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SOME REACTIONS OF TETRASULPHUR TETRANITRIDE

AND TRITHIAZYL TRICHLORIDE

by

G.G. ALANGE

A thesis submitted for the degree of Doctor of Philosophy  
in the University of Durham

August 1969



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## SUMMARY

The thesis can be conveniently divided into two parts (a) the reactions of tetrasulphur tetranitride and (b) the reactions of trithiazyl trichloride.

### (a) Reactions of tetrasulphur tetranitride

The reactions of tetrasulphur tetranitride with many

- i) Lewis acids in inert organic solvents have been studied. Adducts of 2:1, 1:1, 1:2, 1:4 ( $S_4N_4$ : Lewis acid) stoichiometry have been prepared; it is likely that in most of these compounds the nitrogen of  $S_4N_4$  is coordinated to the Lewis acid. The following new compounds have been prepared:  $2S_4N_4 \cdot SnBr_4$ ,  $S_4N_4 \cdot TiBr_4$ ,  $S_4N_4 \cdot 4TiF_4$ ,  $S_4N_4 \cdot TiI_4$ ,  $S_4N_4 \cdot ZrCl_4$ ,  $S_4N_4 \cdot HfCl_4$ ,  $S_4N_4 \cdot SeCl_4$ ,  $S_4N_4 \cdot TeCl_4$ ,  $S_4N_4 \cdot TeF_4$ ,  $S_4N_4 \cdot NbCl_5$ ,  $S_4N_4 \cdot NbF_5$ ,  $S_4N_4 \cdot TaCl_5$ ,  $S_4N_4 \cdot TaF_5$ ,  $S_4N_4 \cdot 2AlCl_3$ ,  $S_4N_4 \cdot 2AlBr_3$ ,  $S_4N_4 \cdot 2GaCl_3$ ,  $S_4N_4 \cdot 2InCl_3$ ,  $S_4N_4 \cdot 2TlCl_3$  (?),  $S_4N_4 \cdot PhBCl_2$ ,  $S_4N_4 \cdot WBr_4$ ,  $S_4N_4 \cdot WOCl_4$  (?). Silicon tetrachloride, germanium tetrachloride and tin tetraiodide do not react under the conditions studied; p-tolytin trichloride gives  $2S_4N_4 \cdot SnCl_4$  due to disproportionation into tin tetrachloride and tetra-p-tolytin.

The infrared spectra of the new adducts and some of the previously reported adducts are recorded and their structures have been discussed. These compounds can be roughly divided into two types (i) adducts with infrared spectra similar to the infrared

of compounds of known structure ( $S_4N_4 \cdot SbCl_5$ ,  $S_4N_4 \cdot BF_3$ ) and (ii) the infrared spectra of products whose spectra differ from the infrared spectra of  $S_4N_4 \cdot SbCl_5$  and  $S_4N_4 \cdot BF_3$ . Compounds of type (i) are considered to contain monodentate  $S_4N_4$ ; in other cases possible structures have been discussed by analogy with other adducts described in the literature.

A study of the reactions between  $S_4N_4$  and (a) sulphuryl chloride and (b) chlorine led to (a) a new convenient synthesis for trithiazyl trichloride and (b) a new compound thought to be  $S_6N_6Cl_4$ .

(b) Reactions of trithiazyl trichloride

The second part of the thesis deals with trithiazyl trichloride reactions. Apart from conversion to the trifluoride no other reactions of this compound are known. Trithiazyl trichloride reacts with epoxides to give the following esters (i)  $(NSO \cdot C_3H_5Cl_2)_3$  (ii)  $(NSOC_3H_5BrCl)_3$ , (iii)  $(NSOC_2H_4Cl)_3$ , (iv)  $(NSOC_4H_8O)_3$ . Trithiazyl trichloride reactions with nitriles yielded a variety of products and possible structures are discussed.

## ACKNOWLEDGEMENTS

The author wishes to express his grateful thanks to Dr. A.J. Banister under whose guidance this research was carried out, for his help, valuable advice and constant encouragement throughout the course of the work. Thanks are due to S.C.S. College Omerga, Dr. N.K.Hazari and Mrs. P. Blair for their help in many ways and the University of Durham for research facilities.

## INTRODUCTION

The chemistry of sulphur nitrogen compounds has been a topic of interest since the first synthesis of tetrasulphur tetranitride.<sup>1</sup> Today many sulphur nitrogen compounds are known which are derived from this nitride and their chemistry has been thoroughly investigated. It shows hardly any analogy with that of nitrogen oxygen compounds. This observation may be ascribed to the facts that (a) nitrogen is the less electronegative partner in binary oxygen nitrogen compounds<sup>2</sup>, (b) many of the characteristic properties of oxygen are related to its small size, thus its ionization potential is appreciably higher than for sulphur, (c) the non-availability to oxygen of d-orbitals limits the covalency maximum to four. The chemistry of sulphur-nitrogen compounds has several interesting and important features, namely, stability of the sulphur-nitrogen bond, tendency to form six and eight membered rings, ring contraction, polymerisation and ion formation. Compounds with six or eight membered rings of alternating sulphur-nitrogen atoms have aroused considerable interest in connection with the bonding properties of their  $\pi$ -electrons<sup>3,4,5</sup>.

### The sulphur nitrides

Monomeric sulphur nitride or 'thiazyl', SN is the thio-analogue of nitric oxide, and like nitric oxide, is a radical<sup>5</sup>.

Nitric oxide exhibits a tendency to lose electrons to form the positively charged nitrosonium ion which is isoelectronic with elemental nitrogen and the cyanide ion. Because of the lower electronegativity of sulphur compared with O, there would appear to be a greater tendency to form a cation but no definite  $\text{NS}^{\oplus}$  compounds have been isolated. There is some evidence however, that a positive  $\text{S}\equiv\text{N}$  species does exist as an intermediate, especially since trithiazyl trichloride,  $(\text{NSCl})_3$ , is obtained by the direct chlorination of  $\text{S}_4\text{N}_4$ .<sup>7</sup> It has only actually been detected (from its emission spectrum) in a mixture of nitrogen and sulphur vapour subjected to an electric discharge.<sup>8</sup> It has also been prepared by the reaction of  $\text{H}_2\text{S}$  with atomic nitrogen,<sup>9</sup> and its presence as an intermediate in reactions of some sulphur-nitrogen compounds has been invoked.<sup>10</sup> Since many reactions of trithiazyl trichloride,  $(\text{NSCl})_3$ , in solution proceed by way of thiazyl chloride,  $\text{NSCl}$ <sup>11</sup>, several reactions of tetrasulphur tetranitride may proceed via monomeric sulphur nitride  $\text{NS}$ .<sup>11</sup>

The structure of monomeric thionitrosyl can be represented by a typical 3-electron bond configuration, as in the case of nitric oxide. In principle a stable ion can be achieved by loss of an electron to give  $\text{N}\equiv\overset{+}{\text{S}}$ , or by electron addition to give  $\bar{\text{N}}=\overset{-}{\text{S}}$ .

The monomer, NS can be represented either by a V.B. representation involving a three electron bond,  $:N \equiv S:$  or more precisely by a M.O. picture similar to that for NO.

The probable analogy between an  $S \equiv N$  and the  $C \equiv N$  groups in the monomeric thiazyl and cyanogen compounds appears worthy of consideration. Such triple bonds to nitrogen are stable among the carbon compounds  $R-C \equiv N$ ; they are apparently not stable in phosphorus chemistry ( $N \equiv PX_3$ ) and are only known in sulphur chemistry for  $NSF_3$ ,  $NSF$  and  $NSCl$ .

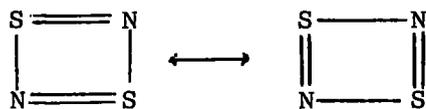
#### Disulphur dinitride

When tetrasulphur tetranitride is sublimed in vacuo and the vapour led through a zone filled with silver wool and heated to  $300^\circ C$  thermal fission of the molecule occurs. Although (SN) and a little sulphur (as  $Ag_2S$ ) and nitrogen are formed, the predominant product (60% yield) consists of a white volatile substance which can be condensed in a trap cooled to  $-196^\circ - 80^\circ C$ .<sup>17</sup> This compound is soluble in benzene, ether, carbon tetrachloride, acetone, tetrahydrofuran, dioxane and can be recrystallised from them, but insoluble in water<sup>13,14</sup>. The colourless product obtained in this way contains equal numbers of sulphur and nitrogen atoms and has the formula  $S_2N_2$ <sup>15</sup>. It sublimes at room temperature at 0.01mm Hg and has a strong unpleasant odour. It has been reported<sup>12</sup> to decompose explosively above  $30^\circ C$  or on impact.

In more recent investigations  $S_2N_2$  vapour was unaffected by glass wool at  $300^\circ$  and on heating above  $30^\circ$ , rapid polymerisation not detonation was observed<sup>17</sup>.

Disulphur dinitride rapidly dimerises to tetrasulphur tetranitride when an alkali metal or an alkali carbonate or cyanide is added to its benzene solution<sup>16</sup>. Spontaneous polymerisation occurs when the compound is stored at below  $30^\circ C$ . A compound with the composition  $(SN)_x$  is formed as well as the tetrasulphur tetranitride. The polymeric sulphur nitride  $(SN)_x$  is the sole product if moisture is rigorously excluded.<sup>13</sup>

The infrared spectrum and chemical properties of  $S_2N_2$  have led to its formulation as a four-membered planar ring with alternating S and N atoms.<sup>14a</sup>



This is supported by X-ray examination of the adduct  $S_2N_2 \cdot SbCl_5$ <sup>17</sup>.

Reactions of disulphur dinitride with antimony pentachloride and boron halides have been studied recently<sup>17</sup> and the effect of donation on the stability and structure of the  $S_2N_2$  ring have been investigated.

Solutions of  $S_2N_2$  in dichloromethane react with antimony pentachloride (in excess) and form a diadduct  $S_2N_2(SbCl_5)_2$  which can further react with  $S_2N_2$  to form a monoadduct  $S_2N_2SbCl_5$ . The

monoadduct can be reconverted to the diadduct by treatment with  $\text{SbCl}_5$ . The physical and chemical properties of these compounds indicate that the  $\text{S}_2\text{N}_2$  ring structure is maintained intact. The monoadduct  $\text{S}_2\text{N}_2 \cdot \text{SbCl}_5$  reacts irreversibly with  $\text{S}_2\text{N}_2$  to form both the previously characterised  $\text{S}_4\text{N}_4 \cdot \text{SbCl}_5$  and, in lower yields, a less reactive material  $(\text{S}_4\text{N}_4 \cdot \text{SbCl}_5)_x$ . Antimony pentachloride acts as a catalyst for the dimerisation of  $\text{S}_2\text{N}_2$ .<sup>17</sup>

Disulphur dinitride reacts with boron trichloride in dichloromethane to form the following compounds:<sup>17</sup>

$\text{S}_4\text{N}_4\text{BCl}_3$ ,  $\text{S}_2\text{N}_2(\text{BCl}_3)_2$  and  $(\text{S}_2\text{N}_2\text{BCl}_3)_2$ . At  $0^\circ\text{C}$   $\text{S}_2\text{N}_2(\text{BCl}_3)_2$  loses  $\text{BCl}_3$  to form the adduct  $\text{S}_2\text{N}_2\text{BCl}_3$  which can be reconverted to the diadduct by treatment with  $\text{BCl}_3$  at  $-78^\circ\text{C}$ . Antimony pentachloride  $\text{SbCl}_5$  displaces boron trichloride;  $\text{BCl}_3$  from  $\text{S}_2\text{N}_2\text{BCl}_3$  to form  $\text{S}_2\text{N}_2(\text{SbCl}_5)_2$ , the polymeric compound,  $(\text{S}_2\text{N}_2\text{BCl}_3)_x$  is inert toward both  $\text{BCl}_3$  and  $\text{SbCl}_5$ . The properties of  $\text{S}_2\text{N}_2\text{BCl}_3$  and  $\text{S}_2\text{N}_2(\text{BCl}_3)_2$  indicate that the  $\text{S}_2\text{N}_2$  ring structure remains intact. Reaction of  $\text{S}_2\text{N}_2$  with  $\text{BF}_3$  yields only  $\text{S}_4\text{N}_4\text{BF}_3$ .<sup>17</sup>

#### Tetrasulphur tetranitride

The earliest known nitride of sulphur is tetrasulphur tetranitride. The compound is formed when disulphur dichloride and ammonia are reacted together and was first discovered by Gregory<sup>15</sup>. Tetrasulphur tetranitride can be formed in a variety of reactions<sup>8</sup>. It can also be obtained from several other sulphur-

nitrogen compounds.  $S_4N_4$  is usually prepared by passing gaseous ammonia into a solution of sulphur dichloride,  $S_2Cl_2$  in an inert solvent such as  $CCl_4$ <sup>16,18</sup> ( $S_2Cl_2 + Cl_2 \rightleftharpoons 2S_2Cl_2$ ;  $6S_2Cl_2 + 16NH_3 \longrightarrow S_4N_4 + 2S + 12NH_4Cl$ ). This preparation is typical for non-metal- nitrogen compounds (viz: non-metal halide and  $NH_3$  or  $NH_4^+$  salt). In organic solvents of low dielectric constant yields of  $S_4N_4$  from disulphur dichloride and ammonia are higher than in solvents of high dielectric constants.<sup>6</sup> Insufficient is known about the course of the sulphur-chloride ammonia reaction to be able to explain these yield variations. It is however, thought that the tetrasulphur tetranitride may be formed via thiodithiazyl dichloride,  $S_3N_2Cl_2$ , containing a five-membered S-N ring and thiotrithiazyl chloride  $S_4N_3Cl$ , which contains a seven membered ring.<sup>6,21,22</sup> A convenient laboratory preparation for small amounts of the tetranitride makes use of the reaction between disulphur dichloride vapour and dry pellets of ammonium chloride at  $160^\circ$  ( $6S_2Cl_2 + 4NH_4Cl \longrightarrow S_4N_4 + 8S + 16HCl$ ).<sup>23</sup>

Tetrasulphur tetranitride can also be prepared by the following methods:-

- (a) Reaction between elemental sulphur and liquid ammonia at room temperature under pressure. While crystalline sulphur is insoluble in this medium below  $11.5^\circ C$ , blue solutions are formed at higher temperatures which remain stable at room temperature ( $10S + 4NH_3 \longrightarrow$

the  
 $6\text{H}_2\text{S} + \text{S}_4\text{N}_4$ ). If  $\text{H}_2\text{S}$  is removed from the equilibrium system, tetrasulphur tetranitride can be isolated from the solid residue after evaporating the ammonia<sup>12</sup>.

(b) It is prepared by the reaction between disulphur dichloride and lithium azide in an inert solvent at  $0^\circ\text{C}$  ( $4\text{LiN}_3 + 2\text{S}_2\text{Cl}_2 \rightarrow 2\text{S}_2(\text{N}_3)_2 + 4\text{LiCl}$ ;  $2\text{S}_2(\text{N}_3)_2 \rightarrow \text{S}_4\text{N}_4 + 4\text{N}_2$ )<sup>24</sup>

(c) It is formed when active nitrogen is allowed to react with sulphur or sulphur compounds ( $\text{S}_2$  (vapour)  $\xrightarrow{(\text{N})} \text{S}_4\text{N}_4 + (\text{NS})_x$ )<sup>25</sup>

(d) It is obtained by the ammonolysis of sulphur tetrafluoride ( $\text{SF}_4 \xrightarrow{\text{NH}_3} \text{S}_4\text{N}_4$ )<sup>19</sup>

Tetrasulphur tetranitride is a pale orange crystalline solid, m.p.  $178^\circ\text{C}$ <sup>26</sup>. It dissolves in many organic solvents but is insoluble in water. It has the following solubilities<sup>27</sup> (moles per 1000 g. solvent): dioxane at  $18^\circ\text{C}$ , 0.20, at  $60^\circ\text{C}$ ., 0.23; carbon disulphide at  $0^\circ\text{C}$ ., 0.0155, at  $30^\circ\text{C}$ ., 0.0573; benzene at  $0^\circ\text{C}$ ., 0.0137, at  $60^\circ\text{C}$ ., 0.121; ethanol at  $0^\circ\text{C}$ ., 0.0043, at  $20^\circ\text{C}$ ., 0.0072.

The molecular structure of tetrasulphur tetranitride, which has been a subject of controversy for a long period of time is now established. Electron diffraction<sup>28</sup> and X-ray analyses<sup>29,30</sup>, show that the  $\text{S}_4\text{N}_4$  molecule is an eight membered ring (Fig.1). In the vapour<sup>28</sup> and in the solid state,<sup>29,30</sup> the tetramer is in the form of

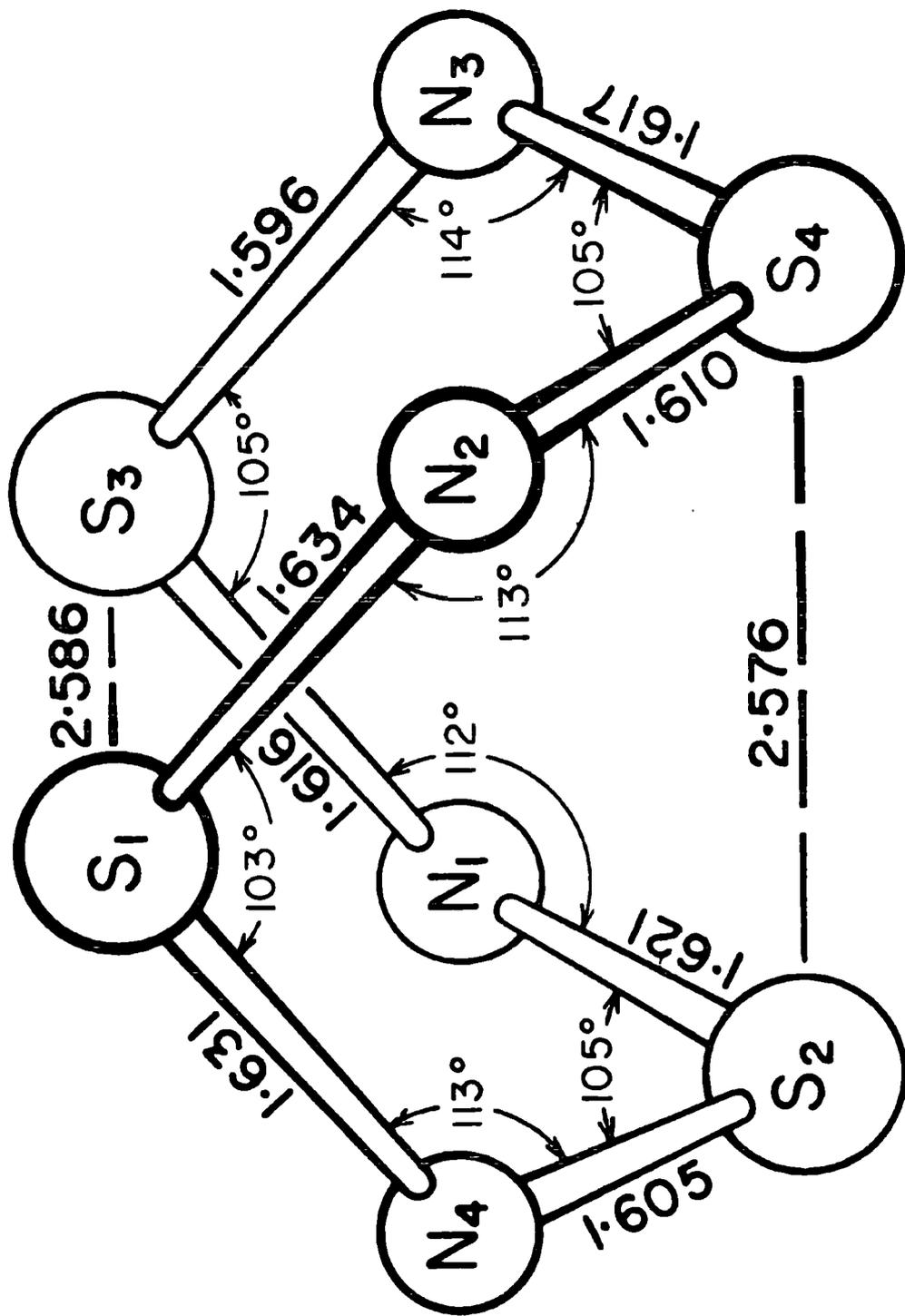


Fig. Bond distances and angles.

of a cradle-type puckered ring with all four nitrogen atoms in the same plane. All the sulphur atoms are chemically and physically identical<sup>31</sup>. Evidence for pi-bonding in the tetramer is provided by the fact that the equal bond length of 1.62Å<sup>28,29</sup> are shorter than the theoretical value of 1.74Å for S-N single bonds, and longer than the calculated value of 1.54Å for S=N double bonds. According to the relationship between S-N bond order and the S-N bond length<sup>32</sup>, a bond length of 1.62Å corresponds to a bond order of 1.5. This is most plausibly explained by the existence of a pi-electron system in the molecule due to overlap between the p-pi orbital of nitrogen and the d-pi orbital of sulphur<sup>3,5</sup>. Self-consistent field molecular orbital calculations suggested that considerable pi electron delocalization takes place in the (SN)<sub>4</sub> system<sup>33</sup>. The calculations also indicate that bonds are polarised as  $\overset{\ominus}{\text{N}} - \overset{\oplus}{\text{S}}$  units and that some sulphur-sulphur bonding occurs mostly by overlap of p orbitals, but one-third by overlap of sulphur d<sub>xy</sub> orbitals.

Electron spin resonance spectra have been observed with (SN)<sub>4</sub> and the spectrum of the anion, (SN)<sub>4</sub><sup>-</sup>, was consistent with a structure in which delocalization occurred over the ring and involved all four nitrogen atoms.<sup>34</sup>

The visible and ultraviolet spectra of  $(S-N)_4$  have been interpreted in terms of a structure in which weak S-S bonding was present<sup>35</sup>.

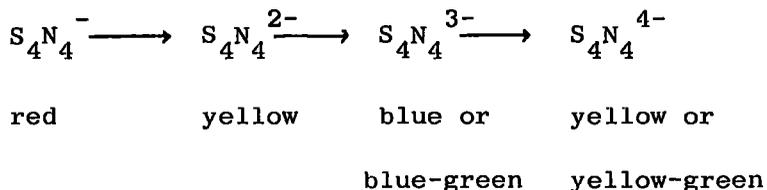
(a) Reduction and oxidation of  $S_4N_4$

The hydrogenation of tetrasulphur tetranitride with stannous chloride<sup>36</sup> or with dithionite,  $S_2O_4^{2-}$  produces tetrasulphur tetraimide<sup>26</sup>. This has not been detected among the products of the sulphur chloride/ammonia reaction but may well be there in very minute quantities. Tetrasulphur tetraimide was discovered by Wolbling.<sup>6</sup> It is colourless and crystallises in the orthorhombic system<sup>38</sup>.

The structure of  $S_4N_4H_4$  has been elucidated<sup>39,40</sup>. The arrangement of the nitrogen and sulphur atoms in the ring is of crown shape like that in the  $S_8$  sulphur ring<sup>40,41</sup>. The sulphur nitrogen bonds in tetrasulphur tetraimide are equal in length and are in the range 1.65 - 1.67 Å<sup>39,40</sup>. This implies that there is an appreciable amount of pi-character in the skeletal bonds, and that some delocalization occurs<sup>42</sup>. The fact that the ring structure is puckered suggests that sulphur d orbitals are involved, and pi-bonding probably takes place by donation of nitrogen lone pair electrons to vacant sulphur d orbitals<sup>42</sup>. The diamagnetic susceptibility, however gives no evidence of any ring current arising from delocalized multiple

bonding<sup>6, 43</sup>, probably because<sup>6(a)</sup> the nitrogen lone pairs will donate into sulphur d orbitals, the symmetry of which (two nodal planes) prevents the formation of uninterrupted molecular orbitals enclosing the whole molecule (cf. chlorophosphazenes<sup>42</sup>).

The hydrogen in tetrasulphur tetraimide can be replaced by metals. Becke-Goehring and Schwarz<sup>44</sup> studied the reaction of  $S_4N_4$  with triphenylmethyl sodium and obtained orange-red solid,  $Na_4S_4N_4$ . Another sodium salt is  $Na_2(H_2S_4N_4)$ , which has been obtained as a lemon yellow precipitate<sup>44</sup>. Stepwise replacement by lithium has been observed<sup>51</sup> in the reaction between  $S_4N_4H_4$  and  $nBuLi$  and the various colour changes are red, yellow, blue, yellow. The  $S_4N_4^{4-}$  ion contained in the sodium salts can be obtained, reducing  $S_4N_4$  by other methods. The reaction of tetrasulphur tetranitride with sodium in dimethoxyethane shows colour changes, red, deep blue, green and yellow green<sup>46</sup>. When  $S_4N_4$  is treated with vacuum-distilled potassium in scrupulously dry dimethoxyethane, various colour changes are exhibited<sup>46</sup>, a scarlet red solution is first observed, on further shaking a green solution is produced. The colour changes have been interpreted as indicating the formation of the following sequence of ions<sup>46</sup>:



Tetrasulphur tetraimide forms adducts, e.g.  $S_4N_4H_4$ .  
 $TeBr_4$ <sup>47</sup>. A tetrameric thionylimide,  $(O_4S_4N_4H_4)$  is produced  
 from the air oxidation of  $S_4N_4H_4$ <sup>48</sup>. Further work on  $S_4N_4H_4$   
 is in progress in this department.

(b) Tetrasulphur tetranitride adducts

In inert organic solvents tetrasulphur tetranitride forms  
 coloured stable adducts with many Lewis acids. The following  
 adducts have been prepared in the past :  $S_4N_4SbCl_5$ <sup>52,53</sup>  
 $S_4N_4.BF_3$ <sup>54</sup>,  $4S_4N_4.BF_3$ <sup>50</sup> (this unusual stoichiometry is probably  
 due to incomplete reaction<sup>54</sup>)  $2S_4N_4.SnCl_4$ <sup>52, 53</sup>,  $S_4N_4.TiCl_4$ <sup>52,53</sup>  
 $S_4N_4.2SO_3$ <sup>49</sup>,  $S_4N_4.4SO_3$ <sup>49</sup>,  $S_4N_4TeBr_4$ <sup>47</sup>,  $S_4N_4.2SbF_5$ <sup>6,57</sup>,  $S_4N_4.4SbF_5$ <sup>55</sup>  
 $S_4N_4.WCl_4$ <sup>52,53</sup>,  $S_4N_4.MoCl_5(?)$ <sup>52,53</sup>,  $S_4N_4.VCl_4$ <sup>56</sup>,  $S_4N_4.BCl_3$ <sup>54</sup>,  
 $S_4N_4.BBr_3$ <sup>54</sup>,  $S_4N_4.BCl_3.SbCl_5$ <sup>54</sup>,  $S_4N_4.2SbBr_3$ <sup>57,6</sup>,  $S_4N_4.2SbI_3$ <sup>57,6</sup>  
 $S_4N_4.Se_2Cl_2(?)$ <sup>53,6</sup>,  $S_4N_4.2TiCl_3(?)$ <sup>53,6</sup>. Adducts queried are  
 not unambiguously established. Further adducts with many other  
 metal halides are discussed in the experimental section.

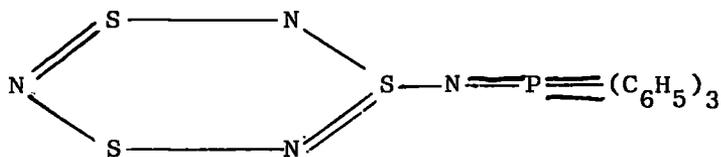
X-ray studies on two of these adducts ( $S_4N_4.SbCl_5$ ,  
 $S_4N_4.BF_3$ ) have been published<sup>58,59</sup>. The structures consist  
 of an eight membered sulphur-nitrogen ring, with one of the nitrogen  
 atoms, bonded to the antimony or boron atom. In adducts the  
 sulphur atoms form a square and the nitrogen atoms a tetrahedron.  
 This conformation differs from that of  $S_4N_4$  in which the nitrogen  
 atoms are square planar and the sulphur atoms (two above and two

below) form a slightly elongated tetrahedron. Infrared spectra and structure of many new  $S_4N_4$  adducts with Lewis acids are considered in the discussion.

Lewis-acid behaviour of  $S_4N_4$  is usually followed by ring contraction or degradation<sup>2</sup>. The observations suggest that nucleophiles invariably attack the more electropositive atoms, viz: sulphur atoms as would be expected. All forms of nucleophilic attack on  $S_4N_4$  break down the ring<sup>6</sup>. The only one which may have the ring preserved is the thiazyl fluoride adduct (it is not well characterized<sup>2</sup>) which can be made by reaction of various fluorinating agents, on  $S_4N_4$ <sup>19</sup> ( $S_4N_4 \xrightarrow{IF_5} I_2 + S_4N_4(NSF)_4$ ).

Ruff and Geisel<sup>60</sup> showed that  $S_4N_4$  and ammonia give an ammoniate of the composition  $S_4N_4 \cdot 2NH_3$ . In a similar reaction  $S_2N_2$  gives an ammoniate  $S_2N_2 \cdot NH_3$ <sup>1</sup>. However according to X-ray patterns and the absorption spectra, the two compounds appear to be identical and since  $S_2N_2$  can be sublimed from these ammoniates even at room temperature, it is assumed that  $S_4N_4$  is cleaved during the reaction with ammonia.

Ring contraction appears to result from the reaction of triphenyl phosphine and  $S_4N_4$  ( $S_4N_4 + 2P(C_6H_5)_3 \rightarrow SP(C_6H_5)_3 + (C_6H_5)_3PN_4S_3$ )<sup>61</sup>. The following structure has been proposed for  $(C_6H_5)_3PN_4S_3$ .



Reactions with Grignard reagents cause ring degradation<sup>62,129(a)</sup>

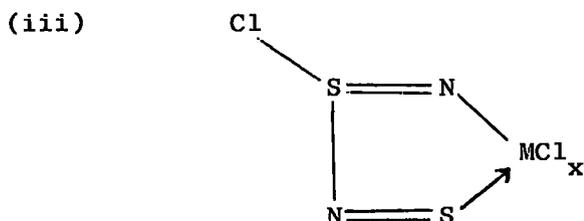
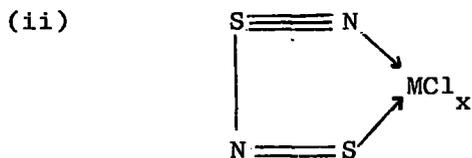
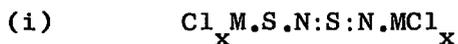
$(C_6H_5MgBr \xrightarrow{S_4N_4} C_6H_5SN=S=NSC_6H_5)$ . Complete degradation has been observed in the reaction of  $S_4N_4$  with  $C_6H_5PCl_2$ <sup>63</sup>.

(c) Reactions of  $S_4N_4$  in polar solvents

In polar solvents more involved reactions of  $S_4N_4$  with Lewis acids have been found to occur<sup>10</sup>. X-ray diffraction<sup>64-68</sup> and spectroscopic<sup>69</sup>, and chromatographic investigations<sup>70</sup> have established that products of three main structural types may be obtained, containing: (i)  $MN_2S_2$  five membered rings ( $PbN_2S_2, NH_3$ <sup>64</sup>,  $Ni(MeN_2S_2)$ <sup>66,67</sup> and  $Pt(HN_2S_2)$ <sup>65</sup>); (ii)  $MNS_3$  five membered rings ( $Pd(NS_3)_2$ <sup>68,70</sup>; and (iii) both  $MN_2S_2$  and  $MNS_3$  rings (Co, Ni and Pd compounds<sup>69, 70</sup>). In dimethylformamide, copper (II) chloride and bromide give low yields of  $S_2N_2 \cdot CuCl_2$  and  $S_2N_2 \cdot CuBr_2$ <sup>71</sup>. In methyl or ethyl alcohol, cobalt, nickel and palladium<sup>70, 73,74</sup> halides react to give mixtures which include compounds of all three types. In organic solvents  $S_4N_4$  reacts with selenium dichloride to give thiotrithiazyl chloride,  $S_4N_3Cl$  and elemental selenium, whereas in thionyl chloride the same reaction may give selenotrithiazyl hexachloroselenate,  $Se_2S_6N_6 \cdot SeCl_6$ , containing a three-element pi-delocalized cation<sup>75</sup>. Reactions of  $S_4N_4$

with several metal halides in thionyl chloride have been studied and products of variety of sulphur-nitrogen-metal ratios have been obtained<sup>10,76</sup> e.g.  $\text{SNMnCl}_2$ ,  $\text{SNCocl}_2$ ,  $\text{S}_2\text{N}_2\text{ZrCl}_4$ ,  $\text{S}_2\text{N}_2\text{CrCl}_3$ . The compounds contain rings or chains involving metal atoms and  $(\text{SN})_n$  units; vibrational spectra suggest 2,3 and 4 as the most likely values for  $n$ <sup>10</sup>.

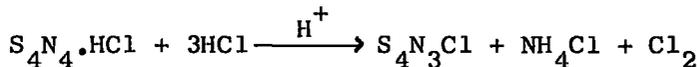
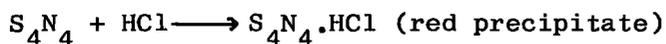
The structures of these compounds involve units of the type 1-3<sup>10</sup>.



(d) Some other important reactions of  $\text{S}_4\text{N}_4$

An important group of reactions illustrating the basic function of the tetranitride is with hydrogen halides. These reactions may well begin with protonation of a nitrogen atom in the ring; in the case of hydrogen chloride, the first product of reaction in carbon tetrachloride is a dark red precipitate which is thought to be  $\text{S}_4\text{N}_4 \cdot \text{HCl}$ . Especially in the presence of water, this changes

to thiotrithiazyl chloride<sup>6</sup>. The overall reaction is consistent with a process proceeding by the following steps<sup>85</sup>,



With HBr or HI in  $\text{CCl}_4$ ,  $\text{S}_4\text{N}_3\text{Br}$  or  $\text{S}_4\text{N}_3\text{I}$  is believed to be formed at once<sup>6</sup>. With excess HI in anhydrous formic acid,  $\text{S}_4\text{N}_4$  is completely broken down ( $\text{S}_4\text{N}_4 + 12\text{HI} \longrightarrow 4\text{S} + 6\text{I}_2 + 4\text{NH}_3$ )<sup>6</sup>.

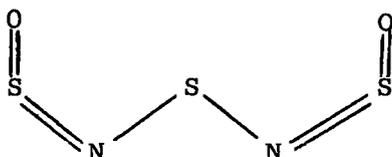
Tetrasulphur tetranitride readily undergoes base hydrolysis ( $2\text{S}_4\text{N}_4 + 6 \text{OH}^- + 9 \text{H}_2\text{O} \longrightarrow 2\text{S}_3\text{O}_6^{2-} + \text{S}_2\text{O}_3^{2-} + 8\text{NH}_3$ )<sup>86</sup>

This result is typical for a substance with sulphur in the plus three oxidation state, since it can readily undergo disproportionation to sulphur (II) and sulphur (IV). Formation of ammonia (rather than hydrazine) and products containing S-S bonds is consistent with the structure of  $\text{S}_4\text{N}_4$ ; the molecule contains S-S bonds rather than N-N bonds. Tetrasulphur tetranitride also undergoes acid hydrolysis<sup>87</sup>.

When  $\text{S}_4\text{N}_4$  is reacted with  $\text{SOCl}_2$  in the presence of  $\text{SO}_2$ , arsenic trichloride or nitric oxide, the compound  $\text{S}_3\text{N}_2\text{O}_2$  is obtained<sup>80,81</sup>. It is also obtained by the reaction between ammonia and  $\text{SOCl}_2$ <sup>82</sup>. Recently it has been shown that  $\text{S}_3\text{N}_2\text{O}_2$  is formed in small yields in the reaction between  $\text{S}_4\text{N}_4$  and  $\text{SOCl}_2$ .<sup>75,83</sup> It is also obtained by the reaction between  $\text{S}_4\text{N}_4$  and certain metal

halides in  $\text{SOCl}_2$ <sup>83</sup>.

The crystal structure of  $\text{S}_3\text{N}_2\text{O}_2$  shows that the molecule consists of a planar zig-zag chain<sup>of</sup> sulphur and nitrogen atoms, as shown below:



Thiodithiazyl dioxide reacts with  $\text{SbCl}_5$  and  $\text{TiCl}_4$  to give  $\text{S}_4\text{N}_4 \cdot \text{SbCl}_5$  and  $\text{S}_4\text{N}_4 \cdot 2\text{TiCl}_4$ , respectively<sup>84</sup>.

Tetrasulphur tetranitride reacts with cyclopentadiene in an inert solvent at  $135-136^\circ\text{C}$  and gives  $\text{S}_4\text{N}_4 \cdot 4\text{C}_5\text{H}_6$ . In a similar way compounds  $\text{S}_4\text{N}_4 \cdot 2\text{C}_7\text{H}_{10}$  and  $\text{S}_4\text{N}_4 \cdot 2\text{C}_7\text{H}_8$  have been prepared by the reaction of the nitride with bicycloheptene (norbornene) and bicyclopentadiene, respectively.<sup>79</sup>

#### Polymeric sulphur nitride, $(\text{SN})_x$

This compound is produced by the polymerisation of disulphur dinitride in the absence of moisture. The polymerisation is best effected by leaving disulphur dinitride in an evacuated desiccator for 30 days at  $20^\circ - 25^\circ\text{C}$ .<sup>6</sup> The product is stable and forms fibrous crystals up to 3mm long with a shiny, brass-like appearance.<sup>6</sup>

The polymer shows evidence of delocalization. It is diamagnetic and conducts electricity<sup>42</sup>. The polymer is more stable than  $S_4N_4$ <sup>1</sup>. The infrared spectrum showed a strong band at  $1225\text{ cm}^{-1}$  which was attributed to an S=N stretching vibration for a bond length of  $1.48\text{Å}$ . A band at  $1015\text{ cm}^{-1}$  was suggestive of an S-N mode with a more single bond character<sup>42</sup>. The optical spectrum showed a strong absorption near  $7000\text{Å}$  which might indicate the presence of a pi-electron delocalised system<sup>77</sup>. The conductance of the polymer increased with rising temperature and also with rising pressure. The semiconductance behaviour might be explained in terms of pi-electron delocalization along the polymer chain in a similar manner to the delocalization of the cyclic tetramer<sup>42</sup>. Each nitrogen atom can contribute one p-pi electron to the pi system and each sulphur can contribute two 3p-pi lone-pair electrons or one or two 3d-pi electrons. However the physical data could be rationalised in terms of a structure which contained alternating sequence of greater and less pi character<sup>77</sup>.

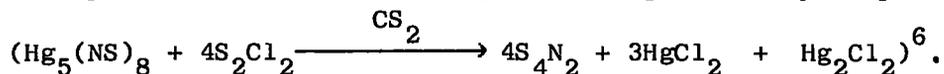
#### Tetrasulphur dinitride

$S_4N_2$  can be prepared by the following methods:-

(a) Tetrasulphur tetranitride is heated with carbon disulphide in an autoclave at  $120^\circ\text{C}$ , (poor yield)<sup>6</sup>.

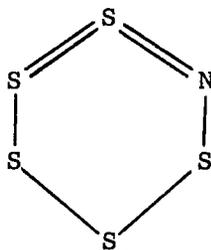
(b) It is prepared in 42% yield by the reaction between

disulphur dichloride and a sulphur-nitrogen-mercury compound



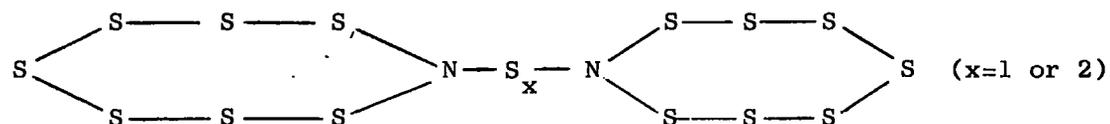
(c) Heating to  $80^\circ\text{C}$ , the reaction products from sulphur dioxide and ammonia<sup>6</sup>. Tetrasulphur dinitride has an unpleasant odour and melts at  $23^\circ\text{C}$ .<sup>78</sup>

No physical structure determination has been reported and the following unsymmetrical cyclic formula has been proposed<sup>6</sup>.



### Polymeric sulphur nitrides

The nitrides  $\text{S}_{15}\text{N}_2$  and  $\text{S}_{16}\text{N}_2$  are derived from the eight-membered ring system of heptasulphur imide. They are made by condensing this imide in carbon disulphide solutions with sulphur dichloride or disulphur dichloride respectively<sup>6</sup>. Their infrared spectra are featureless except broad bands in the S-N stretching region<sup>6</sup>. They have the following structures,



## Sulphur-nitrogen-halogen compounds

These compounds have interesting chemical (see below) and structural properties. They can contain single, double and triple bonds as well as localized and delocalized pi-bonds in rings. Rings with delocalized double bonds may be considered as inorganic aromatic compounds<sup>88</sup>.

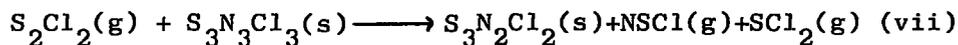
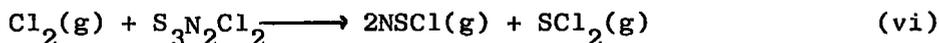
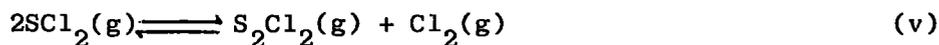
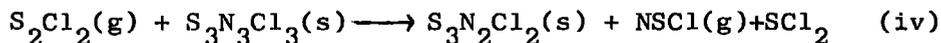
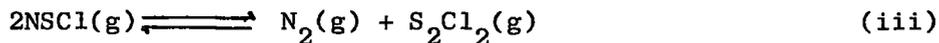
### (i) Monomeric thiazyl halides

The thionitrosyl halides  $S=N-F$ ,  $S=N-Cl$ , and nitrosyl halides,  $O=N-F$ ,  $O=N-Cl$  are isomeric with  $N\equiv S-F$  and  $N\equiv S-Cl$  and  $\bar{N}=\overset{+}{O}-F$ ,  $\bar{N}=\overset{+}{O}-Cl$ , respectively. In reality only nitrosyl halides  $ONF$ ,  $ONCl$  and thiazyl halides  $NSF$ ,  $NSCl$  are known. The monomeric nitrosyl bromide,  $BrNO$  is known but monomeric  $NSBr$  has not yet been prepared. In the nitrosyl halides the halogen is attached to nitrogen, whereas in the thiazyl halides it is attached to ~~nitrogen~~<sup>Sulphur</sup>. This has been ascribed to the fact that the halogen atom would join itself for preference to the atom of lowest electronegativity in these compounds<sup>6</sup>.

### (a) Thiazyl chloride

$NSCl$  is prepared by the depolymerisation of trithiazyl trichloride<sup>90,91</sup>. In a continually evacuated sublimation apparatus,  $S_3N_3Cl_3$  sublimed very slowly at  $55^{\circ}C$ , to a water cooled cold-finger giving yellow  $S_3N_3Cl_3$  on the cold-finger while only traces of  $NSCl$  were pumped out. However, when 40 mm pressure of nitrogen

or helium was present during closed sublimation at 70-80°C, to a liquid nitrogen cold-finger a yellow-white film, and later white to purple crystals, collected, which virtually all pumped out when warmed to 20°C and proved to be NSCl with less than 5% of the material remaining as  $S_3N_3Cl_3$ .<sup>91</sup> The experiments involving depolymerisation of  $S_3N_3Cl_3$  indicated that the depolymerisation is a reversible process, and the following reaction sequence is proposed on the basis of the known species involved during the depolymerisation<sup>91</sup>.



The process explains the observed autocatalytic behaviour by the enhanced occurrence of step 3 with build up of NSCl(g).

The following methods also have been used to prepare NSCl<sup>89,92</sup>.

(i) When a stream of ~~active~~ disulphur dichloride was passed into a stream of active nitrogen, NSCl is formed ( $2N + S_2Cl_2 \longrightarrow 2NSCl$ ).

(ii) It is prepared by heating under reflux a suspension of ammonium chloride in excess of disulphur dichloride ( $NH_4Cl + 2S_2Cl_2 \longrightarrow 3S + NSCl + 4HCl$ ).

(iii) It is an intermediate in the preparation of  $S_3N_3Cl_3$  from  $S_3N_2Cl_2$  and chlorine, and can be isolated ( $S_3N_2Cl_2 + Cl_2 \longrightarrow 2NSCl + SCl_2$ ).

(iv) When  $S_3N_2Cl_2$  is heated in vacuo to 80-90°C., NSCl and  $SCl_2$  are evolved ( $3S_3N_2Cl_2 \longrightarrow S_3N_2Cl + 2NSCl + SCl_2$ ).

(v) NSCl can be obtained by the action of chlorine on gaseous NSF.

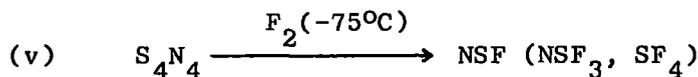
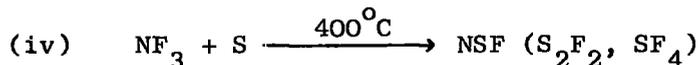
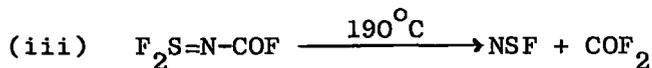
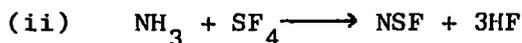
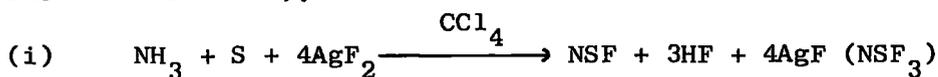
Thiazyl chloride is a greenish-yellow gas. It reacts with water to give ammonia, sulphur dioxide and hydrochloric acid ( $NSCl + H_2O \longrightarrow HNSO + HCl$ ;  $HNSO + H_2O \longrightarrow NH_3 + SO_2$ ).

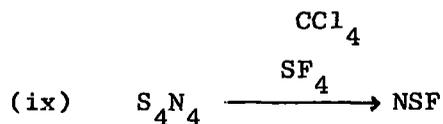
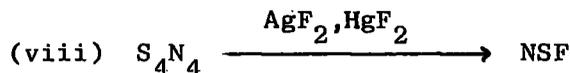
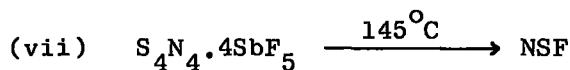
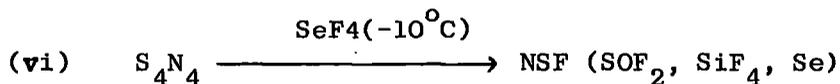
It is possible that NSCl has the structure with chlorine attached to nitrogen, but the very high value of force constant (10.02 m dynes/Å) and the NS bond order,<sup>95,96</sup> 2.3 show that only the structure in which chlorine is attached to sulphur is likely, since in the case of SNCl no expansion of the valency shell of the

nitrogen is possible to give a bond order  $N_{NS} = 2$ .<sup>93</sup> According to the Walsh rule<sup>94</sup>, NSCl should be non-linear. A non-linear asymmetric molecule gives rise (according to the relevant symmetry considerations and selection rules) to three vibrational degrees of freedom, constituting three fundamental frequencies, namely  $\nu_1$  (NS stretching),  $\nu_2$  (S-Cl stretching) and  $\nu_3$  (the NS-Cl bending vibration). The infrared spectrum of NSCl (from 300 to 4000  $\text{cm}^{-1}$ ) showed two fundamental frequencies,  $\nu_1$  (1325  $\text{cm}^{-1}$ ),  $\nu_2$  (414  $\text{cm}^{-1}$ ), and  $\nu_3$  (273  $\text{cm}^{-1}$ ) was calculated from the overtone and combination bands<sup>93</sup>. It was confirmed that NSCl has the structure NSCl with  $C_s$  symmetry and is not SNCl.

(b) Thiazyl fluoride

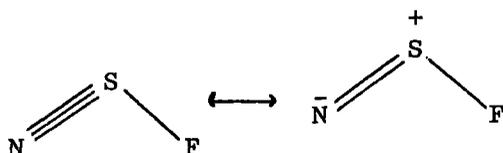
NSF is an unstable colourless gas (m.p.  $-89^\circ\text{C}$ ., b.p.  $0.4^\circ\text{C}$ ). It can be prepared by several methods given below, (minor products shown in brackets).





The fluorination of  $S_4N_4$  using  $AgF_2$  or  $HgF_2$  in boiling  $CCl_4$  is a suitable method. In the case of  $HgF_2$ , the fluorination proceeds under milder conditions and better yields are obtained.

$NSF$  is a bent triatomic molecule with sulphur in the middle and fluorine atom attached to sulphur<sup>a</sup> <sup>97,98</sup>. After  $NSF_3$ , thiazyl fluoride has the highest SN bond order of all the sulphur-nitrogen halides<sup>32</sup>. The bond order of more than two would correspond to resonance structures shown below,



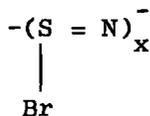
The  $NSF$  molecule can be thought of as being derived from  $SF_4$  with three of the fluorine atoms replaced by a triply bonded nitrogen atom. The  $SF$  distance in  $NSF$  is the same as the  $SF$  distance in  $SF_4$  and the  $SN$  distance of  $NSF$  is only slightly greater than the  $SN$  distance in  $NSF_3$ .<sup>98</sup>

NSF is highly reactive and undergoes hydrolysis with water vapour yielding thionyl imide, HNSO, as an intermediate<sup>97,98</sup>. The final hydrolysis products are sulphite, fluoride and ammonia, the course of this reaction has not yet been elucidated. In copper or teflon vessels, NSF can be stored for a short time without decomposition, but it trimerises to  $S_3N_3F_3$  on standing. It decomposes slowly in glass vessels. The reaction with glass proceeds rapidly at about 200°C and gives  $S_4N_4$ ,  $SOF_2$ ,  $SO_2$ ,  $SiF_4$  and  $N_2$ <sup>32</sup>. NSF polymerises to give  $S_3N_3F_3$  at high pressures, whereas/low pressures, green-yellow crystals of  $S_3N_2F_2$  separate out on the walls of the container. NSF forms a colourless crystalline adduct with boron trifluoride<sup>90,100</sup>. This compound  $NSF.BF_3$  or  $NS^+BF_4^-$  is stable for a short time at low temperatures and dissociates into its components in the gas phase<sup>6</sup>.

(ii) Polymeric thiazyl halides

(a) Polythiazyl bromide

When bromine is allowed to react with  $S_4N_4$  in  $CS_2$ , deep-red brown compound of composition  $(NSBr)_x$  is obtained<sup>26,101</sup>. The infrared spectrum of this compound is given in the experimental section. It is stable in dry air, but hydrolysed in moist air. It is thought to be a bromine derivative of  $(SN)_x$  and the following structure has been proposed.<sup>6</sup>

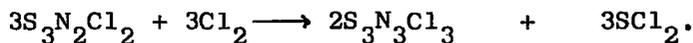


It reacts with ammonia at  $-40^{\circ}\text{C}$  to give a red solution (probably  $(\text{NS-NH}_2)_x$ ) and ammonium bromide<sup>6</sup>.

(b) Trithiazyl trichloride and trithiazyl trifluoride

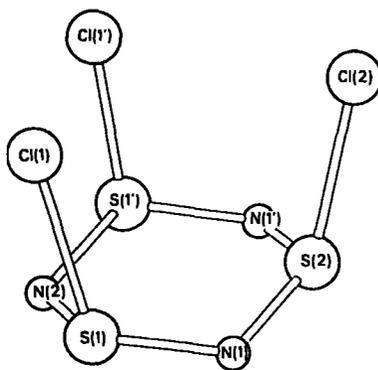
(i)  $\text{S}_3\text{N}_3\text{Cl}_3$

Trithiazyl trichloride may be prepared by the method originally described by Demarcay<sup>127</sup> and Meuwsen<sup>102</sup> and most recently revised by Schroeder and Glemser<sup>117</sup> on passing chlorine through a suspension of  $\text{S}_4\text{N}_4$  in an inert solvent ( $3\text{S}_4\text{N}_4 + 6\text{Cl}_2 \longrightarrow 4\text{S}_3\text{N}_3\text{Cl}_3$ ). A more convenient method recently described by Jolly and Maguire<sup>104</sup> utilising the reaction:



This method, but with  $\text{CCl}_4$  solvent, was first described by Meuwsen<sup>118</sup>. The preparation of  $\text{S}_3\text{N}_3\text{Cl}_3$  from  $\text{S}_4\text{N}_4$  using sulphuryl chloride as the chlorinating agent is described in this thesis.

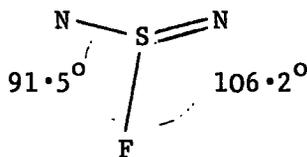
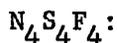
In the structure of  $\text{S}_3\text{N}_3\text{Cl}_3$  shown below



Molecule of  $(\text{NSCl})_3$ . The atoms S(2), N(2) and Cl(2) are on the mirror plane.

the molecule consists of a six-membered ring compound of alternating sulphur and nitrogen atoms in a chair configuration with the three nitrogen atoms below the sulphur atoms and one chlorine bonded to each sulphur in an axial position above the ring.<sup>107,108</sup> One chlorine atom (marked Cl(2) on the previous diagram) differs from the other two - compare (NSOCl)<sub>3</sub>.<sup>110,190</sup> In this structure both sulphur and nitrogen atoms contribute one electron each to the  $\pi$  system. These bonds have been proposed to consist of nitrogen  $p_{\pi}$ -sulphur  $d_{\pi}$  overlap delocalized either over the entire ring<sup>3</sup> as in benzene or over separate three-centre S-N-S bonds.<sup>4</sup> The SN bonds are all short and equal (1.605Å), which indicates the presence of  $\pi$  bonds.<sup>107,108</sup> The aromatic ring of S<sub>3</sub>N<sub>3</sub>Cl<sub>3</sub> is in contrast to the alternating single and double bonds of S<sub>3</sub>N<sub>3</sub>F<sub>3</sub> and S<sub>4</sub>N<sub>4</sub>F<sub>4</sub>. The presence of localised double bonds in S<sub>3</sub>N<sub>3</sub>F<sub>3</sub> is deduced from <sup>19</sup>F n.m.r. data (the trimer and tetramer fluoride show similar shifts);<sup>88</sup> the sulphur-nitrogen distances in S<sub>4</sub>N<sub>4</sub>F<sub>4</sub> are known from an X-ray structure determination.<sup>115</sup> Glemser<sup>88</sup> explains the different ring bonding in the chloride and fluorides as follows (cf. Allen<sup>2</sup>): "Each fluorine atom polarizes the sulphur, by drawing off electrons, to such an extent that, in comparison to S<sub>4</sub>N<sub>4</sub>, a weaker repulsion between the lone electron pair on the S and that on the N results. In this way, the bond length can be decreased and the tendency towards formation of a double bond is enhanced. Alternating shorter and longer S-N distances may frequently be more favourable than two proportionately shorter, but equal distances, such as occur in

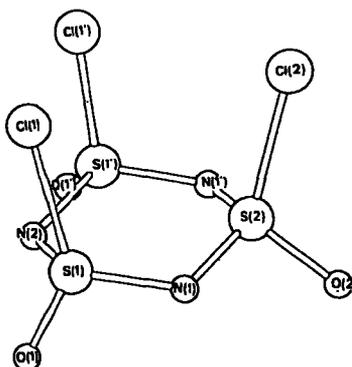
delocalized bonds. That is to say, the attraction term of the bond energy increases exponentially with decreasing distance, so that, in the case of alternating distances, the gain in double bond energy may exceed the delocalisation energy for equal distances. This effect is intensified by the position of the fluorine, which tends to form an N=S-F angle as wide as possible, as is evidenced by the structure of



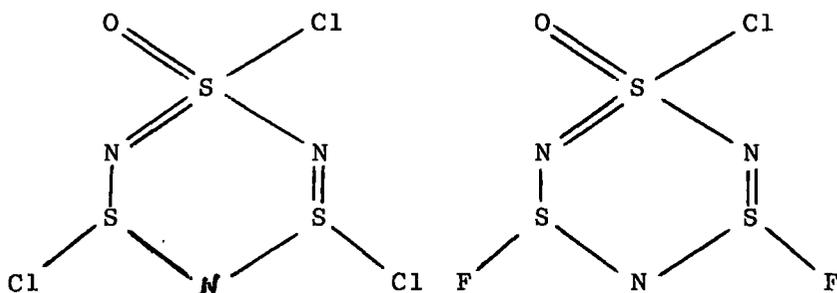
The same assumptions must be valid for  $N_3S_3F_3$ . In  $N_3S_3Cl_3$ , however, the chlorine cannot polarize the sulphur as strongly as fluorine can in  $N_3S_3F_3$ . Therefore, no preponderance is given localized double bonds and S-N distances are longer, i.e. the symmetrical arrangement of chlorine and the gain in delocalizing energy are more favoured."

Trithiazyl trichloride reacts with sulphur trioxide and gives a pale-yellow adduct  $S_3N_3Cl_3 \cdot 3SO_3$  and then the olive-coloured  $S_3N_3Cl_3 \cdot 6SO_3$ .<sup>6</sup> When these adducts are heated to 140-160°C,  $\beta$   $\alpha$ -sulphanuric chloride  $S_3N_3Cl_3O_3$  is formed. The structure of  $\alpha$ -sulphanuric chloride has been determined.<sup>108,109,110</sup> The results show that  $\alpha$ -sulphanuric chloride is trimeric with an  $S_3N_3$  ring (like  $S_3N_3Cl_3$  but with oxygen atoms taking the place of lone pairs

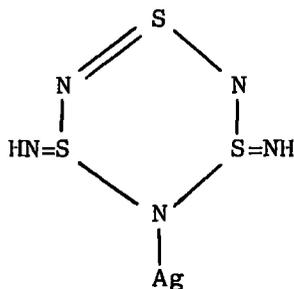
on sulphur). The molecule exists as the chair form with the chlorine atoms in axial positions and with all S-N distances equal ( $1.571\text{\AA}$ )<sup>110</sup> as in  $\text{S}_3\text{N}_3\text{Cl}_3$  there are two types of axial chlorine atoms.<sup>110,190</sup> The shortness and equality of the skeletal bonds probably denotes appreciable  $p_\pi-d_\pi$  overlap; it also seems likely that there is donation of the nitrogen lone-pair to sulphur, to form a co-ordinate  $\pi$ -bond<sup>42</sup> especially since the sulphur atoms in  $(\text{NSOCl})_3$  have considerable Lewis acidity [sulphanuric chloride forms an adduct  $(\text{py}.\text{NSOCl})_3$  with pyridine].<sup>128</sup> Two new sulphur and nitrogen containing six-membered ring compounds ( $\text{S}_3\text{N}_3\text{Cl}_3\text{O}$  and  $\text{S}_3\text{N}_3\text{F}_2\text{ClO}$ ) have recently been reported.<sup>111</sup> Chlorination of  $\text{S}_3\text{N}_2\text{O}_2$ , by means of liquid chlorine yields the crystalline colourless mixed thiazyl-sulphanuric ring compound,  $\text{S}_3\text{N}_3\text{Cl}_3\text{O}$ ; with silver difluoride  $\text{S}_3\text{N}_3\text{Cl}_3\text{O}$  gives another colourless crystalline ring compound  $\text{S}_3\text{N}_3\text{F}_2\text{ClO}$ . The following structures have been proposed for these compounds.<sup>111</sup> Conformations similar to  $(\text{NSCl})_3$  (p.25) and  $(\text{NSOCl})_3$  (below) are to be expected, i.e. axial halogen atoms.



Molecule of  $(\text{NSOCl})_3$ . The atoms S(2), N(2), O(2), and Cl(2) are on the mirror plane.

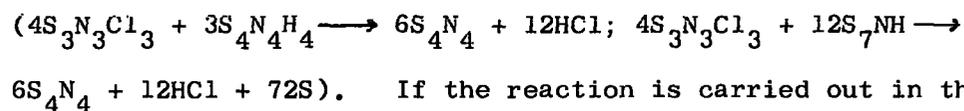


The thermal depolymerisation of  $S_3N_3Cl_3$  to form thiazyl chloride has already been described (page 20).  $S_3N_3Cl_3$  is easily hydrolysed by water, aqueous acid or alkali, presumably by nucleophilic attack on sulphur<sup>6</sup>, giving ammonia and chloride. Ammonolysis of trithiazyl trichloride produces the amide  $(H_2N-SN)_3$ <sup>12</sup>. If the freshly prepared amide is dissolved in aqueous ammonia and then rapidly precipitated with silver nitrate a very explosive yellow silver salt can be isolated after removing ammonia under vacuum<sup>112</sup>. The following probable structure has been proposed for the silver compound<sup>12</sup>.



$S_3N_3Cl_3$  reacts with dimethyl sulphoxide giving new type of sulphur-nitrogen cation ( $S_3N_3Cl_3 + 6(CH_3)_2SO \rightarrow 3 [(CH_3)_2S=\overset{+}{N}=S(CH_3)_2] Cl^- + 3SO_2$ )<sup>6</sup>. When trithiazyl trichloride is allowed to react

with tetrasulphur tetraimide or heptasulphur imide in the presence of pyridine, tetrasulphur tetranitride is formed, suggesting the formation of both the  $N\equiv S^+$  and  $\bar{N}=S$  ions in these reactions<sup>88</sup>



If the reaction is carried out in the absence of pyridine, which is intended to capture HCl, a brown red adduct is formed, which reacts with traces of water to give  $S_4N_3Cl$  ( $S_4N_4 \cdot 4HCl \longrightarrow S_4N_3Cl + NH_4Cl + Cl_2$ )<sup>88</sup>.

Molybdenum hexacarbonyl reacts with trithiazyl trichloride in dichloromethane to give microcrystalline brown solid,  $MoS_3N_3Cl_3$  ( $S_3N_3Cl_3 + Mo(CO)_6 \longrightarrow MoS_3N_3Cl_3 + 6CO$ )<sup>113</sup>. A polymeric structure involving metal-metal bonding was thought, on the basis of its being insoluble in non-polar solvents and the observed low ratio of  $S_3N_3Cl_3$  to Mo.

(ii)  $S_3N_3F_3$

When NSF is allowed to stand in a sealed glass container for three days, a mixture of crystals is formed from which  $S_3N_3F_3$  can be sublimed<sup>97</sup>.  $S_3N_3F_3$  is more conveniently prepared by

fluorinating  $S_3N_3Cl_3$  in  $CCl_4$  using  $AgF_2$ <sup>97</sup>.

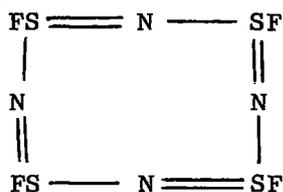
$S_3N_3F_3$  is a colourless, volatile, crystalline compound (m.p.  $74.2^\circ C$ ., b.p.  $92.5^\circ C$ ) and soluble in inert solvents such as benzene,  $CCl_4$ <sup>97</sup>. No X-ray structure determination has been reported, but the cyclic formula can be inferred from the fact that there is only one nuclear magnetic resonance line for fluorine, showing that all three fluorine atoms are in equivalent environments<sup>6</sup>. The infrared spectrum of  $S_3N_3F_3$  shows absorption peaks at 1085, 720 and  $650\text{ cm}^{-1}$ <sup>97</sup>. It is more moisture sensitive than  $S_3N_3Cl_3$  and  $S_4N_4F_4$ . It is stable in dry air and turns black in moist air with decomposition<sup>6</sup>. In cold diluted sodium hydroxide solution  $S_3N_3F_3$  is hydrolysed by the following reaction<sup>32</sup>,

$$S_3N_3F_3 + 9H_2O \longrightarrow 3NH_4F + 3H_2SO_4.$$

(c) Tetrathiazyl tetrafluoride

$S_4N_4F_4$  is prepared from the reaction of  $AgF_2$  on  $S_4N_4$  in  $CCl_4$  (the reaction of elementary fluorine with solid  $S_4N_4$  is too violent and gives sulphur fluorides and nitrogen)<sup>88</sup> but attempts to obtain this compound by the polymerisation of NSF have been unsuccessful<sup>32</sup>. It is therefore considered that the formation of  $S_4N_4F_4$  from  $S_4N_4$  and  $AgF_2$  does not involve intermediate SN radicals but that the fluorine atoms add directly to the sulphur atoms of the  $S_4N_4$  ring.

$S_4N_4F_4$  molecule, has a puckered eight-membered ring type of molecular structure, with the plane of the nitrogen atoms above the plane of the sulphur atoms<sup>2</sup>. X-ray diffraction measurements indicate that in the tetrameric fluoride,  $S_4N_4F_4$ , there is an alternation of double and single bonds<sup>114,115</sup>. Delocalization of  $\pi$  electrons, therefore is minimal. This is in part due to the fact that the  $\pi$  bonding itself is weak, due to a repulsion of the nitrogen lone-pair, by the sulphur-lone-pair<sup>5</sup> and also because the non-bonded interactions (lone-pair, polar and steric repulsions) force the ring to assume a tub configuration. This reduces the possibility that delocalized  $p_{\pi} - p_{\pi}$  bonding can occur. An additional factor which limits  $d_{\pi} - p_{\pi}$  bonding to alternate skeletal bonds is that although there is a large overlap between a sulphur  $d_{\pi}$  orbital and one nitrogen  $p_{\pi}$  orbital, the  $d_{x^2-y^2}$  orbital, which is directed towards the  $p_{\pi}$  orbital of the other neighbouring nitrogen is not polarized sufficiently to form a strong  $\pi$  bond<sup>5</sup>. Thus the aromatic character of the ring is lost and the puckered eight-membered ring has a different shape from that of  $S_4N_4$ <sup>6</sup>. Infrared bands<sup>97</sup> that can be used for the identification of  $S_4N_4F_4$  lie at 1117, 786, 760, 709, 645 and  $520\text{cm}^{-1}$ . The structure of  $S_4N_4F_4$  is shown below:



$\text{S}_4\text{N}_4\text{F}_4$  is a white crystalline compound (m.p.  $153^\circ\text{C}$  (decomp.)). It is soluble in  $\text{CCl}_4$  (3.44g. per litre at  $2^\circ\text{C}$ )<sup>6</sup>. It forms a green adduct  $\text{F}_4\text{S}_4\text{N}_4 \rightarrow \text{BF}_3$  the thermal decomposition of which yields  $\text{NSF}$ <sup>32</sup>. The compound hydrolyses completely in warm sodium hydroxide ( $\text{S}_4\text{N}_4\text{F}_4 + 12\text{H}_2\text{O} \rightarrow \text{NH}_4\text{F} + 4\text{H}_2\text{SN}_3$ ).

(iii) Sulphur-nitrogen halides derived from sulphur hexafluoride

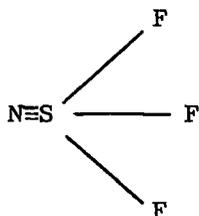
Thiazyl trifluoride

$\text{NSF}_3$  is a derivative of  $\text{SF}_6$  in which three fluorine atoms are replaced by nitrogen atoms and it resembles the hexafluoride to some degree in its stability and lack of reactivity<sup>6</sup>. It is formed when ammonia is passed into a suspension of sulphur and  $\text{AgF}_2$  in  $\text{CCl}_4$ <sup>32</sup> ( $\text{NH}_3 + \text{S} + 6\text{AgF}_2 \xrightarrow{\text{CCl}_4} \text{NSF}_3 + 3\text{HF} + 6\text{AgF}$ ).

$\text{NSF}_3$  is also formed in all fluorinations of  $\text{S}_4\text{N}_4$  with  $\text{AgF}_2$  in  $\text{CCl}_4$ <sup>32</sup> ( $\text{S}_4\text{N}_4 + 12\text{AgF}_2 \xrightarrow{\text{CCl}_4} 4\text{NSF}_3 + 12\text{AgF}$ ).

$\text{NSF}_3$  is a colourless, pungently smelling gas (m.p.  $-72.6^\circ\text{C}$ , b.p.  $-27.1^\circ\text{C}$ )<sup>6</sup>. Its molecular structure has been established from studies of the microwave spectrum, infrared spectrum and fluorine nuclear magnetic resonance<sup>6</sup>.  $\text{NSF}_3$  is isoelectronic with  $\text{OPF}_3$

(tetrahedral, having the symmetry  $C_{3v}$ ) which gives a very similar infrared spectrum to that of  $FCIO_3$ <sup>6,32</sup>. The calculated force constants corresponds to a bond order of 2.7 for the SN bond<sup>32</sup>. Infrared spectrum<sup>97</sup> of  $NSF_3$  shows peaks at 1515, 811, 775, 521, 429 and 342  $cm^{-1}$ . Its structure is shown below:

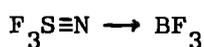


The chemical properties also seem to indicate that it is reasonable to compare  $NSF_3$  with  $SF_6$ . However, whereas the 3s, 3p and 3d electrons in  $SF_6$  are hybridised to the octahedral  $sp^3d^2$  state, the orbitals in  $NSF_3$  are  $sp^3$  hybridised<sup>32</sup>. There are two  $p_\pi - d_\pi$  overlaps between nitrogen and the sulphur in  $NSF_3$ . The fact that the F-N-F angle in  $NSF_3$  ( $94^\circ A$ ) is smaller than the ideal tetrahedral angle indicates some contribution of d and p states in sulphur<sup>32</sup>.

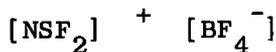
Thiazyl fluoride does not react at room temperature with ammonia gas<sup>6</sup>. It reacts slowly with water at room temperature, but it is hydrolysed by sulphuric acid and fluoride ion when boiled with sodium hydroxide solution<sup>6</sup>. It is stable towards metallic sodium and reacts only at about  $400^\circ C$  to form  $Na_2S$ ,

nitrogen and sodium fluoride<sup>97</sup>.

NSF<sub>3</sub> reacts with BF<sub>3</sub> to form colourless NSF<sub>3</sub>.BF<sub>3</sub>,<sup>88</sup> which can be purified by sublimation. Infrared measurements and molecular weight determinations indicate that the gaseous phase consists of an equimolar mixture of NSF<sub>3</sub> and BF<sub>3</sub>. The spectrum of the solid but not the liquid compound in the near infrared resembles those of the alkali metal tetrafluoroborates. The compound is therefore assumed to have the formula 1 in the liquid state and formula 2 in the solid state<sup>32</sup> as shown below



(1)



(2)

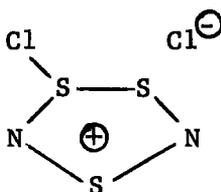
The instability of these adducts indicate that the donor power of nitrogen is considerably weakened by the N≡S bond. In addition to NSF<sub>3</sub>, compounds of the type, F<sub>2</sub>NSF<sub>5</sub>, F<sub>5</sub>SNH<sub>2</sub>, CF<sub>3</sub>N=SF<sub>4</sub> and SF<sub>5</sub>N=SF<sub>2</sub> have been prepared<sup>32</sup>.

(iv) Thiodithiazyl monochloride, dichloride and difluoride

(i) Thiodithiazyl chloride, S<sub>3</sub>N<sub>2</sub>Cl, was first prepared by Demarcay<sup>128</sup>, from the reaction between S<sub>4</sub>N<sub>4</sub> and S<sub>2</sub>Cl<sub>2</sub>. It can be obtained by the vacuum sublimation of S<sub>3</sub>N<sub>2</sub>Cl<sub>2</sub> at 80-90°C (3S<sub>3</sub>N<sub>2</sub>Cl<sub>2</sub>  $\xrightarrow{80-90^\circ C}$  2S<sub>3</sub>N<sub>2</sub>Cl + 2NSCl + SCl<sub>2</sub>)<sup>123</sup>. It is also formed in the reaction of NOCl with S<sub>4</sub>N<sub>4</sub> or when S<sub>3</sub>N<sub>3</sub>Cl<sub>3</sub> reacts with NO in nitromethane.<sup>32</sup>

(ii) Thiodithiazyl dichloride,  $S_3N_2Cl_2$  was reported by Meuwesen<sup>103</sup> in the chlorination of  $S_3N_3Cl_3$  in  $CCl_4$ . It can be prepared by refluxing a mixture of  $S_2Cl_2$  and ammonium chloride ( $2NSCl + S_2Cl_2 \rightarrow S_3N_2Cl_2 + SCl_2$ )<sup>123</sup>.  $S_3N_2Cl_2$  was first identified by Demarcay<sup>124</sup>, who prepared it by allowing  $SCl_2$  or  $S_2Cl_2$  to react with  $S_4N_4$ . It may also be prepared by the reaction of tetrachloro ethylene (or trichloro ethylene) with  $S_3N_3Cl_3$ <sup>125</sup>.

An X-ray crystal structure analysis on  $S_3N_2Cl_2$  shows that the compound is a salt consisting of a chloride anion, and  $S_3N_2Cl^+$  cation, the sulphur and nitrogen atoms form a puckered five membered ring as shown below



The chemistry of  $S_3N_2Cl_2$  has been reviewed<sup>129(a)</sup>.

(iii) Thiodithiazyl difluoride,  $S_3N_2F_2$  is prepared by the decomposition of NSF in a six litre glass flask at pressures of about 600 mm Hg<sup>88</sup>. After one week greenish-yellow crystals are obtained.  $S_3N_2F_2$  sublimes at 40°C and 55°C giving yellowish-green and bright-green crystals respectively<sup>88</sup>.

Both the compounds are soluble in  $\text{CCl}_4$  and have the same molecular weights and ultraviolet spectra (the two compounds are thought to be polymorphic modifications of the same compound). Since  $\text{S}_3\text{N}_2\text{F}_2$  is soluble in  $\text{CCl}_4$ , an ionic structure similar to  $\text{S}_3\text{N}_2\text{Cl}_2$  is less probable, and a structure, which is given below is proposed on the basis of the qualitative conversion of its nitrogen to ammonia by alkaline hydrolysis<sup>6</sup>



(v) Thiotrithiazyl halides

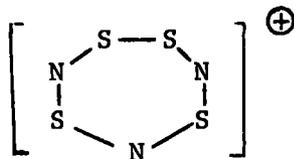
Thiotrithiazyl halides contain the cationic seven-membered ring  $\text{S}_4\text{N}_3^+$ . The relatively stable chloride serves as the starting material for these compounds. All the four halides have been reported by Padley<sup>129</sup>. Later attempts to repeat the preparation of the pure iodide were unsuccessful<sup>125</sup>.

$\text{S}_4\text{N}_3\text{Cl}$  was first prepared by Demarcay<sup>127</sup> by heating together  $\text{S}_4\text{N}_4$  and  $\text{S}_2\text{Cl}_2$  in  $\text{CCl}_4$  ( $3\text{S}_4\text{N}_4 + 2\text{S}_2\text{Cl}_2 \longrightarrow 4\text{S}_4\text{N}_3\text{Cl}$ ). It can be prepared by the action of  $\text{SOCl}_2$  or acetyl chloride on  $\text{S}_4\text{N}_4$ <sup>129</sup> or by the reaction of  $\text{S}_4\text{N}_4$  with diselenium dichloride in  $\text{CCl}_4$ <sup>129</sup>. All other sulphur chlorides as well as the adduct  $\text{S}_4\text{N}_4 \cdot 4\text{HCl}$  can be converted to  $\text{S}_4\text{N}_3\text{Cl}$ . When  $\text{S}_3\text{N}_3\text{Cl}_3$  or  $\text{S}_3\text{N}_2\text{Cl}_2$  is heated with  $\text{S}_2\text{Cl}_2$  in  $\text{CCl}_4$ ,  $\text{S}_4\text{N}_3\text{Cl}$  is formed. Reaction of

$S_3N_3Cl_3$  with diphenyl acetylene or carbon monoxide at about  $40^\circ C$  in  $CCl_4$  gives  $S_4N_3Cl$  (this thesis p. 82 ). It can also be prepared by the reaction between  $S_2Cl_2$  and lithium azide in  $CCl_4$ <sup>32</sup>. Since the same reaction gives  $S_4N_4$  at  $0^\circ C$ , it is assumed that  $S_4N_4$  is the initial product which reacts with  $S_2Cl_2$  to form  $S_4N_3Cl$  ( $4LiN_3 + 2S_2Cl_2 \longrightarrow S_4N_4 + 4LiCl + 4N_2$ ;  $3S_4N_4 + 2S_2Cl_2 \longrightarrow 4S_4N_3Cl$ ).

$S_4N_3Cl$  is a yellow crystalline solid, stable in dry air. It decomposes at  $170^\circ C$  in vacuo to give  $S_4N_4$ <sup>129</sup>. It is insoluble in solvents of low dielectric constants, but soluble in  $SOCl_2$  and formic acid<sup>6</sup>. It can be recrystallised from  $SOCl_2$  in red needles<sup>129</sup>.  $S_4N_3Cl$  decomposes slowly in benzene,  $CHCl_3$ , acetone, and acetic acid by development of a red colour<sup>129</sup>. The course of hydrolysis of  $S_4N_3Cl$  depends on the reaction conditions. With ice-cold sodium acetate solution, the initial product at  $0^\circ C$  is the black  $S_4N_3OH$ , whereas black  $(S_3N_3OH)_2$  is formed at room temperature<sup>129</sup>. The hydroxides are probably polymeric and unstable giving  $S_4N_4$  on standing.

The  $S_4N_3$  cation is a planar seven membered ring with three alternating S-N bonds and one S-S bond<sup>130,131</sup>.

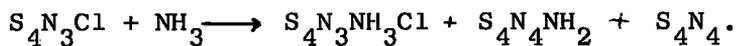
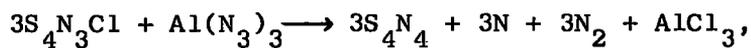


The evidence for pseudoaromaticity in the ring is provided by structural and spectral studies. There is however disagreement in the literature over the extent of  $\pi$  delocalization. Johnson et al<sup>132</sup> reports that, the planar structure and short, equal, S-N bond lengths (1.55Å compared with 1.62Å for (S-N)<sub>4</sub>) of the thiotrithiazyl (S<sub>4</sub>N<sub>3</sub><sup>+</sup>) cation suggest that considerable  $\pi$  bonding occurs in this ring system and the electronic spectrum is consistent with a delocalized, ten electron  $\pi$  system in which sulphur d orbitals are used. Whereas Bailey et al<sup>133</sup> proposed a six or eight  $\pi$  electron system and their results indicate that delocalization does not occur over the whole ring, the delocalized system and the disulphide group are best considered separately, however the existence of a certain amount of delocalization across the disulphide group is quite likely.

S<sub>4</sub>N<sub>3</sub>F is obtained by the replacement of the chloride ion in S<sub>4</sub>N<sub>3</sub>Cl, when anhydrous HF gas is allowed to react with S<sub>4</sub>N<sub>3</sub>Cl in a polyethylene or teflon tube<sup>88</sup> (S<sub>4</sub>N<sub>3</sub>Cl + HF → S<sub>4</sub>N<sub>3</sub>F + HCl). A convenient general method for the preparation of thiotrithiazyl compounds consists in the metathesis of solutions of the chloride in anhydrous formic acid. An orange-yellow bromide, bronze coloured S<sub>4</sub>N<sub>3</sub>SCN, red-brown tetraphenyl borate, S<sub>4</sub>N<sub>3</sub>.B(C<sub>6</sub>H<sub>5</sub>)<sub>4</sub> and S<sub>4</sub>N<sub>3</sub>.SbCl<sub>6</sub> have been made in this way<sup>6</sup>. With nitric

acid and sulphuric acid,  $S_4N_3Cl$  gives  $S_4N_3 \cdot NO_3$  and  $S_4N_3 \cdot HSO_4$  respectively<sup>6</sup>. A novel preparation of the bromide is by the reaction of bromine on  $(HNS)_4$  ( $S_4N_4H_4 + Br_2 \rightarrow S_4N_3Br + NH_4Br$ )<sup>51</sup>.

Ring expansion of  $S_4N_3^+$  can be achieved by reaction of  $S_4N_3Cl$  with aluminium azide or ammonia<sup>6</sup>.



EXPERIMENTAL

PREPARATIONS

Tetrasulphur tetranitride:<sup>14,15,16,18,19,23,26</sup>

A three-necked round-bottomed was used as the reaction vessel. This was fitted with a paddle stirrer through the main neck and a gas inlet tube through one of the side necks.

700 ml of carbon tetrachloride (dried over  $P_4O_{10}$ ) and 25 ml of disulphur dichloride (sulphur monochloride) were added to a one-litre reaction vessel. While stirring briskly dry chlorine gas was passed through the solution until a distinctly green layer of chlorine gas was observed over the solution. After about three quarters of an hour, the apparatus was immersed in an ice-bath and a fast stream of ammonia from a cylinder was passed through the solution as rapidly as possible without causing material to splash from the flask.

Initially copious white fumes were formed which soon disappeared and a thick yellow brown suspension was formed in the flask. The colour then changed to a grey green, brown and finally after about three hours to a reddish brown or yellowish brown suspension. The flow of ammonia was then stopped. During the passage of ammonia the liquid in the flask was maintained to a constant volume by occasionally adding carbon tetrachloride through the third neck of the flask using a funnel.

The reaction mixture was filtered on a sintered-glass funnel and the solid material was slurried with about 500 ml of water for 10-15 minutes. The precipitate was separated by filtration and thoroughly air-dried for a day or two.

To remove  $S_7NH$ , the dried residue was shaken with 150 ml of ether for ten minutes in a wide necked reagent bottle. The solution was decanted off and the process was repeated. (This process removes so little material, there is some doubt if it is necessary). The yellow or yellowish green dry residue was extracted with dry benzene. Either a Soxhlet extractor or an extraction tube was used for this. The extraction was continued until the eluate was colourless or faintly orange yellow. When all the  $S_4N_4$  was extracted, the extraction pot was cooled and pure tetrasulphur tetranitride crystallised from the solution as orange-red or orange-yellow needles. Yields of 12-14 g. of  $S_4N_4$  (m.p.  $178-179^\circ$ ) were obtained. Further purification if necessary may be effected by sublimation in high vacuum with a bath temperature of about  $100^\circ C$ .

Precautions for working with  $S_4N_4$  are as follows<sup>14(b)</sup>.  $S_4N_4$  itself can only become dangerous in a dry state, but one should take note of the following:

Do not work with more than 10g of dry  $S_4N_4$ . Do not touch it with a metal spatula, and do not store the dry substance in bottles

with ground glass stoppers in order to save the crystals from being ground between the two surfaces, which usually causes an explosion. While working with  $S_4N_4$  in dry state normal precautions are sufficient, e.g. a plate of safety-glass.

Phenylboron dichloride ( $PhBCl_2$ ) 54(a),(b),191

Boron trichloride (5.214g., 0.453 mol.) was added to a suspension of tetraphenyl tin (4.205g.,) in dry methylene dichloride (10 ml) at  $-80^{\circ}C$ . The mixture was allowed to warm gradually to between  $0^{\circ}C$  and  $5^{\circ}C$  when a violent reaction occurred. The volatile material (methylene dichloride containing some boron trichloride) was removed and trapped at  $-80^{\circ}C$ . The residue gave a mixture of phenylboron dichloride (b.p.  $65-70^{\circ}C$ ) and phenyltin trichloride (b.p.  $129-130^{\circ}C$ ). Phenylboron dichloride was purified by several distillations under vacuo (Yield 4.2 g., 90% based on the equation,  $Ph_4Sn + 3BCl_3 \longrightarrow 3PhBCl_2 + PhSnCl_3$ ).

Diphenyl mercury:

B.D.H. laboratory reagent was purified by recrystallisation from hot chloroform.

p-Tolytin trichloride: ( $C_7H_7SnCl_3$ ) 52(a),(b)

p-Bromotoluene (171 g, 1 mole) in ether (100 ml) was added to magnesium (24.3 g., 1 g atom) in ether (500 ml) during one and a half hours. The reaction mixture was refluxed for 30 minutes

and then allowed to cool to room temperature. Stannic bromide (76.5 g., 0.175 moles) in benzene was added to the reaction mixture during 40 minutes and then the reaction mixture was refluxed for two and a quarter hours. The reaction mixture was cooled to room temperature and hydrolysed by the addition of ice-water (500 ml) and ice-cold 5% hydrochloric acid (200 ml.) After filtration the organic layer was separated, dried over  $\text{MgSO}_4$ , and solvent was removed under vacuum to give tetra-p-tolytin (71 g., 85%), which was recrystallised from benzene. p-Tolytin trichloride was prepared by the redistribution reaction of tetra-p-tolytin with stannic chloride. The two components in 1:1 ratio were mixed at room temperature and allowed to stand for 2-3 hours.

Stannic chloride (B.D.H. standard laboratory reagent) was purified by distillation under dry nitrogen atmosphere or under vacuo.

Stannic bromide (B.D.H.) was purified by sublimation under vacuum at room temperature.

Stannic iodide (B.D.H.) was purified by recrystallisation from hot chloroform.

Stannic fluoride (Alfa Inorganics Inc.) was used directly without further purification.

Titanium tetrachloride (B.D.H.) was purified by distillation under vacuo.

Titanium tetrabromide (Alfa Inorganics Inc.) purified by sublimation under vacuum at 30-40°C.

Titanium tetraiodide (Alfa Inorganics Inc.) was purified by sublimation under vacuum at 140-160°C.

Titanium tetrafluoride (Alfa Inorganics Inc.) was used without further purification.

Zirconium tetrachloride (B.D.H.) was first refluxed with  $\text{SOCl}_2$  to remove any traces of moisture and then purified by recrystallisation from  $\text{SOCl}_2$ .

Zirconium tetrafluoride (Alfa Inorganics Inc.) was used without further purification.

Hafnium tetrachloride (Alfa Inorganics Inc.) was used without further purification.

Aluminium trichloride was purified by sublimation in a dry nitrogen atmosphere.

Aluminium tribromide (Hopkin and Williams) was purified by sublimation under vacuo.

Gallium trichloride was purchased from Koch-Light Ltd., and used without further purification.

Indium trichloride,  $\text{InCl}_3 \cdot \text{H}_2\text{O}$  was purchased from B.D.H. and water was removed by refluxing with thionyl chloride.

Thallium trichloride was prepared from thallos chloride (Alfa Inorganics Inc.) and chlorine in dry acetonitrile, (pp.67-68).

Selenium tetrachloride was prepared by the reaction between selenium and chlorine in dry  $\text{CCl}_4$ <sup>36</sup>. Pure selenium was suspended in  $\text{CCl}_4$  in a two-necked round-bottomed flask and dry chlorine was then introduced. The Se soon dissolved and the solution turned brown (formation of  $\text{Se}_2\text{Cl}_2$ ); after some time  $\text{SeCl}_4$  separated as a yellow-white powder.  $\text{SeCl}_4$  was filtered in absence of moisture and dried by suction.  $\text{SeCl}_4$  was purified by sublimation at  $196^\circ\text{C}$  in the atmosphere of dry chlorine gas.

Selenium tetrafluoride was prepared by the reaction between  $\text{ClF}_3$  and  $\text{Se}_2\text{Cl}_2$  by analogy with the published preparation viz from fluorine and diselenium dichloride ( $\text{Se}_2\text{Cl}_2 + 5\text{F}_2 \rightarrow \text{SeF}_4 + 2\text{FCl}$ )<sup>47(a)</sup>. The apparatus used was constructed from Pyrex, and employed cone and socket and ball socket joints. It consisted of a 250 ml three-necked round-bottomed flask for mixing dry nitrogen and chlorine-trifluoride and a 100 ml two-necked reaction flask followed by a train of traps at  $-196^\circ\text{C}$  for purification. Each section of the apparatus was capable of isolation by means of stopcocks. All joints were greased with Fluorolube 'W' grease.

Diselenium dichloride (10 g.) was cooled in an ice salt bath. This was found to be necessary to prevent ignition at the commencement of fluorination. The apparatus was flushed with dry nitrogen for about an hour. Chlorine trifluoride from the

cylinder diluted with dry nitrogen was passed slowly for half an hour and then the rate of chlorine trifluoride supply was increased until only a colourless liquid remained in the reaction vessel. The chlorine trifluoride was switched off and the apparatus was flushed with dry nitrogen for about an hour. The product was then purified by trap to trap distillation in vacuo.

Tellurium tetrafluoride<sup>47(b)</sup>

The reaction employed for the preparation of tellurium tetrafluoride was that of selenium tetrafluoride and tellurium dioxide ( $\text{TeO}_2 + 2\text{SeF}_4 \longrightarrow \text{TeF}_4 + 2\text{SeOF}_2$ ). Selenium tetrafluoride was distilled from a storage bulb into a carefully dried, evacuated train of bulbs, the first of which carried the dry tellurium dioxide. The mixture was slowly heated by means of a water-bath. As the temperature approached  $80^\circ\text{C}$  there was a vigorous reaction and the tellurium dioxide dissolved. The temperature was raised until the liquid began to reflux under its own vapour pressure and was kept at that temperature for about 15 minutes, after which the selenium tetrafluoride and selenium oxyfluoride were distilled into another bulb. The last traces being removed from the residue by keeping it at  $100^\circ\text{C}$  in vacuo.  $\text{TeF}_4$  was purified by sublimation in vacuo.

Tellurium tetraiodide<sup>36</sup>:  $\text{TeI}_4$  was prepared by the reaction between telluric/and hydrogen iodide ( $\text{Te(OH)}_6 + 6\text{HI} \xrightarrow{\text{acid}} \text{TeI}_4 + \text{I}_2 + 6\text{H}_2\text{O}$ ).

A very concentrated telluric acid solution is mixed with slightly more than the stoichiometric quantity of fuming hydriodic acid.

A heavy, grey precipitate of  $\text{TeI}_4$  immediately separated. It was suction filtered on a fritted glass filter and washed several times with pure  $\text{CCl}_4$  to remove iodine. The product was analytically pure (Found: I = 80.3%; theory I = 79.93).

Niobium pentachloride was purchased from Alfa Inorganics Inc. and purified by sublimation in vacuo.

Niobium pentafluoride (Koch-Light standard laboratory reagent) was used without further purification.

Tantalum pentachloride and Tantalum pentafluoride (Koch-Light standard laboratory reagents) were used without further purification.

Vanadium oxytrichloride and  $\text{WOCl}_4$  were prepared by the methods described by Brauer.<sup>36</sup>

Tungsten hexachloride was purchased from Koch-Light and used without further purification.

Tungsten hexabromide<sup>120</sup>

$\text{WCl}_6 + 2\text{BBr}_3 \longrightarrow \text{WBr}_6 + 2\text{BCl}_3$  2.1 g. of  $\text{WCl}_6$  was placed in a two-necked round-bottomed flask and excess of boron tribromide (B.D.H.) was condensed on it at  $-196^\circ\text{C}$ . The reaction flask slowly warmed to  $0^\circ\text{C}$  when a vigorous reaction occurred. The flask was allowed to stand in a bath of cold water ( $10^\circ\text{C}$ ) for about an hour and the excess of boron halides were removed by condensing at  $-196^\circ\text{C}$ . The tungsten hexabromide

was obtained as a black powder (Found: Br = 72.18; theory: Br = 72.30).

Trithiazyl trichloride ( $S_3N_3Cl_3$ )<sup>1</sup>

The preparation was carried out in the absence of moisture. A Schlenk or a two-necked round bottomed flask was used as the apparatus for the preparation. Tetrasulphur tetranitride (5 g.) was placed in a Schlenk and freshly purified (p. 50) sulphuryl chloride (25 ml) was added to the  $S_4N_4$ . The reaction mixture was stirred at room temperature using a teflon stirrer. The colour of the reaction mixture slowly changed to red after 1-2 hours, and the stirring was continued for 16-24 hours, until the evolution of sulphur dioxide ceased (the exit gas was led away through rubber (decomposes with  $SO_2Cl_2$ ) or plastic tubing into a fuming chamber).

The pale-yellow-white powdery  $S_3N_3Cl_3$  which settled out was filtered from the supernatant red liquid, washed with sulphuryl chloride (5-10 ml) dried in vacuo, and if necessary purified by recrystallisation from dry  $CCl_4$ . The red liquid was evaporated by pumping and further yellow-white  $S_3N_3Cl_3$  was obtained and recrystallised from dry  $CCl_4$ . The total yield before crystallisation was quantitative.

The trithiazyl trichloride when freshly crystallised was a pale-yellow-white crystalline solid, which changed to yellow after standing for several days. The m.p. of the first batch of  $S_3N_3Cl_3$

was 90-91°C, whereas the  $S_3N_3Cl_3$  recrystallised from  $SO_2Cl_2$  melted at 93-94°C.

$S_3N_3Cl_3$  is soluble in carbon tetrachloride (1 g in 25 ml  $CCl_4$ ), benzene, chloroform, carbon disulphide, thionyl chloride, and sulphuryl chloride. When recrystallised from hot benzene it crystallises as yellow-white flakes.  $S_3N_3Cl_3$  should be stored in glass containers with air-tight polyethylene stoppers or glass stoppers with teflon sleeves.

#### Drying and purification of solvents and other liquid materials

Most of the solvents were dried and purified by the methods described by A. Weissberger<sup>36(a)</sup>. Non-halogenated solvents were dried over sodium wire, redistilled if necessary from sodium and stored in a three-necked flask over clean sodium wire, in a nitrogen atmosphere. Quantities of solvents were removed by using a long needled syringe whilst dry nitrogen was flushed through the vessel.

Carbon tetrachloride<sup>104</sup>  $CCl_4$  (AnalaR grade) was dried on standing over  $P_2O_5$  for a day or two and then if necessary purified by distillation under dry nitrogen atmosphere.

Carbon disulphide<sup>36(a)</sup> Commercial carbon disulphide was agitated with mercury for 4-6 hours, dried with phosphorus pentoxide and fractionally distilled in vacuum avoiding all greased joints.

Methylene dichloride<sup>54</sup>  $\text{CH}_2\text{Cl}_2$  was refluxed for 3-4 hours over phosphorus pentoxide, distilled, and stored in a dry nitrogen atmosphere.

Sulphuryl Chloride<sup>36</sup>  $\text{SO}_2\text{Cl}_2$  (B.D.H. standard laboratory reagent) was fractionally distilled through a twelve inch column packed with glass helices, connected to a reflux distillation head equipped with a calcium chloride drying tube. The middle colourless fraction boiling between  $69-70^\circ\text{C}$  was pure  $\text{SO}_2\text{Cl}_2$ .

Thionyl chloride<sup>119</sup> Triphenyl phosphite (160 ml) was added to the thionyl chloride (1 litre) with vigorous stirring for 30 minutes. The mixture was fractionated and the 'water white' middle fraction was collected and stored.

Nitriles<sup>36(a)</sup> Acetonitrile, propionitrile, isobutyronitrile and tertiarybutyl cyanide were dried over phosphorus pentoxide and purified by fractional distillation.

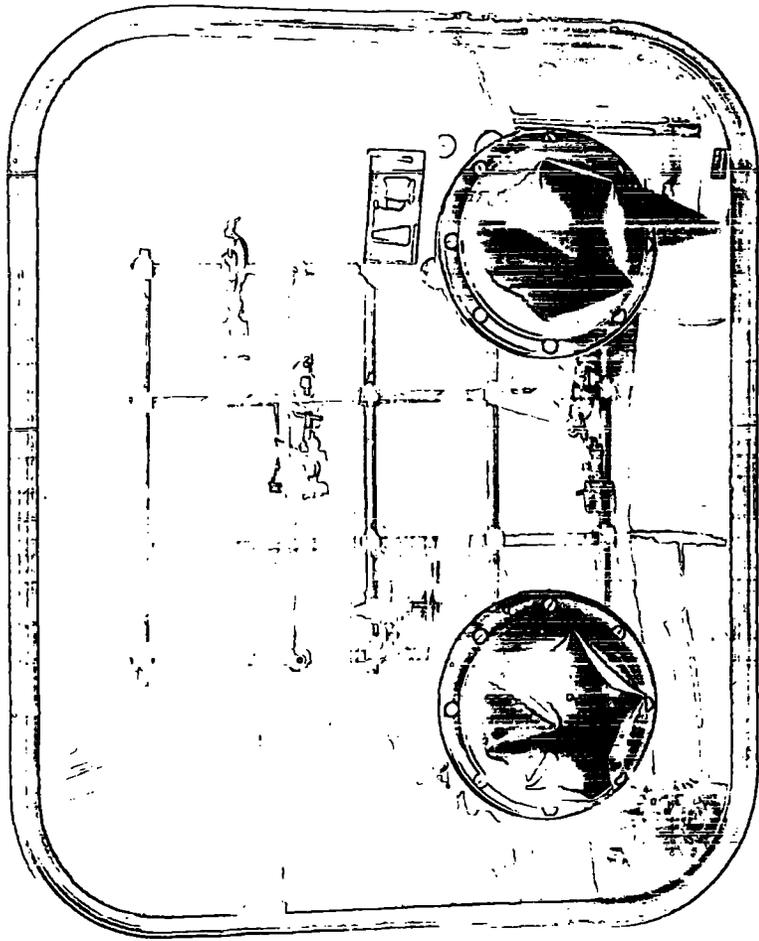
Epoxides<sup>36(a)</sup> Epichlorohydrin was purified by fractional distillation (b.p.  $116^\circ\text{C}$ .) Ethylene oxide and epibromohydrin were vacuum distilled.

### Experimental Techniques

All manipulations of air and moisture sensitive compounds were carried out in the glovebox shown in figure overleaf.

#### The Drybox

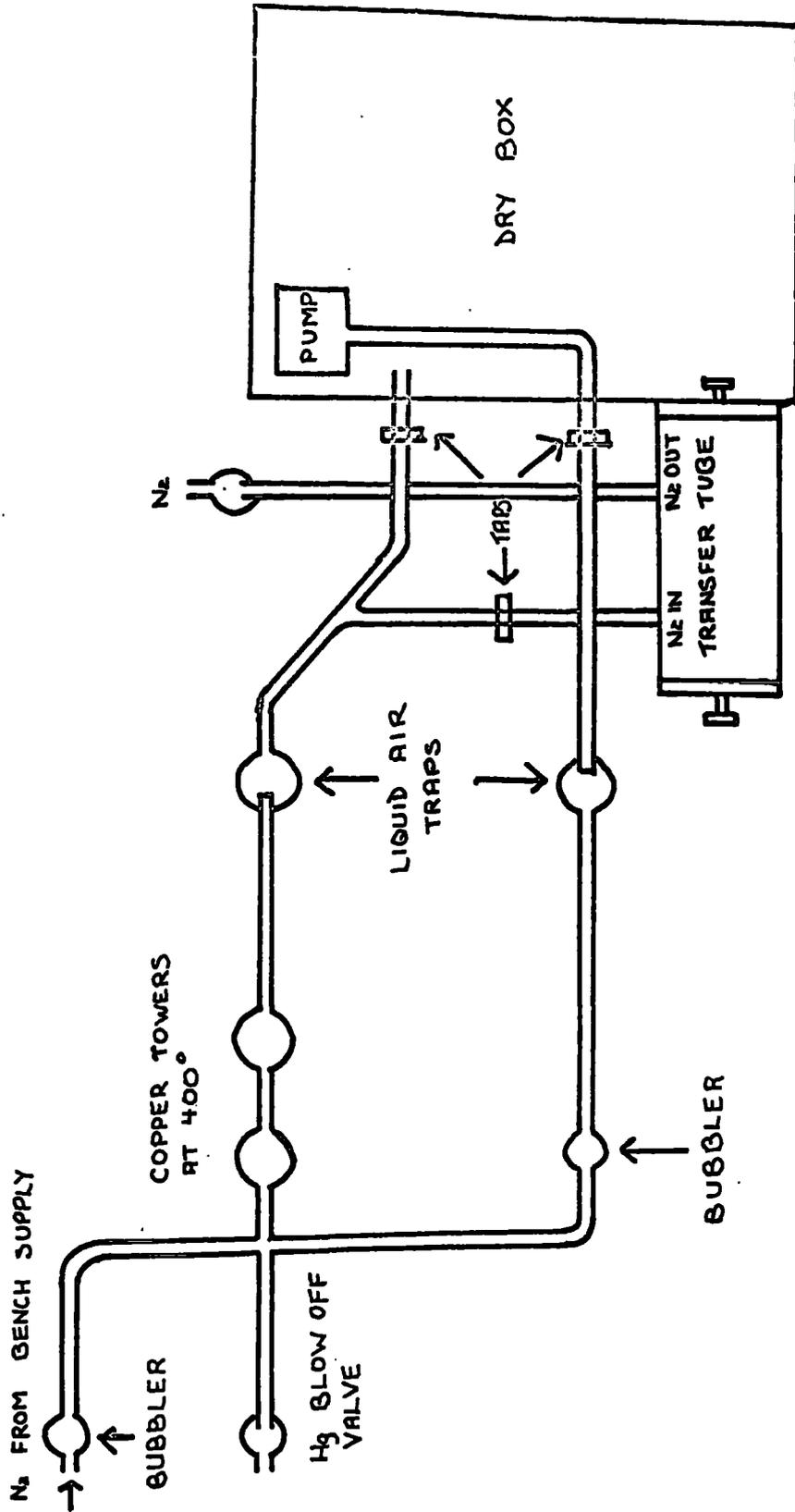
This consisted of a steel box 39 inches long, 29 inches high and 24 inches deep with a perspex roof and front, and with two front



BB



PLAN VIEW OF FLOW



ports used for armholes. It was obtained from Lintott Engineering Ltd., Horsham, Sussex (MK XI Glovebox). The perspex windows were fitted with rubber airtight seals; 'Charco, Buta-sol, 5B 3032' (or neoprene) arm-length gloves were used on the front parts. At one side of the box was a cylindrical transfer tube ('posting port') 18 inches long and 9 inches diameter, which opened into the drybox by means of a screw-in part and which similarly opened to the air at the other end. A strip-light was mounted outside the perspex roof and electricity was carried into the box which contained a recirculating pump. Behind the transfer tube were four 1 cm. diameter tubes leading through the side of the apparatus and closed inside and out by 4 mm. glass high vacuum taps, whilst the floor was covered with a sheet of black plastic material or aluminium kitchen foil.

The nitrogen atmosphere in the dry box was kept free from oxygen and moisture in the following way. The pump which could completely recycle the atmosphere in the box in ten hours, passed nitrogen out through a 4 mm. tap, through a trap 18 inches deep cooled in liquid air, over copper wire packed in two silica towers at 400°C, through a second trap similarly cooled, and back through another 4 mm. tap into the box. This circulation was maintained whenever the dry box was not being used for experiments.

Copper towers and liquid air traps were connected to the drybox by P.V.C. and silicone tubing and normally the pressure in the box was maintained slightly above atmospheric. Nitrogen from the bench supply could be introduced into the system via the copper towers and liquid air cooled traps as shown in the figure.

All the apparatus introduced into the drybox was first placed in the transfer tube which had an inlet connected to the nitrogen system of the drybox, and nitrogen from the bench supply was flushed through via the copper towers and liquid air traps and passed out of the transfer chamber via a gas bubbler into the air. When the transfer tube had been purged for at least one hour the apparatus could be moved into the drybox.

#### Analyses:

Analyses were performed by Messrs. R.Coult and T.Holmes of this department and by Drs. Weiler and Strauss of the Micro-analytical laboratory, Oxford.

#### Molecular Weights:

Mol. wt. determinations were carried out either using a Mechrolab vapour pressure Osmometer, model 301A or the cryoscopic technique usually in benzene adapted to facilitate the use of air and moisture sensitive compounds.

Mass spectra:

Mass spectra were obtained with an A.E.I. (MS9) mass spectrometer on samples mounted on an inert ceramic and introduced on a direct insertion probe.

Infrared Spectra:

Infrared spectra under nitrogen were recorded on Grubb-Parsons GS2A or Spectromaster (4000-400  $\text{cm}^{-1}$ ) and DM2/DB3(475-200  $\text{cm}^{-1}$ ) prism grating spectrophotometers.

Spectra in the potassium bromide region were obtained either as thin liquid films (in the case of low melting compounds) or as Nujol mulls, between KBr plates.

For spectra in the caesium iodide region, the thin liquid films or mulls were supported between two sheets of one tenth mm. thick polyethylene clamped in a cell (Nujol cell) to give an air-tight seal.

Reactions

Most of the reactions were carried out in a Schlenk or in a two-necked round-bottomed flask in an atmosphere of dry nitrogen.

Reaction between tetrasulphur tetranitride and metal halides:

Tin tetrabromide

$\text{SnBr}_4$  (1.2 g.) was dissolved in dry hexane or heptane (40 ml) at room temperature and  $\text{S}_4\text{N}_4$  (1.0 g.) was added to the solution.

The reaction mixture was stirred for 48-60 hours. The reaction was slow and no immediate colour change was observed. After 12-14 hours, the colour of the solution turned reddish brown, finally a deep brown precipitate was obtained, and no further change in the colour of the product was observed after about 48 hours. The precipitate was filtered, washed in hexane (20 ml) and dried in vacuo. The adduct is insoluble in  $\text{CCl}_4$ ,  $\text{CH}_2\text{Cl}_2$ ,  $\text{Et}_2\text{O}$ ,  $\text{CS}_2$ . Found: S = 31.8; N = 13.65; Br = 39.0.  $\text{SnBr}_4 \cdot 2\text{S}_4\text{N}_4$  requires: S = 31.73; N = 13.65; Br = 39.61%. M.P. 198-200°C (decomposition). The compound gradually changed to a yellow product upon exposure to air. The infrared spectrum of the sample exposed to air after several days (30-40) was similar to the i.r. spectrum of  $\text{S}_4\text{N}_4$ , with additional peaks at  $1400 \text{ cm}^{-1}$ ,  $3194 \text{ cm}^{-1}$  probably due to the hydrolysis product of the halide.

Tin tetrachloride<sup>52,53</sup>

Tetrasulphur tetranitride (0.92 g) was dissolved in  $\text{CCl}_4$  (50 ml) and tin tetrachloride (1.3 g) added dropwise at room temperature. A deep red precipitate of  $\text{SnCl}_4 \cdot 2\text{S}_4\text{N}_4$  was formed immediately. The compound was filtered, and purified by washing in  $\text{CCl}_4$  and pumped dry at room temperature. M.P. 200°C (decomp.) The adduct is insoluble in  $\text{CCl}_4$ ,  $\text{CH}_2\text{Cl}_2$ ,  $\text{Et}_2\text{O}$ ,  $\text{CS}_2$ . Found, Cl = 22.54;  $\text{SnCl}_4 \cdot 2\text{S}_4\text{N}_4$  requires: Cl = 22.57.

Tin tetrafluoride:

Attempts were made to prepare the adduct of  $\text{SnF}_4$ . In one experiment tin tetrafluoride (1.0 g) was suspended in 30 ml of acetonitrile and  $\text{S}_4\text{N}_4$  (1.0 g) was added, the solution was refluxed for 24 hours, while in an another experiment,  $\text{SnF}_4$  (0.7 g) was held in 40 ml of dry T.H.F. and  $\text{S}_4\text{N}_4$  (0.7 g) was added, the mixture was refluxed for 14 hours. No colour change or other change in appearance was noted. The i.r. spectra of the products showed only unchanged starting materials.

Tin tetraiodide:

(a)  $\text{SnI}_4$  (1.9 g) was dissolved in dry chloroform (40 ml) and  $\text{S}_4\text{N}_4$  (1.1 g) in 25 ml of hot dry chloroform was added in portions, no immediate reaction was observed. The solution was stirred for 24 hours. No change in appearance was observed; the spectrum of the evaporated solution showed only  $\text{S}_4\text{N}_4$ .

(b)  $\text{SnI}_4$  (1.5 g) was dissolved in  $\text{CS}_2$  (30 ml) and  $\text{S}_4\text{N}_4$  (0.9 g) in  $\text{CS}_2$  (40 ml) was added at room temperature. The solution was stirred for 24 hours and concentrated to a small volume. No reaction was found to take place.

Stannous chloride

Tetrasulphur tetranitride (1.0 g) was suspended in ether (40 ml) and  $\text{SnCl}_2$  (1.0 g) added at room temperature. The reaction mixture was stirred for 48 hours. No obvious reaction was observed.

Germanium tetrachloride

Following attempts were made to study the reaction between  $\text{GeCl}_4$  and  $\text{S}_4\text{N}_4$ .

(a) Tetrasulphur tetranitride (1.2 g) was suspended in  $\text{CCl}_4$  and  $\text{GeCl}_4$  (2 ml) added at room temperature. The solution was stirred for 24 hours. No reaction was found to take place.

(b)  $\text{GeCl}_4$  (10 ml) was added to  $\text{S}_4\text{N}_4$  (1.0 g) at room temperature and the reaction mixture was stirred for 30 hours. Since there was no obvious reaction, the reaction temperature was raised to  $75^\circ\text{C}$  and stirring was continued for 4 hours. No colour change or other change in appearance was noted. The infrared spectrum of the evaporated solution showed only unchanged starting materials.

Silicon tetrachloride

Tetrasulphur tetranitride (1.0 g) was taken in a Schlenk and  $\text{SiCl}_4$  (10 ml) added at room temperature. The reaction mixture was stirred for 48 hours. The infrared spectrum of the evaporated solution showed only unchanged starting materials.

Selenium tetrachloride

$\text{SeCl}_4$  (1.1 g) was suspended in benzene or toluene (20 ml) and tetrasulphur tetranitride added to the solution at  $0^\circ\text{C}$ . The solution was stirred for 24 hours. The reaction was vigorous initially and a bright yellow precipitate was obtained at the end of the reaction after 24 hours. The precipitate was filtered,

washed in benzene (15 ml) and dried in vacuo. Found: Se=20.60, S=28.71, N=13.88, Cl=34.61;  $\text{SeCl}_4 \cdot \text{S}_4\text{N}_4$  requires; Se=19.54; S=31.60, N=13.83, Cl=34.99. M.P. 127-129°C. The compound is insoluble in  $\text{CCl}_4$ ,  $\text{CHCl}_3$ . It turns red upon exposure to air.

#### Tellurium tetrachloride

Tetrasulphur tetranitride (0.46 g) was dissolved in toluene (20 ml) and tellurium tetrachloride (0.73 g) in toluene (10 ml) added at room temperature. An immediate deep red precipitate was formed and filtered off. The compound was washed in toluene and dried by pumping at room temperature. Found: S= 28.75, N =12.45; Cl = 31.60;  $\text{TeCl}_4 \cdot \text{S}_4\text{N}_4$  requires: S= 28.26; N = 12.35; Cl= 31.25. M.P. 140°C. The compound is insoluble in  $\text{CCl}_4$ ,  $\text{CH}_2\text{Cl}_2$ ,  $\text{CS}_2$ ,  $\text{Et}_2\text{O}$ . The adduct changes to a yellow product giving probably tetrasulphur tetranitride and the hydrolysis product of the halide.

#### Tellurium tetrafluoride

The reaction was carried out in a two-necked 100 ml round-bottomed flask. Tellurium tetrafluoride (0.4 g) was dissolved in dry acetonitrile (45 ml) at room temperature and tetrasulphur tetranitride (0.36 g) added to the above solution. No immediate colour change was observed. The solution was refluxed for 72 hours and a deep red solution was obtained. The solution was concentrated to a small volume (10 ml) and a bright deep red precipitate was

obtained. The precipitate was filtered, washed in acetonitrile and dried in vacuo. When dry the compound was brownish-orange in colour. Found: N=15.24,  $\text{TeF}_4 \cdot \text{S}_4\text{N}_4$  requires, N=14.44. M.P.  $92^\circ\text{C}$ . There was insufficient sample for further analysis. The adduct changes to a yellow compound upon exposure to air.

Tellurium tetraiodide

$\text{TeI}_4$  (1.0 g) and tetrasulphur tetranitride (0.29 g) in ether (40 ml) were shaken together for about a week. No reaction was found to take place, probably due to the insolubility of tellurium tetraiodide in ether. Methylene dichloride was also used as a solvent to study the reaction, but no reaction was observed.

Titanium tetrabromide

$\text{TiBr}_4$  (2.0 g) was dissolved in 30 ml of dry methylene dichloride (or o-dichlorobenzene or ether) and tetrasulphur tetranitride (0.67 g) added at room temperature. Immediately a reddish brown precipitate was formed. The solution was stirred for 10 hours. The deep brown precipitate was filtered, washed in methylene dichloride and pumped dry at room temperature. Found: S=22.1, N=10.34, Br=59.1;  $\text{TiBr}_4 \cdot \text{S}_4\text{N}_4$  requires; S=23.2, N=10.15, Br=57.34. M.P.  $138^\circ\text{C}$ . It is insoluble in  $\text{CCl}_4$ ,  $\text{CH}_2\text{Cl}_2$ . When exposed to air, it turns yellow giving probably tetrasulphur tetranitride and the hydrolysis product of the halide.

Titanium tetrachloride<sup>52,53</sup>

Tetrasulphur tetranitride (0.92 g) was dissolved in carbon tetrachloride (40 ml) and titanium tetrachloride (0.81 g) added at room temperature. An immediate yellow-orange precipitate of  $S_4N_4 \cdot TiCl_4$  was obtained and filtered from the solution. The product was washed in  $CCl_4$  and pumped dry. M.P.  $135^\circ$  (decomp.) It is insoluble in  $CCl_4$ ,  $CH_2Cl_2$ .

Titanium tetrafluoride

Attempts to prepare the adduct of  $TiF_4$  using the solvents acetonitrile, T.H.F.,  $CH_2Cl_2$  were unsuccessful. Methylene dichloride was found to be the most suitable solvent. (i)  $TiF_4$  (1.0 g) was refluxed with 30 ml of dry acetonitrile for 24 hours and filtered, to the filtrate added tetrasulphur tetranitride (0.2 g) in acetonitrile (20 ml) at room temperature. The solution was stirred for 12 hours. The infrared spectrum of the evaporated product showed only unchanged starting materials. (ii)  $TiF_4$  (1.0 g) was suspended in acetonitrile and  $S_4N_4$  (0.2 g) added to the solution. The reaction mixture was refluxed for 48 hours at  $92^\circ C$ . No obvious reaction was observed. (iii)  $TiF_4$  (1.1 g) was refluxed with T.H.F. (70 ml) and tetrasulphur tetranitride (0.2 g) added at room temperature. The solution was stirred for 12 hours. No reaction was found to take place.

(iv)  $\text{TiF}_4$  (1.5 g) was suspended in methylene dichloride and tetrasulphur tetranitride (0.75 g) added at room temperature. No immediate reaction was observed. The reaction mixture was stirred for 48 hours. A deep red precipitate was slowly formed. The compound was filtered, washed in  $\text{CH}_2\text{Cl}_2$  and pumped dry at room temperature. When dry the adduct was orange in colour. Found: S=17.90, N=7.81, F=46.60;  $\text{S}_4\text{N}_4\text{TiF}_4$  requires: S=18.83, N=8.24, F=44.70, M.P. decomposed above  $120^\circ\text{C}$ . It is insoluble in  $\text{CH}_2\text{Cl}_2$ ,  $\text{CS}_2$ . The adduct changes to a yellow product upon exposure to air.

#### Titanium tetraiodide

$\text{TiI}_4$  (1.0 g) was dissolved in 40 ml of dry  $\text{CCl}_4$  (or  $\text{CH}_2\text{Cl}_2$  or  $\text{CS}_2$ ) and tetrasulphur tetranitride (0.25 g) added at room temperature. The solution was stirred for 48 hours and a black precipitate was obtained. The compound was filtered, washed in  $\text{CCl}_4$  and dried in vacuo. Found: S=17.05, N=8.74, I=68.70,  $\text{TiI}_4 \cdot \text{S}_4\text{N}_4$  requires, S=17.30, N=7.58, I=68.61. M.P. decomposition above  $100^\circ\text{C}$ . The compound is insoluble in  $\text{CCl}_4$ ,  $\text{CH}_2\text{Cl}_2$ ,  $\text{CS}_2$ . It changed to a yellow product when exposed to air.

#### Zirconium tetrachloride

$\text{ZrCl}_4$  (0.8 g) was suspended in  $\text{CCl}_4$  (30 ml) and tetrasulphur tetranitride (0.63 g) added at room temperature. Immediately the solution turned red. The solution was stirred for 12 hours and a deep reddish-orange precipitate was obtained. The compound was

filtered, washed in  $\text{CCl}_4$  and dried in vacuo. Found: S=29.55, N=12.80, Cl=33.10,  $\text{ZrCl}_4 \cdot \text{S}_4\text{N}_4$  requires: S=30.67, N=13.42, Cl=33.99. M.P.  $260^\circ\text{C}$  (decomp.) It is insoluble in  $\text{CH}_2\text{Cl}_2$ ,  $\text{CS}_2$ . The adduct changed to a yellow product when exposed to air.

#### Zirconium tetrafluoride

$\text{ZrF}_4$  (0.5 g) was suspended in dry methylene dichloride (or o-dichlorobenzene) at room temperature and  $\text{S}_4\text{N}_4$  (0.54 g) added to the solution. The solution was stirred for 48 hours. No reaction was found to take place.

#### Hafnium tetrachloride

$\text{HfCl}_4$  (1.9 g) was suspended in  $\text{CCl}_4$  (25 ml) and tetrasulphur tetranitride added at room temperature. The reaction mixture was stirred for 24 hours and a bright deep red compound was obtained. The precipitate was filtered, washed in  $\text{CCl}_4$  and dried in vacuo. Found: S=25.41, N=10.35, Cl=29.90;  $\text{S}_4\text{N}_4 \cdot \text{HfCl}_4$  requires: S=25.37, N=11.10, Cl=28.14. M.P. decomposition above  $140^\circ\text{C}$ . It is insoluble in  $\text{CH}_2\text{Cl}_2$ . The adduct gave a yellow product when exposed to air.

#### Antimony pentachloride

Antimony pentachloride (1.0 ml) was dissolved in  $\text{CCl}_4$  (20 ml) and a solution of  $\text{S}_4\text{N}_4$  (0.92 g) in  $\text{CCl}_4$  (40 ml) added at room temperature. The solution was stirred for 14 hours. A deep red precipitate was obtained. The precipitate was filtered, washed in

$\text{CCl}_4$  and pumped dry at room temperature. (Obtained for spectrum only; no analyses)

Antimony pentafluoride

$\text{SbF}_5$  (1.9 g) was suspended in 25 ml of  $\text{CH}_2\text{Cl}_2$  and  $\text{S}_4\text{N}_4$  (0.4 g) added at room temperature. The solution was stirred for 14 hours and a green precipitate was obtained. The precipitate was filtered, washed in  $\text{CH}_2\text{Cl}_2$  and dried in vacuo. Found: F, 38.15, N, 5.14; S=11.87;  $\text{S}_4\text{N}_4 \cdot 4\text{SbF}_5$  requires: F, 36.16; N, 5.33; S=12.18. M.P.  $145^\circ\text{C}$  (decomp.)

Niobium pentachloride

$\text{NbCl}_5$  (2.2 g) was suspended in  $\text{CCl}_4$  or  $\text{CH}_2\text{Cl}_2$  (35 ml) and  $\text{S}_4\text{N}_4$  (1.4 g) added at room temperature. The solution was stirred for 12 hours and a reddish-brown precipitate was formed. The precipitate was filtered, washed in  $\text{CCl}_4$  and dried in vacuo. The adduct was recrystallised from methylene dichloride. Found: S=27.15, N=12.68, Cl=39.50;  $\text{S}_4\text{N}_4 \cdot \text{NbCl}_5$  requires: S=28.17, N=12.32, Cl=39.06. M.P.  $106^\circ\text{C}$ . The adduct is soluble in  $\text{CH}_2\text{Cl}_2$ ,  $\text{CS}_2$ . It changed to a yellow product in air.

Niobium pentafluoride

$\text{NbF}_5$  (1.35 g) was suspended in 40 ml of dry methylene dichloride and  $\text{S}_4\text{N}_4$  (0.2 g) was added at room temperature. Immediately a deep red solution and a pinkish-white precipitate was obtained. The solution was stirred for 24 hours. The deep red solution was filtered and evaporated to a small volume (10 ml). A deep red-orange

precipitate was filtered, washed in  $\text{CH}_2\text{Cl}_2$  (5 ml) and vacuum dried. Found: N = 14.35;  $\text{S}_4\text{N}_4 \cdot \text{NbF}_5$  requires: N = 15.04. M.P. decomp. above  $60^\circ\text{C}$ . The adduct changed to a yellow product in moist air. The infrared spectrum of the pinkish-white precipitate showed peaks (at 3030 and  $1612\text{ cm}^{-1}$ ) due to -OH indicating presence of partially hydrolysed  $\text{NbF}_5$ .

#### Tantalum pentachloride

$\text{TaCl}_5$  (2.5 g) was suspended in  $\text{CCl}_4$  or  $\text{CH}_2\text{Cl}_2$  (40 ml) and tetrasulphur tetranitride (1.2 g) added at room temperature. Immediately a red precipitate was formed. The solution was stirred for 14 hours and a deep red compound was obtained. The compound was filtered and dried in vacuo and recrystallised from dry methylene dichloride. Found: S=23.40, N=10.88, Cl=33.20;  $\text{S}_4\text{N}_4\text{TaCl}_5$  requires: S=23.59, N=10.32, Cl=32.72. M.P.  $132^\circ\text{C}$  (decomp). It changes to a yellow product in air. The adduct is soluble in  $\text{CCl}_4$ ,  $\text{CH}_2\text{Cl}_2$ ,  $\text{CS}_2$ . The solubility of  $\text{S}_4\text{N}_4 \cdot \text{TaCl}_5$  in  $\text{CH}_2\text{Cl}_2$  is Ca. 0.8g/100 ml.

#### Tantalum pentafluoride

$\text{TaF}_5$  (1.0 g) was suspended in 70 ml of dry  $\text{CH}_2\text{Cl}_2$  and tetrasulphur tetranitride (0.15 g) added at room temperature. The solution was stirred for 48 hours, a deep red solution and a white precipitate was obtained. The solution was filtered, the filtrate was evaporated to a small volume (10 ml) and a deep

bright red precipitate was obtained. The precipitate was filtered and washed in  $\text{CH}_2\text{Cl}_2$  (5 ml) and pumped dry at room temperature. Found: S=26.59, N=12.24;  $\text{S}_4\text{N}_4 \cdot \text{TaF}_5$  requires: S=27.81, N=12.17. The compound changed to a yellow product when exposed to air.

Tungsten hexachloride

$\text{WCl}_6$  (2.0 g) was suspended in  $\text{CCl}_4$  (40 ml) and  $\text{S}_4\text{N}_4$  (0.72 g) added at room temperature. Immediately a dark-brown precipitate was formed. The solution was stirred for 24 hours. The precipitate was filtered, washed in  $\text{CCl}_4$  and pumped dry at room temperature. (Obtained for spectrum only; no analyses).

Tungsten hexabromide

$\text{WBr}_6$  (1.2 g) was dissolved in carbon disulphide at room temperature and  $\text{S}_4\text{N}_4$  (0.4 g) added to the solution. Immediately a dark-brown precipitate was formed. The solution was stirred for 48 hours. The dark-brown precipitate was filtered, washed in  $\text{CS}_2$  and dried in vacuo at room temperature. Found: S=17.85, N=8.08, Br=44.5.  $\text{S}_4\text{N}_4 \cdot \text{WBr}_4$  requires, S, 18.61, N=8.14, Br, 46.48. M.P.  $251^\circ\text{C}$ .

Tungsten oxytetrachloride

$\text{WOCl}_4$  (0.2 g) was dissolved in dry benzene (20 ml) and  $\text{S}_4\text{N}_4$  (0.1 g) added at room temperature. A dark-brown precipitate was immediately formed. The solution was stirred for 10 hours. The precipitate was filtered, washed in benzene and pumped dry.

Since the infrared spectrum of the compound was similar to that of  $WBr_4 \cdot S_4N_4$ , this compound is probably  $WOCl_4 \cdot S_4N_4$ . There was insufficient compound for analyses and other investigations.

Vanadium oxytrichloride

1 ml of  $VOCl_3$  was dissolved in 20 ml of dry ether and  $S_4N_4$  (1.8 g) added at room temperature. Immediately a dark brown precipitate was formed. The solution was stirred for 14 hours and the precipitate was filtered, washed in ether and dried in vacuo. Since the infrared spectrum of the product showed some hydrolysis of the compound, the compound was not investigated further.

Vanadium trichloride

$VCl_3$  (1.0 g) and tetrasulphur tetranitride in 40 ml of dry ether were shaken together for several hours at room temperature. No reaction was observed.

Aluminium tribromide

The reaction was studied in  $CCl_4$ , toluene,  $CS_2$  and  $CHBr_3$ . Carbon disulphide and bromoform were found to be suitable solvents.

(i)  $AlBr_3$  (1.2 g) was dissolved in  $CCl_4$  or toluene (25 ml) and tetrasulphur tetranitride (0.4 g) added at room temperature.

Immediately <sup>a</sup> dark-red solution was obtained. The solution was stirred for 14 hours and a black sticky mass was obtained. The reaction was not studied further.

(ii)  $\text{AlBr}_3$  (1.5 g) was dissolved in carbon disulphide or bromoform (20 ml) and tetrasulphur tetranitride (0.51 g) added at room temperature. Immediately a red solution was obtained. The solution was stirred for 24 hours and an orange-brown compound was obtained. The compound was filtered, washed in  $\text{CS}_2$  and vacuum dried at room temperature. Found: S=16.04, N=6.97, Br=68.74,  $\text{S}_4\text{N}_4 \cdot 2\text{AlBr}_3$  requires; S=17.83, N=7.80, Br=66.81. M.P.  $144^\circ\text{C}$ . The compound is slightly soluble in  $\text{CS}_2$ . It changed to a yellow product upon exposure to air.

Aluminium trichloride

$\text{AlCl}_3$  (1.9 g) was dissolved in 35 ml of carbon disulphide (or  $\text{CCl}_4$ ) and tetrasulphur tetranitride (1.3 g) added at room temperature. A deep red solution was formed immediately. The solution was stirred for 14 hours and a deep red precipitate was obtained. The compound was filtered, washed in  $\text{CS}_2$  and dried in vacuo. The adduct was recrystallised from  $\text{CH}_2\text{Cl}_2$ . Found: S, 29.45, N, 12.41;  $\text{S}_4\text{N}_4 \cdot 2\text{AlCl}_3$  requires: S=28.38, N=12.41, Cl=48.60, Cl=47.25. M.P.  $89^\circ\text{C}$  (decomp.) It changed to a yellow product in air.

Gallium trichloride

(i)  $\text{GaCl}_3$  (1.05 g) was dissolved in  $\text{CCl}_4$  or pentane (20 ml) and tetrasulphur tetranitride (0.55 g) added at room temperature. A sticky dark-red precipitate was immediately obtained. The solution was stirred for 10 hours and filtered. The product

was pumped dry. The reaction was not studied further since the oily product was difficult to handle.

(ii)  $\text{GaCl}_3$  (1.0 g) was dissolved in carbon disulphide (15 ml) and tetrasulphur tetranitride (0.5 g) added at room temperature. Immediately a deep red precipitate was obtained. The solution was stirred for 24 hours. The deep red precipitate was filtered, washed in  $\text{CS}_2$  and vacuum dried at room temperature. Found: S=23.48, N=11.22, Cl=37.89,  $\text{S}_4\text{N}_4 \cdot 2\text{GaCl}_3$  requires, S=23.87, N=10.44, Cl=39.71. M.P.  $100^\circ\text{C}$  (decomp.) It is soluble in  $\text{CS}_2$ . It changes to a yellow compound in air.

Indium trichloride

$\text{InCl}_3$  (0.8 g) was suspended in methylene dichloride (20 ml) and tetrasulphur tetranitride (0.33 g) added at room temperature. No immediate reaction was observed. The solution was stirred for 48 hours. A deep reddish-brown precipitate was slowly formed. The compound was filtered, washed in  $\text{CH}_2\text{Cl}_2$  and dried in vacuo at room temperature. Found: S=20.30, N=9.33, Cl=34.99;  $\text{S}_4\text{N}_4 \cdot 2\text{InCl}_3$  requires; S=20.42, N=8.94, Cl=33.99. M.P. decomp. above  $100^\circ\text{C}$ . It changed to a yellow product when exposed to air. It is slightly soluble in methylene dichloride.

Thallium trichloride

$\text{TlCl}_3$  (0.4 g) was suspended in dry acetonitrile (25 ml) and chlorine gas (dried over  $\text{P}_2\text{O}_5$ ) was passed through the solution till

all the thallos chloride was dissolved and a clear solution was obtained. Excess of chlorine was removed by flushing out with dry nitrogen and by condensing it at  $-196^{\circ}\text{C}$ . Tetrasulphur tetranitride (0.15 g) was then added to the above solution at room temperature. After about 10-15 minutes an orange-yellow solution was obtained. The solution was stirred for 14 hours and a pale yellow solution was formed. The acetonitrile was removed by pumping at room temperature and a red oily compound was obtained. Since the infrared spectrum of the compound was similar to the I.R. spectra of  $\text{S}_4\text{N}_4 \cdot 2\text{InCl}_3$ ,  $\text{S}_4\text{N}_4 \cdot 2\text{GaCl}_3$  this compound may well be  $\text{S}_4\text{N}_4 \cdot 2\text{TlCl}_3$ . The compound was soluble in  $\text{CH}_2\text{Cl}_2$ . There was not enough material for further investigations.

#### Iron (III) chloride

$\text{FeCl}_3$  (2.2 g) was suspended in 40 ml of dry  $\text{CCl}_4$  and tetrasulphur tetranitride (1.2 g) added at room temperature. There was no immediate reaction. The solution was stirred for 48 hours. A brown-black precipitate was obtained. The precipitate was filtered, washed in  $\text{CCl}_4$  and pumped dry at room temperature. The compound is soluble in  $\text{CS}_2$  and  $\text{CH}_2\text{Cl}_2$  and recrystallised from  $\text{CH}_2\text{Cl}_2$  and a deep red-brown adduct was obtained. Found: S, 24.31, N, 10.5; Cl, 43.72;  $\text{S}_4\text{N}_4 \cdot 2\text{FeCl}_3$  requires: S=25.16, N=11.01, Cl=41.87. M.P.  $80^{\circ}\text{C}$  (decomp.) It changes to a yellow product in air.

Reaction between tetrasulphur tetranitride and phenylboron dichloride

Tetrasulphur tetranitride (0.4 g) was dissolved in dry  $\text{CCl}_4$  (20 ml) and phenylboron dichloride (0.3 ml) added at room temperature. Immediately an orange-red precipitate was obtained. The solution was stirred for 6 hours and a brownish-orange precipitate was obtained. The precipitate was filtered, washed in  $\text{CCl}_4$  and pumped dry at room temperature. Found: S=35.10, N=15.75, C=19.92, Cl=21.30, H=1.33;  $\text{S}_4\text{N}_4 \cdot \text{PhBCl}_2$  requires, S=37.30, N=16.32, C=20.98, H=1.46, Cl=20.69. M.P. 99-102°C. The compound changed to a yellow product when exposed to air. The i.r. spectrum of the product exposed to air for 48 hours indicated the presence of  $\text{S}_4\text{N}_4$  and probably phenylboron dichloride hydrolysis products.

Reaction between tetrasulphur tetranitride and p-tolytin trichloride

0.7 ml (1.2 g) of p-tolytin trichloride was dissolved in dry  $\text{CCl}_4$  (30 ml) and tetrasulphur tetranitride (0.4 g) added at room temperature. No immediate colour change was observed. The solution was stirred for 60 hours. A deep red precipitate was slowly formed and filtered. The precipitate was washed in  $\text{CCl}_4$  and dried in vacuo. The infrared spectrum of the compound was identical to the infrared spectrum of  $\text{SnCl}_4 \cdot 2\text{S}_4\text{N}_4$ . Found: S=38.60, N=17.90, Cl=12.75,  $\text{SnCl}_4 \cdot 2\text{S}_4\text{N}_4$  requires; S=40.73, N=17.80, Cl=22.57. The p-Tolytin trichloride had undergone disproportion<sup>ation</sup> in the presence of  $\text{S}_4\text{N}_4$  giving  $\text{SnCl}_4 \cdot 2\text{S}_4\text{N}_4$  and tetra-p-tolytin.

Reaction between trimethyl aluminium and tetrasulphur tetranitride

The reaction was carried out in dry hexane. Tetrasulphur tetranitride (1.9 g) was suspended in 25 ml of dry  $\text{CCl}_4$  and the solution was cooled to  $-196^\circ\text{C}$ . Trimethyl aluminium (1 ml, 0.75 g) added to the above solution. The solution was slowly warmed to room temperature and stirred for 24 hours. No visible change occurred and the unreacted yellow precipitate of  $\text{S}_4\text{N}_4$  was recovered by filtration.

Reaction between phenylmercuric chloride and tetrasulphur tetranitride

Phenylmercuric chloride (1.0 g) and  $\text{S}_4\text{N}_4$  (0.58 g) were shaken together in 40 ml of dry ether for 14 hours. No reaction was observed.

Reaction between tetrasulphur tetranitride and sulphuryl chloride

Tetrasulphur tetranitride (0.49 g) was suspended in 30 ml of dry toluene at  $-196^\circ\text{C}$ . Sulphuryl chloride (1.0 ml) added under a current of dry nitrogen gas. The reaction mixture was slowly warmed to room temperature, but no obvious reaction was observed. The solution was stirred for 16 hours, the infrared spectrum of the evaporated product showed the unchanged starting material.

In another experiment the reaction was carried out in the absence of the solvent at room temperature (see page 48), and trithiazyl trichloride was obtained. Found: S = 39.4; N=17.60;

Cl= 43.40; mol.wt (cryoscopic in benzene) 244;  $S_3N_3Cl_3$  requires  
S=39.31; N=17.16; Cl=43.45; mol.wt. = 244.57.  $S_3N_3Cl_3$  probably  
gives NSCl on pumping, since the  $S_3N_3Cl_3$  in the flask turned  
slightly green under vacuum. It forms ammonium chloride and  
 $SO_2$  in moist air ( $2S_3N_3Cl_3 + 12H_2O \rightarrow 6NH_4Cl + 6SO_2$ )

Reaction between tetrasulphur tetranitride and chlorine

(a) 1.5 g of finely powdered tetrasulphur tetranitride was  
suspended in dry  $CCl_4$  (20 ml) and chlorine gas (dried over  $P_2O_5$ )  
was carefully passed through the solution at room temperature for  
about 5 minutes until all the  $S_4N_4$  was dissolved and a clear red  
solution was obtained. Excess of chlorine gas was removed by flushing  
out with dry nitrogen gas and condensing it at  $-196^\circ C$ . The red  
solution was cooled to  $-16^\circ C$  using cold refrigerator and bright red  
crystals were obtained. The precipitate was filtered and pumped dry  
at room temperature. The compound was recrystallised from dry  $CCl_4$ .  
Found: S=37.54, N=17.82, Cl=43.30;  $S_3N_3Cl_3$  requires, S=39.36, N=17.16,  
Cl=43.45. M.P.  $89-91^\circ C$ . The compound turns white in moist air (cf.  
 $S_4N_4/SO_2Cl_2$  product but contrast product obtained with a fast flow  
of chlorine (see (b) below). The filtrate was evaporated to dryness  
and more  $S_3N_3Cl_3$  was obtained.

(b) Tetrasulphur tetranitride (1.5 g) was suspended in  $CCl_4$  (20 ml)  
at room temperature and dry chlorine gas was passed at a very fast

rate through the solution. First after 2-3 minutes a red solution was obtained, the bubbling of chlorine gas was continued and a yellow precipitate came out of the solution after 10 minutes. The flow of chlorine gas was stopped after  $4\frac{1}{2}$  hours. The yellow precipitate was filtered and vacuum dried at room temperature. The compound was recrystallised from dry  $\text{CCl}_4$ . Found: (before recrystallisation), S=36.80, N=21.90, Cl=27.60 (2nd. 29.46); (recrystallised compound), S=45.70, N=23.60, Cl=26.90. M.P.  $58-64^\circ\text{C}$  (decomp.) (repeat preparation), S=43.79, N=19.59, Cl=36.90.  $\text{S}_6\text{N}_6\text{Cl}_3$  requires: S=50.19, N=21.90, Cl=27.84;  $\text{S}_6\text{N}_6\text{Cl}_4$  requires: S=45.93, N=20.10, Cl=33.91. The compound changed to a yellow-black compound in moist air.

I.R. spectrum of the black yellow compound exposed to air for 48 hours exhibited peaks mainly due to  $\text{S}_4\text{N}_4$  and -OH. The infrared spectrum of  $\text{S}_6\text{N}_6\text{Cl}_4$  showed the following peaks: 1011 vs, 948 ms(sh), 899 (sh), 780 ms, 699 s(sh), 686 vs, 670 vw(sh), 662 vs, 627 vw(sh), 577 s, 546 vs, 517 w(sh), 504 ms, (452 s).

(c) Tetrasulphur tetranitride was dissolved in dry  $\text{CCl}_4$  (50 ml) and dry chlorine gas was bubbled through the solution at a very slow rate at room temperature for about 3 hours and a red solution was obtained. The solution was evaporated to a small volume (20 ml) by pumping and cooled to  $-16^\circ\text{C}$ . A bright yellow crystalline compound was obtained. Found: Cl=42.90,  $\text{S}_3\text{N}_3\text{Cl}_3$  requires; Cl=43.45. M.P.  $82-85^\circ\text{C}$ .

Reaction between tetrasulphur tetranitride and bromine

The reaction was carried out in an atmosphere of dry nitrogen gas in a 50 ml two-necked round-bottomed flask. Bromine (20 ml) dried over phosphorus pentoxide was condensed on tetrasulphur tetranitride (1.0 g) at  $-196^{\circ}\text{C}$  and the reaction flask was warmed to room temperature. Carbon disulphide (20 ml) was then added to the above solution and the liquid was stirred for 14 hours at room temperature. A deep reddish-brown precipitate was slowly formed. The excess of solvent and bromine was removed by pumping at room temperature and a deep red-brown precipitate was obtained. Found: S=26.40, N=11.50, Br=66.10; (NSBr)<sub>n</sub> requires: S=25.41, N=11.19, Br=63.45. Mol.Wt. The compound was insoluble in CS<sub>2</sub>. It is moisture sensitive. M.P.  $121^{\circ}\text{C}$ . Infrared absorptions occur at: 1169 vs, 1010 vs, 675 vs, 609 w, 574 vw (sh), 562 s, 537 w, 492 vs.

Reaction between S<sub>3</sub>N<sub>3</sub>Cl<sub>3</sub> and bromine

Dry bromine 15 ml was condensed in 1.0 g of S<sub>3</sub>N<sub>3</sub>Cl<sub>3</sub> in a two-necked round-bottomed flask and the solution was stirred for 6 hours at room temperature. Excess of bromine was removed by pumping and a yellow compound was obtained. The compound was found to contain chlorine and bromine. The reaction was not investigated further. Infrared absorptions occur at: 1100 s, 1018 s, 959vw, 763 vw, 724 w, 621 vw, 534 vs, 515 vvw(sh).

### Reactions of trithiazyl trichloride

In all the reactions studied,  $S_3N_3Cl_3$  prepared from  $S_4N_4$  and  $SO_2Cl_2$  was used as the starting material.

### Reaction between trithiazyl trichloride and chlorine

$S_3N_3Cl_3$  (0.7 g) was dissolved in  $CCl_4$  (25 ml) at room temperature and dry chlorine gas passed for 2 hours through the solution. The solution was cooled to  $-16^\circ C$  and a yellow-white precipitate was obtained, filtered and dried in vacuo. The infrared spectrum of the compound showed that  $S_3N_3Cl_3$  had undergone no change.

### Attempted preparation of $S_3N_3Cl$

$S_3N_3Cl_3$  (0.89 g) was dissolved in 20 ml of dry methylene dichloride at room temperature and tetrasulphur tetranitride (1.0 g) added to the solution. (No immediate reaction was observed). The solution was stirred for 12 hours and cooled to  $-16^\circ C$ . A yellow precipitate was obtained. The precipitate was filtered and dried in vacuo. I.R. spectrum showed that the compound was  $S_4N_4$ .  
dryness and  
The filtrate was evaporated to/the infrared spectrum of the yellow product indicating that it was a mixture of  $S_4N_4$  and trithiazyl trichloride.

### Attempted oxidation of trithiazyl trichloride

Attempts were made to prepare sulphanuric chloride ( $S_3N_3O_3Cl_3$ ) by the oxidation of trithiazyl trichloride using selenium dioxide, iodine pentoxide and ozone as the oxidising agents.

(a) Attempted oxidation of  $S_3N_3Cl_3$  using  $SeO_2$

Trithiazyl trichloride (1.0 g) was dissolved in dry  $CCl_4$  (30 ml) and selenium dioxide (0.79 g) added at room temperature. The solution was stirred for 1-2 hours. Since there was no obvious reaction, the solution was refluxed for 6 hours. A red solution and a pinkish-white precipitate was obtained. The solution was filtered and evaporated to dryness. A crude red product was obtained. I.R. spectra of the pinkish-white precipitate ( $SeO_2$ ) and the crude red product indicated that no sulphanic chloride was formed. The reaction was not studied further.

(b) Attempted oxidation of  $S_3N_3Cl_3$  using  $I_2O_5$

$S_3N_3Cl_3$  (0.5 g) was dissolved in 25 ml of dry  $CCl_4$  and iodine pentoxide (0.5 g) added at room temperature. The solution was stirred for 1 hour but no reaction was seen to take place. The solution was refluxed for 24 hours and a pink-white precipitate and a brown-coloured solution were obtained. The solution was filtered and evaporated to dryness and a brown precipitate was obtained. The i.r. spectrum of the pink-white precipitate showed that the compound was a mixture of  $I_2O_5$  and silicone grease, whereas the i.r. spectrum of the brown precipitate indicated that no sulphanic chloride was formed. The product was not investigated further.

(c) Attempted oxidation of  $S_3N_3Cl_3$  using Ozone

(i) Trithiazyl trichloride (2.0 g) was dissolved in dry  $CCl_4$  (50 ml) and ozone-oxygen mixture (dried over  $P_2O_5$ ) was bubbled through the solution at very slow rate at  $-10^\circ C$ . The flow of ozone was discontinued after 48 hours. The solution was evaporated to dryness and a white-yellow precipitate was obtained. I.R. spectrum of the compound showed that  $S_3N_3Cl_3$  had undergone no change.

(ii) Trithiazyl trichloride (2.0 g) was dissolved in 50 ml of dry  $CCl_4$  and ozone-oxygen mixture was passed through the solution at  $60^\circ C$  at slow rate for 24 hours. The i.r. spectrum of product showed that  $S_3N_3Cl_3$  had undergone no change.

(iii) The oxidation was also carried out in the presence of  $MoO_3$  as a catalyst as above, but no  $S_3N_3O_3Cl_3$  formation was noticed.

Reaction between trithiazyl trichloride and pyridine

Trithiazyl trichloride (0.90 g) was taken in a 100 ml two-necked, round-bottomed flask and pyridine (0.9 ml) added at  $0^\circ C$ . The flask was slowly warmed to room temperature. The colour of the solution turned green after about 10 minutes, then changed to a pale yellow and finally a red oily thick pasty mass was obtained. Dry pentane (25 ml) was added to the oily mass and the solution was stirred for 12-14 hours at room temperature. A

yellow-brown precipitate was obtained, filtered, washed in pentane and dried in vacuo. Found: C=31.05, H=3.66, N=15.00, S=17.20, Cl=29.0,  $S_3N_3Cl_3 \cdot 2py$  requires; C=29.81, H=2.46, N=17.39, S=23.85, Cl=26.46, ( $S_3N_3Cl_3 \cdot 3py$  requires; C=37.38, H=3.12, N=17.45, S=19.94, Cl=22.12. Reaction probably needs to be repeated and stopped at pale yellow stage. Infrared spectrum showed peaks at: 1259 vw, 1226 vw, 1180 w, 1122 vvw (sh), 1104 w, 1068 ms, 1047 w(sh), 1022 ms, 1000 w, 961 vvw, (926 w) 841 vs, 779 vs, 758 vs, 743 vvw(sh), 722 vw(sh), 701 vvw, 679 vs, 666 vvw (sh), 660 vw(sh), 621 vs, 608 vw, 600 w, 560 vs, 542 s, 491 w, 454 vw.

Reaction between diphenyl mercury and trithiazyl trichloride

Trithiazyl trichloride (1.2 g) was dissolved in about 25 ml of dry benzene and diphenyl mercury (1.7 g) added at room temperature. Immediately a yellow-green precipitate came out of the solution, the solution turned green after about 5 minutes and after 3 hours a black precipitate was obtained. The solution was stirred for 12 hours. The black precipitate was filtered and the filtrate evaporated to dryness, no ppt was obtained. The black precipitate was washed in benzene and pumped dry at room temperature. Found:  $\overset{5}{\wedge}$  16.50, N=8.06, Cl=18.60, C=23.61, H=1.57;  $S_3N_3Cl_3 \cdot (Ph)_2Hg$  requires; S=16.02, N=7.01, Cl=17.77, Cl=24.03, H=1.67. M.P. 170°C. It is insoluble

in methylene dichloride. Infrared absorptions occur at:  
2198 ms, 1156 vw, 1064 vw(sh), 1047 vs, 1020 vvw, 990 vs,  
916 vvw, 855 ms, 797 vvw, 646 vs, 722 vs, 685 vs, 660 ms(sh),  
609 w, 571 ms, 531 vs, 508 vs, 465 w, 436 w, 431 vs, 408 ms(sh),  
394 vs, 347 vs, 330 vw, (309 w, 279 s), (227 w, 211 w)  $\text{cm}^{-1}$ .

Reaction between trithiazyl trichloride and antimony trichloride in  $\text{SOCl}_2$

$\text{SbCl}_3$  (0.7 g) was dissolved in thionyl chloride (20 ml) and trithiazyl trichloride (2.0 g) added at room temperature. Immediately a dark-brown solution was obtained. The solution was stirred for 12 hours and a dark-brown precipitate was obtained. The precipitate was filtered, the filtrate was evaporated to dryness and a crude dark oil product was obtained. The dark-brown precipitate was washed in  $\text{SOCl}_2$  and a yellow-pale green precipitate was obtained. Found: S=23.10, N=6.76, Cl=48.70;  $\text{S}_4\text{N}_3\text{SbCl}_9$  requires: S=22.25, N=7.3, Cl=49.30. Infrared absorptions occur at: 217 ms, 126 vw, 1193 w, 1149 vw, 1057 s, 1010 vs, 803 ms, 735 vvw(sh), 719 ms, 666 vvw, 626 ms, (450 ms) 418 w.  $\text{cm}^{-1}$ .

Reaction between trithiazyl trichloride and titanium tetrachloride in thionyl chloride.

Trithiazyl trichloride (0.5 g) was dissolved in thionyl chloride (10 ml) and titanium tetrachloride (1 ml) added at room temperature. Immediately<sup>a</sup>/deep red solution was obtained. The solution was stirred for 4 hours and a deep red precipitate was

obtained. The precipitate was filtered, washed in  $\text{SOCl}_2$  and pumped dry at room temperature. Found: S=16.0, N=9.60, Cl=52.00,  $\text{Ti}_2\text{S}_2\text{N}_3\text{Cl}_6$  requires, S=15.43, N=10.31, Cl=51.36. M.P.  $70^\circ\text{C}$  (decomp.) Infrared spectrum showed the following peaks: 1324 w, 1012 vs, 966 vs, 840 vs, 732 vs, 697 s, 662 s, 608 vs, (5000 vs)  $\text{cm}^{-1}$ .

Reaction between trithiazyl trichloride and antimony pentachloride in thionyl chloride

$\text{S}_3\text{N}_3\text{Cl}_3$  (0.2 g) was dissolved in 10 ml of  $\text{SOCl}_2$  and  $\text{SbCl}_5$  (1 ml) added at room temperature. Immediately<sup>a</sup>/bright orange solution was obtained. The solution was stirred for 2-3 hours and excess of the liquid was removed by pumping at room temperature. The infrared spectrum of the compound was comparable to the infrared spectrum of  $\text{Ti}_2\text{S}_2\text{N}_3\text{Cl}_6$ . There was insufficient compound for further investigations. I.R. absorptions occur at: 1156 vw, 1117 ms, 1058 vs, 1017 vs, 866 ms, 722 ms, 687 s, 666 w, 619 w, 599 s, 555 w, 513 vs (454 s), 431 ms  $\text{cm}^{-1}$ .

Reaction between trithiazyl trichloride and epoxides

(i) Epichlorohydrin

Trithiazyl trichloride (2.0 g) was taken in a Schlenk and epichlorohydrin (15-16 ml) added at  $-196^\circ\text{C}$  under a current of dry nitrogen gas. Vigorous reaction was observed and the reaction mixture was slowly warmed to room temperature. After 15-20 minutes a green solution was obtained which changed to a pale-yellow liquid after 1-2 hours. Finally a red liquid was obtained after 12-14 hours,

and there was no further colour change. Excess of epichlorohydrin was removed by pumping at room temperature and a red oil was obtained. The red oil changed to sticky mass after 2-3 days, dry hexane (10 ml) was added to it, and the solution was stirred for 12-14 hours. A reddish-brown solid was formed, the solid was washed in ethanol and fine powdery white compound was obtained. Found: S=18.68, N=8.3, C=20.70, H=2.78, Cl=40.60,  $S_3N_3(O-CH_2-CH-Cl.CH_2.Cl)_3$  requires: S,18.65; N=8.26; C,20.3; H,2.87; Cl,40.90. Mol.wt. 521. M.P. 86-89°C. It is air stable. It is soluble in acetone, insoluble in EtOH, MeOH.

(ii) Epibromohydrin

Trithiazyl trichloride (0.90 g) was taken in a Schlenk and epibromohydrin (6 ml) added at room temperature. Immediately the solution turned green which slowly changed to a pale-yellow liquid after about an hour. The solution was stirred for 20-24 hours at room temperature and a red solution was obtained. Excess of epibromohydrin was removed by pumping, and a red oil was obtained. Dry pentane (10 ml) added to the above oil and the solution was stirred for an hour, pentane was removed by suction and a yellow-white precipitate was obtained. The precipitate was washed in ethanol and a fine powdery solid was formed and dried in vacuo at room temperature. Found: S=13.55, N=7.40, C=16.30, H=2.16, Br=38.30, Cl=14.96;  $S_3N_3(O-CH_2-CH Cl.CH_2Br)_3$  requires, S=14.65, N=6.41, C=16.48, H=2.23, Cl=16.25, Br=36.58. M.P.92-94°C, Mol.wt.in benzene 644; theory 655.34. It is air stable.

### Ethylene oxide

Trithiazyl trichloride (1.0 g) was placed in a Schlenk and ethylene oxide was condensed on it at  $-196^{\circ}\text{C}$ . The reaction mixture was slowly warmed to room temperature. A green solution was obtained immediately which changed to a pale yellow liquid after 2 hours. The liquid was stirred and finally a red solution was obtained after 24 hours. The excess of ethylene oxide was removed by pumping at room temperature and a red oil was obtained. Dry hexane (10 ml) was added to the oil and the solution was stirred for 12 hours. Hexane was removed under suction and a red oil was left behind. Found: S=24.00, N=11.30, Cl=27.14, C=19.96, H=3.06,  $(\text{NSCl.O.CH}_2\text{CH}_2)_3$  requires: S=25.48, N=11.15, Cl=28.27, C=19.2, H=3.18. Mol. wt. 376 in benzene. The red oil became dark red at  $50-60^{\circ}\text{C}$ , probably due to decomposition. It decomposed to a yellow product in air.

### Butylene oxide

Trithiazyl trichloride (1.8 g) was placed in a Schlenk and about 10 ml of butylene oxide added at room temperature. Immediately the solution turned green and there was vigorous reaction after 5 minutes. The solution was stirred for 14 hours and a red liquid was obtained. The excess butylene oxide was removed by pumping and a red oily product was obtained. Found: S=20.2, N,9.55, Cl=22.70, C=31.33, H=5.11;  $\text{S}_3\text{N}_3(\text{O-CH}_2\text{-Cl-CH}_2\text{-CH}_3)_3$  requires, S,20.84, N,9.12, Cl=23.11, C=31.25 H=5.20. It decomposed to a yellow product in air.

Reaction between trithiazyl trichloride and phenyl acetylene

Trithiazyl trichloride (0.5 g) was cooled to  $-196^{\circ}\text{C}$  and phenyl acetylene was condensed on it. The reaction flask was warmed to room temperature. There was a vigorous reaction initially and green, pale-yellow to red colour change was observed. A red oily sticky mass was obtained. The reaction was not investigated further.

Reaction between trithiazyl trichloride and diphenyl acetylene

Trithiazyl trichloride (1.45 g) was dissolved in dry  $\text{CCl}_4$  (45 ml) and diphenyl acetylene (1.2 g) added at room temperature. The solution was stirred for 6 hours at room temperature, but no obvious reaction was observed. The solution was stirred for 18 hours at  $42^{\circ}\text{C}$ . The liquid was changed to a green colour and a yellow precipitate came out of the solution. The precipitate was filtered, evaporated to dryness and a mixture of a red oil and a yellow product was obtained. The precipitate was washed in methylene chloride and pumped dry at room temperature. The infrared spectrum of the compound was identical with the i.r. of  $\text{S}_4\text{N}_3\text{Cl}$ . Found: Cl=17.38,  $\text{S}_4\text{N}_3\text{Cl}$  requires; Cl=17.24. The mixture of the red oil and the yellow compound was ignored.

Reaction between trithiazyl trichloride and carbon monoxide

Trithiazyl trichloride (2.0 g) was dissolved in dry  $\text{CCl}_4$  (50 ml) at room temperature. Carbon monoxide was bubbled through the solution at a very slow rate at room temperature, for 48 hours. The solution was evaporated to dryness and a pale-yellow white precipitate was obtained. The i.r. spectrum indicated that  $\text{S}_3\text{N}_3\text{Cl}_3$  had undergone no change.

In another experiment the reaction was carried out at higher temperature. Carbon monoxide was bubbled through a solution of trithiazyl trichloride (2.0 g) in 50 ml of dry  $\text{CCl}_4$  at  $40^\circ\text{C}$  for 60 hours. A yellow precipitate<sup>(1)</sup> came out of the solution and the colour of the solution was pale red. The precipitate<sup>(1)</sup> was filtered, the filtrate was evaporated to dryness and a yellow compound<sup>(2)</sup> was obtained. The i.r. spectrum of compound no.1 was similar to  $\text{S}_4\text{N}_3\text{Cl}$  while the i.r. spectrum of the compound no.2 was identical with the product obtained by passing chlorine vigorously through a solution of  $\text{S}_3\text{N}_3\text{Cl}_3$  in  $\text{CCl}_4$ . (See page 72)

Reaction between trithiazyl trichloride and nitriles

Acetonitrile

$\text{S}_3\text{N}_3\text{Cl}_3$  (2.0 g) was placed in a Schlenk and 15 ml of dry acetonitrile added at room temperature. The solution was stirred for 12-14 hours at room temperature. The colour of the solution was changed to green, then to pale yellow and finally to red.

Excess of acetonitrile was removed by pumping at room temperature. A crude black mass was obtained. The reaction was not investigated further.

#### Propionitrile

Trithiazyl trichloride (2.5 g) was taken in a Schlenk and dry propionitrile (12-15 ml) added at room temperature. The solution was turned green after 5-10 minutes, which slowly changed to pale yellow. The solution was stirred for 12-14 hours and a red liquid was obtained. The liquid was pumped and a red sticky oil was obtained. The reaction was not studied further.

#### Isobutyronitrile

Dry isobutyronitrile (15 ml) was added to trithiazyl trichloride (1.8 g) in a Schlenk. There was no immediate reaction. The colour of the solution was changed to green, then to yellow and at the end, after 12-14 hours a red oil was obtained. The solution was pumped and a black crude mass was obtained. The reaction was not investigated further.

#### Tertiarybutyl cyanide

Dry tertiarybutyl cyanide (10 ml) was added to  $S_3N_3Cl_3$  (1.8 g) at room temperature in a Schlenk. The solution was stirred for 24 hours and no obvious reaction was seen to take place. The reaction temperature was raised to  $58^{\circ}C$  and the solution was stirred for 10 hours. A very small amount of yellow precipitate (No.1) was formed and the colour of the solution was red.

The precipitate was filtered, filtrate was evaporated to dryness and golden yellow (No.2) precipitate was obtained (M.P. 240°C decomp.) The infrared spectrum of (No.1) precipitate was recorded, but there was insufficient sample of this compound for further investigations. The compound (No.2) was analysed twice. Found: 1st. analysis in this department. C = 28.90, H=3.79, Cl=33.10, S=31.85, N=11.37. 2nd. analysis (Weiler and Strauss). C=29.39, H=4.34, Cl=16.25, S=26.55, N=9.37.  $S_2N_2Cl_2(CH_3)_3Cl$  requires, C=30.56, H=4.58, Cl=18.00, S=32.59, 14.26;  $S_2N_2C_2(CH_3)_3Cl_2$  requires, C=25.86, H=3.88, Cl=30.60, S=27.58, N=12.04;  $S_2N_3C_2(CH_3)_3Cl_2$  requires, C=24.39, H=3.66, Cl=28.86, S=26.02, N=17.07.

The infrared spectrum of compound (No.1) showed the following peaks:

1227w, 1163 ms, 1000 s, 889 s, 858 s, 803 vw, (7335 s, 722 s), 680 s, 607 vw, 565 s, 554 s, 525 vw, 466 vs, 451 vw (sh).

The infrared spectrum of compound (No.2) showed peaks at: 1667 w, 1399 vw (sh), 1368 vs (sh), 1274 w, 1222 s, 1087 w, 1019 w, 980 vw, 943 w, 909 w, 885 vs, 855 s, 803 ms, 733 s, 722 vvw (sh), 590 vvw, 551 vs, 522 vvw, 510 ms, 476 ms, 407 ms, 379 vw, 341 w, 308 w, 288 vw, 253 w, 226 w  $cm^{-1}$ .

#### Trichloroacetonitrile

$S_3N_3Cl_3$  (2.45 g) was placed in a Schlenk and dry trichloroacetonitrile (15 ml) added at room temperature. The reaction mixture was stirred for 24 hours at room temperature, and a yellow solution was

obtained. The liquid was evaporated to dryness and a pale yellow precipitate was obtained. The infrared spectrum of the precipitate indicated that  $S_3N_3Cl_3$  had undergone no change.

In another experiment, trichloroacetonitrile (10 ml) was added to  $S_3N_3Cl_3$  (2.5 g) at room temperature and the solution was stirred for 2-3 days at  $60^\circ C$ . The solution was changed to green after about 1 hour, then to pale yellow after about 2 hours, and finally a red solution and a yellow precipitate was obtained after 14 hours. The precipitate (No.1) was filtered, washed in trichloroacetonitrile (5 ml) and dried in vacuo. The filtrate was evaporated to dryness and a pale yellow precipitate (No.2) was obtained. The compound (No.1) was ignored because there was insufficient compound for further investigations. The compound (No.2) was analysed twice, in this department. Found: 1st analysis, C=9.59, Cl=55.89, S=24.75, N=11.60; 2nd. analysis, C=9.99, Cl=52.80, S=21.98, N=10.51.  $S_2N_2C_2Cl_4$  requires; C=9.53, Cl=55.04, S=24.80, N=10.85;  $S_2N_2C_2Cl_5$  requires, C=8.19, Cl=60.34, S=21.81, N=9.54;  $S_2N_3C_2Cl_5$  requires, C=7.81, Cl=57.72, S=20.81, N=13.66.

The compound changed to a white product in moist air. M.P. decomp. above  $110^\circ C$ . Infrared absorptions occur at: 1299 vw, 1266 vw, 1047 vs, 930 ms, 909 vvw (sh), 855 vs, (813 w (sh), 794 vs), 760 s, 722 vvw, 676 vs, 543 vs, 535 ms (sh), 517 w, 495 vw (sh), 483 s, 471 w(sh), 406 ms, 376 vw, 347 ms, 246 s, 225 vw  $cm^{-1}$ .

Benzonitrile

Trithiazyl trichloride (3.0 g) was placed in a Schlenk and dry benzonitrile/<sup>was</sup>(20 ml) added at room temperature. The solution was stirred, a green clear solution was obtained after 10-15 minutes, which slowly changed to a pale yellow liquid after 2 hours. The solution was concentrated to 10 ml and cooled to 0°C. A pale yellow precipitate was obtained. The infrared spectrum of the precipitate indicated that  $S_3N_3Cl_3$  had undergone no change.

In another experiment the reaction was carried out in a Schlenk clamped in a slightly slanting position. Benzonitrile (25 ml) added to trithiazyl trichloride (3.0 g) at room temperature. The solution was stirred at 60°C. Immediately a green solution was formed, the solution turned yellow after 15 minutes. Stirring was continued and the solution was red after 4 hours. After 3-4 days a bright yellow precipitate (No.1) was settled down the red liquid and bright yellow-orange needles (No.2) collected near the frit of the Schlenk. The red solution was cooled to -196°C and the yellow-orange compound (No.2) pumped dry at room temperature. After removing the compound (No.2), the red solution was warmed to room temperature and the yellow precipitate was filtered, the red filtrate was chilled to 0°C and fine yellow needles came out of the solution. The

solution was transferred to a 50 ml two-necked round bottomed flask and precipitate (No.3) was filtered, the filtrate was vacuum evaporated to dryness and a dark yellow compound (No.4) was obtained. The compound (No.4) was recrystallised from dry  $\text{CCl}_4$  or  $\text{CH}_2\text{Cl}_2$ . The compound (No.1) was dried under vacuo. Some of the compound (No.1) (about 0.5 g) was dissolved in about 20 ml of hot benzonitrile ( $60^\circ\text{C}$ ) and a red solution was obtained, filtered, chilled to  $0^\circ\text{C}$  and fine yellow needles (No.1 and same as No.3) were obtained. The infrared spectra of the compounds (No.1,2 and No.3) were identical and analyses showed that the two compounds are the same.

Compound (No.1)

Found: C=41.72, H=2.55, Cl=14.92, S=26.5, N=14.22;

$\text{S}_2\text{N}_2\text{C}_7\text{H}_5\text{Cl}$  requires: C=38.80, H=2.31, Cl=16.40, S=29.56, N=12.93.

Compound (No.2)

Found: C=32.10, H=1.58, Cl=20.48, S=30.56, N=14.68.

$\text{S}_2\text{N}_2\text{Cl}_2\text{C}_7\text{H}_5$  requires: C=31.6, H=1.89, Cl=26.64, S=24.09, N=15.79.

Compound (No.3)

Found: C=31.2, H=1.14, Cl=22.83, S=29.73, N=16.60.

Compound (No.4)

Found: C=23.42, H=1.12, Cl=28.10, S=24.15, N=16.33.

$\text{S}_3\text{N}_3\text{Cl}_3$ .PhCN requires, C=24.18, H=1.45, Cl=30.59, S=27.67,  
N=16.11.

Infrared spectra showed the following peaks:

Compound (No.1) 1660 w, 1290 vw(sh), 1212 vw, 1170 vw,  
1149 s, 1070 w, 1029 ms, 1000 vw, 935 vvw, 921 s, 892 vs, 834 vs,  
794 s, 781 s, 767 s, 707 w(sh), 699 vs, 662 vw(sh), 548 vs, 515  
ms.  $\text{cm}^{-1}$ .

Compound (No.2 and 3) 1600 w, 1350 vw (sh), 1299 vvw,  
1266 vvw, 1212 vvw, 1176 vvw, 1155 s, 1074 w, 1031 ms, 1002 vw,  
943 vvw, 926 s, 897 vs, 844 vs, 787 s, 699 vs, 664 vw, 549 vs.  $\text{cm}^{-1}$ .

Compound (No.4) 1590 ms, 1290 w (sh), 1179 s, 1093 w,  
1065 w, 1022 ms, 998 vvw (sh), 910 vs, 870 vvw (sh), 842 vvw (sh),  
791 vs, 662 ms, 615 vvw, 525 s, 493 vs, 473 s.  $\text{cm}^{-1}$ .

## DISCUSSION

Tetrasulphur tetranitride adducts with Lewis acids

Tetrasulphur tetranitride reacts with many Lewis acids (e.g. metal halides and  $\text{SO}_3$ ) to give compounds of a variety of empirical compositions. In inert organic solvents, adducts of 2:1, 1:1, 1:2, 1:4 ( $\text{S}_4\text{N}_4$  : Lewis acid) stoichiometry have been prepared, in which the nitrogen of  $\text{S}_4\text{N}_4$  is co-ordinated to the Lewis acid. In these adducts, the  $\text{S}_4\text{N}_4$  ring undergoes a conformational change as a result of donation of electrons from nitrogen and consequent weakening of the sulphur-sulphur bond.

The aims of the research were, to further explore the reactions of  $\text{S}_4\text{N}_4$  as a Lewis base, to study the effects of coordination upon the reactivity of the  $\text{S}_4\text{N}_4$  ring and to gain more information about the structures of the products. It was also hoped to correlate the various properties previously noted of  $\text{S}_4\text{N}_4$ , and the structures of the adducts.

We found that tin tetrachloride and tetrabromide gave adducts in which  $\text{S}_4\text{N}_4$  to metal halide ratio is 2:1; on the other hand, tin tetraiodide, silicon tetrachloride, germanium tetrachloride and stannous chloride, gave no adducts under the conditions studied. No suitable solvent was found (because of insolubility of  $\text{SnF}_4$  in non-coordinating solvents) to study the reaction between  $\text{S}_4\text{N}_4$  and tin tetrafluoride.

Titanium tetrabromide and tetraiodide,  $ZrCl_4$ ,  $HfCl_4$ ,  $SeCl_4$ ,  $TeCl_4$ ,  $TeF_4$ ,  $NbCl_5$ ,  $NbF_5$ ,  $TaF_5$  and  $WOCl_4$  (?) gave adducts of 1:1 composition, whereas  $AlCl_3$ ,  $AlBr_3$ ,  $GaCl_3$ ,  $InCl_3$ ,  $TlCl_3$  (?) and  $FeCl_3$  gave products of 1:2 stoichiometry.

In the reaction of tungsten hexabromide with  $S_4N_4$ , the bromide was first reduced to  $WBr_4$  and gave the adduct,  $S_4N_4$ .  $WBr_4$  (analogous to the reaction of  $S_4N_4$  and  $WCl_6$  to give  $S_4N_4 \cdot WCl_4$ ).

Phenylboron dichloride reacted with  $S_4N_4$  to yield the adduct  $S_4N_4 \cdot PhBCl_2$ , whereas p-tolytin trichloride gave  $SnCl_4 \cdot 2S_4N_4$  due to the disproportion of the p-tolytin trichloride to  $SnCl_4$  and tetra-p-tolytin. Further details are given in Table 1.

Tetrasulphur tetranitride adducts were generally prepared by mixing the solutions of  $S_4N_4$  and Lewis acids in solvents of low polarity, usually under an atmosphere of dry nitrogen. The reaction mixtures were stirred and the coloured products were filtered and dried in vacuo. The reaction time was found to depend on the solubility of the Lewis acid. In those cases, where the Lewis acid was soluble in the solvent, the reaction time was from 1-10 hours (until there was no further change in the colour of the product), whereas, if the Lewis acid was only slightly soluble in the solvent, the procedure was to add  $S_4N_4$  to the suspension of the Lewis acid in the solvent and stir the solution for 12-24 hours or longer.

TABLE 1  
TETRASULPHUR TETRANITIDE ADDUCTS

<u>Metal halide</u>	<u>Stoichiometry</u> ( <u>S<sub>4</sub>N<sub>4</sub>:m-halide</u> )	<u>Colour</u>	<u>M.P.</u> <u>O°C.</u>	<u>Solubility</u>	<u>Remarks</u>
SnBr <sub>4</sub>	2:1	deep brown	198-200 (decomp)	insoluble in CCl <sub>4</sub> , CS <sub>2</sub> CH <sub>2</sub> Cl <sub>2</sub>	slow decomp. in moist air
SnCl <sub>4</sub>	2:1	deep red	200-202 (decomp.)	"	"
TiBr <sub>4</sub>	1:1	deep brown	138 (decomp.)	"	rapid decomp. in moist air
TiCl <sub>4</sub>	1:1	orange yellow	135 (decomp.)	"	"
TiF <sub>4</sub>	1:4	orange	decomp. above 120	"	"
TiI <sub>4</sub>	1:1	black	above 360 (decomp. above 100)	"	"
ZrCl <sub>4</sub>	1:1	red orange	260 (decomp.)	"	"
HfCl <sub>4</sub>	1:1	deep red	decomp. above 140	"	"
SbCl <sub>5</sub>	1:1	deep red	160-162	"	slow decomp. in moist air

TABLE 1 (contd.....)

<u>Metal halide</u>	<u>Stoichiometry</u> ( $S_{4N}^N$ :m-halide)	<u>Colour</u>	<u>M.P.</u> <u>°C.</u>	<u>Solubility</u>	<u>Remarks</u>
$SbF_5$	1:4	green	145 (decomp.)	"	very rapid decomp.in moist air
$NbCl_5$	1:1	red orange	106	soluble in $CH_2Cl_2$	rapid decomp. in moist air
$NbF_5$	1:1	deep red orange	decomp. above 60	"	"
$TaCl_5$	1:1	deep red	132 (decomp)	"	"
$TaF_5$	1:1	bright red	-	"	"
$BBr_3$	1:1	orange brown	-	-	-
$BCl_3$	1:1	red orange	137-138	soluble in $CH_2Cl_2$	slow decomp. in moist air
$BF_3$	1:1	dark burgundy	145-147 (decomp.)	"	rapid decomp. i moist air
$PhBCl_2$	1:1	brown orange	99-101	-	"
$AlCl_3$	1:2	deep red	89(decomp.)	soluble in $CS_2, CH_2Cl_2$	"
$AlBr_3$	1:2	orange brown	144	slightly soluble in $CS_2$	"
$GaCl_3$	1:2	deep red	100(decomp.)	soluble in $CS_2, CH_2Cl_2$	"
$FeCl_3$	1:2	deep red-brown	80(decomp.)	"	"

TABLE 1 (contd.....)

<u>Metal halide</u>	<u>Stoichiometry</u> ( $S_4N_4:m\text{-halide}$ )	<u>Colour</u>	<u>M.P.</u> <u>°C.</u>	<u>Solubility</u>	<u>Remarks</u>
$InCl_3$	1:2	deep red brown	decomp. above 100°C	slightly soluble in $CH_2Cl_2$	rapid decomp. in moist air
$SeCl_4$	1:1	yellow	127-129	insoluble in $CH_2Cl_2, CS_2$	changed to a re <sup>red</sup> comp. in moist air (rapid)
$TeCl_4$	1:1	deep red	140	"	rapid decomp. in moist air
$TeF_4$	1:1	brown orange	92	soluble in $CH_3CN$	-
$WBr_6$	( $S_4N_4 : WBr_4$ )	dark brown	251	-	rapid decomp. in moist air.

In some cases, choice of a suitable solvent was found to be the important factor e.g. it was possible to prepare the  $S_4N_4$  adduct of aluminium tribromide using the solvents bromoform or carbon disulphide, but the reaction of  $S_4N_4$  and  $AlBr_3$  in  $CCl_4$  or toluene gave an oily sticky product. Because of thermal instability of many tetrasulphur tetranitride adducts (e.g.  $S_4N_4 \cdot BF_3$  decomposes above  $90^\circ C$ <sup>54</sup>) most of the reactions were studied between  $0^\circ - 20^\circ C$ .

Many adducts were stable under dry nitrogen atmosphere for several days but decomposed in moist air usually giving  $S_4N_4$  and the hydrolysis product of the Lewis acid.

// The electronegativity difference between sulphur (2.44)<sup>138</sup> and nitrogen (3.07)<sup>138</sup> in tetrasulphur tetranitride would cause partial negative charge on nitrogen atoms and partial positive charge on sulphur atoms. Consequently the compound may act as either a Lewis base through the nitrogen atoms or as a Lewis acid through the sulphur atoms. Since we have only studied the reactions of  $S_4N_4$  with Lewis acids, the Lewis base behaviour of  $S_4N_4$  is considered below.

Recently<sup>134, 135, 136</sup> a rule concerning the stability of acid-base complexes has been suggested "The Principle of Hard and Soft Acids and Bases" or HSAB principle, which may be applied to understand the donor properties of  $S_4N_4$ .

According to this rule, bases in which the donor atom is, N, O, or F (i.e. of high electronegativity and small size) are classified as 'hard' bases, e.g.  $\text{NH}_3, \text{H}_2\text{O}, \text{OH}^-, \text{F}^-$ ; and bases in which the donor atom is P, S, I, Br, Cl or C are called 'soft' bases, e.g.  $\text{R}_2\text{S}, \text{R}_3\text{P}, \text{CN}^-$ ; whereas the borderline category takes into account such factors as, the presence of unsaturation in some nitrogen donors, which should loosen up the valency electrons, e.g.  $\text{C}_6\text{H}_5\text{NH}_2, \text{C}_5\text{H}_5\text{N}$ . From the above classification of hard and soft bases it can be seen that  $\text{S}_4\text{N}_4$  (containing unsaturated nitrogen) may fall in the borderline category (i.e. intermediate between a hard and soft base).

In exactly the same way it is possible to classify hard (Class A) and soft (Class B) Lewis acids: the Class A Lewis acids, in which acceptor atoms are small in size of high positive charge and do not contain unsaturated pairs of electrons in their valency shell (e.g.  $\text{H}^+, \text{Li}^+, \text{BF}_3$ ); the Class B Lewis acids generally have acceptor atoms large in size, of low positive charge and containing unshared pairs of electrons (p or d electrons) in their valency shell (e.g.  $\text{Hg}^+, \text{Cu}^+, \text{Tl}^+, \text{RS}^+$ ). For Lewis acids the important properties that determine softness are size, charge or oxidation state, electronic structure and the nature of the attached groups<sup>135</sup> (for examples see  $\text{S}_4\text{N}_4$  adducts later).

In view of the above principle it was interesting to study the various adducts of tetrasulphur tetranitride with Lewis acids. It was hoped that any radical differences in the structures of the adducts would be revealed by infrared spectra and chemical properties.

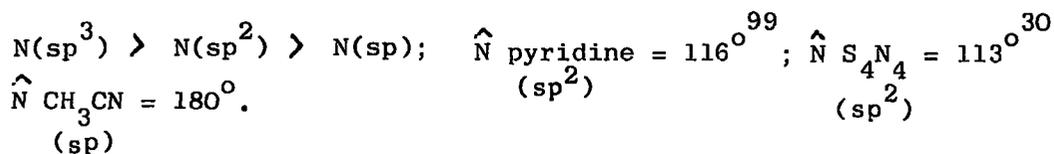
(a) Tetrasulphur tetranitride adducts of tin tetrabromide and tin tetrachloride

The formation of coordination complexes by the tetrahalides of silicon, germanium and tin with pyridine and acetonitrile (border-line bases according HSAB principle) may be compared to the reactions of  $S_4N_4$  with tetrahalides.

The observed ratios of acceptor to donor in these addition compounds are most frequently 1:2 or 1:1, more rarely 1:4 and occasionally ratios other than these<sup>137</sup>. The tetrahalides of silicon, germanium and tin appears to follow the acceptor sequence Sn Ge Si and F Cl Br I. It can be seen from Table 1 that the ratio of  $S_4N_4$  to  $SnCl_4$  and  $SnBr_4$  in these adducts is 2:1, whereas  $SiCl_4$ ,  $GeCl_4$  form no adducts with  $S_4N_4$ . From the above observations we may assign increasing softness in the order  $CH_3CN \gg S_4N_4 \gg C_5H_5N$ . This appears to be reasonable since pyridine forms adducts with  $SiCl_4$ ,  $GeCl_4$  and  $SnI_4$ , whereas in the case of  $CH_3CN$  and  $S_4N_4$ , no adduct formation has been reported or observed with these halides. Tetrasulphur tetranitride can be considered as a stronger base than acetonitrile, because tellurium tetrafluoride

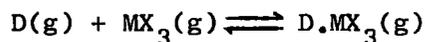
and thallium trichloride form adducts with  $S_4N_4$  in acetonitrile solution (e.g. consider the acid-base substitution reaction,  $B' + A:B \rightarrow AB' + B$ , where  $B'$  and  $B$  are bases and  $A$  is an acid, if the reaction goes as indicated  $B'$  is a stronger base than  $B$ )<sup>135</sup>.

The relative donor ability of nitrogen bases more simply be explained by considering the state of hybridisation of the donor atom. With regard to the donor strength of nitrogen atoms,



In tin tetrahalides the order of acid strength is  $SnF_4 > SnCl_4 > SnBr_4 > SnI_4$  (from size, charge or oxidation state and the nature of the attached groups), because the high electronegativity of fluorine (4.1)<sup>138</sup> leaves higher positive charge on Sn in  $SnF_4$  than on Sn in other tetrahalides of tin (E.N. values, Cl=2.83, Br=2.74, I=2.21)<sup>138</sup> and other factors are equal. Therefore it is not surprising that  $SnI_4$  gave no complex with  $S_4N_4$ . (This does not necessarily mean that  $S_4N_4$  - tin tetraiodide adduct is not preparable. It may be that the reaction has not been examined over sufficiently wide range of experimental conditions). It is generally accepted that intermolecular bonds of the donor-acceptor type are formed as the result of charge transfer from a donor molecule to an acceptor molecule. Consequently the properties of donor bonds should be dependent upon the degree of charge transfer from donor to

acceptor<sup>121</sup>. This has been verified by establishing the relationship between the degree of charge transfer (from the value of the dipole moment of the intermolecular bonds) and the stability (from the heat of complex formation<sup>122</sup>). Strength of a metal-ligand bond is most satisfactorily defined as the enthalpy change,  $\Delta H$ , accompanying the gas-phase dissociation of the complex<sup>118</sup>. Sometimes however, this information is not available and the strength of the donor acceptor bond is estimated from the magnitude of the stability constant, which is the equilibrium constant,  $K_p$ , for the reaction<sup>118</sup>:



D=donor, M=metal, X=halogen

When equilibrium constants are used as a criterion of stability care has to be taken in interpreting the results. This is because equilibrium constants are a measure of a free energy change, not the required enthalpy change,  $\Delta G^\circ = -Rt \ln K_p$ . Therefore, if  $K_p$  for one addition compound is greater than for a second at a given temperature, it does not necessarily follow that the dissociation of the former is accompanied by the smaller enthalpy change. This is only true if the entropy of dissociation in both reactions is very similar. As indicated above, the most satisfactory method of investigating the stability of an adduct is by studying the gas phase dissociation of the compound into its component parts. A knowledge of how the degree of dissociation

varies with temperature permits the thermodynamic functions,  $\Delta H$ ,  $\Delta G^\circ$  and  $\Delta S$  to be calculated and this enables a quantitative measure of the strength of the metal-ligand bond to be obtained. The experimental techniques for studying gas-phase dissociation of molecular addition compounds have been developed by Brown, Taylor and Gerstein<sup>118</sup>. The gas-phase dissociation technique for the study of addition compounds has certain limitations. Thus it is difficult to study in the gas phase adducts which have already attained a high degree of dissociation a few degrees above saturation point. The dissociation method is also unsuitable for the study of complex compounds which do not give a measurable dissociation at a convenient temperature.

In many instances the relative stabilities of molecular addition compounds have been established by displacement reactions (e.g.  $S_4N_4 \cdot BF_3 + BCl_3 \xrightarrow{CH_2Cl_2} S_4N_4 \cdot BCl_3 + BF_3$ )<sup>54</sup>.

It has long been customary to infer orders of relative stability from measurement of saturation pressure<sup>118</sup>. As a general rule for two addition compounds of closely similar type and molecular weight the less stable exhibits the higher saturation pressure (e.g. the order of stability,  $(CH_3)_3N \cdot BF_3 > (CH_3)_3N \cdot BCCH_3)_3$ ; the order of saturation pressure  $(CH_3)_3N \cdot (BCH_3)_3 > (CH_3)_3 \cdot BF_3$ )<sup>118</sup> For addition compounds differing in molecular weight it is to be expected that the lighter would be more volatile (e.g.  $S_4N_4 \cdot BCl_3$   $S_4N_4 \cdot BF_3$ ). If however the heavier complex is found to be more

volatile, this is taken to indicate that it is also more highly dissociated.

It is possible to consider the existence of a coordination complex in terms of an energy cycle<sup>138</sup> and the cycle can be used qualitatively for discussion of real or possible compounds. It should be understood that every donor-acceptor reaction requires adjustment of energy levels in relation to each other to accord with the actual properties of the system. In some instances the adjustment energy (or reorganisation energy) may be greater than the energy released by dative-bond formation so that there is no combination, the gas-phase free energy of formation being positive instead of negative. This may well be true for some of those extreme cases where no reaction takes place between acceptors and donors having large alkyl groups attached to them. On the other hand, from the kinetics of coordinate bond formation in the vapour phase, the energy of readjustment for reactions between some classes of donor and acceptor can be quite small. This is true for complex compound formation between certain amines and boron halides. Alternatively, the Donor.MX<sub>3</sub> standard state may lie above the (MX<sub>3</sub> + D) standard states so that the adduct would not form. All these energy steps are complex. Thus with respect to the acid, adjustment for bonding involves energy of rehybridisation of the metal atom to give the required coordination number, e.g. in the case of SnCl<sub>4</sub> to give an

octahedral coordination (reduction in bond angles from  $109^{\circ}28'$  to approximately  $90^{\circ}$ ). Sometimes the existence of bonding between M and X in  $MX_3$  makes this step energetically more costly than in other situations where such bonding is less or absent, (e.g.  $S_4N_4 \cdot BCl_3$  is more stable than  $S_4N_4 \cdot BF_3$ ).

Rehybridisation considerations also apply to the molecules of base although usually the changes are not as drastic as in the case of acceptors. A further complication occurs if the acceptor molecule exists as a polymer. Then conversion of  $MX_3$  (standard state) to  $MX_3(g)$  requires energy for depolymerisation (e.g. complex formation by dimeric aluminium halides in solution or by solid halides polymerised through halogen bridges). Thus from this brief consideration of the energy steps in complex compound formation, it is readily seen that it is impossible to assign definite strengths to electron-pair donors and acceptors valid for every acid-base reaction<sup>118</sup>.

Since many  $S_4N_4$  adducts are insoluble or slightly soluble in inert organic solvents, any physical measurements such as vapour pressure, dipole moment etc. would be difficult. However, in those cases where the adducts are soluble in inert solvents, it may be possible to gain more knowledge about the properties of  $S_4N_4$  adducts. The adduct  $S_4N_4 \cdot 4SbF_5$  appears to be less stable than  $S_4N_4 \cdot SbCl_5$ , because of the very rapid decomposition of  $S_4N_4 \cdot 4SbF_5$  in moist air. This behaviour may be explained in



terms of two effects (i) the donation of electrons from one of the nitrogens of  $S_4N_4$  causes the weakening of the donor ability of the other nitrogen atoms. Consequently, the antimony pentafluoride molecules will be attached more weakly than in (hypothetical)  $S_4N_4 \cdot SbF_5$  and probably more weakly than in  $S_4N_4 \cdot SbCl_5$ . Rapid hydrolysis of  $S_4N_4 \cdot 4SbF_5$  in moist air is therefore to be expected, (ii) Steric effect: as the adduct gets bigger it may become less stable.

The case with which the  $S_4N_4$  adducts undergo hydrolysis in moist air can be considered in terms of HSAB principle and may in turn probably explain their stabilities. Thus since neither the  $S_4N_4$  is a very strong donor, nor the  $SnCl_4$  is a strong acceptor, in the adduct,  $2S_4N_4 \cdot SnCl_4$  both  $S_4N_4$  and  $SnCl_4$  may be considered as nearly matching partners and consequently one would expect the adduct to be relatively stable. This is shown by the slow decomposition of  $2S_4N_4 \cdot SnCl_4$  in moist air. Further the same argument can be applied to explain the stabilities of  $S_4N_4 \cdot BCl_3$  and  $S_4N_4 \cdot SbCl_5$  adducts where the latter appears to be more stable than  $S_4N_4 \cdot BCl_3$ , since  $S_4N_4 \cdot SbCl_5$  can be obtained from the adduct,  $S_4N_4 \cdot SbCl_5 \cdot BCl_3$  at 85-90°C.<sup>54</sup> Thus  $SbCl_5$  would be a better matching partner or acceptor for  $S_4N_4$  than  $BCl_3$ . However, it is still quite possible for a compound formed from a hard acid and a soft base to be more stable than one made from a better matched pair<sup>135</sup>.

(b) Tetrasulphur tetranitride adducts of titanium, zirconium and hafnium tetrahalides

Titanium tetrachloride, tetrabromide, tetraiodide, zirconium tetrachloride and hafnium tetrachloride, form 1:1 adducts with  $S_4N_4$ . From electronegativity considerations  $TiCl_4$  would be a better acceptor for  $S_4N_4$  than  $SnCl_4$  (the estimated ionic radii,  $Sn^{4+} = 0.71\overset{O}{\text{Å}}$ ,  $Ti^{4+} = 0.68\overset{O}{\text{Å}}$ )<sup>138</sup> since neutral acids and bases will have strength proportional to the local dipoles at the acceptor or donor end. Silicon tetrachloride and  $GeCl_4$  do not form addition compounds with  $S_4N_4$ , although  $TiCl_4$  and  $SnCl_4$  do so, a difference which may be attributed to ability of the halogen atoms to fill the coordination sphere of the smaller Si and Ge atoms.

Zirconium tetrachloride and  $HfCl_4$  (the radii of the  $Zr^{4+}$  and  $Hf^{4+}$  ions are 0.74 and 0.75 respectively<sup>138</sup>) resemble  $TiCl_4$  in their chemical properties<sup>138</sup>. Similar considerations can be applied to other halides of the group. Titanium tetrafluoride gave the adduct  $S_4N_4 \cdot 4TiF_4$ , thus using all the four basic sites in  $S_4N_4$ .

(c) Tetrasulphur tetranitride adducts of boron, aluminium, gallium, indium, thallium and iron trihalides

As previously mentioned (see page 11,91),  $BCl_3$ ,  $BBr_3$ ,  $PhBCl_2$ , form 1:1 adducts with  $S_4N_4$ , whereas in the case of  $BF_3$ , two adducts,  $S_4N_4 \cdot BF_3$  and  $BF_3 \cdot 4S_4N_4$  have been reported. However, the adduct

$\text{BF}_3 \cdot 4\text{S}_4\text{N}_4$  appears to be unusual since the inability of boron to have coordination numbers exceeding four. Aluminium trichloride and tribromide  $\text{GaCl}_3$ ,  $\text{InCl}_3$ , and  $\text{FeCl}_3$  gave 1:2 adducts ( $\text{S}_4\text{N}_4$ : metal halide), while the stoichiometry in thallium trichloride adduct is not known.

In  $\text{BX}_3$  compounds the boron octet is incomplete; boron has a low-lying unfilled orbital, consequently  $\text{BX}_3$  (x=halogen) compounds behave as Lewis acids in which boron achieves its maximum coordination number with approximately  $\text{sp}^3$  hybridisation. There is good evidence that the relative strengths of the boron halides as Lewis acids are in the order  $\text{BBr}_3 > \text{BCl}_3 > \text{BF}_3$ . This order is opposite of what would be expected both in steric grounds and from electronegativity considerations. It can be explained at least partially in terms of the boron halogen bonding. Acceptor atoms are less effective when the vacant orbital can be at least partly used in multiple bonding within the molecule<sup>140</sup>. In an addition compound this  $\pi$  bonding is largely or completely lost so that addition compounds of the boron trihalides with the strongest  $\pi$  bonding will be the most destabilised through loss of the  $\pi$  bonding energy<sup>139</sup>. Calculations<sup>138</sup> indicate that the  $\pi$  bonding energies of the trihalides are in the order  $\text{BF}_3 > \text{BCl}_3 > \text{BBr}_3$ . However certain properties<sup>138</sup> of the  $\text{BX}_3$  adducts with donor molecules suggest that the donor to boron bonds may themselves increase in strength in the order  $\text{BF}_3 < \text{BCl}_3 < \text{BBr}_3$ . This may be

explained by the application of the mutual stabilising effect called symbiosis<sup>141</sup> (i.e. soft bases tend to group together on a given central atom and hard ligands tend to group together). In  $BX_3$  halides boron is formally in a plus three oxidation state. The hard  $F^-$  ligands form a complex which is strongly ionic, the boron atom in  $BF_3$  is appreciably positive and hard. Thus the presence of hard fluoride ion in  $BF_3$  makes it easy to add other hard bases (e.g.  $BF_3 \cdot OR_2$  is more stable than  $BF_3 \cdot SF_2$ ). In the adducts  $S_4N_4 \cdot BF_3$  and  $S_4N_4 \cdot BCl_3$  the latter is more stable (since  $BCl_3$  replaces  $BF_3$  from  $S_4N_4 \cdot BF_3$  in  $CH_2Cl_2$  to give  $S_4N_4 \cdot BCl_3$ )<sup>54</sup> because  $S_4N_4$  is a better matching partner for  $BCl_3$  than for  $BF_3$  or the better stability of  $S_4N_4 \cdot BCl_3$  compared to  $S_4N_4 \cdot BF_3$  can be explained by considering  $BCl_3$  as a better acceptor than  $BF_3$ . Thus both the above explanations can be used to explain the relative stabilities of these adducts.

Aluminium and its congeners Ga, In, Tl are considerably larger than boron (atomic radii of Al and B being 1.26 and 0.88 Å respectively) and their trihalides behave as Lewis acids and can accept either neutral donor molecules or anions to give tetrahedral species, the acceptor ability generally decreases  $Al > Ga > In$  with the position of Tl uncertain. There are however notable distinctions from boron. These arise in part due to the reduced ability to form multiple bonds and to the ability of heavier elements to have coordinate numbers exceeding four.

Thallium (III) chloride is softer than Tl(I) chloride, because of the inert pair of electrons in the 6S orbitals. The presence of electrons in these orbitals decreases softness by a shielding affect on the outer d electrons and consequently  $TlCl_3$  would be a better matching partner for  $S_4N_4$ .

(d) Tetrasulphur tetranitride adducts of antimony niobium and tantalum halides

The pentahalides of Sb, Nb and Ta form adducts with donors, such as oxygen, nitrogen exhibiting various stoichiometries (e.g.  $SbCl_5 \cdot SeOCl_2$ ,  $NbCl_5 \cdot POCl_3$ ,  $NbF_5 \cdot 2NH_3$ ,  $TaF_5 \cdot 2C_5H_5N$ )<sup>142</sup> Antimony pentachloride has been more extensively studied than the other pentahalides of Sb, Nb and Ta and the majority of its adducts conform to 1:1 stoichiometry. Comparison of the values of the heats of reaction of  $BBr_3$ ,  $BCl_3$  and  $SbCl_5$  with pyridine yields the order of acid strengths toward pyridine:  $BBr_3 > BCl_3 > SbCl_5$ . In the boron halide series (as previously described), variations in degree of bonding have been used to explain the order; apparently the pentahalides may coordinate with little disturbance to the degree of bonding present. The physical properties of the adducts of pentahalides vary but the majority are solids at room temperature<sup>142</sup>. Antimony pentafluoride has some unusual chemical behaviour (e.g. it dissolves S, Se, Te and from the solutions crystalline substances such as  $(SbF_5)_2S$  may be isolated)<sup>144</sup>. Antimony pentafluoride (electronegativity values,  $Sb=1.82$ ,  $F=4.1$ <sup>138</sup>),

as would be expected because of the high affinity of antimony (in  $\text{SbF}_5$ ) for electrons, functions as a strong Lewis acid.

The acid strength of  $\text{SbF}_5$  (with respect to  $\text{S}_4\text{N}_4$ ) can be compared with that of sulphur trioxide, since both the acids give  $\text{S}_4\text{N}_4$  adducts of 1:2 ( $\text{S}_4\text{N}_4$  Lewis acids) and 1:4 stoichiometry. When

one of the nitrogen atoms of  $\text{S}_4\text{N}_4$  is involved in the adduct formation, the donor ability of other N atoms is considerably weakened, but in the presence of strong acceptors, the other

donor sites of  $\text{S}_4\text{N}_4$ , though weak can be used in the formation of coordinate bonds, although according to HSAB principle, such

bonds would be weaker than the bonds formed from better matched partners. The pentafluorides of niobium and tantalum give

adducts with various donor ligands (e.g.  $\text{NbF}_5 \cdot \text{OEt}_2$ ,  $\text{TaF}_5 \cdot \text{SeEt}_2$ )

and hexafluoride anions are known for these elements. Niobium and tantalum also exhibit a coordination number greater than six.

A coordination number of seven has been formed for niobium in

$(\text{NbF}_7)^{2-}$ , whereas species up to  $(\text{TaF}_8)^{3-}$  and possibly  $(\text{TaF}_9)^{4-}$  exist in solution<sup>138</sup>. The acceptor strength of  $\text{SbF}_5$ ,  $\text{NbF}_5$  and

$\text{TaF}_5$  toward  $\text{S}_4\text{N}_4$  is probably in the order,  $\text{SbF}_5 > \text{NbF}_5 > \text{TaF}_5$ , since  $\text{SbF}_5$  gives 1:4 and 1:2 adducts, whereas Nb and Ta form

1:1 ( $\text{S}_4\text{N}_4$ : metal fluoride) adducts. However it would be interesting

to see whether  $\text{SbF}_5$  displaces  $\text{NbF}_5$  or  $\text{TaF}_5$  from  $\text{S}_4\text{N}_4 \cdot \text{NbF}_5$  or

$\text{S}_4\text{N}_4 \cdot \text{TaF}_5$  to give  $\text{S}_4\text{N}_4$  adducts of  $\text{SbF}_5$ , because it is not possible

to write down any universal order of acid strength (it varies with the reference donor)<sup>135</sup>. As noted above, adduct formation is observed for oxygen, nitrogen and sulphur donors with the pentachlorides and bromides of Nb and Ta, exhibiting the stoichiometry of 1:1 and 1:2 (e.g.  $\text{NbCl}_5 \cdot 2(\text{CH}_3)_3\text{N}$ ,  $\text{TaCl}_5 \cdot (\text{CH}_3)_2\text{S}$ )<sup>142</sup>.

Tantalum pentafluoride and  $\text{NbX}_5$  (X=Cl, Br, I) are readily reduced by pyridine to give  $\text{MX}_4\text{py}_2$  complexes<sup>138</sup>.

(e) Tetrasulphur tetranitride adducts of selenium (IV) tellurium (IV) and tungsten halides and oxyhalides

The halides of selenium (IV) and tellurium (IV) are generally more stable than those of sulphur and they also differ in showing Lewis acidity<sup>138</sup> (e.g. they form complex halides such as  $\text{K}(\text{SeF}_5)$ ,  $\text{K}_2(\text{SeCl}_6)$ ,  $(\text{C}_5\text{H}_5)_2(\text{TeI}_6)$ ). Selenium tetrachloride forms addition compounds with ammonia,  $\text{SeCl}_4 \cdot 4\text{NH}_3$ , ethylenediamine  $\text{SeCl}_4(\text{en})$ ,  $\text{SeCl}_4 \cdot 2\text{en}$ , and with many amines<sup>145</sup>. The pyridine adduct  $\text{SeCl}_4 \cdot \text{py}_2$  is not analogous to  $\text{SeCl}_6^{2-}$  since in acetonitrile it acts like a salt of the cation  $(\text{SeCl}_3 \cdot \text{py}_2)^+$ , this ion probably has a distorted octahedral structure, like the  $\text{SeOCl}_2 \cdot \text{py}_2$ <sup>138</sup>. Tellurium tetrachloride also gives  $\text{TeCl}_4 \cdot 4\text{NH}_3$  with dry ammonia and adducts of the type  $\text{TeCl}_4 \cdot \text{py}$ ,  $\text{TeCl}_4 \cdot 2\text{py}$ ,  $\text{TeCl}_4 \cdot \text{POCl}_3$  have been obtained<sup>145</sup>. From HSAB principle,  $\text{SeCl}_4$  and  $\text{TeCl}_4$  may be classified as soft Lewis acids, since the soft Lewis acids generally have acceptor atoms large in size, of low positive charge and

containing unshared pairs of electrons (p or d electrons) in their valency shell. Thus in  $\text{SeCl}_4$  and  $\text{TeCl}_4$ , from electronegativity considerations (e.n. values for  $\text{Se}=2.48$ ,  $\text{Cl}=2.83$ ,  $\text{Te}=2.01$ )<sup>138</sup> one would expect relatively small positive charge on Se and Te atoms, and since they contain unshared pairs of electrons in  $sp^3d$  hybrid orbitals and also they are relatively large in size (covalent radii,  $\text{Se}=1.71\text{\AA}$ ,  $\text{Te}=1.37\text{\AA}$ ) consequently  $\text{SeCl}_4$  and  $\text{TeCl}_4$  may form stable complexes with soft bases e.g.  $\text{TeCl}_4 \cdot \text{py}$  would probably be more stable than  $\text{TeCl}_4 \cdot \text{POCl}_3$  and relatively less stable than  $\text{S}_4\text{N}_4 \cdot \text{TeCl}_4$  (however HSAB principle is a qualitative rule based on experimental facts, the above order may be disturbed by other factors).

Selenium tetrafluoride and tellurium tetrafluoride are highly reactive fluorinating agents though tellurium tetrafluoride appears to be less useful as a fluorinating agent. It forms 1:1 addition compound with pyridine in dry ether<sup>145</sup>; the tetrafluoride reacts exothermically with a number of bases, but secondary reactions occurred before the complexes could be isolated in pure form.<sup>146</sup>

Tungsten hexachloride,  $\text{WCl}_6$  is reduced by primary amines to give amido complexes in lower oxidation states<sup>138</sup>, which is in analogy to the  $\text{S}_4\text{N}_4$  reactions with  $\text{WCl}_6$  and  $\text{WBr}_6$ . The reaction of oxytetrahalides  $\text{WOCl}_4$  and  $\text{WOBr}_4$  with various unidentate and bidentate ligands containing group V and group VI donor atoms has been recently studied<sup>147</sup>. Alkyl cyanides, pyridine and cyclic ethers give 1:1 adducts and the alkyl cyanide complexes (e.g.

$\text{WOC1}_4 \cdot \text{CH}_3\text{CN}$ ,  $\text{WOC1}_4 \cdot \text{C}_2\text{H}_5\text{CN}$ ) appear to be six-coordinate complexes. The infrared spectra of  $\text{WCl}_4 \cdot \text{S}_4\text{N}_4$ ,  $\text{WBr}_4 \cdot \text{S}_4\text{N}_4$  and  $\text{WOC1}_4 \cdot \text{S}_4\text{N}_4$  are discussed later.

#### The Structures of $\text{S}_4\text{N}_4$ adducts

The positions of the infrared absorptions of the  $\text{S}_4\text{N}_4$  adducts are given in Table 2. The formation of a coordinate bond by donation of a lone pair of electrons merely perturbs the donor molecule, no great changes in stereochemistry are commonly required and the effect on the spectrum appears as small shifts in frequency, with perhaps spitting of bands and altered intensity<sup>137,142</sup>. In the case of  $\text{S}_4\text{N}_4$  more marked changes occur. Even without change in the geometry of  $\text{S}_4\text{N}_4$ , lowering of the molecular symmetry on coordination gives rise to more infrared-active bands. Since coordination by nitrogen atoms flattens out the  $\text{S}_4\text{N}_4$  molecule with loss of S-S bonds and SN bond lengths no longer equal, further changes are inevitable. As a diagnostic tool infrared spectrum is invaluable and the spectra of coordinated ligands frequently show considerable similarities in a wide variety of compounds. Examination of the element-halogen vibrations as well as the ligand vibrations would appear to offer a tool to investigate the stereochemistry of the adducts. Recent studies have shown that metal-halogen absorption bands (MX) are often intense, and therefore readily identifiable and that the frequencies

TABLE 2 VIBRATIONAL FREQUENCIES OF  $S_4N_4$  ADDUCTS WITH METAL HALIDES

The following symbols are used to denote the relative intensity of the infrared absorptions: vs = very strong, s = strong, m = medium, w = weak, vw = very weak, br = broad, sh = shoulder.

$SnBr_4 \cdot 2S_4N_4$	1156 vw, 1041 vs, 961 vs, 794 vs, 725 vw, 671 ms, 621 ms(Br), 563 w, 513 s, 422 vs, 355 vs, 298 ms, 259 w, 234 s, 219 ms (Br) $cm^{-1}$ .
$SnCl_4 \cdot 2S_4N_4$	1170 vw, 1047 vs, 966 vs, 814 vs, 787 w(sh), 722 vw, 683 w, 623 ms, 568 vw, 516 s, 413 s, 365 vs, 319 vw(sh), 309 vs, 279 ms, 260 vw, 252 w, 245 vw(sh), 236 s, 225 w, 212 vw, 207 vw, 201 vw $cm^{-1}$ .
$TiBr_4 \cdot S_4N_4$	1156 vw, 1036 vs, 936 vs, 929 vs, 807 s, 775 vs, 746 ms (sh), 681 ms, 621 w, 565 ms(br), 508 s, 416 w, 365 w, (322 w, 312 w, 299 w)(br), 280 vw, 279 w, 266 w, 253 w, 245 ms, 226 w, 220 w, 217 vw, 212 w, 211 w(sh), 206 w $cm^{-1}$ .
$TiCl_4 \cdot S_4N_4$	1156 vw, 1041 w, 990 vw, 963 s, 927 vs, 810 w, 760 ms, 728 s, 700 vs, 620 vw, 549 vs, 529 vw(sh), 515 vw, 389 vw (sh), 370 vs, 340 vs $cm^{-1}$ .
$TiF_4 \cdot S_4N_4$	1149 vw, 1059 vs, 985 vs, 724 w(sh), 662 vs(br), 613 vw, 510 ms, 510 vw, 378 ms, 351 vw, 282 s (br), 247 vw $cm^{-1}$ .
$TiI_4 \cdot S_4N_4$	1156 vw, 1098 vw, 1020 w, 934 w, 793 w, 722 vw, 279 s, 248 s (br) $cm^{-1}$ .
$ZrCl_4 \cdot S_4N_4$	1157 vw, 1034 vs, 957 vs, 807 vs, 795 vw(sh), 762 vs, 740 vw, 722 vs, 699 vs, 668 vw(sh), 626 ms, 551 vs, 529 vw, 510 ms, 367 w(sh), 340 vs, 305 ms, 245 vw $cm^{-1}$ .
$HfCl_4 \cdot S_4N_4$	1156 vw, 1037 vs, 991 vw, 958 vs, 800 vs, 724 vw(sh), 682 s, 666 vw, 639 vw(sh), 624 s, 561 vw, 553vw, 514 vs, 422 vw, 399 vw, 359 w(sh), 324 s(br), 303 vw, 290 vw, 279 w, 267 w, 253 ms(sh), 247 s, 226 w, 220 w, 217 vw, 212 w, 206 w.

TABLE 2 (contd...)

$\text{SbCl}_5 \cdot \text{S}_4\text{N}_4$	1156 vw, 1058 vs, 975 vs, 807 vs, 786 vs, 738 w(sh), 722 ms (br), 602 s, 666 vw, 651 w, 623 vs, 608 vw(sh), 563 w, 511 vs, 483 vw, 411 vs, 370 s(sh), 370 w(sh), 361 w(sh), 345 vs, 308 s, 275 vs, 245 s, 239 w(sh), 226 w $\text{cm}^{-1}$ .
$4\text{SbF}_5 \cdot \text{S}_4\text{N}_4$	1143 vw, 1058 vs, 986 vs, 943 vs, 886 vw(sh), 790 ms, 741 ms, 719 vw(sh), 695 s, 625 s, 571 s(br), 429 vs, 357 s, 339 s(br), 291 ms, 268 vw, 259 w, 250 vw(sh), 234 w, 228 w, 223 w, 214 w, 208 w $\text{cm}^{-1}$ .
$\text{NbCl}_5 \cdot \text{S}_4\text{N}_4$	1041 vs, 987 ms, 954 vs, 883 ms, 788 vs, 750 s, 719 vw, 680 ms, 666 vw, 618 s, 506 vs, 431 ms, 365 vs, 340 vs $\text{cm}^{-1}$ .
$\text{NbF}_5 \cdot \text{S}_4\text{N}_4$	1065 vs, 992 vs, 929 w, 891 vw, 800 ms, 722 ms, 676 ms, 606 vs(br), 515 vs.
$\text{TaCl}_5 \cdot \text{S}_4\text{N}_4$	1153 vw, 1045 vs, 957 vs, 797 vs, 749 s, 721 vw(sh), 682 ms, 669 vw, 637 ms(sh), 619 s, 568 vw, 505 vs, 425 ms, 372 w(sh), 359 ms(sh), 322 vs(br), 265 w, 252 vw, 244 vw, 226 w $\text{cm}^{-1}$ .
$\text{TaF}_5 \cdot \text{S}_4\text{N}_4$	1153 vw, 1071 vs, 996 vs, 927 vs, 873 vw(sh), 803 ms, 744 ms, 727 w, 700 vs, 678 ms, 667 vw, 581 vs(br), 516 w $\text{cm}^{-1}$ .
$\text{BF}_3 \cdot \text{S}_4\text{N}_4^{54}$	1171 w, 1138 ms, 1117 s, 1070 s, 1040 vs, 1014 w, 949 s, 908 w, 888 s, 840 w, 724 vw, 697 vw, 682 vw, 658 ms, 623 ms, 567 w, 552 w, 527 s, 502 w, 490 w(sh), 420 ms $\text{cm}^{-1}$ .
$\text{BCl}_3 \cdot \text{S}_4\text{N}_4^{54}$	1064 s, 1042 w, 982 s, 958 s, 864 w, 736 w, 720 w, 695 w, 678 w, 660 w, 625 w, 615 vw(sh), 552 vw, 518 w, 430 w, $\text{cm}^{-1}$ .
$\text{PhBCl}_2 \cdot \text{S}_4\text{N}_4$	1310 vw, 1156 vw(sh), 1087 vw(sh), 1265 vw, 1194 vw(sh), 1186 vw(sh), 1174 vs, 1057 vs, 1029 w(sh), 1000 vw(sh), 971 w(sh), 948 vw(sh), 921 vs, 888 w(sh), 875 s, 857 vw(sh), 797 ms, 762 ms, 738 vw(sh), 725 vw(sh), 704 vs, 693 vw(sh), 659 vs, 628 ms, 615 vw(sh), 551 s, 521 s, 420 vs, 359 vs, 352 vw(sh), 335 vs, 314 vs, 304 vw(sh), 282 vs, 261 w, 250 vs, 241 w, 238 vw(sh), 233 vw(sh), 228 ms, 222 w, 218 vw, 213 vw, 208 w.

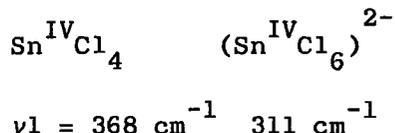
TABLE 2 (contd....)

$2\text{AlBr}_3 \cdot \text{S}_4\text{N}_4$	1157 vw, 1126 vs, 934 ms, 869 vs, 776 ms, 736 ms, 710 vw(sh), 694 vw, 667 w, 633 w, 585 ms, 565 w, 481 vw (sh), 473 vs, 457 w, 437 ms, 414 ms, 395 ms, 349 vs, 318 ms, 276 ms, 259 ms, 251 ms, 244 ms, 238 vw, 226 s, 221 w (sh), 212 ms, 206 ms $\text{cm}^{-1}$ .
$2\text{AlCl}_3 \cdot \text{S}_4\text{N}_4$	1162 vw, 1046 vs, 998 w, 967 vs, 866 vs, 800 vw, 755 ms, 719 w, 680 ms, 623 s, 573 w, 561 w, 530 w(sh), 507 vw(br), 476 w, 454 ms, 403 vs, 355 vs, 324 vs, 238 s, 225 ms $\text{cm}^{-1}$ .
$2\text{GaCl}_3 \cdot \text{S}_4\text{N}_4$	1147 vw, 1033 vs, 993 w, 961 vs, 844 vs, 756 ms, 722 vw(sh), 680 ms, 666 vw(sh), 680 ms, 623 s, 566 w, 516 vs, (420 s, 408 s, 389 s, 374 s)(Br), 297 vs, 267 vs, 228 s $\text{cm}^{-1}$ .
$2\text{InCl}_3 \cdot \text{S}_4\text{N}_4$	1266 ms, 1152 vw, 1040 vs, 954 vs, 893 vw, 824 vs, 777 ms(sh), 730 vs, 704 ms, 681 s, 645 vw(sh), 621 vs, 565 ms, 551 vw(sh), 521 vs, 403 vs, 361 vs, 312 vs, 236 ms(br) $\text{cm}^{-1}$ .
$2\text{TlCl}_3 \cdot \text{S}_4\text{N}_4$	1156 vw, 1059 vs, 971 vs, 803 w, 741 w(sh), 722 s, 702 w, 655 w, 619 ms, 597 s, 580 s, 558 w, 533 ms, 523 w $\text{cm}^{-1}$ .
$2\text{FeCl}_3 \cdot \text{S}_4\text{N}_4$	1162 vw, 1033 vs, 995 w, 957 vs, 797 vs, 737 ms, 720 vw(sh), 679 s, 619 vs, 565 w, 516 vs, (384 vs, 370 vs)(br), 340 s, 308 s, 255 vw, 248 vw, 234 w, 228 vw $\text{cm}^{-1}$ .
$\text{SeCl}_4 \cdot \text{S}_4\text{N}_4$	1190 w, 1124 vs, 1105 ms(sh), 1016 ms, 945 w, 919 ms, 800 vw, 729 vs, 702 vw, 670 ms, 622 vs, 559 s(sh), 546 vs, 403 s, 383 s, 336 s, 309 s $\text{cm}^{-1}$ .
$\text{TeCl}_4 \cdot \text{S}_4\text{N}_4$	1156 vw, 1047 vs, 966 vs, 806 s, 760 vs, 727vw(sh), 671 ms, 635 ms, 613 ms, 563 w, 500 s(br), 360 vs(br), 251 s(br), 225 w $\text{cm}^{-1}$ .

TABLE 2 (contd....)

$\text{TeF}_4 \cdot \text{S}_4\text{N}_4$	1282 w, 1162 vw, 1036 s, 981 vs, 926 vs, 926 vs, 865 vw, 821 w, 768 s, 745 vw, 727 s, 700 vs, 627 vw, 591 vw, 458 vs $\text{cm}^{-1}$ .
$\text{WOCl}_4 \cdot \text{S}_4\text{N}_4(?)$	1164 vw, 1075 vw, 1000 vw(sh), 980 vs, 926 vw, 857 w, 837 w, 792 w, 778 w, (735 w, 723 w)(br), 697 w, 662 vs, 617 vw, 551 w, 543 w, 515 ms $\text{cm}^{-1}$ .
$\text{WCl}_4 \cdot \text{S}_4\text{N}_4$	1162 vw, 1119 w, 1070 vw, 1041 w(sh), 1010 vs, 971 ms, 934 w, 851 ms, 800 vw(sh), 788 vs, 768 w(sh), 723 vw, 703 s, 697 vw(sh), (660 s, 647 s) (br), 576 vw, 554 s, 515 vs, 494 ms(sh), 472 vw, 406 ms, (350 w (sh), 331 vs, 312 w, 294 w(sh),(br), 276 vw, 263 ms, 251 ms, 244 ms $\text{cm}^{-1}$ .
$\text{WBr}_4 \cdot \text{S}_4\text{N}_4$	1169 w, 1066 vw, 1005 vs, 921 vw, (857 s, 837 s) (br), 780 ms, 769 ms, 735 w(sh), 722 w, 689 ms, 673 vw, 660 vw(sh), 653 vs, 623 vw, 548 s, 527 ms, 514 ms, 501 vw(sh), 467 s, 405 vs, 330 vs, 312 ms, 291 s, 279 s, 263 ms, 254 w $\text{cm}^{-1}$ .

of these vibrations are related to the oxidation state and coordination number of the metal and also to the stereochemistry of the complex<sup>148</sup>. Thus an increase in coordination number leads to a decrease in  $\nu$  M-Cl<sup>149</sup>, e.g.



and an increase in oxidation state causes an increase in  $\nu$  M-Cl<sup>149</sup>, e.g.  $(\text{FeCl}_4)^{2-}$ ,  $(\text{FeCl}_4)^{-1}$



Also in using vibrational data, one should be aware of the importance of environmental effects such as field affects, solvent effects, and site symmetry effects. However, the spectra of several adducts containing supposedly chelate ligands, such as 1,10-phenanthroline and 2,2'-bipyridyl show that the assignments of stereochemistry can be made, in the absence of complicating factors such as crystal field affects<sup>137</sup>. For infrared spectroscopy because it involves the direct study of the metal-ligand bond is particularly useful in assigning M-X stretching frequencies.

From Table 2 it can be seen that the spectra of the adducts of  $\text{S}_4\text{N}_4$  with metal halides may roughly be divided into four types. Since the X-ray structures of  $\text{S}_4\text{N}_4 \cdot \text{SbCl}_5$  and  $\text{S}_4\text{N}_4 \cdot \text{BF}_3$  are known, it is useful to compare the infrared spectra of these adducts with the other complexes.

(a) The adducts,  $\text{SnBr}_4 \cdot 2\text{S}_4\text{N}_4$ ,  $\text{SnCl}_4 \cdot 2\text{S}_4\text{N}_4$ ,  $\text{TiBr}_4 \cdot \text{S}_4\text{N}_4$ ,  $\text{ZrCl}_4 \cdot \text{S}_4\text{N}_4$ ,  $\text{HfCl}_4 \cdot \text{S}_4\text{N}_4$ ,  $4\text{TiF}_4 \cdot \text{S}_4\text{N}_4$ ,  $4\text{SbF}_5 \cdot \text{S}_4\text{N}_4$ ,  $\text{SbCl}_5 \cdot \text{S}_4\text{N}_4$ ,  $\text{NbCl}_5 \cdot \text{S}_4\text{N}_4$ ,  $\text{TaCl}_5 \cdot \text{S}_4\text{N}_4$ ,  $\text{TaF}_5 \cdot \text{S}_4\text{N}_4$ ,  $\text{TeCl}_4 \cdot \text{S}_4\text{N}_4$ ,  $2\text{AlCl}_3 \cdot \text{S}_4\text{N}_4$ ,  $2\text{GaCl}_3 \cdot \text{S}_4\text{N}_4$ ,  $2\text{InCl}_3 \cdot \text{S}_4\text{N}_4$ ,  $2\text{TlCl}_3 \cdot \text{S}_4\text{N}_4$  (?) have roughly similar infrared spectra to those of  $\text{S}_4\text{N}_4 \cdot \text{SbCl}_5$  and  $\text{S}_4\text{N}_4 \cdot \text{BF}_3$  with characteristic strong peaks at 1040, 960, 510 and  $360 \text{ cm}^{-1}$ .

(b) The infrared spectra of  $\text{S}_4\text{N}_4 \cdot \text{WOCl}_4$ ,  $\text{S}_4\text{N}_4 \cdot \text{WCl}_4$  and  $\text{S}_4\text{N}_4 \cdot \text{WBr}_4$  are different from  $\text{S}_4\text{N}_4 \cdot \text{SbCl}_5$  and  $\text{S}_4\text{N}_4 \cdot \text{BF}_3$ , but show similarity to one another with characteristic very strong peak near  $1000 \text{ cm}^{-1}$ . The strong peaks at 1040 and 1060 in the above adduct are missing in these adducts, the strong peaks in  $\text{S}_4\text{N}_4$  at 924, 727 and  $698 \text{ cm}^{-1}$  are also missing in these adducts.

(c) The infrared spectra of  $2\text{AlBr}_3 \cdot \text{S}_4\text{N}_4$  and  $\text{SeCl}_4 \cdot \text{S}_4\text{N}_4$  are different from the above and one another.

(d) The infrared spectrum of  $\text{TiI}_4 \cdot \text{S}_4\text{N}_4$  is weak.

The Structures of  $\text{SnBr}_4 \cdot 2\text{S}_4\text{N}_4$  and  $\text{SnCl}_4 \cdot 2\text{S}_4\text{N}_4$

The structures to be expected of these adducts are that based on an octahedral distribution about the central metal atom. A single Sn-Cl band has been observed in tin(IV) chloride complexes with nitrogen donors, such as pyridine<sup>151</sup> (e.g.  $\text{SnCl}_4 \cdot 2\text{py}$ , Sn-Cl,  $324 \text{ cm}^{-1}$ ), but a splitting of this band has been observed in complexes such as  $\text{SnCl}_4 \cdot 2,2'$ -bipyridyl ( $\nu \text{Sn-Cl}$ ,  $327, 280 \text{ cm}^{-1}$ )<sup>151</sup>

From this it was concluded that the former complexes are trans octahedral, whereas the latter are cis octahedral<sup>151</sup>. The infrared spectra of  $\text{SnCl}_4 \cdot 2\text{S}_4\text{N}_4$  and  $\text{SnBr}_4 \cdot 2\text{S}_4\text{N}_4$  in 400-4000  $\text{cm}^{-1}$  region are very similar or virtually identical except that in the case of  $\text{SnCl}_4 \cdot 2\text{S}_4\text{N}_4$  the very strong peak at 813  $\text{cm}^{-1}$  has a shoulder at 986  $\text{cm}^{-1}$ . Hence it is reasonable to conclude that both the adducts have similar structures. The metal-nitrogen stretching frequency is of particular interest since it provides direct information about the coordinate bond. Because of the relatively heavy mass of the metal and low bond order of the coordinate bond, the M-N stretching vibrations may appear in the low frequency region<sup>156</sup>. The assignment of metal-nitrogen stretching frequency is carried out by calculating approximate metal nitrogen force constant from Gordys rule<sup>157</sup> and then calculating the approximate metal-nitrogen stretching frequency.

This method is similar to the method described by Poller<sup>159</sup> for calculating Sn-O stretching frequency from the approximate value of force constant, except that the metal-nitrogen bond lengths used were from the X-ray data of the adduct of  $\text{S}_4\text{N}_4$  with  $\text{SbCl}_5$  ( $\text{Sb-N} = 2.17 \text{ \AA}$ )<sup>58</sup> whereas Poller calculated the Sn-O bond length from the sum of the covalent radii corrected for the electronegativity difference<sup>160</sup>. Since the infrared spectra of  $\text{SnCl}_4 \cdot 2\text{S}_4\text{N}_4$  and  $\text{SnBr}_4 \cdot 2\text{S}_4\text{N}_4$  are very similar to the infrared

spectrum of  $S_4N_4 \cdot SbCl_5$ , it is useful to assign the metal-nitrogen stretching frequency first in  $S_4N_4 \cdot SbCl_5$  and then assign the Sn-N stretching frequencies in  $SnCl_4 \cdot 2S_4N_4$  and  $SnBr_4 \cdot 2S_4N_4$  by comparison. Thus taking electronegativity values of 3.07 for nitrogen (Allred-Rochow scale)<sup>138</sup> and 1.82 for antimony (Allred-Rochow scale)<sup>138</sup> and the N-Sb bond length of  $2.17\text{\AA}$  a force constant of  $2.2 \times 10^5$  dyn./cm. was obtained (see Appendix 1) This gave a value of  $545\text{ cm}^{-1}$  for the N-Sb stretching frequency. If the electronegativity values for nitrogen and antimony are 3.04 and 2.05 (Pauling-type values)<sup>138</sup> respectively, the calculations gave a stretching frequency of  $565\text{ cm}^{-1}$ . These are probably upper limits to the anticipated metal-nitrogen stretching frequency, on account of the large mass of the other (halogens) atoms attached to the metal atom. If such types of calculations are correct as a first approximation, one may assign N-Sb stretching frequencies near the above values. Since tin and antimony are of comparable atomic weights and electronegativities (atomic weights, Sn=118.69, Sb=121.80, E.N. values, Sn=1.96, Sb=2.04)<sup>138</sup> and both have nearly the same covalent radii (Sn= $1.40\text{\AA}$ , Sb= $1.41\text{\AA}$ )<sup>160</sup> it is reasonable to expect the Sn-N stretching frequencies in the region of Sn-N.

The metal-chlorine vibrational frequencies lie in the broad range<sup>149</sup>  $650\text{--}200\text{ cm}^{-1}$  and the octahedral Sn(IV) complexes show no Sn-Cl absorptions above  $400\text{ cm}^{-1}$ . Therefore all the bands

above  $700\text{ cm}^{-1}$  in these adducts are assigned to S-N vibrations. Thus the very strong bands at  $1040$ ,  $940$  and  $800$  are assigned to S-N (no Sn-halogen or Sn-N bands are to be expected in this region, because of the above limits for Sn-N and Sn-halogen frequencies), in these adducts. The very strong bands at  $515$  and  $360\text{ cm}^{-1}$  are assigned to S-N vibrations, because  $\text{S}_4\text{N}_4$  has a ring stretching mode at  $531\text{ cm}^{-1}$  and a ring deformation mode at  $347\text{ cm}^{-1}$ <sup>161</sup>. The very strong band at  $410\text{ cm}^{-1}$  in these adducts may be (1) from the S-N ring system, as the lowering of symmetry of  $\text{S}_4\text{N}_4$  gives rise to additional bands, or (2) Sn-N ( $\text{SnCl}_4 \cdot 2\text{S}_4\text{N}_4 = 413\text{ cm}^{-1}$ ,  $\text{SnBr}_4 \cdot 2\text{S}_4\text{N}_4 = 420\text{ cm}^{-1}$ ). Several papers have appeared in the past few years dealing with the low frequency spectra of some nitrile adducts of tin tetrachloride<sup>150, 151, 152, 153, 154</sup>. There has been controversy over the assignment of the bands below  $500\text{ cm}^{-1}$  in the spectrum of  $\text{SnCl}_4 \cdot 2\text{CH}_3\text{CN}$ . Brown and Kubota<sup>153</sup> originally assigned the bands around  $400\text{ cm}^{-1}$  as Sn-Cl stretching modes, whereas those bands occurring between  $350$  and  $300\text{ cm}^{-1}$  were assigned to the asymmetric and symmetric Sn-N vibrations. Beattie<sup>151</sup> et al., however, showed that the assignments of Brown and Kubota were incorrect; they assigned the bands around  $400\text{ cm}^{-1}$  as ligand vibrations (NCC bending modes) and lower frequency bands as Sn-Cl stretching vibrations. On the basis of simple valency force field calculations, Beattie and Rule<sup>155</sup> predicted that the Sn-N stretching

frequency for  $\text{SnCl}_4 \cdot 2\text{CH}_3\text{CN}$  would occur below  $265 \text{ cm}^{-1}$ .

Aggarwal and Singh on the basis of the low frequency spectra of some amide, urea and aminobenzoic acid adducts of tin tetrachloride, reversed the assignment of Beattie et al., and support those of Brown and Kubota<sup>153</sup>. They observed a strong band in tin(IV) chloride complexes with nitrogen donors at about  $310 \text{ cm}^{-1}$ , but no band is present in this region in the tin (IV) chloride complexes with oxygen donors; had this band been due to a Sn-Cl vibration, then it should have appeared in all the complexes of tin(IV) chloride with nitrogen as well as oxygen donors.

However, Fowles<sup>150</sup> et. al., and Farona<sup>152</sup> et al., support the assignment of Beattie et al. They assigned the bands appearing in the  $300 - 370 \text{ cm}^{-1}$  region, in the spectra of all the  $\text{SnCl}_4$  adducts, but missing in the spectra of corresponding  $\text{SnBr}_4$  and  $\text{SnI}_4$  adducts, to Sn-Cl stretching modes.

In  $\text{SnCl}_4 \cdot 2\text{S}_4\text{N}_4$  there is a very strong broad band at  $308 \text{ cm}^{-1}$  with a very weak shoulder at  $319 \text{ cm}^{-1}$ . Since this band is missing in the infrared spectrum of  $\text{SnBr}_4 \cdot 2\text{S}_4\text{N}_4$ , it is reasonable to assign the band at  $308 \text{ cm}^{-1}$  to Sn-Cl stretching vibration. The medium strong bands at  $235 \text{ cm}^{-1}$  which appear in both the infrared spectra of  $\text{SnCl}_4 \cdot 2\text{S}_4\text{N}_4$  and  $\text{SnBr}_4 \cdot 2\text{S}_4\text{N}_4$ , are assigned to Sn-N. The medium strong broad band at  $219 \text{ cm}^{-1}$  in  $\text{SnBr}_4 \cdot 2\text{S}_4\text{N}_4$  is assigned to Sn-Br vibration, since a medium strong band at  $220 \text{ cm}^{-1}$

has been assigned to Sn-Br mode in the adduct  $\text{SnBr}_4 \cdot 2,2'\text{-bipyridyl}$ <sup>152</sup>. It was found to be difficult to assign the other bands appearing in the infrared spectra of  $\text{SnCl}_4 \cdot 2\text{S}_4\text{N}_4$  and  $\text{SnBr}_4 \cdot 2\text{S}_4\text{N}_4$ .

Beattie et al., have<sup>151</sup> observed one Sn-Cl stretching frequency ( $324 \text{ cm}^{-1}$ ) in the far infrared spectrum of  $\text{SnCl}_4 \cdot 2\text{py}$  and predicted a trans structure for  $\text{SnCl}_4 \cdot 2\text{py}$  whereas in  $\text{SnCl}_4 \cdot 2,2'\text{-bipyridyl}$  two bands (327 vs, br, 280 s, br) were assigned to Sn-Cl and a cis octahedral structure, was proposed. Because usually large ligands (or sterically hindered ligands) such as pyridine give trans octahedral structure, therefore since  $\text{S}_4\text{N}_4$  is also a sterically hindered ligand, the structures of  $\text{SnCl}_4 \cdot 2\text{S}_4\text{N}_4$  and  $\text{SnBr}_4 \cdot 2\text{S}_4\text{N}_4$  may be trans octahedral. However there are other bands in the far infrared spectra of these adducts, which were found to be difficult to assign and some of these bands may be due to Sn-Cl vibrations, which would then favour a cis octahedral structure for these adducts. Thus the choice between cis and trans appears to be difficult.

The Structures of  $\text{S}_4\text{N}_4 \cdot 4\text{TiF}_4$ ,  $\text{S}_4\text{N}_4 \cdot \text{TiBr}_4$ ,  $\text{S}_4\text{N}_4 \cdot \text{TiF}_4$ ,  $\text{S}_4\text{N}_4 \cdot \text{ZrCl}_4$  and  $\text{S}_4\text{N}_4 \cdot \text{HfCl}_4$ .

Titanium, zirconium and hafnium halides form a wide variety of adducts with many oxygen and nitrogen donors, e.g. ethers<sup>170</sup>, nitriles<sup>148</sup>, and amides<sup>171</sup>. These compounds are usually either 1:1 or 2:1 (base:acid) adducts, the latter are six coordinate monomers, but former may be either five coordinate monomers, or six coordinate

dimers as in the compound  $(\text{TiCl}_4 \cdot \text{POCl}_3)_2$ <sup>162</sup> Eight-  
 coordination for titanium has been established for bidentate  
 arsine complexes of titanium (IV) halides<sup>163</sup>.

The structures of  $\text{S}_4\text{N}_4 \cdot \text{TiBr}_4$ ,  $\text{S}_4\text{N}_4 \cdot \text{TiF}_4$ ,  $\text{S}_4\text{N}_4 \cdot \text{ZrCl}_4$   
 and  $\text{S}_4\text{N}_4 \cdot \text{HfCl}_4$ , adducts are expected to contain unidentate  
 $\text{S}_4\text{N}_4$ , since their spectra are similar to the infrared spectra  
 of  $\text{S}_4\text{N}_4 \cdot \text{SbCl}_5$  (major peaks at, 1058, 976, 511 and  $370 \text{ cm}^{-1}$ )  
 and  $\text{S}_4\text{N}_4 \cdot \text{BF}_3$  (major peaks at 1040, 949,  $502 \text{ cm}^{-1}$ ) in which only  
 one nitrogen of  $\text{S}_4\text{N}_4$  is used in coordination. The corresponding  
 characteristic peaks for the new adducts occur at  $\text{S}_4\text{N}_4 \cdot \text{TiBr}_4$ ,  
 1036, 963, 508,  $365 \text{ cm}^{-1}$ ; 957,  $\text{S}_4\text{N}_4 \cdot 4\text{TiF}_4$ , 1059, 985, 510  $351 \text{ cm}^{-1}$ ;  
 $\text{S}_4\text{N}_4 \cdot \text{ZrCl}_4$ , 1034, 957, 510, 368;  $\text{S}_4\text{N}_4 \cdot \text{HfCl}_4$ , 1037, 958, 515,  
 $360 \text{ cm}^{-1}$ . However, the infrared spectra of  $\text{ZrCl}_4$ ,  $\text{HfCl}_4$ ,  
 $4\text{TiF}_4$ ,  $\text{S}_4\text{N}_4$  are different from the infrared spectrum of  
 $\text{S}_4\text{N}_4 \cdot \text{SbCl}_5$  in a number of respects, while the infrared  
 spectrum of  $\text{HfCl}_4 \cdot \text{S}_4\text{N}_4$  is most like the infrared spectrum of  
 $\text{S}_4\text{N}_4 \cdot \text{SbCl}_5$ . Absorption frequencies and the outstanding  
 similarities and differences in the infrared spectra of these  
 adducts and  $\text{S}_4\text{N}_4 \cdot \text{SbCl}_5$  are given below:

$\text{S}_4\text{N}_4 \cdot \text{SbCl}_5$ : 1058 vs, 976 vs, 808 vs, 786 vs, 722 ms, 682 s, 623 vs,  
 511 vs.

$\text{S}_4\text{N}_4 \cdot \text{HfCl}_4$ : 1037 vs, 958 vs, 800 vs, 741 s, 682 s, 624 s, 415 vs  $\text{cm}^{-1}$ .

$\text{S}_4\text{N}_4 \cdot \text{ZrCl}_4$ : 1034 vs, 957 vs, 807 vs, 762 vs, 722 vs, 699 vs, 626 ms,  
 551 vs,  $510 \text{ ms cm}^{-1}$ .

$S_4N_4 \cdot TiBr_4$ : 1037, 963 vs, 829 vs, 807 s, 746 ms, 681 ms,  
621 w, 565 ms, 508  $cm^{-1}$ .

$S_4N_4 \cdot 4TiF_4$ : 1059 vs, 985 vs, 725 w, 662 vs(br), 510 ms.

Since M-X frequencies in the above metal halides lie in the broad range 650-200  $cm^{-1}$  (with exception of  $TiF_4$  highest, Ti-F = 880 w(v.br)<sup>172</sup> all the strong bands above 700  $cm^{-1}$  (except in  $4TiF_4 \cdot S_4N_4$ ) are likely to be S-N stretching frequencies. The common bands at 510 and 365  $cm^{-1}$  in these adducts are assigned to S-N, since  $S_4N_4$  has a bond stretching mode at 545 and a bond bending mode at 347  $cm^{-1}$  respectively.

In the far infrared spectrum of  $TiBr_4 \cdot S_4N_4$ , the band at 416  $cm^{-1}$  can be assigned to either  $\nu$ S-N or  $\nu$ Ti-N, by analogy with other  $S_4N_4$  adducts, in which M-N frequencies are assigned in this region (e.g.  $SnCl_4 \cdot 2S_4N_4$ , Sn-N=413  $cm^{-1}$ ).

There are a number of other peaks in the far infrared spectrum of  $TiBr_4 \cdot S_4N_4$ , which cannot be assigned with certainty.

In the far infrared spectrum of  $ZrCl_4 \cdot S_4N_4$ , the peaks at 340 vs(br) 304 ms  $cm^{-1}$  are assigned to  $\nu$ Zr-Cl, since  $\nu$  Zr-Cl frequencies are assigned in the region 299-354  $cm^{-1}$  in the addition compounds of  $ZrCl_4$ <sup>148</sup>. The infrared spectrum of  $S_4N_4 \cdot 4TiF_4$  has two peaks at 1059 and 985 which are assigned to S-N stretching vibrations. This infrared spectrum differs from the infrared spectrum of  $S_4N_4 \cdot SbCl_5$  in that there is no very strong peak at 800  $cm^{-1}$ . This may be because in  $TiF_4$  the highest metal-

fluorine frequency for  $\text{TiF}_4$  at  $880 \text{ cm}^{-1}$  may couple with the S-N stretching frequencies in this region; all the peaks in this region are probably due to the combination of S-N and Ti-F vibrations. There is broad very strong band at  $662 \text{ cm}^{-1}$  which may be assigned to Ti-F vibrations, since Ti-F stretching frequencies have been assigned in the region  $550\text{-}670 \text{ cm}^{-1}$  in  $\text{TiF}_4 \cdot 2,2'\text{-bipyridyl}$ ,  $\text{TiF}_4 \cdot 2\text{py}$ <sup>167</sup>. However Ti-N vibrations may also occur in this region, and it seems likely that the absorptions in the region  $728\text{-}615$  may be due to combination of S-N, Ti-N and Ti-F modes rather than simple group absorptions. In the far infrared spectrum of  $\text{S}_4\text{N}_4 \cdot 4\text{TiF}_4$  the band at  $283$  (vs,br) is assigned to Ti-F bending vibration, since a mode at  $280$  s(br) is assigned to Ti-F bending vibration in the infrared spectrum of  $\text{TiF}_4$ <sup>172</sup> and also because Ti-F deformations occur at  $254\text{-}311 \text{ cm}^{-1}$  in  $\text{TiF}_4$  complexes<sup>167</sup>. The medium strong band at  $370$  could be due to  $\nu$  S-N or  $\nu$  Ti-N.

In the infrared spectrum of  $\text{S}_4\text{N}_4 \cdot \text{HfCl}_4$  the very strong broad band at  $325 \text{ cm}^{-1}$  (shoulder at  $303 \text{ cm}^{-1}$ ) is assigned to Hf-Cl vibration, by analogy with other  $\text{S}_4\text{N}_4$  adducts of metal halides (e.g.  $\text{S}_4\text{N}_4 \cdot \text{ZrCl}_4$ , Zr-Cl  $340, 305 \text{ cm}^{-1}$ ).

The infrared spectrum of  $\text{TiI}_4 \cdot \text{S}_4\text{N}_4$  is weak even though the mulls were strong; the reason for this is presumably due to reduced polarity of bonds compared with the  $\text{S}_4\text{N}_4$  complexes of the other titanium halides. In the far infrared spectrum of this

there is a strong band at  $279 \text{ cm}^{-1}$  which can be assigned to Ti-I, because metal-iodine bands usually occur at lower frequencies. The commonly occurring bands at  $245 \text{ cm}^{-1}$  in all the titanium halides adducts are assigned to Ti-N (in  $\text{ZrCl}_4 \cdot \text{S}_4\text{N}_4$ ,  $\text{Zr-N} = 245 \text{ cm}^{-1}$ ).

None of the above adducts of  $\text{S}_4\text{N}_4$  with  $\text{TiBr}_4$ ,  $\text{TiCl}_4$ ,  $\text{TiF}_4$ ,  $\text{ZrCl}_4$  and  $\text{HfCl}_4$  has a sharp melting point, in fact for the most part they do not melt below  $250^\circ\text{C}$  although most of them show signs of decomposition below this temperature. These complexes have very little solubility in inert solvents, whereas solvents like water, alcohols decompose these adducts. These properties of the adducts probably indicate that they may not be pentacovalent substances but rather that they are polymeric complexes, at least some of these complexes may be polymeric.

The structures of  $\text{S}_4\text{N}_4 \cdot \text{SbCl}_5$ ,  $\text{S}_4\text{N}_4 \cdot 4\text{SbF}_5$ ,  $\text{S}_4\text{N}_4 \cdot \text{NbCl}_5$ ,  $\text{S}_4\text{N}_4 \cdot \text{NbF}_5$ ,  $\text{S}_4\text{N}_4 \cdot \text{TaCl}_5$  and  $\text{S}_4\text{N}_4 \cdot \text{TaF}_5$

As already mentioned, the X-ray structure of  $\text{S}_4\text{N}_4 \cdot \text{SbCl}_5$  is known in which  $\text{S}_4\text{N}_4$  acts as monodentate ligand. All the above adducts of  $\text{S}_4\text{N}_4$  with the pentahalides of Sb, Nb and Ta may have six coordinate structures since the infrared spectra of these adducts are similar to the infrared spectrum of  $\text{S}_4\text{N}_4 \cdot \text{SbCl}_5$ . Absorption frequencies showing the outstanding similarities and differences, in the infrared spectra of these adducts are given below:

$S_4N_4 \cdot SbCl_5$  1058 vs 975 vs 807 vs 786 vs 722 ms 682 s 623 vs 511 vs  $cm^{-1}$   
 $S_4N_4 \cdot NbCl_5$  1041 vs 987 ms 954 vs 888 ms 788 vs 750 s 680 ms 618 s 506 vs  $cm^{-1}$   
 $S_4N_4 \cdot TaCl_5$  1045 vs 957 vs 797 vs 749 s 682 ms 619 s 505 vs  $cm^{-1}$

Assignments S-N S-N S-N S-N S-N S-N S-N S-N S-N

$S_4N_4 \cdot 4SbF_5$  1058 vs 986 943 790 ms 741 ms 695 s 621 vs 512 ms  $cm^{-1}$   
 (br)

$S_4N_4 \cdot NbF_5$  1065 vs 992 vs 929 w 800 ms 722 ms 676 ms 606 vs 515 s  $cm^{-1}$   
 (br)

$S_4N_4 \cdot TaF_5$  1071 vs 996 vs 927 vs 903 ms 744 ms 700 vs 581 vs 516 w  $cm^{-1}$   
 727 w 678 ms (br)

Assignments S-N S-N S-N M-F S-N

In  $S_4N_4 \cdot SbCl_5$  the very strong bands above  $700\text{ cm}^{-1}$  are assigned to S-N (highest Sb-N =  $565\text{ cm}^{-1}$  (ca), highest Sb-Cl =  $395\text{ cm}^{-1}$  <sup>148</sup>). The very strong band at  $511\text{ cm}^{-1}$  is assigned to S-N vibration, because  $S_4N_4$  has a S-N ring stretching mode at  $545\text{ cm}^{-1}$ .

In the far infrared spectrum of  $S_4N_4 \cdot SbCl_5$  the strong band at  $411\text{ cm}^{-1}$  is either due to S-N or Sb-N vibration. The strong band at  $311\text{ cm}^{-1}$  is assigned as S-N, because  $S_4N_4$  has a ring deformation mode in this region ( $347\text{ cm}^{-1}$ ). The strong band at  $370\text{ cm}^{-1}$  is assigned to Sb-Cl since  $SbCl_5$  has Sb-Cl absorption modes in this region (Sb-Cl =  $395, 371\text{ cm}^{-1}$  in  $SbCl_5$  <sup>148</sup>). However, the bands in this region may arise due to the coupling of S-N and Sb-Cl modes. The very strong broad band at  $345\text{ cm}^{-1}$  in  $S_4N_4 \cdot SbCl_5$  is assigned to Sb-Cl, by analogy with other  $S_4N_4$  adducts, e.g.  $S_4N_4 \cdot 2SnCl_4$ , Sn-Cl =  $310\text{ vbr (sh.319)}\text{ cm}^{-1}$ . The number of other bands appearing in the far infrared spectrum of  $S_4N_4 \cdot SbCl_5$  cannot be assigned with certainty. However, it is likely that the relatively weak bands at  $308$  and  $345\text{ cm}^{-1}$  may be due to Sb-N vibrations, since the polarity of the metal-halogen bonds is higher than the metal nitrogen bonds.

The infrared active bands appearing in the region  $700\text{--}550\text{ cm}^{-1}$  in  $S_4N_4 \cdot SbCl_5$  are difficult to assign, since they may be combination bands rather than simple group absorptions.

In  $S_4N_4 \cdot NbCl_5$  and  $S_4N_4 \cdot TaCl_5$  the strong bands above  $700 \text{ cm}^{-1}$  are assigned to  $\nu \text{ S-N}$  by analogy with  $S_4N_4 \cdot SbCl_5$  (highest  $\nu \text{ Nb-Cl}$  in  $NbCl_5$  is at  $497 \text{ cm}^{-1}$  <sup>156</sup>). The strong band at  $340 \text{ cm}^{-1}$  in  $S_4N_4 \cdot NbCl_5$  is assigned to  $\nu \text{ Nb-Cl}$ , whereas the band at  $363 \text{ cm}^{-1}$  is assigned to  $\text{ S-N}$  analogy  $S_4N_4 \cdot SbCl_5$ . Similarly in  $S_4N_4 \cdot TaCl_5$  the very strong broad band at  $322 \text{ cm}^{-1}$  is assigned  $\text{ Ta-Cl}$  whereas the band at  $360 \text{ cm}^{-1}$  may be due to  $\nu \text{ S-N}$ .

In a series of related molecules, variation of metal-halogen stretching frequency with metal may depend upon several factors. However, it is at least reasonable to expect that an increase in mass of the metal will cause a decrease in  $\nu \text{ M-X}$  (M= metal, X=halogen).

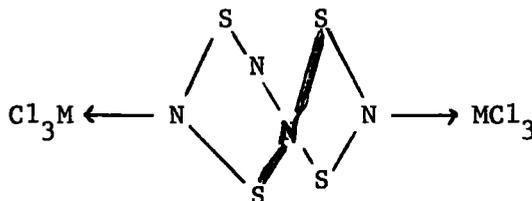
	$S_4N_4 \cdot SbCl_5$	$S_4N_4 \cdot NbCl_5$	$S_4N_4 \cdot TaCl_5$
M-X	345	340	322
( $\text{cm}^{-1}$ )			

In  $S_4N_4 \cdot 4SbF_5$ ,  $S_4N_4 \cdot NbF_5$  and  $S_4N_4 \cdot TaF_5$  the strong bands above  $800 \text{ cm}^{-1}$  are assigned to  $\nu \text{ S-N}$  (highest  $\text{ Sb-F} = 716 \text{ cm}^{-1}$  <sup>156</sup>).

In all these pentafluoride adducts there is a very strong broad band in the region  $666\text{-}526 \text{ cm}^{-1}$  ( $S_4N_4 \cdot 4SbF_5 = 627 \text{ vs}(\text{br})$ ,  $S_4N_4 \cdot NbF_5 = 606 \text{ vs}(\text{br})$ ,  $S_4N_4 \cdot TaF_5 = 581 \text{ vs}(\text{br}) \text{ cm}^{-1}$ , which may be either due to the combination of M-F, S-N and Sb-N modes or may be due to M-F mode only since M-F stretching frequencies in octahedral complexes lie in this region <sup>148</sup> (e.g.  $NbF_6^-$ ,  $\text{ Nb-F} = 585 \text{ cm}^{-1}$ ,  $TaF_6^-$ ,  $\text{ Ta-F} = 560 \text{ cm}^{-1}$ ).

The Structures of  $S_4N_4 \cdot 2AlCl_3$ ,  $S_4N_4 \cdot 2AlBr_3$ ,  $S_4N_4 \cdot 2GaCl_3$ ,  $S_4N_4 \cdot 2InCl_3$   
 $S_4N_4 \cdot 2TlCl_3$ ,  $S_4N_4 \cdot 2FeCl_3$  and  $S_4N_4 \cdot PhBCl_2$

The infrared spectra of these adducts, with the exception of  $S_4N_4 \cdot 2AlBr_3$  and  $S_4N_4 \cdot PhBCl_2$  are similar to the infrared spectrum of  $S_4N_4 \cdot SbCl_5$ . They all may have structures with monodentate  $S_4N_4$  as shown below,



The infrared frequency assignments in the near infrared spectra of these complexes can be done in exactly the same way as for  $S_4N_4 \cdot SbCl_5$ . The far infrared spectra of all these adducts are described below.

In  $S_4N_4 \cdot 2AlCl_3$  the strong band at 403 is assigned to either S-N or Al-N, whereas the band at 354 is assigned to S-N by analogy with other  $S_4N_4$  adducts. The very strong band at 324 is assigned Al-Cl, since metal-halogen frequencies in  $S_4N_4$  adducts appear in this region. The relatively weak band at  $225 \text{ cm}^{-1}$  is assigned to Al-N vibration since this band also appears in  $S_4N_4 \cdot 2GaCl_3$ , at  $228 \text{ cm}^{-1}$ ,  $S_4N_4 \cdot 2InCl_3$  and  $S_4N_4 \cdot 2FeCl_3$  also absorb in this region (high background of spectrum prevents exact location of absorption maximum)

In  $S_4N_4 \cdot 2GaCl_3$ , the bands in the broad envelope at 420, 408, 389 and  $374 \text{ cm}^{-1}$  are probably due to Ga-Cl and S-N combination modes, since gallium trichloride complexes show strong Ga-Cl bands in this region  $340-400 \text{ cm}^{-1}$  ( $\nu \text{ sym. (Ga-Cl)} = 348 \pm 2$  and  $\nu \text{ asym (Ga-Cl)} = 383 \pm 3 \text{ cm}^{-1}$ )<sup>167</sup>. The very strong bands at 297 and 267 are assigned to Ga-Cl vibrations, and the relatively weak band at  $228 \text{ cm}^{-1}$  to Ga-N vibration.

In  $S_4N_4 \cdot 2InCl_3$ , the band at  $361 \text{ cm}^{-1}$  is assigned to  $\nu$  S-N, whereas the band at  $314 \text{ cm}^{-1}$  to  $\nu$  In-Cl. The strong band at 403 may be due to either the In-N or to S-N vibrations.

In  $S_4N_4 \cdot 2FeCl_3$  the very strong band (broad) with peaks at 384 and  $370 \text{ cm}^{-1}$  is probably a combination band due to the coupling of S-N and Fe-Cl modes ( $S-N = 354 \text{ cm}^{-1}$ , Fe-Cl in  $FeCl_4^- = 385 \text{ cm}^{-1}$ <sup>156</sup>). The band at  $308 \text{ cm}^{-1}$  is assigned to

Fe-Cl analogy with other  $S_4N_4$  adducts. The adducts  $S_4N_4 \cdot 2AlCl_3$ ,  $S_4N_4 \cdot 2GaCl_3$ ,  $S_4N_4 \cdot 2InCl_3$ ,  $S_4N_4 \cdot 2TlCl_3$  and  $S_4N_4 \cdot 2FeCl_3$  are all soluble in inert organic solvents (e.g.  $CH_2Cl_2$ ) indicating that they probably are covalent structures rather than ionic structures of the type  $(S_4N_4 \cdot MX_2)^+ MX_4^-$ .

For  $S_4N_4 \cdot PhBCl_2$ , few assignments can be made on account of the large number of additional bands due to the phenyl group. However the far infrared spectrum of the adduct is relatively simple and similar in many respects to other  $S_4N_4$  adducts of group III halides (e.g.  $S_4N_4 \cdot 2AlCl_3$ ). By analogy with other

adducts, it may have a structure with monodentate  $S_4N_4$ .

In the far infrared spectrum of  $S_4N_4 \cdot PhBCl_2$  the strong band at 420 is either due to S-N or B-N vibration. The strong bands at  $360 \text{ cm}^{-1}$  is assigned to S-N as usual. The strong bands at 314 and 282 are assigned to B-Cl by analogy with other  $S_4N_4$  adducts, ( $BCl_2$  assym. deformation =  $330 \text{ cm}^{-1}$ ,  $BCl_2$  sym. deformation  $230 \text{ cm}^{-1}$ )<sup>47a</sup>.

The structure of  $S_4N_4 \cdot 2AlBr_3$  appears to be different from the above adducts, since the infrared spectrum is different (Table 2). The low solubility and relatively high melting point of this adduct indicates that it may have an ionic structure of the type  $(S_4N_4 \cdot AlBr_2)^+ \cdot AlBr_4^-$ . The near infrared spectrum shows three strong peaks at 1126, 869 and 473 in addition to other weak peaks. Since in the complex  $AlBr_3 \cdot Et_2O$ , the band at  $445 \text{ cm}^{-1}$  has been assigned to Al-Br stretching mode<sup>171</sup>, the band at 438 in  $S_4N_4 \cdot 2AlBr_3$  is assigned to  $\nu$  Al-Br. The very strong bands at 1126 and  $869 \text{ cm}^{-1}$  are assigned to S-N. In the far infrared spectrum of this adduct a strong band at  $349 \text{ cm}^{-1}$  can be assigned to Al-Br (cf. Al-Br in  $BrCN \rightarrow AlBr_3$  absorbs at 341 and  $445 \text{ cm}^{-1}$ ).

The structures of  $S_4N_4 \cdot TeCl_4$  and  $S_4N_4 \cdot SeCl_4$

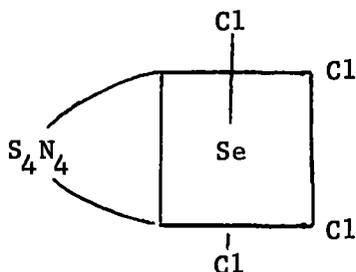
The infrared spectrum of  $S_4N_4 \cdot TeCl_4$  is similar to the infrared spectrum of  $S_4N_4 \cdot SbCl_5$ , as shown below:

$S_4N_4 \cdot SbCl_5$  1058 vs, 975 vs, 807 vs, 786 vs, 722 ms, 682 s, 651 w, 623 vs,  
563 w, 511 vs  $cm^{-1}$ .

$S_4N_4 \cdot TeCl_4$  1047 vs, 966 vs, 806s, 760vs, 727 vw, 671ms, 635ms, 613ms, 563 w,  
SN 500 vs,  $cm^{-1}$ .

In the far infrared spectrum of  $S_4N_4 \cdot TeCl_4$ , there are only three bands, two strong and broad bands at 360 and 251  $cm^{-1}$  and a weak band at 225  $cm^{-1}$ . The very strong broad band at 360 may be due to combination of S-N and Te-Cl modes since both  $TeCl_4$  and  $S_4N_4$  have strong absorption bands in this region ( $TeCl_4$ ; 358 vs and 347 vs  $cm^{-1}$  168,169;  $S_4N_4$ , 347 s 161) or it may only be due to S-N vibration. The broad band in the region 22-286  $cm^{-1}$  centred at 251  $cm^{-1}$  is probably caused by Te-Cl and Te-N vibrations.

The assignment of frequencies in the near infrared spectrum of  $S_4N_4 \cdot TeCl_4$  can be done in the same way as in the case of  $S_4N_4 \cdot SbCl_5$ . The structure of  $S_4N_4 \cdot SeCl_4$  may be either six coordinate as in  $SeCl_4$  ethylenediamine<sup>145</sup> or ionic as in  $SeCl_4 \cdot 2py$ <sup>138</sup>.



Its insolubility in inert organic solvents may indicate an ionic structure. In their discussion of the infrared spectrum of  $SeCl_4$ ,

George, Katsaros and Wynne<sup>169</sup> concluded that the available vibrational data are in accord with the presence of  $\text{SeCl}_3^+$  spectra in solid  $\text{SeCl}_4$  but are inconclusive regarding the nature of the anionic species. Since the far infrared spectrum of  $((\text{CH}_3)_4\text{N})_2\cdot\text{SeCl}_6$  yields absorptions at 294 and 184  $\text{cm}^{-1}$  which are absent in  $\text{S}_4\text{N}_4\cdot\text{SeCl}_4$ , it seems more likely that  $\text{S}_4\text{N}_4\cdot\text{SeCl}_4$  has an ionic structure of the type  $(\text{S}_4\text{N}_4\cdot\text{SeCl}_3)^+\text{Cl}^-$ . In the far infrared spectrum of  $\text{S}_4\text{N}_4\cdot\text{SeCl}_4$ , the bands at 383 is assigned to  $\overset{\text{an}}{\text{S-N}}$  vibration, because  $\text{S}_4\text{N}_4$  has S-N bonding mode at 347  $\text{cm}^{-1}$  which may have shifted to 383  $\text{cm}^{-1}$  on coordination, or it may be due to the coupling of Se-Cl and S-N modes. The band 403  $\text{cm}^{-1}$  may be an additional S-N band due to coordination or it may be due to Se-N vibration. The solid  $\text{SeCl}_4$  shows absorption bands at: 371 vs, 348 vs, 275 s, medium strong (broad) and 205 weak, therefore, the bands at 337 s, 309 s and medium strong bands broad in the region 260-217  $\text{cm}^{-1}$  are assigned to Se-Cl vibrations.

The structures of  $\text{S}_4\text{N}_4\cdot\text{WBr}_4$ ,  $\text{S}_4\text{N}_4\cdot\text{WCl}_4$  and  $\text{S}_4\text{N}_4\cdot\text{WOCl}_4(?)$

The halides  $\text{WX}_4$  (X= halogen) form a number of complexes of the type  $\text{WX}_4\cdot 2\text{L}$  (L=monodentate: pyridine, RCN, dimethyl sulphoxide<sup>173</sup>) and  $\text{WX}_4\cdot\text{L}$  (L= bidentate: 2,2'-bipyridyl)<sup>173</sup>.

The complexes are obtained either from the tetrahalides or from higher halides.

The infrared spectra of  $S_4N_4 \cdot WBr_4$  and  $S_4N_4 \cdot WCl_4$  are different from the infrared spectrum of  $S_4N_4 \cdot SbCl_5$ . By virtue of the chelating nature of the ligand and on account of the tendency for  $WCl_4$  and  $WBr_4$  to achieve six coordination, the adducts  $S_4N_4 \cdot WBr_4$  and  $S_4N_4 \cdot WCl_4$  may have six coordinate structures, with bidentate  $S_4N_4$  (cf.  $MX_4 \cdot 2,2'$ -bipyridyl).

The infrared spectrum of the complex obtained from  $S_4N_4$  and  $WOCl_4$  shows some similarity with the infrared spectra of  $S_4N_4 \cdot WBr_4$  and  $S_4N_4 \cdot WCl_4$  (major peak at  $1000$  ( $vs$ )  $cm^{-1}$ ).

This compound may be  $S_4N_4 \cdot WOCl_4$  (but with structure different from  $S_4N_4 \cdot SbCl_5$ ) or, since  $WOCl_4$  is easily reduced,  $S_4N_4 \cdot WOCl_3$ . The structure of the latter may be similar to  $WOX_3 \cdot 2,2'$ -bipyridyl complexes<sup>147</sup> (formed in reactions of the oxytetrahalides of tungsten with bipyridyl, and which contain six coordinate tungsten).

In the far infrared spectrum of  $S_4N_4 \cdot WCl_4$ , the band at  $406$   $cm^{-1}$  may be due to either S-N or W-N vibration. The strong broad band in the region 286-385 is probably caused by W-N and S-N vibrations ( S-N (deformation) =  $347$   $cm^{-1}$  in  $S_4N_4$ <sup>161</sup>,  $\nu$  W-Cl (stretching) =  $355$   $cm^{-1}$ ). Similarly in  $S_4N_4 \cdot WBr_4$  the band at  $405$   $cm^{-1}$  may be due to either S-N or W-N vibrations and the absorptions in the region 270-357 may be due to combinations of S-N and W-Br modes.

The preparation and reactions of trithiazyl trichloride

Baumgarten<sup>174</sup> has reported that pyridine reacts with sulphuryl chloride to give a complex oil product, which was thought to be  $(C_5H_5NCl)SO_2Cl$  and  $(C_5H_5NCl)_2SO_2$ . This reaction has been repeated by Banister and Moore<sup>128</sup> and obtained an oily product of the formula  $(C_5H_5N)_2SO_2Cl_2$ , irrespective of the mole ratio of the reactants. By analogy with the above reaction, it was decided to study the Lewis acid behaviour of sulphuryl chloride towards tetrasulphur tetranitride. It was found that in this case, no adduct is formed but sulphuryl chloride slowly acts as a chlorinating agent to give trithiazyl trichloride (page 70). This is not surprising, because sulphuryl chloride is used as a chlorinating agent in a number of reactions, e.g.  $Ph_3As + SO_2Cl_2 \rightarrow Ph_3AsCl_2$ <sup>175</sup>.

Trithiazyl trichloride may be prepared by the method described by Demarcay<sup>127</sup> and Meuwsen<sup>103</sup> and revised by Schroder and Glemser<sup>117</sup>, of passing chlorine through a suspension of  $S_4N_4$  in an inert solvent or by the method described by Meuwsen<sup>103</sup> and revised by Jolly and Maguire<sup>104</sup> involving the chlorination of the solid  $S_3N_2Cl_2$ . Jolly and Maguire prepared  $S_3N_3Cl_3$ , with a melting point of  $91^\circ C$ , from  $S_3N_2Cl_2$  and chlorine, while Schroder and Glemser reported a melting point of  $162.5^\circ C$  for the  $S_3N_3Cl_3$  prepared from  $S_4N_4$  and chlorine. Trithiazyl trichloride obtained from the

reaction of sulphuryl chloride and  $S_4N_4$  closely resembles that of Jolly and Maguire. This compound has a melting point of  $89-91^{\circ}C$  (decomp.) before recrystallisation, whereas the recrystallised  $S_3N_3Cl_3$  melted at  $93-94^{\circ}C$ . It has been proposed<sup>91</sup> that this lowering of melting point is not principally due to depression of melting point by significant amounts of impurities, but is decomposition catalysed by small amounts of impurities.

We also prepared trithiazyl trichloride from  $S_4N_4$  and chlorine by the method described previously<sup>117</sup>, but observed that the infrared spectrum of the product varies remarkably with the experimental conditions. The simplest infrared spectrum (below) is obtained if the chlorination of  $S_4N_4$  is carried out under the following conditions:

(i) large volume of the inert solvent in which  $S_4N_4$  is suspended or dissolved.

(ii) slow rate of chlorination

(iii) short time or chlorination until all the  $S_4N_4$  is dissolved; filter as soon as a clear red solution is obtained.

If the volume of the solvent in which  $S_4N_4$  is suspended is small and the rate of chlorination is fast and for a longer time after the stage when a clear red solution is obtained, the reaction gives a product which even after recrystallisation from carbon tetrachloride has a much more complex infrared spectrum. (see section (ii) below)

The compound obtained by slow chlorination (of  $S_4N_4$  suspension or dilute solution) melted at  $89-91^\circ C$  (recryst.  $CCl_4$ ). The infrared spectrum of this compound was similar to the infrared spectrum of the trithiazyl trichloride prepared from  $S_4N_4$  and  $SO_2Cl_2$ ; though the peak  $1015\text{ cm}^{-1}$  was broader than for the latter. This was almost certainly due to difference in particle size in the mull. The crystalline form is identical to the  $S_4N_4/Cl_2$  product as studied by Wiegers and Vos<sup>107,108</sup>.

Sample system	Wiegers monoclinic (from $S_4N_4/Cl_2$ )	Hazell <sup>176</sup> monoclinic ( $S_4N_4/SO_2Cl_2$ )
a	$5.55 \text{ \AA} \pm .01$	$5.54 \text{ \AA}$
b	$11.23 \text{ \AA} \pm .02$	$11.14 \text{ \AA}$
c	$6.13 \text{ \AA} \pm .01$	$6.13 \text{ \AA}$
$\alpha$	90	90
$\beta$	$99.2^\circ \pm .2$	99.5
$\gamma$	90	90
Space group	$P2_1/m$	$P2/m$
	or $P2_1$	or $P2_1$
mols/cell	2	2

The infrared spectrum of  $S_3N_3Cl_3$  obtained from  $S_4N_4 + Cl_2$  (slow chlorination) or  $S_4N_4 + SO_2Cl_2$  showed the following peaks:  $1018\text{ vs}$ ,  $698\text{ ms}$ ,  $621\text{ w(br)}$ ,  $(514\text{ ms}$ ,  $488\text{ ms})\text{ (br)}$ ,  $380\text{ w}$ ,  $320\text{ w (br)}$ .

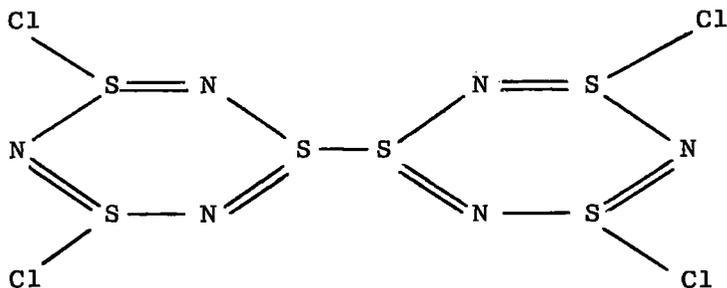
The highest frequency absorption at  $1018 \text{ cm}^{-1}$  is assigned to an S-N stretching frequency, the highest bands in other SN systems occur at:  $1325 \text{ cm}^{-1}$  (NSCl)<sup>93</sup>,  $1153 \text{ cm}^{-1}$  ( $\text{S}_4\text{N}_3\text{Cl}$ )<sup>133</sup>,  $1085 \text{ cm}^{-1}$  ( $\text{S}_3\text{N}_3\text{F}_3$ )<sup>97</sup>,  $925 \text{ cm}^{-1}$  ( $\text{S}_4\text{N}_4$ )<sup>161</sup>. The higher S-N stretching frequency in  $\text{S}_3\text{N}_3\text{Cl}_3$  compared with  $\text{S}_4\text{N}_4$  is expected on account of the higher S-N bond order (sulphur-nitrogen bond) distances are:  $1.60\text{\AA}$  in  $\text{S}_3\text{N}_3\text{Cl}_3$ <sup>107,108</sup> and  $1.62\text{\AA}$  in  $\text{S}_4\text{N}_4$ <sup>30</sup>). The medium strong band at  $698 \text{ cm}^{-1}$  is probably a stretching rather than a bending mode ( $\nu$  (stretching in  $\text{S}_4\text{N}_4$  is at  $696 \text{ cm}^{-1}$ , the highest frequency bend  $\nu$  (deformation) is at  $347 \text{ cm}^{-1}$ ), whereas the weak (broad) band at  $621 \text{ cm}^{-1}$  cannot be assigned with certainty, because S-Cl and S-N modes appear in this region<sup>156</sup>. The medium strong broad band in the region  $526-477 \text{ cm}^{-1}$  with peaks at  $514$  and  $488 \text{ cm}^{-1}$  may be assigned to S-Cl stretching, because S-Cl stretching in NSCl is assigned at  $414 \text{ cm}^{-1}$ <sup>93</sup>. In the far infrared spectrum of  $\text{S}_3\text{N}_3\text{Cl}_3$  (from  $\text{S}_4\text{N}_4$  and  $\text{SO}_2\text{Cl}_2$ ) the weak band at  $380 \text{ cm}^{-1}$  is assigned to S-N bending mode by analogy with  $\text{S}_4\text{N}_4$  (S-N deformation) =  $347 \text{ cm}^{-1}$  whereas the weak broad band centred at  $320 \text{ cm}^{-1}$  is assigned to NSCl ( $\nu$  NSCl (bending) =  $273 \text{ cm}^{-1}$ )<sup>93</sup>.

Mass spectrum of  $\text{S}_3\text{N}_3\text{Cl}_3$

m/e	relative intensity	assignment
32	43	S
46	262	SN
64	100	$\text{S}_2$

m/e	relative intensity	assignment
78	240	$S_2N$
92	372	$S_2N_2$
138	242	$S_3N_3$
174	150	$S_3N_3Cl$
210	170	$S_3N_3Cl_2$

(ii) The rapid chlorination of  $S_4N_4$  with chlorine gave a product which apparently contains a new compound. Chlorine gas was bubbled at a very fast rate through  $S_4N_4$  suspension in carbon tetrachloride and at room temperature (page 72). This compound was prepared twice, but each time the analytical figures were different (page 72) and it was not possible to give definite formula for this compound. However it appears to consist of  $S_3N_3Cl_3$  and a compound containing two cyclotrithiazyl rings as shown below (analytical figures correspond to a 2:3 mixture);



The outstanding difference in the isolation procedure is that this product precipitates out; (this is not just because the reaction solution is stronger; similar quantities of  $S_4N_4 + CCl_4$  solution were used as in the usual  $(NSCl)_3$  preparation).

A relatively large number of extra peaks appear in the infrared spectrum and these are retained on crystallisation. The infrared spectrum is different from  $S_3N_3Cl_3$ , the comparison is given below,

$S_6N_6Cl_4$  : 1011 vs, 943 w(sh), 893 ms(sh), 781 w(sh), 699 w(sh)  
 687 vs, 671 vw(sh), 662 vs, 625 vw(sh), 576 ms, 546 vs,  
 517 w(sh), 504 ms, 452 ms(br)  $cm^{-1}$ .

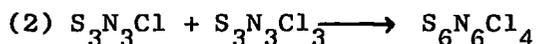
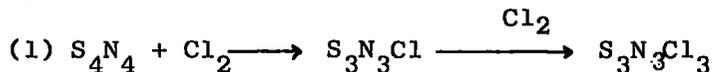
$S_3N_3Cl_3$  (from  $S_4N_4/SOCl_2$ ) : 1018 vs, 698 ms, 621 w(br), (514 ms, 488 ms)  
 (br)  $cm^{-1}$ .

All the bands above  $680\text{ cm}^{-1}$  are assigned to S-N stretching vibrations, by analogy with  $S_3N_3Cl_3$  and other sulphur nitrogen compounds (p.139 ). The medium strong broad band at  $452\text{ cm}^{-1}$  may be assigned to  $\nu S-S$  because S-S modes appear in the region  $400-500\text{ cm}^{-1}$ <sup>177</sup>. The strong band 546 is probably due to S-Cl stretching mode. The strong band at 662 cannot be assigned with certainty.

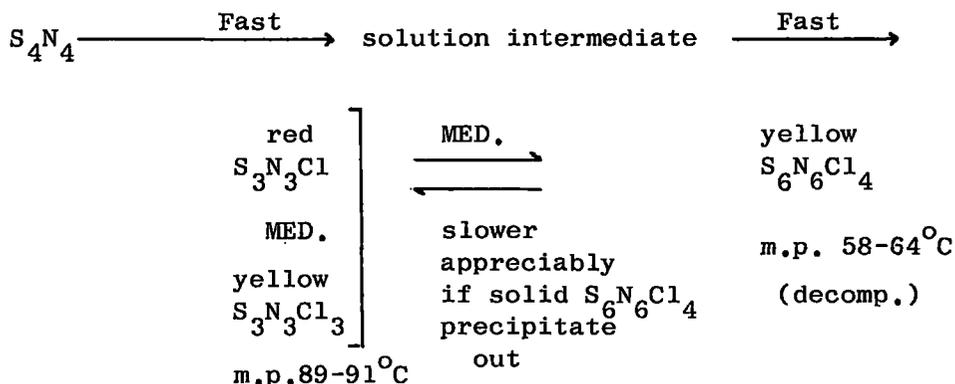
(iii) Trithiazyl trichloride and  $Cl_2$  or CO:-

When trithiazyl trichloride obtained from  $S_4N_4$  and  $SO_2Cl_2$  was dissolved in a large volume of  $CCl_4$  and chlorine gas was slowly bubbled through the solution, it was observed from the infrared spectrum of the evaporated product that  $S_3N_3Cl_3$  does not undergo any further change. However, the compound tentatively proposed as  $S_6N_6Cl_4$  is the major product in a reaction of  $S_3N_3Cl_3$  (from  $S_4N_4/SO_2Cl_2$ ) with carbon monoxide, giving a small amount of  $S_4N_3Cl$ .

The mechanism of the formation of  $S_6N_6Cl_4$  appears to be complex, but may be as follows<sup>178</sup>.



the formation of  $S_6N_6Cl_4$  may well depend upon a build up of concentration of  $S_3N_3Cl$  or some other incompletely chlorinated sulphur-nitrogen species as follows:



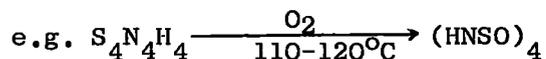
Reactions of trithiazyl trichloride (from  $S_4N_4$  and  $SOCl_2$ ):

(a) Attempted preparation of sulphanuric chloride from trithiazyl trichloride

The preparation of sulphanuric chloride involves the isolation and pyrolysis of the extremely hygroscopic trichlorophosphazosulphuryl chloride<sup>179</sup>. The trichlorophosphazosulphuryl chloride does not pyrolyse to give sulphanuric chloride if the sample is impure. Alternatively sulphanuric chloride can be obtained in a very poor yield by heating the pale yellow adduct of  $S_3N_3Cl_3$  with

6  
sulphur trioxide.

Since  $(\text{NSCl})_3$  is a relatively simple preparation the synthesis of sulphauric chloride by the oxidation of trithiazyl trichloride was attempted. The use of  $\text{SeO}_2$  and  $\text{I}_2\text{O}_5$  as the oxidising agents were unsuccessful, because in each case the oxidising agent gave a new reaction product, which (from the i. r. spectrum) was not sulphauric chloride. Trithiazyl trichloride did not undergo any oxidation, when a mixture of molecular oxygen and ozone was bubbled through a solution in  $\text{CCl}_4$  at room temperature or at  $60^\circ\text{C}$ . Failure of trithiazyl trichloride to undergo direct oxidation with molecular oxygen is in contrast to the reaction that occurs with other sulphur nitrogen compounds



(b) Reaction of trithiazyl trichloride with diphenyl mercury and pyridine

$\alpha$ -Sulphauric chloride reacts with diphenylmercury to form diphenylsulphauric chloride,  $\text{N}_3\text{S}_3\text{O}_3\text{Cl}(\text{C}_6\text{H}_5)_2$ <sup>180</sup>. It was thought to prepare the analogous compound  $\text{S}_3\text{N}_3\text{Cl}(\text{Ph})_2$  by the reaction of trithiazyl trichloride with diphenyl mercury. However, it was found that diphenyl mercury gives an adduct with  $\text{S}_3\text{N}_3\text{Cl}_3$  ( $\text{S}_3\text{N}_3\text{Cl}_3 \rightarrow \text{Hg}(\text{Ph})_2$ ).

By analogy with the reaction of sulphauric chloride with pyridine<sup>128</sup>, it was decided to study the reaction between the trithiazyl trichloride and pyridine. Trithiazyl trichloride reacted with pyridine to give a pale yellow solid. The infrared

spectrum showed retention of the SN ring, shifts in the frequencies were slight. The exact stoichiometry is not established on account of variable analyses (p. 77 )

The above two reactions exhibiting the donor and acceptor behaviour of trithiazyl trichloride.

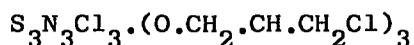
(c) Reaction of trithiazyl trichloride with epibromohydrin, epichlorohydrin, ethylene oxide and butylene oxide

Peters and Kharasch<sup>181</sup> have studied the reaction between sulphuryl halides and epoxides e.g. ethylene oxide reacts with 2,4-dinitrobenzenesulphenyl chloride to give  $\text{Cl}\cdot\text{CH}_2\cdot\text{CH}_2\text{OSC}_6\text{H}_5$ . Since trithiazyl trichloride reacts vigorously with alcohols (not reported in experimental section) to give complex mixtures, it was hoped that epoxides would give trithiatriazene esters without ring cleavage. Epibromohydrin, epichlorohydrin, ethylene oxide, butylene oxide all apparently gave the required compounds. Epibromohydrin and epichlorohydrin gave white solid compounds whereas red oil products were obtained in the case of ethylene oxide and butylene oxide.

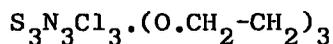
The infrared spectra of these compounds are given below,

$\text{S}_3\text{N}_3\text{Cl}_3(\text{O}\cdot\text{CH}_2\text{CHCH}_2\text{Br})_3$  : 1429 vw, 1370 vs, 1299 vw, 1266 vw, 1235 vw, 1220 vw, 1205 vw, 1176 vw, 1104 vw, 1047 w(sh), 1036 vs, 1011 s, 990 vs, 962 s, 952 s(sh), 901 w(sh), 885 vs, 870 s, 855 vw(sh), 848 vw (sh), 826 vs, 781 ms, 769 vs, 746 s, 719 vs,

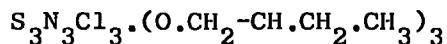
694 s, 685 s, 667 s, 637 ms, 623 ms, 617 w  
(sh), 597 s, 564 ms, 532 vw, 526 vw, 516 vw,  
504 ms, 489 ms, 435 ms, 423 s, 4000 vw(sh),  
388 vs, 361 s, 348 w, 323 ms, 274 vw, 253 w,  
240 ms cm<sup>-1</sup>.



1342 vw, 1290 vw, 1258 vw, 1250 vw, 1212 vw,  
1188 vw, 1149 vw, 1099 vw, 1053 vw(sh), 1036 vs,  
1020 s, 990 vs, 962 vs, 901 vw(sh), 885 vs,  
855 s(sh), 833 vs, 787 w(sh), 775 vs, 763 vw(sh),  
730 vs, 709 vw, 699 ms, 676 s, 658 s, 570 s,  
544 s, 521 vw(sh), 513 s, 495 ms, 442 ms,  
428 s, 408 ms, 392 s, 377 s, 347 s, 331 ms,  
276 s, 258 ms, 245 s, 227 ms(br), 216 vw,  
213 vw cm<sup>-1</sup>.



1453 vw(sh), 1430 w, 1379 vw, 1307 ms, 1258 vw  
(sh), 1198 vw, 1136 vw(sh), 1042 vs, 995 vs,  
876 vs, 855 vs, 766 w(sh), 722 w(sh), 707 vs,  
667 vs, 536 vw, 392 ms cm<sup>-1</sup>.



1471 ms, 1439 vw(sh), 1372 vw(sh), 1370 w,  
1312 w, 1252 vw, 1205 vw, 1042 vs, 980 vw(sh),  
957 vs, 917 s, 866 s, 791 vs, 741 s(br),  
694 vw(br), 673 vs(br), 556 vw, 420 ms, 402 vw,  
395 vw, 387 vw cm<sup>-1</sup>.

The assignment of the infrared active bands in these compounds cannot be done with certainty because S-N vibrational modes occur in the same region in which epoxides give absorption bands e.g. in ethylene oxide the bands at 1165, 1265 and 865 are associated with the epoxy group<sup>182</sup>.

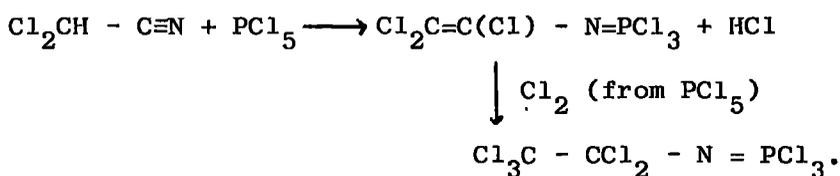
(d) Reaction of trithiazyl trichloride with nitriles

It was considered<sup>125</sup> that trithiazyl trichloride is likely to react in (at least) three ways: (i) as a sulphenyl chloride,  $\text{RSCl}$ , i.e. as an acid chloride of the hypothetical acid  $(\text{NS-OH})_3$  (see ref. 183 for a review of sulphenyl halide reactions). (ii) as a source of  $\text{N}\equiv\text{S-Cl}$  at temperatures sufficiently high to cause significant dissociation:  $\text{S}_3\text{N}_3\text{Cl}_3 \rightleftharpoons 3\text{NSCl}$ . The thiazyl chloride monomer should then be able to copolymerise with other unsaturated systems containing CC, CN or CS multiple bonds, and (iii) reaction with X-H bonds (elimination of HCl).

Olefins can react in all three ways, chlorinated olefins as (i) and (ii); consequently the reaction between trithiazyl trichloride and tetrachloro ethylene was studied in some more detail by Banister<sup>125</sup>; a compound of empirical formula  $\text{S}_2\text{N}_2\text{C}_2\text{Cl}_4$  was isolated.

The first reaction in the nitrile series, viz. the reaction between trithiazyl trichloride and trichloroacetonitrile was

initially performed to check if a reaction of the type (ii) above were possible. It was also hoped that the product(s) obtained from  $S_3N_3Cl_3$  and trichloroacetonitrile might shed some light (e.g. by comparing infrared spectra) on the  $S_3N_3Cl_3/C_2Cl_4$  reaction. A fully chlorinated nitrile was chosen because of the possibility of complications arising due to simultaneous reactions of type (iii), e.g.<sup>184</sup>



(a) Reaction between  $S_3N_3Cl_3$  and  $Cl_3C.CN$

Trithiazyl trichloride ( $S_4N_4/SO_2Cl_2$ ) was found not to react with  $S_3N_3Cl_3$  at room temperature; a reaction temperature of  $60^\circ C$  was chosen by analogy with the reaction between  $S_3N_3Cl_3$  and  $C_2Cl_4$ <sup>125</sup>. The reaction solution slowly undergoes colour changes from green to pale yellow to red and a yellow crystalline product was obtained which was found to be identical to the  $S_2N_2C_2Cl_4$  obtained from  $S_3N_3Cl_3/C_2Cl_4$  (page 85). The colour change which may be ascribed to the intermediate formation in solution of monomeric thiazyl trichloride does not/<sup>seem</sup>very likely since (i) the bright green colour of the solution and (ii) perceptible dissociation in vacuum commences at  $70-80^\circ C$ <sup>91</sup>.

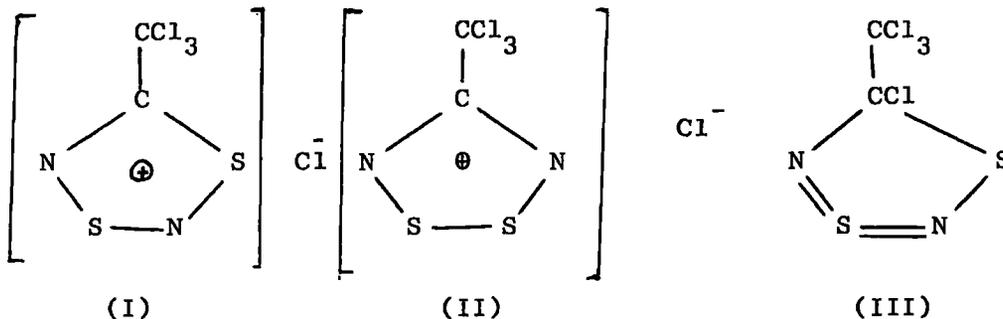
This agrees with the proposal that monomeric thiazyl chloride does not form in solution unless at high temperatures (above 70°C)<sup>91</sup>. Analyses are given below (same batch of compound analysed at Durham).

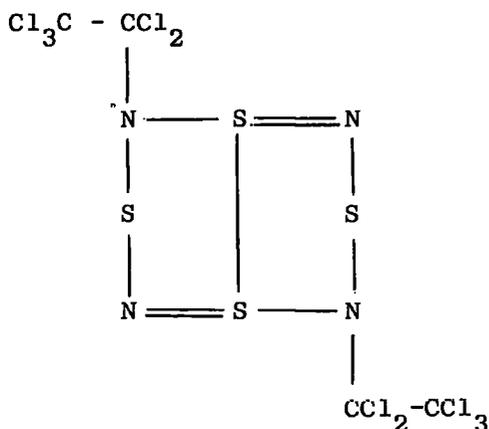
	Found		Calculated		
	anal.1	anal. 2.	S <sub>2</sub> N <sub>2</sub> C <sub>2</sub> Cl <sub>4</sub>	S <sub>2</sub> N <sub>2</sub> C <sub>2</sub> Cl <sub>5</sub>	S <sub>2</sub> N <sub>3</sub> C <sub>2</sub> Cl <sub>5</sub>
C	9.59	9.99	9.53	8.19	7.81
Cl	55.89	52.80	55.04	60.34	57.72
N	11.60	10.85	10.85	9.54	13.66
S	24.75	21.98	24.80	21.81	20.81
Total	101.83	86.28			

Structure and the infrared spectrum of S<sub>2</sub>N<sub>2</sub>C<sub>2</sub>Cl<sub>4</sub>

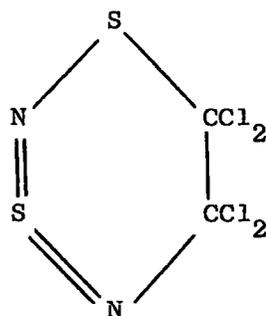
The m.p.(decomp. above 100°C) and the infrared spectrum of this compound is identical to the infrared spectrum of the product of the S<sub>3</sub>N<sub>3</sub>Cl<sub>3</sub> and C<sub>2</sub>Cl<sub>4</sub> reaction (M.P. 205-208 decomp.)

The following structures are proposed on the basis of the information discussed below:





(IV)



(V)

Structure (IV) suffers from the disadvantage that it is difficult to see how it could arise from  $\text{S}_3\text{N}_3\text{Cl}_3/\text{C}_2\text{Cl}_4$ . Similarly it does not seem likely that structure (V) could arise from  $\text{S}_3\text{N}_3\text{Cl}_3/\text{Cl}_3\text{CCN}$ . The infrared spectrum shows no localized C=N ( $1630-1690 \text{ cm}^{-1}$ )<sup>182</sup> or C=C peaks ( $1620-1645 \text{ cm}^{-1}$ )<sup>185</sup> unless the absorptions happen to be very weak (C=N and C=C absorptions are often weak). The doublet at  $1302$  and  $1270 \text{ cm}^{-1}$  is intermediate in frequency between that expected for a C-N single bond ( $1100 \text{ cm}^{-1}$ ) and a C=N double bond ( $1600$  to  $1700 \text{ cm}^{-1}$ )<sup>42</sup> and so could be ring vibration(s) predominantly associated with CN stretching.

In view of the low solubility of  $\text{S}_2\text{N}_2\text{C}_2\text{Cl}_4$  in non-polar (or low polarity) organic solvents and very low volatility (it cannot be sublimed in vacuum until  $100^\circ\text{C}$  and then decomposition occurs), the ionic structure appears to be more likely.

Such a structure is analogous with the structures of  $S_3N_2Cl_2$ <sup>6</sup> and 4-phenyl-1,2-dithiolium iodide,  $S_2C_3PhI$ .<sup>187</sup>

Further evidence for a structure containing a  $CCl_3$  group comes from a study of the infrared spectrum of this compound.  $\nu_{sym} CCl_3$  and  $\nu_{asym} CCl_3$  in  $Cl_3C.CN$  occur at 787 and 491  $cm^{-1}$  respectively<sup>188</sup> and peaks approximately in these positions (781 and 483  $cm^{-1}$ ) occur in  $S_2N_2C_2Cl_4$ . The strong band in the region 833-741  $cm^{-1}$  is assigned to  $\nu_{sym} CCl_3$  by analogy with trichloroacetonitrile. Similarly the medium strong broad band in the region 500-465 centred at 483 with shoulders at 495 and 471  $cm^{-1}$  is assigned to  $\nu_{sym} CCl_3$ . The very strong band at 1052  $cm^{-1}$  may be due to either S=N or C-N since trichloroacetonitrile absorbs in this region ( $\nu C-C = 1000 cm^{-1}$ )<sup>189</sup>. The strong band at 543  $cm^{-1}$  cannot be assigned with certainty.

(b) Reaction between  $S_3N_3Cl_3$  and  $Bu^tCN$

Trithiazyl trichloride was found not to react with tertiarybutyl cyanide at room temperature (for 24 hours). A 58°C reaction temperature was chosen by analogy with the  $Cl_3CCN$  reaction, a golden yellow precipitate was obtained (page 84). The analytical figures are given on page 151, (same batch of compounds).

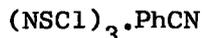
Found		Calculated	
anal.1 (at Durham)	anal.2 (Weiler & Strauss)	$S_2N_2C(CH_3)_3Cl$ , $S_2N(CH_3)_3Cl_2$ , $S_2N_2C_2(CH_3)_3Cl_2$	$S_2N_2C(CH_3)_3Cl$ , $S_2N(CH_3)_3Cl_2$ , $S_2N_2C_2(CH_3)_3Cl_2$
C	28.90	29.39	25.86
H	3.79	4.34	3.88
Cl	33.10	16.25	30.60
N	11.37	9.37	12.04
S	31.85	26.55	27.58
Total	109.01	85.90	26.02

It is likely that this compound is  $S_2N_2C_2(CH_3)_3Cl$ , by analogy with  $S_2N_2C_2Cl_4$  and similar structures can be considered for this compound. The infrared spectrum shows some similarity with the infrared spectrum of  $S_2N_2C_2Cl_4$  (the peaks at 543, 676 and  $855\text{ cm}^{-1}$  in  $S_2N_2C_2Cl_4$  also appear in the presumed  $S_2N_2C_2(CH_3)_3Cl$  at 551, 733, and  $855\text{ cm}^{-1}$ ). The peak at  $733\text{ cm}^{-1}$  may be due to S-N, while the peak at  $551\text{ cm}^{-1}$  cannot be assigned with certainty.

(c) The reaction between  $S_3N_3Cl_3$  and benzonitrile

Trithiazyl trichloride was found not to react with benzonitrile at room temperature. The reaction at about  $60^\circ\text{C}$  gave four products two of which (products 2 and 3, page 88) proved to be the same. The first product settles down from the red solution during reaction and has an infrared spectrum similar to products 2 and 3 but with extra peaks in the region  $794\text{--}767\text{ cm}^{-1}$ , which are lost on recrystallisation from PhCN or  $SOCl_2$  (though the latter recrystallisation gives additional absorption at  $510\text{ cm}^{-1}$ ). Thus after recrystallisation from PhCN product 1 is the same as product 2 (the crystals that collect near the filter frit during reaction) and product 3 (the crystals that deposit on cooling the filtrate). Products 1 (recrystallised 1'), 2 and 3 do not give satisfactory analyses but i.r. similarities (two absorptions between  $910$  and  $833\text{ cm}^{-1}$  one  $\sim 552\text{ cm}^{-1}$  and one near  $700\text{ cm}^{-1}$ ) to the  $Cl_3CCN$  and  $(CH_3)_3CN$  products suggest similar structures for these three compounds.

Product 4 was obtained from the filtrate (left after filtering the product 3) by evaporation to dryness. A dark-yellow precipitate was obtained which was recrystallised from  $\text{CCl}_4$  or  $\text{CH}_2\text{Cl}_2$ . After recrystallisation the compound was pale yellow and analyses (page 88) correspond to an empirical formula:



The infrared spectrum of this compound was different from other products (1 and 2). An 8-membered ring is proposed for this compound by analogy with  $(\text{NSF})_4$ .

Numerous C-H absorptions occur between  $1660\text{-}740\text{ cm}^{-1}$  as in PhCN, though the strong absorptions at  $1342, 1179, 910\text{ cm}^{-1}$  may indicate superimposed CN and/or SN. The strong peaks at  $701$  and  $790$  are probably the characteristic peaks associated with mono-substituted benzene derivatives (usually at  $694\text{-}701\text{ cm}^{-1}$  (CH deformation) and  $758\text{-}747\text{ cm}^{-1}$  (CC stretching)<sup>185,189</sup>. The single absorption in the region  $588\text{-}500\text{ cm}^{-1}$  is replaced by four:  $525, 493, 473, 419\text{ cm}^{-1}$ . SCl may be responsible for one or more of these.

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Calculations of force constants

Gordy's rule:- A relation of the form,

$$k = aN (X_A \cdot X_B / d^2)^{\frac{3}{4}} + b$$

has been found to hold accurately for a large number of molecules in their ground states. Here  $k$  is the bond stretching force constant,  $d$  the bond length,  $N$  the bond order, and  $X_A$  and  $X_B$  are the electronegativities of the bonded atoms.  $k$  is measured in dynes/cm  $\times 10^{-5}$  and  $d$  in Angstrom units,  $a$  and  $b$  have the values 1.67 and 0.30 respectively, for stable molecules exhibiting their normal covalencies, except those in which both bonded atoms have only one electron in their valency shell.

Thus since  $N-Sb = 2.17\text{\AA}$

$$X_A(N) = 3.07 \text{ (Allred-Rochow)}$$

$$X_B(Sb) = 1.82 \text{ (Allred-Rochow)}$$

$$\text{and } N = 1$$

Therefore, the (N-Sb) force constant =

$$\begin{aligned} & 1.67 (3.07 \times 1.82 / 2.17^2)^{\frac{3}{4}} + 0.30 \\ & = 2.2 \times 10^5 \text{ dyne/cm.} \end{aligned}$$

$$\text{Now } \nu_{Sb-N} = 1303.16 ( \lambda )^{\frac{1}{2}}$$

$$\text{Where } \lambda = \frac{\text{force constant}}{\text{reduced mass}} = \frac{k}{\mu}$$

$$\left( \mu = \frac{m_1 m_2}{m_1 + m_2}, \text{ where } m_1 \text{ and } m_2 \text{ are atomic weights of N(14.007) \right. \\ \left. \text{ and Sb(121.75) respectively).} \right.$$

$$\begin{aligned} \text{Sb-N} &= 1303.16 \text{ (2.2 x 0.07959)} \\ &= \underline{545 \text{ cm}^{-1}} \end{aligned}$$

Similarly using the values of electronegatives of 3.04 for nitrogen and 2.05 for antimony (Pauling-type values), a value of 565  $\text{cm}^{-1}$  was obtained for <sup>the</sup> Sb-N stretching frequency.

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