or pseudohalide) counterions forming the close contacts tend to be almost in the plane of the rings approaching collinearity with at least one primary bond. Similarly in the structure of S<sub>3</sub>N<sub>2</sub>Cl<sub>2</sub> (S<sub>3</sub>N<sub>2</sub>Cl<sup>+</sup>Cl<sup>-</sup>) apart from the three center interactions with the disulfide bond the next shortest S···Cl contacts of 3.206 (4) and 3.288 (4) Å are approximately collinear (S-S-Cl angles are 168.6 (1) and 175.3 (1)°) with the disulfide bond.<sup>44</sup>

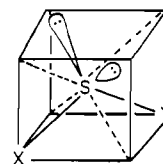
Some other short interionic contacts in sulfur-nitrogen compounds of note include the contacts in the structure of S<sub>4</sub>N<sub>5</sub><sup>+</sup>Cl<sup>-</sup>, where the chloride ion is again involved in short contacts (2.811 (2) Å) to sulfur atoms giving polymeric chains of interacting anions and cations,<sup>34</sup> and in the structure of 1,7-di-4-tolyltetrasulfurtrinitrogen chloride, there are again some significantly short S···Cl contacts of 3.06–3.12 Å.<sup>45</sup> Some other analogous interactions in recent sulfur compounds may also be found in ref 46.

The geometry of these anion-cation interactions can all be accounted for if it is assumed, as seems reasonable, that they are all donor interactions from the oxygen or fluorine atoms of the anion to the sulfur atoms. Each donor interaction is in such a direction as to avoid the bonding and nonbonding electron density on the acceptor S atom. In the S<sub>6</sub>N<sub>4</sub><sup>2+</sup> structure the atoms S(1) and S(2) have an approximately tetrahedral arrangement of three bonds and one nonbonding electron pair. Similarly, the atom S(3) in the S<sub>6</sub>N<sub>4</sub><sup>2+</sup> cation and all the S atoms in the monomeric S<sub>3</sub>N<sub>2</sub><sup>+</sup> cation have an approximately tetrahedral arrangement of two bonds and two nonbonding electron pairs (or one nonbonding pair and one single nonbonding electron). The weak donor-acceptor interactions are then directed toward the regions of minimum electron density on the surface of the sulfur atom, and hence they lie between the tetrahedral concentrations of electron density represented by the bonds and nonbonding pairs. In other words, they are formed approximately toward one or more of the four faces of the tetrahedron describing the location of the maximum bonding and nonbonding electron

Table VIII. Bond Lengths (Å) and Bond Angles (Deg) in the Hexafluoroarsenate, Thiofluorosulfate, and Fluorosulfate Anions

atoms	lengths	atoms	angles
(a) (S <sub>3</sub> N <sub>2</sub> )(AsF <sub>6</sub> )			
As(1)-F(1)	1.719 (8)	F(1)-As-F(2)	88.7 (4)
As(1)-F(2)	1.694 (10)	F(1)-As-F(3)	89.8 (5)
As(1)-F(3)	1.697 (12)	F(1)-As-F(4)	87.7 (4)
As(1)-F(4)	1.707 (9)	F(1)-As-F(5)	178.5 (4)
As(1)-F(5)	1.700 (8)	F(1)-As-F(6)	90.5 (4)
As(1)-F(6)	1.718 (9)	F(2)-As-F(3)	178.5 (4)
		F(2)-As-F(4)	89.5 (5)
		F(2)-As-F(5)	91.8 (4)
		F(2)-As-F(6)	90.2 (5)
		F(3)-As-F(4)	90.7 (5)
		F(3)-As-F(5)	89.7 (5)
		F(3)-As-F(6)	89.6 (6)
		F(4)-As-F(5)	90.9 (4)
		F(4)-As-F(6)	178.2 (4)
		F(5)-As-F(6)	90.9 (4)
(b) (S <sub>6</sub> N <sub>4</sub> )(S <sub>2</sub> O <sub>2</sub> F) <sub>2</sub>			
S(4)-S(5)	2.071 (2)	S(5)-S(4)-X(1)	103.50 (19)
S(4)-X(1)	1.412 (5)	S(5)-S(4)-X(2)	103.68 (20)
S(4)-X(2)	1.410 (4)	S(5)-S(4)-X(3)	102.98 (14)
S(4)-X(3)	1.438 (3)	X(1)-S(4)-X(2)	116.99 (26)
		X(1)-S(4)-X(3)	113.74 (23)
		X(2)-S(4)-X(3)	113.67 (25)
(c) (S <sub>6</sub> N <sub>4</sub> )(SO <sub>3</sub> F) <sub>2</sub>			
S(4)-F	1.537 (2)	F-S(4)-O(1)	104.7 (2)
S(4)-O(1)	1.415 (3)	F-S(4)-O(2)	105.7 (2)
S(4)-O(2)	1.419 (3)	F-S(4)-O(3)	103.3 (2)
S(4)-O(3)	1.415 (3)	O(1)-S(4)-O(2)	112.8 (2)
		O(1)-S(4)-O(3)	114.6 (2)
		O(2)-S(4)-O(3)	114.3 (2)

density, that is, trans to the bonds and nonbonding pairs as shown by



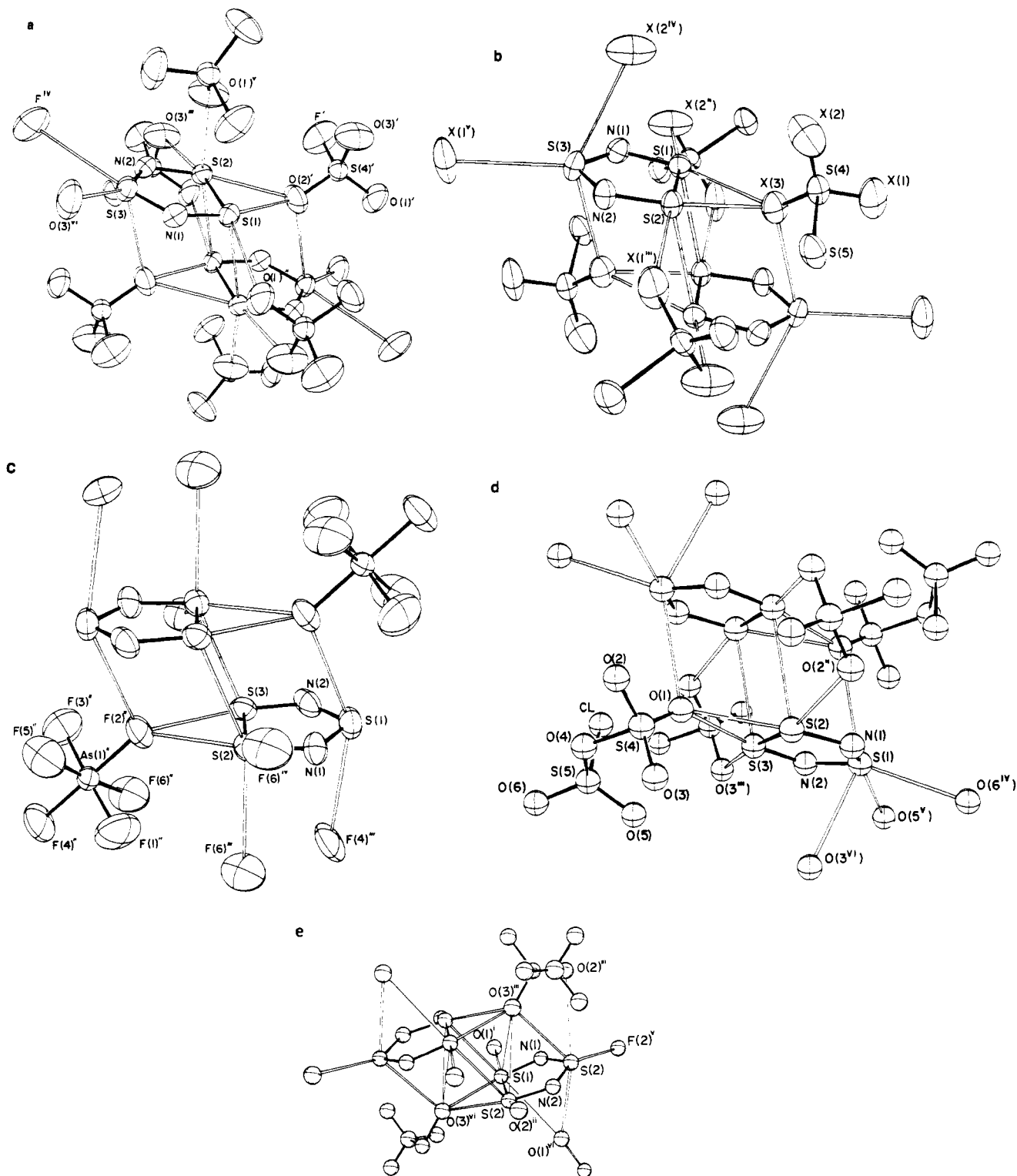
Dunitz et al.<sup>47</sup> have recently made a survey of the directional preferences of nonbonded atomic contacts with divalent sulfur. They show that nucleophiles, i.e., donor atoms such as O and F, tend to form bonds in the plane of the two covalent bonds from sulfur, S-X and S-Y, and approximately trans to these bonds. They interpret this as being due to an interaction of the donor atoms with the LUMO's on sulfur which they identify as the antibonding orbitals associated with the SX and SY bonds, i.e., σ\*(S-X) and σ\*(S-Y). Our observations are in accord with this generalization except that we also observed

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

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

(46) Andersen, O.; Hazell, A. C.; Hazell, R. G. *Acta Crystallogr., Sect. B* **1977**, *B33*, 1109. See also: Heath, G. A.; Murray-Rust, P.; Murray-Rust, J. *Ibid.* **1977**, *B33*, 1209.

(47) Rosenfield, R. E.; Parthasarathy, R.; Dunitz, J. D. *J. Am. Chem. Soc.* **1977**, *99*, 4860.



**Figure 2.** Anion-cation and cation-cation interactions in the following compounds: (a)  $(S_6N_4)(SO_3F)_2$ ; (b)  $(S_6N_4)(S_2O_2F)_2$ ; (c)  $(S_6N_4)(AsF_6)_2$  (redrawn from the original coordinates in ref 14); (d)  $(S_6N_4)(S_2O_6Cl)_2$  (redrawn from the atomic coordinates kindly provided by Dr. Banister); (e)  $(S_6N_4)(SO_3CF_3)_2$  (redrawn from the original coordinates in ref 12b).

weak interactions which are trans to the assumed positions of the nonbonding pairs. These are also regions of low electron density which result from the localization of the S atom electron density into bonding and nonbonding regions.

Dunitz et al. also point out that electrophiles, i.e., acceptor atoms, interact with lone pair orbitals on the S atom to form bonds approximately perpendicular to the plane of the SX, SY bonds.<sup>47</sup> The interring S-S bonds in the dimer molecule can be regarded as being approximately of this type, and they are at 108 and 90° to the SN and SS bonds of the ring.

We may summarize by stating that electrophilic, i.e., acceptor, interactions to sulfur will always be in the direction of the nonbonding pairs on sulfur and therefore in an ideal case at approximately 109° to the SX and SY bonds. Nucleophilic, i.e., donor interactions, will be not only approximately trans to the SX and SY bonds but also in directions at approximately 109° to the interactions in the S-X, S-Y plane, i.e., trans to the nonbonding pairs, making an approximately tetrahedral arrangement of a maximum of four such weak interactions around any S atom.

Table IX. Comparison of the Bond Distances (Å) and Bond Angles (Deg) in Several Thiosulfate Anions

compd	(S <sub>6</sub> N <sub>4</sub> )(SO <sub>3</sub> F) <sub>2</sub> <sup>a</sup>	(CH <sub>3</sub> C(OH) <sub>2</sub> ) <sub>2</sub> <sup>+</sup> (SO <sub>3</sub> F) <sup>b</sup>	(NH <sub>4</sub> )(SO <sub>3</sub> F) <sup>c</sup>	(S <sub>4</sub> N <sub>4</sub> )(SO <sub>3</sub> F) <sub>2</sub> <sup>d</sup>	Li <sup>+</sup> SO <sub>3</sub> F <sup>e,f</sup>
Bond Lengths, Å					
S-F	1.537 (2)	1.561 (4)	1.55 (2)	1.515 (3) (S-OF(1))	1.555 (7)
S-O(1)	1.415 (3)	1.432 (4)	1.45 (2)	1.465 (3) (S-OF(2))	1.455 (6)
S-O(2)	1.419 (3)	1.429 (4)	} 1.45 (2)	1.427 (3) (S-O(1))	} 1.424 (4)
S-O(3)	1.415 (3)	1.418 (5)		1.425 (2) (S-O(2))	
Bond Angles, Deg					
F-S-O(1)	104.7 (2)	102.9 (3)	} 106 (1)	103.8 (2) (OF(1)-S-OF(2))	104.5 (5)
F-S-O(2)	105.7 (2)	103.0 (3)		107.0 (1) (OF(1)-S-O(1))	} 102.8 (3)
F-S-O(3)	103.3 (2)	104.7 (3)		108.0 (1) (OF(1)-S-O(2))	
O(1)-S-O(2)	112.8 (2)	112.4 (3)	} 113 (1)	112.1 (2) (OF(2)-S-O(1))	} 113.5 (2)
O(1)-S-O(3)	114.6 (2)	116.0 (3)		110.8 (1) (OF(2)-S-O(2))	
O(2)-S-O(3)	114.3 (2)	115.7 (3)	113 (1)	114.5 (2) (O(1)-S-O(2))	117.4 (4)

<sup>a</sup> This work. Anion-ordered C<sub>3v</sub> symmetry. <sup>b</sup> Reference 51. Anion-ordered C<sub>3v</sub> symmetry. <sup>c</sup> Reference 18. Anion partially disordered (distances quoted assume symmetry C<sub>3v</sub>). <sup>d</sup> Reference 10. Anion-disordered C<sub>2v</sub> symmetry. <sup>e</sup> Reference 53. Anion-ordered C<sub>3v</sub> symmetry. <sup>f</sup> The fluorosulfate anions in ref 54 were also found to be disordered, and the parameters were constrained in the least-squares refinements.

That it is indeed the unshared electron pairs on the donor atom, O or F in our case, that take part in the interactions with S atoms is confirmed by the fact that the three weak bonds formed by a given O or F atom have an approximately tetrahedral arrangement with respect to the covalent bond between this atom and the central atom of the anion (Table V).

It is interesting to note that all the anion-cation interactions are with sulfur atoms and not nitrogen atoms in the cation. This is consistent with the fact that according to the resonance structures I-VII and particularly the more important structures I-IV the positive charge is concentrated principally on the S atoms which also being larger have a lower surface electron density and therefore more readily accept additional electron density from the donor atom (Table V).

As a consequence of the presumed charge-transfer interactions between the anions and the S<sub>3</sub>N<sub>2</sub><sup>+</sup> and S<sub>6</sub>N<sub>4</sub><sup>2+</sup> cations, it would be expected that there should be a weakening of the primary bond to the donor atom involved in the CT interaction. This lengthening is possibly shown in the dimeric form (S<sub>6</sub>N<sub>4</sub>)(AsF<sub>6</sub>)<sub>2</sub><sup>14</sup> where the bridging fluorine atom F(2) forms an As-F bond of 1.730 (5) Å compared to other As-F distances of 1.658-1.719 Å and a "normal" As-F distance of 1.719 (3) Å in the hexafluoroarsenate anion of KAsF<sub>6</sub>.<sup>48</sup> Due to the relatively high standard deviations associated with the atomic positions in the monomeric salt (S<sub>3</sub>N<sub>2</sub>)(AsF<sub>6</sub>) and the disorder in the anion of the (S<sub>6</sub>N<sub>4</sub>)(S<sub>2</sub>O<sub>2</sub>F)<sub>2</sub>, no conclusive statement on any possible weakening of the primary bonds as a result of the CT interactions can be made. The evidence from the structure of (Se<sub>4</sub>S<sub>2</sub>N<sub>4</sub>)(AsF<sub>6</sub>)<sub>2</sub> is however slightly more reliable despite the more varied nature of the Se...F and S...F contacts present. In particular the distances As(1)-F(12) and As(2)-F(21) are 1.76 and 1.74 Å, and these fluorines appear to be involved in the strongest interactions.<sup>15</sup> Furthermore, in (S<sub>4</sub>N<sub>3</sub>)(NO<sub>3</sub>) the effect of the three-center interactions is clearly apparent in the nitrate group since the N-O bond to the bridging atom is 0.043 Å (ca. 10σ) longer than the other two N-O distances.<sup>5</sup> Moreover, the electron density distribution in this structure has been determined at 90 K with the result that this bridging interaction is represented by a broad region of charge consistent with an appreciable charge transfer from the nitro to the disulfide group.<sup>49</sup> In (S<sub>4</sub>N<sub>3</sub>)(Br<sub>3</sub>), the Br-Br distances in the anion are 2.677 (2) and 2.431 (2) Å where the longer bond is again to the bromine involved in the CT interaction.<sup>6</sup> Also in the structure of (S<sub>4</sub>N<sub>3</sub>)<sub>2</sub>(SbCl<sub>5</sub>) one

of the equatorial chlorines of the SbCl<sub>5</sub><sup>2-</sup> anion (which is a distorted square pyramid) is involved in all four short contacts (3.005-3.073 Å) to the disulfide bonds in two different S<sub>4</sub>N<sub>3</sub><sup>+</sup> cations and forms a substantially longer (2.99 (3) Å) Sb-Cl bond (other Sb-Cl distances 2.38-2.61 Å).<sup>9,50</sup> Overall, it does appear that there is some weakening of some primary bonds to the donor atom in the anions as a result of the charge-transfer interactions.

**Fluorosulfate, Thiofluorosulfate, and Hexafluoroarsenate Anions.** The As-F distances in the hexafluoroarsenate anion of (S<sub>3</sub>N<sub>2</sub>)(AsF<sub>6</sub>) range from 1.694-1.719 Å and are close to accepted values. None of these bonds show any lengthening analogous to the bond to the bridging fluorine in the dimeric compound (S<sub>6</sub>N<sub>4</sub>)(AsF<sub>6</sub>)<sub>2</sub>. Bond angles in the anion in (S<sub>3</sub>N<sub>2</sub>)(AsF<sub>6</sub>) are within ca. 2° of 90° or 180° with no systematic trends (Table VIII).

The dimensions of the fluorosulfate anion in the structure of (S<sub>6</sub>N<sub>4</sub>)(SO<sub>3</sub>F)<sub>2</sub> are compared to those in some related salts containing this anion in Table IX. Of note is the fact that the present anion appears to be completely ordered in the crystal with exact C<sub>3v</sub> symmetry since all the oxygen atoms in the anion are involved in contacts to the sulfur atoms of the S<sub>6</sub>N<sub>4</sub><sup>2+</sup> cation of approximately the same strength. The S-O (1.416 (3) Å) and S-F (1.537 (2) Å) distances in the present anion are however somewhat shorter than those in CH<sub>3</sub>C(OH)<sub>2</sub><sup>+</sup>SO<sub>3</sub>F<sup>2-</sup>, although the SO<sub>3</sub>F<sup>-</sup> anion in this compound is involved in several hydrogen bonds.<sup>51</sup> It may also be noted that the only oxygen atom not involved in any strong hydrogen bonds in this latter compound forms an S-O bond of 1.418 (5) Å, close to the value observed here. The O-S-F and O-S-O angles in the fluorosulfate anions in both of these compounds are very similar, and the average values of 104.4 and 113.9°, respectively, for (S<sub>6</sub>N<sub>4</sub>)(SO<sub>3</sub>F)<sub>2</sub> and 103 and 114.7°, respectively, for [CH<sub>3</sub>C(OH)<sub>2</sub>](SO<sub>3</sub>F) show that the anions in both compounds are flattened tetrahedra. In the structures of ammonium fluorosulfate<sup>19</sup> and (S<sub>4</sub>N<sub>4</sub>)(SO<sub>3</sub>F)<sub>2</sub>,<sup>10</sup> the fluorosulfate anions both have some oxygen/fluorine disorder which results in the anions having only C<sub>2v</sub> symmetry. The two ordered S-O bonds in the anion of (S<sub>4</sub>N<sub>4</sub>)(SO<sub>3</sub>F)<sub>2</sub> are, however, very similar in length (1.426 Å) to the S-O

(50) For comparison the Sb-Cl distances in K<sub>2</sub>SbCl<sub>5</sub> are 2.385 (2) (axial), 2.633 (2), 2.625 (2), 2.799 (2) and 2.509 (2) Å (basal): Wismer, R. K.; Jacobson, R. A. *Inorg. Chem.* **1974**, *13*, 1678.

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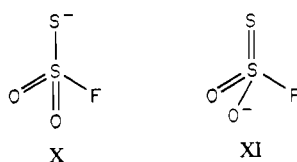
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distances in the present anion and that in  $(\text{CH}_3\text{C}(\text{OH})_2(\text{S}-\text{O}_3\text{F}))^{51}$

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  $\text{SO}_3\text{F}^-$ .

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  $\text{S}_8^{27}$  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<sup>-</sup> whereas S-S<sup>-</sup> 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.

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**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;  $\text{S}_4\text{N}_4$ , 28950-34-7;  $\text{HSO}_3\text{F}$ , 7789-21-1;  $\text{AsF}_5$ , 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 $\text{S}_4\text{N}_4$ with $\text{SbCl}_5$ , $\text{SbF}_5$ , $\text{AsF}_5$ , $\text{PF}_5$ , and $\text{HSO}_3\text{F}$ . 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  $\text{S}_4\text{N}_4$  with the Lewis acids  $\text{SbCl}_5$ ,  $\text{AlCl}_3$ ,  $\text{PCl}_5$ ,  $\text{PF}_5$ ,  $\text{AsF}_5$ , and  $\text{SbF}_5$  with principally  $\text{SO}_2$  as the solvent are reported. It is shown that  $\text{PF}_5$  and  $\text{PCl}_5$  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,  $\text{SbCl}_5$ ,  $\text{AsF}_5$ , and  $\text{SbF}_5$  in a 3:1 or larger mole ratio oxidize  $\text{S}_4\text{N}_4$  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  $\text{AlCl}_3$ , and the  $(\text{S}_4\text{N}_4)(\text{SO}_3\text{F})_2$  salt has been obtained from the reaction of  $\text{S}_4\text{N}_4$  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.<sup>1-4</sup> The majority of these compounds have a 1:1 stoichiometry, and X-ray crystallographic structures of the 1:1 adducts with  $\text{BF}_3$ ,  $\text{SbCl}_5$ ,  $\text{AsF}_5$ ,  $\text{SO}_3$ , and  $\text{FSO}_3\text{NCO}$  show that in each case the Lewis acid is coordinated to a nitrogen atom and the  $\text{S}_4\text{N}_4$  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  $\text{S}_4\text{N}_4 \cdot 2\text{BCl}_3$ ,<sup>5</sup>  $\text{S}_4\text{N}_4 \cdot 2\text{SbCl}_5$ ,<sup>5</sup>  $\text{S}_4\text{N}_4 \cdot 4\text{SbF}_5$ ,<sup>5-7</sup>  $\text{S}_4\text{N}_4 \cdot 2\text{SO}_3$ ,<sup>8</sup> and  $\text{S}_4\text{N}_4 \cdot 4\text{SO}_3$ <sup>8</sup> as well as a number of mixed complexes such as  $\text{S}_4\text{N}_4 \cdot \text{BCl}_3 \cdot \text{SbCl}_5$ ,<sup>5</sup>  $\text{S}_4\text{N}_4 \cdot \text{AlCl}_3 \cdot \text{SbCl}_5$ ,<sup>9</sup>  $\text{S}_4\text{N}_4 \cdot \text{BCl}_3 \cdot \text{SO}_3$ , and

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