LEWIS ACID CHEMISTRY OF SOME SULPHUR-NITROGEN COMPOUNDS

By

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TO MY PARENTS

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ABSTRACT

The compound S_4N_4 has been shown to react with the Lewis acids $SbCl_5$, SbF_5 and AsF_5 to produce the previously unreported cyclotetrathiazyl dication, $S_4N_4^{2+}$, in the form of the salts $S_4N_4(SbCl_6)_2$, $S_4N_4(SbF_6)_2$, $S_4N_4(AsF_6)_2\cdot xSO_2$ and $S_4N_4(Sb_3F_{14})(SbF_6)$. A reaction sequence for the preparation of $S_4N_4(SbCl_6)_2$ has been suggested and the infrared and Raman spectra for each of the salts is reported as well as the crystal structures of the $S_4N_4(SbCl_6)_2$ and $S_4N_4(Sb_3F_{14})(SbF_6)$ salts.

A brief investigation of the reaction of S_4N_4 with the Lewis acids PF_5 and PCl_5 produced, in the S_4N_4/PF_5 system, the new molecular adduct, $S_4N_4\cdot PF_5$, whereas the reaction of S_4N_4 with PCl_5 yielded a complex mixture of products, composed of phosphonitrilic chlorides.

The chemistry of trichlorocyclotrithiazene with $SbCl_5$ has been studied. It has been determined for the first time that $S_3N_3Cl_3$ when oxidized by $SbCl_5$ produces the $S_4N_4(SbCl_6)_2$ salt with the compounds $S_4N_4\cdot SbCl_5$ and $S_5N_5(SbCl_6)$ isolated as intermediates formed during the production of the $S_4N_4^{2+}$ dication. The crystal structures of both $S_4N_4\cdot SbCl_5$ and $S_5N_5(SbCl_6)$ are reported in this thesis.

In contrast, the fluoride, trifluorocyclotrithiazene, $S_3N_3F_3$, when combined with the Lewis acids SbF_5, AsF_5 and SO_3 was not oxidized but rather simple fluoride ion abstraction occurred to yield the thiazyl salts $SN(Sb_2F_{11})$, $SN(AsF_6)$ and $SN(SO_3F)$.

For the first time, the chemistry of the sulphur imides with Lewis acids of oxidative capability has been studied.

Cyclotetrasulphurtetraimide, $S_4N_4H_4$, reacted readily with

$SbCl_5$ to yield the $S_4N_4^{2+}$ salt, $S_4N_4(SbCl_6)_2$. The compound $S_4N_4 \cdot SbCl_5$ has been shown to be an intermediate formed during the oxidation of $S_4N_4H_4$ with $SbCl_5$.

Cycloheptasulphurimide, S_7NH, and 1,4-cyclohexasulphurdiimide, 1,4-$S_6N_2H_2$, produced the previously unknown dithionitronium ion, S_2N^+, when treated with $SbCl_5$. Infrared and Raman spectra for the $S_2N(SbCl_6)$ are reported as well as the crystal structure.

In a limited investigation, the compound $Cl_3PNPCl_3(PCl_6)$, has been isolated from the reaction of S_7NH with PCl_5. The crystal structure of the trichloro[(trichlorophosphoranylidene)amino]phosphorus (V) hexachlorophosphate is reported in this work.

ACKNOWLEDGEMENTS

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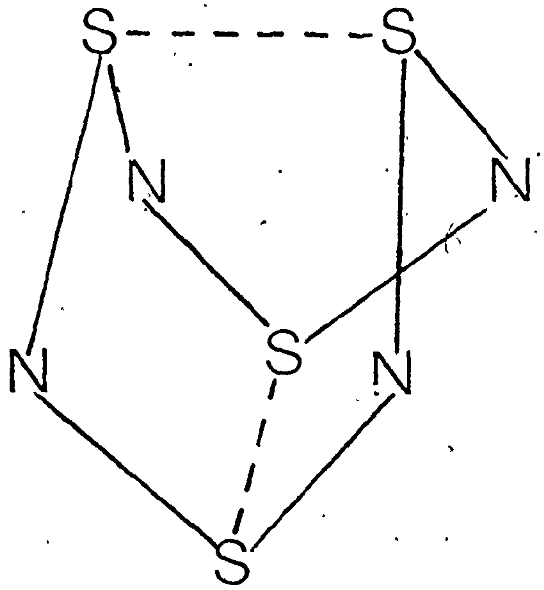
CHAPTER I

INTRODUCTION

I-1 The Chemistry of S_4N_4

In 1835, A. Gregory[1,2] founded sulphur-nitrogen chemistry by preparing cyclotetrathiazene, S_4N_4, by the action of ammonia upon a chloroform solution of sulphur monochloride. There was much debate as to the exact structure of S_4N_4 which continued until 1944 when Lu and Donohue[3] established the geometry, shown below, by electron diffraction studies of the vapour. This structure was confirmed in 1963 by an X-ray crystallographic study of the solid.[4,5] Cyclotetrathiazene is a three-dimensional cage with point group symmetry D_{2d}. The nitrogen atoms occupy the corners of a square while the four sulphur atoms form a disphenoid.



S-S = 2.58 Å

S-N = 1.62 Å

N-N = 2.52 Å

The S-N bond lengths are all 1.62 Å. This is shorter than the normal sulphur-nitrogen single bond length (1.76 Å in sulfamic acid, $H_3N^+-SO_3^-$),[6] or the value obtained from the sum of the single bond radii (1.74 Å) [7] and therefore some double bond character is indicated. The S-S bond distance of 2.58 Å is 1.1 Å shorter than the sum of the Van der Waals radii, 3.7 Å [8] for sulphur and it is reasonable to assume that there is a weak sulphur-sulphur bond. The distance between adjacent nitrogen atoms is 2.52 Å, while the sum of the two nitrogen Van der Waals radii is 3.0 Å,[8] and a single nitrogen-nitrogen bond has a length of 1.40 Å.[7] It would appear that a slight interaction of nitrogen atoms around the ring is also possible.

Due to the difference in the electronegativities of sulphur and nitrogen, it is expected that the sulphur atoms will carry a partial positive charge and that the nitrogen atoms will carry a partial negative charge. As a consequence, S_4N_4 may act either as an electrophile through the sulphur atoms or a nucleophile through the nitrogen atoms.

The chemistry of S_4N_4 may be briefly summarized as follows:

i) Reactions in which the eight-membered ring is maintained intact and substituents are placed on sulphur or nitrogen;
ii) Reactions in which co-ordination complexes are formed;
iii) Reactions in which ring contraction or expansion occurs;
iv) Reactions in which ring fragmentation occurs to produce species containing open S-N chains.

I-2 Reactions of S_4N_4

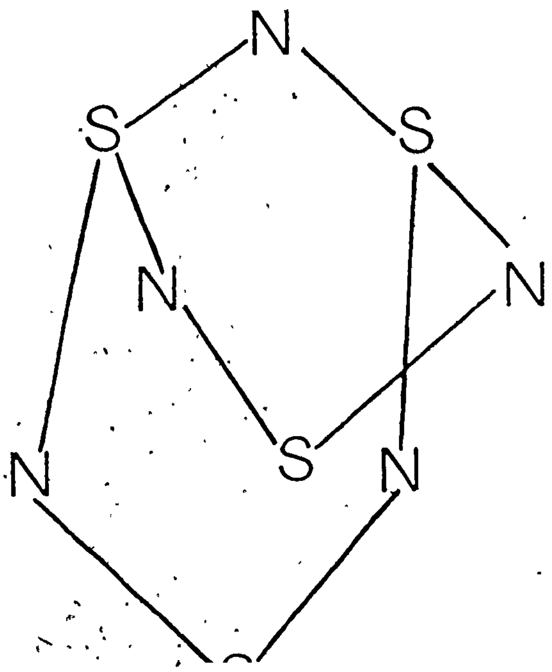
(1) With Lewis Bases

In general, nucleophiles tend to attack the more positive sulphur atom with the S_4N_4 ring being destroyed. There are no Lewis base complexes known in which the S_4N_4 ring is maintained intact.

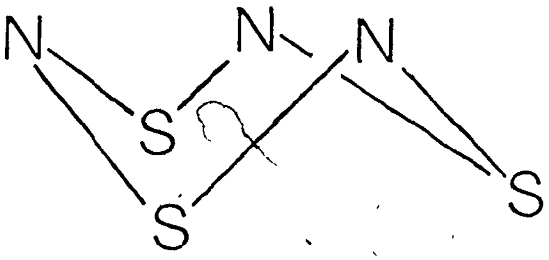
Lewis bases that have been reacted with S_4N_4 include ammonia, amines, phosphines, cyanide ion, Grignard reagents and diazomethane.

The product obtained from the reaction of S_4N_4 with liquid ammonia[9] was originally assumed to be the diammoniate of composition $S_4N_4 \cdot 2NH_3$. This would be a true acid-base adduct in which S_4N_4 functions as a Lewis acid. This complex has not been thoroughly investigated, but the material has been assumed to be $S_2N_2 \cdot NH_3$,[10] since it can be prepared by the reaction of S_2N_2 with liquid ammonia and careful thermal cracking yields NH_3 plus S_2N_2 and not S_4N_4.

Another product of the reaction of S_4N_4 with liquid ammonia is the ammonium salt of the $S_4N_5^-$ anion[11] which has a cage structure similar to that of S_4N_4.



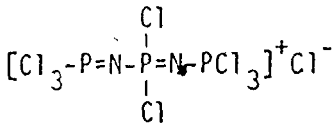
This anion as well as the new $S_3N_3^-$ anion[12] can also be generated by the action of azide salts upon S_4N_4. The structure of the $S_3N_3^-$ anion is not known, but based on spectroscopic data, it is thought to have C_{3v} symmetry.



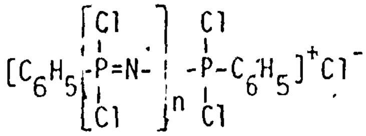
Cyclotetrathiazene is known to readily undergo very complex reactions with primary and secondary amines.[13] The reaction with benzylamine[14] is the most thoroughly studied reaction and yields arylimine polysulfides, Schiff's bases and ammonia as products.

$$S_4N_4 + 8C_6H_5CH_2NH_2 \rightarrow C_6H_5NS_xNCHC_6H_5 + 7NH_3 + 3C_6H_5CHNCH_2C_6H_5 + (4-x)S$$

The phosphorus compounds PCl_3, $(C_6H_5)PCl_2$ and $(C_6H_5)_3P$ give an interesting series of reactions with S_4N_4. Phosphorus trichloride[15,16] and phenyl phosphorus dichloride[17,18] destroy the eight-membered ring to produce short chain phosphorus-nitrogen polymers, such as:



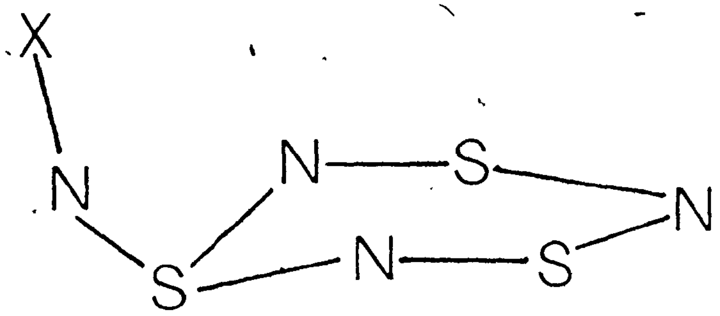
$$[Cl_3\text{-}P{=}N\text{-}\overset{\overset{\textstyle Cl}{|}}{\underset{\underset{\textstyle Cl}{|}}{P}}{=}N\text{-}PCl_3]^+Cl^-$$



$$[C_6H_5\left[\text{-}\overset{\overset{\textstyle Cl}{|}}{\underset{\underset{\textstyle Cl}{|}}{P}}{=}N\text{-}\right]_n\text{-}\overset{\overset{\textstyle Cl}{|}}{\underset{\underset{\textstyle Cl}{|}}{P}}\text{-}C_6H_5]^+Cl^-$$

The other products are $C_6H_5P(S)Cl_2$ and $C_6H_5PCl_2{=}NP(S)(C_6H_5)_2$.

Triphenyl phosphine[19,20] and triphenyl arsine[21] behave differently. One sulphur atom is removed from the S_4N_4 ring as $SP(C_6H_5)_3$ or $SAs(C_6H_5)_3$ and an exocyclic N-P or N-As bond is formed generating a six-membered ring. The compounds formed are $S_3N_4P(C_6H_5)_3$ and $S_3N_4As(C_6H_5)_3$ and in both instances the structures have been determined by X-ray crystallography.

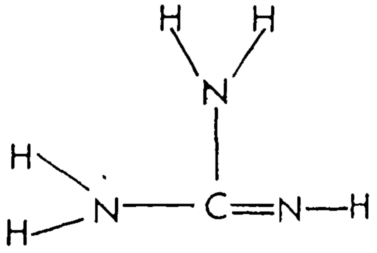


X = $As(C_6H_5)_3$

or $P(C_6H_5)_3$

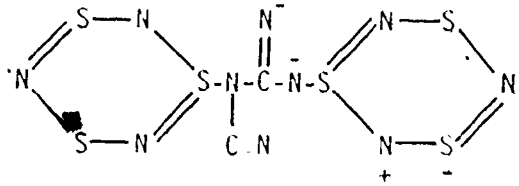
The molecules have an $As(C_6H_5)_3$ or an $P(C_6H_5)_3$ group bonded through nitrogen to an S_3N_3 ring, five atoms of which are co-planar.

Cyanide ion[22] has been found to readily react with S_4N_4. Upon mixing S_4N_4 with KCN in dimethylformamide in a mole ratio of 1:2, a red precipitate was formed which analyzed as KCN_3S_2. This material was proposed to be a complex containing one mole of $K_2(C_2N_{10}S_4)$ per two moles of KSCN based upon a molecular weight determination and an X-ray powder photograph of the mixture. Hydrolysis of the mixture yielded guanidine from ~~which~~ it could be inferred that the carbon was bonded

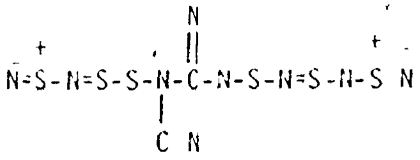


guanidine

to three nitrogens. The structure of the $(C_2N_{10}S_6)^{2-}$ anion has been proposed to be



or



$\overset{-}{N}=\overset{+}{S}-N=S-S-\underset{CN}{\underset{|}{N}}-\overset{N}{\overset{\|}{C}}-N-S-N=S-N-\overset{+}{S}\ \overset{-}{N}$

Grignard reagents[23] are known to completely disrupt the S_4N_4

ring and again the chemistry is not well understood. Aryl Grignard reagents yield thiodithiazyl diaryl compounds.

$$X\text{-}C_6H_5MgBr + S_4N_4 \rightarrow X\text{-}C_6H_4\text{-}S\text{-}N{=}S{=}N\text{-}S\text{-}C_6H_4\text{-}X$$

$$X = H,\ p\text{-}Cl,\ p\text{-}Br,\ p\text{-}CH_3O$$

There are very few physical data on these species other than melting points and solubilities and no information regarding their structures.

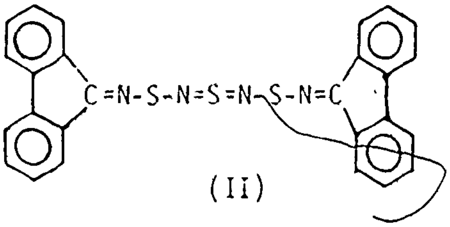
Ethyl magnesium bromide[24] reacts with S_4N_4 to yield a material of composition $C_2H_6S_2N_2$. It has been suggested that this material has a structure consisting of a linear S-N-S-N- chain with a single hydrogen bonded to nitrogen.

$$C_2H_5\text{-}S\text{-}N{=}S{=}N\text{-}H$$

If a substituted diazomethane[25] such as diphenyldiazomethane or 9-diazofluorene is reacted with S_4N_4 in diethyl ether, nitrogen is liberated and products corresponding to the diphenyl trisulphurtetranitride (I) and the difluorenylidenetrisulphurtetranitride (II), respectively, are obtained.

$$(C_6H_5)_2C\text{-}N\text{-}S\text{-}N{=}S{=}N\text{-}S\text{-}N{=}C(C_6H_5)_2$$

(I)



(II)

A crystal structure of (II)[26] has confirmed the structure and has indicated that the -S-N=S=N-S- central portion of the chain is linear.

(ii) With Lewis Acids

The Lewis acid chemistry of cyclotetrathiazene is, at present, not well understood. Depending upon the oxidizing strength of the Lewis acid versus its acceptor strength, the eight-membered ring of S_4N_4 may or may not be destroyed. Thus, a simple molecular adduct may form or if an oxidative process takes place, new cationic species may be generated. Table I-1 summarizes some of the Lewis acid chemistry of S_4N_4.

Many of the complexes in the Table I-1 have only been tentatively identified and the proposed structures are based only on elemental analysis and spectral data.

The best established adducts of S_4N_4 are $S_4N_4 \cdot BF_3$ [27,28] and $S_4N_4 \cdot SbCl_5$ [27,29] for which crystallographic data is available. Upon adduct formation, S_4N_4 undergoes a conformational change with the original disphenoid changing to produce a boat-shaped sulphur-nitrogen ring in which the sulphur atoms form a nearly square planar arrangement.

In 1967, Jolly and co-workers[27] demonstrated that 1:2 complexes of S_4N_4 were possible and could be isolated from the reaction of S_4N_4 with the appropriate amount of Lewis acid.

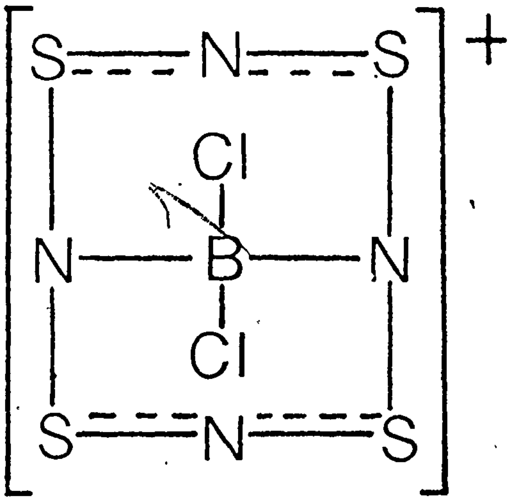
$$S_4N_4 + BCl_3 + SbCl_5 \rightarrow S_4N_4 \cdot BCl_3 \cdot SbCl_5$$

Malhotra et al.[36] have also prepared a 1:2 S_4N_4:$SbCl_5$ species. The exact nature of this compound is not understood but it has been proposed on the basis of spectral data that it is ionic in nature. Jolly has suggested a possible formulation for the $S_4N_4 \cdot BCl_3 \cdot SbCl_5$ species.

Table I-1

Lewis Acid Chemistry of S_4N_4

Lewis Acid	Molar Ratio with Respect to S_4N_4	Complex	References
BCl_3	1:1	$S_4N_4\cdot BCl_3$	27
BCl_3	1:2	$(S_4N_4\cdot BCl_2^+)(BCl_4^-)$	27
BF_3	1:1	$S_4N_4\cdot BF_3$	27,28
$SbCl_5$	1:1	$S_4N_4\cdot SbCl_5$	27,29
	1:2	$S_4N_4\cdot Sb_2Cl_{10}$	27
	1:3	$S_4N_4\cdot Sb_2Cl_{12}$	27
$BCl_3/SbCl_5$	1:1:1	$S_4N_4BCl_2^+SbCl_6^-$	27
BBr_3	1:1	$S_4N_4\cdot BBr_3$	27
SbF_5	1:4	$(S_4N_4SbF_4^+)(Sb_3F_{16}^-)$	36
AsF_5	1:1	$S_4N_4\cdot AsF_5$	30
	1:3	$S_3N_2(AsF_6)$	31
$SnCl_4$	2:1	$(S_4N_4)_2SnCl_4$	32,33
SO_3	1:2	$S_4N_4\cdot 2SO_3$	34
	1:4	$S_4N_4\cdot 4SO_3$	34
$AlCl_3$	1:1	$S_4N_4\cdot AlCl_3$	35
$AlBr_3$	1:1	$S_4N_4\cdot AlBr_3$	35
$SeCl_4$	1:1	$S_4N_4\cdot SeCl_4$	36
$TeCl_4$	1:1	$S_4N_4\cdot TeCl_4$	36
$TeCl_4$, BCl_3	1:1:1	$S_4N_4TeCl_3^+BCl_4^-$	36
$NbCl_5$	1:1	$S_4N_4\cdot NbCl_5$	36
$TaCl_5$	1:1	$S_4N_4\cdot TaCl_5$	38
$AlCl_3$, $SbCl_5$	1:1:1	$(S_4N_4AlCl_2^+)SbCl_6^-$	35
$TiCl_4$	2:1	$(S_4N_4)_2TiCl_4$	37

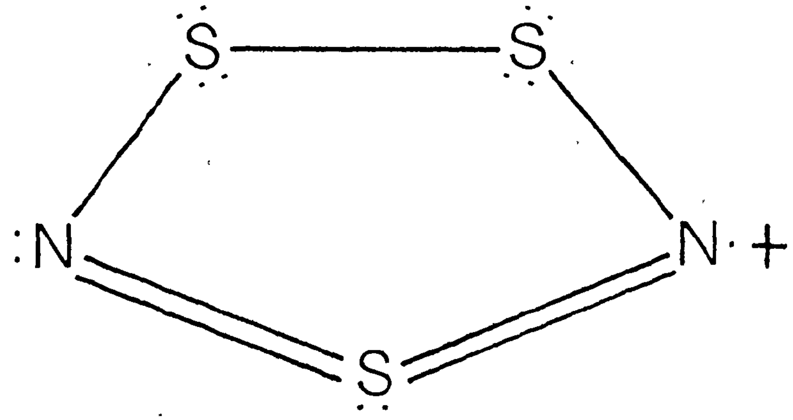


The proposed formulation for the cation is shown above and it has been assumed on the basis of infrared data that the anion is $SbCl_6^-$ rather than BCl_4^-.

Cyclotetrathiazene is oxidized in solution by sulphuric acid and antimony pentafluoride to yield radical species which exhibit a five-line esr spectrum. The observed results were first explained by suggesting the presence of the SN_2^+ ratical,[39] but a later study interpreted the esr spectrum in terms of the $S_2N_2^+$ radical.[40] Although this species was not identified, it is clear that oxidation is occurring.

Gillespie and co-workers[31] have recently shown that S_4N_4 is easily oxidized by arsenic pentafluoride in liquid SO_2. One of the products of the oxidation is the cyclothiodithiazyl radical cation $S_3N_2^+$. The g-value and coupling constants obtained from esr data are compatible with those obtained in the earlier work on S_4N_4-sulphuric acid solutions.

Therefore, it is reasonable to conclude that the $S_3N_2^+$ radical cation is produced in sulphuric acid solutions of S_4N_4. A crystallographic determination indicates that the cyclothiodithiazyl cation is a planar five-membered ring.



Oxidation of S_4N_4 can give other products. Banister has isolated the cyclopentathiazyl cation, $S_5N_5^+$, from the reaction of S_4N_4 with $AlCl_3$ and transition metal halides in thionyl chloride.[41]

I-3 Trichlorocyclotrithiazene

Trichlorocyclotrithiazene was first prepared in 1880 by Demarcay[42] by the action of chlorine gas on a chloroform solution of S_4N_4. The reaction involves an oxidation of sulphur III in S_4N_4 to sulphur IV in $S_3N_3Cl_3$ as well as a ring contraction. Heal[43] has studied the reaction pathway and has concluded that $S_3N_3Cl_3$ is formed via an $S_4N_4Cl_4$ intermediate.

$$S_4N_4 + 2Cl_2 \xrightarrow{\text{minutes}} S_4N_4Cl_4 \xrightarrow{\text{hours}} S_3N_3Cl_3 + NSCl$$

$$NSCl \xrightarrow{\text{days}} \frac{1}{3}\, S_3N_3Cl_3$$

Banister has recently shown that $S_3N_3Cl_3$ can also be prepared by means of sulphuryl chloride as an oxidant.[44]

$$3S_4N_4 + 6SO_2Cl_2 \rightarrow 4S_3N_3Cl_3 + 6SO_2$$

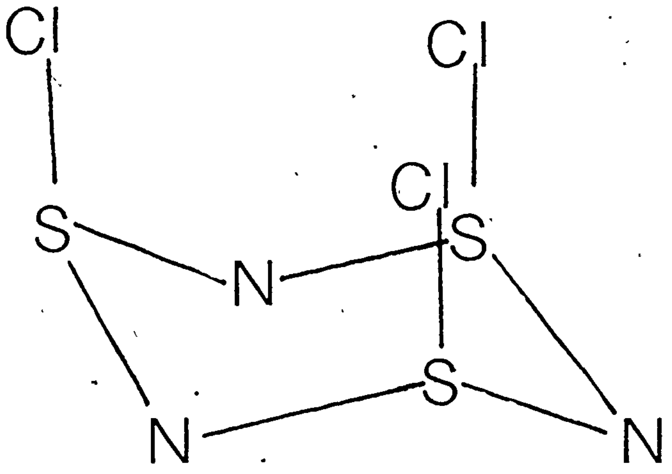
Other methods involve the chlorination of $S_3N_2Cl_2$ by either chlorine gas or sulphuryl chloride.

$$3S_3N_2Cl_2 + 3Cl_2 \rightarrow 2S_3N_3Cl_3 + 3SCl_2 \qquad \text{(ref. 45)}$$

$$3S_3N_2Cl_2 + 3SO_2Cl_2 \rightarrow 2S_3N_3Cl_3 + 3SO_2 + 3SCl_2 \qquad \text{(ref. 44)}$$

The structure of $S_3N_3Cl_3$ has been determined by X-ray crystallography.[46] The molecule consists of a six-membered ring in the chair conformation. Each chlorine is bonded in an exocyclic manner to a sulphur atom such that all the chlorines are <u>cis</u> with respect to each other.

The equivalence of all the sulphur-nitrogen bonds in the ring might imply that it has aromatic character, but it should be noted that it is not planar.



S-N = 1.605 Å

S-Cl = 2.150 Å

If $S_3N_3Cl_3$ is heated under high vacuum in a static system, the cyclic trimer is broken down to produce the monomer, thiazyl chloride. The following thermodynamic data have been obtained.[47]

$S_3N_3Cl_3(s) \rightarrow NSCl(g)$	$\Delta H° = 46.2 \pm 1.5$ kcal mole^{-1}
	$\Delta S° = 129.6 \pm 4.8$ cal deg^{-1}
$S_3N_3Cl_3(s) \rightarrow S_3N_3Cl_3(g)$	$\Delta H° = 24.3 \pm 1.5$ kcal mole^{-1}
	$\Delta S° = 52.1 \pm 4.6$ cal deg^{-1}

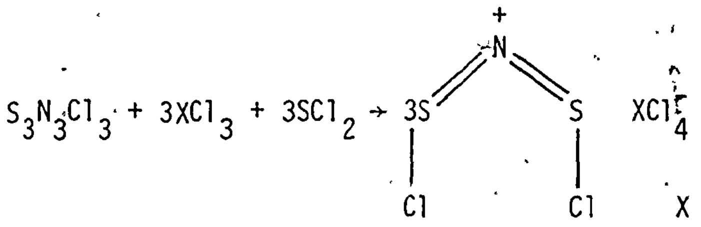
The thiazyl chloride formed has been shown by microwave spectroscopy to be a non-linear molecule.[48]

At room temperature thiazyl chloride trimerizes very readily to $S_3N_3Cl_3$.

Thiazyl Chloride

The known chemistry of $S_3N_3Cl_3$ is not as extensive as that of S_4N_4. Glemser has shown that $S_3N_3Cl_3$ reacts with the Lewis acid $SbCl_5$ to produce the salt $(S_3N_3Cl_2^+)(SbCl_6^-)$ and with BCl_3 and $AlCl_3$ in the presence of SCl_2 to form the $S_2NCl_2^+$ cation

$$S_3N_3Cl_3 + SbCl_5 \rightarrow (S_3N_3Cl_2^+)(SbCl_6^-) \qquad \text{(ref. 30)}$$



(ref. 49,50)

X = B or Al

The reactions involving SCl_2 with BCl_3 and $AlCl_3$ are thought to produce SCl^+ which behaves as an electrophile attacking the $S_3N_3Cl_3$ ring presumably facilitating the breakdown of the ring.

Banister[51] has studied the chemistry of $S_3N_3Cl_3$ with the metal chlorides $AlCl_3$, $FeCl_3$ and $SbCl_5$ in thionyl chloride in the presence of S_4N_4. It was reported that $S_3N_3Cl_3$ initially forms 1:1, 1:2 and 1:3 adducts with $AlCl_3$, $FeCl_3$ and $SbCl_5$, if stoichiometric amounts of reagents are combined. The adducts then react readily with S_4N_4 to yield the $S_5N_5^+$ cation.

The overall reactions are:

$$S_3N_3Cl_3 + 2FeCl_3 \rightarrow S_3N_3Cl_3 \cdot 2FeCl_3$$ (ref. 48)

$$+ 2AlCl_3 \rightarrow S_3N_3Cl_3 \cdot 2AlCl_3$$ (ref. 48)

$$+ 3SbCl_5 \rightarrow S_3N_3Cl_3 \cdot 3SbCl_5$$ (ref. 46,49)

$$S_3N_3Cl_3 \cdot 2FeCl_3 + 3S_4N_4 \rightarrow S_5N_5FeCl_4$$

$$S_3N_3Cl_3 \cdot 2AlCl_3 + 3S_4N_4 \rightarrow S_5N_5AlCl_4$$

$$S_3N_3Cl_3 \cdot 3SbCl_6 + 3S_4N_4 \rightarrow S_5N_5SbCl_6$$

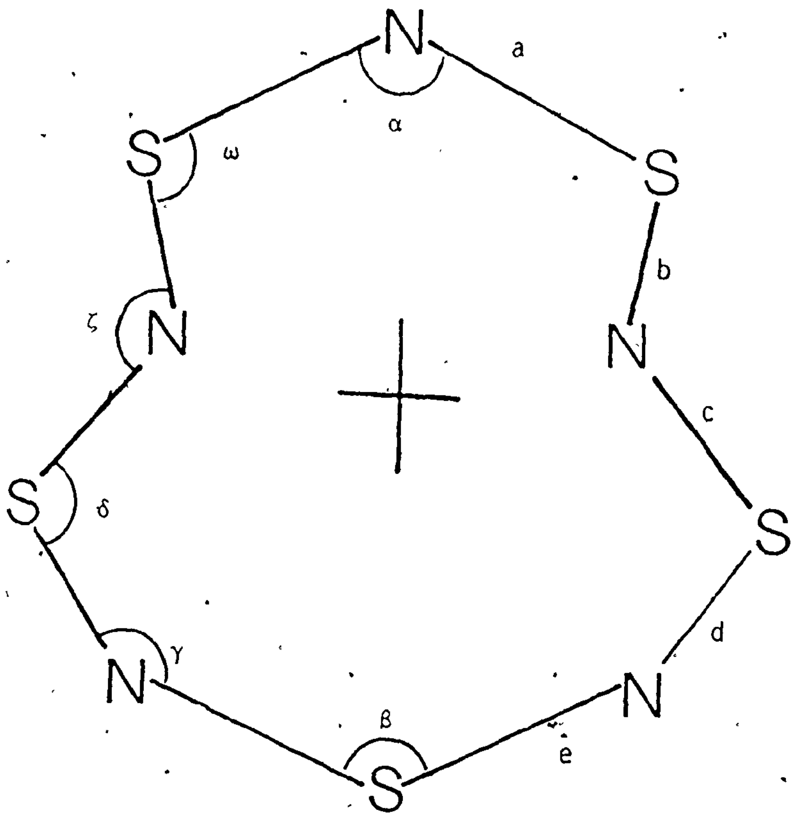
Note: These equations are not balanced as salts of the $S_5N_5^+$ cation were the only characterized products.

The adducts are regarded as potential sources of the thiazyl cation SN^+, which behaves as an electrophile towards S_4N_4 and thus generates the $S_5N_5^+$ cation in the process. Indeed, Mews[50] has demonstrated that the thiazyl cation, SN^+, does react with S_4N_4 to produce $S_5N_5^+$.[52]

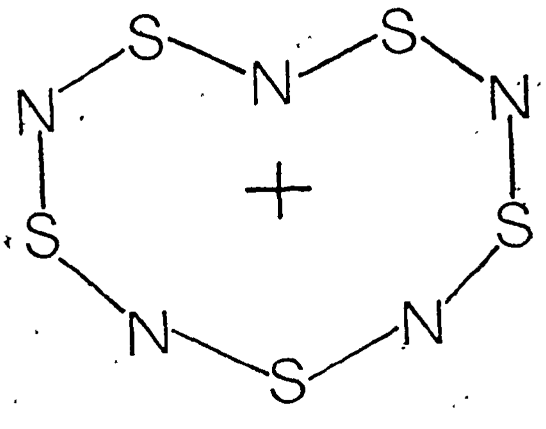
$$(SN^+)(AsF_6^-) + S_4N_4 \rightarrow (S_5N_5^+)(AsF_6^-)$$

The geometry of the $S_5N_5^+$ cation has been found in the species $S_5N_5(S_3N_3O_4)$,[54] and $S_5N_5(SnCl_5OPCl_3)$.[55] In both of these salts, the $S_5N_5^+$ cation has the same azulene shape. Bond lengths and bond angles for the $S_5N_5^+$ rings in these compounds are listed below, and the "azulene" like structure is illustrated on the following page.

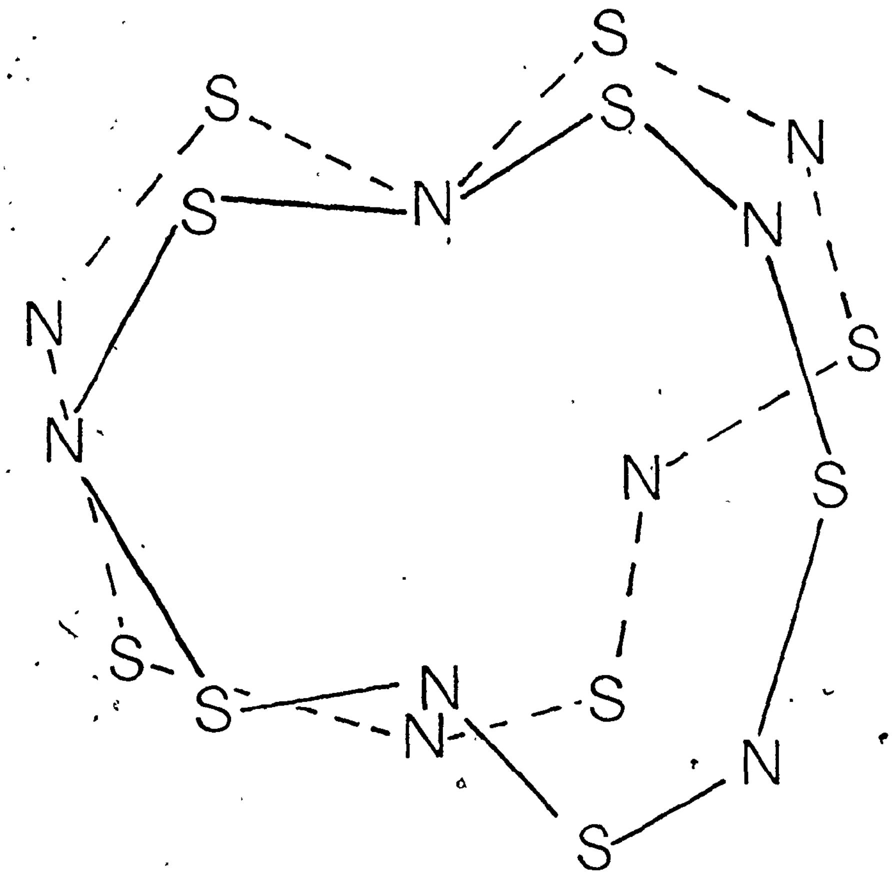
$(S_5N_5^+)(SnCl_5OPCl_3^-)$			$(S_5N_5^+)(S_3N_3O_4^-)$	
a 1.58 Å	α 131.5°		a 1.580 Å	α 133.0°
b 1.52 Å	β 125.0°		b 1.556 Å	β 124.5°
c 1.56 Å	γ 151.0°		c 1.543 Å	γ 151.0°
d 1.56 Å	δ 111.0°		d 1.567 Å	δ 109.6°
e 1.56 Å	ζ 141.0°		e 1.564 Å	ζ 138.3°
	ω 110.5°			ω 108.7°



The ionic structure of the $(S_5N_5^+)(AlCl_4^-)$ salt first isolated by Banister[53] was shown crystallographically not to contain the azulene-shaped $S_5N_5^+$ ring but rather to consist of a heart-shaped, almost planar, $S_5N_5^+$ ring.



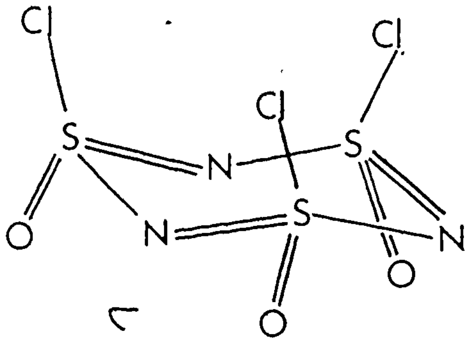
Since the publication of the latter structures, Banister has suggested that the apparent heart-shaped conformation probably arises from a disordering of the "azulene" like structure.[56] The diagram below illustrates the manner by which two azulene-shaped rings may be superimposed to produce an apparent heart-shaped $S_5N_5^+$ ring.



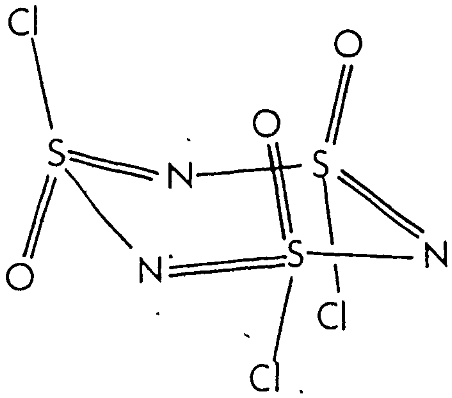
Sulphur trioxide combines with $S_3N_3Cl_3$ to yield the adduct $S_3N_3Cl_3 \cdot 6SO_3$,[57] which decomposes at 100°C to $S_3N_3Cl_3 \cdot 3SO_3$, and at slightly higher temperatures (140°C, 20 atm) to trioxotrichlorocyclotrithiazene. Thus, SO_3 is capable of oxidizing $S_3N_3Cl_3$ without ring cleavage.

$$S_3N_3Cl_3 + 3SO_3 \xrightarrow[20\ \text{atm}]{140°\text{C}} S_3N_3Cl_3O_3 + 3SO_2$$

The oxychloride[58] is a six-membered ring with sulphur in the oxidation state VI. Both the cis and trans isomers are known.



Cis



Trans

Trichlorocyclotrithiazene reacts with the sulphur imides[59,60] S_7NH and $S_4N_4H_4$ in the presence of pyridine to yield S_4N_4. In the absence of pyridine which acts as an acid scavenger, S_4N_3Cl is formed. This may be a result of the initial formation of the $S_4N_4 \cdot HCl$ adduct.[61]

$$4S_3N_3Cl_3 + 3S_4N_4H_4 \xrightarrow{\text{pyridine}} 6S_4N_4 + 12HCl$$

$$4S_3N_3Cl_3 + 3S_4N_4 \rightarrow 3S_4N_4\ HCl \rightarrow 3S_4N_3Cl + 3NH_4Cl + 3Cl_2 + 3S_4N_4$$

$$4S_3N_3Cl_3 + 12S_7NH \xrightarrow{\text{pyridine}} 3S_4N_4 + 12HCl + 84S$$

$$4S_3N_3Cl_3 + 12S_7NH \rightarrow 3S_4N_4 + 3S_4N_3Cl + 3NH_4Cl + 3Cl_2 + 72S$$

Other reactions in which the $S_3N_3Cl_3$ ring is destroyed are summarized in Table I-2.

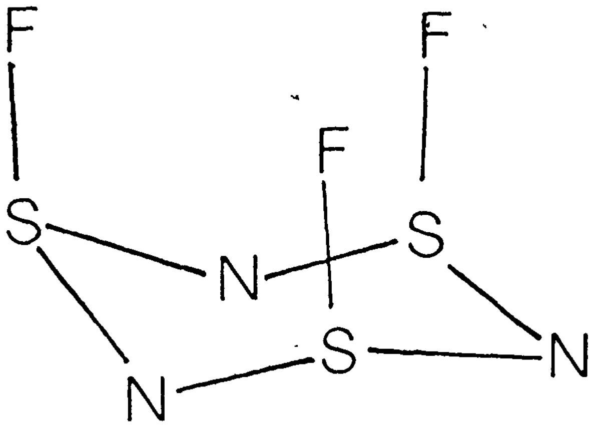
Table I-2

Reactions of $S_3N_3Cl_3$

Reactant	Product	References
H_2O	$S_2O(NH_2)_2$ SO_3^{2-}, NH_3, Cl^- (in alkaline solution.	(62,62,64)
EtOH	$S(OEt)_4$, NH_3, NH_4Cl	(64)
NH_3	$S(NH_2)$	(65)
$Mo(CO)_6$	$Mo(ClSN)_3$	(69)
$(CH_3)_2SO$	$((CH_3)_2S{=}N{=}S(CH_3)_2)Cl$	(66)
NO_2	$(NO)_2S_2O_7$	(64)
SO_3^{2-}	$S_2O_3^{2-}$	(62,64)
KCN	KSCN	(67,68)

I-4 Trifluorocyclotrithiazene

Trifluorocyclotrithiazene was first prepared by Glemser[70] by the action of silver(II)fluoride on $S_3N_3Cl_3$ in carbon tetrachloride solution. An alternative method is the polymerization of thiazyl fluoride formed by the reaction of AgF_2 or HgF_2 upon S_4N_4.[67,71] The structure of $S_3N_3F_3$ [72,73] is comparable to that of $S_3N_3Cl_3$.



S-F = 1.61 Å

S-N = 1.59 Å

It consists of a puckered six-membered ring with alternating sulphur-nitrogen atoms, in the chair conformation. The fluorine atoms are all bonded in an exocyclic manner to sulphur in the axial position. Sulphur-nitrogen bond equivalence in the ring would tend to suggest delocalized bonding, but like $S_3N_3Cl_3$ the ring is not planar.

Our present knowledge of the chemistry of $S_3N_3F_3$ is very limited. If heated to 250°C, it decomposes to the monomer thiazyl fluoride.[74] Thiazyl fluoride readily trimerizes at room temperature to yield $S_3N_3F_3$. Trifluorocyclotrithiazene acts as a fluoride ion donor to Lewis acids which are good fluoride ion acceptors.[30]

$$\begin{aligned} S_3N_3F_3 &+ BF_3 \rightarrow S_3N_3F_2(BF_4) \\ &+ AsF_5 \rightarrow S_3N_3F_2(AsF_6) \\ &+ SbF_5 \rightarrow S_3N_3F_2(SbF_6) \end{aligned}$$

Upon heating the hexafluoroarsenate salt, the ring is destroyed to produce SN^+, the thiazyl cation, and thiazyl fluoride.

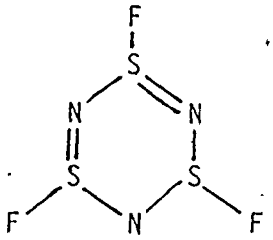
$$S_3N_3F_2^+AsF_6^- \xrightarrow{\Delta} 2FSN + SN(AsF_6)$$

The trimer decomposes in an all-glass vessel in the presence of trace amounts of water.[74] The products that have been characterized are NSF, SO_2, SOF_2, NH_3, SiF_4 and HNSO.

Hydrolysis[75] of $S_3N_3F_3$ results in the formation of NSF, HNSO, SO_2, SOF_2, SF_4 and NH_3. The hydrolysis has been interpreted as proceeding by nucleophilic attack of hydroxide ion on sulphur.

It has also been shown that dilute NaOH solutions hydrolyse $S_3N_3F_3$.[76]

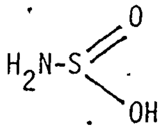
$$S_3N_3F_3 + 9H_2O \rightarrow 3NH_4F + 3H_2SO_3$$



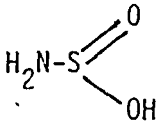
$$+ OH^- \rightarrow 2NSF + N{\equiv}S\text{-}OH + F^-$$

$$NSF + OH^- \rightarrow N{\equiv}S\text{-}OH + F^-$$

$$H\text{-}N{=}S{=}O + H_2O \rightarrow$$



$$H_2N\text{-}S(=O)OH$$



$$H_2N\text{-}S(=O)OH \rightarrow NH_3 + SO_2$$

I-5 The Chemistry of the Sulphur Imides

Cycloheptasulphurimide

Cycloheptasulphurimide was first discovered in 1923 as one of the products resulting from the action of NH_3 on S_2Cl_2.[77,78]

Earlier in the introduction, it was stated that the ammonia/S_2Cl_2 or SCl_2 system in non-polar solvents may be used to prepare S_4N_4. The yield of the tetrasulphur tetranitride can be reduced almost to zero, while that of the imide is maximized if a more polar solvent such as dimethyl formamide is used. The mechanism of the formation of S_7NH is not clear, but the following reaction scheme has been suggested.[79]

$$S_2Cl_2 \rightleftarrows Cl\text{-}S\text{-}S^+ + Cl^-$$

$$Cl\text{-}S\text{-}S^+ + NH_3 \rightarrow (Cl\text{-}S\text{-}S\text{-}NH_3)^+$$

$$(Cl\text{-}S\text{-}S\text{-}NH_3)^+ + S_2Cl_2 \rightarrow (H_3N\text{-}S\text{-}S\text{-}S\text{-}Cl)^+ + SCl_2$$

The first step is the ionization of S_2Cl_2 in a polar solvent. The second step involves a chain lengthening process which continues until all seven sulphur atoms have been incorporated in the chain. Formation of the S_7N ring requires elimination of HCl. There is little support for the above mechanism and in fact it is known that S_2Cl_2 ionizes very little in acetonitrile[79] which has a higher dielectric constant than dimethylformamide. Thus, it has been suggested that a more plausible mechanism is an S_N2 displacement of chloride ion by ammonia rather than the S_N1 pathway described earlier.[80]

Other preparative routes to S_7NH are listed below:

i) S_nCl_2 (n = 2,3,etc.) + $LiN_3 \xrightarrow{HCl} LiCl + S_7NH$ (ref. 81)

ii) $2S_4N_4 + N_2H_4 \rightarrow S_7NH + S + 4N_2 + NH_3$ (ref. 82)

iii) $2S_4N_3Cl + 3N_2H_4 \rightarrow S_7NH + S + NH_3 + 4N_2 + 2NH_4Cl$ (ref. 82)

iv) $S_8 + 2NH_3 \xrightarrow[-H_2S]{} H_2NS_7NH_2 \rightarrow S_7NH + NH_3$ (ref. 83)

The crystal structure of S_7NH has been recently redetermined.[84] The molecule consists of an eight-membered puckered ring. The co-ordination of the nitrogen is almost planar and there is an indication of weak intermolecular S---H-N hydrogen bonding.

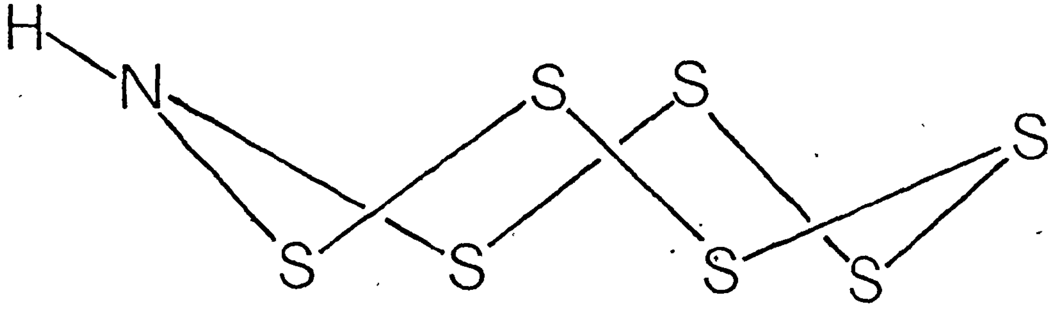
The reactions of S_7NH may be classified as follows:

(a) Ring cleavage reactions;

(b) Addition reactions to nitrogen; and,

(c) Condensation reactions.

Note: equation (i) is not balanced but is meant only to indicate observed products.



(i) Ring Cleavage

Hydrolysis[83,85] in alkaline solutions entirely destroys the S_7NH ring to yield ammonia, thiosulphate and polysulphides. In acid solution, the products of hydrolysis are hydrogen sulphide, sulphur dioxide and sulphur.[86] Sulphite ion and hydrogen iodide also destroy the ring:

$$S_7NH + 8HSO_3^- \rightarrow S_3O_6^{2-} + 6S_2O_3^{2-} + NH_4^+ + 5H^+ \qquad \text{(ref. 37)}$$

$$2HI + S_7NH \rightarrow 7S + I_2 + NH_3 \qquad \text{(ref. 86)}$$

It has also been demonstrated that 20% oleum solutions of S_7NH exhibit an esr spectrum consisting of one sharp line;[39] the spectrum is identical to that produced when sulphur is reacted with 20% oleum.

(ii) Additional Reactions

Addition reactions are listed in Table I-3. They involve either condensation processes or insertion of the reagent into the N-H bond.

Table I-3

Reactions of S_7NH

Reagent	Product	References
CH_2O	S_7NCH_2OH	88,89
SO_3	S_7NSO_3H	85
*HgX_2	$(S_7N)_2Hg$	89,90
*Hg_2X_2	$(S_7N)_2Hg_2$	90,89
BBr_3	S_7NBBr_2	92
BCl_3	S_7NBCl_2	91,92
ClCOR	S_7NCOR	93,94,88
†S_nCl_2	$S_7NS_n NS_7$	95
$Me_3SiNHSiMe_3$	S_7NSiMe_3	96
$HOCH_2N(CH_3)_2$	$S_7NCH_2N(CH_3)_2$	97
$R_2N\text{-}S\text{-}NR_2$	$S_7N\text{-}S\text{-}NR_2$	98
$[(CH_3)_2N]_3PO$	$[(CH_3)_2N]_3PO\cdot 2S_7NH$	99
RLi	S_7NLi	100

The last reaction in Table I-3 has been demonstrated to be a good synthetic pathway for the production of alkylated heptasulphur imides.[100]

---

* $X = CH_3COO^-$, NO_3^-.

† n = 1, or 2.

$$S_7NH + RLi \rightarrow S_7N^-Li^+ + RH$$

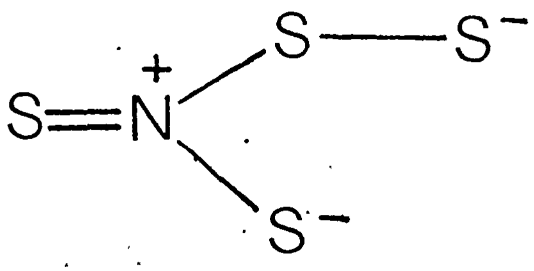
$$S_7N^-Li^+ + R'I \rightarrow S_7N\text{-}R' + LiI$$

These compounds are normally prepared by using the appropriate primary amine in a SCl_2 solution.[101,102]

It was shown that the blue solutions of S_7NLi contain the anions S_7N^- and S_4N^-. The blue colour is due to the presence of the S_4N^- anion which is in equilibrium with the yellow S_7N^- anion. The equilibrium is temperature-dependent, and the S_7N^- anion formed by deprotonation of S_7NH at lower temperatures rearranges to the S_4N^- ion and elemental sulphur upon warming.

$$\begin{array}{l} S_7NH + \text{Base} \rightleftarrows S_7N^- + (\text{Base})(H^+) \\ \qquad\qquad\qquad\quad \updownarrow \\ \qquad\qquad\qquad\quad S_4N^- + \frac{3}{8}\,S_8 \end{array}$$

Based on infrared and Raman data, a branched chain structure has been suggested for the S_4N^- anion.[103,104]

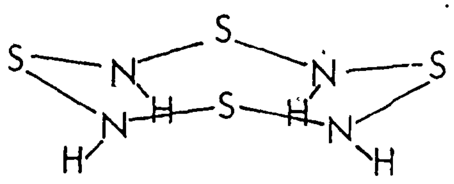


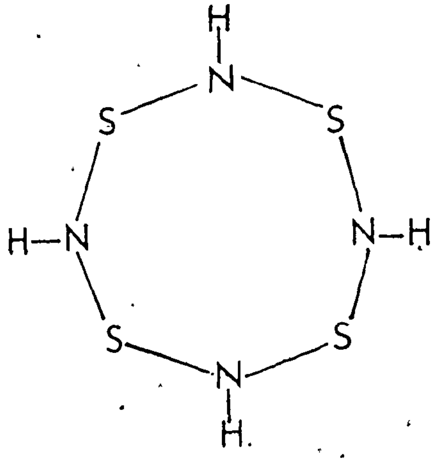
Cyclotetrasulphurtetraimide

Cyclotetrasulphurtetraimide was first prepared in 1908 by Wolbing by the reduction of S_4N_4 with stannous chloride in benzene/methanol solution.[32,104]

$$S_4N_4 + 2SnCl_2 + 4H_2O \rightarrow (SNH)_4 + 2SnCl_2(OH)_2$$

The crystal structure of the $S_4N_4H_4$ molecule has been determined and the structure of the molecule is shown below.[105]





Cyclotetrasulphurtetraimide is a puckered eight-membered ring with a geometry closely resembling that of the S_8 ring. The positions of the hydrogen atoms were not located, however the stereochemistry around each nitrogen is based on a planar arrangement of three atoms. The sulphur bond angles in $S_4N_4H_4$ and S_8 are not significantly different being 108.4° and 107.8°, respectively. The dihedral angles are 99.4° in $S_4N_4H_4$ and 99.3° in S_8. These similarities would tend to suggest that the bonding in both molecules is very similar.

In the presence of hydrogen iodide or sulphurous acid, the eight-membered ring is cleaved.[106]

$$S_4N_4H_4 + 9HI \rightarrow 4S + 4I_2 + 4NH_3$$

$$S_4N_4H_4 + 8H_2SO_3 \rightarrow 4S_3O_6^{2-} + 4H^+ + 4\ NH_4^+$$

According to Chapman and Massey, sulphuric acid oxidizes the ring to produce a radical species which has been assumed to be SN_2^+.[39]

Upon reaction of $S_4N_4H_4$ with certain metal ions, it has been proposed that the hydrogen atoms are replaced. Thus, species such as $Li(Al(SN)_4)$,[107] $Cu_4(NS)_4$,[108] $Hg_2(NS)_4$,[109] $Hg_4(NS)_4$,[90] $Hg_5(NS)_8$,[109] $\{CuCl)_2H_2N_4S_4$,[110] and $(AgNS)_4$,[108,111] are formed from $S_4N_4H_4$. There is very little structural evidence concerning these metal complexes and it is not known whether the eight-membered ring is still intact.

Becke-Goehring and Schwarz[110] reacted $S_4N_4H_4$ with triphenyl methyl sodium, $NaC(C_6H_5)_3$, to yield an explosive salt, $Na_4(S_4N_4)$. The structure of the $S_4N_4^{4-}$ anion is not known, however; it has been assumed that the ring is still intact, as shown in Figure I-1.

The tetraimide reacts with formaldehyde[112,113] and the intermediate formed is then a convenient starting point for the preparation of organo derivatives.

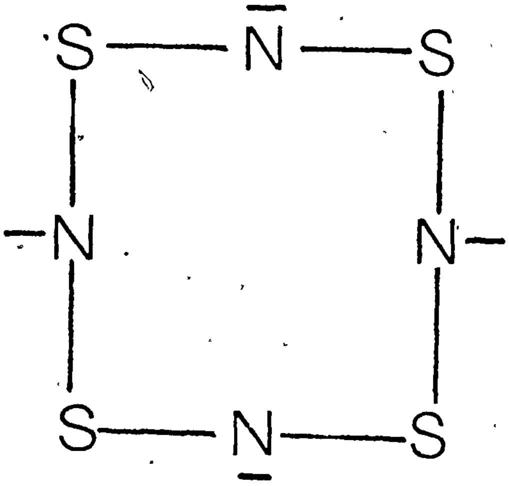
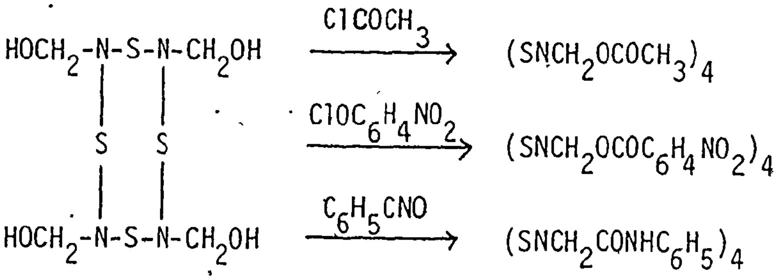


Figure I-1 The $S_4N_4^{4-}$ Anion

$$S_4N_4H_4 + 4CH_2O \rightarrow S_4N_4(CH_2OH)_4$$



$$(HOCH_2NSNCH_2OH)(S)_2 \xrightarrow{ClCOCH_3} (SNCH_2OCOCH_3)_4$$

$$\xrightarrow{ClOC_6H_4NO_2} (SNCH_2OCOC_6H_4NO_2)_4$$

$$\xrightarrow{C_6H_5CNO} (SNCH_2CONHC_6H_5)_4$$

(ref 112)

The Lewis acid chemistry of $S_4N_4H_4$ is essentially undeveloped. Reported reactions are:[114]

$$S_4N_4H_4 + AlCl_3 \rightarrow S_4N_4H_4 \cdot AlCl_3$$

$$+ AlBr_3 \rightarrow S_4N_4H_4 \cdot AlBr_3$$

$$+ SnBr_4 \rightarrow (S_4N_4)_2 \cdot SnBr_4$$

The 1:1 adducts are poorly characterized and further work is required to understand the behaviour of $S_4N_4H_4$ towards Lewis acids.

I-6 Bonding in Cyclic Sulphur-Nitrides (Neutral, Anionic, and Cationic Species)

At present, it is not possible to discuss the bonding in the sulphur nitrides in any detail. This is a consequence of the fact that a good general bonding scheme has not been developed that will readily apply to inorganic ring systems such as the sulphur nitrides. Such a bonding scheme would have to explain the following:

i) The wide variation in bond angles around nitrogen. This angle has been observed to vary from 90° in S_2N_2 [115] to 151° in $S_5N_5^+$;[54,55]

ii) The smaller variation in N-S-N bond angles from 90° in S_2N_2 [115] to 125° in $S_5N_5^+$;[54,54]

NOTE: The smaller bond angles in S_2N_2 are a requirement of the square planar geometry, however the values do indicate the minimum value for these angles in cyclic sulphur nitrides.

iii) The fact that some species are nearly flat rings while others are puckered or form cage structures and yet multiple bond character is observed in all;

iv) That some rings have equivalent S-N bond lengths while in other rings non-equivalent S-N bond distances are observed; and,

v) If one considers that nitrogen and sulphur each donate one and two electrons, respectively, to the π system, many of the anionic and cationic ring systems obey the Hückel 4n + 2 rule.

At present, two CNDO calculations[116a, 116b] have been done for cyclic sulphur nitrogen systems in an attempt to further understand the bonding in these systems. Although the results of one calculation supports the validity of Dewar's "islands" model, while the other calculation is consistent with electron delocalization in unsaturated sulphur-nitrogen rings such as S_4N_4, neither calculation proposes a viable bonding scheme.

I-7 Aims of the Present Work

The purpose of this introduction was to briefly sketch the wide variety of cyclic sulphur-nitrogen chemistry. In particular, the Lewis acid chemistry and chemistry in oxidative media was reviewed with the intention of presenting a complete and up-to-date survey of the present knowledge of the behaviour of the sulphur nitrides under these conditions. From this review, it is clear that a large number of experimental results have been obtained, but there has been little understanding or rationalization of these results. In addition, many of the species isolated have been inadequately characterized. The purpose of the present work was to investigate the reactions of certain sulphur nitrides with Lewis acids of oxidative capability, to characterize the products, and ultimately, to attempt to obtain some understanding of the reactions.

CHAPTER II

PREPARATION AND PURIFICATION OF STARTING MATERIALS

II-1 Preparation of S_4N_4

Cyclotetrathiazene was prepared according to the method of Becke-Goehring[117] with some alterations. Carbon tetrachloride (2 ℓ) and disulphur dichloride (125 ml) were placed in a 5-litre round-bottom three-neck flask. The flask was fitted with a mechanical stirrer, a condenser that has a central bore diameter of 2 cm (to ensure that the condenser does not become plugged with the large amounts of solid material produced during the preparation) and a gas inlet tube which extended below the surface of the solution and terminated in a porous filter. Anhydrous chlorine was bubbled through the stirred solution for approximately 2 h. The solution was then cooled to 0°C and the ammonia cylinder connected to the flask.

The ammonia flow was monitored by use of a flow meter and was not allowed to exceed 50 ℓ/h. An open-ended tube of 1 cm diameter that extended beneath the solution was used to deliver the ammonia. As the anhydrous ammonia was added, a vigorous reaction occurred and much solid material issued from the condenser. For the first few hours, the reaction flask was kept cool in ice to prevent the temperature from rising above 50°C. The mixture gradually turns from red-brown to gray-green and finally after six hours, the product is salmon-red. The mixture was stirred constantly and the salmon-red end-point detected by examining, from time to time, the colour of some product extracted from the inside of the flask. Once the end-point was reached, the ammonia flow was stopped and the material filtered and slurried (for 30 minutes) with water. It was not allowed to dry before washing with water because of the possible presence of NCl_3 as a side-product. After washing, the material was filtered and then allowed to dry for 24 hours in the air. It was observed that at this point the colour of the crude material may range from a yellow-green to bright yellow. The S_4N_4 was obtained upon working up the material, and the yield was lower whenever the crude material obtained had a greenish colouration. The crude dried material was Soxlet extracted with benzene (1 ℓ) and then recrystallized twice from benzene (m.p. 178°C, lit. m.p. 178°C[117]). Typical yields ranged from 25 to 35 g.

Cyclotetrathiazene is known to decompose explosively on striking or if heated above 100°C. Consequently, the obtained yield was divided into 2 g. amounts and stored in plastic vials. The material may be ground safely if amounts less than 250 mg are used and the grinding is done with moderation.

II-2 Preparation of $S_4N_4H_4$

Cyclotetrasulphur tetraimide was prepared by reduction of S_4N_4 with an alcoholic solution of $SnCl_2$.[118]

Cyclotetrathiazene (10 g) and 300 ml of benzene were heated to 80°C in a 500 ml round-bottom three-neck flask equipped with a condenser and a pressure equalizing dropping funnel containing a solution of 35 g. of $SnCl_2 \cdot 2H_2O$ in 80 ml of CH_3OH that contained approximately 5% water.

The latter solution was added as quickly as possible but care must be taken that the reaction does not become too violent. The precipitate that formed was filtered, washed with 2N HCl until no $SnCl_2(OH)_2$ remained. It was then washed with methanol. The crude $S_4N_4H_4$ was recrystallized from CH_3OH to give colourless crystals (m.p. 145°C, lit. m.p. 145°C[118]). Typical yields were between 4 and 5 g.

II-3 Preparation of S_7NH

Cycloheptasulphurimide was prepared using a similar procedure to that outlined by Brauer.[119] Dimethylformamide (3.5 ℓ) was cooled in a 5-litre three-neck flask to -20°C using a dry-ice-acetone bath. Anhydrous ammonia was bubbled into the vigorously stirred solution at a flow rate of about 100 ℓ/h for 30 minutes. Sulphur monochloride (350 ml) was then added in 15 ml aliquots from a 100 ml syringe equipped with a 18 G x 5 $\frac{1}{2}$" stainless steel needle. The sulphur monochloride was injected below the surface of the solvent. Due to the vigor of the reaction protective gloves were necessary for this step. After the solution had again cooled to -20°C, another aliquot of S_2Cl_2 was added. This procedure was repeated until all 350 ml of S_2Cl_2 had been added.

Additions of S_2Cl_2 were not made faster than the solution could be kept saturated in NH_3. If the reaction appeared to decrease in vigor as S_2Cl_2 addition occurred, the solution was allowed to further saturate with ammonia before the next addition of S_2Cl_2. Approximately 30 minutes was required for further saturation with NH_3. After the addition of all the S_2Cl_2, the passage of ammonia was continued for another 15 minutes. The ammonia addition, cooling and stirring were then stopped and the resulting deep blue solution was allowed to stand for 30 minutes. The solution was then slowly added to 50 ℓ of 1% HCl in a 100 ℓ container with constant stirring. The pink-purple solution that forms was neutralized with 10% HCl until an orange colour was obtained at the end-point. The solid material was allowed to settle overnight and the solution was decanted leaving a yellow solid. The solid was allowed to dry in the air for 24 hours and then Soxlet extracted with tetrahydrofuran (1 ℓ). The tetrahydrofuran was removed using a rotory evaporator, and the resulting brown oil dissolved in a minimum amount of hot methanol. Upon cooling, yellow platelets were obtained. The material was again recrystallized from benzene to remove final traces of sulphur. Resulting yields were typically 20-30 g (m.p. 113°C, lit. m.p. 113°C[119]).

II-4 Preparation of S_7NCH_3

N-methylcycloheptasulphurimide was prepared using the method of the late Dr. F.P. Olsen.[100] Purity of the sample was checked by comparison of its infrared and nmr spectra with published spectra. To ensure that no sulphur was present in the $S_7N\text{-}CH_3$, the obtained sample was twice eluted from a Silica-gel chromatographic column.

II-5 Preparation of $S_3N_3Cl_3$

Trichlorocyclotrithiazene was prepared using the method of Schröder and Glemser.[70] This involved chlorination of a stirred solution of S_4N_4 in CCl_4 at room temperature. The $S_3N_3Cl_3$ was crystallized from CCl_4 and stored in dry evacuable bulbs with a slight pressure of anhydrous chlorine gas. A sample was analyzed by the Schwarzkopf Microanalytical Laboratory:

	Calculated For SNCl	Found
Sulphur	39.50%	38.87%
Nitrogen	17.28%	17.4%
Chlorine	43.21%	43.20%

The melting point of $S_3N_3Cl_3$ that had been recrystallized from hot CCl_4 had been previously reported to be 142.5°C. Jolly and Patton[47] noted that whenever CCl_4 solutions of $S_3N_3Cl_3$ were heated above 60°C, green solutions were obtained and samples isolated from these solutions had variable and high melting points. It has therefore been suggested by Jolly and Patton that the melting point of 162.5°C quoted by Schröder and Glemser[70] corresponds to the melting or decomposition of a solid decomposition product of $S_3N_3Cl_3$. Crystals obtained in this laboratory from solutions that had not been heated above 50°C, melted consistently at 90-91°C and this melting point is in agreement with that reported by Patton and Jolly for crystals obtained by a similar procedure. Thus, it is important that solutions of $S_3N_3Cl_3$ not be heated above 50°C during crystallization procedures.

II-6 Preparation of $S_3N_3F_3$

Trifluorocyclotrithiazene was prepared by fluorination of $S_3N_3Cl_3$ with AgF_2 in CCl_4, according to the method of Glemser and Schröder.[120] The preparative procedure and equipment employed were essentially identical to those used by Glemser and Schröder, however a number of modifications were employed. The quartz reaction vessel was fitted with a Teflon

Rota-flo valve and did not contain a stirring bar. This enabled the flask to be rigorously flame-dried under high vacuum. The AgF_2 was placed in a Monel bomb and subjected to a pressure of fluorine of 1000 lb/sq. in. at 150°C for one week to ensure complete fluorination. The required amount of $S_3N_3Cl_3$ and AgF_2 were transferred to the quartz reaction bulb in a dry box and CCl_4 (40 ml), that had been dried over molecular sieves, was then distilled onto the $S_3N_3Cl_3/AgF_2$ mixture. The bulb was then placed on a mechanical agitator for 3 days. After this time, a yellow solution was obtained rather than a colourless solution as reported by Glemser and Schröder. The vessel was then connected to the trap assembly which had been previously leak checked and flame dried under high vacuum. The procedure from this point was identical to that outlined by Glemser and Schröder. Due to the reactivity of $S_3N_3F_3$ with glass, it was sublimed into a Kel-F trap that had been previously conditioned with HF and fluorine. The $S_3N_3F_3$ was then stored in this trap under 25 lbs/sq. in. of dry argon.

It was noted, however, that when $S_3N_3F_3$ was sublimed into either Kel-F or glass vessels, it initially formed as a colourless crystalline solid that turned yellow with time. This suggested that decomposition may be occurring, and no explanation is offered to explain this observation. The ^{19}F nmr spectrum of the material was consistent with that reported by Glemser[121] and indicated that no other fluorine-containing species were present.

II-7 Preparation and Purification of Materials

Sulphur Dioxide

Anhydrous sulphur dioxide (Canadian Liquid Air) was stored as a liquid over P_4O_{10} prior to use.

Sulphur Trioxide

Sulphur trioxide (Baker and Adamson) was distilled under vacuum into a dry glass storage vessel.

Arsenic Pentafluoride and Phosphorus Pentafluoride

Arsenic pentafluoride and phosphorus pentafluoride (Ozark Mahoning Co.) were used directly from the cylinder and were measured on a calibrated Pyrex vacuum line.

Antimony Pentafluoride

Antimony pentafluoride (Ozark Mahoning Co.) was doubly distilled in a Pyrex glass still before use. Distilled samples were stored in dry Pyrex bottles in the dry box.

Antimony Pentachloride

Antimony pentachloride (Baker Analyzed Reagent) was used directly without any purification.

Chlorine and Ammonia

Both gases were anhydrous grade (Canadian Liquid Air) and were used directly from the cylinder.

Silver Difluoride

Silver difluoride (Ventron Alfa Products) was subjected to

1000 lb/sq. in. of fluorine at 150°C for one week prior to use.

Disulphur Dichloride

Disulphur dichloride (Eastman Kodak) was used directly without any purification.

Thionyl Chloride

Thionyl chloride (J.T. Baker Chemical Co.) was distilled twice from triphenyl phosphate to remove traces of SCl_2, S_2Cl_2 and SO_2Cl_2 and used immediately after purification.

Carbon Tetrachloride

Carbon tetrachloride (Mallinckrodt Analytical Reagent) was dried over molecular sieves.

Methylene Chloride

Methylene chloride (Mallinckrodt Analytical Reagent) was stored over phosphorus pentoxide and degassed prior to use. The purpose of the degassing was to remove any dissolved O_2 which could cause paramagnetic line broadening during esr measurements on samples in which CH_2Cl_2 was used as a solvent.

Anhydrous Hydrogen Fluoride

Anhydrous hydrogen fluoride was stored under a pressure of 100 lbs/sq. in. of F_2 to remove traces of water.

II-8 General Experimental Techniques

In most instances, compounds were prepared in the reaction vessel shown in Fig. II-1. The vessel consists of two reaction bulbs

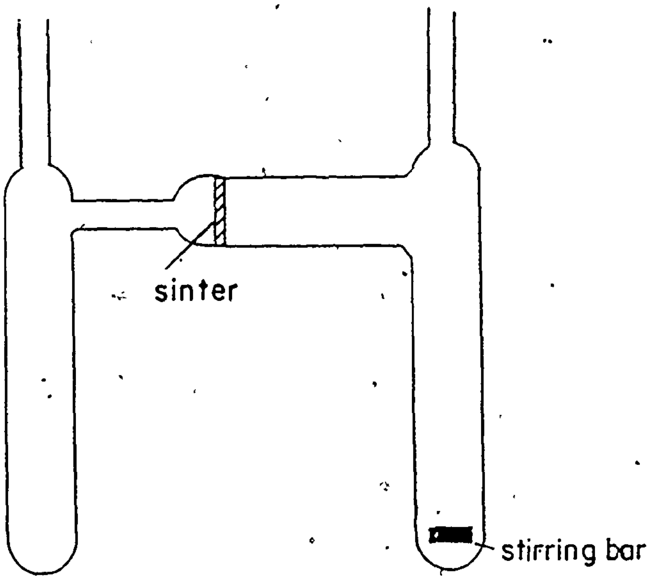


Figure II-1
Double Bulb Reaction Vessel

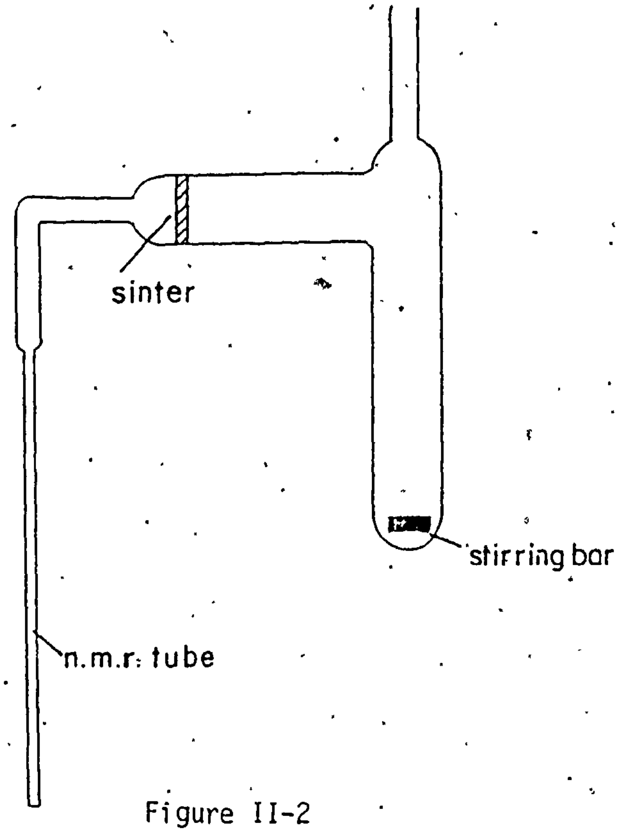


Figure II-2

Single Bulb Reaction Vessel with nmr Tube separated by a medium glass frit. Since many of the reactants used were moisture sensitive, the vessel was flame dried under vacuum before use. All transfers of liquid and solid into the vessel were done in a dry box. In the case of gaseous components, transfers were carried out on a vacuum line. The vessel was sealed by use of Teflon valves which also allowed convenient connection to vacuum lines. Details of individual preparations are given in the appropriate chapters.

Experiments that required the use of Kel-F or FEP plastic equipment are described in the individual chapters. Techniques concerning the manipulations of plastic equipment have been described elsewhere.[122]

II-9 Instrumentation

(i) Infrared Spectroscopy

Infrared spectra were recorded on a Perkin Elmer Grating Infrared spectrometer type 283. Samples were prepared from Nujol that had been dried over sodium wire and spectra were recorded in the 4000 cm^{-1} to 200 cm^{-1} range using CsI windows.

(ii) Raman Spectroscopy

Raman spectra were recorded on a Spex Industries Model 1400 3/4 meter Czerny-Turner double monochromator using a Spectra Physics model 164 argon ion laser giving up to 900 milliwatts at 5145 Å or a Spectra Physics Model 125 He-Ne laser giving up to 50 milliwatts at 6328 Å. All spectra were obtained at -196°C to prevent decomposition from the laser. Samples were run in 1/4" O.D. glass sample tubes or in the double bulb vessel in which they were prepared.

(iii) Electron Spin Resonance Spectroscopy

Electron spin resonance spectra were obtained on a Jeolco Model J.E.S. 3BS-X spectrometer. The g-values and hyperfine constants were obtained by comparison with a sample of Mn^{2+} in MgO (g = 1.981) and are accurate to ± 0.001. Samples were prepared by the use of the apparatus in Figure II-2. This apparatus conveniently fitted into the resonance cavity and allowed adjustment of sample concentration to obtain maximum signal intensity and resolution.

In some instances, samples were prepared by transferring an appropriate amount of sample and solvent to a glass nmr tube sealed with a Teflon valve.

(iv) Nuclear Magnetic Resonance Spectroscopy

(a) ^{19}F NMR Spectra

All fluorine nmr spectra were obtained at room temperature using either a Varian DA-60 spectrometer operating at 56.4 MHz or a Varian HA-100 spectrometer operating at 96.4 MHz. Samples which did not attack glass were prepared in 5 mm o.d. medium precision polished glass nmr tubes (Wilmad Glass Co.) glass blown onto 2" lengths of 1/4" O.D. glass tubing. These tubes could be conveniently attached to the vacuum line by means of a Teflon valve. Samples were transferred to the tubes in the dry box, followed by condensation of an appropriate volume of sulphur dioxide.

Samples that were recorded in anhydrous hydrogen fluoride were prepared in tubes that were made from 3.91 mm o.d., 0.31 mm wall FEP tubing (Warehoused Plastics, Toronto). The tube and Teflon valve assembly for vacuum line manipulations have been described previously. The tubes were washed with anhydrous HF several times before use. All ^{19}F spectra were measured with respect to external $CFCl_3$, positive chemical shifts being to high field.

(b) ^{31}P NMR Spectra

Phosphorus nmr spectra were recorded on a Bruker WH90 nmr spectrometer at 36.43 MHz. The spectrometer was internally locked to the deuterium signal of CD_2Cl_2 in the sample solution. All chemical shifts are reported with reference to 85% phosphoric acid, positive chemical shifts being to high field.

(v) Mass Spectroscopy

Mass spectra were obtained on a Consolidated Electrodynamics Corporation Model No. 21-110B double focussing mass spectrometer. Spectra were referenced to perfluorokerosene and the normal energy of the bombarding electrons was 70 e.v. The mass spectrum of $S_3N_3F_3$ was recorded by connection of an evacuated Kel-F trap, containing the sample, to the gas inlet system of the spectrometer by means of a Teflon valve.

(vi) Dry Box

All materials sensitive to moisture were handled in a Vacuum Atmospheres Dry Box Model HE-43 equipped with a dry train model HE-373-B.

(vii) Analyses

Analyses were done by the Schwarzkopff Microanalytical Laboratory, 56-19 37th Avenue, Woodside, N.Y. and Pascher Mikroanalytisches Laboratorium, 53, Bonn, Buschstrasse 54, West Germany.

CHAPTER III

LEWIS ACID CHEMISTRY OF S_4N_4

III-1 Reaction of S_4N_4 with Lewis Acids

The only results that are certain from the previous work of S_4N_4 with Lewis acids is that S_4N_4 forms molecular adducts with $SbCl_5$,[29] and BF_3,[27,28] and that the oxidation of S_4N_4 by AsF_5 produces the radical cation $S_3N_2^+$.[53] The crystal structures of both the molecular adducts and the $S_3N_2^+$ cation have been determined.

A systematic study of the reactions of S_4N_4 with the Lewis acids $SbCl_5$, PCl_5, PF_5, AsF_5, SbF_5 and WF_6 was initiated in an attempt to isolate new sulphur-nitrogen compounds as well as perhaps gain insight into reaction pathways.

III-2 The PCl_5/S_4N_4 and PF_5/S_4N_4 Systems

The chemistry of these systems was studied in an attempt to determine if the phosphorus pentahalides PCl_5 and PF_5 are capable of oxidizing S_4N_4 or forming molecular adducts. In general, it was observed that PF_5, whether present in excess or equimolar amounts, formed only a 1:1 molecular adduct with S_4N_4. Phosphorus pentachloride, however, reacted quickly to yield a complicated mixture.

The ^{31}P nmr spectra of the mixtures obtained for the reaction of S_4N_4 with one and three moles of PCl_5 are shown in Figure III-1. The spectra consist of a number of single lines and the chemical shifts relative to H_3PO_4 are listed in Table III-1. From the nmr data, it is clear that with higher molar ratios of PCl_5 to S_4N_4, the reaction proceeds

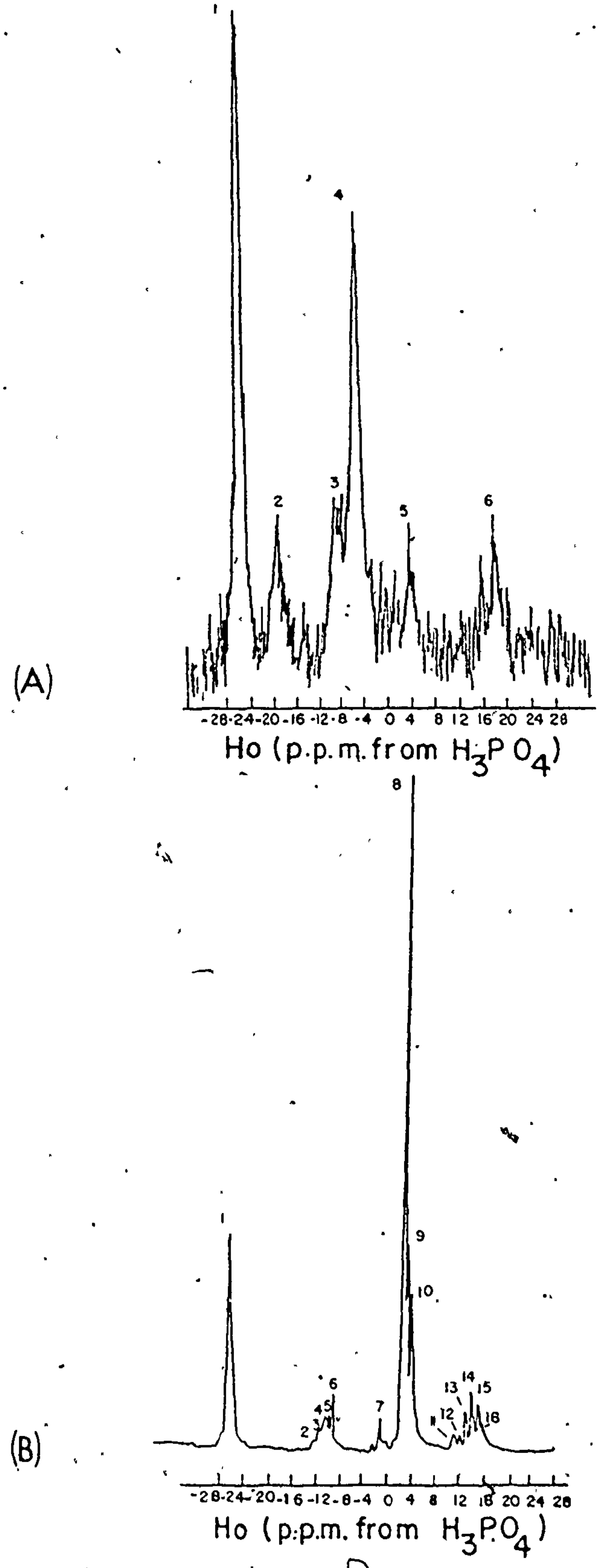


Fig. III-1 ^{31}P nmr spectra of (a) S_4N_4 with PCl_5 in a 1:1 molar ratio, (b) S_4N_4 with PCl_5 in a 1:3 molar ratio.

Table III-1

^{31}P nmr Signals Obtained from S_4N_4/PCl_5 Mixtures

S_4N_4/PCl_5		$S_4N_4/3PCl_5$	
Signal number	δ (p.p.m.) from H_3PO_4	Signal number	δ (p.p.m.) from H_3PO_4
1	-25.8	1	-25.7
2	-19.3	2	-10.5
		3	-10.1
		4	-9.6
3	-8.84	5	-8.9
		6	-8.4
4	-6.56	7	-0.1
5	2.55	8	3.12
		9	3.72
		10	4.65
		11	11.56
		12	12.36
		13	13.56
		14	14.47
		15	15.48
6	16.32	16	16.18

Table III-2

Reported ^{31}P nmr Chemical Shifts For Possible Reaction Products of the S_4N_4/PCl_5 System

Compound	δ (p.p.m.)	Compound	δ (p.p.m.)
$P_3N_3Cl_6$	-19.8, -20.0 -20.2, -19.0 -19.1	PCl_3	-219.4, -220
$P_4N_4Cl_8$	6.8, 4.6 7.0, 7.0	$PSCl_3$	-28.8, -30.8 -29, -20.6, -34
$P_5N_5Cl_{10}$	17.0	PCl_6^-	281, 300, 305
$P_6N_6Cl_{12}$	16.0	PCl_5	80
$P_7N_7Cl_{14}$	18.0		
$P_8N_8Cl_{16}$	18.0		

further to produce a complex mixture.

Assignment of the signals in the spectra is difficult and further experiments were not carried out. However, some speculative assignments can be made. The chemical shifts of some possible products are listed in Table III-2.

It would appear that there is no PCl_3, $PSCl_3$, unreacted PCl_5 or PCl_6^- containing species present. It is noteworthy, however, that the singlets at -19.3 ppm and 16.38 or 16.32 ppm are perhaps due to the trimer $P_3N_3Cl_6$ and hexamer $P_6N_6Cl_{12}$, respectively. The other singlets are left uncharacterized.

The reactions were carried out in CH_2Cl_2 and removal of the solvent gave, in both instances, yellow viscous oils that had the distinct odour of chlorosulphanes. A black solid was dispersed in the oil obtained from the 1:1 S_4N_4:PCl_5 reaction mixture. The Raman spectra of these oils were recorded at -196°C and the observed bands are listed in Table III-3. Again these spectra represent complex mixtures and the observed band frequencies are used only as a guide for discussion.

The two bands at 512 cm^{-1} and 210 or 212 cm^{-1} are assigned to ν_1 and ν_2 of SCl_2. The band due to ν_3 is observed only as a poorly resolved shoulder. This is perhaps a result of its lower intensity in comparison to ν_1 and ν_2.

There are also bands that are coincident with those observed for $P_3N_3Cl_6$ although many of the recorded bands of $P_3N_3Cl_6$ may be masked by the broad bands obtained in the spectra of the oils.

It was mentioned earlier in this chapter that PF_5 combines with

Table III-3

Raman Frequencies for the S_4N_4/PCl_5 System

S_4N_4/PCl_5		$S_4N_4/3PCl_5$		SCl_2[124]	S_2Cl_2[125]	$P_3N_3Cl_6$[126]
Δν, cm^{-1}	relative intensity	Δν, cm^{-1}	relative intensity	Δν, cm^{-1}	Δν, cm^{-1}	Δν, cm^{-1}
130	15	128	13			97(m)
167	63	178	39			157(m)
195	36	197	20			172(m)
210	23	212	22	208(s)	210(s)	202(m)
237	16				242(m)	
265	14	271	44			298(vw)
309	sh					
320	60					334(w)
336	53	336	77			364(vs)
352	100	353	50			
415	27	436	27		443(s)	
463	65	465	100		455(s)	
512	29	512	28	514(s)		529(vw)
		531	(sh)	535(w)	540(m)	584(w)
666	28	666	25			669(s)
		700	13			
		715	18			

s = strong; m = medium; vw = very weak; w = weak.

S_4N_4 to produce the molecular adduct $S_4N_4 \cdot PF_5$. This is not surprising since phosphorous pentafluoride is known to form addition compounds with a variety of Lewis bases such as ethers, amines, amides and esters.[126,127] Also, it was observed that PF_5 did not oxidize S_4N_4 under the described experimental conditions.

The 94.1 MHz ^{19}F nmr AB_4 room temperature spectrum of $S_4N_4 \cdot PF_5$ in liquid SO_2 is illustrated in Fig. III-2B. The spectrum consists of two doublets and two apparent quintets which show additional splittings under higher resolution. The quintet showed all nine of the expected transitions for the A spin system. The second order transitions for the B system were not observed because the lines are rather broad and the line width is comparable with the expected separation of the lines. The second order effects for the quintet are shown in Fig. III-2A.

Figure III-3 illustrates the ^{31}P room temperature nmr spectrum of the adduct. The spectrum consists of a multiplet of lines which arises from the P-F_{axial} and P-$F_{equatorial}$ coupling. Fig. III-4 illustrates how a simple first order stick diagram may be used to predict the theoretical intensities of the multiplet.

Table III-4 lists observed chemical shifts and coupling constants for the $S_4N_4 \cdot PF_5$ adduct as well as for other PF_5 adducts.

Table III-4

^{19}F nmr Data for Molecular Adducts of PF_5

	$S_4N_4 \cdot PF_5$	$(CH_3)_2O \cdot PF_5$ [126]	$(C_2H_5)_2O \cdot PF_5$ [127]	$CH_3N \cdot PF_5$ [126]
$J_{P\text{-}F\ axial}$ (Hz)	755.8	777	745	747
$J_{P\text{-}F\ eq}$ (Hz)	789.7	820	790	848
F_{ax}-F_{eq} (Hz)	57.3	65	62	55
δF_{eq} (p.p.m.)	65.4	69.6	66.3	71.1
δF_{ax} (p.p.m.)	82.8	88.8	86.0	83.6

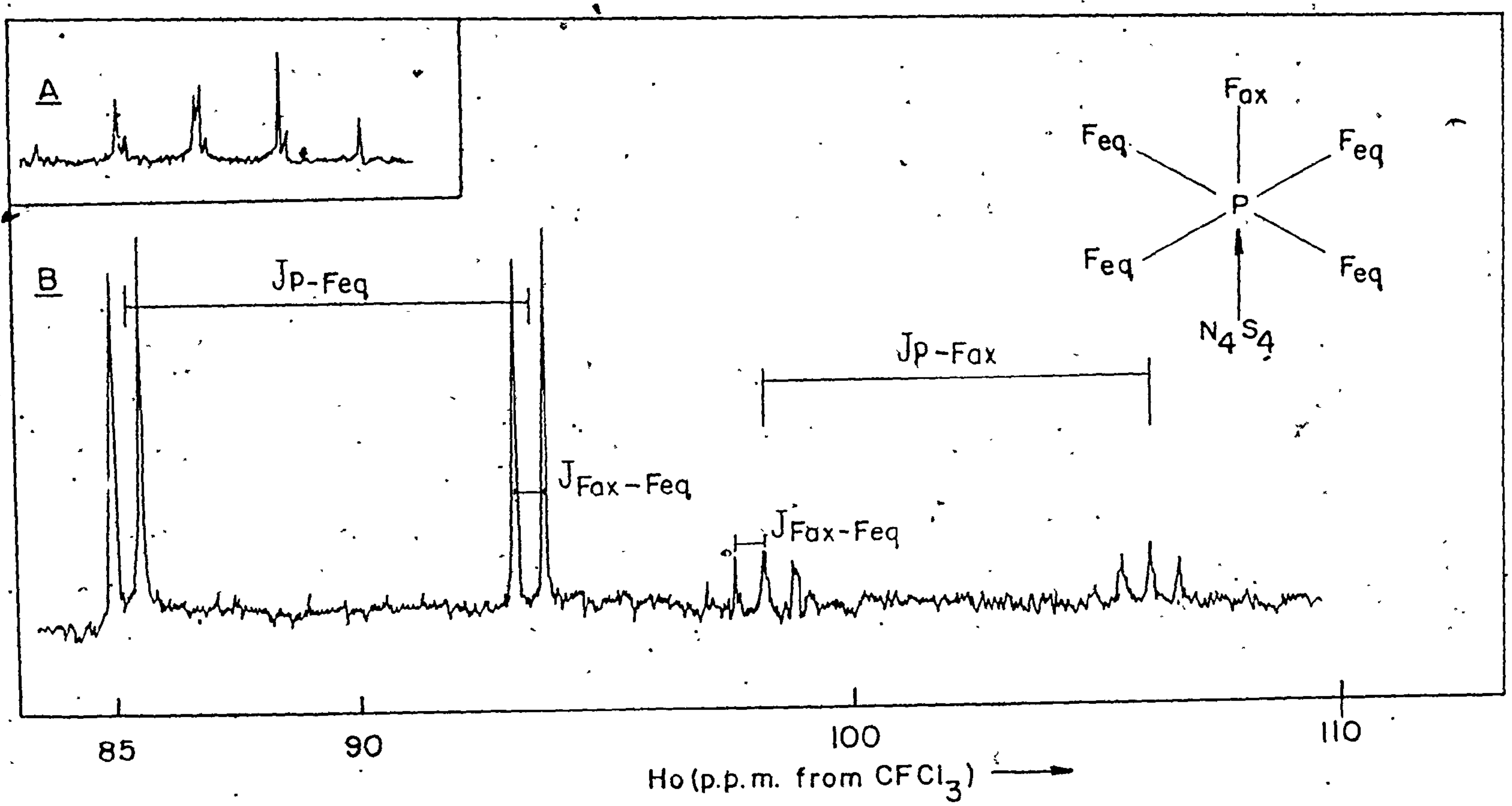


Figure III-2 Room temperature ^{19}F nmr spectrum of the $S_4N_4 \cdot PF_5$ adduct.

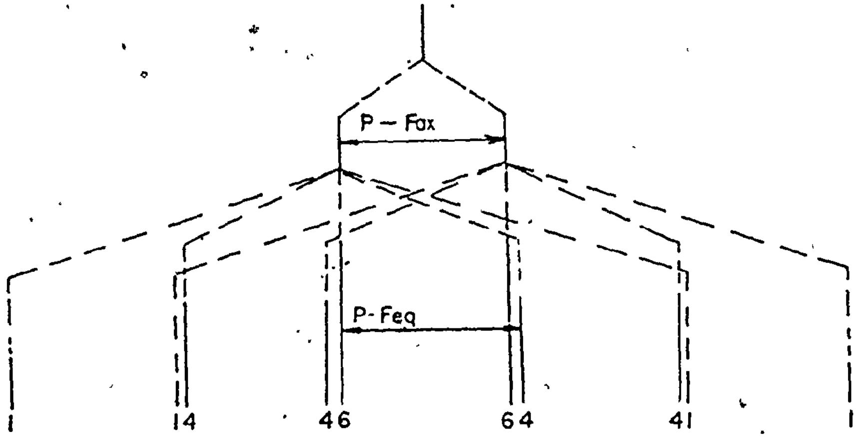


Figure III-4

First order stick diagram illustrating the ^{31}P nmr spectrum of the $S_4N_4 \cdot PF_5$ adduct

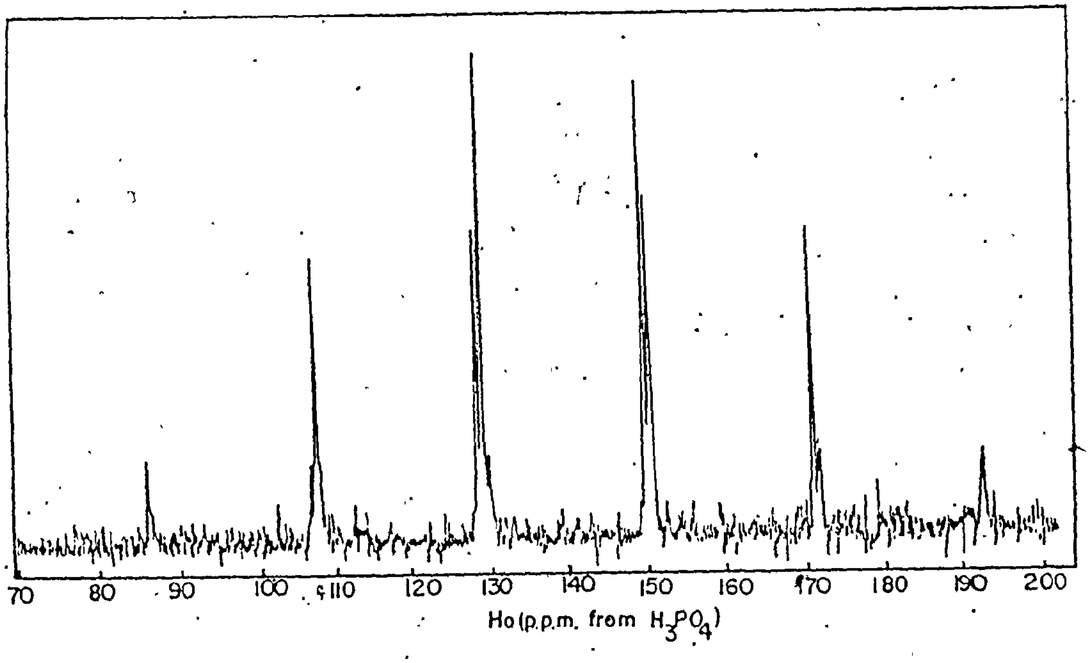


Figure III-3

Room temperature ^{31}P nmr spectrum of $S_4N_4 \cdot PF_5$ adduct.

The spectra of PF_5 adducts with donor organic molecules were all obtained at temperatures below -60°C. At higher temperatures intermolecular fluorine exchange occurs which has been attributed to the rapid equilibrium[127]

$$PF_5 + \text{base} \rightleftarrows PF_5 \cdot \text{base}$$

The exchange process does not occur to a significant extent at room temperature in the case of the $S_4N_4 \cdot PF_5$ adduct since well-resolved spectra were obtained.

Analogy with other known structures of molecular adducts of S_4N_4 allows one to assume that the PF_5 is co-ordinated to the nitrogen in the S_4N_4 ring. The stability of the adduct shows that the lone pair on the nitrogen atom is available for donation to donor sites and that formation of a dative bond as in the $S_4N_4 \cdot SbCl_5$ adduct, results in a change in the geometry of the S_4N_4 ring.

III-3 Raman and Infrared Spectra of the Molecular Adducts of S_4N_4

Table III-5 contains a list of vibrational frequencies for some of the known adducts of S_4N_4 as well as for S_4N_4 itself, and Figure III-5 illustrates the infrared spectra of $S_4N_4 \cdot SbCl_5$ and $S_4N_4 \cdot PF_5$ while Figure III-6 shows the Raman spectrum of $S_4N_4 \cdot SbCl_5$. The point group symmetry of S_4N_4 is D_{2d} and the vibrational spectrum of free S_4N_4 has been extensively discussed.[128] Upon co-ordination with a Lewis acid the symmetry becomes C_s with a possibility of 18 infrared and Raman active fundamentals. In addition, the penta co-ordinated Lewis acids such as $SbCl_5$ and PF_5 once complexed have approximately C_{4v} symmetry (octahedral co-ordination)

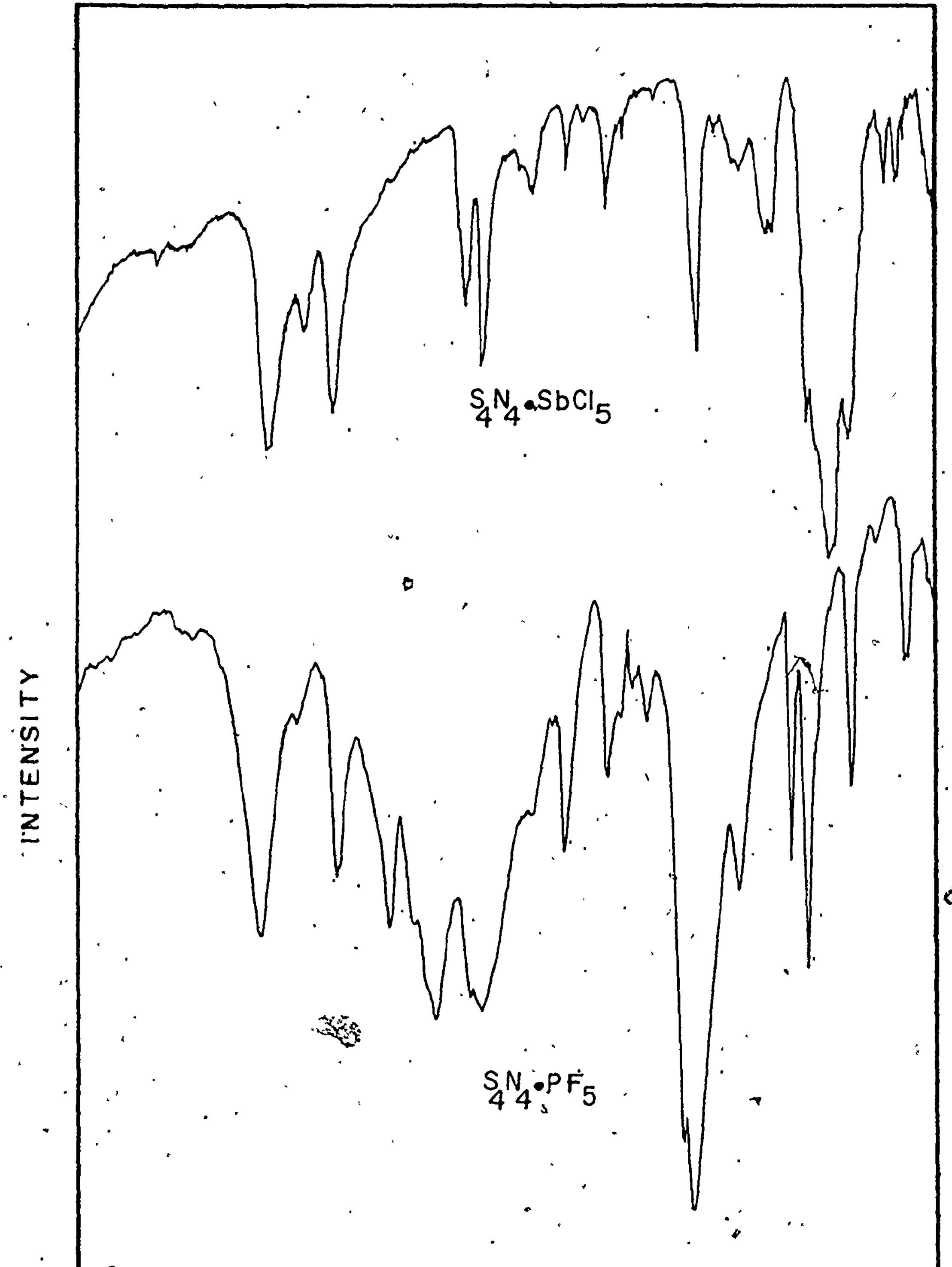
Table III-5

Infrared and Raman Spectra of Some Molecular Adducts of S_4N_4

S_4N_4 [128]			$S_4N_4\cdot SbCl_5$*	$CH_3CN\cdot SbCl_5$ [129]		$S_4N_4\cdot SbCl_5$*	$S_4N_4\cdot BF_3$ [27]	$CH_3CN\cdot BF_3$ [130]	$S_4N_4\cdot PF_5$*
Infrared (cm^{-1})		Raman* $\Delta\nu$, (cm^{-1})	Infrared (cm^{-1})	Infrared (cm^{-1})	Raman $\Delta\nu$, (cm^{-1})	Raman $\Delta\nu$, (cm^{-1})	Infrared (cm^{-1})	Infrared (cm^{-1})	Infrared (cm^{-1})
Solution	Solid								
		38(14)							
		42(14)				75(100)			
		50(29)							
	77.5								
		82(25)							
						156(22)			
	190	107(7)		174(sh)	Sb-Cl def. 174(sh)	172(7)			
		200(43)			Sb-Cl def. 187(23)	191(63)			
		202(100)							
						212(52)			
		219(96)							
	226	227(23)		232(w)	Sb-N str. 222(1)	234(17)			239(w)
						241(17)			
			242 (wsh)						
330(m)			257(w)						
			270(w)		$SbCl_4$ eq. str. 295(14)	278(19)			
			309 (wsh)		315(77)				
			320(m)						311(m)
		340(3)	340(s)	341(s)	Sb-Cl_4 eq. str. 344(100)	335(31)			
	347(s)	345(5)				354(34)			
		352(10)	360(s,sh)	352	Sb-Cl axial str. 348(30)	360(34)			
			370(s)	370(vs)	Sb-Cl_4 eq. str. 367(1)				369(s)
			412(m)		371(3)		420(ms)		
			450(m)						389(m)
			482(vw)						455(s)
							490(vs)		
			510(m)				502(m)		
519.3(w)	519.3(w)	519(2)	516(vw)						519(s)
		522(5)					527(s)	asym. BF_3 def 519,522	
	529.7(w)	529(3)					552(w)		
	552.2(s)	559(45)				556(45)	567(w)		570(w)
									598(w)
556.5(m)			580(vw)						610(sh)
			600(w)						623(w)
			620(w)				623(ms)		
			648(w)				658(ms)	657(w) B-N	680(mw)
			681(w)				697(wv)		
702(m)	701(s)		721(w)			718(22)	724 wv		720(sh)
705(vs)	726(s)	720(37)							
	760(w)	731(4)							785(m)
	766(w)	768(5)	787(m)			781(22)			803(sh)
	798(w)								842(m)
			805(m)				888(s)		877(sh)
							908(m)		902(m)
	925(s)						949(s)		
938(s)			976(ms)						969(ms)
	1007(w)		1010(m)				1040(vs)		1010(sh)
	1046(w)		1055(s)				1070(s)		1069(s)
	1067(w)						1117(s)	asym BF_3 str. 1188	

* This work; s = strong; m = medium; w = weak; sh = shoulder.

Figure III-5 Infrared spectra of the $S_4N_4 \cdot SbCl_5$ and $S_4N_4 \cdot PF_5$ molecular adducts



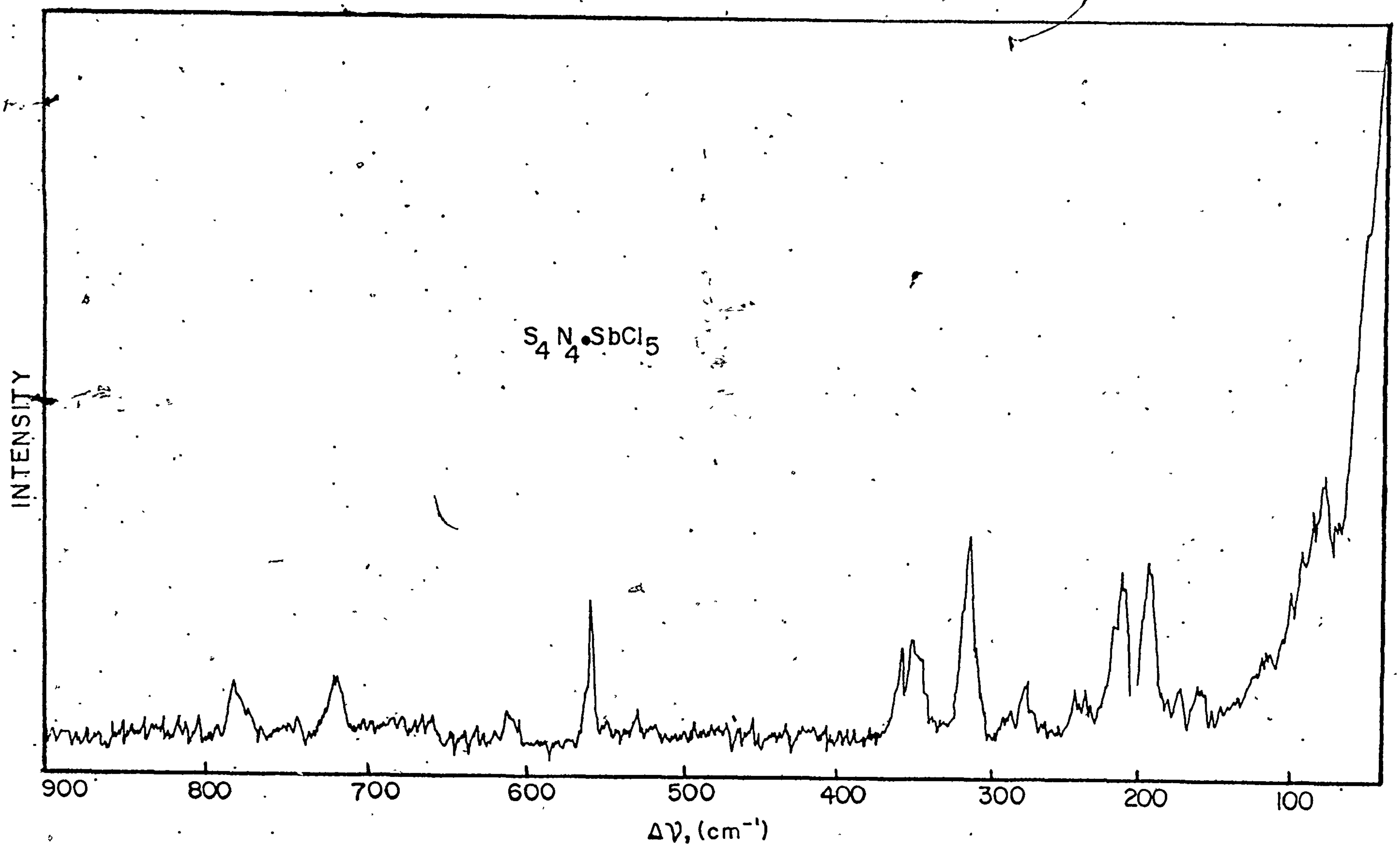


Figure III-6 Raman spectrum of the $S_4N_4 \cdot SbCl_5$ adduct recorded at -196°C.

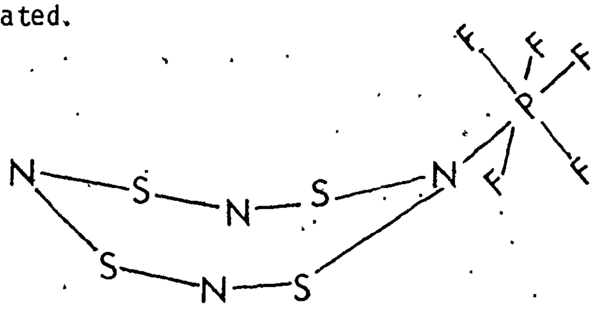
about the central atom. Considered as a rigid structure, the highest symmetry possible for an $S_4N_4 \cdot MX_5$ adduct is C_s for which the selection rules predict 36 Raman and infrared active fundamentals. Utilizing a local symmetry approximation to the selection rules results in the $N\text{-}MX_5$ portion having 4 A_1, 2 B_1, 1 B_2 and 4 E fundamentals with the $S_4N_4\text{-}M$ portion contributing 12 A' and 9 A" fundamentals. It is beyond the scope of this thesis to attempt a complete vibrational analysis of the molecular adducts of S_4N_4, although some discussion of the S-N vibrational frequencies will be given.

A complete vibrational analysis of molecular adducts of acetonitrile with $SbCl_5$,[129] and BF_3 [130] has been given. Their assignments are given in Table III-5 in order to indicate frequency ranges over which Sb-Cl and B-F vibrations are observed. Thus, it is possible to assign the vibrations involving the co-ordinated Lewis acid. For instance, the high frequency band at 1117 cm^{-1} in the $S_4N_4 \cdot BF_3$ adduct which has no corresponding bands in the other adducts may be assigned as an assymetric BF_3 stretch by analogy with the spectrum of the acetonitrile-BF_3 complex. Assignment of P-F vibrations in the $S_4N_4 \cdot PF_5$ adduct is not possible due to the lack of good vibrational data on other PF_5 adducts.

The vibrational spectrum of S_4N_4 has been studied by Bragin and Evans.[128] A valence force field calculation allowed comparison of predicted frequencies with observed infrared and Raman frequencies. Twelve observed fundamentals, seven of which are infrared active were assigned. Of the six N-S stretching fundamentals, two (A_1 and B_1 symmetry) are active in the Raman only and a third (the A_2 band) is inactive in both the infrared and Raman spectra. Therefore, the remaining three bands are a strong B_2 vibration at 705 cm^{-1} and vibrations of E symmetry at 766 cm^{-1} and 930 cm^{-1}. The strong vibration has historically been referred to as "the S-N stretch".

Bragin and Evans have classified the vibrational frequencies of free S_4N_4 into three classes. The high frequency bands above 700 cm^{-1}, bands in the 340-615 cm^{-1} range and the low frequency bands below 250 cm^{-1}. The high frequency bands above 750 cm^{-1} have been identified as combination bands. The larger number of bands observed in the vibrational spectra of the molecular adducts makes such a classification difficult. However, it is noted that each of the molecular adducts exhibits strong bands above 1000 cm^{-1}. These bands cannot be reasonably assigned as combination bands as in S_4N_4, but since a drastic change in geometry of the S-N ring occurs upon complexation, they may be due to the stretching of the shorter SN bands of 1.60 Å to 1.55 Å.[27,29] Similarly bands due to the S-N stretch associated with the co-ordinated nitrogen would be expected to have lower frequencies, 700-900 cm^{-1}, due to the longer S-N bond of 1.65 Å.[27,29] Assignment of S-N vibrations due to motion involving the co-ordinated nitrogen atom is difficult as there are a large number of bands in the required range.

Infrared and nmr data indicates that the $S_4N_4 \cdot PF_5$ adduct is iso-structural with the other adducts. The expected geometry is as illustrated.



III-4 The Reaction of S_4N_4 with Anhydrous HF

The purpose of this work was to investigate the possibility of using anhydrous HF as an alternative solvent for S_4N_4-Lewis acid systems. MacDiarmid[61] has demonstrated that S_4N_4 reacts with HCl in carbon tetrachloride to yield the cyclothiotrithiazyl cation $S_4N_3^+$ according to the following sequence

$$S_4N_4 + HCl \rightarrow S_4N_4{\cdot}HCl \text{ (red ppt)}$$

$$S_4N_4{\cdot}HCl + 3HCl \rightarrow S_4N_3Cl + NH_4Cl + Cl_2$$

The ^{19}F nmr room temperature spectrum of the mixture obtained from the reaction of S_4N_4 with HF in a 100:1 HF:S_4N_4 molar ratio exhibited two singlets at δ = -70.9 ppm and -33.8 ppm as well as a peak due to unreacted HF. The ^1H nmr spectrum consisted of a triplet at 4.9 ppm from tetramethylsilane. The singlets observed in the ^{19}F nmr spectrum are in the correct region for fluorine bonded to sulphur. Table III-6 lists possible S-F species that may be formed as well as their chemical shifts. The signal at -33.8 ppm may correspond to that reported for F on $S_4N_4F_4$ (-35 ppm). The lower field singlet could not be identified by analogy with any known S species. The triplet in the proton nmr spectrum is due to the ammonium ion NH_4^+. Although nitrogen has a quadrupole moment, quadrupole broadening is minimized as the electric field gradient is very small because of the high symmetry of the ammonium ion. As a result, the ^1H nmr spectrum of the NH_4^+ consists of three lines due to N-H coupling.

The chemistry of the S_4N_4/HF system is complex. This system does

Table III-6

^{19}F nmr Chemical Shifts of Possible Reaction Products from the S_4N_4/HF System.

Compound	δ (p.p.m.) from $CFCl_3$
$S_3N_3F_3$	-44.1 [131]
$S_4N_4F_4$	-35.0 [131]
NSF	-23.3 [132]
NSF_3	-61.7 [133]

not behave analogously to the HCl system; as only an extremely powerful oxidizer could be reduced by hydrogen fluoride as the product of the reaction would be elemental fluorine.

It is also necessary to explain the downfield shift of the ^{19}F nmr signal due to HF, as the reaction proceeds. The chemical shift of HF in liquid SO_2 is +193.1 ppm. The fluorine signal of the HF/S_4N_4/SO_2 reaction mixture was observed at +182.0 ppm after the reaction had been allowed to proceed for two hours. Over a period of several days, the signal moved downfield to +173.1 ppm and bands due to F bonded to S appeared in the appropriate region. The continual downfield snift of the HF line is attributed to an exchange process between free fluoride ion and HF. One possible source of fluoride ion is obviously NH_4F . As the reaction proceeds, the concentration of free fluoride increases and the exchange process becomes more important.

Due to the complexity of this system and the lack of utility of HF as either a solvent or a synthetic reagent, the HF-S_4N_4 reaction was not further investigated.

III-5 The Reaction of S_4N_4 with WF_6 in a 1:3 Mole Ratio

The purpose of this work was to determine the reaction of S_4N_4 with WF_6. That is, would it be possible to form an $S_4N_4 \cdot WF_6$ adduct or would an oxidative process occur?

Generally, the results are not readily interpretable. Tetrasulphur tetranitride, when combined with WF_6 in a 1:3 molar ratio, produced an SO_2 insoluble black material and an SO_2 soluble material that gave a red solution which yielded a green solid upon solvent removal.

An esr spectrum of the red solution showed a five-line pattern which is consistent with the presence of a radical containing two equivalent nitrogen atoms. The radical has a g-value of 2.011 and a hyperfine coupling constant of 3.14 gauss. These values are very similar to those reported for $S_3N_2{}^+ AsF_6{}^-$ which has a g-value of 2.011 and a coupling constant of 3.15 gauss.[31] The ^{19}F nmr spectrum of the SO_2 soluble material consisted of one line with a chemical shift of -147.6 ppm. Comparison with the chemical shifts of $Tl(WF_7)$ and $Cu(N(CH_3)_5(WF_7)_2)$ suggests that the anion may be WF_7^-.[134] The infrared spectra of the isolated materials are not very informative. The WF_7^- ion has been reported to have a strong vibration at 620 cm^{-1} in the NO^+ and NO_2^+ salts.[135,136,137] Both sets of infrared spectra have bands in this region as well as higher frequency bands in the 800-1150 cm^{-1} region which are probably due to

S-N vibrations. The infrared spectra of the radical containing material was not similar to the infrared spectrum of $S_3N_2AsF_6$. This is not conclusive proof that the radical is not $S_3N_2^+$ since it may only be present in very small amounts. Analysis of the insoluble black material failed to produce meaningful results. This system was not further investigated due to its complexity. It is apparent that S_4N_4 does not co-ordinate with WF_6 to form a stable molecular adduct, but instead, a complex process occurs that probably involves oxidation of S_4N_4.

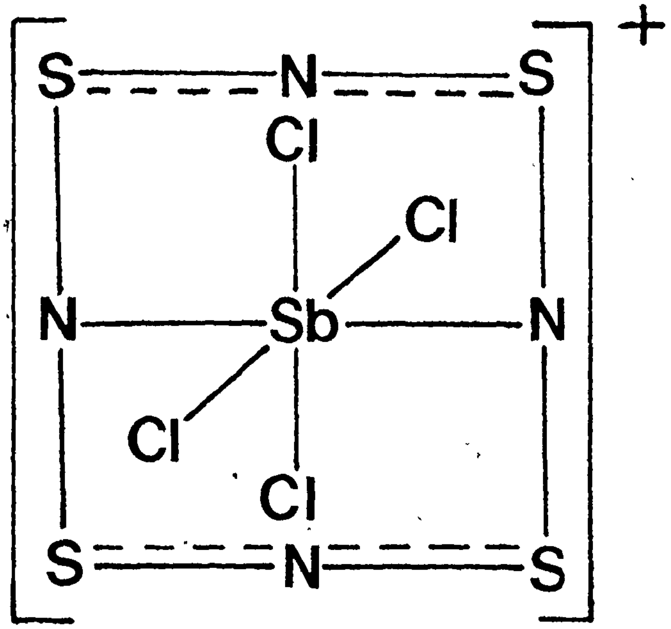
III-6 The $S_4N_4/SbCl_5$ System

Adducts of S_4N_4 were first prepared in 1906.[138] However, it was not until 1960 that the first crystal structure of one of these adducts, $S_4N_4 \cdot SbCl_5$,[29] was determined. Jolly and Wynne, in 1967 prepared for the first time the $S_4N_4 \cdot BF_3$ [27,28] adduct and found it to be structurally similar to the $SbCl_5$ adduct.

The species $S_4N_4 \cdot Sb_2Cl_{10}$ has also been prepared from the reaction of S_4N_4 with $SbCl_5$ in a 1:2 mole ratio. Based on vibrational data and comparison with the results of Jolly for the species $S_4N_4 \cdot BCl_3 \cdot SbCl_5$ Malhotra, et al.[36] have suggested that the $S_4N_4 \cdot Sb_2Cl_{10}$ species is an ionic compound containing the $S_4N_4 \cdot SbCl_4^+$ cation and the proposed structure is illustrated on the next page.

Jolly[27] has reported the isolation of a yellow material, obtained from the reaction of $S_4N_4 \cdot SbCl_5$ with $SbCl_5$ in a 1:2 mole ratio, which analyzed as $S_2N_2 \cdot SbCl_6$. There is little information concerning the material since the initial investigation was very limited.

At the time work was begun on this system, it was clear that S_4N_4 formed molecular adducts with $SbCl_5$, but the nature of the species $S_4N_4Sb_2Cl_{10}$ and $S_2N_2SbCl_6$ was still not clear. An attempt was therefore made to clarify this $S_2N_2SbCl_6$ system.



When S_4N_4 is mixed with $SbCl_5$ in a 1:3 molar ratio, it is easily oxidized to produce a yellow crystalline material that analyzes as $S_2N_2SbCl_6$. By means of an X-ray structural determination, it was shown to be $S_4N_4(SbCl_6)_2$ and is clearly identical with the material first prepared by Jolly.

$$S_4N_4 + 3SbCl_5 \rightarrow S_4N_4(SbCl_6)_2 + SbCl_3$$

Jolly[27] originally obtained a solution having the yellow colour of the cyclotetrathiazyl dication by reaction of the molecular adduct $S_4N_4 \cdot SbCl_5$ with $SbCl_5$. This reaction was checked in this laboratory and found to be correct. It was also demonstrated that one mole of S_4N_4 could be combined directly with two moles of $SbCl_5$ or one mole of $S_4N_4 \cdot SbCl_5$ with one mole of $SbCl_5$ to yield an orange solid, the infrared spectrum of which was different from that of the 1:1 molecular adduct or from $S_4N_4(SbCl_6)_2$. These reactions are summarized in Table III-7.

TABLE III-7

A Summary of the Chemistry of S_4N_4 with $SbCl_5$

$$S_4N_4 + 1SbCl_5 \xrightarrow{SO_2} S_4N_4\cdot SbCl_5$$

$$S_4N_4 + 2SbCl_5 \xrightarrow{SO_2} S_4N_4\cdot Sb_2Cl_{10}$$

$$S_4N_4 + 3SbCl_5 \xrightarrow{SO_2} (S_4N_4)(SbCl_6)_2 + SbCl_3$$

$$S_4N_4\cdot SbCl_5 + SbCl_5 \xrightarrow{SO_2} S_4N_4\cdot Sb_2Cl_{10}$$

$$S_4N_4\cdot SbCl_5 + 2SbCl_5 \xrightarrow{SO_2} (S_4N_4)(SbCl_6)_2 + SbCl_3$$

$$S_4N_4\cdot 2SbCl_5 + SbCl_5 \xrightarrow{SO_2} (S_4N_4)(SbCl_6)_2 + SbCl_3$$

It is noteworthy that $S_4N_4(SbCl_6)_2$ and $SbCl_3$ were the only detectable products from the reaction of one mole of S_4N_4 with ten moles of $SbCl_5$. Thus, no further oxidation or cleavage of the S_4N_4 ring was observed. Also, it was observed that SO_2 solutions resulting from the preparation of the cyclotetrathiazyl dication exhibited an esr signal with a g-value of 2.016. The signal was in the form of a very broad line with a width of 20 gauss. This indicates the presence of at least one competing side reaction. No attempt was made to establish the identity of the radical giving rise to the esr spectrum.

The above reactions suggest a possible sequence for the preparation of the cyclotetrathiazyl dication from $SbCl_5$.

(1) $S_4N_4 + SbCl_5 \rightarrow S_4N_4 \cdot SbCl_5$

(2) $S_4N_4 \cdot SbCl_5 + SbCl_5 \rightarrow S_4N_4Sb_2Cl_{10}$

(3) $S_4N_4Sb_2Cl_{10} + SbCl_5 \rightarrow S_4N_4(SbCl_6)_2 + SbCl_3$

The first step is the formation of the molecular adduct which then reacts further to form the 1:2 species, $S_4N_4Sb_2Cl_{10}$. Based on experimental data, there can be no doubt that the first step in the reaction sequence is the formation of the 1:1 adduct.

The structure of the 1:2 species is not known, however, some speculation can be made based on spectral data.

The following information is available:

(1) Infrared and Raman spectral data show that the compound is an $SbCl_6^-$ salt.

(2) Mössbauer data indicate that it contains no $SbCl_3$ but do not clearly show the presence of two distinct antimony sites. A broad signal was obtained that may consist of two signals with similar isomer shifts.

Crystals suitable for X-ray analysis could not be obtained. Whenever crystallization was attempted the material appeared to dissociate to some extent to $S_4N_4^{2+}$ and $S_4N_4 \cdot SbCl_5$. The remaining orange material was not suitable for crystallographic studies. At this point, it is not possible to draw any certain conclusions about the structure of the $S_4N_4 \cdot 2SbCl_5$ intermediate. However, it is reasonable to assume, based on the available information, that $S_4N_4 \cdot 2SbCl_5$ is probably $S_4N_4SbCl_4^+SbCl_6^-$ and that the structure of the cation is probably as shown in Figure III-7.

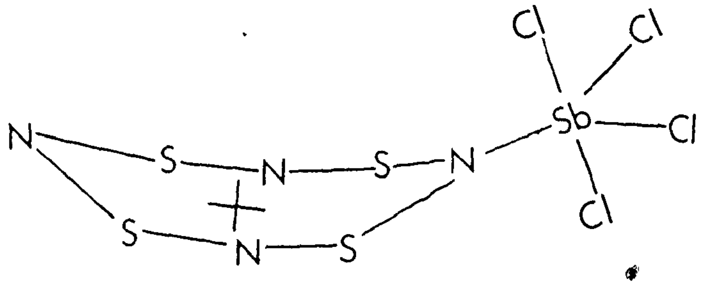
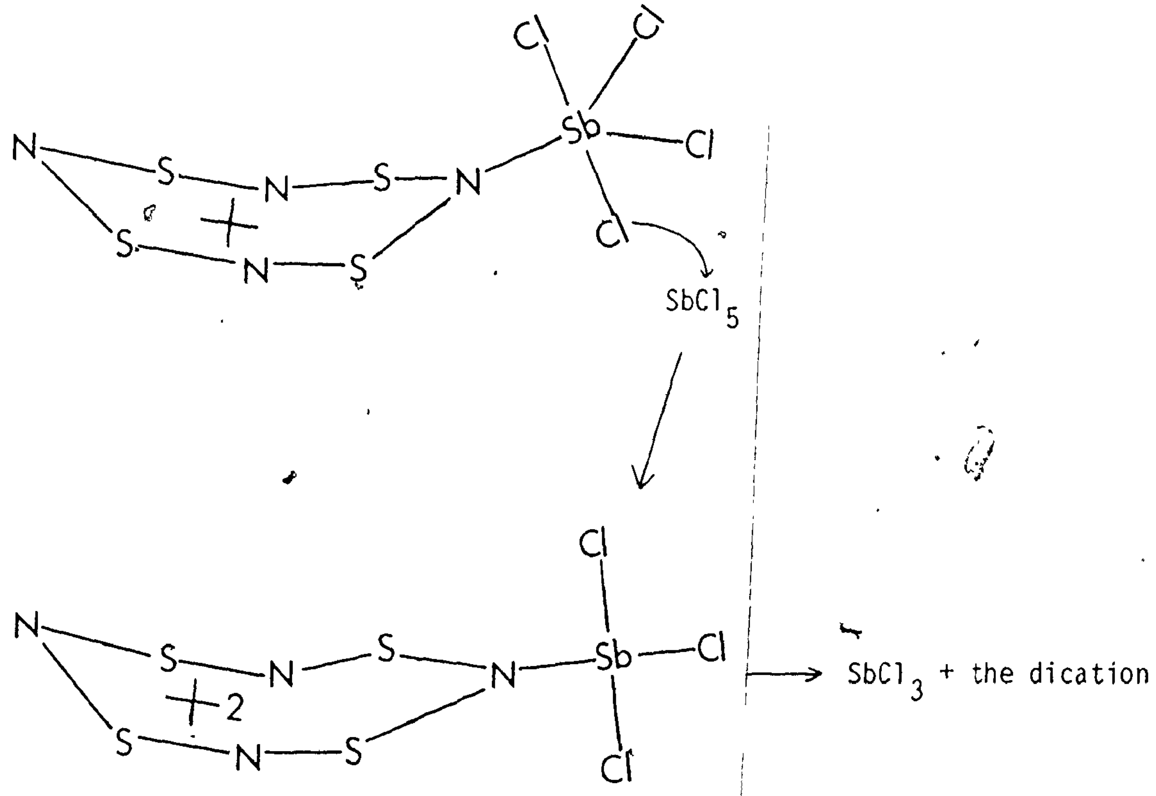


Figure III-7 Proposed structure of the $S_4N_4SbCl_4^+$ intermediate



Proposed reaction sequence for the production of the $S_4N_4^{2+}$ cation

The addition of a mole of $SbCl_5$ to one mole of $S_4N_4 \cdot SbCl_5$ simply removes a chloride ion from the coordinated $SbCl_5$ to give the $S_4N_4SbCl_4^+$ cation. The orange 1:2 species must then, in the presence of one mole of $SbCl_5$, undergo further reaction to produce the $S_4N_4^{2+}$ cation, presumably by loss of a second chloride ion to give $S_4N_4SbCl_3^{2+}$ followed by loss of $SbCl_3$.

It is important to note that, according to Jolly,[27] the $(S_4N_4BCl_2^+)(SbCl_6^-)$ complex does not undergo reaction with $SbCl_5$. This would indicate that the $[\geq N\text{-}SbCl_4]^+$ unit in the intermediate is an active site capable of producing $SbCl_3$ and thus completing the oxidation, whereas the corresponding $\geq\overset{+}{N}\text{-}BCl_2$ unit is not capable of undergoing oxidation and therefore the reaction stops at this point.

III-7 The S_4N_4/AsF_5 and S_4N_4/SbF_5 Systems

In Chapter I, mention was made of the fact that S_4N_4 forms a compound with SbF_5 which was first assumed to have the composition $(S_4N_4SbF_4^+)(Sb_3F_{16}^-)$.[36] It has been confirmed that SbF_5 is indeed capable of oxidizing S_4N_4, however the two $S_4N_4^{2+}$ salts, $S_4N_4(Sb_3F_{14})(SbF_6)$ and $S_4N_4(SbF_6)_2$ were obtained rather than the assumed $(S_4N_4SbF_4)(Sb_3F_{16})$.

In every instance S_4N_4 was mixed with 1:3, 1:4, and 1:6 molar ratios, the solutions produced underwent a variety of colour changes to yield crystalline materials.

The reaction of S_4N_4 with SbF_5 in 1:4 and 1:6 molar ratios produced green solutions from which a golden yellow crystalline material was obtained. X-ray analysis of the crystals indicated the formation of the salt of the cyclotetrathiazyl dication $S_4N_4^{2+}(Sb_3F_{14}^-)(SbF_6^-)$. Formation of this compound is consistent with the following stoichiometry

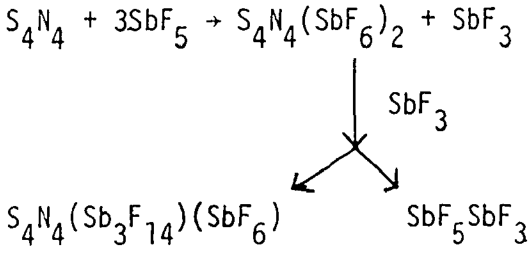
$$S_4N_4 + 4SbF_5 \xrightarrow{SO_2} S_4N_4(Sb_3F_{14})(SbF_6)$$

ratio to produce the species $S_4N_4(SbF_6)_2$

$$S_4N_4 + 3SbF_5 \xrightarrow{SO_2} S_4N_4(SbF_6)_2 + SbF_3$$

This salt was identified by comparison of its Raman and infrared spectra with the spectral data of the other $S_4N_4^{2+}$ salts.

It is worthy of note that in the production of the $Sb_3F_{14}^-$ salt, some $SbF_3 \cdot SbF_5$ [139] was formed. This is a result of the one further mole of SbF_5 reacting with free SbF_3, which is generated in the first step of the reaction



Thus, care must be taken not to obtain a product contaminated with $SbF_3 \cdot SbF_5$ and $S_4N_4(SbF_6)_2$.

The AsF_5/S_4N_4 system behaves somewhat differently from SbF_5 system and observations have been made which are at present difficult to explain. It has been previously reported that AsF_5, when mixed with S_4N_4 in a 3:1 stoichiometry, produces the $S_3N_2^+$ radical ion[31] as well as other unidentified species. The reaction of one mole of S_4N_4 with both three and six moles of AsF_5, in SO_2 solution, has been shown to produce the $(S_4N_4)(AsF_6)_2 \cdot xSO_2$ salt. This has been established by comparison of the infrared and Raman spectra of this salt with those of $S_4N_4(Sb_3F_{14})(SbF_6)$

$$S_4N_4 + 3AsF_5 \xrightarrow{SO_2} S_3N_2(AsF_6) + AsF_3 + \text{other products}$$

or

$$S_4N_4 + 3AsF_5 \xrightarrow{SO_2} S_4N_4(AsF_6)_2 \cdot xSO_2 + AsF_3$$

The reaction with AsF_5 has been repeated many times in this laboratory and only on one occasion was $S_3N_2^+$ obtained. In all other instances, the $S_4N_4^{2+}$ cation was isolated. It is also significant that in the SbF_5 system, the $S_3N_2^+$ cation was not observed in a reaction using identical stoichiometries. At present, these conflicting results cannot be explained. It is felt that the formation of these different products is a function of two competing reactions. It is not clear, however, how to influence the system so as to obtain $S_3N_2^+$ or the $S_4N_4^{2+}$ cation. Although the $S_3N_2^+$ cation is not as highly oxidized as the $S_4N_4^{2+}$ cation, it seems unlikely that it is an intermediate on the way to formation of $S_4N_4^{2+}$. It is difficult to visualize the $S_4N_4^{2+}$ dication being formed by first cleavage and cyclization to produce a five-membered ring species followed by ring expansion to produce the required eight-membered ring.

In the reactions of S_4N_4 with SbF_5 or AsF_5, regardless of the molar ratio employed, the resulting solutions exhibited one line esr spectra with a g-value of 2.011. This value is in the range of the values reported for the radical species S_5^+.[140]

Solutions of S_4N_4 in 20% oleum were observed by Chapman and Massey[39] to yield first a five line esr spectrum which then changed with time to produce an esr spectrum identical to that produced by sulphur in 20% oleum. Presumably, this can now be interpreted as formation of $S_3N_2^+$ initially which then reacts to yield S_5^+ and other unidentified species. In no case was a five line esr spectrum, that could be attributed to $S_3N_2^+$, observed from the solutions resulting from the oxidation of S_4N_4 to $S_4N_4^{2+}$ with SbF_5 or AsF_5.

A reaction sequence for the production of $S_4N_4^{2+}$ via SbF_5 or AsF_5 cannot be proposed at present. It is reasonable to speculate that the first step is the formation of the molecular adduct. Although there is no evidence for the existence of a molecular adduct of S_4N_4 with SbF_5, Glemser has prepared the $S_4N_4 \cdot AsF_5$ [30] adduct in CCl_4 solution. Identification of this adduct was based on analysis and infrared data.

III-8 Infrared and Raman Spectra of $S_4N_4^{2+}$ Salts

In Table III-8 and Figures III-8, III-9, III-10, III-11, III-12 and III-13, the infrared and Raman spectra of $S_4N_4(SbCl_6)_2$, $S_4N_4(AsF_6) \cdot xSO_2$, $S_4N_4(SbF_6)_2$ and $S_4N_4(Sb_3F_{14})(SbF_6)$ are presented. The infrared and Raman spectra of the anion in each of these salts will be discussed first.

The site group symmetry of the $SbCl_6^-$ anion in the crystal $S_4N_4(SbCl_6)_2$ is C_2. Table III-9 gives the correlation of the point group O_h with the site group symmetry C_2.

This site group symmetry implies that the degeneracy of the doubly and triply degenerate vibrations should be lifted and ν_3 and ν_4, which are Raman inactive in the purely octahedral environment, become Raman active. Similarly, the vibrations due to ν_1, ν_2 and ν_5 may now also be infrared active.

Table III-8

Infrared and Raman Spectra of $S_4N_4^{2+}$ Salts

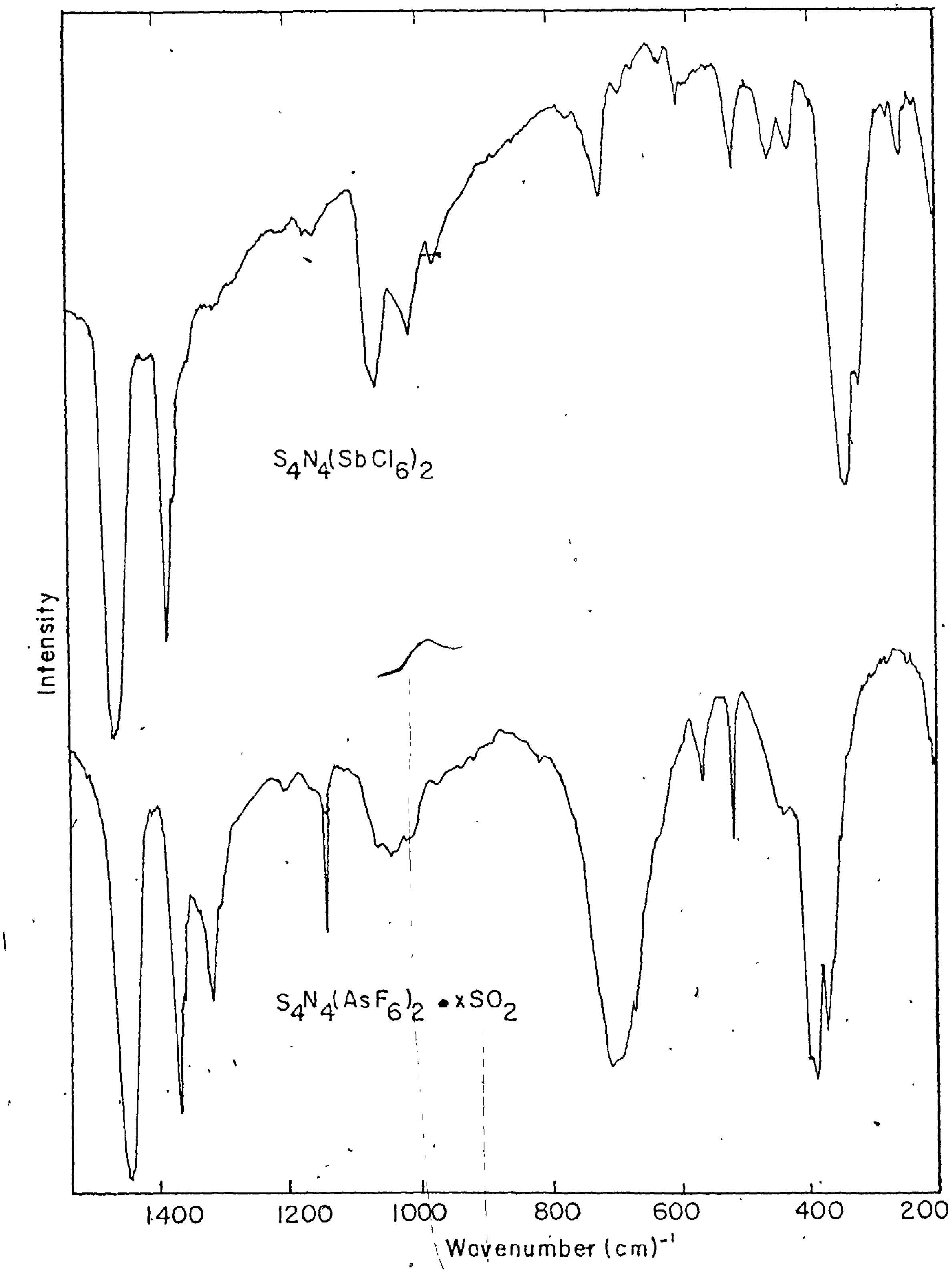
$S_4N_4(SbCl_6)_2$		$S_4N_4(AsF_6)_2\cdot xSO_2$		$S_4N_4(SbF_6)_2$		$S_4N_4(Sb_3F_{14})(SbF_6)_2$	
Raman $\Delta\nu$,(cm^{-1})	Infrared (cm^{-1})	Raman $\Delta\nu$,(cm^{-1})	Infrared (cm^{-1})	Raman $\Delta\nu$,(cm^{-1})	Infrared (cm^{-1})	Raman $\Delta\nu$,(cm^{-1})	Infrared (cm^{-1})
44(21)		42(50)				40(57)	
63(25)		55(35)		40(45)		48(40)	
74(32)				74(45)		61(32)	
83(54)		81(35)		96(45)		81(56)	
91(sh)		102(49)		104(48)		98(24)	
121(10)		115(19)		145(23)		111(16)	
134(4)							
145(6)		160(19)		150(sh)		145(21)	
173(20)		165(17)			205(w)	152(13)	
180(28) ν_5 $SbCl_6^-$				223(51)	210(w)		
191(sh)					215(w)	188(33)	205(w)
193(sh)							210(w)
225(48)		230(87)		230(sh)		230(100)	217(w)
241(2)	255 (mw)	241(3)		234(67)			
271(2) ν_2 $SbCl_6^-$		245(3)				274(3)	270(s)
283(4)				282(9) ν_5 SbF_6^-		287(21)	282(s)
289(4)					280(s)ν_4 SbF_6^-		292(s)
293(4)				294(4)			
324(10)	320 (m)						
338(63) ν_1 $SbCl_6^-$	340(s)ν_3 $SbCl_6^-$						
362(6)							
369(6)		367(6) ν_5 AsF_6^-					
		373(7)	373(s) ν_4 AsF_6^-		381(s)		380(w)
			390(s)				
			400(sh)		395(s)	415(1)	387(w)
		418(3)					415(w)
	425(mw)		449(sh)				421(sh)
	460(mw)	461(2)			465(m)		433(vw)
							475(m)
		478(2)					
		503(100)				496(84)	
501(74)		524(4) νSO_2	521(m)	501(100)	520 mw νSO_2	501(66)	
	515(mw)	567(4)				564(16)	
	599(w)	572(8) ν_2 AsF_6^-	568 mw	561(2)	568(m)	583(22)	587(ms)
	610(vw)	578(4)		615(5)		615(13)	615(s)
	615(vw)	622(10)				620(13)	630(s)
				630(3) ν_2 SbF_6^-		629(8) ν Sb-F	
						643(59)	
				647(71) ν_1 SbF_6^-		650(sh)	
					655(s) $\nu_3 SbF_6^-$	656(45)	662(s)
			672(s)			673(10)	670 sh
		677(sh)	700(s) ν_3 AsF_6^-		720(s)		687(s)
		682(14) $\nu_1 AsF_6^-$	1015 mw	668(8)	990(m)		695(s)
	690(vw)		1040 mw		1045 mw	1122(8)	1020(m)
	721(mw)	1138(4)	1054 mw		1082(m)		1060(m)
1175(6)	972(w)	1142(50) νSO_2	1145(m) νSO_2	1141(31) νSO_2	1150(mw) νSO_2		1155(w)
1197(100)	1010(mw)	1210(42)	1200(w)	1210(96)	1170(w)	1205(80)	1205(vw)
	1060(m)	1218(55)			1205(mw)	1217(60)	
		1325(8)	1325 νSO_2		1339(m) νSO_2		

In some instances, a bracket indicates several vibrational frequencies over which a fundamental may occur, rather than attempting a definitive assignment.

sh = shoulder; ( ) = band intensities, all frequencies reported in cm^{-1}.

The Raman frequencies for the co-ordinated SO_2 in $S_4N_4(AsF_6)_2\cdot xSO_2$ are taken from Ref. 141.

Figure III-8 Infrared spectra of $S_4N_4(SbCl_6)_2$ and $S_4N_4(AsF_6)_2 \cdot xSO_2$.



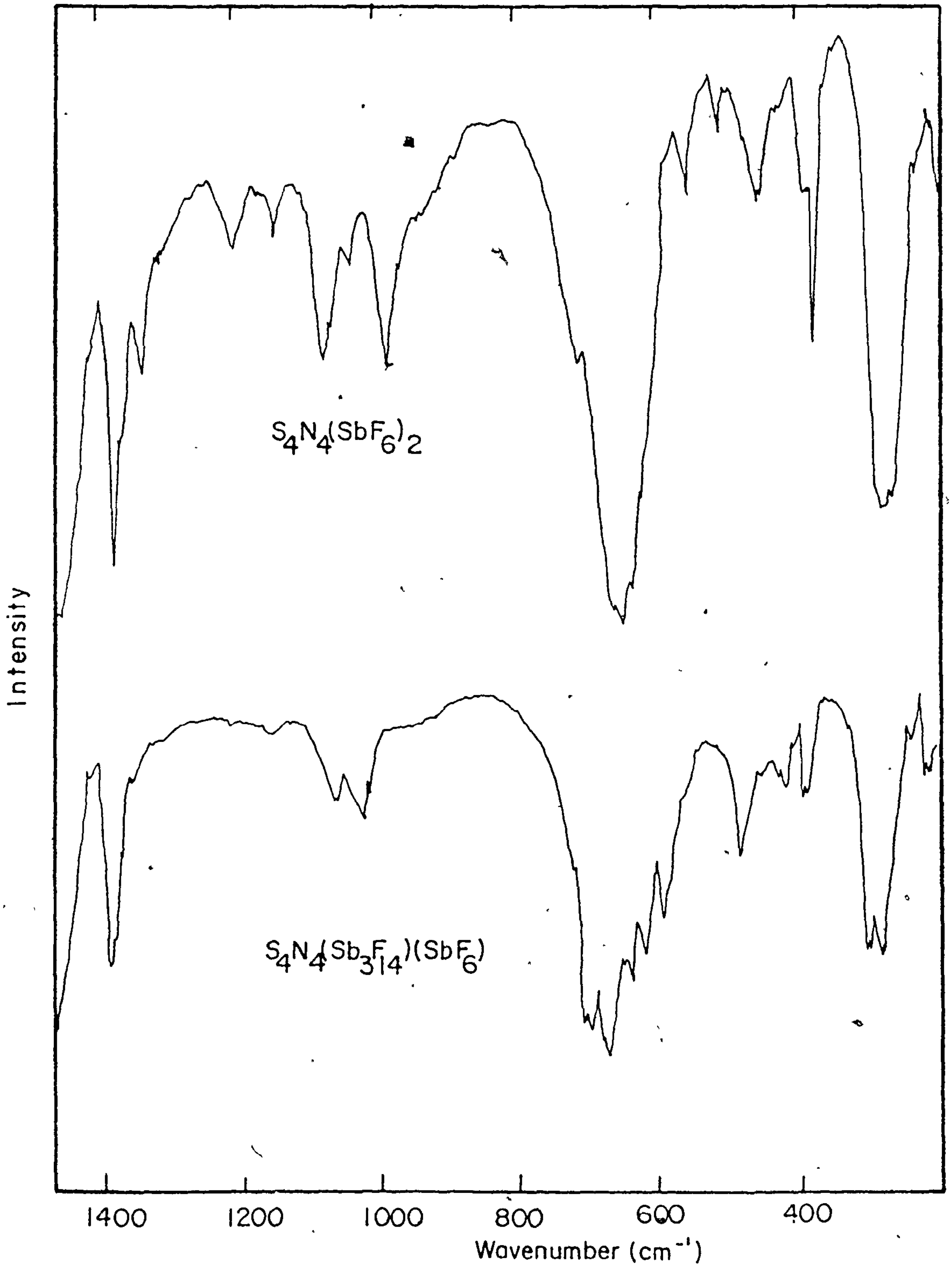


Figure III-9 Infrared spectra of $S_4N_4(SbF_6)_2$ and $S_4N_4(Sb_3F_{14})(SbF_6)$.

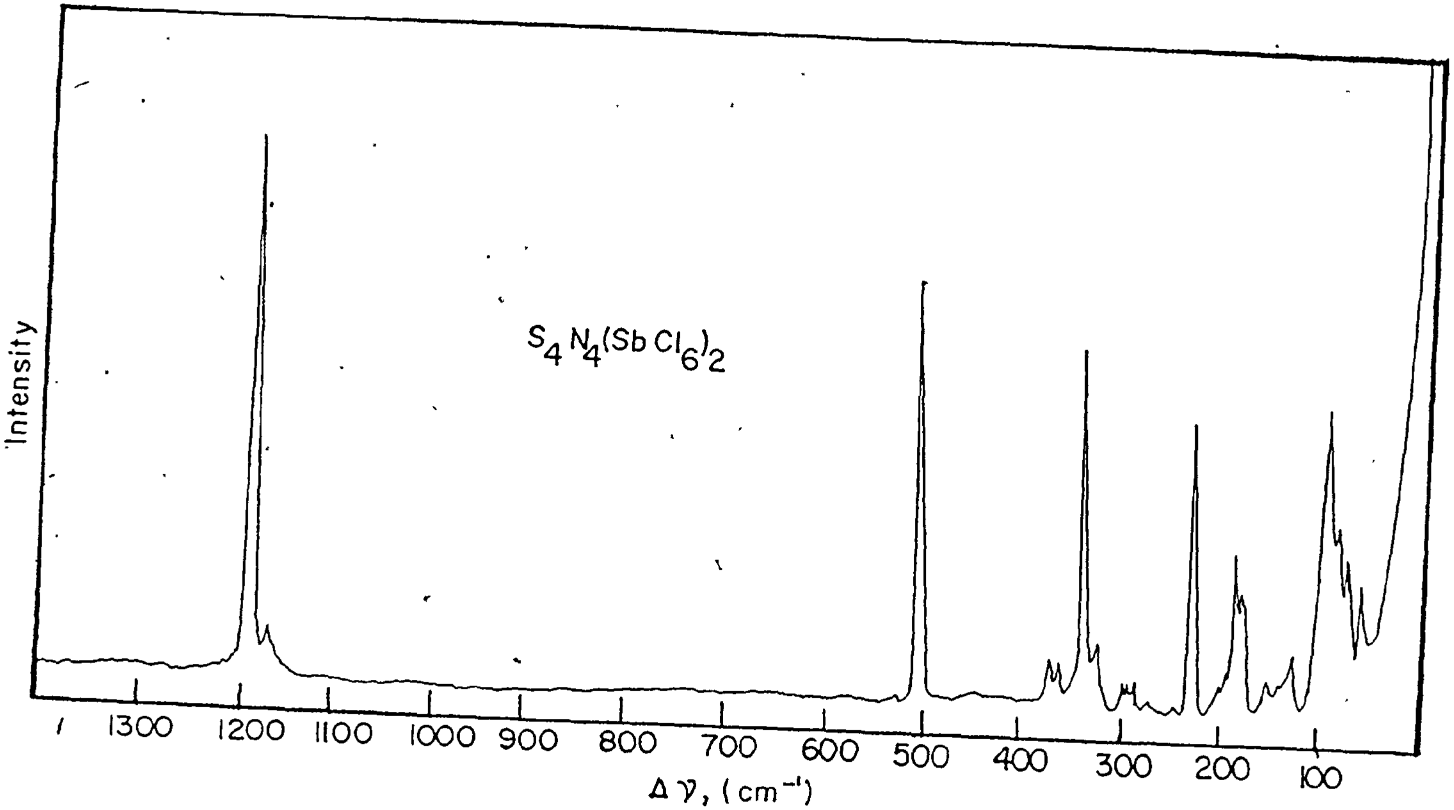


Figure III-10 Raman spectrum of $S_4N_4(SbCl_6)_2$ recorded at -196°C.

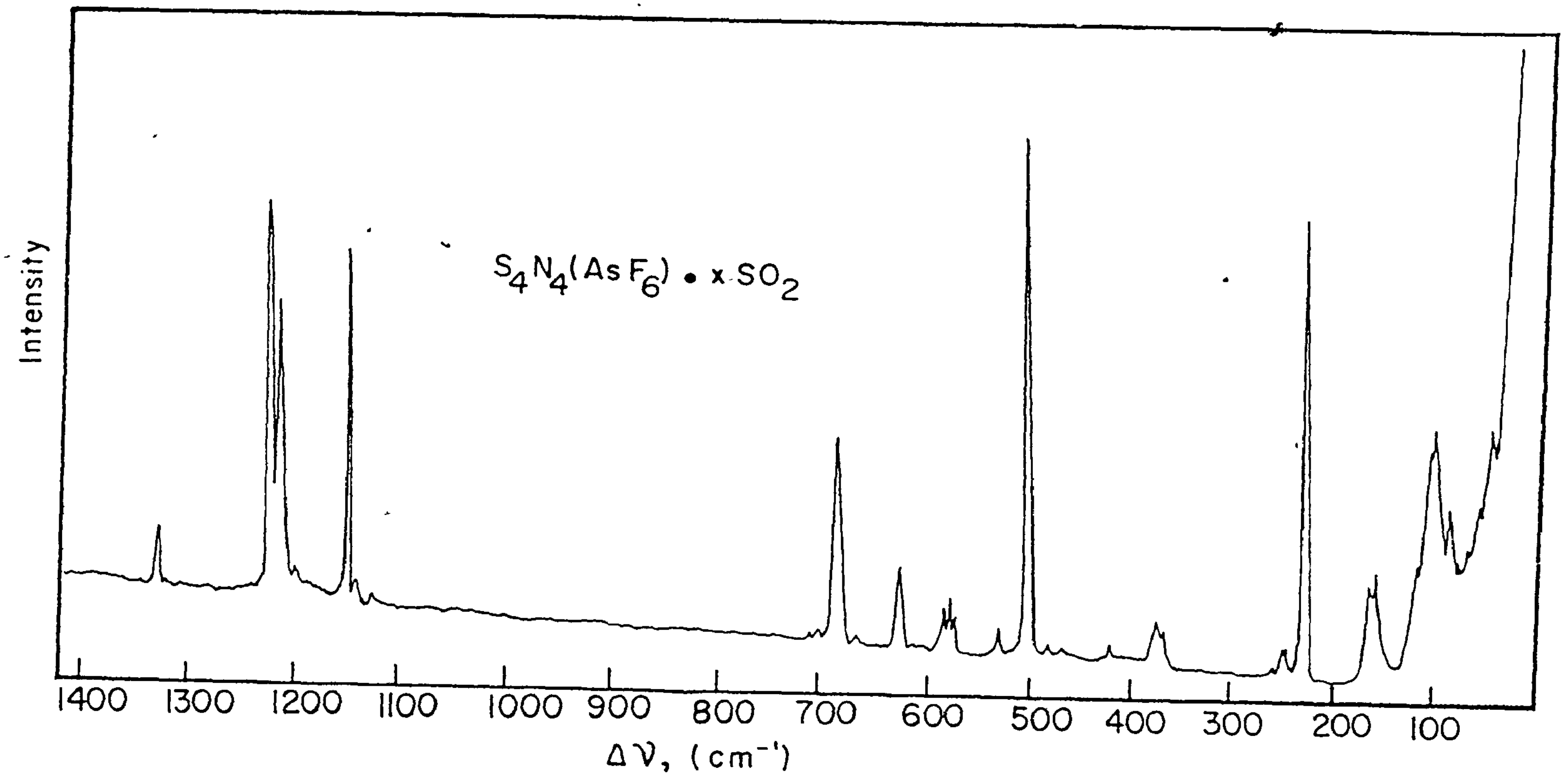


Figure III-11 Raman spectrum of $S_4N_4(AsF_6)_2 \cdot xSO_2$ recorded at -196°C.

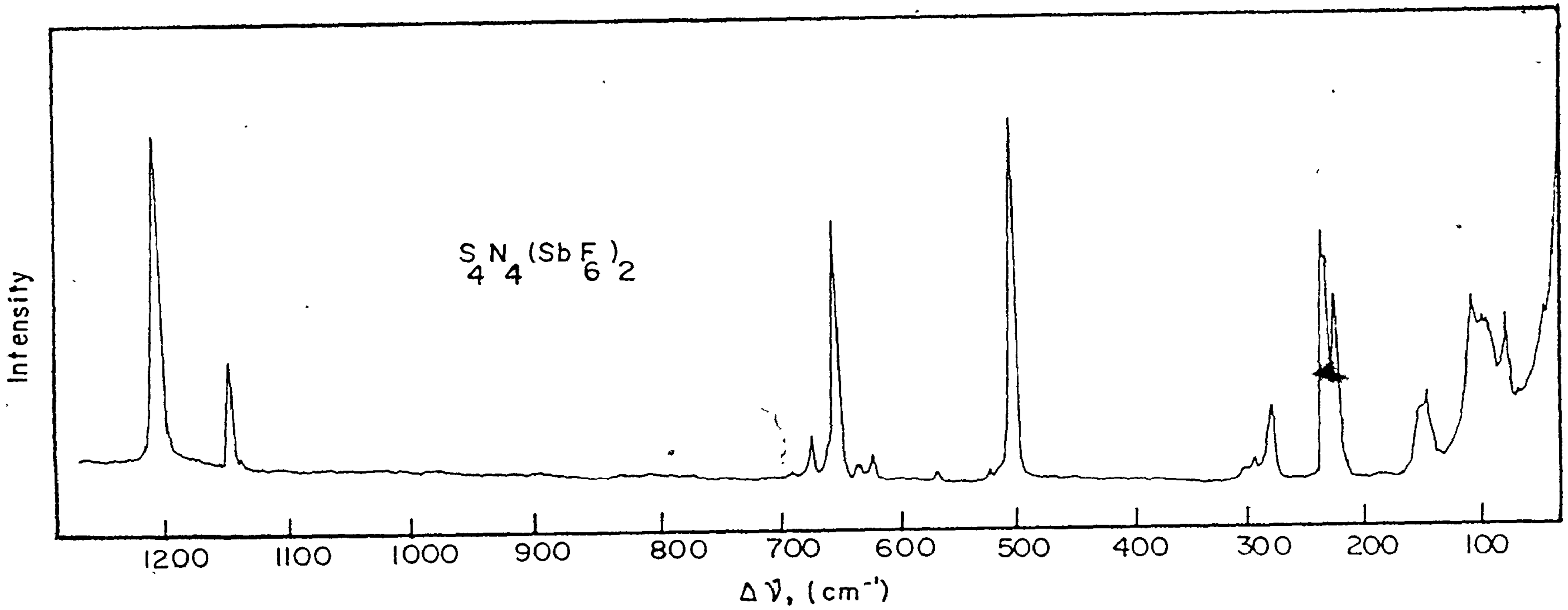


Figure III-12 Raman spectrum of $S_4N_4(SbF_6)_2$ recorded at -196°C.

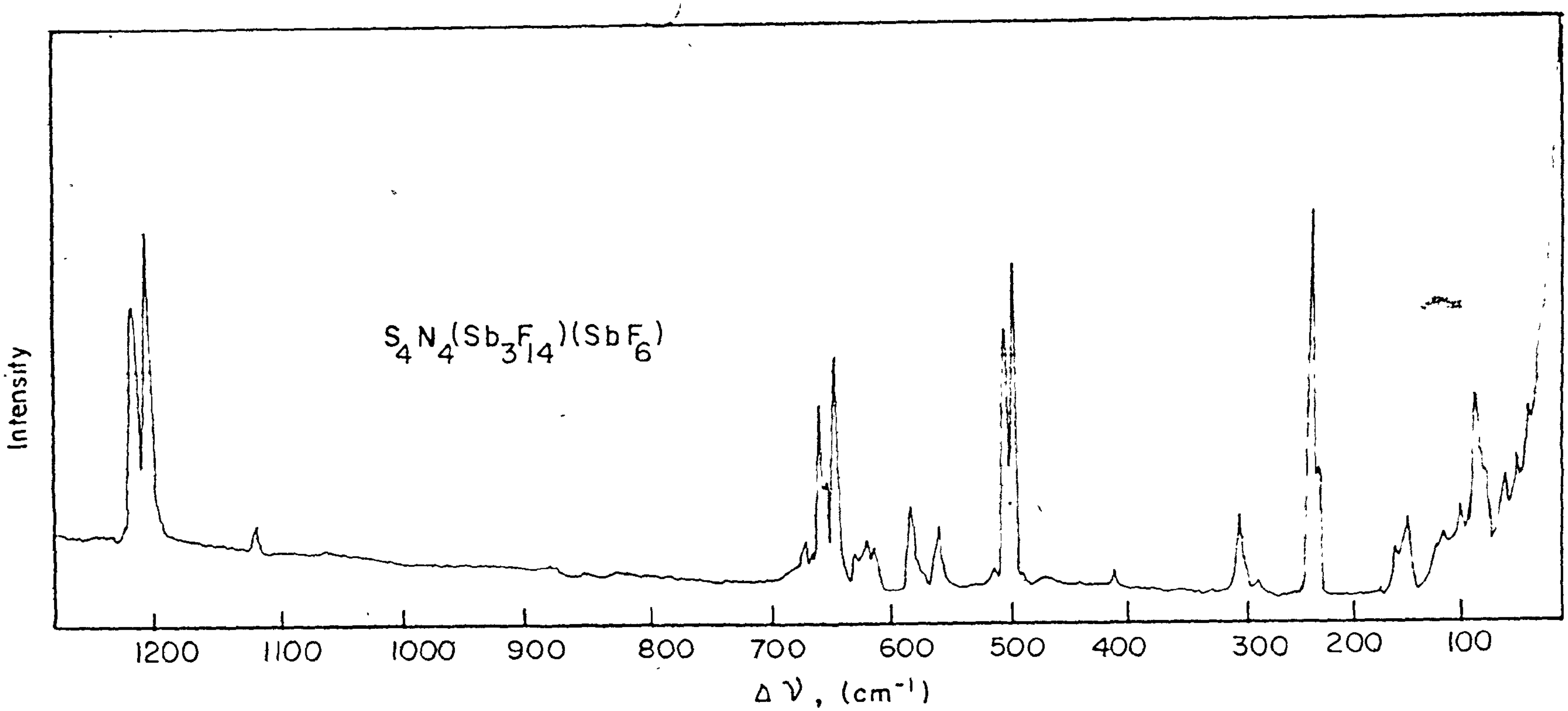


Figure III-13 Raman spectrum of $S_4N_4(Sb_3F_{14})(SbF_6)$ recorded at -196°C.

Table III-9

Correlation Table for the Point Groups O_h, D_4 and C_2

	O_h	D_4	C_2
ν_1	A_{1g}(R)	A_1(R)	A(IR),(R)
ν_2	E_g(R)	A_1(R) + B_1(R)	2A(IR),(R)
ν_3	T_{1u}(IR)	A_2(IR) + E(IR),(R)	(A+2B),(IR)(R)
ν_4	T_{1u}(IR)	A_2(IR) + E(IR),(R)	(A+2B),(IR)(R)
ν_5	T_{2g}(R)	B_2(R) + E(IR),(R)	(A+2B)(IR),(R)

The vibrations due to the $SbCl_6^-$ unit are reasonably consistent with C_2 site symmetry. The Raman active band at 338 cm^{-1} is assigned to ν_1 which is a non-degenerate vibration and therefore no splitting is expected. The second Raman active vibration, ν_2, is a degenerate vibration and appears to be split. It has been assigned to the two bands at 283 cm^{-1} and 271 cm^{-1}. The final Raman active mode, ν_5, is triply degenerate and again the degeneracy appears to have been lifted. Thus, the vibrations at 173 cm^{-1}, 180 cm^{-1} are possibly due to ν_5. There are also two shoulders at 191 cm^{-1} and 193 cm^{-1}, either one of which may be due to the other component of the triply degenerate vibration.

The infrared active mode, ν_3, is triply degenerate and is assigned to the strong band at 340 cm^{-1}. There is also one other band present at 320 cm^{-1}. This may also be due to lower site group symmetry and a consequence of the degeneracy of ν_3 being destroyed. The other infrared active vibration ν_4 was not observed since it was outside the scanning region of the spectrometer employed.

The crystal structure of the $S_4N_4(AsF_6)_2 \cdot xSO_2$ salt was not determined and therefore site symmetry effects cannot be discussed. The Raman spectrum does, however, indicate that the AsF_6^- unit is not in a purely octahedral environment. The band at 682 cm^{-1} has been assigned to ν_1 while as in the $SbCl_6^-$ salt, ν_2 and ν_5 appear to be split. Two of the three bands at 567 cm^{-1}, 572 cm^{-1} and 578 cm^{-1} can be assigned to the doubly degenerate E_g modes. The third component may possibly arise from either factor group splitting or site symmetry lowering effects. Two bands were observed at 373 cm^{-1} and 367 cm^{-1} which may be assigned to the triply degenerate ν_5 mode, the band at 373 cm^{-1} is somewhat broad and may be composed of two unresolved bands. Again, the apparent loss of degeneracy is due to the effects mentioned above.

The infrared active fundamental, ν_3, is assigned to the bands at 700 cm^{-1} and 672 cm^{-1}. This fundamental is triply degenerate and the band at 672 cm^{-1}, which appears as a sharp spike on the side of the broad band at 700 cm^{-1}, is assumed to be a result of solid state effects which destroy the degeneracy of the fundamental ν_3.

The other infrared active fundamental, ν_4, is also triply degenerate and is assigned to the bands at 400 cm^{-1}, 390 cm^{-1} and 373 cm^{-1}.

In the SbF_6^- salt, the intense line at 647 cm^{-1} in the Raman spectrum is assigned to ν_1. Bands due to ν_2 have been observed in the region 574-594 cm^{-1} in $KSbF_6$.[142] The two bands at 630 cm^{-1} and 615 cm^{-1} are assigned therefore to ν_2 of SbF_6^-. The bands at 294 cm^{-1} and 282 cm^{-1} are assigned to ν_5 of SbF_6^- and are comparable to the frequencies reported for ν_5 (295, 284, 269 cm^{-1}) in $KSbF_6$. Again, loss of degeneracy in the E_g and T_{2g} modes are presumably a result of solid state effects.

The infrared spectrum has two intense bands at 280 cm^{-1} and 655 cm^{-1} and these are assigned to ν_4 and ν_3 for the anion.

The vibrational bands due to the anions in the $S_4N_4(Sb_3F_{14})(SbF_6)$ salt are difficult to assign. This is possibly due to the lack of vibrational data concerning the $Sb_3F_{14}^-$ anion. In the Raman spectrum, there are three bands in the region where ν_1 of SbF_6^- would be expected. These three bands occur at 656 cm^{-1}, 650 cm^{-1} and 643 cm^{-1} with the band at 650 cm^{-1} being observed as a shoulder. The band at 643 cm^{-1} may be due to ν_1 of SbF_6^- and the remaining bands a consequence of a symmetric ν_1 type vibration of the Sb(v) units of the $Sb_3F_{14}^-$ anion. The other two Raman active vibrations, ν_2 and ν_5, resulting from the SbF_6^- anion are difficult to assign. In Table III-9, the bands from 629 cm^{-1} to 564 cm^{-1} are attributed to Sb-F vibrations, and no attempt has been made to make definite assignments. The infrared spectrum of the salt is very complex. There are a large number of bands in the region from 700 cm^{-1} to 200 cm^{-1} and many of these are due to vibrations involving the $Sb_3F_{14}^-$ and SbF_6^- anions. Assignment of these bands is also not attempted.

The bands remaining in the infrared and Raman spectra are therefore due to vibrations involving the $S_4N_4^{2+}$ ring. The Raman and infrared active bands common to all the salts are listed in Table III-10. Infrared bands solely attributable to the sulphur nitrogen ring are more difficult to identify especially the higher frequency bands, due to the possibility of overlap with overtone and combination bands of the anion.

Table III-10

Vibrational Frequencies Common to All $S_4N_4^{2+}$ Salts

$S_4N_4(SbCl_6)_2$		$S_4N_4(AsF_6)_2 \cdot xSO_2$		$S_4N_4(SbF_6)_2$		$(S_4N_4)(Sb_3F_{14})(SbF_6)$	
R (cm^{-1})	I.R. (cm^{-1})	R (cm^{-1})	I.R. (cm^{-1})	R (cm^{-1})	I.R. (cm^{-1})	R (cm^{-1})	I.R. (cm^{-1})
1197		1218				1217	
1175		1210	1200	1210	1205	1205	1205
			1054		1170		
	1060		1040		1082		1060
	1010		1015				1020
501		503		501		501	
225		230		223		236	

R = Raman active; I.R. = Infrared active.

The data in Table III-10 makes it clear that there are three characteristic groups of bands associated with the $S_4N_4^{2+}$ cation. There are single bands in the 225 cm^{-1} to 230 cm^{-1} and 500 cm^{-1} to 505 cm^{-1} region as well as a group of bands above 1,000 cm^{-1} that are common to all four salts. The high frequency bands are due to vibrations of the S-N framework.

III-9 Structure of the Cyclotetrathiazyl Dication

The X-ray crystallographic determinations were performed by Dr. D.R. Slim of this department and pertinent crystal data are listed in Tables III-11, III-12 and III-13. Unit cell diagrams are shown in Figures III-14 and III-15 for $S_4N_4(SbCl_6)_2$ and $S_4N_4(Sb_3F_{14})(SbF_6)$.

Table III-11

Crystal Data for $S_4N_4^{2+}$ Salts

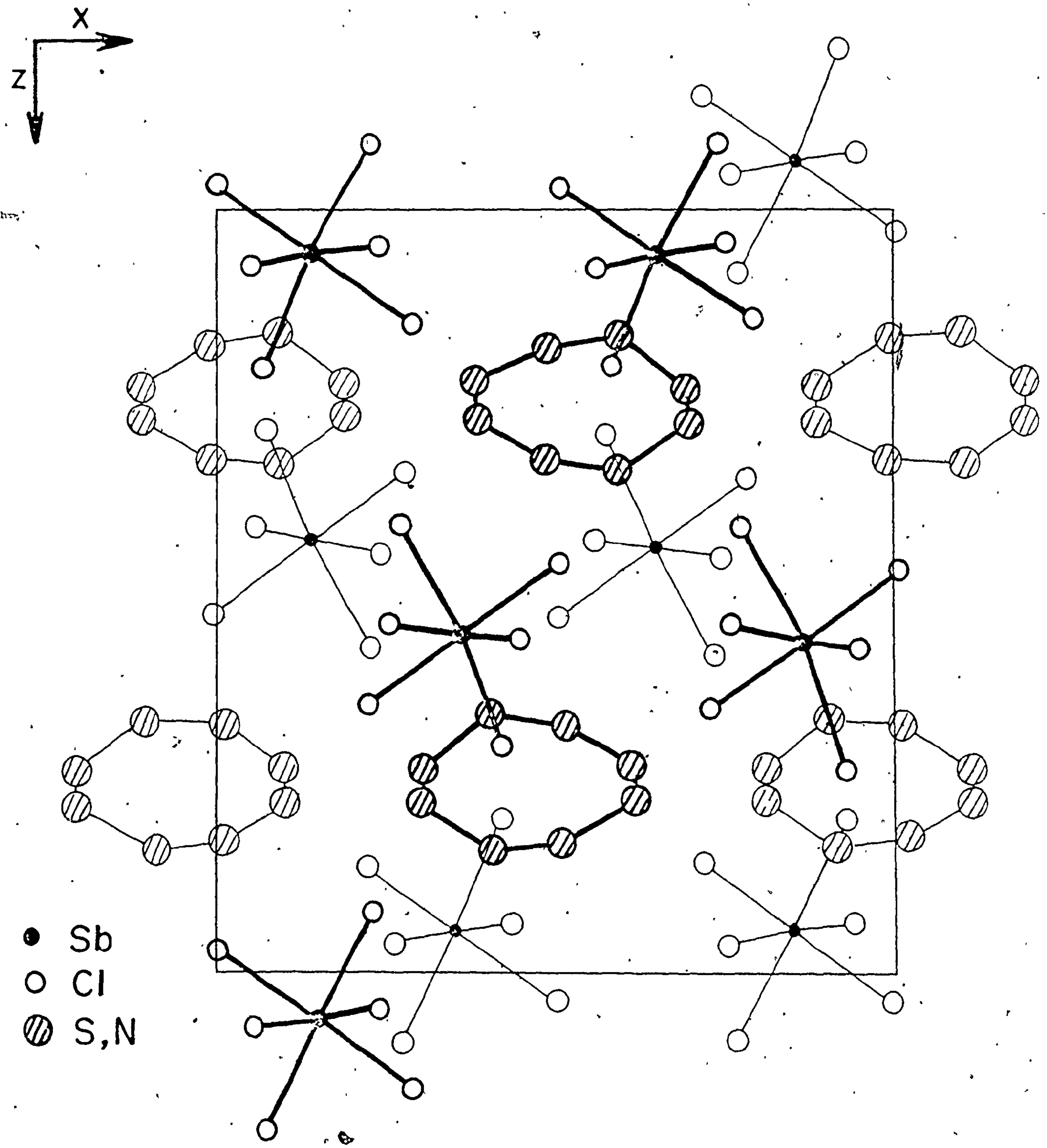
	$S_4N_4(SbCl_6)_2$	$S_4N_4(Sb_3F_{14})(SbF_6)$
Space Group	P_{bcn} orthorhombic	$P_{21/n}$ monoclinic
Unit Cell Dimensions	a = 12.873(8) Å	a = 16.382(8) Å
	b = 12.602(7) Å	b = 16.200(8) Å
	c = 13.557(8) Å	c = 8.454(6) Å
		β = 109.3°(7)
Final unweighted R-factor	0.073	0.10

Note: The final unweighted R-factor is defined as

$$R = \frac{\Sigma(|F_o| - |F_c|)}{\Sigma|F_o|}$$

These studies have indicated that the cyclic $S_4N_4^{2+}$ cation has different ring geometries in the compounds $S_4N_4(SbCl_6)_2$ and $S_4N_4(Sb_3F_{14})(SbF_6)$.

Figure III-14 Unit cell diagram of $S_4N_4(SbCl_6)_2$.



A PROJECTION OF THE STRUCTURE DOWN THE b-AXIS

THE PROJECTION OF THE STRUCTURE DOWN THE C-AXIS

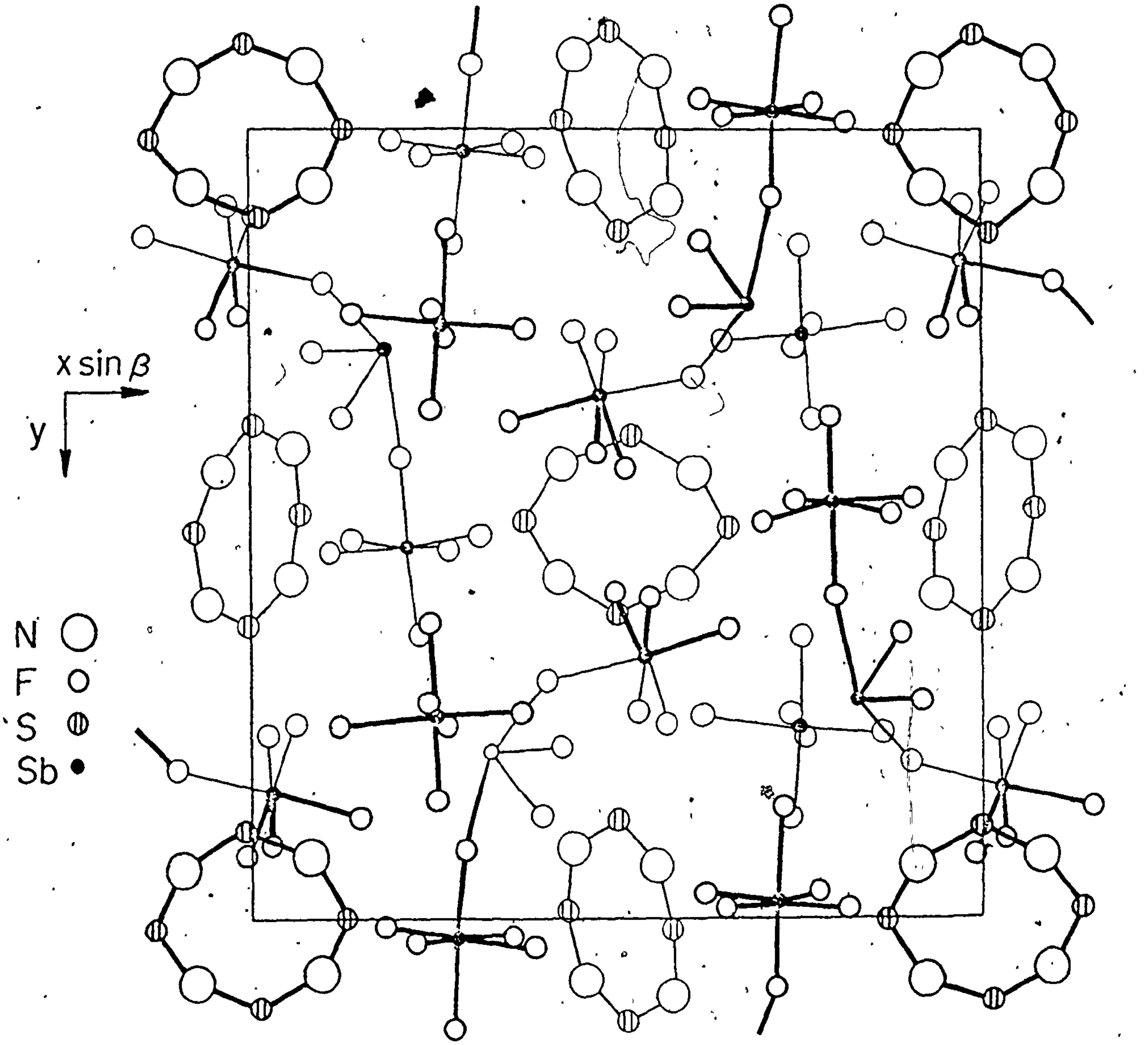


Figure III-15 Unit cell diagram of $S_4N_4(Sb_3F_{14})(SbF_6)$.

Table III-12

Bond Lengths and Bond Angles for $S_4N_4(SbCl_6)_2$

Bond Lengths Å		Bond Angles in Degrees	
SN(1)-SN(2)	1.73(2)	SN(1)SN(2)SN(3)	135.0(1)
SN(2)-SN(3)	1.40(2)	SN(2)SN(2)SN(4)	132.0(1)
SN(3)-SN(4)	1.75(2)	SN(3)SN(4)SN(4')	133.0(1)
SN(4)-SN(4')	1.39(2)	SN(4)SN(4')SN(3')	134.0(1)
SN(4')-SN(3')	1.75(2)	SN(4')SN(3')SN(2')	133.0(1)
SN(3')-SN(2')	1.40(2)	SN(3')SN(2')SN(1')	135.0(1)
SN(2')-SN(1')	1.73(2)	SN(2')SN(1')SN(1)	133.0(1)
SN(1')-SN(1)	1.42(2)	SN(1')SN(1)SN(2)	133.0(1)
Sb-Cl(1)	2.438(6)	Cl(1)SbCl(2)	178.9(2)
Sb-Cl(2)	2.370(7)	Cl(1)SbCl(3)	88.3(2)
Sb-Cl(3)	2.365(6)	Cl(1)SbCl(4)	89.6(2)
Sb-Cl(4)	2.355(8)	Cl(1)SbCl(5)	88.9(2)
Sb-Cl(5)	2.335(7)	Cl(1)SbCl(6)	89.1(2)
Sb-Cl(6)	2.374(6)	Cl(2)SbCl(3)	90.6(2)
		Cl(2)SbCl(4)	91.4(2)
		Cl(2)SbCl(5)	91.2(2)
		Cl(2)SbCl(6)	90.6(2)
		Cl(3)SbCl(4)	177.0(2)
		Cl(3)SbCl(5)	90.4(2)
		Cl(3)SbCl(6)	88.0(2)
		Cl(4)SbCl(5)	91.7(2)
		Cl(4)SbCl(6)	89.8(2)
		Cl(5)SbCl(6)	177.5(2)

Table III-13

Bond Lengths and Bond Angles for $S_4N_4(Sb_3F_{14})(SbF_6)$

Bond Lengths (Å)

Ring (A)

S(1)N(1)	1.55(2)
S(1)N(2)	1.54(2)
S(2)N(2)	1.54(2)
S(2)N(1')	1.55(2)
S(1')N(1')	1.55(2)
S(1')N(2')	1.54(2)
S(2')N(2')	1.54(2)
S(2')N(1)	1.55(2)

Ring (B)

S(3)N(3)	1.62(2)
S(3)N(3)	1.54(2)
S(4)N(4)	1.60(2)
S(4)N(3')	1.52 (2)
S(3')N(3')	1.62(2)
S(3')N(4')	1.54(2)
S(4')N(4')	1.60(2)
S(4')N(3)	1.52(2)

$(Sb_3F_{14}^-)$

Sb(1)-F(1)	1.85(2)
Sb(1)-F(2)	1.78(3)
Sb(1)-F(3)	1.89(2)
Sb(1)-F(4)	1.87(2)
Sb(1)-F(5)	1.84(2)
Sb(1)-F(6)	1.94(2)
Sb(2)-F(3)	2.27 (2)
Sb(2)-F(6)	3.01(2)
Sb(2)-F(7)	1.89(2)
Sb(2)-F(8)	1.91(2)
Sb(2)-F(9)	2.99(2)
Sb(2)-F(12)	2.29(1)
Sb(2)-F(15)	2.73(2)
Sb(2)-F(20)	2.72(2)
Sb(3)-F(9)	1.88(2)
Sb(3)-F(10)	1.83(2)
Sb(3)-F(11)	1.84(2)
Sb(3)-F(12)	1.95(1)
Sb(3)-F(13)	1.81(2)
Sb(3)-F(14)	1.86(2)

SbF_6^-

Sb(4)-F(15)	1.85(2)
Sb(4)-F(16)	1.87(2)
Sb(4)-F(17)	1.87(2)
Sb(4)-F(18)	1.87(2)
Sb(4)-F(19)	1.88(1)
Sb(4)-F(20)	1.86(2)

Table III-13 (Continued)

Bond Angles in Degrees

Ring (A)		SbF_6^-	
S(1)N(2)S(2)	150(1)	F(15)Sb(4)F(16)	88.3(7)
N(2)S(2)N(1')	120(1)	F(15)Sb(4)F(17)	91.0(8)
S(2)N(1')S(1')	151(1)	F(15)Sb(4)F(18)	88.2(8)
N(1')S(1')N(2')	119(1)	F(15)Sb(4)F(19)	91.4(7)
S(1')N(2')S(2')	150(1)	F(15)Sb(4)F(20)	178.6(8)
N(2')S(2')N(1)	120(1)	F(16)Sb(4)F(17)	89.7(6)
S(2')N(1)S(1)	151(1)	F(16)Sb(4)F(18)	89.5(7)
N(1)S(1)N(2)	119(2)	F(16)Sb(4)F(19)	177.8(6)
Ring (B)		F(16)Sb(4)F(20)	90.5(8)
S(3)N(4)S(4)	141(1)	F(17)Sb(4)F(18)	178.9(7)
N(4)S(4)N(3')	127(1)	F(17)Sb(4)F(19)	92.4(7)
S(4)N(3')S(3')	145(1)	F(17)Sb(4)F(20)	89.5(7)
N(3')S(3')N(4')	127(1)	F(18)Sb(4)F(19)	88.4(7)
S(3')N(4')S(4')	141(1)	F(18)Sb(4)F(20)	91.2(8)
N(4')S(4')N(3)	127(1)	F(19)Sb(4)F(20)	89.7(7)
S(4')N(3)S(3)	145(1)		
N(3)S(3)N(4)	127(1)		

$(Sb_3F_{14}^-)$			
F(1)Sb(1)F(2)	93.1(11)	F(8)Sb(2)F(9)	144.3(6)
F(1)Sb(1)F(3)	89.5(7)	F(8)Sb(2)F(12)	78.9(6)
F(1)Sb(1)F(4)	173.2(9)	F(8)Sb(2)F(15)	77.7(6)
F(1)Sb(1)F(5)	90.5(9)	F(8)Sb(2)F(20)	150.3(5)
F(1)Sb(1)F(6)	93.8(8)	F(9)Sb(2)F(12)	136.8(5)
F(2)Sb(1)F(3)	87.9(11)	F(9)Sb(2)F(15)	81.3(5)
F(2)Sb(1)F(4)	90.6(10)	F(9)Sb(2)F(20)	65.1(5)
F(2)Sb(1)F(5)	173.9(9)	F(12)Sb(2)F(15)	119.2(5)
F(2)Sb(1)F(6)	92.4(12)	F(12)Sb(2)F(20)	72.0(6)
F(4)Sb(1)F(3)	88.4(7)	F(15)Sb(2)F(20)	121.5(5)
F(4)Sb(1)F(5)	85.4(8)	F(9)Sb(3)F(10)	93.2(8)
F(4)Sb(1)F(6)	91.8(8)	F(9)Sb(3)F(11)	91.3(7)

Table III-13 (Continued)

Bond Angles in Degrees

($Sb_3F_{14}^-$)

F(5)Sb(1)F(3)	87.5(7)	F(9)Sb(3)F(12)	178.2(8)
F(5)Sb(1)F(6)	92.3(9)	F(9)Sb(3)F(13)	90.9(8)
F(6)Sb(1)F(3)	179.6(9)	F(9)Sb(3)F(14)	89.8(7)
F(3)Sb(2)F(6)	130.6(5)	F(11)Sb(3)F(10)	175.2(9)
F(3)Sb(2)F(7)	80.9(6)	F(11)Sb(3)F(12)	88.3(7)
F(3)Sb(2)F(8)	81.7(6)	F(11)Sb(3)F(13)	89.9(10)
F(3)Sb(2)F(9)	64.9(5)	F(11)Sb(3)F(14)	88.8(9)
F(3)Sb(2)F(12)	152.4(5)	F(12)Sb(3)F(10)	87.1(8)
F(3)Sb(2)F(15)	74.9(5)	F(12)Sb(3)F(13)	90.8(8)
F(3)Sb(2)F(20)	123.1(6)	F(12)Sb(3)F(14)	88.4(6)
F(6)Sb(2)F(7)	135.5(7)	F(13)Sb(3)F(10)	91.6(11)
F(6)Sb(2)F(8)	120.1(6)	F(13)Sb(3)F(14)	178.5(10)
F(6)Sb(2)F(9)	77.3(5)	F(14)Sb(3)F(10)	89.7(10)
F(6)Sb(2)F(12)	76.5(5)		
F(6)Sb(2)F(15)	68.8(5)		
F(6)Sb(2)F(20)	58.4(6)		
F(7)Sb(2)F(8)	91.1(7)		
F(7)Sb(2)F(9)	95.8(6)		
F(7)Sb(2)F(12)	80.1(6)		
F(7)Sb(2)F(15)	154.5(6)		
F(7)Sb(2)F(20)	78.6(7)		

In Tables III-12 and III-13, the bond lengths and bond angles are listed for the two salts.

Figure III-16 illustrates the ring geometries found in $(S_4N_4)(Sb_3F_{14})(SbF_6)$ and $S_4N_4(SbCl_6)_2$. Structure A is planar with equal bond lengths about sulphur and nitrogen, structure B is also planar but has alternating bond lengths, while structure C is non-planar, has S_4 symmetry and a very pronounced alternation in bond lengths while the bond angles are all equal.

It is noteworthy that the contact distances between chlorine on $SbCl_6^-$ and the cation range from 3.22 Å upwards and when compared to the sum of the Van der Waals radio for nitrogen and chlorine and sulphur and chlorine (3.30 Å $r_N + r_{Cl}$, and 3.55 Å $r_S + r_{Cl}$),[143] may be significant.

The possibility of a genuine secondary bonding effect is best reflected in the elongated Sb-Cl bond of 2.43 Å. Comparison of this bond length to the usual Sb-Cl bond distance found in the $SbCl_6^-$ anion of 2.36 Å would imply that there is an interaction between the $S_4N_4^{2+}$ ring and one chlorine of the $SbCl_6^-$ anion in the compound $S_4N_4(SbCl_6)_2$. However, the elongated Sb-Cl bond could be a result of thermal motion and, consequently, the problem of the existence of a genuine secondary bonding effect could be best resolved by a redetermination of the structure at a lower temperature.

At present, there is no bonding scheme that adequately explains the ring geometries observed in cyclic sulphur nitrogen ring systems. A valence bond description is completely inadequate for the $S_4N_4^{2+}$ cation.

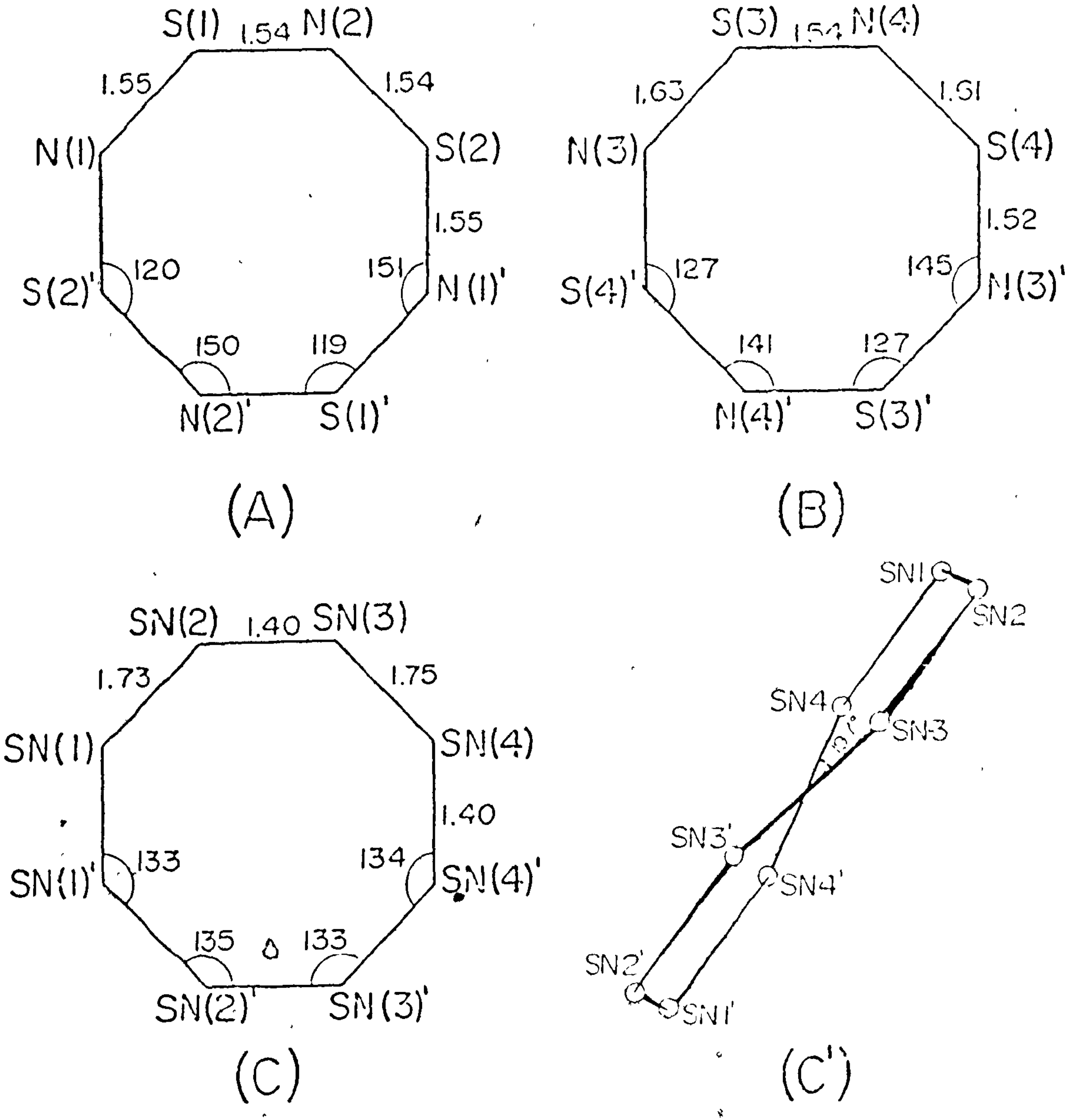


Figure III-16 (A) Structure of ring (A) in $[S_4N_4][SbF_6][Sb_3F_{14}]$;

(B) Structure of ring (B) in $[S_4N_4][SbF_6][Sb_3F_{14}]$;

(C) Structure of ring (C) in $[S_4N_4][SbCl_6]_2$ viewed down the S_4 axis;

(C') Structure of ring (C) viewed down the pseudo-C_2' axis.

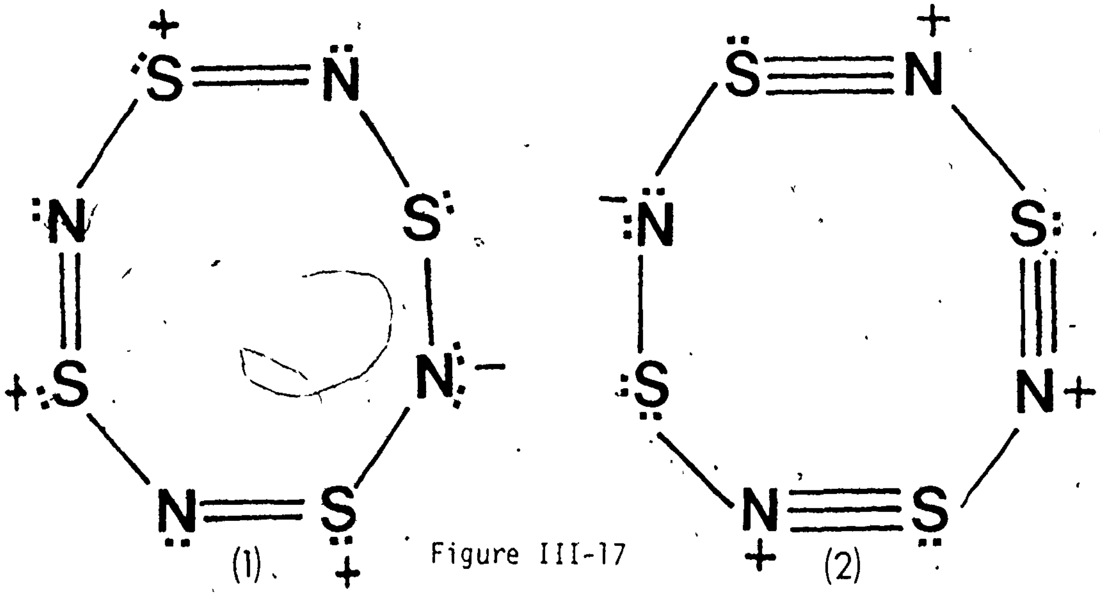


Figure III-17

In Figure III-17, valence bond type structures (1) and (2) are illustrated with a possibility of sixteen resonance forms for both structures. Structure (1) is consistent with an S-N bond order of 1.37 whereas structure (2) predicts an S-N bond order of 1.75. The large S-N-S bond angles in ring forms (A) and (B) are consistent with contribution of a resonance form such as type 2 in which lone pairs on three of the nitrogens have been utilized by forming additional S-N bonds. The valence bond diagrams also suggest possible resonance stabilization of the ring. However, this may not be an important factor due to the observation that the flat ring form (A), with equal bond lengths in which resonance stabilization would be expected to occur, is readily distorted to structure (B) and to the non-planar ring (C) with strongly alternating bond lengths. It is important to note that planarity and bond equivalence may not be necessary for resonance stabilization in SN ring systems. All of these ring forms must have similar energies and the differences between the ring geometries must be due to interactions with neighbouring ions in the crystal lattice.

If it is assumed that each sulphur and nitrogen has a lone pair of electrons and there is one sigma bond between each pair of atoms,

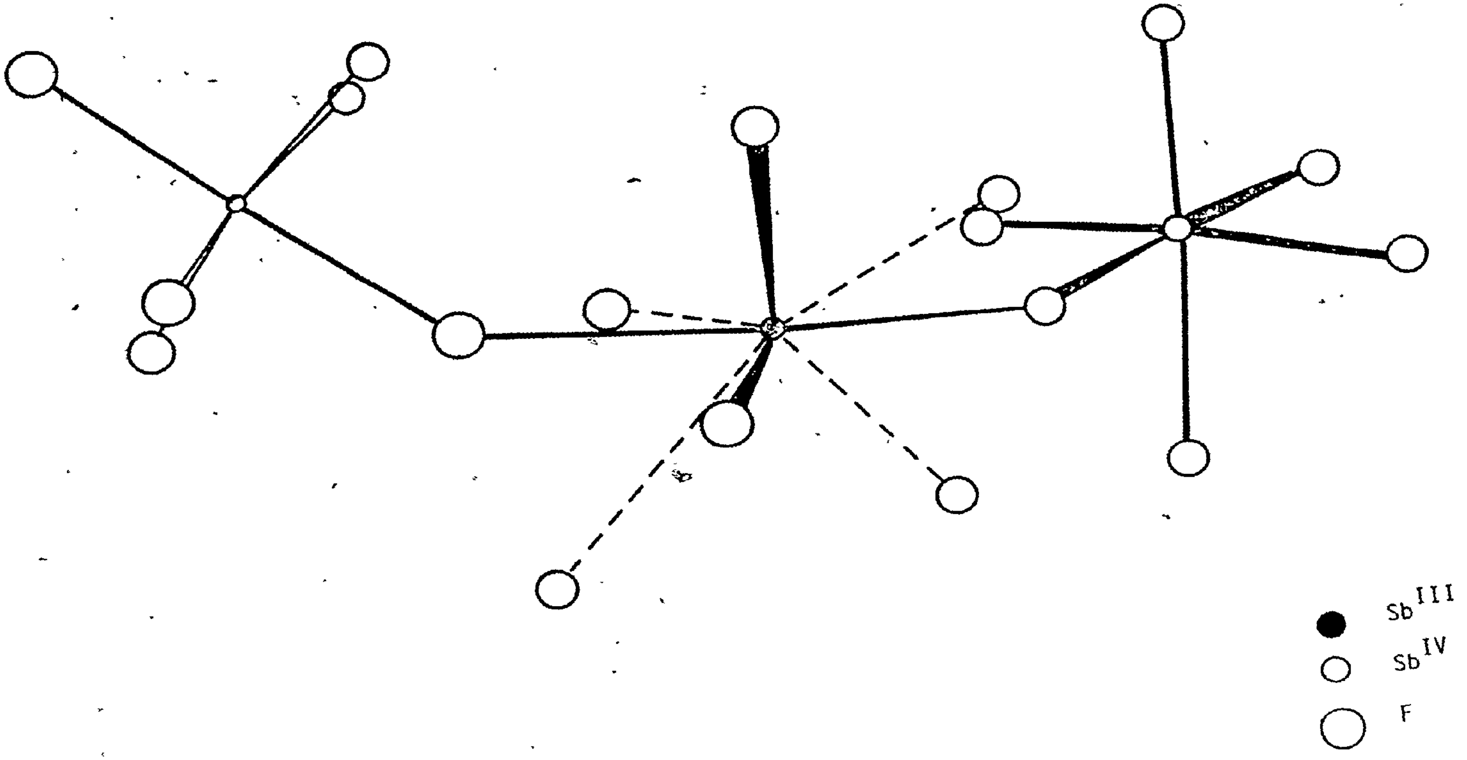


Figure III-18. The $Sb_3F_{14}^-$ anion. --- long contacts to neighbouring F atoms.

then there are ten remaining valence electrons in $S_4N_4^{2+}$, this may be described as a 10 π electron aromatic system. Utilization of the lone pair on nitrogen, in the bonding, as in structure (2), is clearly inconsistent with the 10 π molecular orbital description. Valence bond descriptions do not, therefore, adequately describe the observed ring geometries.

III-10 The $Sb_3F_{14}^-$ Anion

The geometry of the $Sb_3F_{14}^-$ anion in the salt $S_4N_4(Sb_3F_{14})(SbF_6)$ is illustrated in Fig. III-18. This is the first time that this anion has been prepared and characterized crystallographically. The crystallographic data indicates that the anion consists of an SbF_2^+ ion linked by two trans assymetric fluorine bridges to two SbF_6^- anions, thus giving to a first approximation an AX_4E configuration[144] about the central Sb(III).

III-11 Experimental Section

The Reaction of S_4N_4 with a Large Excess of $SbCl_5$

In a typical experiment (250 mg, 1.35 mmol) of S_4N_4 was added to one arm of a double bulb reaction vessel fitted with a medium glass frit separating each of the bulbs. To the other bulb, $SbCl_5$ (4.06 g, 13.5 mmol) was added using a glass syringe. All transfers were carried out in a dry-box containing an atmosphere of dry nitrogen. Sulphur dioxide (10 ml) was condensed at -196°C into each bulb and the ampoule was then flame sealed. Upon warming to room temperature, the $SbCl_5$ completely dissolved in the liquid SO_2, but some S_4N_4 remained undissolved. The $SbCl_5$ solution was poured onto the S_4N_4 solution and immediately a deep red solution formed, with the undissolved S_4N_4 developing a red coating. After stirring for 24 hours, a yellow-orange solution was obtained with some undissolved bright yellow solid. The solution was filtered and the SO_2 slowly removed resulting in the formation of small yellow needles which were very sensitive to moisture. Antimony(III)chloride was sublimed from the crude reaction mixture and characterized by comparison of its Raman spectrum with that of a sample of pure $SbCl_3$.

The Reaction of S_4N_4 with $SbCl_5$ in a 1:3 Mole Ratio

The experimental procedure was essentially as described above. In this instance, S_4N_4 (250 mg, 1.35 mmol) was reacted with (1.22 g, 4.07 mmol) of $SbCl_5$. The resulting SO_2 solution immediately became dark red upon mixing the two reactants. After stirring for 48 h. the red solution faded to again yield a yellow-orange solution that contained some undissolved bright yellow solid. The solution was filtered and left undisturbed for approximately one week to give yellow crystalline needles. Again, $SbCl_3$ was characterized as a component of the reaction mixture by Raman spectroscopy.

The Raman spectrum of the yellow needles was identical to that of the product of the previous reaction. Analysis of this material by two independent laboratories yielded the following results:

	Found		Calculated for $S_2N_2SbCl_6$
S	14.18%	14.81%	15.03%
N	6.54%	6.74%	6.56%
Sb	28.83%	30.77%	28.54%
Cl	46.82%	48.74%	49.86%

A crystal suitable for X-ray analysis was chosen and it was demonstrated that the yellow material was $(S_4N_4^{2+})(SbCl_6^-)_2$. Thus, S_4N_4 is oxidized by $SbCl_5$ to the cyclotetrathiazyl dication

$$S_4N_4 + 3SbCl_5 \xrightarrow{SO_2} (S_4N_4)(SbCl_6)_2 + SbCl_3$$

The preparation of $S_4N_4^{2+}$ as outlined above may also be carried out in CH_2Cl_2.

The Reaction of $S_4N_4 \cdot SbCl_5$ with $SbCl_5$ in a 1:2 Mole Ratio

The 1:1 molecular adduct which has been previously reported by Jolly was prepared in a double bulb reaction vessel. S_4N_4 (250 mg, 1.3 mmol) and $SbCl_5$ (388 mg, 1.3 mmol) were each added to separate bulbs of the double bulb reaction vessel, SO_2 (10 ml) was condensed at -196°C onto each of the reactants and the reaction vessel was allowed to warm to room temperature. The $SbCl_5/SO_2$ solution was poured through the frit onto the S_4N_4/SO_2 solution and a dark red solution formed immediately. The solution was stirred for 24 h. to ensure complete reaction. The SO_2 was then removed to yield a solid red material. The infrared spectrum of a small amount of this material was found to be identical with that of a genuine sample of $S_4N_4 \cdot SbCl_5$ prepared from a methylene chloride solution.

It is clear, therefore, that the nature of the product is not affected by changing the solvent from CH_2Cl_2 to SO_2.

To the arm of the bulb not containing the molecular adduct $SbCl_5$ (810 mg, 2.17 mmol) was added and SO_2 (10 ml) was condensed at

-196°C into both bulbs. The vessel was allowed to warm to room temperature. The $SO_2/SbCl_5$ solution was poured through the frit onto the molecular adduct which was only moderately soluble in liquid SO_2.

The solution was stirred for 48 h during which time a yellow solid formed and the solution became yellow-orange in colour. The yellow solid was identified as $(S_4N_4)(SbCl_6)_2$ and $SbCl_3$ was sublimed from the reaction mixture and characterized by its Raman spectrum. The reaction sequence may be summarized as follows:

$$S_4N_4 + SbCl_5 \xrightarrow{SO_2} S_4N_4 \cdot SbCl_5$$

$$S_4N_4 \cdot SbCl_5 + 2SbCl_5 \xrightarrow{SO_2} S_4N_4(SbCl_6)_2 + SbCl_3$$

It should be noted that the reaction of the molecular adduct with further $SbCl_5$ was also carried out by Jolly et al.[27] in an attempt to prepare the diadduct of S_4N_4 with $SbCl_5$. The experimental procedure was not the same as outlined above but they probably obtained the same product.

The Reaction of S_4N_4 with $SbCl_5$ in a 1:2 Mole Ratio

The compounds S_4N_4 (250 mg, 1.3 mmol) and $SbCl_5$ (810 mg, 2.71 mmol) were each added to separate bulbs of a double bulb reaction vessel and SO_2 (10 ml) was condensed at -196°C into each bulb. The vessel was allowed to warm to room temperature and the $SbCl_5/SO_2$ solution was then poured onto the S_4N_4/SO_2 solution. Immediately, a red coloured solution formed and the mixture was stirred for 48 h. to yield an orange coloured solid. This material would appear to be the same as that prepared by Malhotra et al.[36] and suggested by them to be the compound $(S_4N_4SbCl_4^+)(SbCl_6^-)$.

The orange material was reacted further with one additional mole of $SbCl_5$. The SO_2 was removed from the ampoule and $SbCl_5$ (556 mg, 1.86 mmol) was added to the bulb not containing the orange material and SO_2 (10 ml) was distilled at -196°C into both bulbs and the vessel was allowed to warm to room temperature. The $SbCl_5/SO_2$ solution was poured onto the orange material and after several days, a yellow material formed which was characterized as $S_4N_4(SbCl_6)_2$.

The above reaction was repeated a number of times in an effort to obtain crystals of this material. It was generally found that the material would not crystallize well and if solvent was slowly removed from a saturated solution, both $S_4N_4 \cdot SbCl_5$ and $S_4N_4(SbCl_6)_2$ were formed.

The Reaction of S_4N_4 with PF_5 in a 1:3 Mole Ratio

The compound S_4N_4 (250 mg, 1.3 mmol) was placed in one arm of a double bulb vessel. Phosphorus pentafluoride (488 mg, 3.9 mmol) was then condensed at -196°C onto the S_4N_4 followed by SO_2 (20 ml). The vessel was flame sealed and allowed to warm to room temperature. As the mixture warmed, a deep red colour formed to eventually produce a deep red solution with some unreacted S_4N_4 present. The mixture was stirred for several days and no further colour change occurred. Filtration of the solution and slow solvent removal yielded a bright red crystalline material. The yield based on S_4N_4 was 70%. The reaction was repeated with an S_4N_4:PF_5 molar ratio of 1:1 and the red material obtained was found to be identical to that produced in the 1:3 S_4N_4:PF_5 reaction. Infrared and nmr data which have been discussed indicate that the product is the molecular adduct, $S_4N_4 \cdot PF_5$.

The Reaction of S_4N_4 with One Mole of PCl_5 in CH_2Cl_2

The reaction of S_4N_4 with PCl_5 was performed in CH_2Cl_2 rather than liquid SO_2 due to the solvolysis reaction which occurs between PCl_5 and SO_2 to produce thionyl chloride and oxyphosphorus trichloride

$$SO_2 + PCl_5 \rightarrow OPCl_3 + SOCl_2$$

Phosphorus pentachloride (112 mg, 0.543 mmol) and S_4N_4 (100 mg, 0.543 mmol) were placed together in the same arm of a double reaction vessel fitted with a medium glass frit. It was necessary to place both solid reactants in the same bulb due to their limited solubilities in CH_2Cl_2. It is also important to note that S_4N_4 and PCl_5 did not react in the solid phase. Methylene chloride (20 ml) was condensed at -196°C onto the two solids and the ampoule was allowed to warm to room temperature. As the reaction mixture reached room temperature, the materials present combined to yield a bright orange solid. Within one-half hour, the orange material darkened to produce a black-green solid and an orange solution. After 24 hours, there was no further change. Removal of the solvent yielded a viscous liquid with a black solid dispersed in the liquid. The presence of several phosphorus-containing species in the solution was indicated by ^{31}P nmr data.

The Reaction of S_4N_4 with PCl_5 in CH_2Cl_2 in a 1:3 Mole Ratio

The reaction was performed as described above in the procedure for the reaction of one mole of S_4N_4 with one mole of PCl_5. Again, a bright orange solid formed and the solution was yellow-orange. The orange solid disappeared within one-half hour to yield a black solid which within 24 hours disappeared to produce a clear orange liquid. Removal of the methylene chloride produces an orange viscous oil. This oil had the distinct odour of sulphur chlorides and ^{31}P nmr data indicated the presence of a large number of species.

The Reaction of S_4N_4 with SbF_5 in a 1:4 Mole Ratio

In general, whenever SbF_5 was used in an experiment, efforts were made to measure the required quantity as accurately as possible. This was best accomplished by syringing an estimated amount of SbF_5 into a preweighed reaction vessel; the vessel could then be weighed in order to find the exact amount of SbF_5 added. Other materials could then be added in the required amounts.

Using a syringe, SbF_5 (937.6 mg, 4.376 mmol) was placed into one bulb of a double bulb vessel and S_4N_4 (0.1990 g, 1.08 mmol) was placed in the other bulb. It was observed that the surface of the S_4N_4 turned red with time as it came in contact with SbF_5 vapour. SO_2 (10 ml) was condensed at -196°C onto both the S_4N_4 and SbF_5. It is important to add enough SO_2 to the SbF_5 to solubilize the $SO_2 \cdot SbF_5$ adduct that forms. The vessel was allowed to warm to room temperature and the SbF_5 completely dissolved in the SO_2. The SbF_5/SO_2 solution was then poured through the frit onto the S_4N_4/SO_2 mixture. Immediately, a red colour formed, which faded within a few minutes to produce a purple solution, which in turn, within one-half hour, turned green. During this time, some solid was present, presumably unreacted S_4N_4. After several days, the green colour still persisted and some white solid had precipitated from solution. The solution was filtered and slow removal of solvent yielded a solid crystalline material. This material was washed with fresh SO_2 to produce golden yellow crystals that were characterized by X-ray studies and shown to be $S_4N_4(Sb_3F_{14})(SbF_6)$. The white material was identified as $SbF_3 \cdot SbF_5$; no free SbF_3 was isolated from the mixture.

The above reaction sequence was also repeated using a 1:6 molar ratio of $S_4N_4 \cdot SbF_5$. The same sequence of colour changes was observed and again $S_4N_4(Sb_3F_{14})(SbF_6)$ was obtained.

Analysis of the material yielded the following results:

	Found	Calculated for $SNSbF_5$
S	11.16%	12.20%
N	4.53%	5.33%
Sb	47.87%	46.33%
F	37.10%	36.10%

The percentages of antimony and fluorine are somewhat higher than expected and this is attributed to the presence of some $SbF_3 \cdot SbF_5$ in the sample.

It is important to note that the solution should be left for several days before being filtered. A white precipitate, $SbF_3 \cdot SbF_5$, tends to form rather slowly and if the solution is filtered too early in the preparation, the $S_4N_4(Sb_3F_{14})(SbF_6)$ produced is significantly contaminated with $SbF_3 \cdot SbF_5$.

The Reaction of S_4N_4 with SbF_5 in a 1:3 Mole Ratio

The procedure was as outlined for the reaction of S_4N_4 with four moles of SbF_5. In this instance, S_4N_4 (617 mg, 3.35 mmol) was added to SbF_5 (2.16 gm, 10.05 mmol) in liquid SO_2. The same sequence of colour changes was observed as was described in the previous preparations. The green SO_2 solution was allowed to stand for 24 h. An SO_2 insoluble material precipitated out which was characterized as SbF_3 by comparison of its Raman spectrum with that of a genuine sample. The solution was filtered and allowed to stand for several days; after this time a yellow crystalline material formed. This was characterized as $S_4N_4(SbF_6)_2$ by comparison of its Raman and infrared spectra with the spectra of other $S_4N_4^{2+}$ salts.

The Reaction of S_4N_4 with Anhydrous HF

The reaction of S_4N_4 with anhydrous hydrofluoric acid was carried out in a preconditioned FEP nmr tube. Two FEP nmr tubes equipped with Teflon valves were conditioned with HF and evacuated for 24 hours. S_4N_4 (50 mg, 0.271 mmol) was transferred in the dry box to one tube and HF (500 mg, 25.1 mmol) was distilled into the other tube.

The HF was then distilled onto the S_4N_4 at -196°C. The tube was placed in a dry-ice acetone bath (-78°C) and kept at this temperature for one hour. After this time, no apparent reaction had occurred, therefore, the tube was allowed to warm to room temperature.

The solution turned deep red in colour as it warmed and a considerable quantity of a red-black material was also present. The solution was investigated by means of nmr spectroscopy.

The Reaction of S_4N_4 with Anhydrous HF in Liquid SO_2

Anhydrous HF (26 mg, 1.3 mmol) and S_4N_4 (242 mg, 0.131 mmol) were each transferred to preconditioned FEP nmr tubes. Hydrogen fluoride was then distilled onto the S_4N_4 at -196°C followed by (2 ml) SO_2. The mixture was warmed to room temperature and no immediate colour change occurred. After two hours, the ^{19}F nmr spectrum was recorded. Over a period of several days, the solution became dark red and considerable unreacted S_4N_4 was present. The ^{19}F nmr spectrum of this mixture was obtained and the reaction was not investigated further.

The Reaction of S_4N_4 with WF_6 in a 1:3 Mole Ratio

In working with WF_6, it is most important that all glassware is dried thoroughly, otherwise hydrolysis readily occurs to produce tungsten oxyfluoride , WOF_4.

In the dry box, S_4N_4 (298 mg, 1.61 mmol) was transferred to one bulb of a flame dried double bulb reaction vessel. A three molar equivalent of WF_6 (4.83 mmol) was condensed onto the S_4N_4 at -196°C followed by 20 ml of SO_2. The ampoule was flame sealed and allowed to warm to room temperature. No immediate reaction occurred, but within one-half hour, the mixture slowly became brown-red. After 24 hours, the solution was a very deep red colour and a black purple SO_2 insoluble solid had formed. The solution was filtered and the SO_2 slowly removed. This left a green solid material, which did not crystallize. The infrared spectra of both the green material and the SO_2 insoluble material were recorded.

The experiment was then repeated using the apparatus in Fig. II-2. Nuclear magnetic resonance and esr spectra were obtained for the SO_2 soluble material.

The Reaction of S_4N_4 with AsF_5 in 1:3 and 1:6 Mole Ratios

In a typical reaction, S_4N_4 (250 mg, 1.35 mmol) was added to one side of a double arm ampoule. The other side of the ampoule had been previously flame sealed. AsF_5 (692 mg, 4.07 mmol) was condensed onto the S_4N_4 at -196°C, followed by SO_2 which was also condensed at -196°C. The ampoule was flame sealed and the solution was allowed to warm to room temperature. As the solution warmed, a pink colour formed which then darkened to a deep red. Within minutes of warming completely to room temperature, the solution became green, most of the solid material was dissolved or had reacted after approximately one hour. A brown-green solution formed within 24 hours and no further colour change was observed, even after one week. It is important to note that if no solid material is present in the original reaction mixture, it should be left undisturbed to allow crystal growth, but if some solid material is present, the solution should be filtered. In both instances, if crystals did not form after several days, the solvent was slowly removed. Yellow cubic crystals were obtained and these were demonstrated to be $S_4N_4(AsF_6)_2 \cdot xSO_2$ by comparison of the Raman spectrum with that of $S_4N_4Sb_4F_{20}$. The observed reaction sequence was identical for both the 1:3 and 1:6 stoichiometries. It is important to note that the reaction of S_4N_4 with three moles of AsF_5 in liquid SO_2 has been previously reported to yield the $S_3N_2^+$ cation. This preparation was repeated seven times and in one instance only $S_3N_2^+$ was obtained. In all other cases, $S_4N_4(AsF_6)_2 \cdot xSO_2$ was isolated. At this time, no explanation is offered for this discrepancy.

CHAPTER IV

THE LEWIS ACID CHEMISTRY OF $S_3N_3Cl_3$ AND $S_3N_3F_3$

IV-1 Reactions of $S_3N_3Cl_3$ and $S_3N_3F_3$ with Lewis Acids

Ionic compounds may be produced by the reaction of $S_3N_3Cl_3$ with Lewis acids. A summary of the known reactions is given below:

(i) $S_3N_3Cl_3 + SbCl_5 \xrightarrow{CCl_4} (S_3N_3Cl_2)(SbCl_6)$ 30

(ii) $S_3N_3Cl_3 + 3SbCl_5 + 3S_4N_4 \xrightarrow{SOCl_2} 3S_5N_5(SbCl_6)$ 145,51

(iii) $3S_4N_4 + 2S_3N_3Cl_3 \rightarrow 6S_3N_3Cl$ 146

Reaction (i) is a simple chloride ion abstraction whereas reactions (ii) and (iii) involve more complicated pathways. Reaction (ii) has been rationalized by considering that $S_3N_3Cl_3$ in the presence of $SbCl_5$ is a source of thiazyl cation which behaves as an electrophile towards S_4N_4 to generate the $S_5N_5^+$ cation.

In contrast, the Lewis acid chemistry of $S_3N_3F_3$ is much more limited, but there has been some indication that $S_3N_3F_3$ reacts with certain Lewis acids to form the $S_3N_3F_2^+$ cation.[30]

Due to the very limited knowledge concerning the behaviour of $S_3N_3Cl_3$ and $S_3N_3F_3$ towards Lewis acids, a study was initiated to further investigate the trihalocyclotrithiazene-Lewis acid system.

IV-2 The $S_3N_3Cl_3/SbCl_5$ System

It had been assumed by earlier workers that $S_3N_3Cl_3$ was capable of forming 1:1, 1:2 and 1:3 molecular adducts[50,51] with Lewis acids such as $SbCl_5$. The exact nature of these adducts was not understood and no studies had been made to determine the structures of the adducts. Banister has done much work on the $S_4N_4/SOCl_2/SeCl_2$,[145] and $S_4N_4/SOCl_2/$ Lewis acids systems.[146] The results of this work formed the basis of the $S_4N_4/S_3N_3Cl_3/SOCl_2$/Lewis acid system which has been demonstrated to be a source of $S_5N_5^+$. It is also known that S_4N_4 will react with thionylchloride to produce S_4N_3Cl and $S_3N_2Cl_2$,[147] but the role of thionyl chloride in the production of $S_5N_5^+$ is not known. The chemistry of $S_3N_3Cl_3$ with $SbCl_5$ was, therefore, studied in $SOCl_2$, as well as in the solvents SO_2 and CH_2Cl_2.

It was observed that when $S_3N_3Cl_3$ was combined with $SbCl_5$ in liquid SO_2 in a 1:2 molar ratio at room temperature, at least two products were formed. One of these was characterized as the $SbCl_6^-$ salt of the cyclotetrathiazyl dication, $S_4N_4(SbCl_6)_2$ by comparison of its Raman spectrum with the Raman spectrum of a pure sample of $S_4N_4(SbCl_6)_2$. The Raman spectrum of the other product, a green solid, suggested that it contained an $SbCl_5$ molecule co-ordinated to a nitrogen atom.

The Raman spectrum is shown in Fig. IV-1 and Table IV-1 lists the observed Raman frequencies and intensities as well as some assignments, made by Byler and Shriver,[129] for the vibrational modes involving the $SbCl_5$ unit in the adduct $CH_3CN{\cdot}SbCl_5$. It was also observed that $SbCl_3$, the usual reduction product formed whenever $SbCl_5$ acts as an oxidizing agent, could not be isolated by normal chemical means nor could any Sb(III) be detected in the Mössbauer spectrum of the crude mixture obtained from the reaction of $S_3N_3Cl_3$ with $SbCl_5$ in a 1:2 molar ratio.

Table IV-1

Raman Frequencies for $Cl_3S{\equiv}N{\cdot}SbCl_5$

$Cl_3S{\equiv}N{\cdot}SbCl_5$ $\Delta\nu$, (cm^{-1})	$CH_3C{\equiv}N{\cdot}SbCl_5$[129] $\Delta\nu$, (cm^{-1})	
44(19)		
66(14)		
74(17)		
83(13)		
102(9)		
126(6)		
130(7)	135(33)	$SbCl_4$ in-plane def.
149(9)		
167(18)	169(11)	$Cl-SbCl_4$ wag
171(19)		
175(13)	174(sh)(1)	$SbCl_4$ out-of-plane def.
184(17)	187(23)	$SbCl_4$ in-plane def.
192(8)		
280(11)	295(16)	$SbCl_4$ eq. str.
329(64)	344(100)	$SbCl_4$ eq. str.
336(49)	348(30)	Sb-Cl ax. str.
351(10)		
360(10)		
376(22)		
1394(6)		
1403(100)		

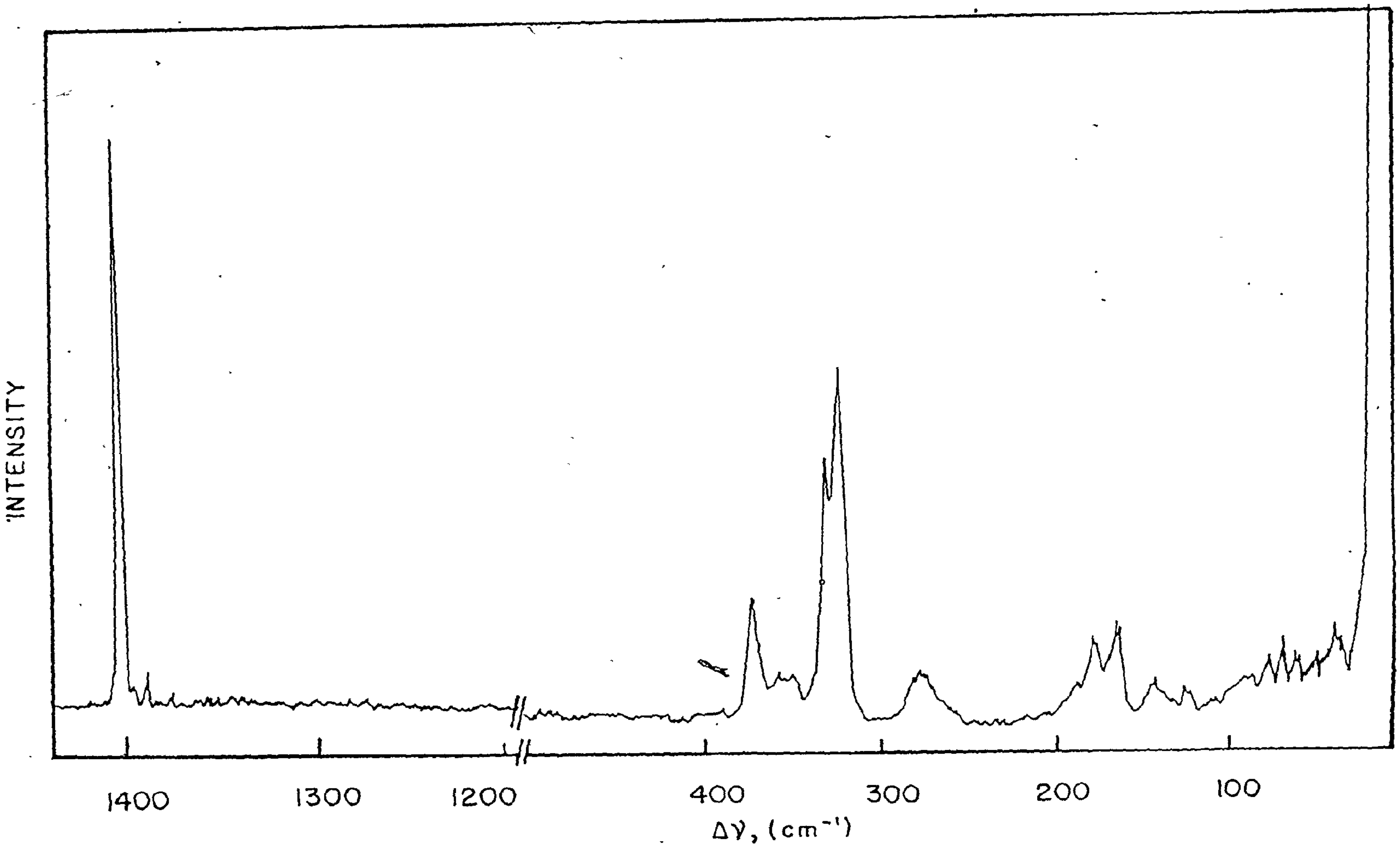
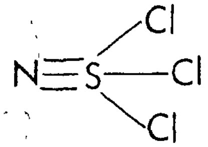


Figure IV-1 Raman spectrum recorded at -196°C of the green material isolated from the reaction of $S_3N_3Cl_3$ with $SbCl_5$ in a 1:2 molar ratio in liquid SO_2.

The oxidation state of the sulphur in $S_4N_4^{2+}$ is +3.5 which is consistent with $S_4N_4^{2+}$ being the reduction product in the oxidation of $S_3N_3Cl_3$ with $SbCl_5$. The green material may then be the oxidation product and the oxidation must involve a change in the valency of sulphur from four in $S_3N_3Cl_3$ to six in the product. The green material is therefore assumed to be a molecular adduct of $SbCl_5$ with thiazyl trichloride, $Cl_3S{\equiv}N{\cdot}SbCl_5$. The overall stoichiometry for the reaction of $S_3N_3Cl_3$ with $SbCl_5$ may perhaps be described by the following equation:

$$5S_3N_3Cl_3 + 9SbCl_5 \xrightarrow{SO_2} 3(S_4N_4)(SbCl_6)_2 + 3Cl_3S{\equiv}N{\cdot}SbCl_5$$

The assumption that the green material is $Cl_3S{\equiv}N{\cdot}SbCl_5$ seems to be reasonable but further proof is required. An attempt has been made to correlate the observed frequencies with those of the $SbCl_5{\cdot}CH_3CN$[129] adduct. The assignment of Sb-Cl vibrations by comparison with the work of Byler and Shriver is difficult due to the S-Cl vibrations in the same frequency range. The remaining vibrations are presumably due to thiazyl trichloride portion of the adduct. Thiazyl trichloride is unknown, however the corresponding fluoride and thiazyl trifluoride-antimony pentafluoride adduct[148] are known and thiazyl trichloride is expected to be isostructural with the fluoride, i.e., to have the following structure



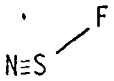
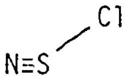
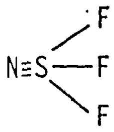
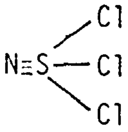
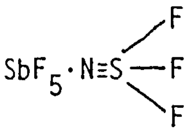
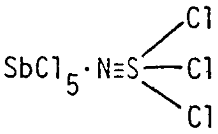
The molecule would be expected to have C_{3v} symmetry and, therefore, $3A_1$ and 3E Raman active fundamentals. Complexation with $SbCl_5$ would not change the symmetry of the thiazyl trichloride, however, it would cause shifts in observed band frequencies. It is important to note that the Raman spectrum of complexed $Cl_3S{\equiv}N$ would have only one high frequency fundamental involving motion of the sulphur and nitrogen atoms. Consequently, only one S-N vibration should be observed at a frequency above 1,000 cm^{-1}, the range for S-N triple bonds. The Raman spectrum in Fig. IV-1 shows only one high frequency vibration at 1403 cm^{-1}. Table IV-2 compares the high frequency fundamental for the thiazyl fluorides and chlorides.

In a molecular adduct of Cl_3SN with $SbCl_5$, the fundamental involving the S-N vibration would have a frequency lower than 1650 cm^{-1}, as observed in $SbF_5 \cdot F_3SN$, due to the lower Lewis acidity of $SbCl_5$ compared to SbF_5 and the lower electronegativity of chlorine in comparison to fluorine. The location of a band at 1403 cm^{-1} is reasonably consistent with this evaluation.

However, this comparison of thiazyl frequencies is not completely convincing. In going from thiazyl fluoride to thiazyl trifluoride, there is a frequency increase of 143 cm^{-1}. Once the thiazyl trifluoride is complexed to SbF_5, an additional frequency increase of 135 cm^{-1} occurs in the high frequency vibration involving the thiazyl group. This is an overall increase of 278 cm^{-1}. In comparison, it is expected that in going from NSCl to $Cl_3SN \cdot SbCl_5$ that the increase in S-N frequency would be greater than 78 cm^{-1}. Also, assuming that adduct formation of $NSCl_3$ with $SbCl_5$ would raise the S-N frequency by at least 50 cm^{-1}, then the difference between the S-N frequencies in NSCl and $NSCl_3$ would be rather small. More work is required on this system to identify the green material

Table IV-2.

Comparison of High Frequency Fundamentals for Thiazyl Halides

	1372 cm^{-1}. [150]		1325 cm^{-1} [149]
	1515 cm^{-1} [148]		1350 cm^{-1}
	1650 cm^{-1} [148]		1403 cm^{-1}

with certainty.

It was found that the use of thionyl chloride as a solvent in place of SO_2 did not change the reaction products obtained in the $S_3N_3Cl_3/SbCl_5$ system. It is therefore concluded that

i) Thionyl chloride does not react significantly with $S_3N_3Cl_3$ to produce unwanted side products;

ii) The $S_3N_3Cl_3 \cdot xSbCl_5$ (x = 1, 2 or 3) adducts, referred to by Banister, formed by the reaction of $S_3N_3Cl_3$ with $SbCl_5$ in a 1:3 molar ratio in $SOCl_2$ do not exist, but that rather the yellow-green precipitate formed consists of $S_4N_4(SbCl_6)_2$ and perhaps $SbCl_5 \cdot NSCl_3$;

iii) That there is no thiazyl cation generated and although Glemser and Mews[52] have shown that $S_5N_5^+$ may be obtained from S_4N_4 and SN^+, in the $S_3N_3Cl_3/S_4N_4/SbCl_5$ system the $S_5N_5^+$ must result from an oxidation of S_4N_4 by $S_4N_4^{2+}$ and $Cl_3S{\equiv}N \cdot SbCl_5$.

Banister's[46] preparation of $S_5N_5^+$ referred to in (ii) above was repeated and the reaction proceeds identically as described. Indeed, $S_4N_4^{2+}$ and $Cl_3NS \cdot SbCl_5$ were initially formed and these further reacted with added S_4N_4 to produce $S_5N_5^+$. The reaction sequence is then best described as follows

$$5S_3N_3Cl_3 + 9SbCl_5 \rightarrow 3(S_4N_4)(SbCl_6)_2 + 3Cl_3SN \cdot SbCl_5$$

$$Cl_3SNSbCl_5 + S_4N_4(SbCl_6)_2 + S_4N_4 \rightarrow (S_5N_5)(SbCl_6) + \text{other products}$$

It was also observed that $S_4N_4^{2+}$ could be obtained from $S_3N_3Cl_3$ and $SbCl_5$ if the reaction was carried out in methylene chloride. However, the reaction mixture first became orange-red in colour before yellow $S_4N_4(SbCl_6)_2$ was formed. If $S_3N_3Cl_3$ and $SbCl_5$ were combined in a 1:1 molar ratio in CH_2Cl_2, it was found that the red-orange mixture persisted and could be isolated if the solvent was removed. The material could most easily be crystallized from liquid SO_2 and the resulting material consisted of two crystalline forms. A crystal representative of each form was removed for X-ray crystallographic studies and they were shown to be $S_5N_5(SbCl_6)$ and $S_4N_4 \cdot SbCl_5$. The structures are discussed later in this chapter. Addition of one further mole of $SbCl_5$ to the red-orange mixture yielded within 24 h. the yellow $S_4N_4(SbCl_6)_2$.

The crystals of $S_5N_5SbCl_6$ obtained in this manner were red, however; Banister[146] has reported that $S_5N_5SbCl_6$ is yellow-orange. The $S_5N_5SbCl_6$ prepared by the reaction of the $S_4N_4(SbCl_6)_2/Cl_3SN \cdot SbCl_5$ mixture with S_4N_4 was also yellow-orange in colour. It was found that the red material exhibited an esr spectrum consisting of five lines with a g-value of 2.01 and a hyperfine coupling constant of 2.52 gauss. Comparison of these values with those obtained for $S_3N_2AsF_6$ ($g = 2.01$, $a = 3.15$ G) tend to suggest that the radical is not $S_3N_2^+$ but the data is nevertheless consistent with that of a sulphur-nitrogen radical containing two equivalent nitrogen atoms. The red colour is presumably due to the presence of this unidentified radical. The radical is possibly $S_2N_2^+$ which could readily dimerize to produce $S_4N_4^{2+}$.

In each instance, whenever $SbCl_5$ was added to $S_3N_3Cl_3$, a yellow solid immediately formed regardless of the solvent used in the reaction. This yellow material is the salt $(S_3N_2Cl_2^+)(SbCl_6^-)$, first prepared by Glemser by the action of $SbCl_5$ on $S_3N_3Cl_3$ in carbon tetrachloride.

$$S_3N_3Cl_3 + SbCl_5 \xrightarrow{CCl_4} (S_3N_3Cl_2^+)(SbCl_6^-)$$ 30

Thus, it was concluded that $S_3N_3Cl_2SbCl_6$ once formed in carbon tetrachloride does not undergo further reactions to produce any of the products obtained in other solvents.

A Raman spectrum of the solid material obtained was consistent with that reported for $S_3N_3Cl_2^+$,[30] and indicated no evidence for $S_4N_4^{2+}$, $S_5N_5^+$ or $S_4N_4 \cdot SbCl_5$.

It is worthy of note, that if $S_3N_3Cl_3$ is combined with $SbCl_5$ in a 1:1 molar ratio in liquid SO_2 for 24 h, no $S_4N_4 \cdot SbCl_5$ or $(S_5N_5)(SbCl_6)$ is produced. However, a Raman spectrum of the solid material indicated the presence $(S_4N_4)(SbCl_6)_2$ and $(S_3N_3Cl_2)(SbCl_6)$.

The results discussed to this point tend to suggest that the polarity of the solvents used in the oxidation process may have some effect upon reaction pathways. In CH_2Cl_2 or SO_2, the $S_3N_3Cl_2^+$ cation gave a red solution and some orange-red solid. A Raman spectrum of this material indicated that $S_5N_5^+$ and $S_4N_4 \cdot SbCl_5$ were formed in both instances. However, $S_4N_4^{2+}$ was also observed when SO_2 was employed as a solvent. A summary of the reactions is presented in Table IV-3.

Although the results obtained from this system are difficult to rationalize, the following conclusions seem to be reasonable.

i) The first step in the reaction of $S_3N_3Cl_3$ with $SbCl_5$ is formation of $(S_3N_3Cl_2)(SbCl_6)$, by simple chloride ion abstraction. It would appear that the subsequent oxidation process is inhibited by a non-polar solvent such as CCl_4, but is facilitated by use of more polar solvents such as CH_2Cl_2 and SO_2.

Table IV-3

A Summary of the Reactions of $S_3N_3Cl_3$ with $SbCl_5$ in Various Solvents

i) $S_3N_3Cl_3 + SbCl_5 \xrightarrow{CCl_4} (S_3N_3Cl_2^+)(SbCl_6^-)$

ii) $S_3N_3Cl_3 + SbCl_5 \xrightarrow{CH_2Cl_2} S_4N_4 \cdot SbCl_5 + (S_5N_5^+)(SbCl_6^-) + [(S_2N_2^+)(SbCl_6^-)]$

iii) $S_3N_3Cl_3 + SbCl_5 \xrightarrow{SO_2} (S_3N_3Cl_2)(SbCl_6) + (S_4N_4)(SbCl_6)_2$

iv) $5S_3N_3Cl_2 + 9SbCl_5 \xrightarrow[SOCl_2]{SO_2 \text{ or}} 3(S_4N_4)(SbCl_6)_2 + [3Cl_3SN \cdot SbCl_5]$

v) $S_3N_3Cl_3 + 2SbCl_5 \xrightarrow{CH_2Cl_2} S_4N_4(SbCl_6)_2$

vi) $(S_3N_3Cl_2)(SbCl_6) \xrightarrow{CH_2Cl_2} S_4N_4 \cdot SbCl_5 + S_5N_5(SbCl_6)$

vii) $(S_3N_3Cl_2)(SbCl_6) \xrightarrow{SO_2} S_4N_4(SbCl_6)_2 + S_4N_4 \cdot SbCl_5 + S_5N_5(SbCl_6)$

Note: a) Equations (ii), (iii), (v), (vi) and (vii) are not balanced and are meant only to indicate observed products.

b) The compounds $Cl_3SN \cdot SbCl_5$ and $(S_2N_2^+)(SbCl_6^-)$ enclosed in square brackets in the above equations are only suggested products.

ii) That the $(S_3N_3Cl_2)(SbCl_6)$ once formed in a polar solvent may produce $S_5N_5^+$, $S_4N_4^{2+}$ and $S_4N_4\cdot SbCl_5$, in a manner that is not clear, without addition of further $SbCl_5$.

iii) The product that has been assumed to be $Cl_3SN\cdot SbCl_5$ was observed only in preparations involving SO_2 or $SOCl_2$ as solvents.

iv) Addition of one further mole of $SbCl_5$ to reaction mixtures from $S_3N_3Cl_3$ and $SbCl_5$ in a 1:1 molar ratio in SO_2 or CH_2Cl_2 produced the $S_4N_4^{2+}$ cation. The fate of any $S_5N_5^+$ present is not known. It was observed that $S_5N_5^+$ does not react with $SbCl_5$ in SO_2. The $S_4N_4\cdot SbCl_5$ present is readily further oxidized to $S_4N_4^{2+}$.

v) The formation of $S_4N_4\cdot SbCl_5$; $S_5N_5(SbCl_6)$ and the unidentified radical would seem to occur more readily in CH_2Cl_2.

It is difficult to explain the observation that $S_4N_4\cdot SbCl_5$ and $S_5N_5\cdot SbCl_6$ were produced when $(S_3N_3Cl_2)(SbCl_6)$ was in contact with SO_2 but not when $S_3N_3Cl_3$ was reacted directly with $SbCl_5$ in SO_2.

The conclusions are summarized in the following proposed reaction sequence.

$$S_3N_3Cl_3 + SbCl_5 \rightarrow (S_3N_3Cl_2^+)(SbCl_6^-)$$

$$\downarrow$$

$$S_4N_4\cdot SbCl_5 + (S_5N_5^+)(SbCl_6) + S_2N_2SbCl_6$$

$$\downarrow + SbCl_5$$

$$(S_4N_4^{2+})(SbCl_6^-)_2 + \text{other products}$$

This sequence is speculative and no attempt will be made to give any mechanistic explanation for the formation of the products. This study does, however, indicate that the oxidation of $S_3N_3Cl_3$ with $SbCl_5$ is complex and more work is required to fully understand the system.

IV-3 The $S_3N_3F_3$/Lewis Acid System

The Lewis acid chemistry of $S_3N_3F_3$ was reviewed in the introduction. Glemser has demonstrated, with Lewis acids such as AsF_5 and SbF_5 that $S_3N_3F_3$ behaves as a fluoride ion donor to give the cation $S_3N_3F_2^+$.[30]

$$S_3N_3F_3 + MF_5 \xrightarrow{SO_2} (S_3N_3F_2^+)(MF_6^-) \qquad M = Sb \text{ or } As$$

Thus, it is apparent that $S_3N_3F_3$ behaves somewhat similarly to $S_3N_3Cl_3$ in this respect. Glemser has shown that $S_3N_3F_2^+$ is obtained from $S_3N_3F_3$ and SbF_5 in a 1:1 molar ratio, whereas $S_3N_3F_2^+$ is obtained from $S_3N_3F_3$ and AsF_5 in a 1:4 molar ratio.

The purpose of the present study was to determine if $S_3N_3F_3$ could be oxidized, to produce new cationic species, by reaction with higher molar ratios of Lewis acid to $S_3N_3F_3$. For this purpose, $S_3N_3F_3$ was combined with AsF_5, SbF_5 and SO_3 in the molar ratios 1:6, 1:6 and 1:3, respectively. The results obtained are summarized in the equations, for formation of the SN^+

$$S_3N_3F_3 + AsF_5 \xrightarrow{SO_2} (SN^+)(AsF_6^-) + \text{at least one unidentified product}$$
$$S_3N_3F_3 + 6SbF_5 \xrightarrow{SO_2} 3(SN^+)(Sb_2F_{11}^-)$$
$$S_3N_3F_3 + 3SO_3 \xrightarrow{SO_2} 3(SN^+)(SO_3F)$$

cation was verified in each instance by Raman spectroscopy. Figures IV-2, IV-3 and IV-4 illustrate the spectra and Table IV-4 lists the vibrational frequencies for each of the thiazyl salts.

Note: All products of the reaction of $S_3N_3F_3$ with AsF_5 were not characterized and therefore a stoichiometric equation is not given.

Table IV-4

Raman Frequencies for Thiazyl Salts

(SN)(SO$_3$F) Δν,(cm^{-1})	KSO$_3$F 152 Δν,(cm^{-1})		(SN)(Sb$_2$F$_{11}$) Δν,(cm^{-1})	Cs(Sb$_2$F$_{11}$) 153 Δν,(cm^{-1})	XeF$^+$Sb$_2$F$_{11}^-$ 153 Δν,(cm^{-1})		(SN)(AsF$_6$) + unidentified product Δν,(cm^{-1})		(S$_3$N$_3$F$_2$)(AsF$_6^-$) 30 Δν,(cm^{-1})
52(26)									
							64(28)		
68(18)									
							109(30)		
78(11)									
							139(24)		225(s)
85(9)									
							176(10)		258(m)
100(15)									
							225(20)		329(s)
113(6)									
							327(6)		362(m)
119(9)									
							360(14)	ν_5(AsF$_6^-$)	390(m)
130(33)									
							369(28)		430(vw)
139(11)									
							407(8)		457(m)
150(6)									
			222(59)	232(26)	212(5)		497(28)		524(m)
163(13)									
			233(21)	291(39)	226(12)		553(24)		572(m)
178(7)									
			271(5)		269(11)		558(18)		627(vw)
221(3)									
			300(32)	330(39)	293(8)		572(18)		677(vs)
405(6)	405(3)	ν_6(e) S-F defn							
				332(4)			580(sh)	ν_2(AsF$_6^-$)	695(m)
420(10)									
							608(20)		713(m)
499(4)									
							680(88)	ν_1(AsF$_6^-$)	729(m)
562(2)									
			497(44)	521(15)		Sb$_2$F$_{11}^-$			
									733(vw)
572(2)	571(2)	ν_3(a) SO$_3$ sym defn							
					518(16)				761(vw)
581(3)	587(2)	ν_5(e) SO$_3$ asym defn	585(32)	597(4)	603(< 1)				
									785(w)
594(2)									
					651(39)				800(w)
			647(94)	603(15)	669(9)				825(vw)
778(2)	741(2)	ν_2(a) S-F str							
				654(100)					901(w)
794(7)	821(1)	2 x ν_6(e)	673(sh)		678(8)				
1058(100)									
	1084(10)	ν_1(a) SO$_3$ sym str	680(100)	685(93)	688(48)				
1063(55)									
				692(93)			1023(8)		1059(s)
210(7)									1120(w)
228(6)									
	1285(1)	ν_4(e) SO$_3$ asym str					1190(20)		
256(41)									
263(16)									
							1428	S^{34}≡N(4)	
425(4)	S^{34}≡N str						1438	S≡N(100)	
438(90)	S≡N str		1436(100) S≡N str						

sh = shoulder; vs = very strong; s = strong; m = medium, w = weak; vw = very weak

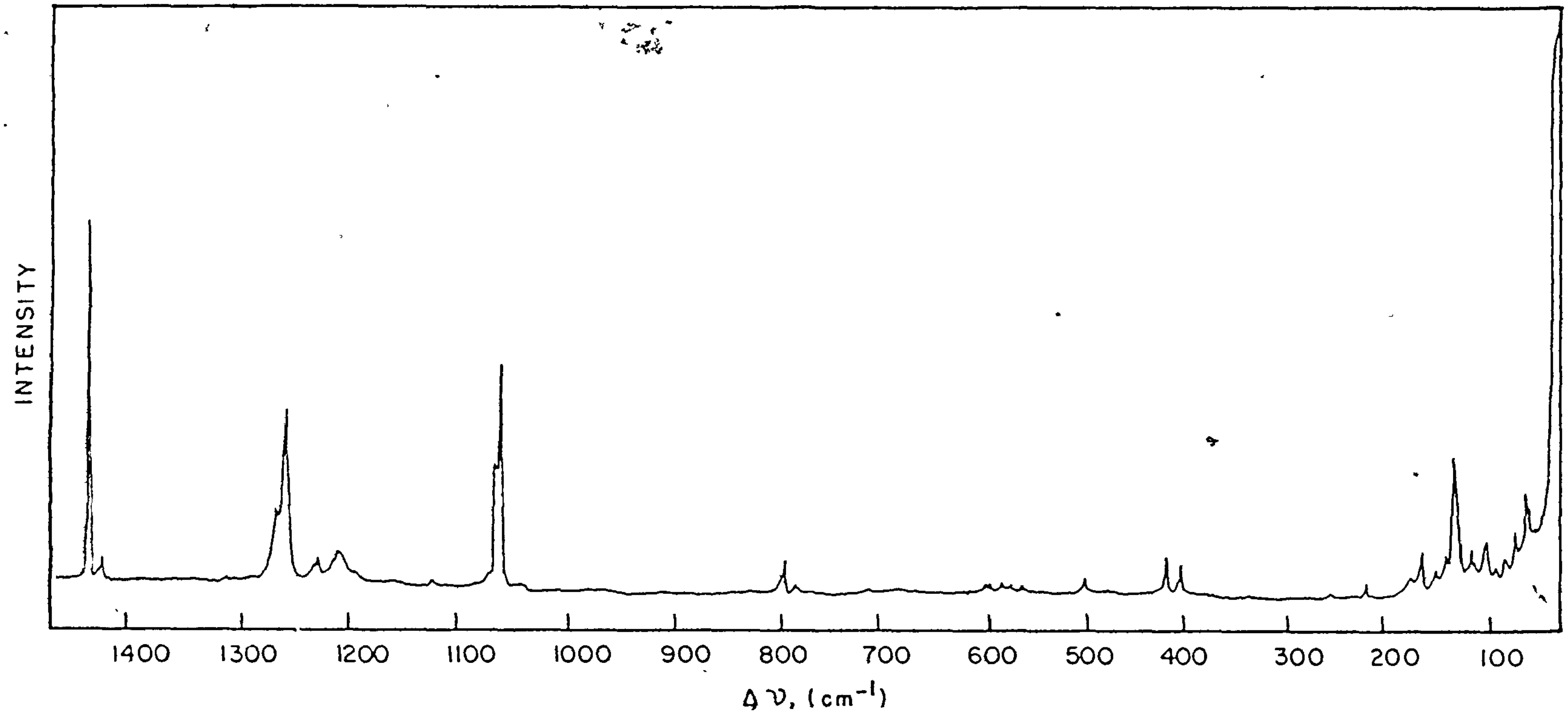


Figure IV-2 Raman spectrum of $SN(SO_3F)$ recorded at -196°C.

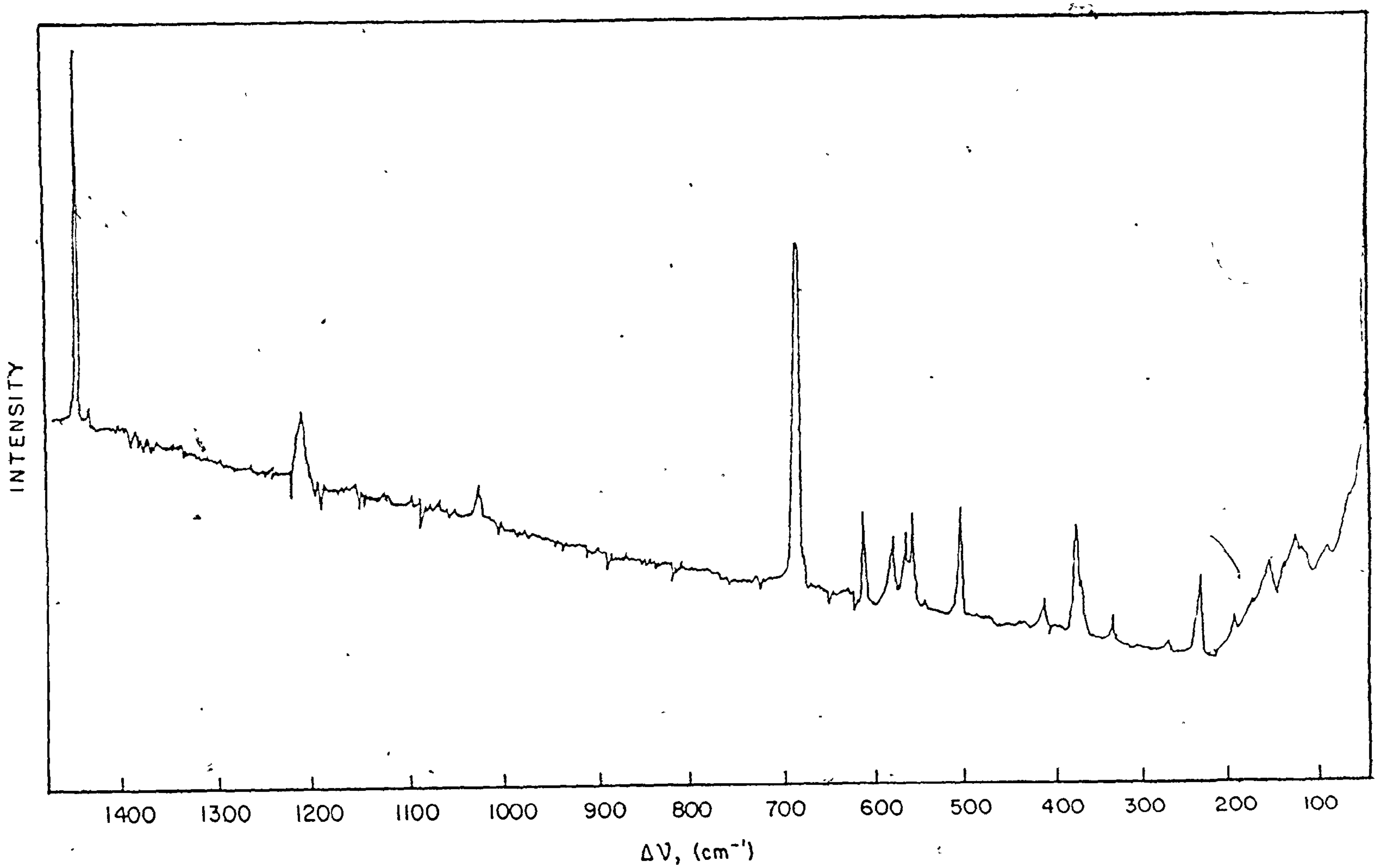


Figure IV-3 Raman spectrum of $SN(AsF_6)$ and other unidentified products recorded at -196°C.

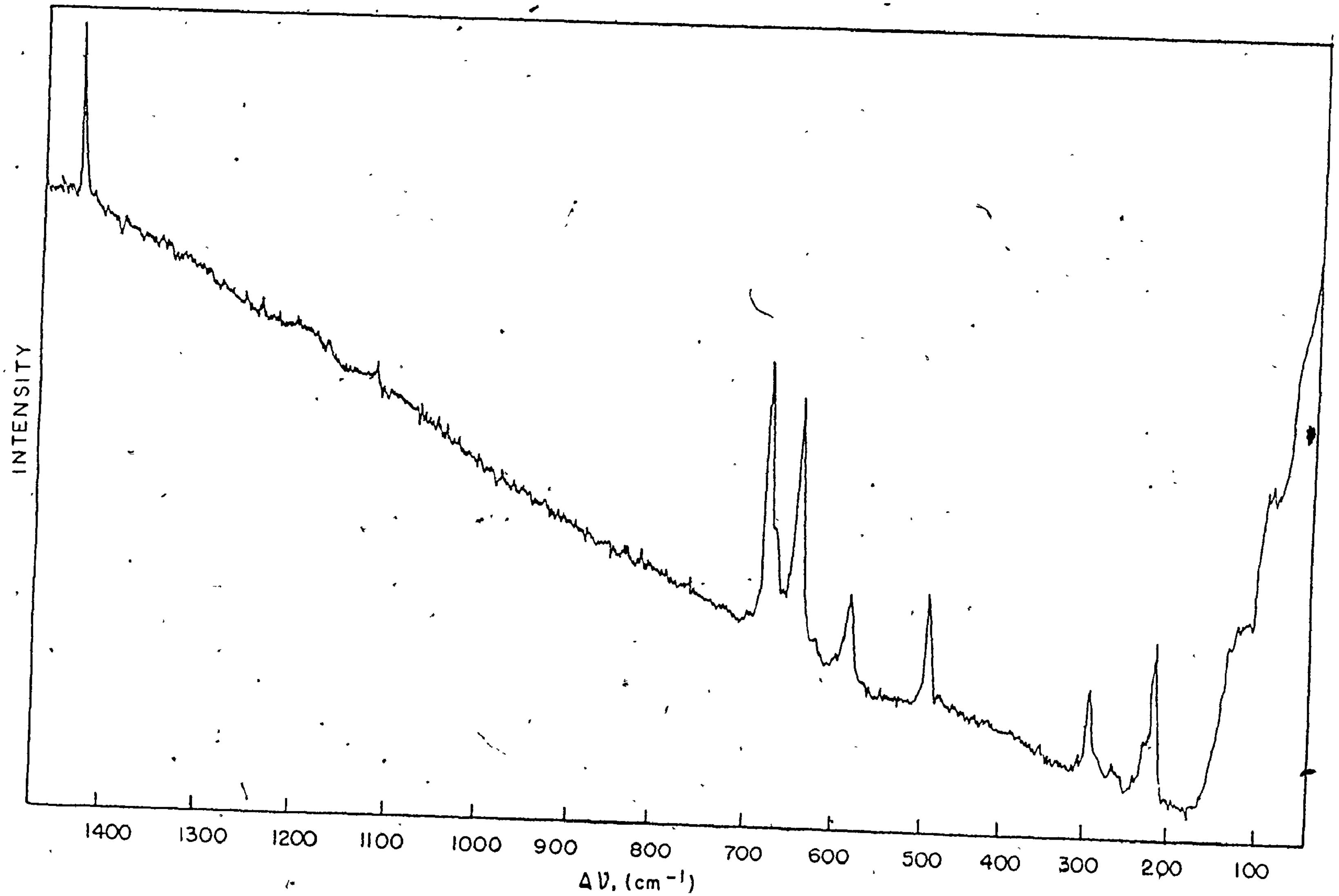


Figure IV-4 Raman spectrum of $SN(Sb_2F_{11})$ recorded at -196°C.

An attempt has been made to correlate the Raman spectrum of (SN)(SO_3F) with that reported for KSO_3F. The band due to the SN stretch is located at 1438 cm^{-1} and is comparable to that reported by Glemser for SN^+ (1437 cm^{-1}) in (SN)(AsF_6). This indicates that there is probably little cation-anion interaction in the form of a fluorine bridge. However, the Raman spectrum of (SN)(SO_3F) indicates that ν_1 (1058 cm^{-1}, 1063 cm^{-1}), the totally symmetric vibration for the anion, is split. This must be a result of factor group splitting since site symmetry lowering cannot split a non-degenerate vibration. It is also noted that ν_4, the SO_3 asymmetric stretch is split into four bands. Again, this is a result of either factor group splitting or site symmetry lowering. Due to the absence of crystallographic data, it is not possible to analyze the spectrum in terms of site symmetry and/or factor group splitting effects. Many of the weak bands cannot be assigned and are attributed to impurities.

In a 1:2 molar ratio, $S_3N_3F_3$ was also combined with AsF_5 and SbF_5. The Raman spectrum of the products could not be obtained due to strong background fluorescence; however, ^{19}F nmr spectra were obtained. The ^{19}F nmr spectra each contained a singlet at -5.38 ppm for the SbF_5 system and -5.34 ppm for the AsF_5 system. The signals are presumably due to $S_3N_3F_2^+$ although Glemser reported δ = -6.12 ppm for $S_3N_3F_2(AsF_6)$ and δ = -6.7 ppm for $S_3N_3F_2(SbF_6)$ with respect to external $CFCl_3$.[30] One additional singlet was observed at δ = -2.17 ppm in the nmr spectra of solutions obtained by combining $S_3N_3F_3$ and AsF_5 in 1:2 and 1:6 molar ratios. The species responsible for this singlet is probably also responsible for the vibrational bands observed in the reported Raman spectrum in Table IV-4 for the $S_3N_3F_3/AsF_5$ system which were not interpreted. It is reasonable to speculate that this unidentified compound may be $S_3N_3F^{2+}$ for the following reasons:

i) it is not $S_3N_3F_2^+$, since its vibrational spectrum is not comparable to that of $S_3N_3F_2^+$;

ii) although some $(SN^+)(AsF_6^-)$ is produced, the existence of $S_3N_3F^{2+}$ is consistent with the fact that AsF_5 is a poorer fluoride ion acceptor than SbF_5 and therefore removal of the final fluorine from $S_3N_3F^{2+}$ would be less efficient than in the SbF_5 system.

The Raman frequencies of $(SN)(Sb_2F_{11})$ are listed in Table IV-4 and are compared to the Raman data for $CsSb_2F_{11}$[153] and $XeFSb_2F_{11}$.[153] A complete assignment of the anion frequencies of $SN(Sb_2F_{11})$ is not possible but there is generally good agreement with the frequencies observed for other compounds containing this anion. Again, the stretch due to the SN^+ cation occurs at the expected frequency (1436 cm^{-1}).

The Raman spectrum of the product of the reaction of one mole of $S_3N_3F_3$ with 6 moles of AsF_5 is consistent with the formation of $SN(AsF_6)$. Table IV-4 shows that ν_3 and ν_5 of the AsF_6^- anion are split and this is due to the lowering of symmetry of the AsF_6^- anion as a result of solid state effects. The S-N stretch occurs at 1438 cm^{-1} and is essentially identical to that reported previously for $SN(AsF_6)$.

In the Raman spectra of $SN(SO_3F)$ and $SN(AsF_6)$, resolution was sufficient to detect one additional high frequency band at 1427 cm^{-1}. This band is attributed to the presence of $^{34}S{\equiv}N^+$ for which the calculated frequency is 1426 cm^{-1}.

It has been shown previously that $S_3N_3Cl_3$ combines with SO_3 to form the trichlorotrioxocyclotrithiazene $S_3N_3Cl_3O_3$ via the molecular adduct $S_3N_3Cl_3 \cdot 6SO_3$.[57] However, this study has indicated that the analogous $S_3N_3F_3O_3$ is not produced if $S_3N_3F_3$ is combined with SO_3, but rather the $S_3N_3F_3$ ring is depolymerized to produce thiazyl fluorosulphate.

It is apparent, therefore, that $S_3N_3F_3$ does not undergo oxidation in the presence of oxidizing Lewis acids as $S_3N_3Cl_3$ does. Instead, the fluoride acts as a fluoride ion donor with successive loss of fluoride ion to yield the thiazyl cation.

$$S_3N_3F_3 + MF_5 \rightarrow (S_3N_3F_2^+)(MF_6^-)$$

$$\downarrow MF_5$$

$$(S_3N_3F^{+2})(MF_6^-)_2$$

$$\downarrow MF_5$$

$$3(SN^+)(MF_6^-)$$

IV-4 Mass Spectra of $S_3N_3F_3$ and $S_3N_3Cl_3$

The mass spectral data for the fluoride and chloride are listed in Table IV-5. In each instance, m/e intensities that were less than 10% relative to the most intense band are not reported unless their identity was obvious. The mass spectral data is in agreement with the respective chemical behaviour of the cyclotrithiazenes with Lewis acids. That is, $S_3N_3Cl_3$ undergoes successive loss of chloride ion while the

Table IV-5

Mass Spectra of $S_3N_3F_3$ and $S_3N_3Cl_3$

$S_3N_3Cl_3$	m/e	Relative Intensity	$S_3N_3F_3$	m/e	Relative Intensity
			S_8^+	256	
$S_3N_3{}^{37}Cl_2^+$	213	13	S_7^+	224	
$S_3N_3{}^{35}Cl^{37}Cl^+$	210	46	S_6^+	192	
$S_3N_3{}^{35}Cl_2^+$	208	65	S_5^+	160	< 1%
$S_3N_3{}^{37}Cl^+$	175	6	$S_3N_3^+$	138	
$S_3N_3{}^{35}Cl^+$	173	13	NSF_3^+	103	
$S_3N_3^+$	138	41	$S_2N_2^+$	92	3
$S_2N_2{}^{37}Cl^+$	129	25	?	85	13
$S_2N_2{}^{35}Cl^+$	127	53	?	81	9
$N^{35}Cl_2{}^{37}Cl^+$	121	< 1	S_2N^+	78	7
$N^{35}Cl_3^+$	119	3	FSN	65	94
$NS^{35}Cl^{37}Cl^+$	118	< 1	?	48	11
$NS^{35}Cl_2^+$	116	2	SN^+	46	100
?	94	6	S^+	32	11
$S_2N_2^+$	92	60			
$NS^{37}Cl^+$	83	10			
$NS^{35}Cl^+$	81	26			
${}^{37}Cl_2^+$	74	3			
${}^{37}Cl^{35}Cl^+$	72	19			
${}^{35}Cl_2^+$	70	28			
${}^{37}S\text{-}Cl^+$	69	5			
${}^{35}S\text{-}Cl^+$	67	13			
S_2^+	64	6			
?	48	11			
SN^+	46	100			
$H^{37}Cl^+$	38	4			
${}^{37}Cl^+$	37	13			
$H^{35}Cl^+$	36	12			
${}^{35}Cl^+$	35	28			

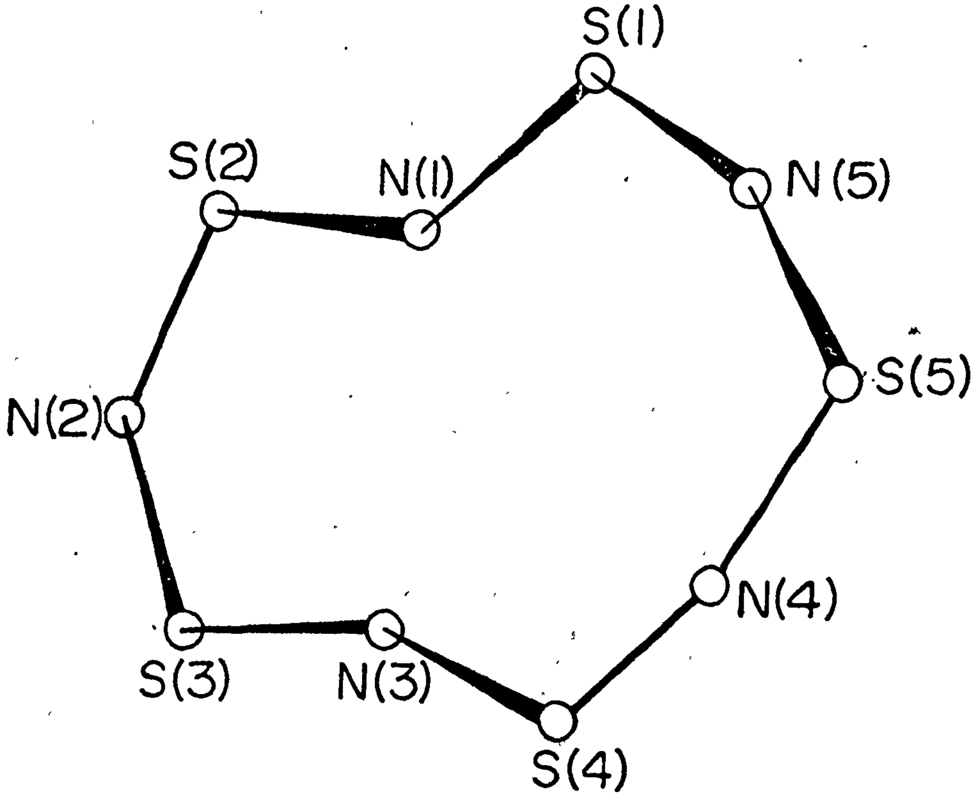
fluoride in contrast simply depolymerizes to produce thiazyl fluoride which ultimately produces SN^+. It is also important to note that the species $S_2N_2^+(S_4N_4^{2+})$ is observed in much greater abundance in the mass spectrum of the chloride than the fluoride. Again this is consistent with what is observed chemically in that $S_3N_3Cl_3$ is a source of $S_4N_4^{2+}$ in the presence of an oxidizing Lewis acid whereas $S_3N_3F_3$ is not. It would appear therefore that the mass spectra of the sulphur nitrides may give some insight into their chemical behaviour in oxidizing media.

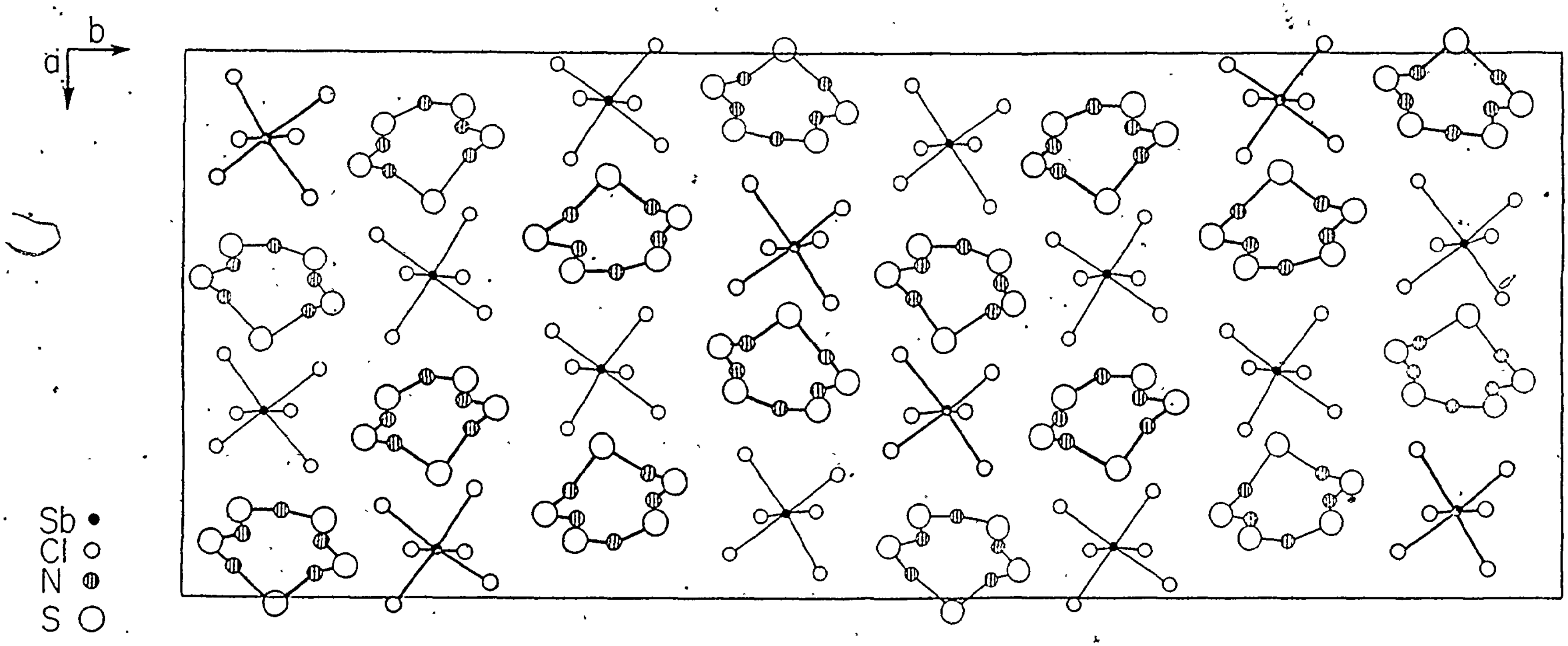
IV-5 The Crystal Structure of $S_5N_5(SbCl_6)$

The X-ray crystallography was performed by Dr. D.R. Slim of this department and the relevant crystal data are reported in Table IV-6. Bond lengths and bond angles are given in Table IV-7. The $S_5N_5^+$ cation and unit cell for $S_5N_5(SbCl_6)$ are shown in Figures IV-5 and IV-6, respectively.

The $S_5N_5^+$ ring in the $SbCl_6^-$ salt is structurally somewhat different to the regular azulene-like geometries reported for the $S_5N_5^+$ ring in the compounds $S_5N_5(S_3N_3O_4)$ [54] and $S_5N_5(SnCl_5OPCl_3)$.[55] This is a result of the sulphur-nitrogen bond distances in the two latter salts varying to a lesser extent (1.52 Å to 1.58 Å in $S_5N_5(S_3N_3O_4)$ and 1.54 Å to 1.58 Å in $S_5N_5(SnCl_5OPCl_3)$) than in the $SbCl_6^-$ salt in which the sulphur-nitrogen bond distances vary from 1.43 Å to 1.66 Å. This variation in bond distances is more pronounced on one-half of the ring and has not been observed in the other $S_5N_5^+$ systems. It is worthy of note that both $S_5N_5(S_3N_3O_4)$ and $S_5N_5(SnCl_5OPCl_3)$ belong to the space group $P_{21/c}$. This particular space group has no crystallographic mirror plane that would bisect the $S_5N_5^+$ ring thus making equivalent sulphur-nitrogen bond distances and angles equal. However, both of these $S_5N_5^+$ salts have been

Figure IV-5 The $S_5N_5^+$ Cation





PROJECTION OF THE STRUCTURE DOWN THE "C"-AXIS

Figure IV-6 The unit cell diagram of $S_5N_5(SbCl_6)$.

Table IV-6

Crystal Data for $S_5N_5(SbCl_6)$

Space Group	Fddd orthorhombic
Unit Cell Dimensions	a = 18.05(1)
	b = 46.72(1)
	c = 7.68(3)
Final unweighted R-factor	0.0392

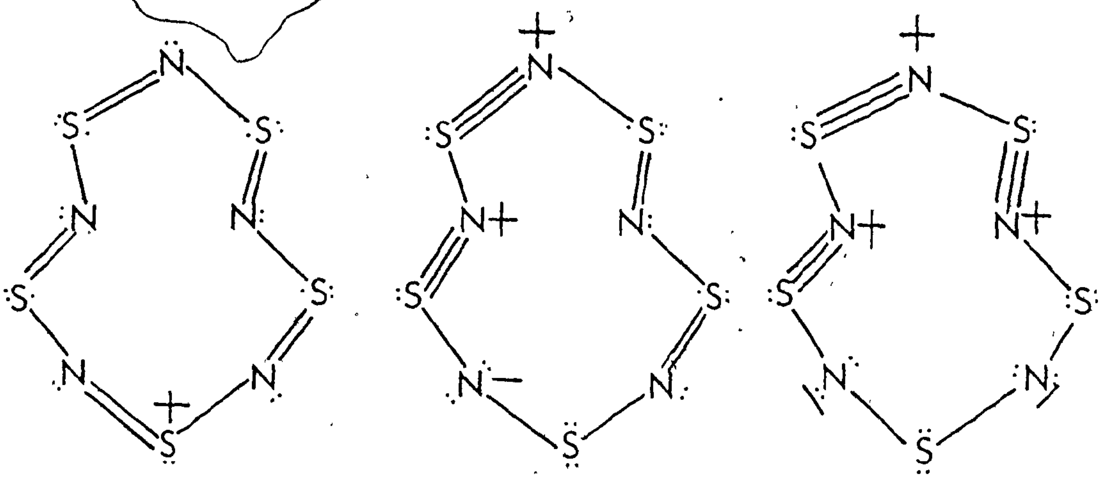
Table IV-7

Bond Lengths and Bond Angles for $(S_5N_5)(SbCl_6)$

Bond Lengths (Å)		Bond Angles in Degrees	
Sb-Cl(1)	2.346(4)	Cl(1)-Sb-Cl(2)	177.2(2)
Sb-Cl(2)	2.381(4)	Cl(1)-Sb-Cl(3)	89.7(1)
Sb-Cl(3)	2.370(4)	Cl(1)-Sb-Cl(4)	89.6(2)
Sb-Cl(4)	2.373(5)	Cl(1)-Sb-Cl(5)	92.1(2)
Sb-Cl(5)	2.322(5)	Cl(1)-Sb-Cl(6)	90.8(1)
Sb-Cl(6)	2.352(4)	Cl(2)-Sb-Cl(3)	89.8(1)
		Cl(2)-Sb-Cl(4)	87.6(2)
		Cl(2)-Sb-Cl(5)	90.7(2)
S(1)-N(1)	1.55(1)	Cl(2)-Sb-Cl(6)	89.6(1)
S(1)-N(5)	1.53(2)	Cl(3)-Sb-Cl(4)	89.8(2)
S(2)-N(1)	1.56(1)	Cl(3)-Sb-Cl(5)	89.4(2)
S(2)-N(2)	1.54(1)	Cl(3)-Sb-Cl(6)	179.4(2)
S(3)-N(2)	1.56 (1)	Cl(4)-Sb-Cl(5)	178.1(2)
S(3)-N(3)	1.49(2)	Cl(4)-Sb-Cl(6)	89.8(2)
S(4)-N(3)	1.53(2)	Cl(5)-Sb-Cl(6)	91.0(2)
S(4)-N(4)	1.43(2)		
S(5)-N(4)	1.66(2)	S(1)N(5)S(5)	151.2(13)
S(5)-N(5)	1.56(2)	N(5)S(5)N(4)	121.1(10)
		S(5)N(4)S(4)	157.8(13)
		N(4)S(4)N(3)	115.7(10)
		S(4)N(3)S(3)	154.5(12)
		N(3)S(3)N(2)	111.3(9)
		S(3)N(2)S(2)	137.6(12)
		N(2)S(2)N(1)	108.7(8)
		S(2)N(1)S(1)	136.6(8)
		N(1)S(1)N(5)	107.6(8)

described in the literature as having bond distances and angles that are related by a mirror plane. At present, the larger variation in the sulphur-nitrogen bond distance in $S_5N_5(SbCl_6)$ is an observation that is not possible to explain. It may, however, be a result of thermal motion that was not corrected for in the present structural determination.

The $S_5N_5^+$ cation obeys the Hückel 4n + 2 rule having 14π electrons and therefore may perhaps be considered to be an aromatic S-N ring system. As for $S_4N_4^{2+}$, a valence bond description of $S_5N_5^+$ does not adequately explain the observed bond distances.


A B C

Resonance forms of type A are not sufficient since participation of the lone pair on nitrogen in the bonding is required to explain the large S-N-S bond angles. Forms B and C account for this as well as the short bond lengths observed of 1.43 Å and 1.49 Å, which would indicate some triple bond character, but have charges on many of the atoms making these forms unfavourable. Participation of the nitrogen lone-pairs in the bonding is also inconsistent with the idea of a Hückel 14π-electron molecular orbital description.

IV-6 The Crystal Structure of $S_4N_4\cdot SbCl_5$

The crystal structure of $S_4N_4\cdot SbCl_5$ was first determined in 1960 by Neubauer and Weiss.[33] The structure was not refined and high accuracy was not claimed. As a consequence, the SN bond distances and bond angles are not comparable to those reported for the $S_4N_4\cdot BF_3$[28] adduct. In the course of this work, the structure of the $S_4N_4\cdot SbCl_5$ adduct was redetermined with greater accuracy than reported by earlier workers. The crystallographic data are reported in Tables IV-8 and IV-9, the unit cell diagram and molecular structure are illustrated in Figures IV-7 and IV-8.

The structure is comparable with the BF_3 adduct and there are no significant differences in bond lengths and bond angles between the two adducts. It is apparent that co-ordination with a Lewis acid results in an opening of the S_4N_4 cage to a puckered ring as electron density is removed in the formation of a bond between nitrogen and antimony. The resulting geometry places each of the sulphur atoms in a plane with the nitrogen atoms arranged so that the S_4N_4 ring is boat-shaped.

Fig. IV-9 illustrates some valence bond resonance forms for the molecular adduct. Resonance forms of this type give approximate proper weighting to each S-N bond such that the S-N bond involving the nitrogen co-ordinated to a donor site would be expected to be the longest. However, such explanations are very inadequate and do not properly explain the bonding in the ring.

IV-7 Bonding in Sulphur-Nitrogen Ring Systems

The literature contains papers which attempt to rationalize the bonding in sulphur nitrides, particularly the cyclic sulphur nitrides.

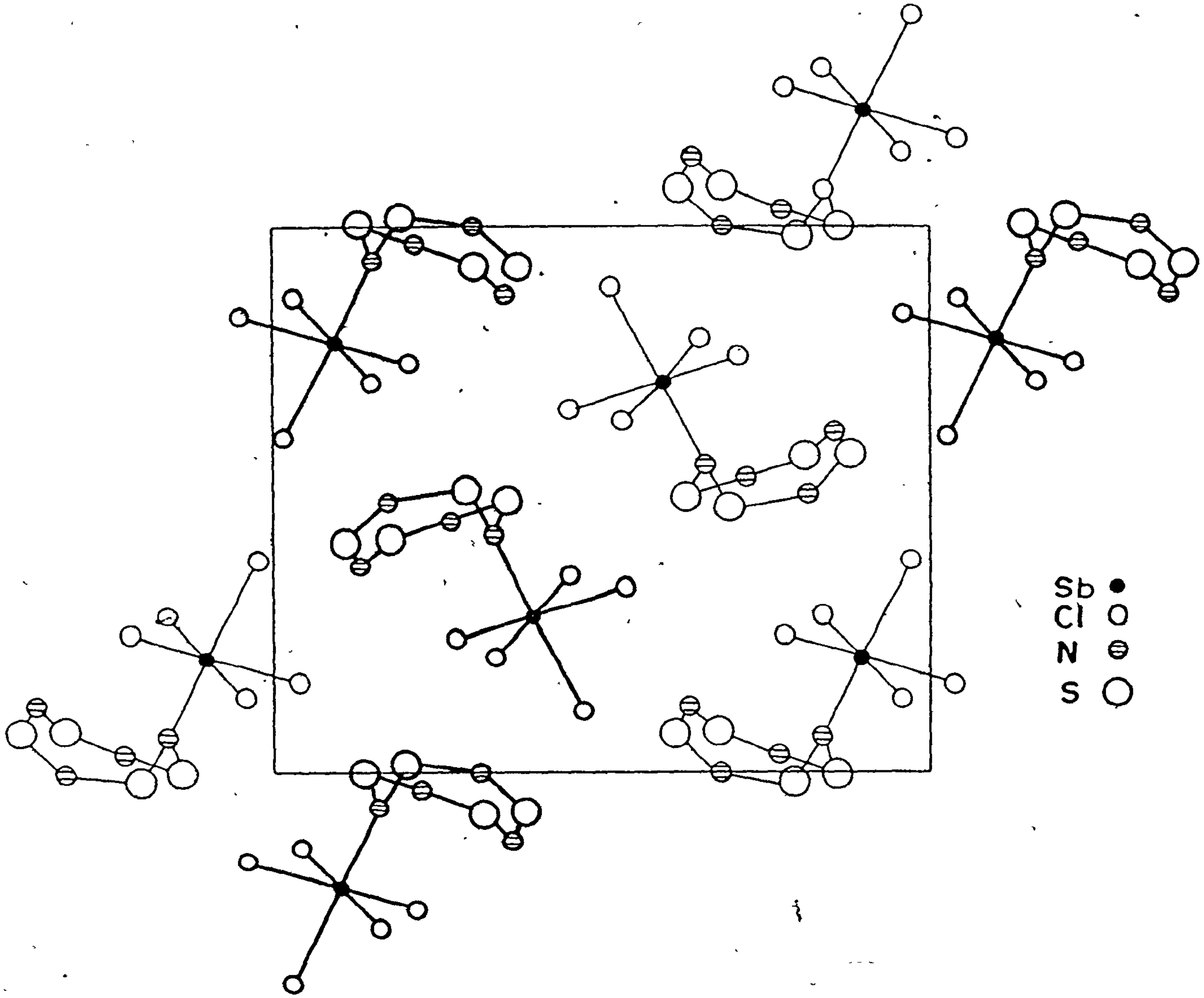
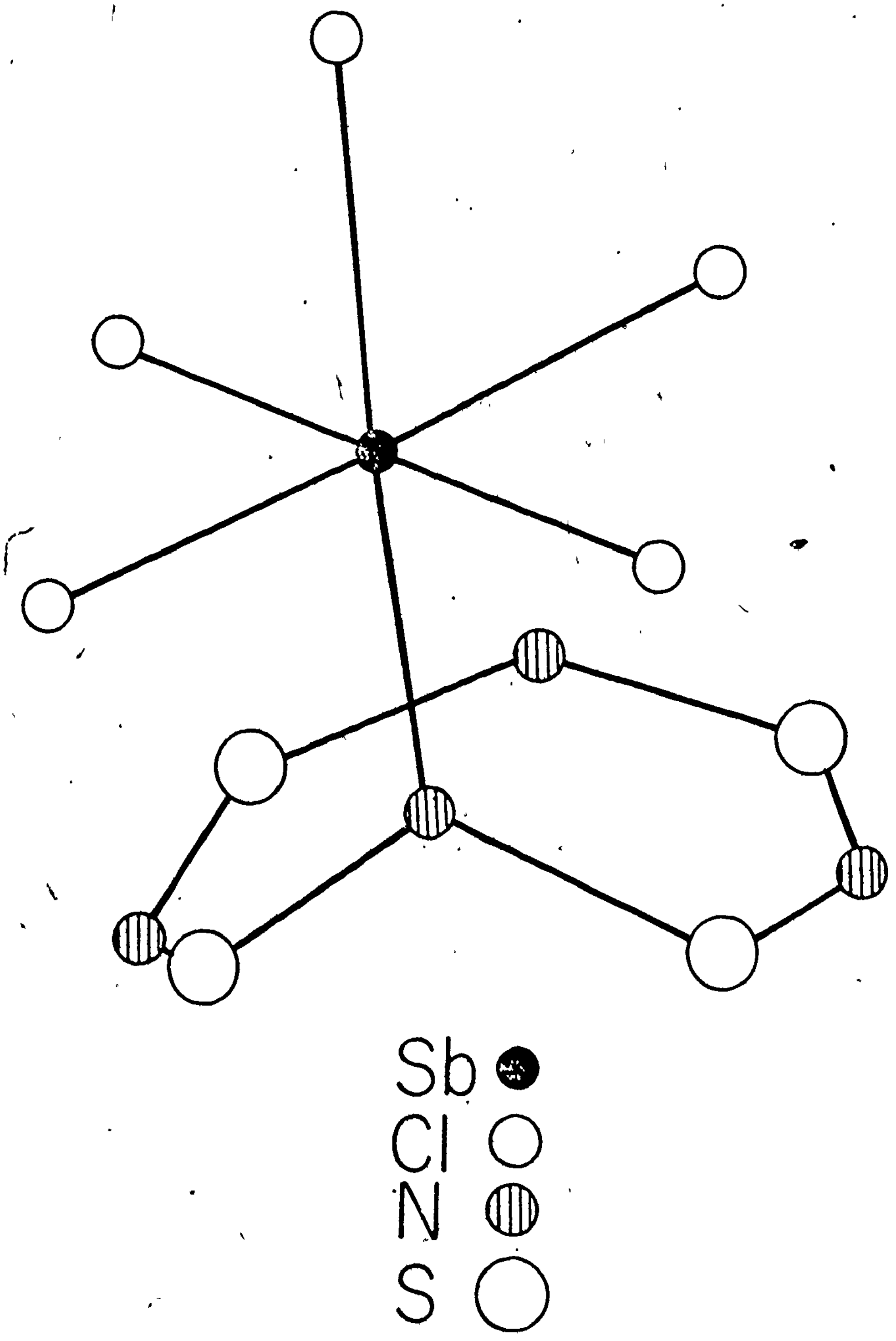


Figure IV-7 The unit cell diagram of $S_4N_4 \cdot SbCl_5$

Figure IV-8 The Molecular Adduct $S_4N_4 \cdot SbCl_5$



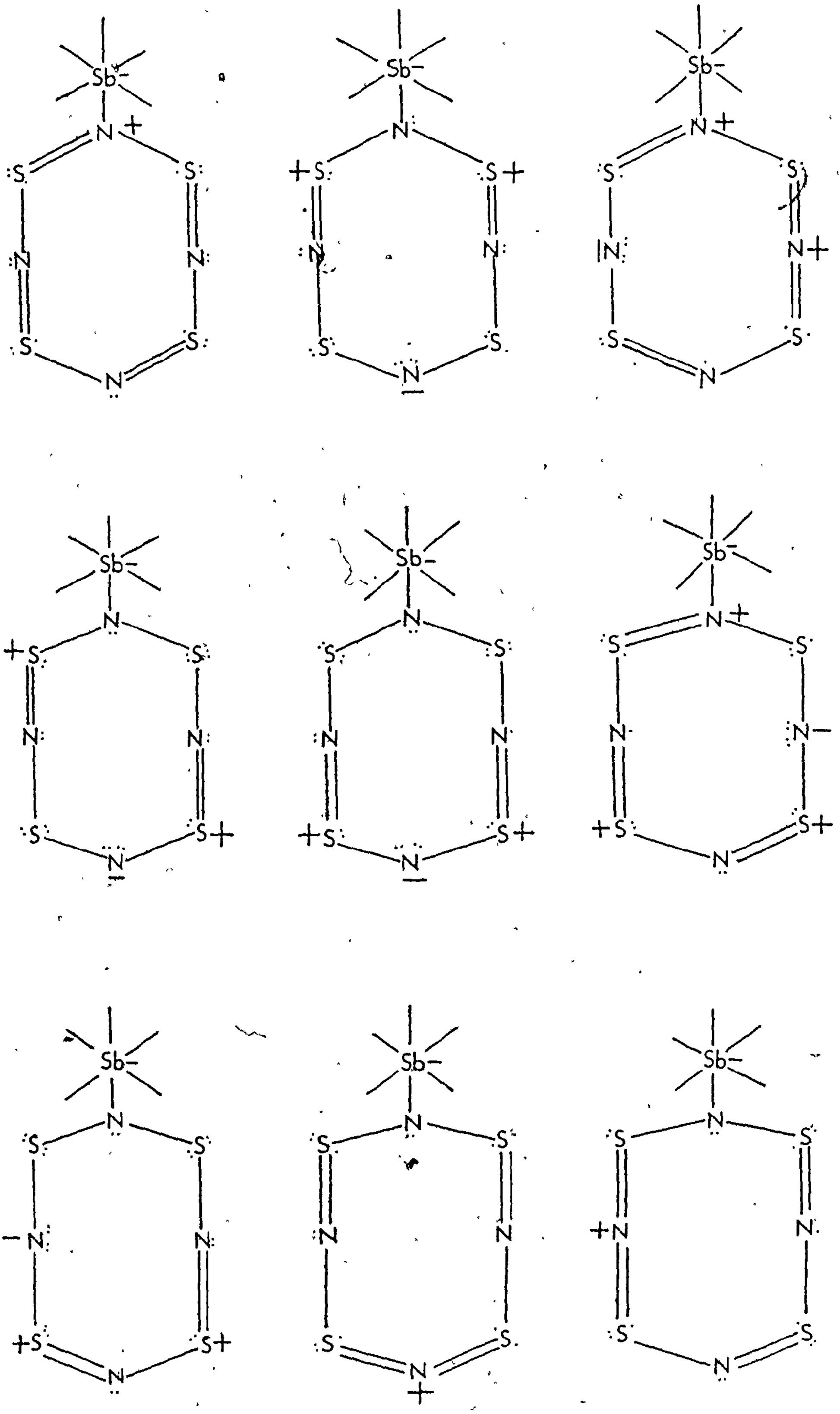


Figure IV-9. Valence Bond Resonance Forms for the Molecular Adduct $S_4N_4 \cdot SbCl_5$

Table IV-8

Crystal Data for $S_4N_4 \cdot SbCl_5$

Space Group	$P_{21/c}$ monoclinic	
Unit Cell Dimension	a = 6.96	
	b = 12.40	β = 107.1(0)
	c = 15.22	
Final unweighted R-factor	0.0527	

Table IV-9

Bond Lengths and Bond Angles for $S_4N_4 \cdot SbCl_5$

Bond Lengths in Å		Bond Angles in Degrees	
Sb-Cl(1)	2.334 (3)	Cl(1)-Sb-Cl(2)	91.71 (1)
Sb-Cl(2)	2.359 (3)	Cl(1)-Sb-Cl(3)	91.74 (1)
Sb-Cl(3)	2.360 (3)	Cl(1)-Sb-Cl(4)	90.92 (1)
Sb-Cl(4)	2.352 (3)	Cl(1)-Sb-Cl(5)	91.88 (1)
Sb-Cl(5)	2.342 (3)	Cl(1)-Sb-N(1)	179.78 (2)
Sb-N(1)	2.134 (7)	Cl(2)-Sb-Cl(3)	176.50 (1)
		Cl(2)-Sb-Cl(4)	88.80 (1)
		Cl(2)-Sb-Cl(5)	90.65 (1)
S(1)-N(1)	1.651 (9)	Cl(2)-Sb-N(1)	88.48 (3)
S(1)-N(2)	1.569 (11)	Cl(3)-Sb-Cl(4)	90.55 (1)
S(2)-N(2)	1.541 (10)	Cl(3)-Sb-Cl(5)	89.83 (1)
S(2)-N(3)	1.580 (13)	Cl(3)-Sb-N(1)	88.07 (2)
S(3)-N(3)	1.585 (13)	Cl(4)-Sb-Cl(5)	177.16 (1)
S(3)-N(4)	1.533 (11)	Cl(4)-Sb-N(1)	89.19 (2)
S(4)-N(4)	1.581 (9)	Cl(5)-Sb-N(1)	88.01 (2)
S(4)-N(1)	1.662 (9)		
		Sb-N(1)-S(1)	123.35 (4)
		Sb-N(1)-S(4)	123.35 (4)
		N(1)-S(1)-N(2)	109.75 (5)
		S(1)-N(2)-S(2)	139.65 (8)
		N(2)-S(2)-N(3)	119.63 (6)
		S(2)-N(3)-S(3)	138.45 (8)
		N(3)-S(3)-N(4)	120.79 (5)
		S(3)-N(4)-S(4)	138.33 (7)
		N(4)-S(4)-N(1)	110.14 (5)
		S(4)-N(1)-S(1)	112.59 (5)

For instance, a CNDO/BW[116b] calculation on S_4N_4 suggests that there is electron delocalization in the molecule, whereas a CNDO/2 [116a] calculation suggests that there are three delocalized "islands" in S_4N_4 similar to those found by Dewar[154] for the phosphonitrilic halides. At present, a good rational bonding scheme has not been developed.

Table IV-10 lists some S-N bond distances and N-S-N and S-N-S bond angles for neutral and cationic SN ring systems and Figures IV-10 and IV-11 graphically illustrate variation in S-N-S bond angles and N-S-N bond angles with S-N bond distance. The purpose of these figures is not to establish a relationship between S-N bond distance and $N\hat{S}N$ or $S\hat{N}S$ bond angles, but rather to illustrate the greater variation in bond angle about nitrogen, as compared to the bond angle about sulphur, with S-N bond distance.

The following facts may be important in the development of any bonding scheme.

1) The largest S-N-S bond angles are found in the cyclic cationic compounds composed of seven to ten-membered rings. The increase in bond angle that is required with increasing ring size is almost entirely at nitrogen while there is little variation in the angle at sulphur. The fact that the N-S-N bond angle is less dependent on ring size is readily illustrated by the azulene-type geometry of $S_5N_5^+$. There are two re-entrant angles at nitrogen in the $S_5N_5^+$ ring and presumably this is due to the fact that a ten-membered $S_5N_5^+$ ring with no reentrant angles at nitrogen would be energetically less favourable due

Table IV-10

Bond Distances and Bond Angles for Some Sulphur-Nitrogen Compounds

Compound	dSN(Å)	$S\text{-}\hat{N}\text{-}S$	dSN(Å)	$N\text{-}\hat{S}\text{-}N$°	References
S_4N_4	1.62	112.6	1.62	104.4	5
S_2N_2	1.65	90.4	1.65	89.6	115
$S_3N_3Cl_3$	1.61	123.9	1.61	113.6	46
$S_3N_3F_3$	1.59	123.2	1.59	112.6	72,73
$S_4N_3^+$	1.58 1.54	134.4	1.55 1.58	111.8 110.9	156
	1.58 1.49	153.3	1.55 1.58	118.8	
	1.55 1.55	151.5	1.54 1.49	119.0	
$S_6N_4^{2+}$	1.61 1.57	119.0	1.57	108.0	155
$S_3N_2^+$	1.61 1.55	119.9	1.61 1.59	96.6 96.4	31
	1.57 1.59	119.8	1.54 1.58	107.2	
$S_3N_2Cl^+$	1.58 1.62	118.0	1.62	95.5	157
			1.58	97.8	
	1.62 1.54	120.7	1.62 1.54	106.3	
$S_5N_5^+$	1.58 1.55 1.56	133.0 138.3 151.0	1.56 1.55 1.56	108.7 109.6 124.5	55
$S_4N_4^+$(A)	1.55	150.0	1.55	120.0	
$S_4N_4^+$(B)	1.57	143.0	1.57	127.0	

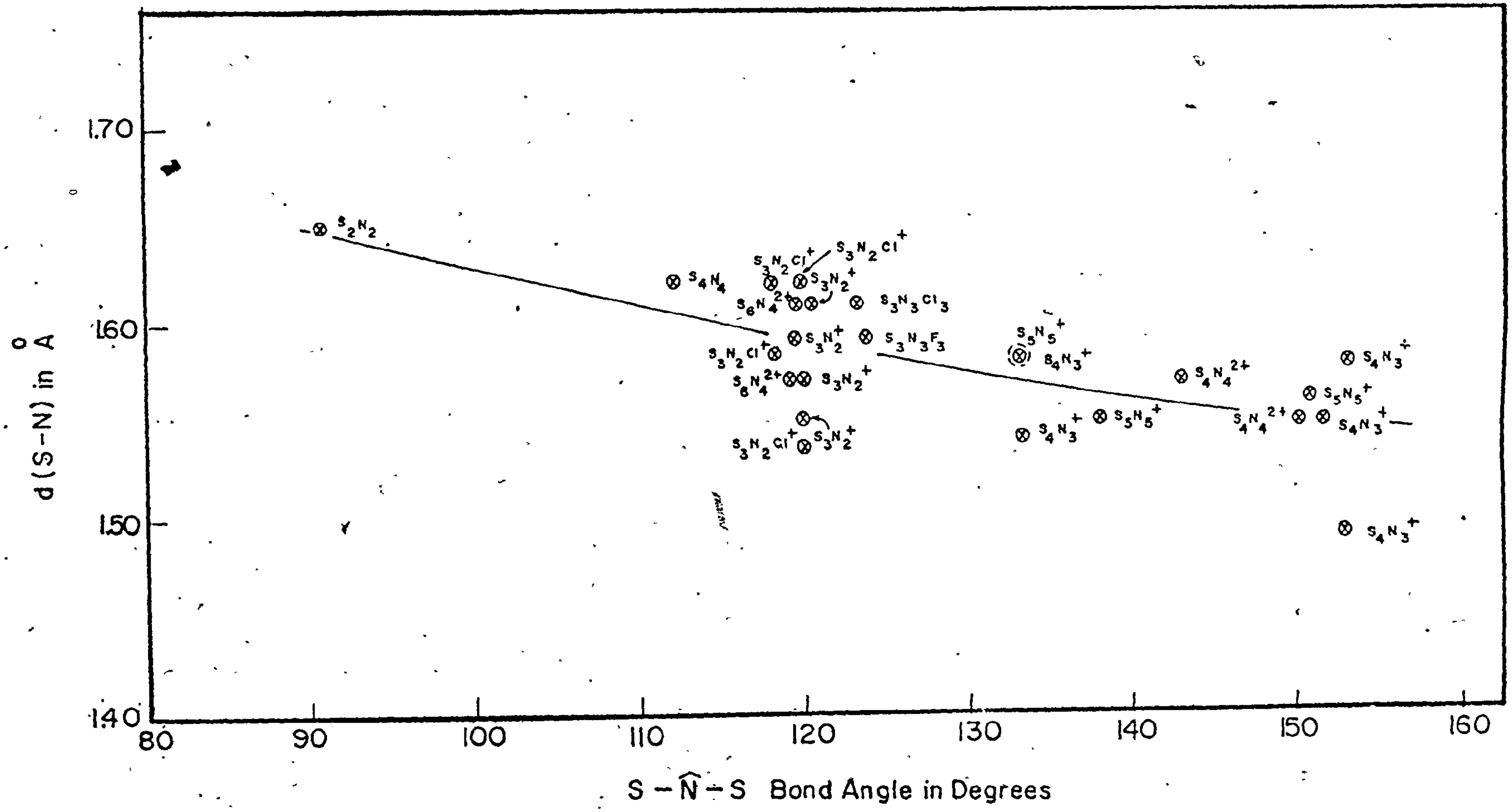


Figure IV-10 Variation of S-N̂-S Bond Angle with S-N Bond Distance.

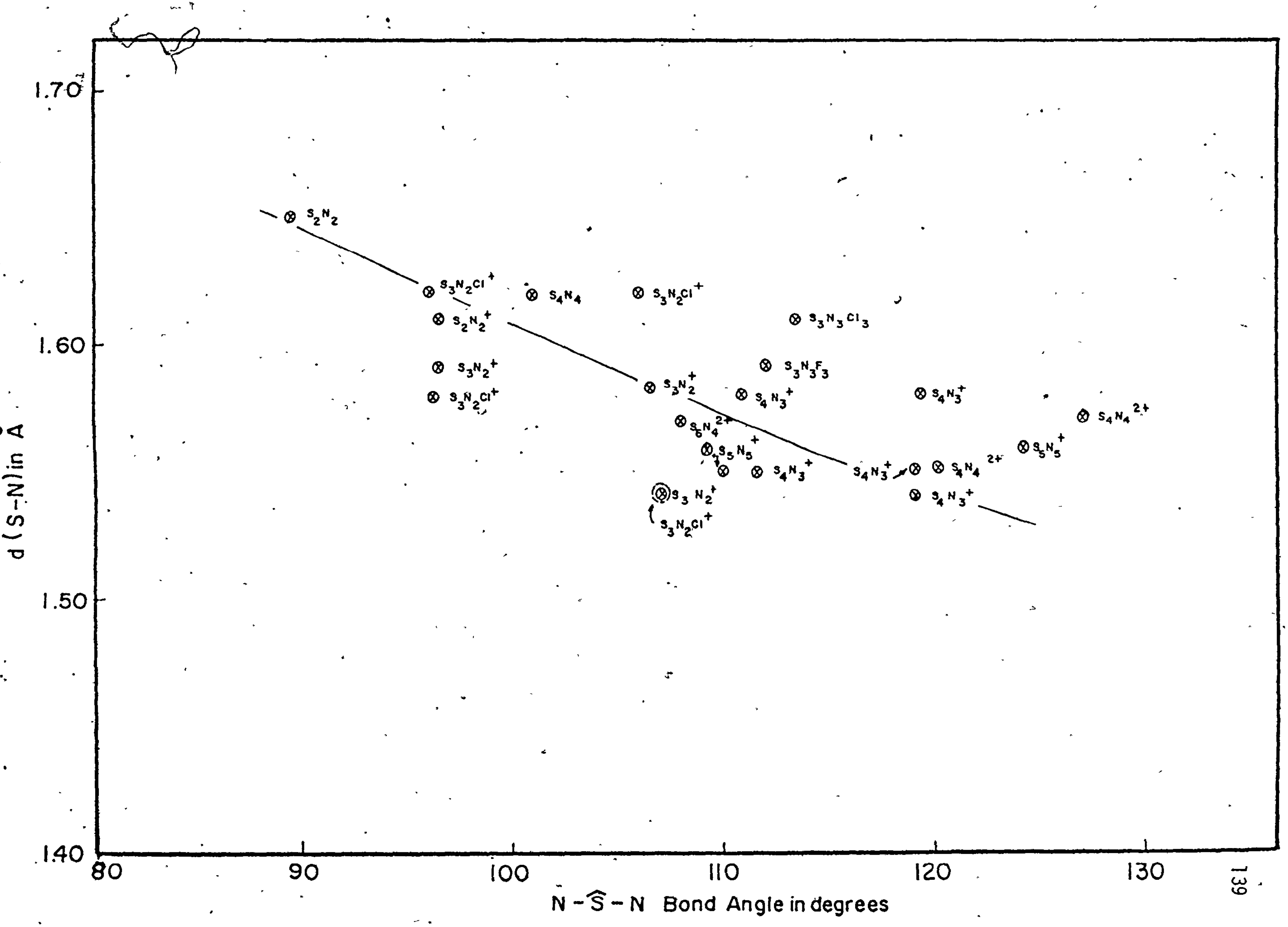


Figure IV-11 Variation of N-Ŝ-N Bond Angle with S-N Bond Distance to the necessity of having larger bond angles at sulphur.

2) The observance of nitrogen bond angles in excess of 120° suggests a change in hybridization at nitrogen from sp^2 to a hybrid orbital that has a larger degree of s character. The N-S-N bond angle is apparently less flexible to change and it is presently not understood why. Presumably, donation of the nitrogen lone pair to the empty sulphur d-orbitals does not affect the hybridization at sulphur.

3) Participation of the lone pair on nitrogen in the π-system of S-N cationic rings destroys the concept of a Hückel 4n + 2 system. Although many of the ring systems obey the Hückel 4n + 2 rule, this may in fact just be a fortuitous coincidence. For instance, the cation $S_3N_2^+$ exists and yet has 7π electrons; the stability of the ring is not apparently affected by the fact that it is not Hückel precise.

IV-8 Experimental Section

The Reaction of $S_3N_3Cl_3$ with $SbCl_5$ in Liquid SO_2 in a 1:2 Mole Ratio

The compounds $S_3N_3Cl_3$ (250 mg, 1.02 mmol) and $SbCl_5$ (615 mg, 2.05 mmol) were both added, in the dry box, to separate bulbs of a double bulb reaction vessel fitted with a medium glass frit. The reaction vessel was connected to a vacuum line evacuated and SO_2 (5 ml) was condensed at -196°C onto both reactants. The reaction vessel was allowed to warm to room temperature, the $SbCl_5$ completely dissolved in the SO_2 while $S_3N_3Cl_3$ was only moderately soluble. The $SbCl_5/SO_2$ solution was poured onto the $S_3N_3Cl_3/SO_2$ solution and a yellow solid initially formed. After stirring for 24 h, the solution was green-brown in colour with a yellow solid present. The solution was filtered and left undisturbed for 24 h. At this time, yellow needles formed along with a few green needles. Continual washing with SO_2 removed the green material yielding a pure yellow crystalline sample. This was shown to be $S_4N_4(SbCl_6)_2$ by comparison of its Raman spectrum with that of a pure sample.

The above procedure was repeated one further time, only in this instance the solution was not filtered, but the solvent was removed on the vacuum line, yielding a crude solid mixture. The Mössbauer spectrum of this crude mixture indicated only the presence of Sb(V) with no signal due to Sb(III) being observed. A Raman spectrum of the crude material showed that $S_4N_4(SbCl_6)_2$ was present, with bands due to at least one other product that was not $SbCl_3$. This other product, the green crystalline material, was extracted from the crude mixture with methylene chloride. The bands in the Raman spectrum of the extracted green material were identical to those not due to $S_4N_4^{2+}$ in the Raman spectrum of the crude material. This reaction may also be done using excess $SbCl_5$, with no change in the observed reaction products.

The Reaction of $S_3N_3Cl_3$ with $SbCl_5$ in $SOCl_2$ in a 1:2 Mole Ratio

The experimental procedure was as described above, $S_3N_3Cl_3$ (250 mg, 1.02 mmol) and $SbCl_5$ (6.5 mg, 2.05 mmol) were transferred in a dry box to separate bulbs of a double-bulb reaction vessel. $SOCl_2$ (10 ml) was also transferred to each of the separate bulbs in the dry box. The vessel was then evacuated and the $SbCl_5/SOCl_2$ solution was poured through the frit onto the $S_3N_3Cl_3/SOCl_2$ solution. After 24 h, a yellow solution was formed with a yellow powder present. Filtration of the solution yielded yellow crystals that were shown to be $S_4N_4^{2+}$ by comparison of their Raman spectrum with a Raman spectrum of a pure sample of $S_4N_4(SbCl_6)_2$. A Raman spectrum of the crude mixture indicated the presence of at least one other product different to that obtained in the SO_2 solvent system.

The Reaction of $S_3N_3Cl_3$ with $SbCl_5$ in CH_2Cl_2 in a 1:2 Mole Ratio

The procedure was identical to that outlined above for the reaction of $S_3N_3Cl_3$ with $SbCl_5$ in SO_2. In this instance, $S_3N_3Cl_3$ (200 mg, 0.823 mmol) was combined with $SbCl_5$ (492 mg, 1.65 mmol) in 20 ml of dry CH_2Cl_2. The $SbCl_5$ dissolved completely in the CH_2Cl_2 while $S_3N_3Cl_3$ was only moderately soluble. Upon addition of the $SbCl_5/CH_2Cl_2$ solution to the $S_3N_3Cl_3/CH_2Cl_2$ solution, a yellow precipitate formed. Within one-half hour, the stirred solution became increasingly orange in colour and finally orange-red to red. This experiment was repeated several times and it was found that the solutions varied from orange-red to deep red in colour. After 24 h. the solution became bright yellow with a yellow solid present. This solid was shown to be $S_4N_4(SbCl_6)_2$ by comparison of its Raman spectrum with that of a pure sample of $S_4N_4(SbCl_6)_2$. Other products from the reaction were not characterized. The green material obtained in the SO_2 solvent system was not observed.

The Reaction of $S_3N_3Cl_3$ with $SbCl_5$ in CH_2Cl_2 in a 1:1 Mole Ratio

The procedure is identical to that described in the previous section. In this instance, $S_3N_3Cl_3$ (175 mg, 0.720 mmol) and $SbCl_5$

(215 mg, 0.720 mmol) were reacted in dry CH_2Cl_2 to yield a red solution. After 24 h, there was no further change and the CH_2Cl_2 was removed on the vacuum line to give a black-green residue that contained some patches of red and yellow. SO_2 (20 ml) was condensed at -196°C onto the solid. Upon warming to room temperature, the solution again became red in colour with some undissolved red solid present. The solution was filtered and left undisturbed for several days. After this time, many crystals formed, three sets of distinct crystals were isolated from the mixture. Light red and dark red needles were shown to be, by an X-ray crystallographic study, $S_4N_4 \cdot SbCl_5$ and $(S_5N_5^+)(SbCl_6^-)$, respectively. A few yellow crystals were also present and these were characterized as $S_4N_4(SbCl_6)_2$. It should be noted that the Raman spectra of the mixture before and after addition of SO_2 were identical.

The Reaction of $S_3N_3Cl_3$ with $SbCl_5$ in SO_2 in a 1:1 Mole Ratio

The compounds $S_3N_3Cl_3$ (2.50 mg, 1.02 mmol) and $SbCl_5$ (307 mg, 1.02 mmol) were each transferred in a dry box to separate bulbs of a double bulb reaction vessel fitted with a medium glass frit. Sulphur dioxide (10 ml) was condensed at -196°C onto both reactants and the vessel was allowed to warm to room temperature. The $SbCl_5/SO_2$ solution was poured through the frit onto the $S_3N_3Cl_3/SO_2$ solution and a yellow precipitate immediately formed. After 24 h, the solution was yellow-orange and a yellow solid was present. The solution was filtered and after several days a yellow crystalline solid formed. This was shown to be $S_4N_4(SbCl_6)_2$. The SO_2 was removed from the crude reaction mixture and Raman data indicated it contained $S_3N_3Cl_2^+$ as well as some $S_4N_4^{2+}$.

Preparation of $(S_3N_3Cl_2)(SbCl_6)$ from the Reaction of $S_3N_3Cl_3$ with $SbCl_5$ in CCl_4 in a 1:1 Mole Ratio

This was done according to the method of O. Glemser,[120] $S_3N_3Cl_3$ (200 mg, 0.823 mmol) and $SbCl_5$ (246 mg, 0.823 mmol) were added, in a dry box, to separate bulbs of a double bulb reaction vessel fitted with a medium filter. CCl_4 (20 ml) was distilled at -196°C onto both reactants and the vessel was allowed to warm to room temperature. The $SbCl_5/CCl_4$ solution and a yellow precipitate formed. The mixture was stirred for 24 h to yield a yellow solid that is insoluble in CCl_4. The CCl_4 was removed and a Raman spectrum of the yellow material was identical to that reported by O. Glemser for $(S_3N_3Cl_2^+)(SbCl_6^-)$.

Solutions of $S_3N_3Cl_2(SbCl_6)$ in CH_2Cl_2 and SO_2

The compound $S_3N_3Cl_2(SbCl_6)$ was prepared as described in the previous section. Methylene chloride was condensed at -196°C onto the yellow $S_3N_3Cl_2(SbCl_6)$ and the mixture was allowed to warm to room temperature. Upon reaching room temperature, the solution turned orange-red in colour and appeared to be very similar to solutions obtained directly from the reaction of $S_3N_3Cl_3$ with $SbCl_5$ in CH_2Cl_2. The CH_2Cl_2 was removed and a Raman spectrum of the solid mixture was identical to that obtained from the crude mixture prepared directly in CH_2Cl_2. Similar observations were made using liquid SO_2 as a solvent.

Preparation of $(S_5N_5)(SbCl_6)$ by the Method of Banister

Cyclotetrathiazyl bis hexachloroantimonate(V) was prepared in thionyl chloride according to the procedure outlined earlier in this chapter.

Trichlorocyclotrithiazene (320 mg, 1.32 mmol) and $SbCl_5$ (1.17 g, 3.94 mmol) were the molar amounts used in the preparation. After 24 h, formation of $S_4N_4(SbCl_6)_2$ was complete and S_4N_4 (0.727 g, 3.95 mmol) was added in the dry box to the stirred $SOCl_2$ solution containing the $S_4N_4^{2+}$ as well as other unidentified products. The solution immediately turned green and after 24 h a dark red-green dichroic solution remained. Filtration yielded a yellow-brown solid that when washed with thionyl chloride produced a yellow-orange material, the infrared spectrum of which was identical to that reported by Banister for $S_5N_5(SbCl_6)$.

The Reaction of $S_3N_3F_3$ with SO_3 in a 1:3 Mole Ratio

Under dynamic vacuum, $S_3N_3F_3$ (0.1395 g, 0.715 mmol) was sublimed from a Kel-F storage trap to one bulb of a double bulb reaction vessel, at -196°C, that had been previously weighed and flame dried under vacuum for 48 h. SO_3 (0.1716 g, 2.14 mmol) was then sublimed onto the $S_3N_3F_3$ at -196°C, followed by 10 ml of SO_2. The solution was allowed to warm to room temperature and turned orange-brown with all the solid material dissolving. After three hours, large cream coloured needles appeared and the solution was leaf green in colour. At this point, the solution was filtered, and the crystals were washed with SO_2 until they were white in colour. The solvent was removed from the reaction vessel and the bulb containing the crystalline material was flame sealed and stored at -196°C. A Raman spectrum of the white crystalline material was consistent with the formation of $(SN)(SO_3F)$. It is important that once the crystalline material is formed that it is soon isolated and stored at -196°C.

The Reaction of $S_3N_3F_3$ with SbF_5 in a 1:6 Mole Ratio

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

The Reaction of $S_3N_3F_3$ with SbF_5 in a 1:2 Mole Ratio

As described in the previous section, $S_3N_3F_3$ (2.43 g, 12.4 mmol) and SbF_5 (5.41 g, 249 mmol) were combined in a double bulb reaction vessel. Sulphur dioxide (5 ml) was condensed at -196°C onto both bulbs and the vessel was allowed to warm to room temperature. The resulting two solutions were mixed by pouring the SbF_5/SO_2 solution through the frit onto the $S_3N_3F_3/SO_2$ solution. A cream coloured solution was formed and after 24 h, the solvent was removed under vacuum to yield a cream coloured solid. A Raman spectrum could not be obtained due to strong background fluorescence; however, an ^{19}F nmr spectrum of the solid was obtained and consisted of one line at δ = -5.38 ppm.

The Reaction of $S_3N_3F_3$ with AsF_5 in a 1:6 Mole Ratio

Into one bulb of a double reaction vessel, at -196°C, $S_3N_3F_3$ (52.3 mg, 0.268 mmol) was sublimed under dynamic vacuum from a

Kel-F storage vessel. AsF_5 (0.257 g, 1.61 mmol) and SO_2 (10 ml) were condensed at -196°C onto the $S_3N_3F_3$ and the vessel was allowed to warm to room temperature. The $S_3N_3F_3$ reacted quickly to yield a yellow solution from which a yellow solid was isolated. The Raman spectrum of this material showed the presence of $(SN)(AsF_6)$ and one other unidentified product.

The Reaction of $S_3N_3F_3$ with AsF_5 and SbF_5 in a 1:2 Mole Ratio

The procedure was as described in the previous section, $S_3N_3F_3$ (372 mg, 1.91 mmol) was combined with AsF_5 (0.610 g, 3.82 mmol) and SO_2 (10 ml). The resulting solution was yellow with no undissolved solid present. The SO_2 was removed to produce a yellow solid, the ^{19}F nmr of which indicated the presence of $(S_3N_3F_2)(AsF_6)$ based on comparison with nmr data reported by Glemser for $(S_3N_3F_2)(AsF_6)$. A Raman spectrum could not be obtained due to strong background fluorescence.

CHAPTER V

THE LEWIS ACID CHEMISTRY OF THE SULPHUR IMIDES

V-1 Reactions of the Sulphur Imides with Lewis Acids

Very little is known about the reactions of the sulphur imides with Lewis acids. The chemistry of S_7NH is dominated by the acidity of the hydrogen atom as Heal[79] has demonstrated. A few poorly characterized adducts of $S_4N_4H_4$ have been prepared. The reactions of other imides, such as 1,4-$S_6N_2H_2$, with Lewis acids, have not been investigated at all.

A study was, therefore, undertaken to attempt to understand the behaviour of some sulphur amides with group (V) pentahalides which have both oxidizing and Lewis acid properties.

V-2 The $S_4N_4H_4/SbCl_5$ System

The compound $SbCl_5$ has proven to be of great utility as a synthetic reagent with other sulphur nitrogen systems and thus reactions with $S_4N_4H_4$ were studied.

It was found that when $SbCl_5$ was reacted with $S_4N_4H_4$ in a 3:1 molar ratio, the products were $S_4N_4 \cdot SbCl_5$, $SbCl_3$ and HCl. The stoichiometry may be described by the equation

$$S_4N_4H_4 + 3SbCl_5 \xrightarrow{SO_2} S_4N_4 \cdot SbCl_5 + 2SbCl_3 + 4HCl$$

The isolation of the $SbCl_5$ adduct of S_4N_4 implies that cyclotetrathiazene could be obtained by the action of $SbCl_5$ on S_4N_4 if a lower molar ratio was used.

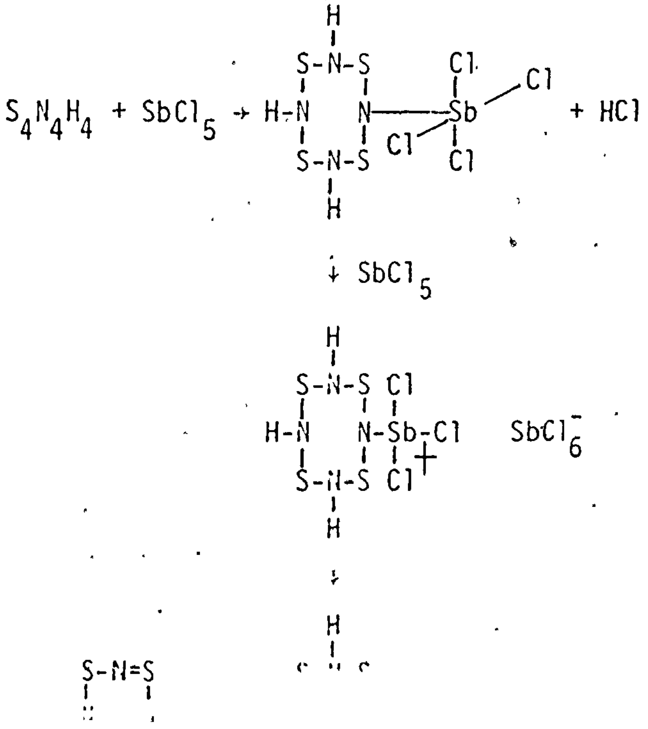
$$S_4N_4H_4 + 2SbCl_5 \xrightarrow{SO_2} S_4N_4 + 4HCl + 2SbCl_3$$

It had previously been shown that $S_4N_4H_4$ is oxidized to S_4N_4 by chlorine and by nitrate ion

$$S_4N_4H_4 + 2Cl_2 \rightarrow S_4N_4 + 4HCl \quad ^{158}$$

$$S_4N_4H_4 + 2NO_3^- \rightarrow 2H_2O + S_4N_4 + 2NO_2^- \quad ^{108}$$

It is known that the hydrogen of sulphur imides is acidic and salts containing S-N anions may be prepared. Heal[91] has also demonstrated that the N-H group in cycloheptasulphur imide is capable of undergoing condensation reactions with the boron trihalides. Thus it is reasonable to speculate that the first step in the oxidation process is the formation of the imido antimony tetrachloride complex. This could be followed by chloride ion abstraction and liberation of $SbCl_3$ with a positive charge simultaneously generated at the nitrogen.



The overall result of this is to increase the acidity of the remaining hydrogen atoms and generation of a neutral $S_4N_4H_2$ intermediate may be expected. This process could then be repeated to give the final product S_4N_4.

The formation of the molecular adduct $S_4N_4 \cdot SbCl_5$ in this system suggests that $S_4N_4H_4$ may be a starting material for the preparation of the dication $S_4N_4^{2+}$. It was shown in Chapter III that $S_4N_4 \cdot SbCl_5$ reacts with additional $SbCl_5$ to produce $S_4N_4(SbCl_6)_2$. Thus, it was not surprising that $S_4N_4H_4$ was found to react with $SbCl_5$ in a 1:5 molar ratio to produce the $S_4N_4^{2+}$ salt. The required stoichiometry may perhaps be described by the equation

$$S_4N_4H_4 + 5SbCl_5 \xrightarrow{SO_2} S_4N_4(SbCl_6)_2 + 4HCl + 3SbCl_3$$

The reaction of $S_4N_4H_4$ with the Lewis acids SbF_5 and AsF_5 was also investigated to determine if these Lewis acids would also oxidize the tetraimide to the corresponding $S_4N_4^{2+}$ salts. In both instances, the cyclotetrathiazyl cation was not produced and consequently the reactions were not studied further.

It is noteworthy that in the three Lewis acid systems, the solutions obtained were paramagnetic. The esr spectra consisted of one single sharp line with a g-value of 2.013. This value is in the reported range for S_5^+ which is possibly an intermediate or a by-product of the formation of $S_4N_4^{2+}$.

V-3 The Dithionitronium ion S_2N^+

The chemistry of cycloheptasulphurimide is quite extensive and much of it is dominated by the known acidity of hydrogen atom. Heal[79,92] has demonstrated that the compounds boron trichloride and boron tribromide are capable of abstracting the hydrogen atom from S_7NH to generate the appropriate heptasulphurimide boron dihalides.

$$S_7NH + BX_3 \rightarrow S_7N\text{-}BX_2 + HX \qquad X = Cl \text{ or } Br$$

As the boron trihalides have no oxidizing capability, it seemed appropriate to determine the behaviour of S_7NH in the presence of a Lewis acid of oxidizing ability.

It was observed that $SbCl_5$ readily reacted with S_7NH in liquid sulphur dioxide in a 2:1 molar ratio to produce an orange crystalline material. This material was characterized by X-ray crystallography as the dithionitronium hexachloroantimonate(V), $(S_2N)(SbCl_6)$. In addition, the other characterized reaction products were elemental sulphur, antimony(III)chloride and HCl. The stoichiometry of the reaction may perhaps be described by the equation

$$S_7NH + 2SbCl_5 \rightarrow HCl + (S_2N)(SbCl_6) + \frac{5}{8}S_8 + SbCl_3$$

It is difficult to propose a mechanism for this reaction at the present time. However, it seems reasonable to suggest that the first step is the loss of the acidic proton from S_7NH with the formation of heptasulphurimido antimony tetrachloride analogous to the compound formed in the reaction with boron trichloride.

$$S_7NH + SbCl_5 \rightarrow S_7NSbCl_4 + HCl$$

Indeed, it was found that S_7NBCl_2, formed by the reaction of S_7NH with BCl_3, reacts with $SbCl_5$ to give $(S_2N)(SbCl_6)$.

$$S_7NH + BCl_3 \rightarrow S_7NBCl_2 + HCl$$

$$S_7NBCl_2 + 2SbCl_5 \rightarrow (S_2N)(SbCl_6) + \frac{5}{8} S_8 + SbCl_3 + BCl_3$$

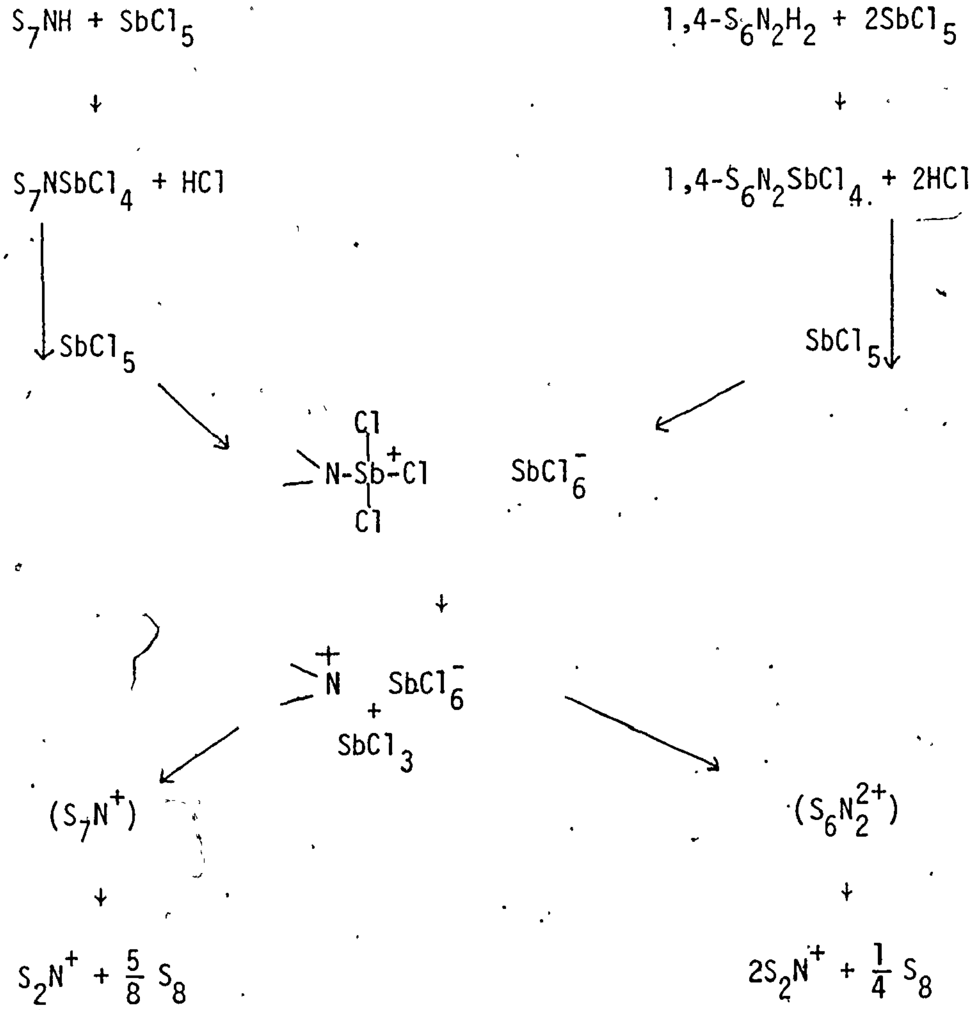
The initial formation of S_7NSbCl_4 must be followed by a series of rather complex steps that produces S_2N^+ and other products. It is interesting that the red-brown solutions obtained from the above reactions exhibited an esr signal consisting of one sharp line with g = 2.016. This can probably be attributed to the radical S_5^+ for which the g-values in the range 2.013 - 2.016 have been reported, and which is obtained when sulphur is oxidized by SbF_5 or AsF_5 or by certain strong oxyacids.[140] It is noteworthy that the formation of S_2N^+ from the S_7N ring leaves an S_5 fragment. Presumably S_8 is then formed from the S_5 fragment by a series of complex reactions.

The dithionitronium cation can also be obtained from the reaction of 1,4-$S_6N_2H_2$ with $SbCl_5$. This implies a stoichiometry given by the equation

$$1,4\text{-}S_6N_2H_2 + 4SbCl_5 \rightarrow 2(S_2N)(SbCl_6) + \frac{1}{4} S_8 + 2HCl + 2SbCl_3$$

The mechanism of this reaction is not obvious. There have been no prior studies of the behaviour of the diimide with Lewis acids. The solution obtained from this reaction exhibited a 5-line esr spectrum with g = 2.002 and a = 3.15 gauss. This is consistent with a radical containing two equivalent nitrogen atoms. A signal due to the S_5^+

Figure V-1 Proposed Reaction Sequence for the Oxidation of S_7NH and $1,4\text{-}S_6N_2H_2$ with $SbCl_5$



radical was not observed. The identity of the radical is not known. Comparison of the g-value and coupling constant with those of $S_3N_2^+$ [31] tend to rule out the cyclothiodithiazyl cation as a possibility.

Again as in the S_7NH system, the first step may be the formation of hexasulphurdimido bis antimony tetrachloride which then reacts further to produce the products

$$1,4\text{-}S_6N_2H_2 + 2SbCl_5 \rightarrow S_6N_2(SbCl_4)_2 + 2HCl$$

The next step in the reaction sequence for both the S_7NH and the $1,4\text{-}S_6N_2H_2$ systems is assumed to be chloride ion abstraction by one further mole of $SbCl_5$ from the N-$SbCl_4$ site. This is outlined in the reaction sequence in Fig. V-1. The resulting complexes would lose $SbCl_3$ to generate the cations S_7N^+ and/$S_6N_2^{2+}$. These species were not observed and either fragment as soon as they formed or simultaneously as loss of $SbCl_3$ occurs. It is not clear why the above cationic species are not stable enough to be isolated from the reaction mixture.

It is noteworthy that $S_7N\text{-}CH_3$ does not react with $SbCl_5$, in liquid SO_2, in a 1:2 molar ratio to produce the S_2N^+ cation. This observation is consistent with the fact that the acidic hydrogen is necessary for the formation of the dithionitrionium cation in that loss of CH_3^+ from $S_7N\text{-}CH_3$ is very unlikely.

The reaction of S_7NH with the Lewis acids SbF_5, AsF_5 and PF_5 was also investigated.

The Lewis acids AsF_5 and SbF_5 were observed to produce a brown solution when combined with S_7NH in liquid SO_2 in a 1:3 molar ratio of imide to Lewis acid.

The esr spectrum of this solution consisted of two signals, one sharp line at g = 2.028 and a five-line signal at g = 2.013 with a coupling constant of 3.2 gauss. Increasing the molar ratio of imide to Lewis acid to 1:9 caused the solution to turn deep blue. The intensity of the single line at g = 2.038 decreased relative to that of the five-line signal at g = 2.013. It was also noted that the resolution of the five-line signal decreased somewhat. An infrared spectrum of the solid blue material isolated after solvent removal, was consistent with the presence of the AsF_6^- anion (ν_3 692 cm^{-1} and ν_4 388 cm^{-1}) and the absence of an N-H stretch. These results can be best explained by the following sequence

$$S_7NH + XF_5 \xrightarrow{SO_2} (S_y^+)_n(XF_6^-)_n + XF_3 + HF + (S_xN_2^+\cdot)(AsF_6^-)$$

$$\text{further } XF_5 \downarrow$$

$$(S_5^+\cdot)(XF_6)$$

X = As or Sb

The S_7NH first loses H^+ to yield HF and then, in a manner that is not clear, a sulphur radical is produced that has been observed in SO_2 solutions of S_{19}^{2+}. The S_{19}^{2+} cation has recently been shown by an X-ray crystallographic determination in this laboratory to be the true identity of the previously reported S_{16}^{2+}. Therefore, the esr signal at g = 2.028 is due to an unknown sulphur radical that is also present in SO_2 solutions of S_{19}^{2+}. However, it is noted that the observation of this radical does not necessarily imply that the S_{19}^{2+} cation is present. The five-line pattern is consistent with a radical containing two equivalent nitrogen atoms, the identity of the radical is not known and comparison with the coupling constant and g-value for $S_3N_2^+$ would tend to rule out $S_3N_2^+$ as a possibility. Further addition of Lewis acid results in a blue solution. Blue solutions of sulphur in oleum have recently been shown to contain the S_5^+ radical which has g-values reported in the range of g = 2.013-2.016.[140] Thus, it is reasonable to assume that upon further oxidation the S_5^+ radical is formed. This may explain the decrease in intensity of the signal at g = 2.038 and the loss of resolution for the five-line signal at g = 2.013.

Cycloheptasulphurimide was also oxidized with PF_5 in a 1:2 molar ratio in SO_2 and elemental sulphur was characterized as one of the products. The esr spectrum of this solution consisted of a five-line pattern, the g-value and coupling constant of which were identical to those obtained in the AsF_5 and SbF_5 systems. Apparently, PF_5 also oxidizes the S_7N ring, however due to its lesser oxidizing power, in comparison to SbF_5 and AsF_5, sulphur is produced rather than S_{19}^{2+} or S_8^{2+}. However, the same nitrogen containing radical was formed as was observed in the SbF_5 and AsF_5 systems.

Due to the complexity of the S_7NH/AsF_5, S_7NH/SbF_5 and S_7NH/PF_5 systems and the fact that these systems did not appear to be a source of new S-N cations, they were not explored further.

The reaction of S_7NCH_3 with AsF_5 and PF_5 was also studied briefly to determine if the addition of the methyl group to the S_7N ring would facilitate production of new S-N species. It was found that AsF_5 when combined with S_7NCH_3 in a 9:1 molar ratio in liquid SO_2 produced a dark blue solution. The esr spectrum of this solution exhibited a sharp singlet at g = 2.016 and a broad line at g = 2.028. The signal was too broad to observe the fine structure associated with a nitrogen containing radical.

The reaction of S_7NCH_3 with PF_5 in a 1:2 molar ratio in SO_2

produced S_8 and the esr spectrum of the resulting solution again as in the case of S_7NH with PF_5 exhibited a five-line pattern with a g-value of 2.012 and a coupling constant of 3.52 gauss. This radical is therefore probably the same species observed in all the other esr spectra. The fate of the methyl group in these reactions is not known. As no evidence was obtained for new SN species, the reactions were not further investigated.

V-4 The Infrared and Raman Spectra of $(S_2N)(SbCl_6)$

The infrared and Raman spectra of solid $(S_2N)(SbCl_6)$ are given in Table V-1. The Raman spectrum of $(S_2N)(SbCl_6)$ is shown in Fig. V-2. The spectra can be interpreted in terms of the ionic structure $(S_2N^+)(SbCl_6^-)$. In the Raman spectrum of the solid, the three bands at 333 cm^{-1}, 293 cm^{-1} and 175 cm^{-1} can be readily assigned as $\nu_1(A_{1g})$, $\nu_2(E_g)$ and $\nu_3(T_{2g})$ of the $SbCl_6^-$ ion. As the site symmetry of $SbCl_6^-$ is D_2, the degeneracy of the E_g and T_{2g} modes is lifted and they are observed as a doublet and a triplet, respectively. In the infrared spectrum, the band at 320 cm^{-1} may be assigned to $\nu_3(T_{1u})$ of $SbCl_6^-$. In addition to the above mentioned bands, the most prominent band in the Raman spectrum is that at 688 cm^{-1} which may clearly be assigned as the single Raman active fundamental of the linear triatomic S_2N^+. The analogous band of the isoelectronic CS_2 molecule is observed at 656.5 cm^{-1}.[159] However, in addition to this band, there are two additional bands; a moderately intense band at 766 cm^{-1} and a very weak band at 680 cm^{-1}. The former is assigned as $2\nu_2$ which should normally be very weak but appears to have its intensity enhanced by Fermi resonance with ν_1.

Table V-1

Raman and Infrared Spectra of $S_2N^+SbCl_6^-$ and CS_2.

$(S_2N^+)(SbCl_6^-)$		CS_2 [a]		
R(cm^{-1})	I.R.(cm^{-1})	R(cm^{-1})	I.R.(cm^{-1})	
solid	solid			
	1498 m		1523	ν_3 $S_2N^+(CS_2)$
766(17)		796		$2\nu_2$ $S_2N^+(CS_2)$
747(2)				$2\nu_2$ $S_{32}S_{34}N^+(CS_{32}S_{34})$
688(44)		656.5		ν_1 $S_2N^+(CS_2)$
680(8)		648.8	396.7	ν_1 $S_{32}S_{34}N^+(CS_{32}S_{34})$
	374 m			ν_2 $S_2N^+(CS_2)$
333(100)				ν_1 (A_{1g}) $SbCl_6^-$
	320 s			$\nu_3(T_{1a})$ $SbCl_6^-$
293(12)				ν_2 (E_g) $SbCl_6^-$
283(8)				
180(26)				ν_5 (T_{2g}) $SbCl_6^-$
175(48)				
167(4)				
78(100)				Lattice modes
62(76)				

[a] Reference 159.

s = strong; m = medium

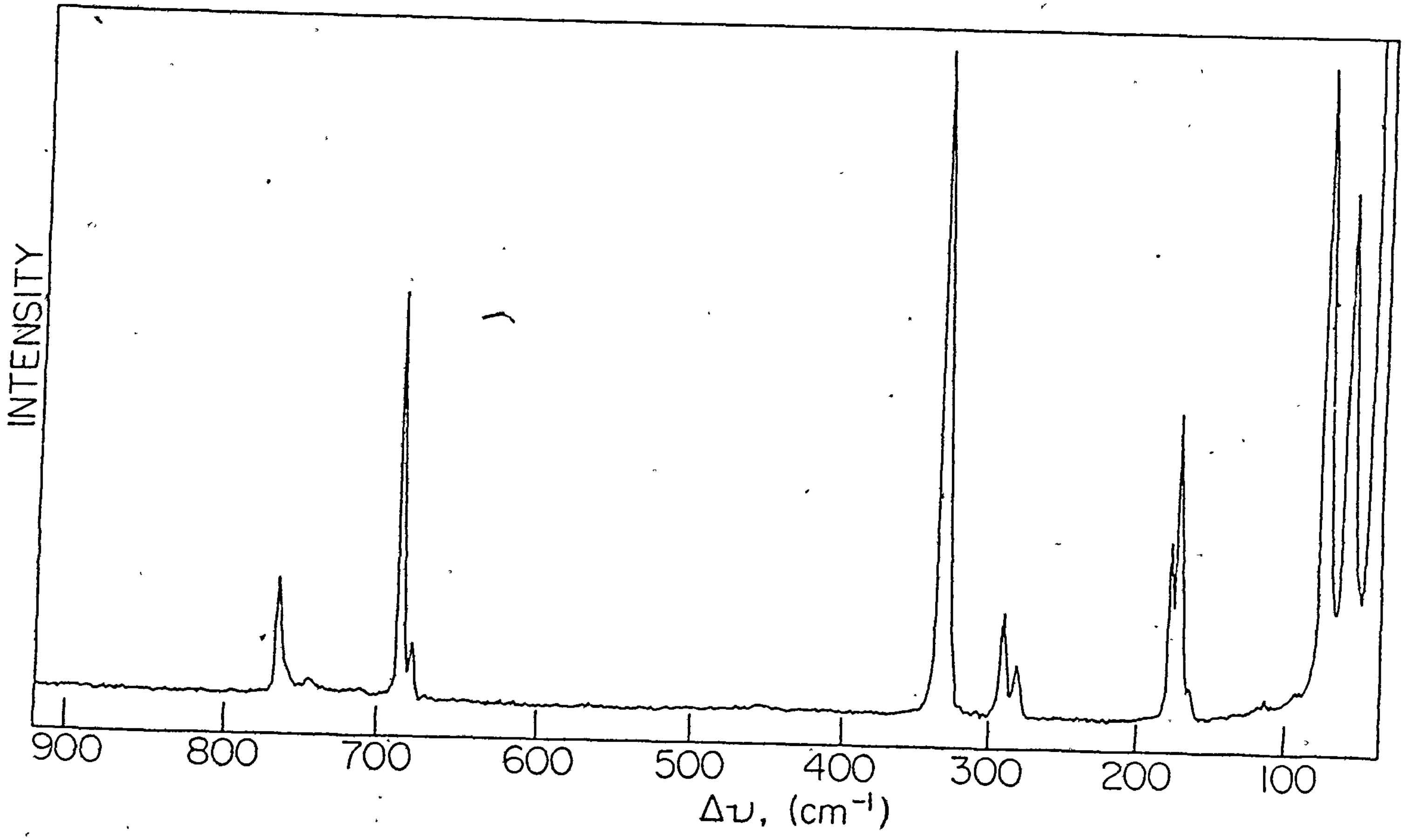


Figure V-2 Raman spectrum of $S_2N(SbCl_6)$ recorded at -196°C.

A similar band is observed at 648 cm^{-1} in the Raman spectrum of CS_2 and is similarly assigned to $2\nu_2$ enhanced by Fermi resonance with ν_1.[160] The weak band at 680 cm^{-1} can be assigned as ν_1 of the $S^{32}S^{34}N^+$ molecule for which the calculated value of ν_1 is 678 cm^{-1}. The other Raman inactive but infrared active fundamentals of the S_2N^+ ion, ν_2 and ν_3, are observed at 374 and 1498 cm^{-1}, respectively, and have frequencies close to the corresponding bands for CS_2. Satisfactory solution Raman spectra of $(S_2N)(SbCl_6)$ could not be obtained due to interference of solvent lines, low solubility or reaction with the solvent.

V-5 The Crystal Structure of $S_2N(SbCl_6)$

The crystal structure of $S_2N(SbCl_6)$ was determined by Dr. C.J.L. Lock and Mr. R. Faggiani of this department. The crystal data is presented in Table V-2 and Fig. V-3 illustrates the unit cell of $S_2N(SbCl_6)$. The S_2N^+ cation is linear and has $D_{\infty h}$ symmetry, and has an S-N bond length of 1.46 Å. This SN bond is shorter than the CS bond in the isoelectronic CS_2 molecule (1.55 Å),[160] just as the NO bond in NO_2^+ (1.10 Å)[161] is shorter than the CO bond in the isoelectronic CO_2 molecule (1.16 Å).[162] The differences are consistent with the presence of the positive charge and the greater electronegativity of nitrogen in comparison to carbon. All of these molecules have bond lengths that are smaller than those predicted from double bond covalent radii such as those given by Pauling.[163] This may suggest that all of these molecules have bond orders greater than two and that the simple valence bond structure

$$\underset{\cdot\cdot}{\overset{\cdot\cdot}{S}}=\overset{+}{N}=\underset{\cdot\cdot}{\overset{\cdot\cdot}{S}}$$

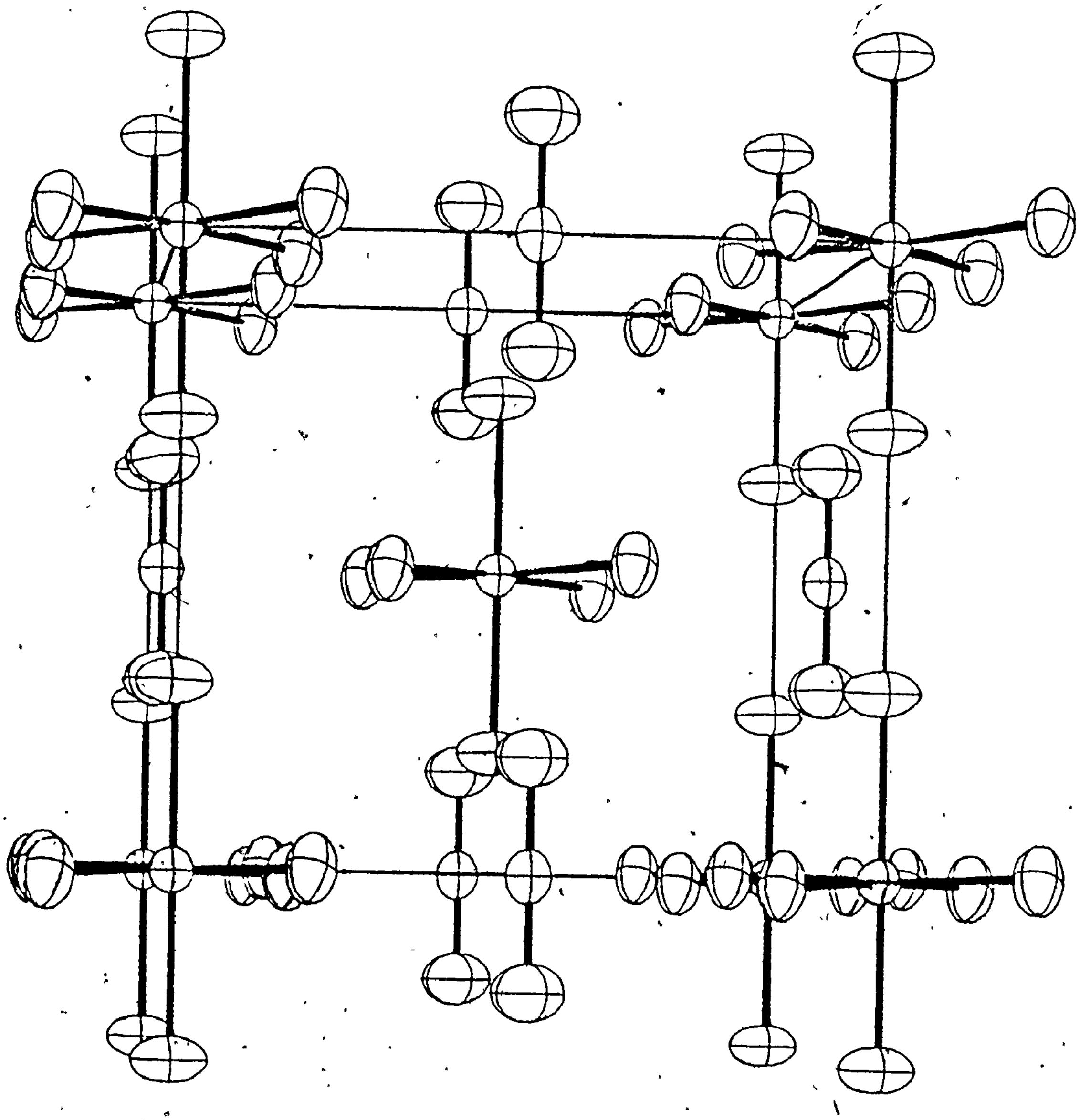
is not an adequate representation of the molecule.

Table V-2

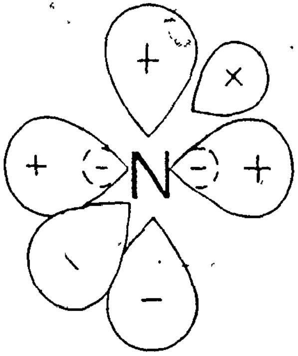
Crystal Data for $(S_2N)(SbCl_6)$

Space Group	I_{mmm}	Orthorhombic
Unit Cell Dimensions	a = 9.299(3) Å	
	b = 7.976(3) Å	
	c = 7.070(2) Å	
Unweighted R-factor	0.0377	
Bond Lengths	S-N	1.463(4) Å
	Sb-Cl(1)	2.351(3) Å
	Sb-Cl(2)	2.363(2) Å
Bond Angles in Degrees	Cl(1)-Sb-Cl(2)	90.0(0)
	Cl(1)-Sb-Cl(2)	90.0(0)
	Cl(2)-Sb-Cl(2)	90.0(0)
	Cl(2)-Sb-Cl(2)	90.0(0)
	Cl(2)-Sb-Cl(2)	180.0(0)

Figure V-3. The unit cell diagram of $S_2N(SbCl_6)$. a and b are parallel to the top and side of the page, respectively, and the view is down c.



The S-N-S bond angle of 180° at nitrogen would tend to suggest that the nitrogen atom is sp hybridized, leaving two orthogonal p-orbitals to participate in a π-system with sulphur. Due to the presence of the positive charge, the 3d orbitals on sulphur would be contracted inward, and may be available for overlap with the 2p orbitals on nitrogen. However, it is not known how important this is in contributing to the overall bonding.



sp hybridization
at nitrogen

V-6 The S_7NH/PCl_5 System

The reaction of S_7NH with PCl_5 in a 1:2 molar ratio in methylene chloride was observed to produce sulphur and a white crystalline material.

An X-ray study of a single crystal (taken from the mixture) provided sufficient evidence to assign the identity of the crystal as the salt $(Cl_3XNXCl_3^+)(PCl_6^-)$ where X must be either sulphur or phosphorus. Difficulty is encountered in assigning the identity of the atom X since crystallographically it is not possible to distinguish between sulphur and phosphorus in the cation due to their similarities in atomic number.

Difficulty also arises because the P-Cl bond distance, 1.94 Å, is comparable to observed S-Cl bond distances in similar sulphur nitrogen cations, for instance 1.985 Å in $Cl_2S_2N^+$.[50] The crystal of (Cl_3PNPCl_3)-(PCl_6) used in the X-ray study was obtained from a mixture containing sulphur and other products and consequently a chemical analysis was not performed. The Raman spectrum of $(Cl_3PNPCl_3)(PCl_6)$ has been published[164] and therefore a Raman spectrum of the single crystal used in the X-ray determination was obtained for comparison with the published data. Table V-3 lists the Raman frequencies for the published and observed values. The two spectra are comparable, however more bands were observed in the Raman spectrum of the single crystal presumably due to solid state crystal effects. It should be noted that the crystal was colourless as $(Cl_3PNPCl_3)(PCl_6)$ should be, whereas all S-N cations except SN^+ are coloured. Although crystallographically it is not possible to definitely assign the identity of the cation as $Cl_3PNPCl_3^+$, rather than $Cl_3SNSCl_3^+$, the Raman data coupled with the ^{31}P nmr data, to be discussed, favour the assignment of the cation as $Cl_3PNPCl_3^+$.

The ^{31}P nmr spectrum of the product mixture illustrated in Fig. V-4 contains several signals. Possible assignments for these signals are listed in Table V-4. The band at -219.5 ppm is assigned to PCl_3, one of the two signals at -33.0 and -29.4 ppm is likely due to $P(S)Cl_3$ and the large singlet at -20.3 ppm is attributed to the $Cl_3PNPCl_3^+$ cation. Assignment of the other bands is difficult especially when the intensities are too low to allow observation of phosphorus-phosphorus coupling. The products of the reaction of S_7NH with PCl_5 are summarized in the form of a non-stoichiometric equation.

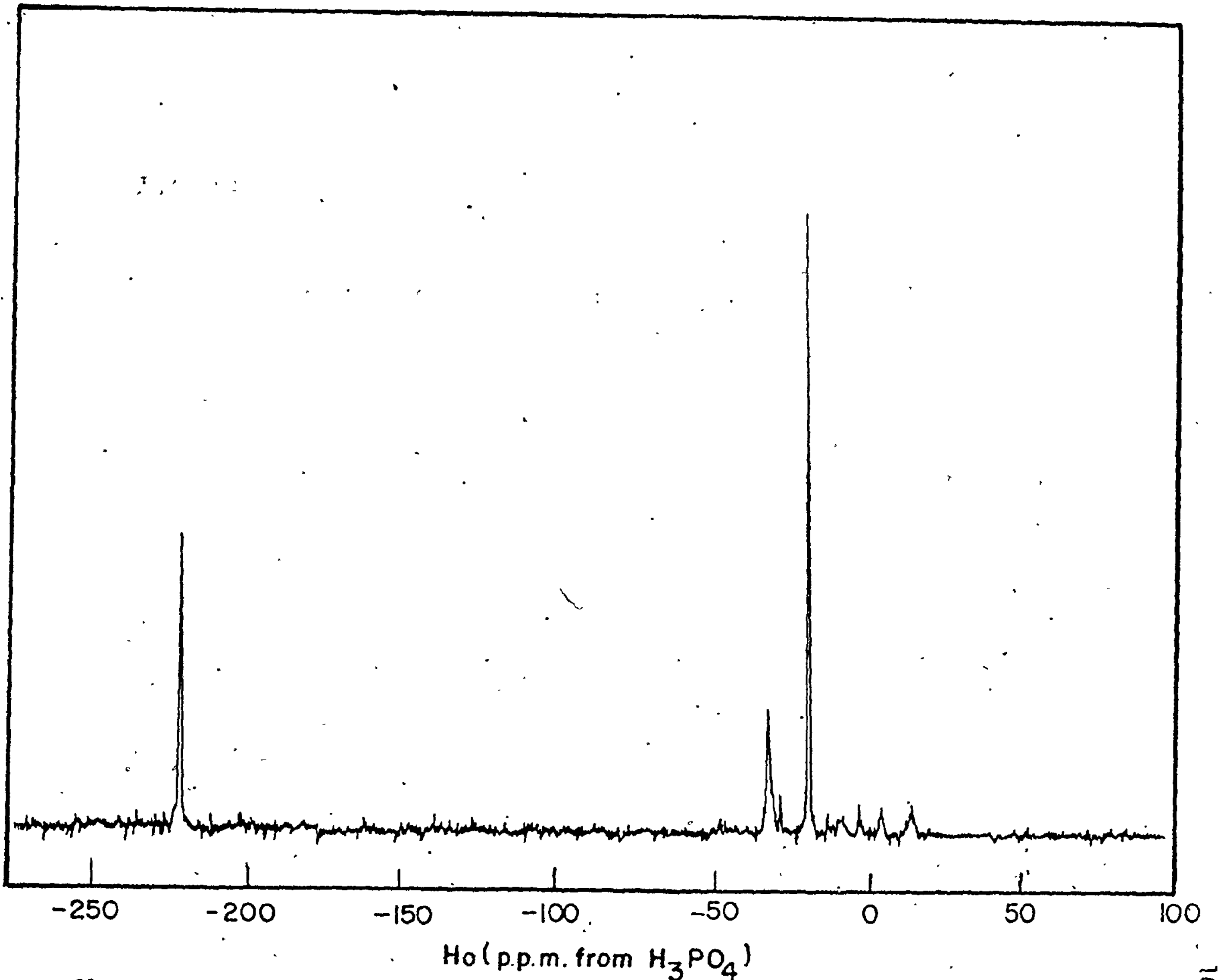


Figure V-4 . ^{31}P room temperature nmr spectrum of the mixture obtained from the reaction of S_7NH with PCl_5 in a 1:2 molar ratio

Table V-3

Raman Frequencies for $(Cl_3PNPCl_3)(PCl_6)$

$\Delta\nu$, (cm^{-1})		$\Delta\nu$, (cm^{-1}) [a]	
87(4)			
116(4)			
154(12)		163(2)	
160(11)			
169(14)			
206(7)		210(0)	
213(9)			
216(9)			
240(18)			
249(14)		247(7)	ν_5 PCl_6^-
266 sh	ν_2 & ν_5 PCl_6^-		
276(21)		276(3)	ν_2 PCl_6^-
288(9)			
357(100)	ν_1 PCl_6^-	358(10)	ν_1 PCl_6^-
467(11)	broad	468(4)	
629 < 1		495(0) 611(0)	
637 < 1		632(1)	
647 < 1		648(0)	
661 < 1			
836 < 1		820(1)	

[a] Reference 164.

Table V-4

^{31}P nmr Data for Possible Reaction Products of S_7NH/PCl_5 System

δ (ppm) from H_3PO_4	Literature Values	
-219.5	PCl_3	-219.4, -220, -215 ppm
- 33.0	$SPCl_3$	-28.8, -30, -30.8,
- 29.4		-29, -30.6, -34 ppm
- 20.3	$(Cl_3PNPCl_3)^+$	-21.4 ppm
- 14.3	$(Cl_3P_\alpha NP_\beta(Cl_2)P_\alpha Cl_3)^+$	α = -12.5 ± 1.0 ppm
- 10.4		
- 4.5		
+ 3.1		
+ 13.0	$(Cl_3P_\alpha NP_\beta(Cl_2)NP_\alpha Cl_3)^+$	β = 14.0 ± 1.0 ppm

All nmr data from Reference 123.

NOTE: The P-P coupling constant in $(Cl_3P_\alpha NP_\beta(Cl_2)NP_\alpha Cl_3)^+$ has been observed to be 45.3 Hz.[165] This value is compatible with the line widths observed for the signals assigned to this cation. However, these signals were much too weak to observe the actual triplet and doublet that would be required of $Cl_3P_\alpha NP_\beta(Cl)_2P_\alpha Cl_3^+$.

$$S_7NH + PCl_5 \xrightarrow{CH_2Cl_2} S + PCl_3 + PCl_3(S) + HCl + (Cl_3PNPCl_3)(PCl_6)$$
$$+ (Cl_3PNP(Cl)_2PNPCl_3)(PCl_6)$$

The intensity of the nmr signal due to the $(Cl_3PNPCl_3^+)$ cation indicates that it is one of the major products from the reaction of S_7NH and PCl_5. The trichloro[(trichlorophosphoranylidene)amino]phosphorous (V) hexachlorophosphate has been prepared by two other routes.[166]

(1) $3PCl_5 + NH_4Cl \rightarrow [Cl_3P{=}N{-}PCl_3][PCl_6] + 4HCl$

$[H_3NOH]Cl + PCl_5 \rightarrow Cl_3P{=}NOH + 3HCl$

(2) $Cl_3P{=}NOH + PCl_5 \rightarrow Cl_3P{=}N{-}Cl + HCl + POCl_3$

$Cl_3P{=}N{-}Cl + 2PCl_5 \rightarrow [Cl_3P{=}N{-}PCl_3]PCl_6 + Cl_2$

Both of these synthetic routes for the production of $(Cl_3P{=}N{-}PCl_3)(PCl_6)$ are more involved than the method used in this thesis. However, more work would be required in order to maximize the yield of the $(Cl_3P{=}N{-}PCl_3)$-(PCl_6) obtained from S_7NH.

It should be noted that although the trichloro[(trichlorophosphoranylindene)amino]phosphorous (V) cation was present as the hexachlorophosphate (in the crystal used for the X-ray study), PCl_6^- was not observed in the ^{31}P nmr spectrum of the crude mixture.

Presumably, chloride is the major anion because very little free PCl_5 is available to form the PCl_6^- anion. Consequently, the ^{31}P nmr signal due to PCl_6^- is too weak to be seen.

The reaction of PCl_5 with S_7NH is clearly very complicated.

It is reasonable to assume, as in the $SbCl_5^-$ system, that the first step is the removal of hydrogen as HCl with subsequent formation of $S_7N{\cdot}PCl_4$. A complex series of reactions must follow to produce the observed products.

V-7 The Crystal Structure of $(Cl_3P\text{-}N\text{-}PCl_3^+)(PCl_6^-)$

A crystal of $(Cl_3PNPCl_3^+)(PCl_6^-)$ was removed from the reaction mixture and the crystal structure determined. The structural determination was carried out by Dr. J. Sawyer of this department. The pertinent crystal data is listed in Tables V-5 and V-6. The unit cell and the cation are depicted in Figures V-5 and V-6. It should be noted that the unit cell contains two non-equivalent cations. The environment around the phosphorus atoms in the cation is essentially tetrahedral with the average ClPN and ClPCl bond angles for the two cations being 112° and 107°, respectively. The average P-Cl bond length in the cation, 1.94 Å, is consistently shorter, due to the presence of the positive charge, than the average P-Cl bond distance of 2.13 Å in the anion. The P-N bond distances observed are 1.56 Å and 1.51 Å, the difference is not considered significant for the error limits involved in these bond lengths and also due to the fact that thermal corrections were not applied. The length of a P-N single bond has been assumed to be in the region of 1.77-1.78 Å,[167] as observed in $(CH_3NPCl_3)_2$ and $(CH_3NPF_2(C_6H_5))_2$. The bond lengths in cyclo- and polyphosphazenes are in the range of 1.47-1.62 Å,[167] and this is consistent with the P-N bonds having some multiple bond character.

As with sulphur-nitrogen compounds, the angle about the nitrogen atom, whether in an acyclic or cyclic (phosphorus-nitrogen) compound has been observed to vary quite widely. In Table V-7, some P-N-P bond angles are given for some phosphorus-nitrogen compounds and it is clear

Table V-5

Crystal Data for $(Cl_3PNPCl_3)(PCl_6)$

Space Group	$P2_1/c$	Monoclinic
Unit Cell Dimension	a = 11.692(5) Å	α = 90°
	b = 20.898(9) Å	β = 119.00(3)°
	c = 15.872(6) Å	γ = 90°
Final unweighted R-factor	0.053	

Table V-6 Bond Lengths and Bond Angles for $(Cl_3PNPCl_3)(PCl_6)$

Bond Lengths in (Å)

$P(1)Cl_6^-$		$P(2)Cl_6^-$	
P(1)-Cl(1)	2.127(6)	P Cl(7)	2.120(7)
P(1)-Cl(2)	2.111(6)	P Cl(8)	2.134(6)
P(1)-Cl(3)	2.138(6)	P Cl(9)	2.145(8)
P(1)-Cl(4)	2.111(6)	P Cl(10)	2.146(6)
P(1)-Cl(5)	2.120(8)	P Cl(11)	2.101(6)
P(1)-Cl(6)	2.146(8)	P Cl(12)	2.105(6)
$Cl_3P(11)N(1)P(12)Cl_3^+$		$Cl_3P(21)N(2)P(22)Cl_3^+$	
P(11)-N(1)	1.561(11)	P(21)-N(2)	1.551(14)
P(11)-Cl(13)	1.926(7)	P(21)-Cl(19)	1.946(7)
P(11)-Cl(14)	1.943(7)	P(21)-Cl(20)	1.934(5)
P(11)-Cl(15)	1.945(7)	P(21)-Cl(21)	1.956(8)
P(12)-N(1)	1.521(13)	P(22)-N(2)	1.521(11)
P(12)-Cl(16)	1.955(8)	P(22)-Cl(22)	1.931(7)
P(12)-Cl(17)	1.947(8)	P(22)-Cl(23)	1.947(8)
P(12)-Cl(18)	1.939(5)	P(22)-Cl(24)	1.962(7)

Bond Angles in Degrees

$P(1)Cl_6^-$		$P(2)Cl_6^-$	
Cl(1)-P-Cl(2)	89.93(23)	Cl(7)-P-Cl(8)	89.36(27)
Cl(1)-P-Cl(3)	178.90(36)	Cl(7)-P-Cl(9)	178.65(29)
Cl(1)-P-Cl(4)	90.43(24)	Cl(7)-P-Cl(10)	89.65(26)
Cl(1)-P-Cl(5)	91.27(28)	Cl(7)-P-Cl(11)	90.88(27)
Cl(1)-P-Cl(6)	89.45(30)	Cl(7)-P-Cl(12)	91.05(30)
Cl(2)-P-Cl(3)	90.38(24)	Cl(8)-P-Cl(9)	89.99(24)
Cl(2)-P-Cl(4)	178.68(36)	Cl(8)-P-Cl(10)	88.70(23)
Cl(2)-P-Cl(5)	90.20(27)	Cl(8)-P-Cl(11)	179.07(32)
Cl(2)-P-Cl(6)	89.21(29)	Cl(8)-P-Cl(12)	90.09(23)
Cl(3)-P-Cl(4)	89.24(23)	Cl(9)-P-Cl(10)	89.15(29)
Cl(3)-P-Cl(5)	89.79(30)	-P-Cl(11)	

Table V-6 (Continued)

$P(1)Cl_6^-$		$P(2)Cl_6^-$	
Cl(3)-P-Cl(6)	89.50(27)	Cl(9)-P-Cl(12)	90.13(28)
Cl(4)-P-Cl(5)	91.06(30)	Cl(10)-P-Cl(11)	90.41(24)
Cl(4)-P-Cl(6)	89.54(27)	Cl(10)-P-Cl(12)	178.60(26)
Cl(5)-P-Cl(6)	179.07(31)	Cl(11)-P-Cl(12)	90.80(26)

$Cl_3P(11)N(1)P(12)Cl_3^+$		$Cl_3P(21)N(2)P(22)Cl_3^+$	
P(11)-N(1)-P(12)	135.73(79)	P(21)-N(2)-P(22)	139.02(79)
Cl(13)-P(11)-Cl(14)	106.65(35)	Cl(19)-P(21)-Cl(20)	107.04(28)
Cl(13)-P(11)-Cl(15)	106.76(32)	Cl(19)-P(21)-Cl(21)	106.45(34)
Cl(14)-P(11)-Cl(15)	196.52(31)	Cl(20)-P(21)-Cl(21)	106.96(36)
Cl(13)-P(11)-N(1)	113.22(54)	Cl(19)-P(21)-N(2)	112.60(62)
Cl(14)-P(11)-N(1)	110.85(51)	Cl(20)-P(21)-N(2)	111.08(47)
Cl(15)-P(11)-N(1)	112.43(65)	Cl(21)-P(21)-N(2)	112.36(56)
Cl(16)-P(12)-Cl(17)	106.34(34)	Cl(22)-P(22)-Cl(23)	197.37(38)
Cl(16)-P(12)-Cl(18)	196.27(29)	Cl(22)-P(22)-Cl(24)	106.22(29)
Cl(17)-P(12)-Cl(18)	197.49(35)	Cl(23)-P(22)-Cl(24)	106.17(28)
Cl(16)-P(12)-N(1)	112.86(63)	Cl(22)-P(22)-N(2)	110.79(51)
Cl(17)-P(12)-N(1)	114.26(58)	Cl(23)-P(22)-N(2)	113.07(54)
Cl(18)-P(12)-N(1)	109.19(38)	Cl(24)-P(22)-N(2)	113.73(69)

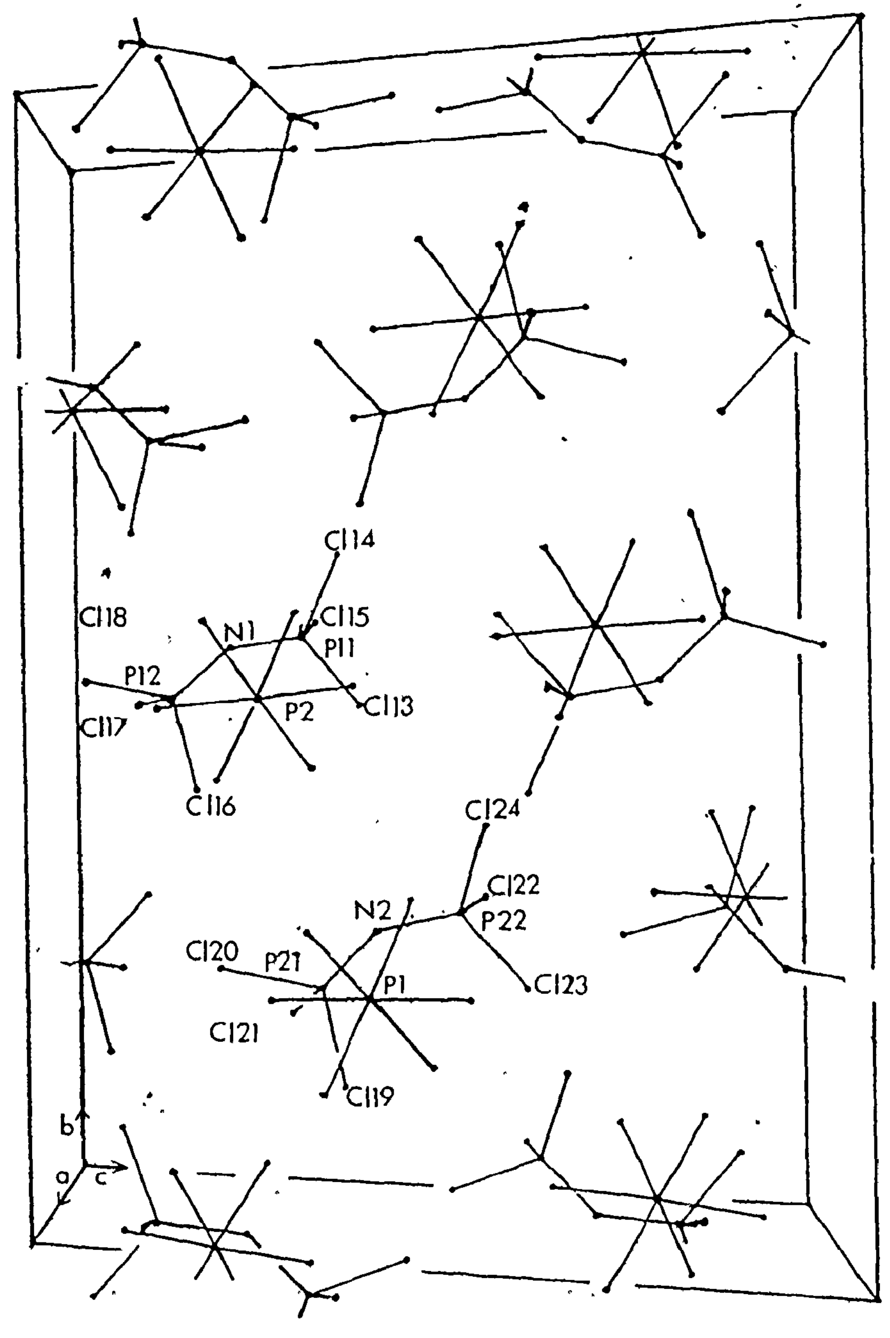


Figure V-5. Unit cell diagram of $(Cl_3PNPCl_3)(PCl_6)$.

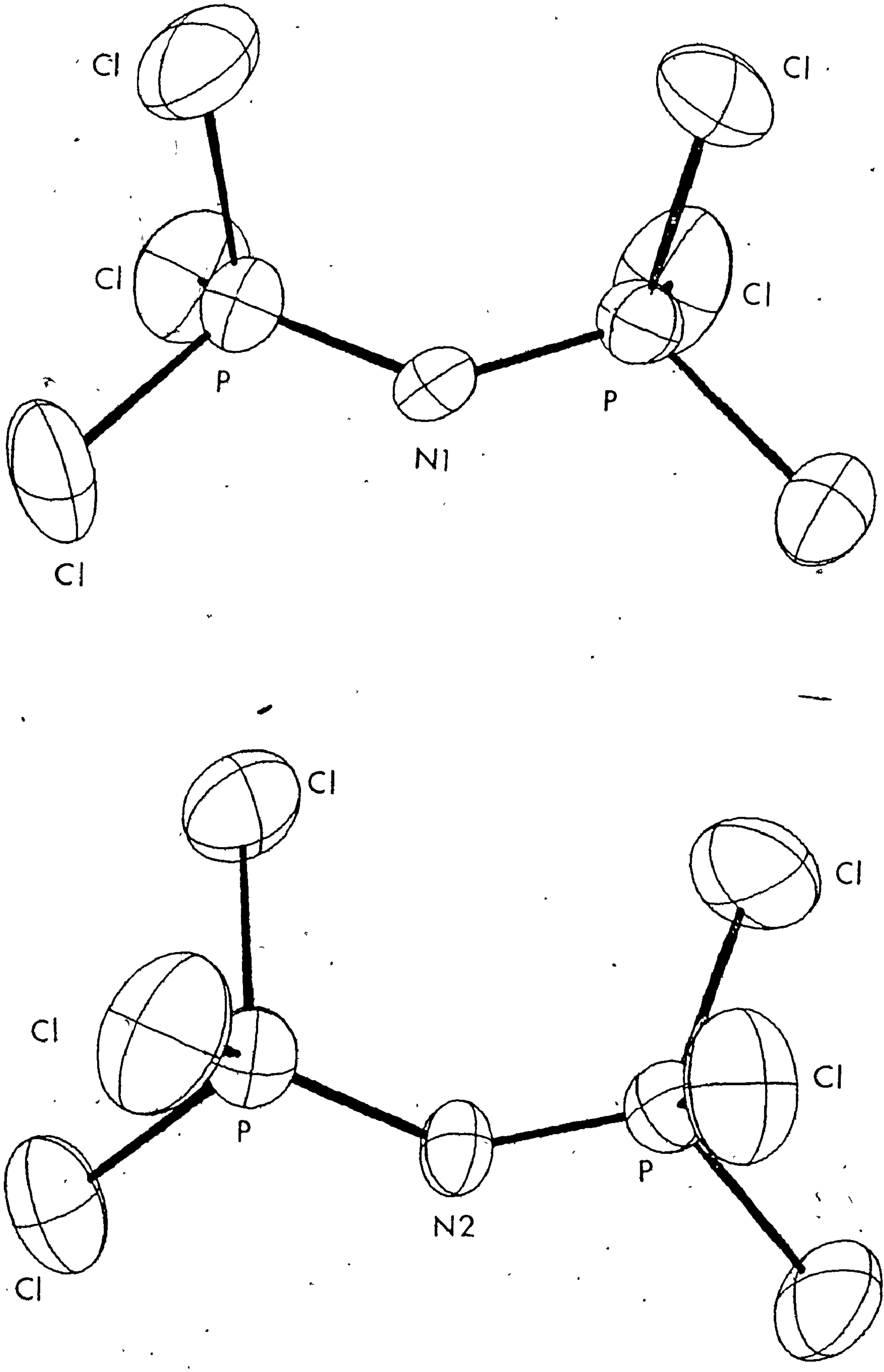
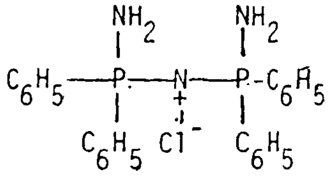
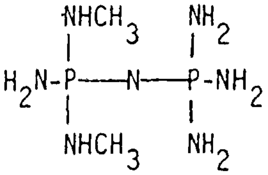
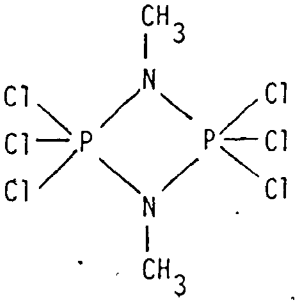
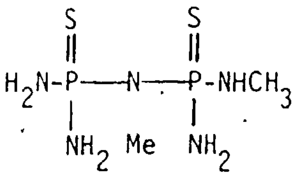


Figure V-6. The $Cl_3PNPCl_3^+$ cation.

Table V-7 Variation in P-N̂-P Bond Angle in Cyclic and Acyclic Phosphorus-Nitrogen Compounds

Compound	P-N̂-P
	136° (a)
	129° (a)
	98.9° (b)
$P_3N_3Cl_6$	121.4° (b)
$P_3N_3F_3$	120.3° (b)
$P_4N_4F_8$	147.4° (b)
$(NPF_2)_n$	136° (b)
$(NPCl_2)_n$	127° (b)
	

(a) Reference 168; (b) Reference 167.

that the angle about nitrogen may vary as much as 48° depending upon ring size, conformation and charge.

Another important factor that must influence the P-N-P bond angle is the type of orbital hybridization occurring at the nitrogen atom. It has been assumed in the cyclic phosphonitrilic halides in which the P-N-P bond angle closely approximates 120°, that the nitrogen is sp^2 hybridized. Again, as in sulphur-nitrogen compounds, observance of angles at nitrogen in excess of 120° must indicate a greater degree of s character in comparison to p-character in the hybridization scheme at nitrogen. This must be the situation in the $Cl_3PNPCl_3^+$ cation in whi[illegible] the average observed P-N-P bond angle is 137.5°.

V-8 Experimental Section

The Reaction of Heptasulphurimide with $SbCl_5$ in a 1:2 Mole Ratio

Heptasulphurimide (0.287 g, 1.20 mmol) and $SbCl_5$ (0.717 g, 2.40 mmol) were each transferred in a dry-box to separate bulbs of a double bulb reaction vessel fitted with a medium glass frit. Sulphur dioxide (5 ml) was then condensed at -196°C into each bulb and the apparatus was flame-sealed. The mixtures were then allowed to warm to room temperature. The $SbCl_5$ completely dissolved in the SO_2 at room temperature but as S_7NH is only moderately soluble in liquid SO_2, some remained undissolved. The $SbCl_5$ solution was then poured through the glass frit into the bulb containing the S_7NH. There was an immediate reaction with the formation of a deep red-brown solution. On shaking for 48 h a yellow powder formed which was characterised as S_8, by means of its Raman spectrum. After filtering at room temperature and slowly removing the solvent, an orange crystalline material was obtained which was shown to be $(S_2N)(SbCl_6)$. The reaction must be allowed to proceed for at least 48 hours prior to filtration to ensure that the S_2NSbCl_6 is not contaminated with sulphur. Hydrogen chloride produced during the reaction was identified by means of its infrared spectrum and $SbCl_3$ sublimed from the reaction mixture was characterised by comparison of its Raman spectrum with a pure sample.

The Reaction of Heptasulphurimide with BCl_3 and $SbCl_5$

The compounds S_7NH (0.5448 g, 2.27 mmol) and $SbCl_5$ (1.3631 g, 4.56 mmol) were transferred in the dry box to separate bulbs of a double bulb reaction vessel. This vessel was fitted with a glass frit as well as a Rota-flo valve between the frit and the bulb containing the $SbCl_5$. In addition, the bulb containing the S_7NH was equipped with a stirring bar. Boron trichloride (0.5288 g, 4.51 mmol) and SO_2 (5 ml) were condensed onto the S_7NH at -196°C, the solution was allowed to warm to -48°C (n-hexanol slush bath) and maintained at this temperature for approximately 1 hour until all the S_7NH was consumed to yield the heptasulphurimide boron dichloride. It was important not to allow the mixture to warm to a higher temperature as a red tar-like material was then produced. Sulfur dioxide (5 ml) was then condensed onto the $SbCl_5$ at -196°C and the solution was allowed to warm to room temperature. The resulting $SO_2/SbCl_5$ solution was then poured through the frit onto the S_7NBCl_2, at -48°C, by opening the Rota-flo valve. The solution immediately turned red-brown and was kept at -48°C for one hour. After this time the solution was allowed to warm to room temperature and stirred for another 48 hours to give a yellow-orange solution containing much solid yellow material. The solution was then filtered and the solvent slowly removed to yield large orange crystals characterized as $(S_2N)(SbCl_6)$. Sulfur and $SbCl_3$ were characterized as other reaction products as outlined previously.

The Reaction of 1,4-$S_6N_2H_2$ with $SbCl_5$ in a 1:4 Mole Ratio

The compounds 1,4-$S_6N_2H_2$ (0.3166 g, 1.42 mmol) and $SbCl_5$ (1.7052 g, 5.71 mmol) were transferred in a dry box to separate bulbs of a double bulb reaction vessel fitted with a medium glass frit and a stirring bar containing the heptasulfurdiimide. Sulfur dioxide (5 ml) was condensed at -196°C into each bulb and the apparatus was flame-sealed. The $SbCl_5$ completely dissolved in the SO_2 at room temperature but as 1,4-$S_6N_2H_2$ is only moderately soluble, some remained undissolved. The $SbCl_5$ solution was then poured through the glass frit into the bulb containing the 1,4-$S_6N_2H_2$. There was an immediate reaction with the formation of deep red-brown solution. The solution was stirred for 48 hours by which time a yellow powder had formed, which was characterized as elemental sulfur by means of its Raman spectrum. The solution colour had also faded from a deep brown to a yellow-orange. After filtering at room temperature and slowly removing the solvent, an orange crystalline material formed which was shown to be $S_2N(SbCl_6)$. Hydrogen chloride produced during the reaction was identified by means of its infrared spectrum and $SbCl_3$ which sublimed from the reaction mixture was characterized by comparison of its Raman spectrum with a pure sample.

The Reaction of $S_4N_4H_4$ with $SbCl_5$ in a 1:3 Mole Ratio

The compounds $S_4N_4H_4$ (0.2268 g, 1.21 mmol) and $SbCl_5$ (1.08 g, 3.62 mmol) were each transferred in a dry box to separate bulbs of a double bulb reaction vessel fitted with a medium glass frit. Sulfur dioxide (5 ml) was then condensed at -196°C into each bulb and the apparatus was flame sealed. The mixtures were then allowed to warm to room temperature. The $SbCl_5$ completely dissolved in the SO_2 at room temperature but $S_4N_4H_4$ was only moderately soluble and consequently some remained undissolved. The $SbCl_5$ solution was then poured through the glass frit into the bulb containing the $S_4N_4H_4$. There was an immediate reaction with the formation of a deep red solution. The reaction mixture was stirred at room temperature for 24 hours and after this time filtered and the solvent was slowly removed. A red crystalline material was obtained which was shown to be $S_4N_4 \cdot SbCl_5$ by comparison of its Raman spectrum with that of a genuine sample. Hydrogen chloride produced during the reaction was identified by means of its infrared spectrum and $SbCl_3$ sublimed from the reaction mixture was characterized by comparison of its Raman spectrum with a pure sample.

The Reaction of $S_4N_4H_4$ with $SbCl_5$ in a 1:5 Mole Ratio

The reaction procedure was identical to that outlined in the previous section. In this instance, $S_4N_4H_4$ (0.1771 g, 0.942 mmol) and $SbCl_5$ (1.41 g, 4.71 mmol) were transferred in the dry box to separate bulbs of a double bulb reaction vessel. Sulphur dioxide solutions of each reactant were formed and the $SbCl_5/SO_2$ solution was poured through the frit onto the $S_4N_4H_4/SO_2$ solution. The reaction mixture immediately turned red and after several hours it faded to an orange-red colour. The mixture was stirred for 24 h and finally became yellow with much yellow solid present. The saturated yellow solution was washed through the frit and yellow crystals formed on slow removal of the solvent. These crystals were shown to be $S_4N_4(SbCl_6)_2$ by comparison of their Raman spectrum with that of a pure sample. The other products HCl and $SbCl_3$ were characterized as before.

The Reaction of S_7NCH_3 with $SbCl_5$ in a 1:3 Mole Ratio

The compound S_7NCH_3 (0.0886 g, 0.350 mmol) was transferred in the dry box to one bulb of a double reaction vessel. Due to the fact that S_7NCH_3 is an oil, the transfer was accomplished by first dissolving the S_7NCH_3 in dry CCl_4 (5 ml) and the resulting solution was then syringed into the reaction vessel. The CCl_4 was then evacuated from the vessel. The other reactant, $SbCl_5$ (0.314 g, 1.05 mmol), was transferred in the dry box to the other bulb and then SO_2 (5 ml) was condensed at -196°C into both bulbs and the reaction vessel was flame sealed. The $SbCl_5/SO_2$ solution was poured through the frit onto the S_7NCH_3/SO_2 mixture and an orange-red mixture formed. The mixture was stirred for 24 h. and the solution became deep orange in colour and a cream coloured solid precipitated from solution. The solid was identified as sulfur by comparison of its Raman spectrum with that of pure sulphur and $SbCl_3$ was isolated and characterized as described previously. The other products formed were not characterized and there was no evidence for the formation of S_2NSbCl_6.

The Reaction of S_7NH with AsF_5 in a 1:3 Mole Ratio

This reaction was carried out in the vessel illustrated in Fig. II-2. The compound S_7NH (0.176 g, 0.735 mmol) was transferred in the dry box to the vessel. The vessel was then evacuated and AsF_5 (0.375 g, 2.20 mmol) and SO_2 (10 ml) were condensed at -196°C onto the S_7NH. The ampoule was not flame sealed and the contents were allowed to warm to room temperature. At room temperature, the solution was red-brown and no solid material was present. The esr spectrum of the solution was obtained after one hour and then further AsF_5 (1.12 g, 6.62 mmol) was condensed into the reaction vessel at -196°C. After warming to room temperature, the solution was dark blue and again no solid material was observable. The esr spectrum was obtained again after one hour. The solvent was then removed under vacuum to yield a dark blue solid. The u.v. absorption spectrum of this solid material was consistent with the presence of S_8^{2+}.

The Reaction of S_7NH with SbF_5 in a 1:3 Mole Ratio

The compound SbF_5 (1.56 g, 6.92 mmol) was transferred in the dry box to one bulb of preweighed double bulb reaction vessel. The vessel used was similar to the one illustrated in Fig. II-2 but an nmr tube had been blown onto the bulb not containing the stirring bar. The ampoule was weighed to determine the exact amount of S_7NH required (0.551 g, 2.30 mmol) and this amount was transferred, in the dry box to the remaining empty bulb. Sulphur dioxide (5 ml) was condensed onto each reactant, at -196°C, and the vessel was allowed to warm to room temperature. Upon reaching room temperature the SbF_5/SO_2 solution was poured through the frit onto the S_7NH/SO_2 solution. An immediate reaction occurred with the formation of a red-brown solution. The S_7NH became coated with a red-brown material and within 24 hours no solid material was present. The reaction mixture was filtered and the esr spectrum was obtained. Removal of the solvent produced a red-brown solid that was extremely soluble in SO_2.

The entire procedure was then repeated using S_7NH and SbF_5 in a 1:6 molar ratio. The resulting SO_2 solution initially became red-brown, however within 24 hours a dark blue solution was obtained that contained little undissolved solid. The esr spectrum of the solution was obtained and removal of the solvent produced a dark blue solid. The u.v. spectrum was consistent with this material containing S_8^{2+}.

The Reaction of S_7NCH_3 with AsF_5 in a 1:10 Mole Ratio

The reaction was carried out in the vessel described in Fig. II-2. The S_7NCH_3 (0.257 g, 1.02 mmol) was transferred to the vessel in a manner described previously. AsF_5 (1.72 g, 10.1 mmol) and SO_2 (10 ml) were condensed at -196° onto the $S_7N\ CH_3$, the vessel was flame sealed and warmed to room temperature. The solution turned red-brown as it warmed and after several hours was a deep dark blue. The solution was filtered and the u.v. absorption spectrum indicated the presence of S_8^{2+}.

The Reaction of S_7NH with PCl_5 in a 1:2 Mole Ratio

The compounds S_7NH (0.184 g, 0.770 mmol) and PCl_5 (0.317 g, 1.54 mmol) were each transferred in the dry box to the same bulb of a double bulb reaction vessel; no reaction of the mixed solid materials was noticed. Methylene chloride (10 ml) was condensed onto the reactants, at -196°C and the mixture was allowed to warm to room temperature. Upon reaching room temperature, no immediate reaction occurred but within one hour, the solid material slowly dissolved to produce a clear yellow solution, after 24 hours no solid material was present. The clear yellow solution was stirred for a further 24 hours and then filtered. The solvent was slowly removed to yield a mixture of yellow and colourless crystals. The yellow crystals were demonstrated to be sulphur by comparison with the spectrum of a pure sample of sulphur. A ^{31}P nmr spectrum of the solvent was obtained and one of the colourless crystals was isolated for X-ray crystallographic studies and was shown to be $(Cl_3PNPCl_3)(PCl_6)$. The presence of HCl was verified as previously described.

The Reaction of S_7NH with PF_5 in a 1:2 Mole Ratio

The compound S_7NH (0.459 g, 1.92 mmol) was transferred in a dry box to one bulb of a double bulb reaction vessel that had an nmr tube attached to one of the bulbs. Phosphorous pentafluoride (0.484 g, 3.84 mmol) and SO_2 (10 ml) were condensed at -196°C onto the S_7NH and the reaction vessel was flame sealed. The reaction mixture was allowed to warm to room temperature to give a red-pink solution with much unreacted S_7NH. After 24 hours, the solution became clear yellow and a considerable amount of yellow solid was present. The solution was filtered and the esr spectrum was obtained. The Raman spectrum of the yellow solid indicated that it was sulphur. It was noted that after approximately two weeks the SO_2 solution became increasingly blue-green in colour.

The Reaction of S_7NCH_3 with PF_5 in a 1:2 Mole Ratio

The reaction procedure was similar to that described above for the S_7NH/PF_5 system. The S_7NCH_3 (0.280 g, 1.12 mmol) was transferred as described in previous sections to the vessel illustrated in Fig. II-2. The compounds PF_5 (0.239 g, 2.21 mmol) and SO_2 (10 ml) were condensed at -196°C onto the S_7NCH_3 and the reaction mixture was warmed to room temperature. A pink-red solution formed initially and the S_7NCH_3 was consumed over a 24 hour period to yield a yellow solution and a yellow solid. The solution was filtered and the esr spectrum was obtained. A Raman spectrum of the yellow solid indicated the presence of sulphur.

CHAPTER VI

VI-1 Conclusions

At the commencement of this work, the Lewis acid chemistry of the sulphur nitrides was poorly developed. A number of the products of the reactions between sulphur nitrides and Lewis acids had been only poorly characterized and almost nothing was known about the mechanisms of these reactions. Attention had been largely focused on the formation of donor-acceptor complexes between S_4N_4 and Lewis acids and some of these adducts, particularly those with $SbCl_5$ [27] and BF_3,[27,28] had been characterized crystallographically.

Little attention had been paid, however, to other types of reactions that might occur between S_4N_4 and Lewis acids although it had been shown that S_4N_4 can be oxidized by AsF_5 [31] to the stable radical cation $S_3N_2^+$. One important result of the present work was the demonstration that S_4N_4 is rather readily oxidized by $SbCl_5$, AsF_5 and SbF_5 to the hitherto unknown $S_4N_4^{2+}$ cation. Phosphorus pentafluoride, however, apparently is not a strong enough oxidizing agent to oxidize S_4N_4 to the dication but it forms the previously unreported adduct $S_4N_4 \cdot PF_5$. In contrast PCl_5 was found to react vigorously with S_4N_4 to give sulphur chlorides and phosphonitrilic halides. The results of the Lewis acid chemistry of S_4N_4 are summarized in Table VI-1.

It was of considerable interest to find that the new species $S_4N_4^{2+}$ was also formed when $S_3N_3Cl_3$ was reacted with $SbCl_5$. There is at

Table VI-1

Summary of the Lewis Acid Chemistry of S_4N_4

Lewis Acid Ratio of S_4N_4 to Lewis Acid	$SbCl_5$	SbF_5	AsF_5	PF_5	PCl_5
1:1	$S_4N_4 \cdot SbCl_5$		$S_4N_4 \cdot AsF_5$ (a)	$S_4N_4 \cdot PF_5$	complex mixture of P-N compounds produced
1:2	$S_4N_4 \cdot Sb_2Cl_{10}$				
1:3	$S_4N_4(SbCl_6)_2$	$S_4N_4(SbF_6)_2$	$S_4N_4(AsF_6)_2$ $S_3N_2(AsF_6)$ (b)	no further oxidation	
1:4		$S_4N_4(Sb_3F_{14})$-(SbF_6)			

(a) Reference 30.

(b) Reference 31.

least one other product of this reaction which was identified as $Cl_3SN \cdot SbCl_5$. However, as Cl_3SN has not been previously prepared and as a full structural study of the new compound was not carried out, this conclusion can only be regarded as tentative. It was demonstrated that the first step in the oxidation process is the formation of the cation $S_3N_3Cl_2^+$ and the compounds $S_4N_4 \cdot SbCl_5$ and $S_5N_5(SbCl_6)$ were shown to be intermediates in the reaction. The detailed investigation of this reaction has thrown considerable doubt upon the previous claim that $SbCl_5$ forms the adducts $S_3N_3Cl_3$-$xSbCl_5$, where x = 1,2, and 3.

The trifluoride $S_3N_3F_3$ reacts in a different manner with AsF_5, SbF_5 and SO_3 in each case giving a salt of the SN^+ cation, namely $SN(AsF_6)$, $SN(SbF_6)$ and $SN(SO_3F)$. The chemistry of the trihalocyclothiazenes is summarized in Fig. VI-1.

It appears that $S_4N_4^{2+}$ is a common product of the oxidation of SN compounds since this apparently rather stable ion was also obtained as the product of the oxidation of $S_4N_4H_4$ with $SbCl_5$. However, oxidation of heptasulphurimide, S_7NH and 1,4-$S_6N_2H_2$ led to the formation of the previously unreported S_2N^+ cation.

It was found that PCl_5 reacts with S_7NH in a similar manner to its reaction with S_4N_4 to produce phosphonitrilic halides and in this case the compound $(Cl_3PNPCl_3)(PCl_6)$ was identified among the products. The Lewis acid chemistry of the sulphur imides is summarized in Fig. VI-2. Clearly, these reactions are very complex and need considerable further study. Indeed, it is true to say that details of almost all the reactions described in this thesis are poorly understood. The chemistry of the sul-

Figure VI-1

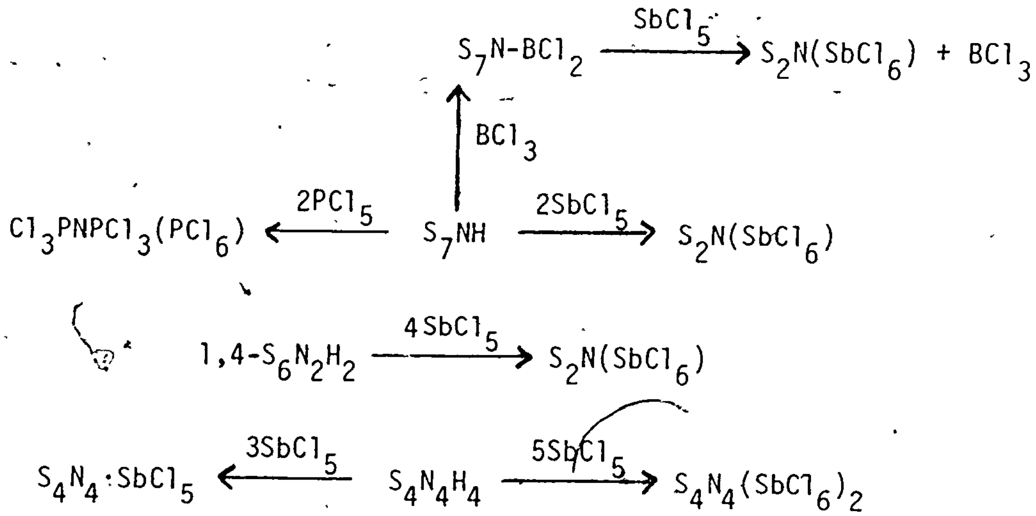
A Summary of the Lewis Acid Chemistry of the Trihalocyclotrithiazenes

$$\begin{tikzcd}
Cl_3SN\cdot SbCl_5 + S_4N_4(SbCl_6)_2 + S_4N_4(SbCl_6)_2 & S_3N_3Cl_3 \arrow[l, "2SbCl_5"', "SO_2"] \arrow[r, "1SbCl_5", "SO_2"'] \arrow[d, "CH_2Cl_2"', "1SbCl_5"] & S_3N_3Cl_2(SbCl_6) \\
 & S_4N_4\cdot SbCl_5 & \\
 & S_5N_5(SbCl_6) &
\end{tikzcd}$$

$$\begin{tikzcd}
SN(MF_6) & S_3N_3F_3 \arrow[l, "3MF_6"'] \arrow[r, "1MF_5"] \arrow[d, "3SO_3"] & (S_3N_3F_2)(MF_6) & M = As,Sb \\
 & SN(SO_3F) & &
\end{tikzcd}$$

Figure VI-2

Lewis Acid Chemistry of the Sulphur Imides



phur nitrides is still in a very early state of development and it seems unlikely that much progress will be made in understanding these reactions until all products have been isolated and identified and at least some of the intermediates have been characterized.

The known sulphur-nitrogen cations are listed in Table VI-2. All cyclic cations are planar except for one of the forms of $S_4N_4^{2+}$. Banister has pointed out that most of the cyclic cations are Hückel precise and obey the Hückel 4n + 2 rule. The only clear exception to the rule is the radical cation $S_3N_2^{+}$ which has seven π electrons. However, it should be noted that although these species apparently conform to the Hückel rule they do not necessarily have equal bond lengths as in aromatic carbon compounds. Moreover, these rings are not necessarily planar as exemplified by one form of $S_4N_4^{2+}$.

It should also be noted that in many cases, the bond angles at nitrogen are considerably in excess of that expected for sp^2 hybridization which is, of course, characteristic of aromatic carbon compounds.

VI-2 Suggestions for Future Work

The cations S_2N^+ and SN^+ are isovalent with NO_2^+ and NO^+ and at present it is not known whether they would exhibit similar chemical behaviour to the nitronium and nitrosonium ions. Thus, it may be possible to produce thiazyl benzene and dithionitronium benzene derivatives by reactions such as

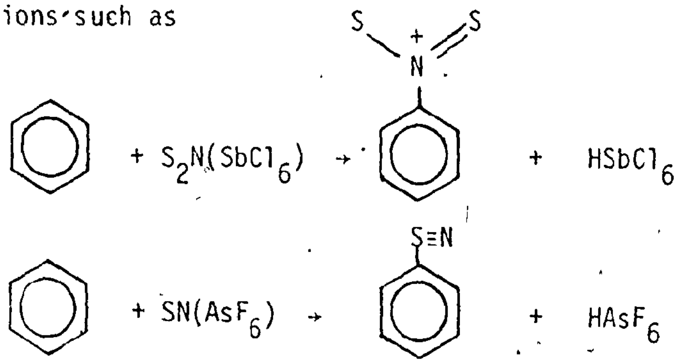


Table VI-2

The Known Sulphur–Nitrogen Cations

Cyclic Cations	Number of π Electrons
$S_5N_5^+$	14π
$S_4N_4^{2+}$	10π
$S_4N_3^+$	10π
$S_3N_2^+$	7π
$S_3N_2^{2+}$	6π
$S_3N_2Cl^+$	6π

Open Chain Cations

$Cl_2S_2N^+$

S_2N^+

SN^+

It has been demonstrated that the SN^+ cation may act as an electrophile toward S_4N_4 to yield $S_5N_5^+$.[52] There is therefore the likely possibility that SN^+ and S_2N^+ might react with other SN species to generate new ring systems. Possible reactions are listed

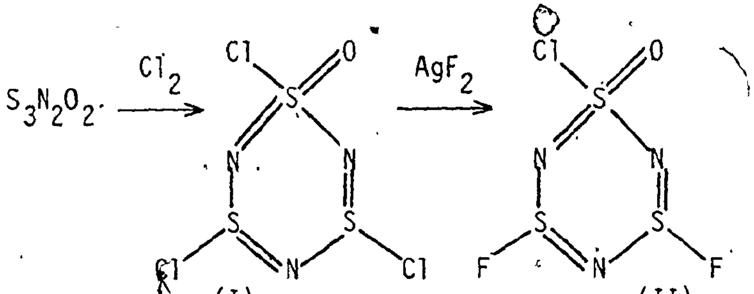
$$S_3N_3^- + SN^+ \rightarrow S_4N_4$$
$$S_3N_3^- + S_2N^+ \rightarrow S_5N_4$$
$$S_4N_5^- + S_2N^+ \rightarrow S_6N_6$$

It was observed during the course of this work that S_4N_4 is easily oxidized by the cations S_8^{2+} and Se_8^{2+}. The reduction products of these reactions are elemental sulphur and selenium. The yield of sulphur produced was lower than expected and this may be indicative of sulphur atoms being inserted into the S_4N_4 ring. No evidence for the $S_4N_4^{2+}$ cation could be found and thus these reactions may provide synthetic routes to new S-N cations. The oxidation of S_4N_4 with Se_8^{2+} may be a synthetic route to mixed S-Se-N cations. The oxidation of S_4N_4 by other polyatomic cations of group VIa may be a good source of new cations.

The group $S_3N_3Cl_3$ was shown to be easily oxidized by $SbCl_5$ to produce the $S_4N_4^{2+}$ dication and a green material which is believed to be $Cl_3SN\text{-}SbCl_5$. It would be of interest to study the reaction of thiazyl chloride, NSCl, with $SbCl_5$. If oxidation occurs, rather than chloride ion abstraction, it is possible that the sulphur(VI) compound $Cl_3S{\equiv}N$ thiazyl trichloride could be prepared.

$$ClSN + SbCl_5 \rightarrow Cl_3SN + SbCl_3$$

The chlorination of $S_3N_2O_2$ produces the compound $S_3N_3Cl_3O$ which can be easily fluorinated to $S_3N_3F_3ClO$.[169]



Lewis acid oxidation of I could be a source of oxygen containing S-N cations. It is perhaps possible that $S_4N_4O^{2+}$ may be synthesized in this manner. Oxidation of II would be of interest, in that II may be a source of SN^{+} and the unknown cation, SNO^{+}, then this would seem to imply that the new cation SNO^{+} may be prepared.

$$S_3N_3F_2OCl + AsF_5 \rightarrow 2SN(AsF_6) + (SNO)(AsF_5Cl)$$

The Lewis acid PCl_5 apparently reacts with the sulphur nitrides to produce phosphorus-nitrogen compounds. Due to the complexity of these reactions, they were not fully investigated. However, the PCl_5/sulphur nitride system may be a good source of phosphorus compounds that are difficult to obtain by other means.

The chemistry of the sulphur nitrides is a field which needs to be studied further. More work is required to understand synthetic pathways and bonding in sulphur-nitrogen systems which have already presented many challenges to both the synthetic and physical chemist.

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