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ELECTROSYNTHETIC AND OTHER STUDIES OF SULFUR IMIDES AND AROMATIC THIAZENES

by

H.G. CLARKE, B.Sc.

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

September 1974

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Acknowledgments

The author wishes to express his gratitude to Dr. A.J. Banister, under whose supervision this research was carried out, for his unflagging enthusiasm, constant interest and valuable advice throughout the whole period of study.

My thanks are also due to the Science Research Council and Staveley Chemicals Limited for providing a research grant, to the Senate of the University of Durham for research facilities, to many of the departments technical staff and to Dr. O.R. Brown of Newcastle University, for assistance in the research, and to Staveley Chemicals Limited for valuable industrial experience.

Finally, my thanks are due to Mrs. Janet Dunford, for the many hours spent in typing this thesis.

Memorandum

The work described in this thesis was carried out in the University of Durham between September 1970 and September 1973, apart from:-

(i) a period in December 1970 at Newcastle University, studying the electrolytic reduction of tetrasulfur tetranitride in organic solvents, and

(ii) three months between July and September 1972 at Staveley Chemicals Limited (See Chapter 8).

The work described in this thesis has not been submitted for any other degree and is the original work of the author, except where acknowledged by reference. Parts of this thesis have been the subjects of the following publications:-

1. Banister, A.J., and Clarke, H.G.
"The Preparation of Cyclopentathiazenium ($S_5N_5^+$) Salts and some Observations on the Structure of the Cyclopentathiazenium Cation".
J. Chem. Soc. Dalton, 1972, 23, 2661.
CA. 1973, 78, 23432s.

2. Zahradnik, R., Banister, A.J., and Clarke, H.G.
"Electronic Spectrum of the Pentathiazyl Cation".
Collect. Czech. Chem. Communs., 1973, 38, 998.
CA. 1973, 79, 36830r.

3. Banister, A.J., and Clarke, H.G.
"Preparation of Cyclopentathiazenium ($S_5N_5^+$) Salts".
Inorganic Synthesis (in press).

4. Banister, A.J., Clarke, H.G., Raimant, I., and Shearer, H.M.M.
"The Structure of Thiodithiazyl Chlorodisulfate, ($S_3N_2\ S_2O_6Cl$), and its Preparation from Thiodithiazyl Monochloride, S_3N_2Cl".
J. Inorg. Nuclear Chem. (in press)

To my Mother and Father

"Great are the works of the Lord,

studied by all who have pleasure in them".

Psalm 111, v.2

Abstract

This thesis describes the work carried out by the author between September 1970 and September 1973.

The electrolysis products of sulfur and S_4N_4 in liquid ammonia, and S_4N_4 in organic solvents were studied with a view to devising improved routes to S_7NH, $S_4(NH)_4$ and other imides. The reactions of these two compounds as model sulfur imides were also investigated.

Addition reactions of $(NSCl)_3$ were studied because it is the cheapest source of SN and NSCl fragments, and because it was hoped to convert the imides into SN compounds with exocyclic S-Cl bonds. It was found that $(NSCl)_3$/metal chloride adducts behaved as a source of NS^+ ions in thionyl chloride solution, which reacted with SCl_2 and S_4N_4 to form the cations $S_2NCl_2^+$ and $S_5N_5^+$ respectively. The structures of these two cations were discussed, in particular the structure and reactions of $S_5N_5^+$ as a member of the "electron rich" aromatic series of sulfur-nitrogen compounds. Other as yet unknown species were predicted as also being members of this series, and their possible stability and preparative routes discussed.

A study was also carried out on the little investigated compound "S_3N_2Cl". The chlorodisulfate derivative:- $S_6N_4^{2+}(ClS_2O_6^-)_2$ - was prepared, and the structure (obtained from x-ray crystallographic studied) discussed with reference to the unusual bonding observed in this compound.

Finally, a summary of the work carried out at Staveley Chemicals Limited is included.

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INTRODUCTION

CHAPTER 1

Introduction

The introductory chapter to this thesis is rather longer than would be normal, since it includes reviews on a large number of sulfur-nitrogen compounds, most of which have been studied in this thesis. A background knowledge of their properties and reactions is of value in understanding their role in the reactions described in the remainder of the thesis. Since sulfur-nitrogen-fluorine, sulfanuric halides and related compounds, have not been studied in this thesis, they are only referred to in passing. Overlap with the remaining chapters of the thesis is kept to a minimum by cross-referencing.

The introductory review is based on information available up to August 1973, with some additions made prior to submission for typing.

S_4N_4 reviews have been written by Allen,[1] Becke-Goehring,[2,3,4] Christopher,[5] Emeléus,[6] Goehring,[7] and Heal.[8,9] Sulfur-nitrogen halogen compounds have been reviewed by Glemser,[10,11,12,13] and sulfur-nitrogen reviews have also been written by Allcock,[14] Becke-Goehring,[15] Gmelin,[16] Glemser,[17] Haiduc,[18] and Schmidt.[19]

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(A) Tetrasulfur Tetranitride S_4N_4

1. Physical Properties

Tetrasulfur tetranitride (S_4N_4) is formed as monoclinic crystals,[20,21] of density 2.20–2.23 g/cc,[16,22] whose colour varies with temperature. It is nearly colourless at -190^oC, bright yellow at -30^oC, orange-yellow at room temperature (20^oC), orange-red at 100^oC and dark red at higher temperatures.[23] The colour changes above room temperature have been attributed to the Boltzman effect.[24] Crystals of S_4N_4 have the property of being birefringent, with refractive indices of 1.908 and 2.046.[25]

S_4N_4 usually melts between 178^o and 179^oC,[7,21,22,26] however, by repeated recrystallisations from benzene, or by purification on an alumina chromatographic column, melting points as high as 187^o–187.5^oC have been obtained.[26] The main impurity is usually sulfur, which is formed during the preparations of S_4N_4, and which depresses the melting point.[22] S_4N_4 is potentially explosive due to its endothermic nature. (Standard heat of formation $\Delta Hf^o = + 110.0 \pm 2.0$ K.cal.mole^{-1} = 460 ± 8 KJ mole^{-1}).[27] It can detonate on shock or on heating above 195^oC, and so should be handled with care, especially since its sensitivity towards shock and temperature increases with purity.[26] S_4N_4 can be sublimed at 100^oC and 10^{-3}mm mercury pressure.[21]

S_4N_4 has a dipole moment of 0.52 (benzene) and 0.72 (CS_2) (Debye units).[28] However, by correcting for atomic polarisation (from the comparison with S_8), the true dipole moment must be much less than 0.5D, and is probably zero, as required by the symmetry of the structure.[23,28] S_4N_4 has a molar susceptibility $\chi = -102 \times 10^{-6}$/mole which is considered as evidence of a diamagnetic ring current.[24]

S_4N_4 can be purified by chromatography using dried alumina or silica gel as the column adsorbent, and benzene, carbon tetrachloride[29] or carbon disulfide[30] as elutant. (See experimental section, Chapter 2).

S_4N_4 is air stable, and is insoluble and not wetted by water, but is soluble in a wide range of organic solvents.[16,22]

e.g.	Solvent	Solubility moles/1000g solvent					
	Dioxane	18°C	0.20	60°C	0.23[22,31]		
	CS_2	0°C	0.0155	30°C	0.0573 [22]		
	Benzene	0°C	0.0137	30°C	0.0526	60°C	0.121
	Ethanol	0°C	0.0043	20°C	0.0072	50°C	0.0116

Tetrasulfur tetranitride is also appreciably soluble in liquid ammonia,[32,33,34] in which it forms an ammoniate of composition: S_4N_4, $2NH_3$.[33,35,36] It is identical to the ammoniate formed by S_2N_2[36,37] and has been formulated as H.N:S:N.S.NH_2. The solutions of S_4N_4 in ammonia are fairly strong electrolytes.[32] (See Chapter 3, S_4N_4 in liquid ammonia).

The ultraviolet,[24,38] visible,[24] near[31] and far infrared,[39] Raman[31,39] and ^{14}N nmr[23] spectra for S_4N_4 have been recorded. (See also section on S_4N_4 structure, this Chapter). Ultraviolet and visible spectrum:[24]

ν max.(kK)	ε max.	Assignment	Comments
~ 24.5	est. 250	$B_2^2 \rightarrow B_1^1$	Vibronic shoulder
~ 30.6	est. 1000-2000	$A_1^1 \rightarrow B_1^1$ (or $B_2^2 \rightarrow B_1^{1a}$)	Shoulder
38.9	19000	$B_2^2 \rightarrow E^2$	Very broad
~ 40.0	~ 5500	σ -system	Shoulder
> 54.0	> 6000	σ -system	Off scale

Infrared and Raman spectra

The infrared and Raman spectra of S_4N_4 have been assigned.[39] There are 14 vibrational fundamentals for the D_{2d} structure of S_4N_4. Two of these are inactive both in the Raman and infrared, the remaining 12 being Raman active while 7 are also infrared active. Weak combination tones have also been assigned.

^{14}N nmr. spectrum[23]

The ^{14}N nmr. spectrum of S_4N_4 is a single signal (showing that all four nitrogens are equivalent) with a chemical shift of +485 $\pm$ 220 ppm., from saturated aqueous nitrite ion. The value is much nearer the shifts observed for singly bonded S-N compounds (530-540 ppm.), than the range of 200-300 ppm. observed for thiazenes such as $S_4N_3^+$.[23]

2. Preparative routes

Tetrasulfur tetranitride is formed in a wide variety of reactions, and a number of new preparative routes have recently been described ((ii) to (vii) below). The original synthesis from sulfur dichloride and ammonia[40] is probably still the best (see (i) below).

(i) Preparation from sulfur dichloride and ammonia

In the methods described by Jolly,[26] Becke-Goehring,[41] and Rougier,[42] sulfur monochloride (S_2Cl_2) is mixed with dry carbon tetrachloride or chloroform,[42] and a stream of chlorine gas passed into the solution while stirring, until the solution is saturated with the gas. This conversion to $S\ Cl_2$ improves the yield. The flow of chlorine is then stopped, and ammonia gas passed into the solution, maintaining the mixture below 50°C. After about 2 hours, the mixture is filtered, the filtrate washed with water, and allowed to dry. The tetrasulfur tetranitride is extracted with dioxane or benzene, using a Soxhlet extractor, the S_4N_4 crystallising out on cooling the solution.

The reactions may be summarised:-

$$6S\ Cl_2 + 16NH_3 \longrightarrow S_4N_4 + 2S + 12NH_4Cl$$

$$6S_2Cl_2 + 16NH_3 \longrightarrow S_4N_4 + 8S + 12NH_4Cl$$

The reaction mechanism is still in some doubt, and S_7NH is also formed in small amounts during the reaction. By varying the conditions of the reaction, and the state of the starting materials,[43] the proportions of S_4N_4 to S_7NH and their respective yields can be varied. Continuous passage of ammonia does not affect the proportion of the two, but higher temperatures favour S_4N_4 and lower temperatures S_7NH. The reaction of S_2Cl_2 with aqueous ammonia solution has been studied.[44] (See Chapter 2, experimental section, preparation of S_7NH). S_7NH is the main product, but S_4N_4 is also formed in lower yields together with other imides, the relative proportions depending upon temperature, solvent and duration of reaction. The products may be separated chromatographically.[29,43,44,45]

Selenium and tellurium nitrides can also be prepared by the reaction between ammonia and the respective halides, but with modifications imposed by their lower stability.[46]

The mechanisms for the reactions involved in the preparations are complex, but probably involve the formation of various 'SNH' fragments. These first form a gummy residue,[44] and then rearrange to give the various stable compounds (S_4N_4, S_7NH, other sulfur imides, sulfur and some polymeric sulfur nitride), the relative proportions depending upon the conditions employed.

(ii) Preparation from S_2Cl_2 and Ammonium chloride

A similar preparation involving the reaction between S_2Cl_2 vapour and ammonium chloride has been described.[47]

S_2Cl_2 vapour was passed over hot ammonium chloride, and the vapours condensed. S_4N_4 was formed in yields of 12 to 26% (based on S_2Cl_2) together with $S_3N_2O_2$ and traces of S_2N_2. The reaction may be summarised -

$$6S_2Cl_2 + 4NH_4Cl \longrightarrow S_4N_4 + 8S + 16HCl.$$

The reaction between thionyl chloride vapour ($SOCl_2$) and sulfur and ammonium chloride, gives good yields of $S_3N_2O_2$.[47]

This preparative route for S_4N_4 requires very little attention and very little solvent manipulation,[47] however, the yields are low and the extraction and purification rather difficult.

(iii) Preparation from azides and S_2Cl_2 or S_4N_3Cl

Preparations of S_4N_4 based on the reactions of S_2Cl_2 or S_4N_3Cl with azides have been described.[48,49,50]

When S_4N_3Cl is added to excess, freshly prepared $Al(N_3)_3$ in THF, S_4N_4, together with nitrogen and $AlCl_3$, is formed in high yield (85 to 90%),[48] and with LiN_3, a 70% yield of S_4N_4 is obtained.

S_4N_4 is also formed when S_2Cl_2 is added to a stirred suspension of LiN_3 in benzene, carbon tetrachloride or methylene dichloride at 20°C, although S_4N_3Cl is the main product.[50] This suggests that the reaction may proceed via $S_2(N_3)_2$ and SN radicals.[50] For example:-

$$4LiN_3 + 2S_2Cl_2 \longrightarrow [2S(N_3)_2] + 4LiCl$$
$$[2S_2(N_3)_2] \longrightarrow S_4N_4 + 4N_2$$
$$3S_4N_4 + 2S_2Cl_2 \longrightarrow 4S_4N_3Cl$$

Activated sodium azide[51] has been used instead of aluminium or lithium azide with S_4N_3Cl to prepare S_4N_4, but the yield was very low.[49]

These preparations are simple to carry out, and give good yields of S_4N_4 from S_4N_3Cl (which can easily be prepared from $S_3N_2Cl_2$[52]). The main difficulties are the explosive nature and commercial unavailability of the azides used.

(iv) Preparation from ammonia and sulfur fluorides

S_4N_4 has been prepared in good yields by the reaction of ammonia with sulfur fluorides.[53,54] At -95°C, SF_4 reacts instantaneously with ammonia in a static system to form S_4N_4 in up to 70% yields, (presumably based on SF_4).

i.e. $$12SF_4 + 64NH_3 \longrightarrow 3S_4N_4 + 2N_2 + 48NH_4F$$

The yields of S_4N_4 are reduced to 15 to 40% at higher temperatures (-45° to +160°C).

The reaction of SF_4 with ammonia probably proceeds initially by simple metathesis to form NSF, and then the NSF reacts with ammonia to form S_4N_4, probably through NS$^{\bullet}$ radicals as intermediates.[53] S_2F_{10} and excess ammonia also form S_4N_4,[55] as do S_2F_2 and ammonia, although in this case the reaction is very complex. With SF_6 and ammonia, no S_4N_4 is formed.

The yields from these preparations are good, and the preparations are fairly simple to carry out, however, the methods are of little practical importance since the sulfur fluorides are expensive and due to the considerable risk of an explosion during the preparations.

(v) Preparation of S_4N_4 from its elements

S_4N_4 can be formed when active nitrogen (produced by an electrical discharge) reacts with sulfur or sulfur compounds.[56] With sulfur vapour, S_4N_4 and at least two other sulfur nitrides were formed. There was a marked induction period before any nitrides were formed, and not all the atomic nitrogen was converted into products. This was explained by a mechanism in which the NS$^{\bullet}$ radical was formed in the initial reactions, and rapidly destroyed in the presence of excess nitrogen atoms.

This method is not a suitable preparative route to S_4N_4, since a great deal of effort is required to obtain little product. The reaction of active nitrogen with S_2Cl_2 also produces $(NSCl)_3$ and traces of S_4N_4.[57,58]

(vi) Preparation of S_4N_4 using liquid ammonia

S_4N_4 is formed from solutions of sulfur in liquid ammonia, by the addition of silver salts to the solution, to precipitate out the insoluble Ag_2S.[33,34,59,60] (See Chapter 2, this thesis).

(vii) Other reactions producing S_4N_4

S_4N_4 is formed in small amounts in many other reactions involving sulfur nitrogen compounds. The thermal decomposition of the sulfur imides S_7NH, 1,3 and 1,4 $S_6(NH)_2$, and the nitrides $S_{11}N_2$ (fused ring), $S_{15}N_2$, $S_{16}N_2$ and $S_{17}N_2$ (coupled rings) produces some S_4N_4 on thermal decomposition,[61] as does $S_4(NH)_4$.[62] S_4N_4 is also produced in the preparation of sulfur imides from sulfur chlorides and ammonia.[41,43,44]

S_4N_4 is produced in high yields by the reaction:

$$3S_4(NH)_4 + 4(NSCl)_3 \longrightarrow 6S_4N_4 + 12HCl$$ [63]

but since $S_4(NH)_4$ can only be prepared from S_4N_4 in yields of about 40%,[64] the reaction is of no preparative significance, and none of the above reactions are regarded as preparative routes, due to the low yields and poor availability of the starting materials.

3. The Structure of Tetrasulfur Tetranitride

(i) Introduction

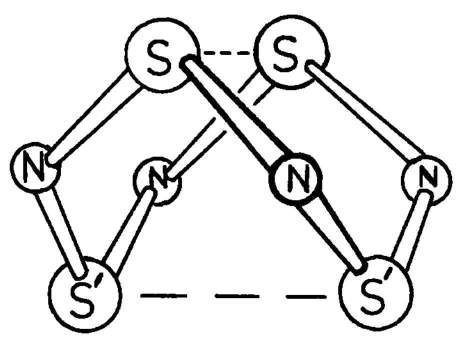
Tetrasulfur tetranitride was first prepared by Gregory in 1835,[65] and the correct formula was established by 1896.[66,67,68]

The structure was in dispute until 1963.[69] Many workers were misled in formulating a structure for S_4N_4, by classical valence theory, which demanded that nitrogen should be trivalent and sulfur di-, quad- or hexavalent. Hydrolysis reactions implied that two sulfur atoms were in the +2 oxidation state, and two in the +4 state.[70] Many unlikely structures were therefore proposed, based both on chains[22,71,72] and rings.[16,73,74,75] Goehring showed that all four sulfur atoms are equivalent,[76] x-ray emission data supported this,[77] and therefore sets of resonance structures were proposed,[7,20] based on an 8-membered ring structure. The shape of the ring was disputed, Lu and Donohue suggested a square of nitrogen atoms and tetrahedral sulfur atoms[78] whereas others suggested the reverse.[31,73]

Jaeger reported that the structure consisted of two interpenetrating bispheroids of sulfur and nitrogen atoms,[79] but these results were questionable.[80] Lindquist showed that the structure could be written without the use of resonance forms, and suggested the existence of S-S bonds,[81] but the structure was eventually finalised by Sharma,[69] and is the accepted structure today. S_4N_4 consists of a square of coplaner nitrogen atoms and a tetrahedron of sulfur atoms. The S-S distance (2.58 Å) is much shorter than the sulfur Van der Wall's diameter (ca. 3.7 Å [82]), but longer than the S-S single bond distance (2.04 Å [83]), implying considerable transannular interactions. (Figure 1.1)

Figure 1.1

S_4N_4



NSS = 90°
NSN = 105°
SNS = 113°
S···S = 2.58 Å
S-N = 1.61 Å
S···S^1 = 2.69 Å (mean values)

The visible, ultraviolet[24,84] infrared, Raman[31] and ^{14}N nmr. spectra[23] have been shown to be consistent with the structure, as have molecular orbital calculations,[85,86] hydrolysis reactions with acids and alkalis,[87] and oxidation by chloramine-T[88,89] (see following discussion on bonding).

(ii) Bonding in S_4N_4

Once the structure of S_4N_4 had been established, the problem was to rationalise its electronic structure, and despite the large number of papers published, this problem has still to be finally resolved.

From a study of cyclic $p\pi - d\pi$ systems and $p\pi - d\pi$ delocalisation in cyclophosphazenes, Craig[90,91] suggested that S_4N_4 is forced to adopt the observed structure, by the formation of weak bonds between p_z orbitals of alternate sulfur atoms which automatically equalised the $d\pi - p\pi$ interactions and bond lengths. Lindquist considered the S-S bonds to be single σ bonds with pure p character.[81] This was based on the NSS angle being close to 90°.

Braterman[24] rationalised the electronic spectra in terms of a molecular orbital scheme involving weak S-S bonding, using standard Hückel-type treatment. The sulfur d-orbitals were also included in the structure. S-S bonding was shown to be necessary to account for the properties of the molecule.

Turner and Mortimer also carried out molecular orbital calculations on S_4N_4 and derived ions, using extended Huckel molecular orbital calculations and including 2s and 2p-type orbitals on nitrogen and 3s, 3p and 3d-type orbitals on sulfur.[85,92] They concluded that:

(a) The structure found by Sharma[69] is to be preferred over one involving coplaner sulfur atoms.

(b) Appreciable S-S bonding between sulfur atoms on the same side of the plane defined by the four nitrogen atoms is to be expected.

(c) Negative ions of S_4N_4 ($S_4N_4^{n-}$, n=1 to 4)[93] should exist and exhibit π-electron delocalisation.

(d) The sulfur d-orbitals are a contributing but not a main factor in describing the electronic structure.

(e) There is no bonding between nitrogen atoms. (This was contrary to previous calculations by Chapman and Waddington[94]).

Bragin and Evans[39] have assigned the infrared and Raman spectra of solid S_4N_4. Excellent agreement was observed with calculated values. (See section on physical properties of S_4N_4).

The ^{14}N nmr. spectra[23] showed that all four nitrogen atoms are equivalent (as expected from the structure). The single peak was observed at +485 ± 20 ppm. (from saturated aqueous nitrite ion). The signal was at unexpectedly high fields, and is much nearer that for single S-N bonds (530-540 ppm.) than for delocalised systems (e.g. for $S_4N_3^+$, lines are observed at 241 and 229 ppm.)[95] This was rationalised in terms of the highly symmetrical nearly spherical structure of S_4N_4, in comparison to the planar thiazenes.

Gleiter[86] treated S_4N_4 as a planar 8-membered S-N ring with a 12π electronic system orthogonal to the σ system, which then undergoes a Jahn-Teller distortion due to the triplet ground state predicted for the planar model. The structure of lowest energy therefore formed was shown to correspond to the accepted structure of S_4N_4, with two transannular S-S bonds. The sulfur d-orbitals do not contribute significantly to the structure. The structure of S_4N_4/Lewis acid adducts was also rationalised.

The bond energy of the S-N bond in S_4N_4 was estimated as 72 K cal/mole, 301 KJ/mole.[96] This is intermediate between the single and double S-N bond energies of 59 and 80 K cal/mole respectively.[96] The corresponding bond length is also intermediate, implying bond delocalisation in S_4N_4.

Cassoux and co-workers[97] investigated the electronic structure of S_4N_4 within the framework of the C NDO/2 approximation. It appears to be composed of three highly delocalised "islands" as defined by Dewar in the case of cyclophosphazines,[98] where there exists a system of weakly interacting 3-centre π bonds, embracing two phosphorus and a central nitrogen atom. Each phosphorus atom uses two $d\pi$ orbitals, which interact with the nitrogen p-orbital. The shape of S_4N_4 was said to be due to strong spatial interactions between non-bonded sulfur atoms, and for this reason, the S_4N_4 molecule was referred to as "inorganic" cyclo-octatetraene".[97] This comparison seems to be rather dubious, since whereas S_4N_4 is a delocalised system, cyclo-octatetraene contains four localised double and four localised single bonds, and the shapes of the molecules are only superficially similar, as there is no transannular bonding in cyclo-octatetraene.

Mingos[99] has adopted a different approach in considering the structures of S_4N_4 and other similar cage and cluster compounds. He used correlations which have been discussed by Wade[100] who noted that boranes (Bn Hm) and carboranes (C_2 Bn-2 Hm) with (n+1) skeletal electron pairs and n-skeletal atoms adopt the shapes of closed polyhedra with triangular faces. In particular, the following polyhedra are adopted for closoboranes with five to eight carbon and boron atoms: trigonal bipyramid (5), octahedron (6), pentagonal bipyramid (7), and dodecahedron (8). If the structures are held together by (n+2) electron pairs, atoms adopt nido structures, and arachno structures with (n+3) electron pairs.

Mingos extended this theory to rationalise the structures of electron-precise and electron-rich polyhedra, and ring compounds. Electron-precise polyhedra have just the correct number of electron pairs to form two centre two-electron bonds along all the edges of the relevent polyhedron, and an electron-rich polyhedron has more electron pairs than those necessary for forming two centre two-electron bonds along all the edges. Electron-deficient polyhedra, such as the boranes and carboranes discussed by Wade,[100] have insufficient electron pairs for forming two centre two-electron bonds along all the edges.

Mingos assumed that: "each electron pair in excess of that required for an electron-precise polyhedra will result in the breaking of one of the edge bonds". This assumption resulted from a very localised view of the bonding in this type of molecule which suggests that each edge bond has a well defined bonding and antibonding molecular orbital, and that the latter is occupied in the electron-rich polyhedra.

Mingos used this theory to rationalise the structures of several cage compounds, including S_4N_4. He assumes that S_4N_4 consists of 14 electron pairs. (Each nitrogen contributes three bonding electrons, and each sulfur four bonding electrons, giving a total of 14 electron pairs; in addition, each atom has one non-bonding pair of electrons).

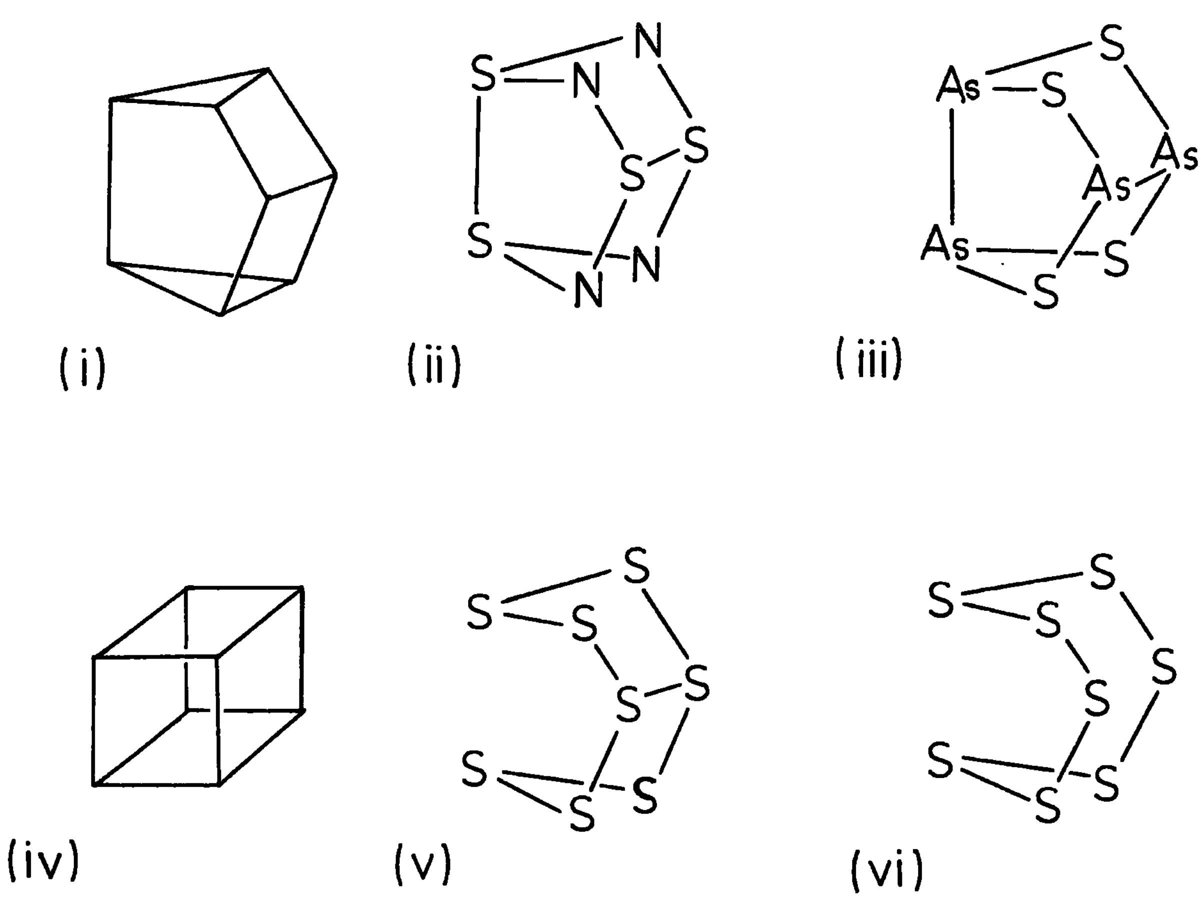
electronic structures:

				2s	2p		
N	:	He	+	↑↓	↑ ↑ ↑		= lone pair + 3 e's
				3s	3p	3d	
S^*	:	Ne	+	↑↓	↑ ↑ ↑	↑	= lone pair + 4 e's

Since S_4N_4 contains eight skeletal atoms, and fourteen electron pairs, it is based on a polyhedra with eight corners. Mingos defines the polyhedron as cuneane, (Figure 1.2(i)) with ten edges, requiring two edge bonds to be broken, although he does not explain why a cube, (with twelve edges requiring the breaking of one edge bond), is not a possibility. (Figure 1.2(iv)).

He assumes that in the cuneane structure, the bonds that are broken are perpendicular in S_4N_4(ii), whereas they are parallel in the related structure of As_4S_4(iii). (The structure described by Mingos for S_4N_4 contains N-N bonds and is incorrect,[69] however this feature was later corrected[101] and does not alter his argument.) Since the submission of Mingos' article a second (β) form of As_4S_4 has been described[102] in which the molecular packing is different although the molecular shapes are the same, the space groups being $\underline{P}2_1/n$ and C2/C for the α and β forms respectively.

Figure 1.2



On the basis of his theory Mingos concludes that S_8^{2+} and S_8 (15 and 16 "skeletal electron pairs" respectively) should adopt the endo, endo configuration shown in Figure 1.2(v) and (vi). The observed structures are exo, endo and exo, exo respectively. Mingos suggested that the difference in energy between the various arrangements is small and that solid state forces determine the actual configuration adopted. On the other hand it has been shown[103] that there are two distinct S_8^{2+} cations in $S_8(AsF_6)_2$ occupying different lattice sites. The authors commented that the close similarity of the two S_8 rings suggests that their conformation is the most stable one for the ion and is not forced by the exigencies of crystal packing. This is further supported by the very similar shape of Se_8^{2+} in $Se_8\ (Al\ Cl_4)_2$.[104]

A later paper by Banister[101] also bases the structures of S_4N_4 and other cage compounds on polyhedra, but disagrees with Mingos' interpretation. Banister proposed that:[101]

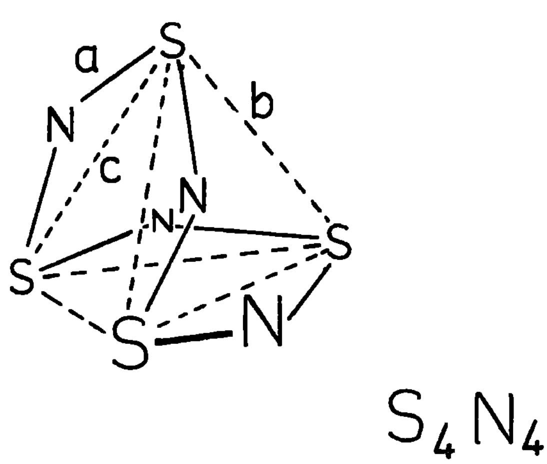
(i) "Many unsaturated flat or cluster compounds can, at a simple level, be regarded as being composed of a σ-bonded molecular framework, with a superimposed set of higher energy electron pairs in relatively delocalised molecular orbitals", (as distinct from Mingos' localised molecular orbitals).

(ii) "Two-co-ordinate sulfur consistently provides two electrons for the σ-bonds and one of the two "lone pairs" on each sulfur atom, interacts with sulfur (empty) d-orbitals to give, as in the Huckel species,[105,106] S_2N_2, $S_4N_3^+$, $S_5N_5^+$, two further bonding electrons of higher energy. Owing to their partial d character, the stability of these latter electrons, and consequently their bonding power decreases with diminishing positive charge on sulfur", (since increases in positive charge causes contraction of d-orbitals, and hence better overlap).[107]

(iii) "The σ-bonded molecular framework is flexible, and will tend to adopt a shape such that the maximum number of the constituent atoms occupy corner positions of a polyhedron of shape compatible with the number of higher energy bond pairs, and with the number and symmetry of the available atomic orbitals not involved in the σ -framework".

The structure of S_4N_4 was rationalised in terms of a total of fourteen bond pairs of electrons. Eight of these bond pairs can be allocated to the sulfur-nitrogen σ -framework, leaving six pairs of higher energy, a number appropriate for the S_4 tetrahedron, similar to P_4. These can be treated as six electron-pair bonds along the tetrahedron edges. Thus S_4N_4 is based on a tetrahedron rather than on a cuneane structure, and is consistent with six S-S distances, (2 x 2.58 Å and 4 x 2.69 Å), which are shorter than Van der Waal's contact for sulfur atoms (3.64 Å in solid S_4N_4), so that there appears to be interaction between all four sulfur atoms, and not just between two pairs. (Figure 1.3)

Figure 1.3

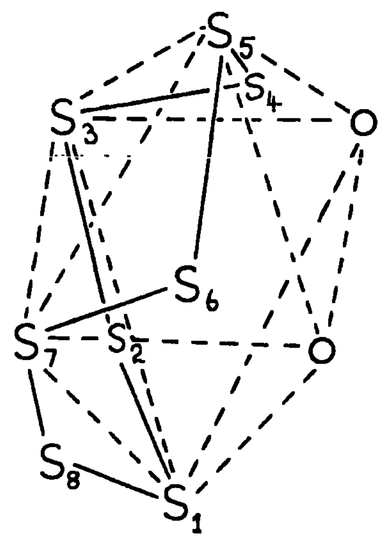


a = 1.62 Å   b = 2.58 Å   c = 2.69 Å

The S-N distances (1.62 Å) are appreciably shorter than normally associated with a single bond (ca. 1.74 Å).[69] Although the four identical N-N distances (2.55 Å) are shorter than the Van der Waal's diameter (3.1 Å), there is no conclusive evidence for N-N bonding, and the nitrogen atoms occupy bridging positions on the sulfur tetrahedron.

This treatment also predicts the correct structure for S_8^{2+},[108] which is based on an octahedron (Figure 1.4) and therefore does not have to introduce special energy considerations to modify the predicted structure.

Figure 1.4



S_8^{2+}

There are numerous intra-molecular distances well below the sulfur Van der Waal's diameter, showing that all the atoms are involved in the cage bonding. The total electron count for S_8^{2+} (in addition to eight lone pairs) is fifteen bond pairs. Eight of these are allocated to the σ -framework, leaving seven for the cage, which is what is required for an octahedron.

In the Mingos treatment of S_8^{2+}, it is regarded as a nine bond pair ion, based on cureane, with three bonds broken. Eight S-S distances in the range 2.01 to 2.07 Å, and one at 2.86 Å, are regarded as single bonds, whereas several other S-S distances slightly longer than the last, (2.94, 3.00, 3.07, 3.09 Å etc.) are treated as non-bonded.

(iii) S_4N_4 structure, conclusion

Despite the apparent disagreements concerning the electronic structure of S_4N_4, the most recent papers agree on several points:

(a) The structure, as determined by Sharma[69] is correct.

(b) There is considerable interaction between sulfur atoms in the molecule, (two pairs or all four) and, negligible interaction between nitrogen atoms.

(c) The structure is more complex than a simple σ-bonded cage, and electrons are present in delocalised molecular orbitals.

(d) Electrons in sulfur d-orbitals make some contribution to the bonding.

Molecular orbital calculations are necessarily very complex and inevitably involve approximations, so that a theory involving a few assumptions and a simple model is often more useful. Since this is always an over-simplification of the true situation, there are bound to be conflicts over the model to be used, the assumptions made and the interpretation of the results. The most recent theories regard S_4N_4 as a cage structure by analogy with the boranes, carboranes and other cage structures, where although simple two atom σ-bonds are present, the system is held together by electron pairs in delocalised molecular orbitals. The molecular shape depends upon the number and type of molecular orbitals available. In S_4N_4, the fourteen electron pairs available for bonding are arranged into eight bond pairs, forming the σ-framework (to a first approximation) the other six forming higher molecular orbitals. A further problem is that there are few other known species for comparison with S_4N_4. Selenium nitride (Se_4N_4) and S_4N_4 both have the same cage-like molecular structure,[109] and exhibit similar x-ray diffraction patterns and infrared spectra[110] although Se_4N_4 is less well characterised than S_4N_4. Tetra-arsenic tetrasulfide (As_4S_4) (both the α and β forms) have a related structure to S_4N_4 but consist of a square of sulfur atoms and a tetrahedron of arsenic atoms with As-As bonds.[102,111] (i.e. the reverse of S_4N_4), and is probably fairly well represented by ten localised single bonds[101] rather than by delocalised molecular orbitals. Tetra-arsenic tetraselenide (As_4Se_4) is isostructural with α-As_4S_4.[112]

S_4N_4 is thought to be a member of a hitherto unexplored series of sulfur-nitrogen cage compounds.[113]

4. S_4N_4 Inorganic Reactions

S_4N_4 is one of the most important sulfur-nitrogen compounds, since many other sulfur-nitrogen compounds can be derived from it by ring expansion, contraction, halogenation or reduction (oxidation leads to ring degradation). S_4N_4 can act both as a Lewis base through the nitrogen atoms with Lewis acids, to give a large number of adducts, or as a Lewis acid, but in this case, ring degradation or contraction usually follow. A large number of "thionitrosyl" complexes are also formed by reaction between S_4N_4 and metal halides, carbonyls or other metal salts.[114] Many of these compounds have novel structures and some contain exocyclic hydrogen and are therefore not strictly thionitrosyl complexes.

The reactions of S_4N_4 with phosphorus compounds, and its ion and free radical formation have also been studied.

(i) Reactions involving ring contraction or expansion

(a) Chlorination

S_4N_4 may be chlorinated in quantitative yields to give $(NSCl)_3$, by passing chlorine into a suspension of S_4N_4 in C Cl_4 or CS_2,[115,116] or by reacting with sulfuryl chloride.[279] (See Chapter 2, experimental section).

These reactions are thought to proceed via a moderately stable intermediate, probably $(NSCl)_4$.[115]

(b) Fluorination

S_4N_4 may be fluorinated in considerably less than theoretical yields, by gradually heating a solution in carbon tetrachloride to the boiling point with silver difluoride and then cooling to yield $(NSF)_4$, (colourless tetragonal needles).[117,118] The $(NSF)_4$ molecule consists of a puckered eight-membered S-N ring, in which the S-N bonds alternate in length around the ring (1.55 and 1.65 Å [119]). $(NSF)_4$ is the only thiazyl halide tetramer to be isolated,[120] although a related sulfanuric tetramer $(NSOF)_4$ is known.[121]

Trithiazyl trifluoride $(NSF)_3$, may be prepared by stirring a solution of $(NSCl)_3$ in CCl_4 with AgF_2 for 18-20 hours at room temperature, distilling off the solvent and purifying by sublimation. $(NSF)_3$ forms as colourless crystals (m.pt 74.2°C, B.pt 92.5°C[122]). It is the fluorine analogue of $(NSCl)_3$ and has a similar structure[123] (see discussion on $(NSCl)_3$).

S_4N_4 may be fluorinated directly to $(NSF)_3$ by controlled fluorination using elemental fluorine diluted with helium at -78°C. $(NSF)_4$ is also formed, and it is probably an intermediate in the reaction.[124] More vigorous fluorination of S_4N_4 with elemental fluorine gives a number of sulfur, nitrogen and sulfur-nitrogen-fluorine compounds by ring degradation.[125,126] Electrochemical fluorination in liquid HF also gives ring degradation.[127]

S_4N_4 can also be fluorinated by other fluorinating agents.[125] Selenium tetrafluoride at -10°C yields NSF (15% yield), IF_5 forms the compound $S_4N_4(NSF)_4$ which decomposes at 50°C to NSF, and SF_4 reacts only slowly under pressure at 160°C to form a little NSF. Antimony pentafluoride combines slowly to give a green solid of composition: $S_4N_4\ (SbF_5)_4$ which melts with decomposition to give NSF (10%) and HF forms thiotrithiazyl fluoride S_4N_3F by ring contraction.[54]

(c) Reaction with bromine

The reaction of S_4N_4 with bromine was found to give a mixture of mainly S_4N_3Br (7-membered ring) and $S_3N_2Br_2$ (probably a 5-membered ring), from which S_4N_3Br could be separated by dissolution in liquid SO_2.[128]

(d) Ring contraction to $S_4N_3^+$ salts

S_4N_3Cl is formed in 90% yield when a solution of S_4N_4 is boiled in carbon tetrachloride with S_2Cl_2.[129] The reaction may be summarised:

$$3S_4N_4 + 2S_2Cl_2 \longrightarrow 4S_4N_3Cl$$

S_4N_3Cl is also produced when S_4N_4 is dissolved in thionyl chloride for 24 hours.[130] It contains the cation $S_4N_3^+$, which is a member of the electron-rich aromatic sulfur nitrogen series (see later discussions).

A possible selenium analogue of $S_4N_3^+$, $SeS_3N_3^+$ has also been reported.[130] S_4N_4 reacts with Se_2Cl_2 in the presence of $SOCl_2$ to form S_4N_3Cl and a compound $(SeS_2N_2Cl_2)_n$ tentatively proposed as either $S_4N_3^+$ $Cl_2Se\text{-}N\text{-}SeCl_2^-$ or $(SeS_3N_3^+)_2$ $(SeCl_6)^{2-}$.

(e) Ring expansion to $S_5N_5^+$ salts (this thesis)

S_4N_4 reacts with metal chloride adducts of $(NSCl)_3$ in thionyl chloride to yield $S_5N_5^+$ salts. (See Chapter 6, this thesis, for a full description and discussion).

(f) Ring contractions to other sulfur nitrides

The sulfur nitrides: S_2N_2, S_4N_2 and $(SN)_x$ can also be prepared from S_4N_4 (see section on other sulfur nitrides).

(ii) Reduction of S_4N_4

S_4N_4 in benzene solution undergoes mild reduction, with tin (II) chloride in methanol/water solution to form the sulfur imide: $S_4(NH)_4$ in about 40% yield.[64,131] (See section on sulfur imides this Chapter, experimental section, Chapter 2, and sulfur imides, Chapter 4).

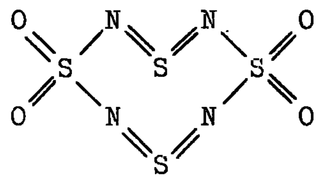
(iii) Oxidation of S_4N_4

In contrast to reduction, oxidation of S_4N_4 leads to ring degradation. S_4N_4 (and $S_4(NH)_4$), can be quantitatively oxidised by Chloramine-T in acidified dioxane, consuming 12 and 16 equivalents of Chloramine-T respectively per mole, and forming H_2SO_4 and NH_3.[88]

An oxide of S_4N_4: $S_4N_4O_4$ has been prepared,[132] although the preparation does not involve S_4N_4. It is prepared through the reaction of N,N$'$ Bis (trimethylsilyl) sulfur diimide with the anhydride of fluorosulfuric acid:

$$2(CH_3)_3\ Si{-}N{=}S{=}N{-}Si(CH_3)_3 + 2FSO_2{-}O{-}SO_2F$$

$$\xrightarrow{CCl_4}$$



$+2(CH_3)_3$ SiF+

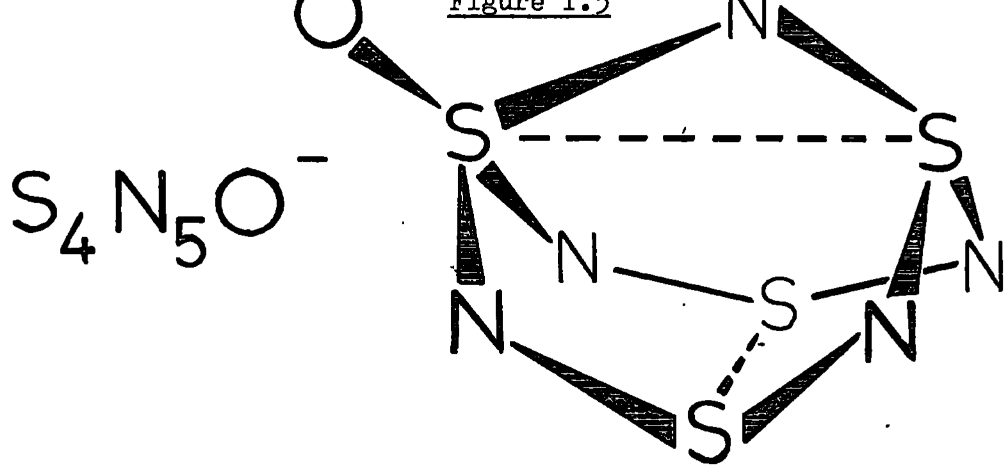
$2(CH_3)_3$ Si·O·SO$_2$F

$S_4N_4O_4$

$S_4N_4O_4$ is a yellow solid which sublimes at 80°-90°C in vacuo, and decomposes at 115-120°C.[132]

An oxy-anion of S_4N_4, $S_4N_5O^-$ has also been prepared, although again the route does not involve S_4N_4.[134,135] The ammonium salt is prepared, in very low yields, by the reaction of thionyl chloride with liquid ammonia to give S_4N_4, $2NH_3$, which is then air oxidised in pyridine solution to give NH_4^+ $S_4N_5O^-$. The compound forms as yellow crystals soluble in and stable to water and pyridine. Other salts, e.g. Thallium (I), Sodium, Potassium, Silver (I) and pyridinium have also been prepared, showing that $S_4N_5O^-$ behaves as a normal anion. Its structure has been recently determined, and as was previously suggested:[134] It is based on the S_4N_4 molecule, with one nitrogen bridging two sulfur atoms, and the oxygen exocyclically attached to one of these two sulfur atoms.[136] (Figure 1.5)

Figure 1.5



(iv) Reaction of S_4N_4 with metals and metal compounds

S_4N_4 undergoes a large number of reactions with metal compounds. These are of two main types:

(a) Adduct formation with metal (and other) halides, in which S_4N_4 functions as a Lewis base, and the halides as Lewis acids.

(b) Reaction with metal halides, other metal salts, metal carbonyls, or pure metals, to form complexes, which are usually termed as thionitrosyl or hydrothionitrosyl complexes. S_4N_4 also reacts with thiophilic reagents, (e.g. CN^-, triphenyl phosphine, etc.) to give compounds of novel structure. The chemistry of sulfur-nitrogen metal compounds has been extensively reviewed.[114]

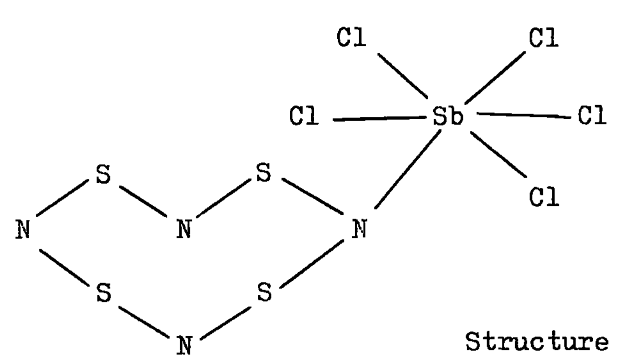
(a) Adduct formation by S_4N_4

S_4N_4 acts as a Lewis base through its nitrogen atoms to form a large series of adducts with Lewis acids. Lewis acid behaviour by S_4N_4 usually leads to ring contraction or degradation.

Reactions of S_4N_4 with Lewis acids

The best characterised of these S_4N_4 adducts is S_4N_4, Sb Cl_5, which is formed when Sb Cl_5 is added to a solution of S_4N_4 in CH_2Cl_2.[137,138] It forms monoclinic crystals, and the crystal structure shows that the Sb Cl_5 is as expected, attached to nitrogen via an antimony-nitrogen bond. The S_4N_4 ring changes conformation but remains intact.[138,139] (Figure 1.6)

Figure 1.6



Structure of S_4N_4, Sb Cl_5

The antimony atom is surrounded octahedrally by five chlorine and one nitrogen atom, but is slightly above the plane of the four chlorine atoms. The sulfur atoms form a square plane, and the nitrogen atoms a bispheroid.[139] The four closest S-S distances (average 2.92 Å), are within the sulfur Van der Waal's diameter (3.7 Å[140]) and this may indicate transannular interactions.

The conformational change in the S_4N_4 ring on forming the adduct may be due to a drain of electron density from the ring by the Sb Cl_5 group. The sulfur-sulfur bonds, being the weakest bonds present are broken, causing the ring to open up into a more sterically favoured conformation.[1]

The crystal structure of the adduct: S_4N_4, BF_3 has also been determined.[141] The structure is similar to that of S_4N_4, Sb Cl_5. The BF_3 group is bonded via boron to a nitrogen atom of the S_4N_4 ring. The four sulfur atoms are near the corners of a square, while the nitrogen atoms are alternately above and below the plane.[141] There is no S-S interaction.[142]

S_4N_4, BF_3 was prepared by reacting S_4N_4 in methylene chloride with BF_3. The adduct S_4N_4, B Cl_3 can be similarly formed with B Cl_3.[137] The BF_3 adduct decomposes reversably to S_4N_4 and BF_3 when heated, whereas the B Cl_3 adduct sublimes with slight decomposition.

The adduct S_4N_4, B Cl_3, Sb Cl_5 has been prepared by the reaction of S_4N_4, B Cl_3 with Sb Cl_5.[137] This is unusual since no diadducts were formed with S_4N_4 and either Sb Cl_5 or B Cl_3 alone. The compound $4S_4N_4$, BF_3 has been reported[143] but discounted by Jolly.[144]

The following adducts of S_4N_4 have been reported. (Table 1.1)

Table 1.1

Adduct	Reference	Adduct	Reference
S_4N_4 BF_3	137,141,145	S_4N_4 $2SO_3$	138,152
BCl_3	137,145,146	$2SbF_5$?	153
BBr_3	137	$2TiCl_3$	151
$AlCl_3$	147	$2TiCl_4$	154
$AlBr_3$	147	$2SbCl_5$	146
$TeCl_4$	146,148	$2BCl_3$	146
$TeBr_4$	149	$2SbBr_3$?	153
$SeCl_4$	146,148	$2SbI_3$?	153
$TiCl_4$	138,150	$4SO_3$	138,152
VCl_4	138,150	$4SbF_5$	53
WCl_4	138,151	$\frac{1}{2}SnCl_4$	138,150,155
$TiBr_4$	150	$\frac{1}{4}BF_3$?	143
$ZrCl_4$	150	$BCl_3,SbCl_5$	137,145
$MoCl_5$	138,151	$AlCl_3,SbCl_5$	147
$NbCl_5$	150	BCl_3,SO_3	146
$TaCl_5$	150	$SbCl_5,SO_3$	146
SbF_5	125	$TeCl_4,BCl_3$	146
$SbCl_5$	137,138,139,146	$TeCl_4,SO_3$	146
Se_2Cl_2 ?	25	$TeCl_4,SbCl_5$	146
		$SeCl_4,SO_3$	146

The structures of many of these adducts are still in doubt although in many cases (e.g. the $NbCl_5$, $TaCl_5$, $TiCl_4$ and $ZrCl_4$ adducts[150]) the structures are probably similar to those of S_4N_4, $SbCl_5$ and S_4N_4, BF_3, where the metal atom is attached directly to nitrogen. Bidentate ligand structures (suggested for VCl_4[150] and $2TiCl_4$[150,154] adducts) are unlikely. Ionic structures are probable for diadducts; e.g. $[S_4N_4, SbCl_4]^+$ $SbCl_6^-$, $[S_4N_4, BCl_2]^+$ BCl_4^- [146] and

$[S_4N_4, BCl_2]^+ SbCl_6^-$.[145] Evidence for these and similar structures has been obtained from infrared and conductivity measurements,[146] although conductivity measurements (in acetonitrile) are not conclusive, and x-ray diffraction data would be required for complete characterisation.[9] A few S_4N_4 adducts have also been prepared using $S_3N_2O_2$ instead of S_4N_4.[154]

(b) Reactions of S_4N_4 with other metal compounds

S_4N_4 undergoes reactions with other metal compounds in which, instead of forming adducts, the S_4N_4 breaks up into SN chains, which then act as ligands around the central metal atom to give "thionitrosyl" derivatives. These may be prepared from the metal, metal halide, carbonyl or other metal salts, using a variety of solvents.

The following thionitrosyl compounds have been described:

Table 1.2

Compound	Reference
$Tl(NS)_3$	156
$Tl(NS), 5Tl(NS)_3$	156
$Cn(NS)_2$	156
$Ag(NS)_2$	156
Cu(NS)	156
Ag(NS)	156
K(NS)	156,157
$K_2(N_2S)$	156,157
$Hg(N_2S)$	74,156
$Hg(NS)_2, NH_3$	74,156
$Pb(NS)_2, NH_3$	74,156,158,159
$Ni(NS)_4$?	65,160
$Co(NS)_4$	65
$Pb(NS)_4$	65
$Fe(NS)_4$?	65,161

Table 1.2
(continued)

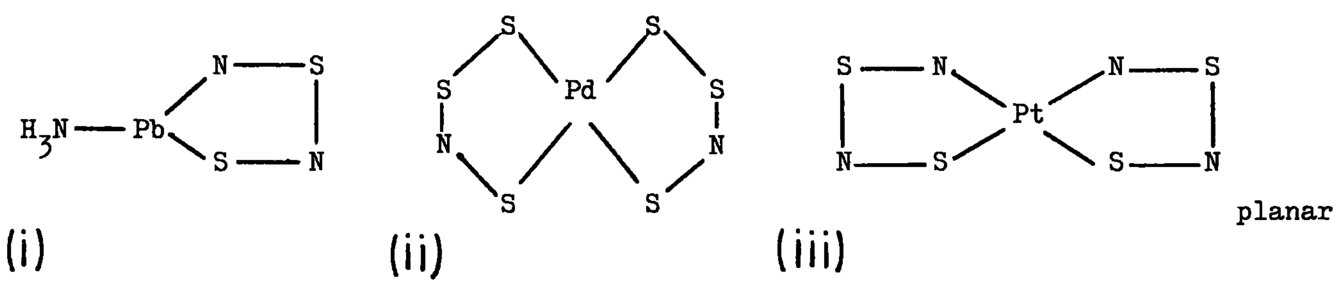
Compound	Reference
$Cu(NS)_2Cl_2$	162
$Cu(NS)_2Br_2$	162
$Pd(NS)_4$?	163
$Pt(NS)_4$	163,164,165
$Co(NS)_4$	166
$Pd(NS_3)_2$	167
$Ni(HN_2S_2)_2$	168,169
$Pd(HN_2S_2)_2$	168
$Co(HN_2S_2)_2$	168,169
$Pt(HN_2S_2)_2$	168,169
$Fe(HN_2S_2)_2$?	168
$Ni(S_4N_4H_2)$	170
$Ni\ S_5N_3H$	169,170
$Ni\ S_6N_2$	170
$Cu_7\ S_4N_4$	171
$Ag_5\ S_4N_4$	171
$Mo\ S_3N_3Cl_3$	172
$Mo\ S_5N_5CO$	172
$Ir\ Cl(CO)(Ph_3P)(S_4N_4)$	173
$Ni(CH_3N_2S_2)_2$	174,175
$Ni(CH_3S_2N_2)(HS_2N_2)$	174,175
$Ni(C_2H_5S_2N_2)(HS_2N_2)$	175
$Fe(CO)\ S_4N_4$	176
$Co_2(CO)\ S_4N_4$	176
$K\left[Ni(CN)_2(S_2N_2H)\right]$	177
$Ni(S_2N_2H)(S_2N_2CONH\ Ph)$	178
$Ni(S_2N_2)(en)_2$	179

The structure and composition of many of these derivatives is still in doubt and others have been disputed. Weiss and Becke-Goehring[168] showed that the compounds formulated as: $M(NS)_4$ (M = Ni, Pd, Co or Pt) by previous workers[65,160,163] contain hydrogen, and should be formulated as $M(HN_2S_2)_2$. A crystal structure on $Pt(NS)_4$ (omitting hydrogen) shows it to be[164]: (Figure 1.7(iii))

Further work suggests that the hydrogens are attached to the nitrogen atoms nearest to platinum.[180]

Crystal structures have also been determined for $Pb(NS)_2$, NH_3[159] and $Pd(NS_3)_2$[167] (Figure 1.7 (i) & (ii))

Figure 1.7



The sulfur nitrogen chains act as bidentate ligands to the central metal atom, forming a planar structure.

Organic derivatives of nickel complexes have been prepared: e.g. $Ni(CH_3N_2S_2)$, $Ni(CH_3N_2S_2)(HN_2S_2)$,[174,175] $Ni(S_2N_2H)(S_2N_2CONH\ Ph)$,[178] $Ni(S_2N_2)(en)_2$,[179] and $K\left[Ni(CN)_2\ H(NS)_2\right]$.[177]

The thionitrosyl compounds may be prepared in a variety of ways:

(I) Reactions of S_4N_4 with metal halides

Compounds of the type $M(SN)_4$ (also containing hydrogen[168]) (M = Fe, Co, Ni, Pd, Pt) have been prepared by reacting an alcoholic solution of S_4N_4 with the anhydrous metal halide in the +2 oxidation state,[163,170] or in the case of platinum with $H_2Pt\ Cl_6$ under carefully controlled conditions.[163] $Cu(SN)_2Cl_2$ and $Cu(SN)_2Br_2$ have been prepared from S_4N_4 and the corresponding metal halide in DMF.[162] The reaction of nickel II chloride with S_4N_4 in alcoholic solution yields a series of compounds: Ni $S_4N_4H_2$, Ni S_5N_3H and Ni S_6N_2.[170] The hydrogen must come from the alcoholic solvent, implying fairly complex reaction mechanisms.

(II) Reaction of S_4N_4 with metal carbonyls

Metal carbonyls can be used in place of metal halides to yield thionitrosyl compounds. Iron,[161] cobalt,[166], nickel,[160] and palladium[165] carbonyls react with S_4N_4 in benzene to yield the corresponding thionitrosyl derivative, $M(SN)_4$ and carbon monoxide.

With molybdenum carbonyl in refluxing benzene, Mo S_5N_5CO is formed as a black amorphous explosive solid, insoluble in all common organic solvents.[172] It reacts with $(NS\ Cl)_3$ to form Mo $S_3N_3Cl_3$.[172]

S_4N_4 reacts with Ir $Cl(CO)(P(C_6H_5)_3)_2$ in benzene at 50^oC to form Ir $Cl(P(C_6H_5)_3(S_4N_4)$.[173] The structure is unknown, although it is probable that the S_4N_4 ring remains intact, and is bonded through nitrogen in a similar way to the adducts previously discussed.

S_4N_4 reacts with iron and cobalt carbonyls in dry deoxygenated benzene to form $Fe(CO)N_4S_4$ and $Co_2(CO)N_4S_4$ respectively.[176] These complexes have been formulated as polymeric thionitrosyl carbonyl compounds.

(III) Reaction of S_4N_4 with metals

Copper and silver foils react slowly with S_4N_4 in carbon tetrachloride, copper reacting over a period of hours, and silver over a period of days. The black powdery product formed by copper is paramagnetic and corresponds to $Cu_7S_4N_4$. The silver complex approximates to $Ag_5S_4N_4$. The structure of these compounds is unknown.[171]

(IV) Reactions of S_4N_4 with metal compounds in liquid ammonia

S_4N_4 dissolves in liquid ammonia to give a red solution which conducts electricity. (See Chapter 3, S_4N_4 in liquid ammonia). When metal ions, as anhydrous salts, are added to the solution, thionitrosyl compounds are precipitated.[74,181]

e.g.

$$S_4N_4 + 2NH_3 \rightleftharpoons 2HN{=}S{=}N{-}S{-}NH_2 \rightleftharpoons 2H{-}N{=}S + 2H{-}N{=}S{=}N{-}H$$

$$2H{-}N{=}S \longrightarrow 2K(NS)+2NH_3 \qquad 2H{-}N{=}S{=}N{-}H \longrightarrow 2K_2(N_2S)+4NH_3$$

$$2H{-}N{=}S \xrightarrow{Pb^{2+}} 2H^+ + Pb(NS)_2 \qquad 2H{-}N{=}S{=}N{-}H \xrightarrow{2Hg^{2+}} 2Hg(N_2S)+4H^+$$

The thionitrosyl compounds: $Tl(NS)_3$; $Tl(NS)$; $5Tl(NS)_3$; $Cu(NS)_2$; $Ag(NS)_2$; $Cu(NS)$ and $Ag(NS)$ have similarly been prepared.[181] The compounds $K(NS)$ and $K_2(N_2S)$ (prepared as above) are solid yellow salts, stable in vacuo or dry nitrogen, but traces of KNH_2 cause explosions in air.[182]

(V) Reactions of S_4N_4 with metal halides in thionyl chloride

Thionyl chloride is an active solvent towards S_4N_4,[183] the S_4N_4 cage structure being broken up, and the fragments reforming in solution to give other stable species, if suitable Lewis acids are present to stabilise them. S_4N_4 reacts with $SO\,Cl_2$, in the presence of iron (III) or aluminium chlorides, to give a mixture of the tetrachloro metallates of the cations $S_3N_2Cl^+$, $S_4N_3^+$ and $S_5N_5^+$.[184] The reaction with other metal chlorides also yields salts containing the $S_3N_2Cl^+$ and $S_4N_3^+$ cations, together with other compounds of unknown structure.[185]

(vi) Reaction of S_4N_4 with phosphorus compounds

(a) $P\,Cl_3$

S_4N_4 reacts with $P\,Cl_3$, to form the ionic compound: $P\,Cl_4^+\ NP\,Cl_3^-$,[186] as concluded from infrared and ^{31}P nmr data. The reaction may be summarised:

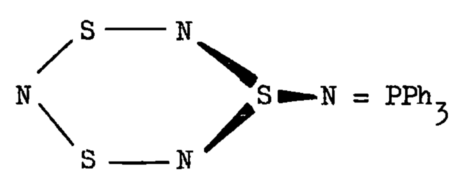
$$S_4N_4 + 10\ PCl_3 \longrightarrow 2NP_2Cl_7 + 2NPCl_2 + 4SPCl_3$$

NP_2Cl_7 is obtained as colourless crystals, when recrystallised from chloroform at -55°C. The reaction involves the complete breakdown of the S_4N_4 cage.

(b) Triphenyl phosphene, Ph_3P, and $(C_6H_{11})_3P$

S_4N_4 reacts with triphenyl phosphene in dimethylformamide,[187] or benzene[188] to give Ph_3PS, and a second substance, $S_3N_4PPh_3$, with the structure (Figure 1.8)

Figure 1.8



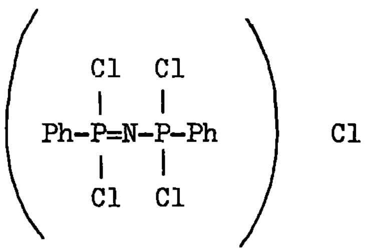
$S_3N_4PPh_3$

The ring is planar, apart from the sulfur atom bonded to the $-N{=}PPh_3$ group, which is 139° out of plane. This partial planarity is unusual, although a similar structure is exhibited by the $S_3N_2Cl^+$ cation, where the sulfur atom bonded to exocyclic chlorine, is out of the plane of the ring.[189] The exocyclic group may therefore be causing the non-planarity of the sulfur atom, by perturbing the "aromatic" delocalised bonding in the ring. All the S-N bond lengths in S_3N_4 PPh_3 (Average = 1.62 Å) are shorter than the S-N single bond (1.76 Å), and two (average 1.57 Å) are close to the S-N double bond (1.55 Å). This implies multiple delocalised bonding in the system.

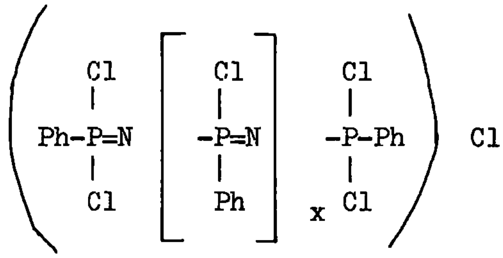
The compound: S_3N_4 P(cyclo-$C_6H_{11})_3$ has been prepared by the same procedure as S_3N_4 PPh_3,[188] and they probably have analogous structures.

(c) Phenyl dichloro phosphene $PhPCl_2$

S_4N_4 reacts with $PhPCl_2$, to form salt-like products, which can be regarded as chlorides of imido-diphenyl-diphosphonic acid, and of higher imido-polyphosphonic acids.[190]



Imido diphenyl diphosphonic acid chloride

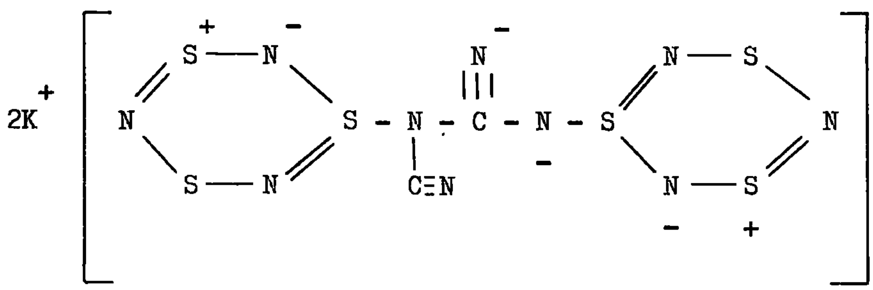


Imido polyphosphonic acid chloride (x = 1 or 2)

PhPS Cl_2 and PhP Cl_2: N PS(Ph)Cl, are also among the reaction products.[190]

(vii) <u>Reaction of S_4N_4 with CN^-</u>

S_4N_4 is readily attacked by CN^- (a powerful thiophile) to form a red solid of composition $(KCN_5S_3)_2$ which could not be obtained free from KNO_3.[187] It appears that one sulfur is removed from the S_4N_4 ring forming a six membered ring as for triphenyl phosphene (above). The tentative structure is proposed:[187]



(viii) <u>Ion and free radical formation by S_4N_4</u>

In the reaction between tetrasulfur tetraimide $S_4(NH)_4$, and triphenyl sodium, various colour changes are observed, and the compound $(Na^+)_4\ S_4N_4^{4-}$ is finally formed.[36] S_4N_4 reacts with potassium metal in dimethoxyethane under vigorously dry conditions to again give various colour changes which have been interpreted as the following anion formations:-

$$S_4N_4 \longrightarrow S_4N_4^- \longrightarrow S_4N_2^{2-} \longrightarrow S_4N_4^{3-} \longrightarrow S_4N_4^{4-}$$ [93]

An esr. spectrum of the solution shows nine lines of relative intensities: 1:4:10:16:19:16:10:4:1, which is consistent with a hyperfine interaction with four equivalent nitrogen atoms, showing that the negative charge on the S_4N_4 anions is delocalised throughout the ion.[191]

S_4N_4 reacts with 100% sulfuric acid via a complicated mechanism to give a number of decomposition products.[192] The overall reaction may be summarised:

$$S_4N_4 + 6.8\ H_2SO_4 \longrightarrow 2SO_2 + 1.5\ NH_3SO_3 + 1.5\ NH_4^+ + 0.1\ S$$
$$+\sim 1.6\ HS_2O_7^- + \sim 0.4\ HSO_4^- + \sim 0.3\ H_2S_2O_7 + \sim\left[0.5\ S_6N_2O_8H^+\right]$$

The coefficients of several of the species are very inaccurately known, and the last species in the equation was empirically formulated to balance atoms and charges, and therefore its formula has practically no significance, although it probably contains an S-N bond.[192] It has been suggested[113] that this species may be S_3N^+ which is the missing member of the series: S_2N_2, S_3N^+, S_4^{2+}, stable to concentrated sulfuric acid.[193]

The radical ion $S_2N_2^+$ has been identified by epr. spectroscopy when S_4N_4 is dissolved in 100% sulfuric acid. It contains two equivalent nitrogen atoms and sulfur atoms (by using S_4N_4 enriched with ^{33}S). In 95% sulfuric acid, coupling between two equivalent hydrogen atoms was observed, and also weak coupling due to ^{33}S atoms, but lines due to nitrogen coupling were absent.

At temperatures below 0^oC, chemical or electrolytic reduction of S_4N_4 in THF produces a nine-line esr. spectrum characteristic of a radical with four equivalent nitrogen atoms,[194] however the isotropic spin Hamiltonian parameters obtained from the observed spectrum are significantly different from those found by Chapman and Massey and assigned by them to the radical anion $S_4N_4^-$.[191] It was concluded that the radical produced below 0^oC is $S_4N_4^-$ which then decomposes at higher temperatures to give a series of products which appear to be precursors of the radical observed by Chapman and Massey.[194]

Radicals produced by the chemical and electrolytic reduction of S_4N_4 and S_4N_3Cl have also been studied by Pratt, and the radical anion of S_4N_4 ($S_4N_4^{\bullet -}$) prepared.[195]

The cyclic radical $S_2N_2^+$ has been observed from the esr. spectrum of S_4N_4 in concentrated sulfuric acid and in antimony pentafluoride (strong Lewis acid).[196]

From a study of the electrochemical reduction of S_4N_4 in pyridine solution,[197] the values of the diffusion coefficient, $D = 2.7 \times 10^{-5}$ Cm^2 s^{-1}, and the coulometric number in the absence of slow coupled chemical reactions, n = 1.05 Faraday mole^{-1}, have been reported with an accuracy of approximately 10%. (See also electrolysis of S_4N_4 solutions, Chapter 3, this thesis).

(ix) <u>Reaction of S_4N_4 with free radicals</u>

Liquid bis(trifluoromethyl) nitroxide radical, $(CF_3)_2NO^{\bullet}$ reacts quantitatively at room temperature with S_4N_4, $S_4(NH)_4$ or $(NSCl)_3$ to form in each case, tetrathiazyl tetra [bis(trifluoromethyl) nitroxide],[198] $S_4N_4[ON(CF_3)_2]_4$, (a white, stable, crystalline solid). X-ray diffraction studies show that the structure resembles that of $(NSF)_4$.[199,200]

(x) <u>S_4N_4, hydrolysis and decomposition reactions</u>

S_4N_4 is quantitatively hydrolysed by 0.5 M NaOH solution in a homogeneous medium to form sulfite, thiosulfate, sulfate and a small quantity of sulfide, the relative proportions depending upon the conditions of hydrolysis.[201] With aqueous ammonia solution, thiosulfate, sulfite, sulfate and sulfamate (via trithionate) are formed, but at 100°C with an ammonia concentration greater than 15 M, an explosive reaction occurs.[202]

Hydrolysis in acid is slower than in alkali, the main product being sulfur dioxide. Other products are elemental sulfur, hydrogen sulfide, and small amounts of thiosulfate and tetrathionate.[201]

Hydrolyses in neutral media have also been studied. With sodium sulfite, S_4N_4 quantitatively forms trithionate[201] and with anhydrous hydrogen iodide in carbon tetrachloride, the quantitative reaction occurs:

$$S_4N_4 + 20\ HI \longrightarrow 4\ H_2S + 4\ NH_3 + 10\ I_2$$ [203]

In all hydrolytic reactions, there is complete conversion of nitrogen to ammonia.

High voltage paper ionophoresis has been used to identify the hydrolysis products of S_4N_4.[87] In strong alkali solutions, the hydrolysis proceeds:

$$S_4N_4 + 6\ OH^- + 3\ H_2O \longrightarrow S_2O_3^{2-} + 2\ SO_3^{2-} + 4\ NH_3$$

and in weak alkali:

$$2\ S_4N_4 + 6\ OH^- + 9\ H_2O \longrightarrow 2\ S_3O_6^{2-} + S_2O_3^{2-} + 8\ NH_3$$

The reactions in concentrated sulfuric acid have been discussed (previous section) and the oxidative reactions with chloramine-T are discussed in the organic section.[88,89]

5. Organic Chemistry of S_4N_4

S_4N_4 has been recently shown to have a wide organic chemistry. It can behave as an inorganic diene towards olefins and other hydrocarbons, where the S-N ring is preserved but changed in conformation. It is also quite reactive towards nucleophilic substitution, and although the products differ considerably from one reaction to another, they generally arise from a nucleophilic attack on sulfur, with the destruction of the sulfur-nitrogen ring system.[204]

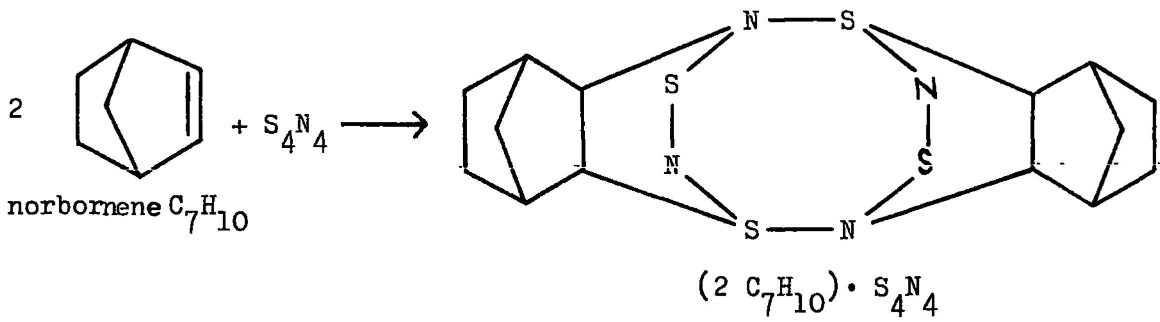
(i) Reactions of S_4N_4 as an inorganic diene

S_4N_4 reacts with dieneophiles, such as cyclopentadiene (C_5H_6), bicycloheptene (norbornene, C_7H_{10}) and bicycloheptadiene (C_7H_8) to form $(C_5H_6)_4\ S_4N_4$, $(C_7H_{10})_2S_4N_4$ and $(C_7H_8)_2\ S_4N_4$ respectively.[205]

The products were thought to have the structures (Figure 1.9):-

Figure 1.9

e.g.



Similarly for the other olefins where the olefin is bonded to alternate sulfur and nitrogen atoms, however these structures were based on uv. data only, and Gleiter on theoretical grounds argued that this structure was unlikely, and suggested that the olefin adds to the transannular bond in the first step.[86] Later work[206,207] showed that the dieneophile is bonded to S_4N_4 through the nitrogen atoms, and proposed the exo-cis stereochemistry. The shape of the S_4N_4 cage is not drastically altered as the ring remains intact, and only the S-S interactions are lost (Figure 1.10). The reactions were carried out in refluxing diethyl ether (24 hours). The yields were high (94-98%).

Figure 1.10

e.g.

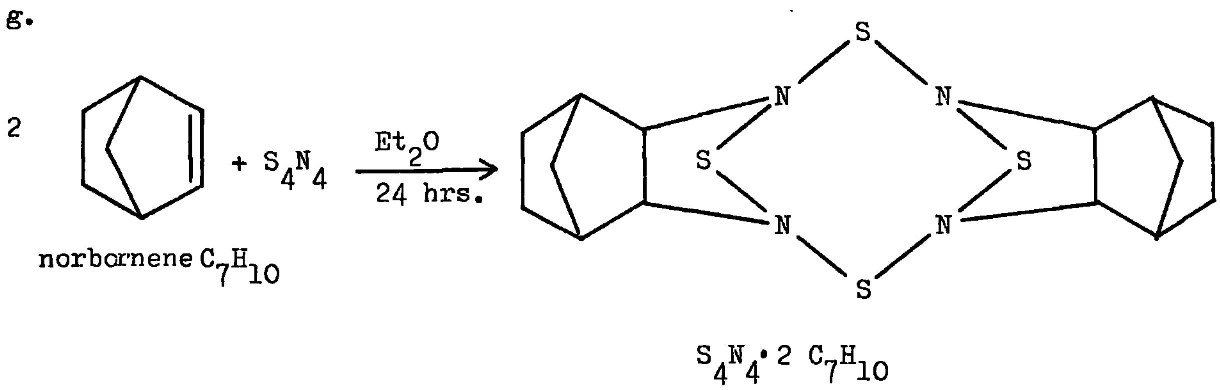
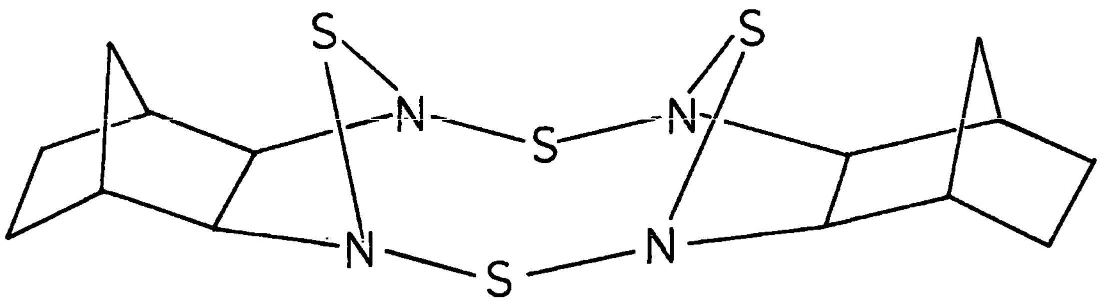


Figure 1.10 (Contd...)



exo-cis

$S_4N_4 \cdot (2C_7H_{10})$

S_4N_4 failed to react with many other dieneophiles and active olefins, and it was concluded that the observed reactions are examples of 1,3-dipolar additions to a class of dipolarophilic olefins.[207]

(ii) Reactions of S_4N_4 with negatively-substituted acetylenes

S_4N_4 reacts with negatively-substituted acetylenes in refluxing benzene to give the corresponding 3,4-disubstituted 1,2,5-thiadiazoles[208] (Figure 1.11).

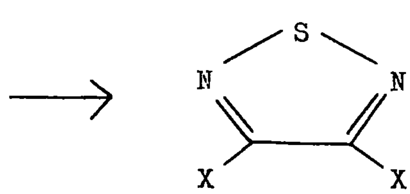
In addition there is isolated from the dicyano-acetylene (X = CN) reaction, a second cyano compound for which the structure II(a) is proposed:

Figure 1.11

e.g.

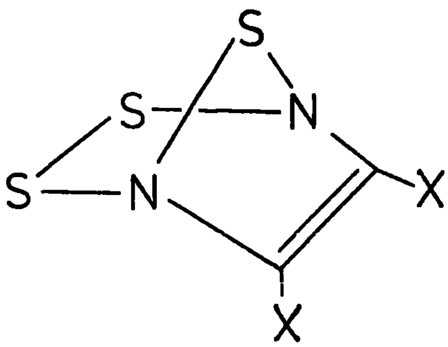
S_4N_4 + X - C ≡ C - X

X = CN, CO_2CH_3



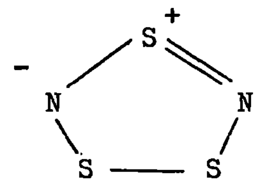
(I)

Figure 1.11 (Contd...)



(II)

(a) X = CN
(b) X = CF_3

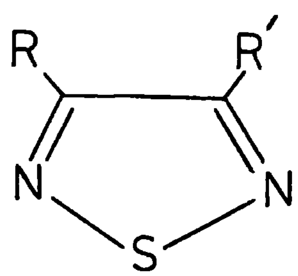


(III)

The formation of the above products has been rationalised on the basis of a 1,3 addition of the acetylene to the ($N = S^{+}N^{-} \leftrightarrow NSN$) portion of S_4N_4, to give a bicyclic intermediate which can collapse to I and III. A similar addition of acetylene to III may then lead to II.[208]

(iii) Reactions of S_4N_4 with saturated and aromatic hydrocarbons[209,210,211]

A mixture of S_4N_4 and ethyl benzene was refluxed, diethyl ether added, the mixture filtered and the filtrate distilled. Products of the type:



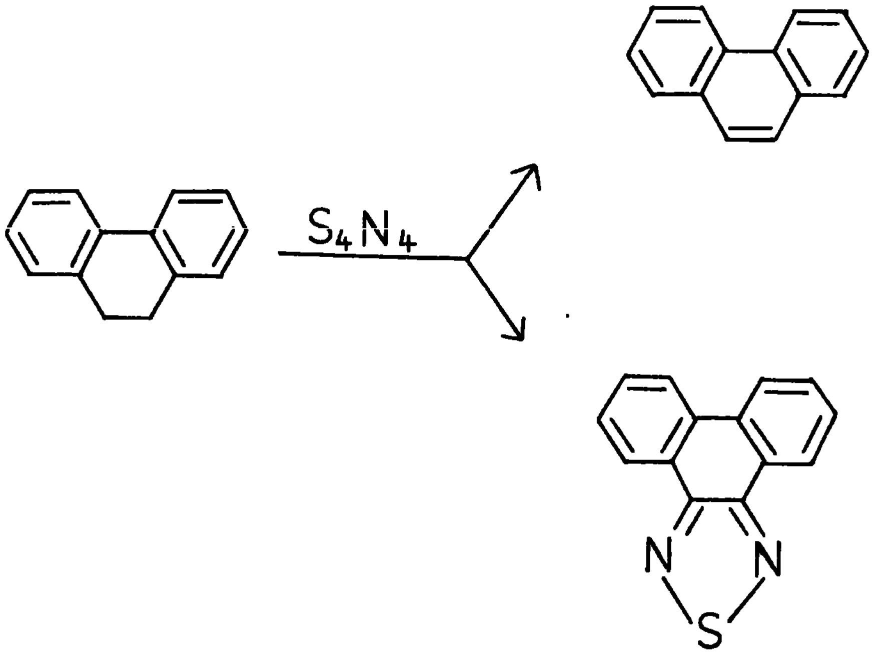
R=Et
R'= Ph

were formed. (1,2,5 thiadiazoles)

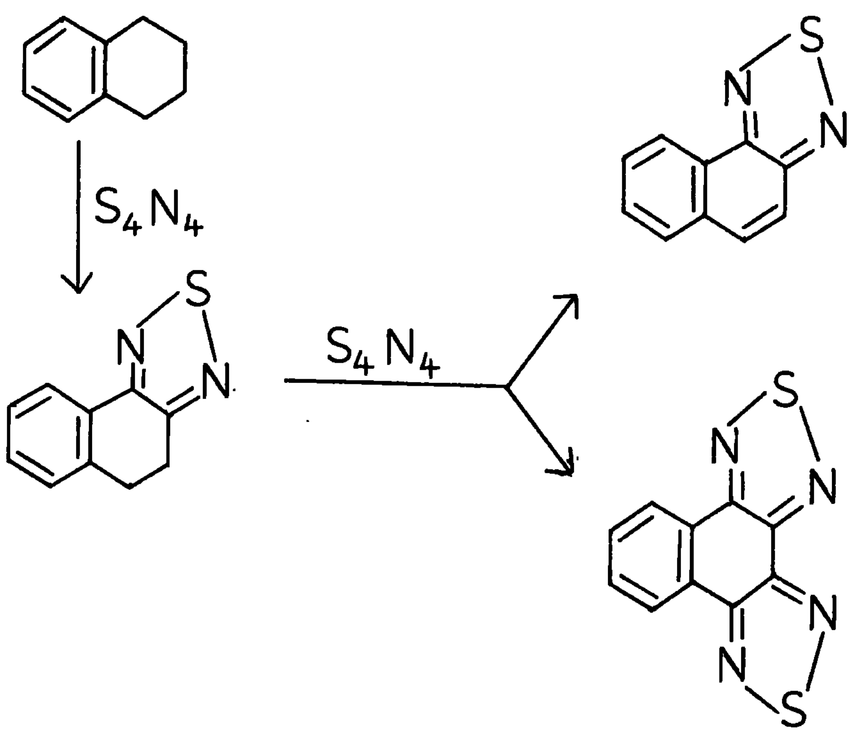
Other hydrocarbons were also used. Similar 1,2,5 thiadiazoles were prepared by reacting S_4N_4 with compounds containing R CH_2R' (R = aryl, R' = aryl, H), acyclic N-C-C-N or R-CH_2-$CH(NH_2)R'$, (R = aryl, R' = alkyl, H) in refluxing xylene.[210]

S_4N_4 also reacts with some fused aromatic ring systems to give 1,2,5 thiadiazoles as well as causing dehydrogenation in the hydrocarbon.[211] The reactions were carried out either in refluxing xylene, or by initiation with U.V. radiation. (Figure 1.12)

Figure 1.12



(i)



(ii)

(iv) Reaction of S_4N_4 with Grignard Reagents

S_4N_4 reacts with Grignard reagents (R Mg Br, R = aryl, alkyl) to form crystalline stable compounds of the type: $R.C_6H_4.SN:S:NS.C_6H_4R$ (linear) (R = H,Cl,Br and OMe).[212] The ether solution of the Grignard reagent is added to a benzene solution of S_4N_4. With ethyl magnesium bromide, a red unstable oil, of composition $C_2H_6S_2N_2$ and proposed structure: Et SN:S:NH is formed. Phenyl magnesium bromide reacts with S_4N_4 or $S_3N_2Cl_2$ to form Ph S.N:S:N.SPh.[213]

(v) Reaction of S_4N_4 with acetyl chloride

S_4N_4 reacts with refluxing acetyl chloride to yield S_4N_3Cl and diacetamide.[214,215] It is thought that the reaction proceeds via traces of HCl in the acetyl chloride, forming S_4N_4-HCl as an intermediate.

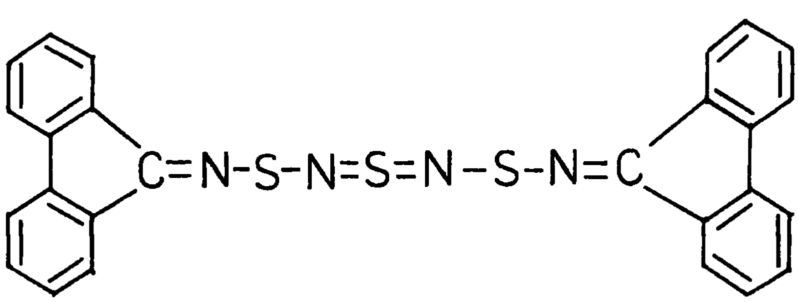
(vi) Reaction of S_4N_4 with substituted diazo methanes

S_4N_4 reacts with diphenyl diazo methane (Ph_2CN_2) in diethyl ether, and with 9-diazofluorene in benzene to form diphenylidene-trisulfurtetranitride $(Ph_2C:)_2\ S_3N_4$ (orange-brown needles) and $(C_{13}H_8:)_2\ S_3N_2$ (green-black metallic needles) respectively. The compounds have the structures:[216] (Figure 1.13)

Figure 1.13

$Ph_2\ C{=}N{-}S{-}N{=}S{=}N{-}S{-}N{=}CPh_2$ $(Ph_2C:)\ S_3N_4$

(I)



$(C_{13}H_8:)_2\ S_3N_4$

(II)

A crystal structure on $(Ph_2C:)_2\ S_3N_4$ has confirmed the chain structure and has shown that the five central members of the sulfur nitrogen chain are coplanar.[217] This indicates some π bonding along the chain.

(vii) Reaction of S_4N_4 with amines

Schenk reported that S_4N_4 reacted with benzylamine at 100°C to form ammonia, sulfur and triphenyl-S-triazene, and at 20°C, the thioamide of thio-benzoic acid,[218] but the structures of these materials remains in doubt.[204] More recent work has shown that S_4N_4 reacts with benzylamine to form benzylidinimine tetrasulfide (yellow needles) ammonia and sulfur.[204,219,220] Di- and probably trisulfides of benzylidinimine are also formed:

$$S_4N_4 + C_6H_5\ CH_2NH_2 \longrightarrow S_8 + NH_3 + C_6H_5CH = N\text{-}S_x\text{-}N\text{=}CH\ C_6H_5$$
$$(x = 2,3 \text{ or } 4)$$

The reaction was carried out in the pure liquid since the yields are quantitive and the presence of other solvents reduces the yields. The structure of the tetrasulfide (x = 4) has been determined.[221] It shows alternating S-S bond lengths, and a short S-N bond. There is probably little π bonding along the sulfur chain, although there may be some π bonding in the S-N bonds.

The reaction is quite sensitive to structural changes in substituents on the aromatic ring.

(a) The reaction appears to be limited to ring substituted benzylamines.

(b) Electron withdrawing groups result in more sulfur and less imides,[219] while electron releasing groups favour the formation of the imide tetrasulfide.

(c) The reaction is fairly specific; for example, benzylamine and α-methyl benzylamine do not appear to give similar species, and phenyl hydrazine with S_4N_4 gives diphenyl sulfide and diphenyl disulfide as major products, along with sulfur and ammonia.[219,220]

Benzylidinimine tetrasulfide undergoes thermal decomposition to yield hydrogen sulfide, benzonitrile, sulfur and triphenyl-S-triazene as the major products.[204]

(B) Other Sulfur Nitrides

1. Introduction

Several other sulfur nitrides are known, as well as S_4N_4 which is the most important sulfur nitride. These are: S_2N_2, S_4N_2, $(SN)_x$ (polymeric sulfur nitride), the fused ring nitride: $S_{11}N_2$, and the coupled ring nitrides: $S_7N-S_x-NS_7$ (x = 1,2,3 or 5). The fused and coupled ring nitrides are structurally closely related to the sulfur imides, and so are discussed in that section. Very little is at present known about the other three nitrides, and these are discussed in this section.

2. Disulfur Dinitride S_2N_2

(i) Preparation

Disulfur dinitride is prepared in good yield by passing S_4N_4 vapour at low pressure (10^{-3}mm. mercury) through heated silver wool at about 300°C,[222,223] lower temperatures and pressures may also be used.[224] The silver wool removes the sulfur decomposition product as silver sulfide. The S_2N_2 is purified by sublimation under high vacuum at room temperature.[222,223,225]

(ii) Physical properties

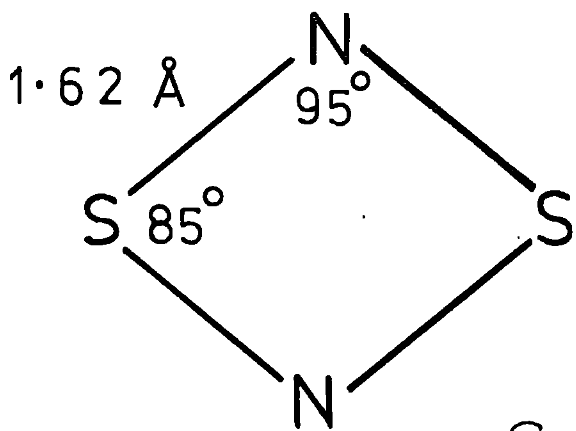
S_2N_2 forms large colourless crystals,[222,226] which are insoluble in water, but soluble in benzene, carbon tetrachloride, ether, acetone and particularly tetrahydrofuran and dioxane.[223] It is also soluble in liquid ammonia to give red solutions which are identical to solutions of S_4N_4 in liquid ammonia.[34,227,228] It can be recrystallised from ether at -70°C.

S_2N_2 has a repulsive smell, and is the least stable of the sulfur imides, detonating with friction, shock, or on heating above 30°C.[8,9,222,233]

(iii) S_2N_2 Molecular structure

The cryoscopic molecular weight in benzene corresponds to S_2N_2,[226] and the infrared spectrum indicates a planar, nearly square ring structure with alternating S and N atoms.[230] (Figure 1.14) The Raman spectrum could not be obtained due to its reactivity.[229]

Figure 1.14



S_2N_2

S_2N_2 has been considered as a member of the "electron rich" aromatic series of sulfur-nitrogen compounds, together with S_4N_2, $S_4N_3^+$, and $S_5N_5^+$, S_2N_2 being a 6π electron system.[101,106] (See discussions in Chapter 6).

(iv) S_2N_2 Reactions

S_2N_2 is a very reactive compound. Its reactions may be divided into five types: (a) Polymerisation; (b) Adduct formation; (c) Ring expansion; (d) Formation of thionitrosyl complexes; (e) Decomposition and hydrolysis.

(a) Polymerisation

S_2N_2 is easily polymerised. In the presence of traces of alkali or cyanide in an organic solvent, S_2N_2 rapidly and quantitatively polymerises to S_4N_4. However, when pure, dry S_2N_2 is stored in an evacuated desiccator for 30 days, almost quantitative conversion to $(SN)_x$ occurs. (See later discussion on $(SN)_x$)

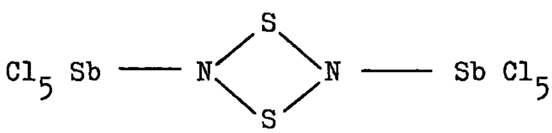
(b) Adduct formation

S_2N_2 forms adducts with $SbCl_5$, BCl_3 and BF_3. The reactions with $SbCl_5$ are represented by the equations:[231]

$$S_2N_2 \xrightarrow[CH_2Cl_2]{SbCl_5\ \text{excess}} S_2N_2,\ 2\,SbCl_5 \underset{SbCl_5}{\overset{S_2N_2}{\rightleftharpoons}} S_2N_2,\ SbCl_5$$

$$S_2N_2,\ SbCl_5 \xrightarrow{S_2N_2} S_4N_4,\ SbCl_5\ \text{(mainly)}$$

The crystal structure of the diadduct shows a planar S-N ring, with antimony bonded directly to nitrogen:[232]



With BCl_3 in CH_2Cl_2; S_4N_4, BCl_3; $S_2N_2(BCl_3)_2$; and apparently polymeric $(S_2N_2, BCl_3)_x$ can be formed; whereas with BF_3, only S_4N_4, BF_3 is formed.[144]

(c) Ring expansion

S_2N_2 reacts with S_2Cl_2 to form S_4N_3Cl,[233] thus showing the same reaction as S_4N_4.

(d) Formation of thionitrosyl complexes

S_2N_2 reacts with finely divided metals (e.g. Pd, Ni, Co) to form metal thionitrosyls:[233] e.g. $2\,S_2N_2 + Pd \rightarrow Pd(SN)_4$.

Nickel carbonyl also reacts with S_2N_2 to give $Ni(SN)_4$[226] (See also section on metal thionitrosyls of S_4N_4).

(e) Decomposition and hydrolysis

S_2N_2 decomposes to its elements when heated in a sealed tube at 250°C.[144] In alkaline solution it rapidly hydrolyses to $S_3O_6^{2-}$, $S_2O_3^{2-}$ and NH_3,[233] and in moist air to a mixture of products including S_4N_4 and a little $(SN)_x$.[224,233]

3. Tetrasulfur Dinitride S_4N_2

This compound has been reviewed in detail by Heal.[9]

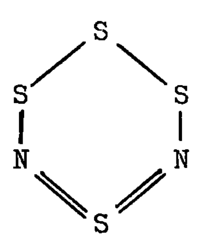
S_4N_2 was first prepared in 1897,[234] and is normally prepared by heating S_4N_4 with sulfur at 100° to 120° in CS_2 solution in an autoclave.[222] The reaction mechanism is complex and not yet completely understood.[4,222] S_4N_2 may also be prepared by the unusual reaction:

$$Hg_5(NS)_8 + 4\ S_2Cl_2 \xrightarrow[20^oC]{CS_2} Hg_2\ Cl_2 + 3\ HgCl_2 + 4\ S_4N_2$$ [131]

Other preparative routes include the combination of SO_2 with NH_3 at 80°, followed by hydrolysis,[235] and refluxing S_4N_4 for several hours in benzene or xylene, to produce small yields of S_4N_2, although this has not been fully investigated.[4,236]

S_4N_2 forms opaque, dark red crystals,[4,222,237] which melt at 23° [222,238] to a dark red liquid resembling bromine.[239] It has a density of 1.71g cm^{-3}.[238] When pure, it decomposes in a few hours at room temperature, and explosively at 100°.[4] It is more stable in CS_2 solution, and can be sublimed at room temperature, at pressures below 1 mm. mercury. It may be purified by sublimation or by chromatography (CS_2 elutant).[237] It is soluble in a variety or organic solvents, including benzene, nitrobenzene, hexane, carbon disulfide, carbon tetrachloride and ether,[238] but is insoluble and slowly hydrolysed by water. The various spectra of S_4N_2 have been extensively studied.[237]

Cryoscopy in benzene gave the formula S_4N_2,[236] and Heal[237] showed that S_4N_2 is a single substance, with the structure:



S_4N_2

from a study of the UV, visible, infrared, Raman, ^{14}N nmr and mass spectra, chromatography and dipole moments. The ring may be planar or puckered.

S_4N_2 can be regarded as a member of the "electron rich" sulfur-nitrogen ring systems,[101,106] and should be planar (unless the π-bonding is too weak for the sulfur atom bonded only to sulfur). So far, no x-ray crystallographic work has been undertaken, mainly due to the instability of the S_4N_2 crystals.

The chemistry of S_4N_2 has been little studied. It combines with Sb Cl_5, to give a moisture sensitive compound of approximately 1:1 stoichiometry together with S_4N_4, Sb Cl_5 and S_4N_3 Sb Cl_6,[9,240] but there is no reaction with B Cl_3. With chlorine, S_4N_4, S_4N_3Cl, and S_3N_2Cl are formed. S_4N_2 is easily reduced by HI in anhydrous formic acid: $S_4N_2 + 6H^+ + 6I^- \longrightarrow 3I_2 + 4S + 2NH_3$.[238]

Reduction with hydrogen and palladium, potassium borohydride, sodium dithionate, lithium aluminium hydride or hydrazine, gives a mixture of cyclic eight membered sulfur imides,[9] and a report that $S_4(NH)_2$ could be prepared by the reduction of S_4N_2 by tin II chloride[241] could not be repeated.[9]

In concentrated sulfuric acid, S_4N_2 gives rise to a weak esr. spectrum, identical to that of S_4N_4, and a reaction of the form: $S_4N_2 - e^- \longrightarrow SN_2^+ + 3S$ is postulated.[242]

4. Polythiazyl $(SN)_x$

The only known preparative route to this compound is to store purified S_2N_2 for 30 days at room temperature or at $-195^\circ C$ in an evacuated desiccator, during which time polymerisation occurs.[222,233,243]

$(SN)_x$ is of interest mainly due to its unusual electrical properties. It conducts electricity,[9,244] is diamagnetic[245] and has been reported to exhibit semi-conductor properties,[245] although a later paper showed it to be metallic over the entire temperature range 4.2 to $300^\circ K$.[246]

$(SN)_x$ appears as fibrous crystals[246] up to 3 mm. long and of density 2.19 g cm^{-3} [244] which have a brass-like metallic lustre, the layers appearing blue to transmitted light.[233] It is insoluble in common organic solvents,[244] hydrolysed by concentrated aqueous alkali and slowly hydrolysed by moisture.[233] With B Cl_3 at 20°C a reaction occurs over several days to form a compound postulated as $(S_2N_2, B Cl_3)_x$ based on infrared studies.[144]

The precise structure of $(SN)_x$ is unknown, since sufficiently good crystals for x-ray diffraction work have not yet been obtained, however a partial structure has been deduced. The dimensions of the unit cell have been determined, it is monoclinic and contains four S-N radicals per unit cell.[243]

The structure is usually considered as a zig-zag chain of alternating S and N atoms,[4,8,226,245,246] with electron delocalisation,[247] and rings and ring currents are probably absent.[51] Simple Huckel theory has been applied to $(SN)_x$, assuming it to be a linear polymer.[247]

(C) Sulfur-Nitrogen Chlorine Compounds

1. Thiotrithiazyl Chloride S_4N_3Cl

S_4N_3Cl is one of the most stable, and also one of the easiest sulfur-nitrogen compounds to prepare. It can be prepared from most other sulfur-nitrogen compounds and is often formed quite unexpectedly[17] or appears as an impurity in many other reactions.

(i) Preparative routes

(a) Preparation from S_4N_4, $S_3N_2Cl_2$ or $(NSCl)_3$

When either S_4N_4 or $S_3N_2Cl_2$ is refluxed in CCl_4 with excess S_2Cl_2, S_4N_3Cl is formed in quantitative yields.[26,52,129,248,249]

i.e. $3\ S_4N_4 + 2S_2Cl_2 \longrightarrow 4\ S_4N_3Cl$

$3\ S_3N_2Cl_2 + S_2Cl_2 \longrightarrow 2\ S_4N_3Cl + S\ Cl_2$

These are the best preparative routes to S_4N_3Cl.[52] S_4N_3Cl is also formed when $(NSCl)_3$ reacts with S_2Cl_2[248] and when $S_3N_2Cl_2$ is refluxed in CCl_4 or $SOCl_2$.[148] Thionyl chloride[130,148] and acetyl chloride[214,215,248] also chlorinate S_4N_4 to yield S_4N_3Cl, although the yields are lower than with S_2Cl_2. S_4N_3Cl may be recrystallised from thionyl chloride or anhydrous formic acid.[130,148,185]

(b) Reaction of sulfur halides with ammonia

S_4N_3Cl may be prepared directly by passing ammonia gas into a solution of S_2Cl_2 diluted ten to fifteen times with an inert solvent.[253] The yield is about 45%.[250,251,252] Sulfur bromides may also be used to form S_4N_3Br.[253]

(c) Reaction of sulfur chlorides with azides

S_4N_3Cl can be prepared by stirring S_2Cl_2 into a suspension of lithium azide in an inert solvent. Some S_4N_4 is also produced, and the reaction is thought to proceed via intermediates such as $S_2(N_3)_2$ and S-N$^{\bullet}$ radicals.[50]

(d) Preparation from S_3N_2Cl

If S_3N_2Cl is heated between 130° and 150° in vacuo, NSCl, SCl_2 and S_4N_3Cl are formed.[52]

(e) Preparation from S_4N_4 and bromine

S_4N_4 reacts with bromine to give a mixture of mainly S_4N_3Br and $S_3N_2Br_2$; S_4N_3Br may be separated by extraction with liquid SO_2.[128]

(ii) Physical properties

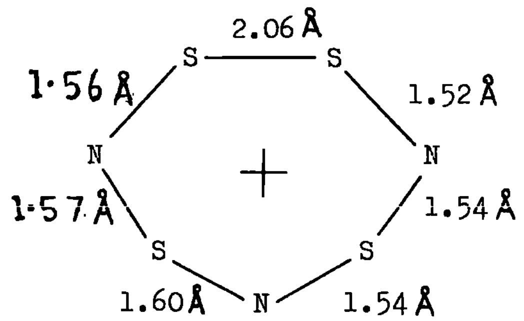
S_4N_3Cl is normally formed as small shining golden-yellow tablets, or as a brilliant yellow powder. Very slow recrystallisation from thionyl chloride yields orange-red crystals.[49] It is insoluble in most solvents, except thionyl chloride and anhydrous formic acid, and decomposes in many organic solvents, including acetone, benzene, acetic acid and chloroform, developing a red colouration.[148]

It melts, with decomposition, in the range 180°-200°C,[26] with the development of red fumes.[251] A blue luminescence on heating in air has also been reported.[254] It is stable in dry air, but is slowly hydrolysed by moisture.[26]

(iii) Structure

S_4N_3Cl was first prepared in 1880,[255,256] and the correct formula soon established, although various structures were proposed.[16,248,257] Salt formation, cryoscopy and conductivity measurements in anhydrous formic acid showed that it was ionic.[258] The average oxidation state of sulfur was 2.5,[259] and the correct structure was determined by Weiss,[260,261] from an x-ray diffraction study of $S_4N_3NO_3$. The $S_4N_3^+$ cation is a seven membered planar ring with short S-N bonds. The structure has been confirmed by Cordes,[262] and Kruss.[263,264] (Figure 1.15)

Figure 1.15



$S_4N_3^+$ (planar)

Several theories were advanced to rationalise the bonding in $S_4N_3^+$, the main problems being the nature of the disulfide S-S bond, and the contribution of π electron delocalisation. Bond lengths (N-S = 1.55 Å) suggested a bond order of 2 for NS bonds, but a single disulfide bond (2.06 Å), and Bailey,[265] from infrared, Raman and ultraviolet data, concluded that there was incomplete electron delocalisation in the ring, due to the disulfide bond. These spectra, and the ^{15}N nmr spectra,[95] were shown to be consistent with the proposed ring structure.

From its ultraviolet spectra, in acidic media, Johnson[266] proposed a model which involved a delocalised 10π electronic system involving sulfur d-orbitals, which was interrupted by the disulfide link. Friedman[267] also proposed a 10π delocalised system with limited delocalisation across the disulfide bond, by application of a semi-emperical self consistent field Molecular Orbital Procedure.

The most recent theories on $S_4N_3^+$ treat it as a member of the "electron rich aromatic" sulfur-nitrogen series,[105,106] being a completely delocalised 10π electronic system. (See discussion in Chapter 6).

(iv) S_4N_3Cl Reactions

S_4N_3Cl contains a stable unsubstituted ring and therefore its chemistry is less varied than for other sulfur-nitrogen compounds. The main types of reaction are: (a) salt formation, (b) ring expansion, (c) hydrolysis and decomposition. A few other reactions of S_4N_3Cl, e.g. with triphenyl phosphine and amines, have also been described.

(a) Salt formation

S_4N_3Cl readily forms salts with other anions. There are three main methods of salt formation:-

(i) Metathesis in water, formic acid or other solvents.

(ii) Reaction with liquid concentrated acids, displacing Cl^- as HCl.[268]

(iii) Reaction with a Lewis acid, e.g. in thionyl chloride, to form the tetrachloro metallate, or with SO_3 to form SO_3Cl^-.

The following $S_4N_3^+$ salts have been described (Table 1.3):

Table 1.3

$S_4N_3^+$ anion	Preparative Method	Reference	$S_4N_3^+$ anion	Preparative Method	Reference
Cl^-	-	-	SO_3F^-	(ii) & (iii)	272,273
Br^-	(i)	258,269	SO_3Cl^-	(ii) & (iii)	272,273
SCN^-	(i)	258,269	$Sb\ Cl_6^-$	(iii)	258
$B\ Ph_4^-$	(i)	258	$Sb\ Cl_4^-$	(iii)	258
NO_3^-	(ii)	256,260 261,270	$Sb\ Cl_5^-$	(iii)	258
HSO_4^-	(ii)	256,266	$Fe\ Cl_4^-$	(iii)	184
ClO_4^-	(ii)	266	$Al\ Cl_4^-$	(iii)	184
$N(SO_2Cl)^-$	(ii)	271	$\frac{1}{2}Sb\ Cl_5^-$	(iii)	286
1.5 HF	(ii)	16	$Bi\ Cl_4^-$		287
			$As\ Cl_4^-$	Recryst. from $As\ Cl_3$	113

S_4N_3Cl also forms adducts with SO_3 of composition: S_4N_3Cl, $(2.7\text{-}2.9)SO_3$, which forms $S_4N_3Cl{\cdot}2SO_3$ on heating.[152] The compounds $S_4N_3^+OH^-$ and $[(SN)_2\ SOH]_2$, are formed by reacting S_4N_3Cl with aqueous sodium acetate at 0° and 20°C respectively.[251,257]

(b) Ring expansion

S_4N_3Cl reacts with aluminium or lithium azides to form S_4N_4. (See preparative routes to S_4N_4(iii)).

(c) Hydrolysis and decomposition

S_4N_3Cl hydrolyses slowly in strong acid, to form NH_4^+ and SO_2, and in strong base to give NH_3, SO_2 and $S_2O_3^{2-}$.[257] The decomposition of S_4N_3Cl by dilute acid and piperidine was studied to determine the average oxidation state of sulfur.[259] In all these reactions, nitrogen is quantitatively converted to ammonia, which is consistent with the absence of N-N bonds in $S_4N_3^+$.

(d) Reactions with triphenyl phosphine

S_4N_3Cl gives a complex series of reactions with Ph_3P, in which compounds of the type: $[Ph_3P{:}NP{\cdot}Ph_3]Cl$, $[Ph_3PNH_2]Cl$, and $[(Ph_3PN)_3S]Cl_3$ are formed. Further reactions also occur.[274]

(e) Reaction with amines

S_4N_3Cl reacts with amines, even in trace quantities, to form highly coloured, unidentified compounds which decompose in a few minutes.[275]

(v) S_4N_3Cl uses

The compounds $S_4N_3^+X^-$ (X = Cl, Br, SCN) have found uses as vulcanizing agents with certain types of rubber,[276] and S_4N_3Cl is also a useful fungicide.[250]

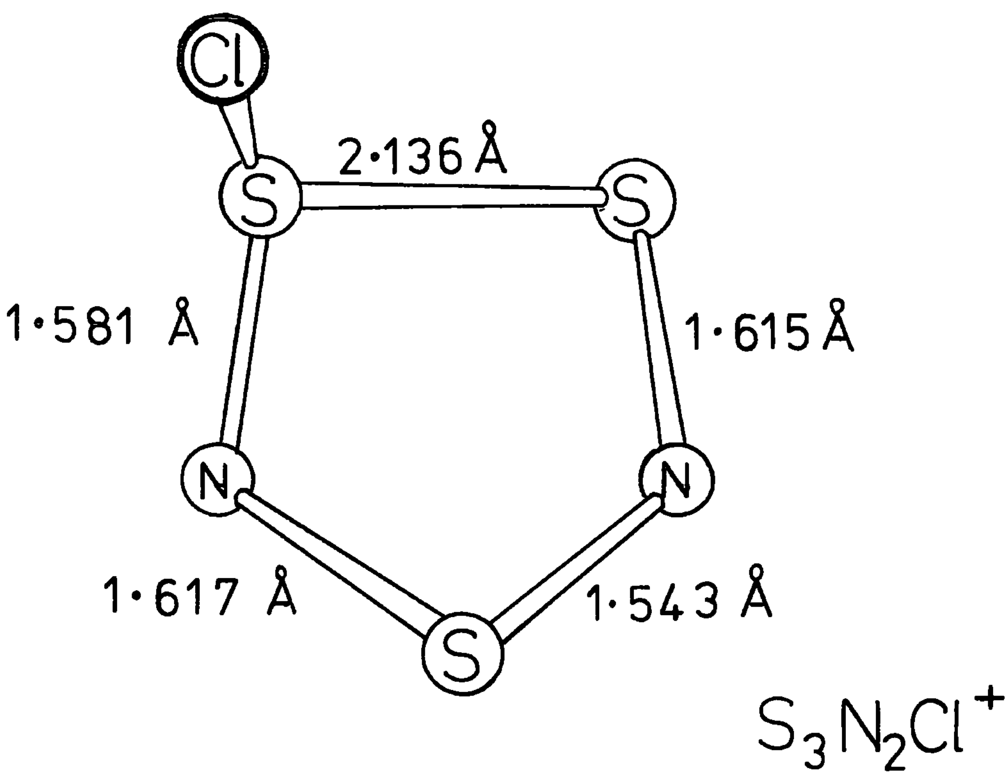
2. Thiodithiazyl Dichloride $S_3N_2Cl_2$

(i) $S_3N_2Cl_2$ Structure

Very little work had been undertaken on $S_3N_2Cl_2$ before the structural determination by Zalkin in 1966.[189]

The structure[189] shows $S_3N_2Cl_2$ to be monoclinic of space group $P2_1$ and with the ionic structure: $S_3N_2Cl^+Cl^-$, $S_3N_2Cl^+FCl_4^-$ has a similar structure.[277] The S-N atoms form a puckered five membered ring (Figure 1.16)

Figure 1.16



The sulfur atom bonded to exocyclic chlorine is out of the plane of the other four ring atoms. $S_3N_2Cl^+$ is regarded as a "pseudo" electron rich aromatic ring, containing a 6π delocalised electronic system.[105,106] (See discussion, Chapter 6).

(ii) $S_3N_2Cl_2$ Preparative routes

(a) Preparation from sulfur, ammonium chloride and S_2Cl_2

This is the most convenient preparative route, and involves heating the reagents in a large flange topped flask, fitted with an air condenser; the crystals form on the sides of the condenser,[52,249] (see experimental section). The $S_3N_2Cl_2$ is thought to be formed by the reaction of S_2Cl_2 with NH_4^+ to give NSCl which then reacts with hot S_2Cl_2 (acting as a source of sulfur) to give $S_3N_2Cl_2$ which crystallises out as the S_2Cl_2/NSCl mixture cools.[113,278]

(b) Preparation from trithiazyl trichloride and S_2Cl_2

As indicated by the above preparation, $S_3N_2Cl_2$ can be formed when $(NSCl)_3$ and S_2Cl_2 are shaken together.

(c) Formation from S_4N_4 in thionyl chloride

S_4N_4 reacts with $SOCl_2$, in the presence of Fe Cl_3 or Al Cl_3 to give a mixture of tetrachloro metallates (MCl_4^-) of the cations $S_3N_2Cl^+$, $S_4N_3^+$ and $S_5N_5^+$.[184]

(d) Chlorination of S_3N_2Cl

S_3N_2Cl can be chlorinated in thionyl chloride solution in the presence of Fe Cl_3 or Al Cl_3 to give the corresponding $S_3N_2Cl^+$ salt. (See Chapter 7, this thesis).

(iii) $S_3N_2Cl_2$ Reactions

$S_3N_2Cl_2$ is an important starting material for other sulfur-nitrogen compounds, and is the easiest one to prepare from compounds not containing S-N bonds.

The following reactions summarise the main preparative uses of $S_3N_2Cl_2$. (See experimental section).

(a) $3\ S_3N_2Cl_2 \xrightarrow[\text{Vacuum}]{80^\circ C} 2\ S_3N_2Cl + 2\ NSCl + SCl_2$ [249]

(b) $3\ S_3N_2Cl_2 + S_2Cl_2 \xrightarrow[CCl_4]{\text{reflux}} 2\ S_4N_3Cl + SCl_2$ [249]

(c) $S_3N_2Cl_2 + SOCl_2 \longrightarrow S_4N_3Cl$ (+ other products)[148]

(d) $3\ S_3N_2Cl_2 + 3\ SO_2Cl_2 \xrightarrow[\text{24 hrs.}]{SO_2Cl_2} 2(NSCl)_3 + 3\ SO_2 + 3\ SCl_2$ [279]

Reactions (b) and (d) are essentially quantitative.

$S_3N_2Cl_2$ also forms salts of the type: $S_3N_2Cl^+A^-$, formed by reacting $S_3N_2Cl_2$ with a Lewis acid in thionyl chloride, or with a sulfonic acid.[280]

e.g. (i) $S_3N_2Cl_2 + MCl_3 \xrightarrow{SOCl_2} S_3N_2Cl^+\ MCl_4^-$ (M = Al,Fe. this thesis)

(ii) $S_3N_2Cl_2 + HSO_3Cl \longrightarrow S_3N_2Cl\ SO_3Cl$[280]

(iv) $S_3N_2Cl_2$ Physical properties

$S_3N_2Cl_2$ is an orange crystalline solid which is very sensitive to moisture, reacting instantly with water to form sulfur dioxide, ammonium chloride and sulfur but is indefinately stable to dry nitrogen at 20°C. It is insoluble in anhydrous organic solvents, and reacts with concentrated sulfuric acid, a uv. spectrum showing decomposition over a period of a few minutes (this thesis, Page 240). $S_3N_2Cl_2$ melts with decomposition at 90° to 92°C.[249]

3. Thiodithiazyl Monochloride S_3N_2Cl

S_3N_2Cl is prepared by heating powdered $S_3N_2Cl_2$ in vacuo at 80° to 90°C,[52,249] (see experimental section, Chapter 2), by stirring powdered $S_3N_2Cl_2$ with anhydrous formic acid at room temperature (Chapter 7, this thesis), by the reaction of S_4N_4 with S_2Cl_2 ($S_4N_4 + S_2Cl_2 \rightarrow 2\ S_3N_2Cl$),[4] by the reaction of S_4N_4 with NOCl:[4]

$$S_4N_4 + 2\ NOCl \longrightarrow S_3N_2Cl + \tfrac{1}{2}\ S_2Cl_2 + NO$$

or by the action of nitric oxide on $(NSCl)_3$ in nitro methane:[4]

$$8(NSCl)_3 + 24\ NO \longrightarrow 6\ S_3N_2Cl + 12\ NOCl + 3\ S_2Cl_2 + 12\ N_2O$$

The last reaction is thought to go via S_2N_2 as an intermediate.

S_3N_2Cl is a dark green powder with a metallic lustre, stable to dry air, but hydrolysed slowly by moisture. It does not have a sharp melting point, decomposing in vacuo between 120° and 140°C, yielding SCl_2, NSCl and S_4N_3Cl.[249] It is insoluble in organic solvents, but slightly soluble in liquid SO_2 (this thesis). The properties, reactions and structure of S_3N_2Cl and its derivatives, form the subject of Chapter 7 of this thesis.

4. Trithiazyl Trichloride $(NSCl)_3$

(i) Physical properties

$(NSCl)_3$ forms yellow needles of density 2.09. It is stable in a dry atmosphere, but is decomposed by water to yield sulfur dioxide and ammonium chloride. Its melting point has been stated as: 75° (decomp.) crude product, 91° (pure product),[249] and 162.5° (decomp.).[17,116,120] It is soluble in benzene, carbon disulfide, carbon tetrachloride (24g/litre at 21°C[214]), thionyl chloride, sulfuryl chloride and liquid SO_2.

$(NSCl)_3$ undergoes a reversible decomposition into the monomeric NSCl, when $(NSCl)_3$ is heated in high vacuum[281,282,283]: $(NSCl)_3 \rightleftharpoons 3NSCl$. This system has been studied, and the pressure of NSCl vapour measured in a static system.

The following thermodynamic values were calculated:

$$(NSCl)_3\ (s) \longrightarrow 3\ NSCl\ (g) \quad \Delta H^\circ = 46.2 \pm 1.5\ \text{K.cal.mole}^{-1}$$
$$\Delta S^\circ = 129.6 \pm 4.8\ \text{cal.deg.}^{-1}$$

and

$$(NSCl)_3\ (s) \longrightarrow (NSCl)_3\ (g) \quad \Delta H^\circ = 24.3 \pm 1.5\ \text{K.cal.mole}^{-1}$$
$$\Delta S^\circ = 52.1 \pm 4.6\ \text{cal.deg.}^{-1}$$

The large value of ΔS^o for entropy of sublimation, (52.1 ± 4.6 cal.deg.$^{-1}$), was indicative of the existence of many degrees of freedom in the $(NSCl)_3$ molecule, implying a puckered rather than a flat ring.[283]

The electric dipole moments of the NSCl molecule have been measured as:

$$|\mu_{Total}| = 1.87 \pm 0.02 \text{ D}^{282}$$
$$|\mu_a| = 0.57 \pm 0.03 \text{ D}$$
$$|\mu_b| = 0.57 \pm 0.03 \text{ D}$$

The NSCl molecule is therefore not linear.[284] (See section on structure of $(NSCl)_3$).

(ii) Preparative routes

(a) Chlorination of S_4N_4 or $S_3N_2Cl_2$

$(NSCl)_3$ may be formed by the chlorination of $S_3N_2Cl_2$ or S_4N_4 by chlorine gas, or SO_2Cl_2. The reactions may be summarised:

(i) $3\ S_3N_2Cl_2 + 3\ SO_2Cl_2 \xrightarrow[20^oC]{SO_2Cl_2,\text{24 hrs.}} 2\ (NSCl)_3 + 3\ SO_2 + 3\ SCl_2$ [279]

(ii) $3\ S_4N_4 + 6\ SO_2Cl_2 \xrightarrow[20^oC]{SO_2Cl_2,\text{24hrs.}} 4\ (NSCl)_3 + 6\ SO_2$ [279]

(iii) $3\ S_3N_2Cl_2 + 3\ Cl_2 \longrightarrow 2\ (NSCl)_3 + 3\ SCl_2$ [249]

(iv) $3\ S_4N_4 + 6\ Cl_2 \longrightarrow 4\ (NSCl)_3$ [115]

All the above methods are easily carried out, and give high yields of $(NSCl)_3$. The reactions of S_4N_4 with chlorine and SO_2Cl_2 probably go via $(NSCl)_4$ as an intermediate.[115,279]

(b) Reaction of ammonium chloride with S_2Cl_2

When a suspension of ammonium chloride in S_2Cl_2 is refluxed, the main product is NSCl. $S_3N_2Cl_2$ is produced if larger amounts of ammonium chloride are used.[52,285]

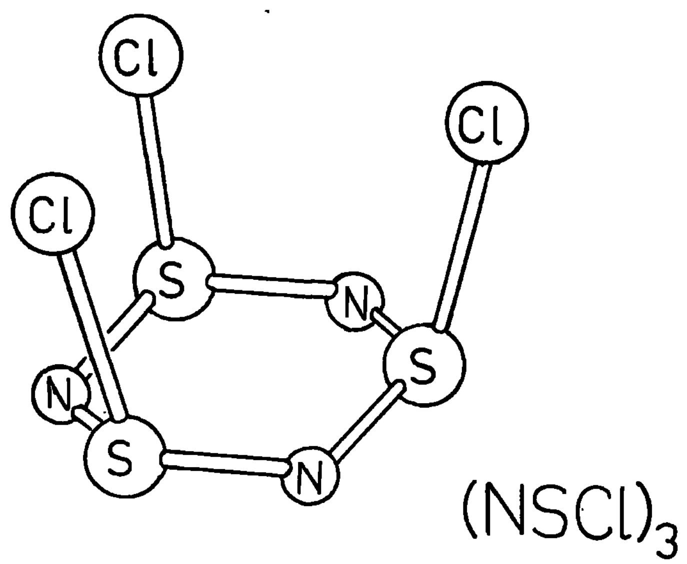
(c) Reaction of S_2Cl_2 with activated nitrogen

When S_2Cl_2 is passed into nitrogen, activated by microwave discharge, the main products are NSCl and SCl_2, with small amounts of $S_3N_2Cl_2$.[285] This method has been studied briefly in Durham. It requires much effort for relatively little product,[113] and so is of little preparative significance.

(iii) Structure of $(NSCl)_3$

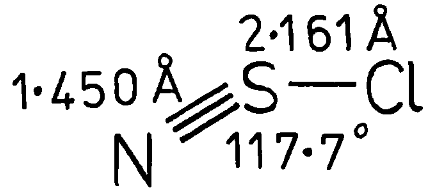
Crystalline $(NSCl)_3$ is monoclinic, the molecule existing in the chair form with chlorine atoms in the axial positions (Figure 1.17):[286]

Figure 1.17



All S-N bonds are equal (1.61 Å,[286] 1.65 Å [287]) as are the S-Cl bonds (2.15 Å [286]). The fact that all S-N bonds are short and equal, indicates that delocalised $p\pi$ -$d\pi$ bonds are present.[17,286]

$(NSCl)_3$ undergoes reversible thermal dissociation into the green gaseous monomer NSCl.[1,281,282,284] Microwave analysis shows the structure to be non-linear:[284]



$(NSCl)_3$ is regarded as a 6π delocalised system containing $p\pi - d\pi$ bonds,[286] although the ring is not planar due to the exocyclic chlorine atoms. The presence of a "pseudo" 6π system probably explains why $(NSCl)_3$ is more stable than $(NSCl)_4$, (probable intermediate), and in the corresponding $(NSF)_4$, the S-N bonds alternate in length between single and double bond lengths (1.660 and 1.540 Å)[287] indicating little or no delocalisation.

(iv) <u>$(NSCl)_3$ Reactions</u>

$(NSCl)_3$ is a fairly reactive compound. Its main types of reaction are: (a) fluorination; (b) adduct formation with Lewis acids and subsequent reactions; (c) hydrolysis and decomposition; (d) reaction with imides; (e) reaction with epoxides.

(a) <u>Fluorination</u>

$(NSCl)_3$ can be fluorinated by AgF_2 in CCl_4, to form $(NSF)_3$ (m.pt. 74.2°, B.pt. 92.5°C).[116]

(b) <u>Adduct formation</u>

$(NSCl)_3$ forms adducts with Lewis acids (e.g. $AlCl_3$, $FeCl_3$, $SbCl_5$) in thionyl chloride, for example: $(NSCl)_3$, x $SbCl_5$ (x = 1 to 3).[288,289] These adducts are of unknown structure, and extremely air sensitive. They undergo further reactions with S_4N_4 and SCl_2 to yield $S_5N_5^+$ [288] and $S_2NCl_2^+$ salts[289,290,291] (this thesis). The $S\text{-}N^+$ ion has been observed in certain compounds with a very strong Lewis acid.

e.g. $(NS^+)(XF_6^-)$, (X = As,Sb).[292,293]

$(NSCl)_3$ also forms adducts with SO_3, to form $(NSCl)_3$, 6 SO_3, and $(NSCl)_3$, 3 SO_3 on heating in vacuo,[152] $(NSCl)_3$, 2.8 SO_3 is also reported.[63] When heated between 140° and 160°C, SO_2 is lost and α-sulfanuric chloride $N_3S_3O_3Cl_3$ is formed.[63] It has a similar structure to $(NSCl)_3$, with oxygen atoms, as well as chlorine, attached to each sulfur.[294]

(c) Hydrolysis and decomposition

$(NSCl)_3$ is hydrolysed by alkali, according to the equations:[295]

(i) $(NSCl)_3 + 9OH^- \longrightarrow 3\ SO_3^{2-} + 3\ Cl^- + 3\ NH_3$

(ii) $(NSCl)_3 + 3\ SO_3^{2-} \xrightarrow{9H_2O} 3\ S(OH)_2 + 3\ SO_4^{2-} + 3\ Cl^- + 3\ NH_4^+$

(d) Reaction with imides

$(NSCl)_3$ reacts with sulfur imides, to form S_4N_4.

i.e. $4\ (NSCl)_3 + 3\ (SNH)_4 \xrightarrow[CCl_4]{boil} 6\ S_4N_4 + 12\ HCl$ [63]

and $4\ (NSCl)_3 + 12\ S_7NH \longrightarrow 6\ S_4N_4 + 12\ HCl + 84S$ [254]

(e) Reaction with epoxides

$(NSCl)_3$ reacts with epoxides to give esters of the hypothetical acid $(NS.OH)_3$[296]

e.g. $(NSCl)_3 + \underbrace{CH_2 - CH}_{O} - CH_2\ Cl \longrightarrow [NS.OCH(CH_2Cl)_2]_3$

The esters are obtained as moisture sensitive red oils.

5. Trithiazyl Monochloride S_3N_3Cl

S_3N_3Cl has been known since 1932,[248] but only recently has a repeat preparation been reported, although with very little practical detail.[128] It is obtained in 50% yield from $(NSCl)_3$, S_4N_4 and some free chlorine in an inert solvent, and separates as brick red crystals (M.pt. 165°C). Very little work has been done on this compound, and its structure is unknown.

6. The Compounds: $(S_5N_4Cl)_n$, $S_{10}N_8Cl_2$ and $S_6N_2Cl_2$

$(S_5N_4Cl)_n$ has been reported as being formed from the solid phase reaction between sulfur and nitrogen (as ammonium chloride) in the presence of thio urea.[297] It is obtained as a brownish silky powder, insoluble in water and acids but completely soluble in alkali. On pyrolysis (400°-500°C), the compounds $S_{10}N_8Cl_2$ and $S_6N_2Cl_2$ are formed. The structure of all three compounds is unknown, although several cage structures based on two linked S_4N_4 cages were suggested for $S_{10}N_8Cl_2$.[297]

(D) The Sulfur Imides

1. Introduction

The sulfur imides form a large section of sulfur-nitrogen compounds containing "saturated" S-N bonds. The first members to be discovered are based on the S_8 ring, and are of the general formula: $S_x(NH)_{(8-x)}$, but more recent work has produced a much wider range of compounds and structures, containing linked and fused rings, but retaining the same basic structure. The bonding is thought to involve some π-bonding as well as simple σ-bonding.

Reviews which include a detailed consideration of sulfur imides have been written by Allcock,[14] Becke-Goehring,[2,15,227] Haiduc,[18] Gmelin,[16] Heal[8] and Schmidt.[19] The sulfur imides[298] and nitrides[9] have also been reviewed by Heal. The preparation, properties and reactions of the sulfur imides ($S_4(NH)_4$ and S_7NH) are the subject of chapters 3 and 4 (this thesis).

2. The Sulfur Imides based on the S_8 ring Structure and Bonding

The S_8 ring has a crown conformation and by replacing one or more non-adjacent sulfur atoms by >NH groups, the sulfur imides are theoretically formed. All the possible imides based on the S_8 ring and not containing N-N bonds are known. These are: S_7NH, $S_6(NH)_2$ (three isomers), $S_5(NH)_3$ (two isomers) and $S_4(NH)_4$.

The molecular structures of all these imides have been determined by x-ray diffraction, and for $S_4(NH)_4$, also by neutron diffraction.[299] In every case the molecule consists of a puckered 8-membered ring of approximately C_{4v} symmetry[300] as in S_8.[301-308]

The S-N bond distances decrease from 1.73 Å in S_7NH to 1.67 Å in $S_4(NH)_4$,[305] and the SNS bond angle increases from 115.8° in S_7NH to 128.5° in $S_4(NH)_4$. The average 1.3 sulfur-sulfur separation also decreases from 3.23 Å in S_7NH to 2.98 Å in $S_4(NH)_4$.[278]

The bonding in these imides is still a subject of discussion, particularly with regard to the importance of π-bonding. Heal[309] considers that the hindrances to rotation about S-N bonds, and hence the shape and stability of the S-N frameworks are likely to be affected by repulsive interactions between lone pairs, and by π-bonding between p-electrons on nitrogen and 3d-orbitals on sulfur. Gleiter[86] however, discounts π-bonding in such systems, and by comparing bond angles in S_8 and $S_4(NH)_4$ considers that the same character of bonds is present. The variation in the length of an S-S "single" bond is solely due to changes in the orbital character of the bond.[81] In $S_4(NH)_4$ the S-N bond is taken to contain ca.22% s-character, and is essentially single. Garcia-Fernandez [310,311] has correlated the S-N bond ir. stretching frequencies of the sulfur imides, and other 8-membered sulfur-nitrogen rings, with the bond lengths and strengths, and with the sulfur oxidation numbers. He concludes that, whereas in S_7NH, there is little π-bonding in the ring, it increases to near the theoretical maximum of half a π-bond per S-N link in $S_4(NH)_4$; therefore the lone pair involvement increases, and this is supported by the diminishing Lewis base and stereochemical activity of the nitrogen lone pair electrons.[298]

Banister,[101,106] considers that both the sulfur and nitrogen lone pairs make important contributions to the bonding, the lone pairs on nitrogen interacting with the vacant sulfur d-orbitals, so that the imides can be regarded as an isoelectronic series in which the nitrogen atoms induce a positive charge on neighbouring sulfur atoms, the changes in the 1:3 sulfur-sulfur mean distances and in the ring bond angles at both nitrogen and sulfur, are considered indicative of the increasing involvement of the nitrogen and sulfur lone pairs in the cage bonding, reaching a maximum at $S_4(NH)_4$. As a result, the structures are regarded as being composed of a σ-framework, and a superimposed set of higher energy electrons in delocalised "cage" molecular orbitals.

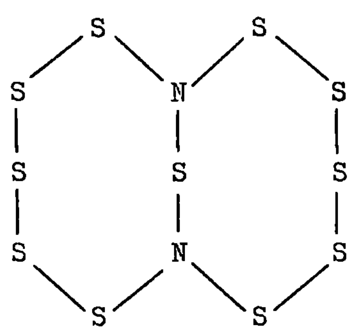
In $S_4(NH)_4$, the $\genfrac{}{}{0pt}{}{S}{S}\!>$N-H groups are coplanar,[299] indicating a considerable loss in stereochemical activity of the nitrogen lone pairs, although there is some doubt as to whether similar groupings in the other imides are also coplanar.

3. Structures of the other Sulfur Imides

Other sulfur imides are also known, and can be regarded as being derived from the imides based on S_8, by coupling together two rings by sulfur chains, or by fusing two rings together. These are: $HN(S_3)_2N.S_2.N(S_3)_2NH$,[312] $S_7N-S_x-NS_7$ ($x = 1,2,3$ or 5),[235] and the fused ring $S_{11}N_2$.[313] (The compounds $S_7N-S_x-NS_7$ and $S_{11}N_2$ are strictly nitrides rather than imides, since they do not contain hydrogen).

$S_{11}N_2$ has an interesting structure.[314,315] It crystallises in two forms, α and β, which differ only in the mode of packing of the crystals. X-ray data shows it to consist, as expected, of two crown-shaped rings, fused in the 1,3 positions. Each of the two $\frac{S}{S}{>}N-S$ units is planar, and π-bonding therefore probably occurs between the nitrogen and neighbouring sulfur atoms. (Figure 1.18)

Figure 1.18



$S_{11}N_2$

$S_4(NH)_2$ has been reported as the product of the reduction of S_4N_2 in ethanol by stannous chloride[241] although this could not be repeated.[9]

4. Imides with N-N Bonds

Organic derivatives of sulfur imides containing N-N bonds, have recently been prepared.[316-320]

5. Imides based on other rings

Sulfur rings of sizes other than S_8 are known; for example: S_6,[321-324] S_7,[325,326] S_9,[322] S_{10},[323,325] S_{11},[322] S_{12},[327,328,329] S_{18},[330] and S_{20},[322,330] but no imides based on these rings are known (apart from possible $S_4(NH)_2$), although they should be preparable. The nitride: $S_{14}N_4$, consisting of three fused rings should be very stable, but all attempts to prepare it via condensation reactions have so far failed.[9]

Imides in which selenium partially replaces sulfur should also be preparable, since selenium analogues of S_8, e.g. S_7Se,[331,332] S_6Se_2 and S_5Se_3, have been prepared.[322]

6. Sulfur Imides Physical Properties

S_7NH forms almost colourless rhombic bipyramids of density 2.01 at 20°C.[8] It is insoluble in, and unaffected by water, but is readily soluble in most organic solvents, particularly carbon disulfide, and pyridine to which it hydrogen bonds.

Its melting point has been reported as 113.5°C,[8,333,334] and 111°C[41,335] (with decomp.), the lower value probably being due to traces of sulfur as impurity. Its standard enthalpy of formation has been estimated as -67.4 K.cal/mole.[129]

The other sulfur imides, $S_6(NH)_2$ and $S_5(NH)_3$ also form colourless crystals, 1,4-$S_6(NH)_2$ however darkens superficially in light.[8] The melting points are: 1,5-$S_6(NH)_2$: 153°C,[306] 1,4-$S_6(NH)_2$: 130°C,[306] 1,3-$S_6(NH)_2$: 123°C,[306] 1,4,6-$S_5(NH)_3$: 131°C,[336] 1,3,5-$S_5(NH)_3$: 124°C.[336,337] The imides may be separated chromatographically,[30] the di-imides being separated from each other by recrystallisations from carbon disulfide.

The infrared and Raman spectra of S_7NH and the hexa-sulfur imides have been recorded and analysed.[241,338,339] Characteristic absorptions of the imides occur at 3,220-3,380 cm^{-1} (NH stretch), 1,260-1,310 cm^{-1} (NH bend), and 690-920 cm^{-1} (S-N stretch). The infrared spectra of the methyl derivatives: $S_x(NMe)_{8-x}$, (x = 1 to 4) have also been recorded.[340-343]

$S_4(NH)_4$ forms small colourless crystals, M.pt = 145°C.[226] It is insoluble and stable to water and insoluble in most non-polar organic solvents. It is soluble in pyridine, to which it hydrogen bonds. The enthalpy of formation from its atoms has been determined as 754 K.cal/mole^{-1} from combustion calorimetry.[96]

$S_{11}N_2$ forms amber coloured crystals. Slow evaporation from CS_2 gives the more stable α form, whereas rapid evaporation yields the β form. $S_{11}N_2$ is slightly soluble in other organic solvents and is insoluble and unaffected by water.[314] It melts at 150°C,[313,314,315] and has a heat of formation of 282 KJ/mole.[314]

$S_{15}N_2$ (M.pt 137°C),[235] $S_{16}N_2$ (M.pt 122°C) and $S_{17}N_2$ (M.pt 97°C) (coupled rings), are yellow crystalline solids, fairly soluble in CS_2, but only slightly soluble in other non-polar solvents.

The infrared spectra of all these compounds show a strong characteristic S-N stretch in the region 750-775 cm.$^{-1}$ [9]

7. Sulfur Imides Preparative Routes

The most widely used preparative routes for sulfur imides are from ammonia and chlorosulfanes. All sulfur imides based on S_8 (apart from $S_4(NH)_4$) are formed together, S_7NH being the main imide product, and are separated chromatographically.[29,30]

(i) Preparation from ammonia and chlorosulfanes

S_7NH was the first imide to be prepared by the reaction of ammonia gas with S_2Cl_2 in chloroform.[344,345] The present preparations are similar, dimethyl formamide or carbon disulfide being used as solvents.[41,44,45,335,346,347] (See preparation of S_7NH, Chapter 2, this thesis). The effect of solvent, temperature, ammonia flow rate, type of chlorosulfane and duration of run on the yields of imide, have been studied.[43,348]

(ii) Preparation of S_7NH using hydrazine

Anhydrous hydrazine on silica gel reacts with S_4N_4 or S_4N_3Cl at 45° to 50°C in an inert organic solvent (benzene or CCl_4) to give S_7NH and other imides in an overall reaction:[301,333,334]

e.g. $$2\ S_4N_4 + N_2H_4 \longrightarrow NH_3 + 4\ N_2 + S + S_7NH$$

(iii) Preparation of S_7NH using azides

Chlorosulfanes react with alkali metal azides (except LiN_3) in polar organic solvents to form S_7NH and some $S_6(NH)_2$ (all three isomers).[339]

(iv) Reduction with $LiAlH_4$ or Raney nickel

S_4N_4 or S_4N_3Cl can be reduced with $LiAlH_4$ or using Raney nickel to yield S_7NH.[333]

(v) Preparation using liquid ammonia

S_7NH has been prepared by adding heavy metal ions to solutions of sulfur in liquid ammonia at room temperature, to precipitate out the insoluble sulfide (see Chapter 3, this thesis).

(vi) Preparation of other imides

(a) $S_4(NH)_4$

This imide and also imides not based on S_8, are not formed in any detectable quantities in the above reactions, therefore other preparative routes are used.

$S_4(NH)_4$ is conveniently prepared by the reduction of S_4N_4 with an alcoholic solution of $SnCl_2$ in benzene.[64,75,131,350] This is the only known method of preparing this compound. (See Chapter 2, experimental section).

(b) $S_{11}N_2$

This has been prepared via a double condensation of Cl_2S_5 (or other chlorosulfanes), with $1,3(NH)_2S_6$ in carbon disulfide containing pyridine.[313,315,351]

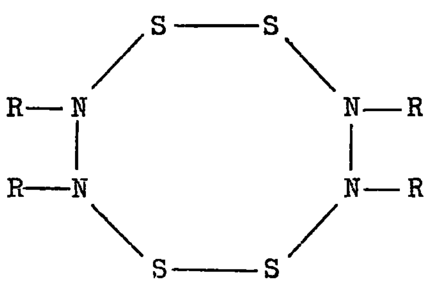
(c) Preparation of the coupled ring nitrides, S_7N-S_x-NS_7

These nitrides (x = 1,2,3 and 5) can be synthesised by the condensation of two molecules of S_7NH with a chlorosulfane in CS_2, in the presence of pyridine.[9] Efforts to prepare $(S_7N)_2$ have so far failed.[352]

(d) Preparation of imides containing N-N bonds

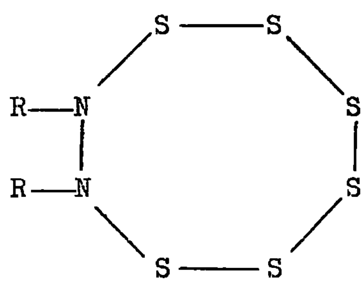
Substituted sulfur imides containing N-N bonds have recently been prepared by the reaction between chlorosulfanes and organic hydrazine derivatives.[316-320]

e.g.



I

R = Me, $MeCO_2$, $EtCO_2$



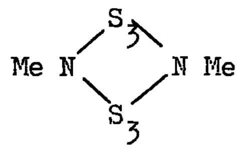
II

R = $MeCO_2$, $EtCO_2$

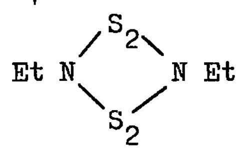
Attempts to prepare the unsubstituted imide, by reacting chlorosulfanes with hydrazine, or by removing the organic groups by acidolysis or pyrolysis have so far failed.[316]

(e) Imide derivatives

Imide derivatives are usually prepared from the parent imide (see reactions of imides: section (d)), however, alkyl derivatives can be prepared from chlorosulfanes and an amine: RNH_2,[340,341] as well as alkyl derivatives of S_6 rings.[353,354]

e.g. (i) $S_3Cl_2 + Me\ NH_2 \longrightarrow$  [341]

(ii) $S_7Cl_2 + Me\ NH_2 \longrightarrow S_7N\ Me$ [340]

(iii) $S_2Cl_2 + Et\ NH_2 \longrightarrow$  [353,354]

(iv) $S_7Cl_2 + H_2N.N\ (COOEt)_2 \longrightarrow S_7N.N\ (COOEt)_2$ [318]

Ethoxy carbonyl derivatives of S_7NH and $S_6(NH)_2$ have been prepared directly from sulfur and ethylazidoformate in decalin at 125°C.[355]

$$S_8 + N_3\ COOEt \longrightarrow S_7N\,COOEt + S_6(N\,COOEt)_2$$

Crystal structure determinations have been carried out on the compounds $S_7N\text{-}N(CO_2Et)_2$,[356] and $S_4(NCH_3)_4$[357].

8. Reactions of Sulfur Imides

The reactions of the sulfur imides are of seven main types:[278] (i) Addition reactions with organic substrates; (ii) Adduct formation with Lewis acids; (iii) Hydrogen substitution; (iv) Hydrogen abstraction; (v) Oxidation to a corresponding thionyl imide; (vi) Ring contraction; (vii) Ring degradation.

(i) Addition reactions with organic substrates

$S_4(NH)_4$ reacts with excess aqueous alkaline formaldehyde to form $(SN\cdot CH_2OH)_4$ in high yields.[64,75] The product is easily recrystallised from water or organic solvents. (See Chapter 4, this thesis). Similar reactions occur with $S_5(NH)_3$ and S_7NH to give $S_5N_3(CH_2OH)_3$[181] and $S_7N\ CH_2OH$[344] respectively, although $S_7N\cdot CH_2OH$ is only formed in very low yields.[344]

Addition reactions also occur with isocyanates (Chapter 4, this thesis).
e.g. $S_4(NH)_4 + 4\ Ph{\cdot}NCO \longrightarrow (SN{\cdot}CONHPh)_4$.[64]

(ii) <u>Adduct formation with Lewis acids</u>

The reactions of sulfur imides with Lewis acids normally lead to rearrangement or elimination reactions, however $S_4(NH)_4$ reacts with $AlCl_3$ and $AlBr_3$ to form 1:1 adducts in which the imide ring is still intact.[358]

(iii) <u>Hydrogen substitution</u>

The sulfur nitrides: $S_{11}N_2$ and $S_7N\text{-}S_x\text{-}NS_7$ (x = 1,2,3 and 5) have been prepared by the action of chlorosulfanes on sulfur imides with the elimination of HCl[9,313,314,315,359] (See sulfur imides, preparative routes). Similar condensations of S_2Cl_2 with the hexasulfur di-imides, give rise to linear polymers in which eight membered sulfur nitrogen rings are coupled together by $-S_2-$ groups.[312]

S_7NH reacts with acetyl chloride to form $S_7N{\cdot}COCH_3$ in fair yields,[360] and other similar derivatives may be formed from S_7NH and free carboxylic acid.[361] With diborane, S_7NH forms S_7NBH_2 which forms 1:1 adducts with ethers and pyridine,[362] and with BCl_3 and BBr_3 to give the corresponding dihalo (heptasulfurimido) boron,[363] however with BI_3, decomposition occurs.

S_7NH reacts with di(trimethyl silyl) amine, $(Me_3Si)_2NH$, to yield $Me_3Si\text{-}NS_7$.[364]

(iv) <u>Hydrogen abstraction</u>

The S_7NH,[365] 1,4-and 1,5- $S_6(NH)_2$[343] and $S_4(NH)_4$[358] rings can be metallated stepwise using alkyl lithium reagents or other strong basis,[366] producing the corresponding sulfur imide anion.

e.g. (a) $S_4(NH)_4 \xrightarrow{n\,Bu\text{-}Li}$ several steps $\longrightarrow (SN\ Li)_4$[358]

(b) $S_7NH + NaCPh_3 \xrightarrow{Et_2O} Na\ S_7N$[36]

(c) $Li\,[AlH_4] + S_4(NH)_4 \xrightarrow{THF} Li\,[Al(S_4N_4)]$ [367]

Alkyl derivatives have been obtained by treating the metallated products with alkyl halides.[342,343,365]

e.g. $S_7NH \xrightarrow{R'Li} S_7N^- \xrightarrow{RX} S_7NR$ [365]

(v) Oxidation

When a 4:1 mixture of sulfur and $S_4(NH)_4$ is heated to 110° to 120°C in air, oxidation occurs and an orange-red tetramer of thionyl imide $(OSNH)_4$ is formed,[368] which slowly polymerises at room temperature. Ozone reacts with $S_4(NH)_4$ in CCl_4 to form a compound of formula $(OSNH)_x$, however the infrared spectrum shows it to be a different compound from the polymeric thionyl imide obtained by Böing and Fluck.[369]

(vi) Ring contraction

$S_4(NH)_4$ reacts with chlorine or sulfuryl chloride to form trithiazyl trichloride $(NSCl)_3$, with bromine or excess bromosuccinimide to form thiotrithiazyl bromide S_4N_3Br, and with acetyl chloride to yield thiotrithiazyl chloride, S_4N_3Cl, by ring contraction.[358] With $(NSCl)_3$, $S_4(NH)_4$ forms S_4N_4 in high yields.[63]

$S_4(NH)_4$ reacts with mercuric acetate in methanol at -10°C to form $Hg_5(NS)_8$ (greenish yellow powder) and with excess mercuric acetate, in the presence of pyridine to yield $Hg(NS)_2$ $Hg_5(NS)_8$ which is said to be a molecular compound of 3 $Hg(NS)_2$ and $Hg_2(NS)_2$.[131]

(vii) Ring degradation

The epr. spectra of the red solution formed during the decomposition of S_7NH in concentrated sulfuric acid at 25°C, shows five equidistant lines with intensity ratios 1:2:3:2:1, which was attributed to the dimeric radical cation $(S_7N)_2^{+\cdot}$.[370] The ion NS_4^- has been identified from solutions of S_7NH in basic media.[371,133]

$S_7(NH)_4$ and S_7NH are quantitatively oxidised in homogeneous acid solution by chloramine-T, to sulfuric acid.[89,372,373] S_7NH hydrolyses rapidly in homogeneous alkali solution to form a mixture of sulfide, sulfite and thiosulfate.[372]

The thermal decomposition of sulfur imides produces S_4N_4 as the only sulfur nitrogen decomposition product.[61,62]

9. Sulfur Imides, Practical Applications

S_7NH has found uses as a fungicide[334] and an insecticide, with a low toxicity for higher organisms,[374] and also as an effective vulcanising agent for rubbers,[1,375,376,377] as have imide derivatives.[378]

EXPERIMENTAL

CHAPTER 2

Experimental

(A) Handling Techniques

1. The Glove Box

Most of the compounds dealt with were air and moisture sensitive, and were therefore handled in a vacuum line or under nitrogen. The nitrogen was obtained from the head of a tank of liquid nitrogen and dried by passing through several bottles of concentrated sulfuric acid and finally by passing over P_2O_5. Removal of oxygen was unnecessary, since the nitrogen from the source was practically oxygen free and none of the compounds handled were found to be oxygen sensitive.

Samples for infrared, ultraviolet and mass spectra and analysis were prepared in a glove box connected to a continuous supply of dry nitrogen.

The box was also fitted with two entry ports which could be purged individually or simultaneously. Traps of fresh P_2O_5 were kept in the entry ports and inside the box to remove any traces of moisture accidentally introduced. The box and ports were made of perspex so that their contents could be observed from any position. The box itself was mounted on wheels so that it could be moved when it was necessary to improve the access to the ports.

2. Spectra

Infrared spectra were recorded on Grubb-Parsons prism grating spectrophotometers (the GS 2A and spectromaster) in the range 4,000 to 400 cm^{-1} (2.5 to 25 $m\mu$). Most samples were prepared either in the form of nujol mulls between potassium bromide plates or as potassium bromide discs.

Ultraviolet and visible spectra were obtained with a Unicam SP.800 spectrophotometer on solutions in concentrated sulfuric and nitric acids, anhydrous formic acid, dioxane, benzene and triethylamine, using quartz cells of 1 cm. path length. The spectrophotometer was also used for the quantitative determination of extinction coefficients.

In this thesis, 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; sh = shoulder;

b = broad; vb = very broad (approximate range of absorption is also given)

obsc = absorption probably obscured by solvent.

Mass spectra were obtained on an AEl,(MS9) mass spectrometer; the samples were mounted on an inert ceramic and introduced on a direct insertion probe.

NQR spectra for nitrogen (14) and chlorine (35 and 37) were recorded by Waddington and Lynch, (this department).[379]

3. Chromatography

Chromatography was frequently used to separate and identify reaction products. For column chromatography a silica gel column of length 40 cm., diameter 2 cm., was used with CS_2 or CCl_4 as elutants.[29] The flow rate was approximately 5 ml/minute. The products were normally identified by their position on the column, and from their infrared spectra. In the thin layer chromatography experiments, plates of ca. 20 cm. in length and of various widths were used.

The plates were "spotted" with the solution from a dropping pipette, and supported in an airtight tank. (Shandon-Southern, "TLC. Chromatank") The plate material was silica, which was impregnated with a fluorescent material, so that after a chromatographic run the spots on the plates could be located and identified by their dark appearance under ultraviolet light.

4. High Pressure Reactions

Reactions involving the use of liquid ammonia or liquid sulfur dioxide at temperatures above their normal boiling points at atmospheric pressure (-37°C for NH_3 and -10°C for SO_2), were carried out in Carius tubes. The reagents and magnetic stirrer (if necessary) were placed in the tube and the gas transferred from the vacuum line cold trap in which it had been dried (see purifications of solvents, Page 76), into the Carius tube, which was cooled in liquid nitrogen. After a suitable amount of gas had been condensed the tube was sealed in vacuo using a hand blow torch. It was placed behind a brick wall and blast screen and allowed to slowly warm up to room temperature. If necessary the Carius tube was heated above room temperature (but not above 60°C), using a water bath.

When the reaction had been completed the tube was cooled to -195°C, the neck of the tube was scratched with a glass knife and inserted (beyond the scratch) into a length of rubber tubing under a pressure of dry nitrogen. The neck was broken inside the tubing thus filling the tube with dry nitrogen. The solvent was then slowly pumped off under reduced pressure through a vacuum line and condensed out in a cold trap. Finally the dry reaction products were removed from the Carius tube in the dry box.

5. Electrolytic Apparatus

The electrolytic cells are described in Chapter 3.

6. Melting and Decomposition Points

These were determined by heating the compound in sealed tubes.

7. Analyses

Analyses were carried out, in this department, by Mr. R. Coult.

(B) Preparation and Purification of Starting Materials

1. Solvents

Thionyl chloride was purified by one of two methods: Method (i) gave a purer product; Method (ii) was more convenient and was used where high purity was not essential.

Method (i)

Triphenyl phosphite (10 per cent wt.) was added to the thionyl chloride with vigorous stirring for 30 minutes. The mixture was fractionated through a twelve inch column packed with glass helices and connected to a reflux distilling head equipped with a calcium chloride drying tube. The first and last fractions distilling over were discarded, and the middle fraction collected. Redistillation of this with more triphenyl phosphite gave a practically clear liquid.[380]

Method (ii)

Thionyl chloride was refluxed with flowers of sulfur for three hours, and then distilled under dry nitrogen. The first and last fractions were discarded and the middle fraction, distilling at 75° to 76°C, was collected. The thionyl chloride was redistilled to give an almost colourless product.[381]

Thionyl chloride was stored in a stoppered flask under vacuum or dry nitrogen. The liquid attacks grease and so contact with greased joints during storage was kept to a minimum. The liquid gradually turns from colourless to pale yellow over a period of a week or so, and so stored samples of thionyl chloride were purified by redistillation on a weekly basis as necessary. Since thionyl chloride reacts with water to form the gases hydrogen chloride and sulfur dioxide: $SOCl_2 + H_2O \longrightarrow SO_2 + 2HCl$,[382] a dehydrating agent was not required. Thionyl chloride has an appreciable vapour pressure at room temperature (e.g. 96.65 mm. at 20°C).[383]

Sulfuryl chloride. AnalaR "redistilled" sulfuryl chloride was used without further purification, since the reactions for which this liquid was used did not require a high purity.

Sulfur dichloride (SCl_2) and disulfur dichloride (S_2Cl_2) were used without further purification since the reactions for which they were used did not require a high purity. A purification procedure for S_2Cl_2 has been described.[384]

Formic acid was dried over boric oxide (which had previously been heated to ca. 120°C for 24 hours), and fractionally distilled.[385] It was stored under dry nitrogen at -15°C (solid) since it decomposes slowly at room temperature to H_2O and CO.

Concentrated sulfuric acid (98%) was used without further purification after examining the uv. and visible spectra for any spurious absorptions. The strength of the acid was determined by dilution and titration against standard sodium hydroxide solution.

Chlorosulfonic acid was freshly distilled under reduced pressure at ca. 60°C before use.

Diethyl ether, benzene, toluene and petroleum ether were dried over sodium wire.[385]

Pyridine was dried over caustic soda pellets.[385]

Carbon tetrachloride was distilled at 77°C and dried over P_2O_5.

Dioxane was dried over caustic soda pellets, distilled, dried over sodium metal, distilled, and stored under nitrogen over sodium metal.[385]

Ammonia (for use as a non-aqueous solvent) was distilled from an ammonia cylinder via a vacuum line into a cold trap containing a few pieces of sodium metal and cooled in liquid air. The ammonia could be temporarily stored in liquid air under dry nitrogen. For use in reactions, the cold trap was warmed and the ammonia transferred via a vacuum line or in a current of dry nitrogen to the cooled reaction vessel.

Sulfur dioxide (for use as a non-aqueous solvent) was distilled from a cylinder via a vacuum line into a cold trap containing P_2O_5 as drying agent and cooled in liquid air. The sulfur dioxide could then be transferred to a reaction vessel in the same way as for ammonia (above).

Cold baths were used for handling liquid NH_3 and SO_2:

Carbon tetrachloride slush: $-22.9^{\circ}C$ (for liquid SO_2)

Chlorobenzene slush: $-45.2^{\circ}C$ (for liquid NH_3)

Dry ice/acetone or methanol bath: $-78.5^{\circ}C$

Liquid nitrogen: $-196^{\circ}C$ (solid SO_2 and NH_3)

Ammonia: Boiling point = $-33.35^{\circ}C$ (atmospheric pressure)

Melting point = $-77.7^{\circ}C$

Sulfur dioxide: Boiling point = $-10^{\circ}C$ (atmospheric pressure)

Melting point = $-72.7^{\circ}C$ [386]

2. Metal Chlorides

Ferric chloride was purified by refluxing under thionyl chloride for one hour, and then removing the thionyl chloride by distillation.

Aluminium chloride was sublimed under vacuum at *ca.* $120^{\circ}C$ onto a cold finger at $-78^{\circ}C$.

Antimony V and tin IV chlorides were freshly distilled at reduced pressure under dry nitrogen.

3. Organic Solvents

Nitrobenzene was distilled under reduced pressure and stored over calcium chloride.

Acetyl chloride was freshly distilled before use.

Trichloromethyl sulfenyl chloride was freshly distilled under reduced pressure before use.

4. Sulfur Nitrogen Starting Materials

(i) S_4N_4 was prepared by the method described by Jolly,[26] in which chlorine gas is passed through a solution of S_2Cl_2 in CCl_4 until the solution is saturated with the gas, followed by ammonia gas (2 hours). The solid product is washed with water, then diethyl ether, and finally extracted with benzene. (See description in the section on S_4N_4 preparations on Page 4 of the introduction).

Infrared spectrum: 1,160 (s), 1,125 (sh), 998 (vs), 682 (s), 637 (w), 603 (w), 565 (s), 466 (vs), ca. 450 (sh,b) cm^{-1}. (See spectrum in Appendix)

Ultraviolet spectrum: (200 to 700 nm) λ max. = 260 nm, (ε max. = 1.9×10^4) (dioxane) (See spectrum in Appendix)

(ii) Thiodithiazyl chloride, $S_3N_2Cl_2$ was prepared by a method[388] similar to that of Jolly.[52,249]

Dry powdered ammonium chloride (200 g) and powdered "flowers" of sulfur (40 g), were mixed in a large straight-sided flange-topped reaction vessel, fitted with an air condenser (about 50 cm. in length) topped with a calcium chloride drying tube and insulated from the reaction vessel by an asbestos sheet or cotton wool. The air condenser was temporarily removed and S_2Cl_2 (200 ml. 336 g) quickly added to the sulfur/ammonium chloride mixture. The mixture was heated to about 150°C on an oil bath for about 12 hours. During this time orange crystals formed on the sides of the air condenser. A critical factor in this preparation was that the highest point of reflux in the air condenser should slowly fall, and this was achieved by keeping the temperature of the oil bath and the air currents around the air condenser constant; the reflux position then gradually fell, as the S_2Cl_2 was consumed.

After the 12 hours, the condenser was quickly removed and attached to a two necked round bottomed flask (a stopper replacing the drying tube). It was then evacuated using a vacuum line trapping out excess liquid in a cold trap. Meanwhile, a second air condenser had replaced the original air condenser on the reaction vessel and the reaction continued. After evacuating the flask and the condenser containing the $S_3N_2Cl_2$ crystals for about half an hour, they were let down to atmospheric pressure with dry nitrogen and the crystals scraped into the flask using a stiff metal spatula or a glass rod under a back current of nitrogen ($S_3N_2Cl_2$ is very moisture sensitive). This was repeated for the second crop of product.

IR: (nujol mull): 1,015 (s), 936 (vs), 752 (w), 719 (sh), 712 (s), 578 (s), 458 (s), ca. 400 (s,b) cm^{-1}

UV: (conc. H_2SO_4 solvent): λ max. ca. 416 nm. and ca. 235 nm. (decomp. with time). (See Appendix for ir. and uv. spectra).

(iii) Trithiazyl trichloride, $(NSCl)_3$ was obtained from $S_3N_2Cl_2$ (prepared as above) by the method described by Alange, Banister and Bell.[279] Crystals of $S_3N_2Cl_2$ were placed in a dry, round bottomed flask, excess SO_2Cl_2 added and the mixture stirred for about 24 hours, the gases formed were allowed to escape via a conc. sulfuric acid bubbler. Evaporation to dryness under reduced pressure, and recrystallisation from dry CCl_4 (or from SO_2Cl_2 and filter at -10^oC), gave pale yellow needles of $(NSCl)_3$. The reaction is essentially quantitative.

$$3\ S_3N_2Cl_2 + 3\ SO_2Cl_2 \longrightarrow 2(NSCl)_3 + 3\ SO_2 + 3\ SCl_2$$

S_4N_4 may also be used in place of $S_3N_2Cl_2$ but the former preparation is to be preferred since $S_3N_2Cl_2$ is more easily prepared than S_4N_4.

The preparation from S_4N_4 may be summarised:-

$$3\ S_4N_4 + 6\ SO_2Cl_2 \longrightarrow 4(NSCl)_3 + 6\ SO_2$$

The reaction is again quantitative.

IR: (nujol mull): 1,015 (s,b), 699 (s), 623 (m,b), ca. 500 (s,vb) cm^{-1}
(See Appendix)

(iv) Thiotrithiazyl chloride (S_4N_3Cl), was prepared by the method described by Jolly.[249] The $S_3N_2Cl_2$ prepared previously was powdered and added to a mixture of excess S_2Cl_2 in dry carbon tetrachloride in a round bottomed flask fitted with a reflux condenser. The mixture was refluxed for ca. 4 to 6 hours, or until all the orange crystals of $S_3N_2Cl_2$ were replaced by a yellow powder. The $S_3N_2Cl_2$ turned green before the yellow S_4N_3Cl was formed, and this is thought to be due to the presence of S_3N_2Cl as an intermediate.[52]

Alternatively the crystals of $S_3N_2Cl_2$ adhering to the inside of the air condenser may be used directly by quickly transferring the air condenser onto the round bottomed flask containing S_2Cl_2 and CCl_4 and allowing the refluxing liquids to wash the crystals into the flask.

The product (yellow solid) was filtered off while still warm, washed with 20 ml. aliquots of dry carbon tetrachloride and dried by pumping off excess solvent, using a vacuum line. S_4N_3Cl is usually formed as a bright yellow powder, though very slow cooling of a hot saturated solution in thionyl chloride produces small orange crystals.[49] S_4N_3Cl is slowly attacked by moist air and so was stored under dry nitrogen, or in sealed bottles.

The conversion of $S_3N_2Cl_2$ to S_4N_3Cl is quantitative according to the equation:

$$3\ S_3N_2Cl_2 + S_2Cl_2 \longrightarrow 2\ S_4N_3Cl + 3\ SCl_2$$ [249]

S_4N_3Cl may also be prepared from $S_3N_2Cl_2$ by refluxing the latter in carbon tetrachloride only, S_4N_3Cl being slowly formed.[52]

IR spectrum: (as a nujol mull and as a KBr disc):

1,400 (w), 1,160 (s), 1,125 (sh), 998 (vs), 682 (s), 637 (w), 606 (w), 565 (s), 466 (vs), 450 (sh) cm^{-1}

UV spectrum: (conc. H_2SO_4 solvent) λmax. = 335, 262 nm. (slowly decomposes).

(See spectra in Appendix)

(v) <u>Thiodithiazyl chloride S_3N_2Cl</u>

S_3N_2Cl was prepared from thiodithiazyl dichloride ($S_3N_2Cl_2$) by the method described by Jolly.[249] Powdered $S_3N_2Cl_2$ was heated (<u>ca</u>. 80° to 90°) in vacuo with stirring for about 40 minutes. The $S_3N_2Cl_2$ gradually turned to a very dark green powder (S_3N_2Cl) and dark volatile (unidentified) products were deposited in the vacuum line and in the cold trap. After the reaction had been completed, the flask was let down to atmospheric pressure with dry nitrogen. The purity of the product was determined from ir. and uv. spectra (See Appendix) and by analysis:

IR (nujol mull): 1,015 (w), 962 (s), 943 (s), 746 (w), 716 (sh), 709 (s), 699 (s), 667 (sh), 584 (s), 570 (w), 500 (w,b), 431 (m) cm^{-1}

For UV. spectrum and analysis, see Chapter 7 on S_3N_2Cl.

(vi) Tetrasulfur tetraimide, $S_4(NH)_4$ was prepared from S_4N_4 in benzene by reduction with an alcoholic solution of $SnCl_2$.[64,75,131,349,350]

A solution of 10 g. of S_4N_4 in 300 ml. of dry benzene was heated to 80^o in a flask fitted with a condenser and dropping funnel. A solution of 35 g of $SnCl_2$ $2H_2O$ in 80 ml. of methanol containing about 5% water was added through the dropping funnel over a period of ca. 15 seconds. Vigorous boiling occurred and a white precipitate started to form immediately. After filtering the solid was washed with 200 ml. of dilute HCl, until the excess tin had dissolved, then washed with alcohol and finally ether. Yield: approximately 40%.

The product was identified by analysis and ir. spectrum:

Analysis:	Found %	$S_4(NH)_4$ requires %
	S = 67.60	S = 68.17
	N = 29.63	N = 29.75
	H = 1.93	H = 2.14

IR spectrum: (nujol mull and KBr disc): 3,226 (s), 3,125 (s), 2,222 (w), 1,299 (m), 901 (vs), 719 (w), 699 (w), 538 (s,b), 416 (s), 458 (sh) cm^{-1} (See Appendix)

(vii) Heptasulfur imide, S_7NH was prepared from the reaction of concentrated aqueous ammonia solution with S_2Cl_2 in CS_2.[44,45] Disulfur dichloride (S_2Cl_2) (10 ml) was dissolved in 40 ml. of carbon disulfide and gradually added, with vigorous stirring to 150 ml. of cooled concentrated aqueous ammonia solution. The optimum temperature for the reaction was -10 to -15^{o}C so an ice-salt cooling bath was used. After the addition the red CS_2 phase was separated, washed well with water, and the CS_2 was allowed to evaporate slowly in a fume cupboard. The gummy residue was extracted with about three 30 ml. portions of warm CS_2. The resulting solution contained some S_4N_4, sulfur, other sulfur imides, and polymeric SN compounds (of unknown structure) as well as S_7NH. These could be separated chromatographically using a column of silica gel (standard chromatographic reagent), and CS_2 as the elutant.[30] The flow rate was ca. 5 ml/minute. About ten fractions in all were collected, the CS_2 was allowed to evaporate and the residual products were identified by their infrared spectra. Sulfur came off the column first, followed by S_7NH, and then S_4N_4 in fairly well separated bands. Polymeric SN compounds moved very slowly, and remained trapped on the column. Other imides are also formed in smaller quantities,[29,30] but these were not detected in the S_7NH as collected from the column. The S_7NH was recrystallised several times from dry benzene, and dried in vacuo to yield white, plate-like crystals. It was identified by its infrared spectrum and by TLC (Rf value = 0.8, CS_2 elutant).

IR (as a nujol mull and as a KBr disc) - See Appendix.

3,230 cm^{-1},	3.1 μ (w)	-	N-H stretch
812 cm^{-1},	12,32 μ (m)	-	N-H bend

Sulfur (the main impurity) could not be detected by infrared spectroscopy since it is essentially transparent; however, it could be quantitatively separated by thin layer chromatography.

5. Preparation of Other Compounds

(i) Dimethyl Chloramine $(CH_3)_2NCl$

Dimethyl chloramine was prepared by the method described by Stevenson and Schomaker.[389] Stoichiometric quantities of cold concentrated calcium hypochlorite and concentrated aqueous dimethyl amine hydrochloride were reacted together and the resulting solution acidified by the addition of dilute hydrochloric acid. The solution was fractionally distilled, collecting the fraction distilling between 35° and 50°C. This crude dimethyl chloramine was refractionated (boiling point at atmospheric pressure = 45°C).

(ii) Reinecke's Salt - $NH_4[Cr(NH_3)_2(SCN)_4]H_2O$.[390]

Ammonium thiocyanate (40 g) was heated in an evaporating basin with stirring until it melted (140° - 150°C). Ammonium dichromate (6.8 g) was then carefully sifted onto the surface in small portions with stirring, not allowing the temperature to rise above 160°. The melt was then allowed to cool and solidify in a desiccator. After it had cooled, it was added to powdered ice with stirring and the crude product filtered. Recrystallisation was from water at 65°C. The pure product was dried in a vacuum desiccator. Yield approximately 50%.

ELECTROLYTIC REDUCTION OF SULFUR AND S_4N_4 IN LIQUID AMMONIA

CHAPTER 3

Electrolytic Reduction of Sulfur and S_4N_4 in liquid Ammonia

(A) Introduction

The sulfur imides, S_7NH and $S_4(NH)_4$, are compounds of important potential value. S_7NH has found uses as a fungicide,[334] an insecticide (with low toxicity for higher organisms[374]), and also as an effective vulcanising agent for rubbers,[1,375,376,377] as have its derivatives.[378] Some aspects of their chemistry are discussed in the following chapter.

Their preparation, however, is difficult and inconvenient, particularly the preparations of S_7NH, which involve the use of ammonia[41,335,344,346] or ammonia solutions,[41,45] and chlorosulfanes.[43,348] The products have to be separated using column chromatography[29] and the final yields are low. The preparation is fairly difficult and time consuming. Alternatively, one of the more recent preparations may be used involving hydrazine,[301,333,334] $LiAlH_4$[333] or Raney nickel[333] with S_4N_4 or S_4N_3Cl, or involving chlorosulfanes and metal azides.[339] The main problem here is the unavailability and potentially hazardous nature of the materials used.

The only preparation of $S_4(NH)_4$ is from S_4N_4 and alcoholic $SnCl_2$,[64,75,131 349,350] (see introduction on preparations of sulfur imides, and experimental section for details), and an alternative preparation would be of value, since the difficulty (and hence high cost) of making it and also S_7NH, severely limit their potential commercial value.

It was therefore decided to try and find simpler and cheaper routes to these imides and related compounds which would make them more readily available in larger quantities. Chemical and electrolytic methods of reduction of cheap SN compounds were considered. The electrolysis of sulfur in liquid ammonia appeared to be a good system for the electrosynthesis of S_7NH and other imides.

This was studied under various conditions including the addition of other reagents to accelerate the dissolution of sulfur in liquid ammonia. The electrolysis of S_4N_4 in various solvents was studied as an alternative route to $S_4(NH)_4$; selenium in liquid ammonia was also studied briefly.

(B) Solutions of Sulfur in Liquid Ammonia

Elemental sulfur is very soluble in liquid ammonia over a wide range of temperatures[391] forming green/blue electrically conducting solutions.[228]

An equilibrium of the type: $10S + 4NH_3 \rightleftharpoons S_4N_4 + 6H_2S$[59] has been postulated as occurring in such solutions, since S_4N_4 can be formed by the addition of silver salts, precipitating out the insoluble Ag_2S.[33,34,59,60] Nelson and Lagowski[34] however showed that this equilibrium does not exist to any appreciable extent in anhydrous solutions, and instead postulated that species of the type: $S_x(NH_3)_y$, $S_x(NH_2)_y^{y-}$ and/or $S_x(NH)_y^{2y-}$ may be present, the first of these species being of the ammoniated sulfur type previously reported by Ruff;[391] the others explain the observed conductivity of the solutions. The formation of small quantities of S_7NH has been reported from solutions of sulfur in liquid ammonia without electrolysis on evaporating off the ammonia although this has been disputed. (We also obtained detectable quantities of S_7NH by this method). S_7NH has also been reported to be formed by the reactions of heavy metal compounds with solutions of sulfur in liquid ammonia.[374]

e.g. (i) $S_8 + PbO + NH_3 \xrightarrow{NH_3(l)} S_7NH + PbS + H_2O$

(ii) $S_8 + 2\,AgI + 3NH_3 \longrightarrow S_7NH + Ag_2S + 2NH_4I$

Although solutions of sulfur in liquid ammonia conduct electricity, the products of electrolysis have not been studied. The reactions which could occur to produce S_7NH through electrolysis are -

(i) $2NH_3 \rightleftharpoons NH_2^- + NH_4^+$ self ionisation

(ii) $\frac{7}{8}\,S_8 + NH_2^- \rightleftharpoons S_7NH_2^-$

(iii) $S_7NH_2^- \longrightarrow S_7NH_2 + e^-$ electrolysis at anode

(iv) $S_7NH_2 \longrightarrow S_7NH + \frac{1}{2}H_2$

Other sulfur imides could also be similarly formed.

The availability and cheapness of the starting materials was also an important consideration.

After the construction and setting up of the apparatus (see pages 93ff), the first problem encountered was the slowness of dissolution of sulfur in liquid ammonia which is dealt with in the next section.

(C) Dissolution of Sulfur in Liquid Ammonia

Sulfur probably dissolves in liquid ammonia by chain fragmentation, to form the species: $S_x(NH_3)_y$, $S_x(NH_2)_y^{y-}$ and/or $S_x(NH)_y^{2y-}$ as postulated by Nelson and Lagowski.[34] Since the S-S bond is strong (264 KJ/mole, 63 K.cals/mole)[140] chain fragmentation at -37^oC (B.pt. of ammonia) is the slow rate determining step in the dissolution.

Two methods were investigated to speed up the dissolution:-

(a) The addition of an appropriate electrolyte, which would attack and fragment the S_8 ring without interfering with the electrolytic process:

Liquid ammonia undergoes slight self-ionisation:

$$2NH_3 \rightleftharpoons NH_2^- + NH_4^+$$

The presence of the NH_2^- or NH_4^+ ions may be responsible for the fragmentation of the sulfur ring, by nucleophilic or electrophilic attack on the ring causing dissolution, the slowness being due to the low concentration of these ions in pure liquid ammonia.

e.g. $S_8 + NH_2^- \longrightarrow S_8\ (NH_2)^-$ etc.

The species described by Nelson and Lagowski,[34] could be formed by this mechanism.

H_2S could also aid dissolution without interfering with the electrolytic system by forming HS^- or S^{2-} ions in solution.[392] These could also fragment the ring by nucleophilic attack.[393]

e.g. $\underset{\text{ring}}{S_8} + SH^- \longrightarrow \underset{\text{chain}}{{}^-S\cdots\cdots SH}$

(b) Fragmentation could also be achieved by heating sulfur to near its boiling point (444.6°C), where it exists as sulfur chains and then rapidly quenching in liquid nitrogen before dissolution in liquid ammonia. Experiments to speed up the dissolution of sulfur in liquid ammonia, were carried out simultaneously with the electrolytic experiments.

1. Addition of Ammonium Ion

Ammonium ion, as ammonium tetrafluoroborate, was added to the liquid ammonia before the addition of sulfur. (Ammonium tetrafluoroborate is soluble in liquid ammonia and the anion does not interfere with the electrolysis). However, this had little effect on the rate of dissolution of sulfur.

2. Addition of Amide Ion

Potassamide (KNH_2) was dissolved in the liquid ammonia.[394] In one experiment the sulfur dissolved rapidly, however this could not be repeated and it is thought that traces of moisture may impede the nucleophillic attack of NH_2^- on the sulfur ring since amide is rapidly hydrolysed to ammonia and OH^-, however in strictly anhydrous conditions, NH_2^- ions may well aid dissolution.

3. Addition of H_2S[393]

Addition of H_2S gas to the solution, with sulfur present, did speed up the dissolution of the sulfur considerably, however on evaporation, after electrolysis, the residue was found to consist of of quantities of ammonium polysulfide (red solid) and sulfur. No other products (e.g. imide) were detected.

It was concluded that the hydrogen sulfide formed polysulfides (S_x^{n-}) in solution which contaminated the product and possibly also inhibited the formation of imides.

4. Fragmentation of Sulfur by Heating

Boiling sulfur was poured into liquid nitrogen to fragment the rings before adding to the ammonia. However, it was found that this process did not increase the rate of dissolution of the sulfur partly due to the physical state of the quenched sulfur which was in lump, rather than powder form (thus decreasing the surface area). A further problem was that the process is more susceptible to contamination by moisture since the quenching process invariably causes moisture to condense on the surface of the sulfur.

5. Conclusion

Since none of the above methods were found to be satisfactory, and since sulfur does eventually dissolve, after a period of hours, it was eventually decided not to use added support electrolytes in later experiments but to allow the sulfur to dissolve without any added reagent.

(D) Electrolytic Cell

1. Description
(See Diagram)

The cell for the electrolysis of sulfur in liquid ammonia was obtained from Dr. O.R. Brown (Newcastle University).

The whole apparatus was constructed of glass with platinum electrodes. The anode and cathode compartments of the cell were separated by a sintered disc and both compartments were fitted with a reflux condenser (dry ice/methanol coolant). The base of the cell was enclosed in a vacuum jacket calibrated in ml. by marks on the outside. The apparatus was maintained under a back pressure of dry nitrogen.

The electric current was supplied from AC. mains electricity (240v, 50 cps) and transformed to DC. Current and emf. could be measured simultaneously and the emf. varied continuously from 0 to 50v.

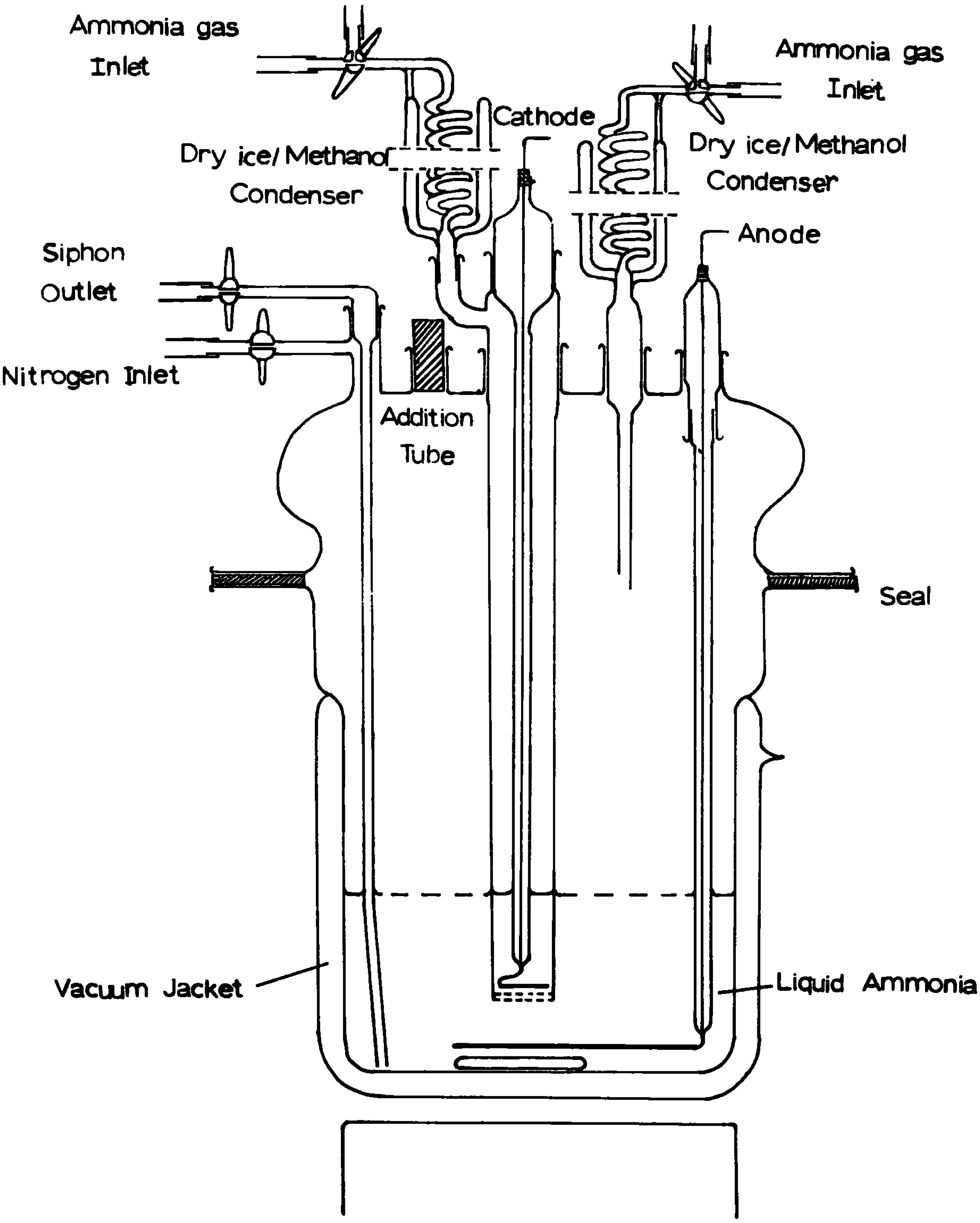
2. Experimental

In a typical experiment about 300 ml. of dry ammonia was condensed into the cell via the reflux condensers. The cell was maintained under reflux conditions. Weighed amounts of sulfur (and other reagents as required) were added to the ammonia, and the solution stirred using a PTFE-coated magnetic stirrer. Up to 60g of sulfur could be dissolved by adding in batches of about 15g over a period of about 2 hours. The conductivity of the solution increased with increasing concentration of sulfur (graph 1), and with increasing emf. (graphs 2 and 3).

Considerable heating effects were noted at higher emfs, which caused brisk boiling of the ammonia from the electrodes and so a working voltage of between 20 and 25 volts was used. It was not possible to determine visually the complete dissolution of sulfur due to the opaqueness of the solution;

Figure 3.1

LIQUID AMMONIA CELL



however, since the conductivity of the solution increased with increasing weight of dissolved sulfur, reaching a maximum with complete dissolution, this was used as an indication when complete dissolution had occurred. An increase in conductivity on adding a further small amount of sulfur was taken to indicate an unsaturated solution.

Current was usually passed for about two hours during which time the conductivity gradually decreased, the solution remaining very dark blue/green.

It was found that the platinum electrodes sometimes became coated with sulfur during electrolysis, thus affecting their efficiency. This coating could be removed by passing current in the reverse direction for a few minutes.

After the completion of a run the solution was removed from the cell via a syphon into a vacuum Dewar, using a back pressure of nitrogen, and then allowing the ammonia to evaporate off under nitrogen. Any support electrolyte which had previously been added was washed out from the residue with water. The residues were then analysed by TLC (CS_2 elutant).

3. Analysis of Residue

The TLC analysis of the residues showed two main spots on the plate (Rf values = 0.95 and 0.8). The first spot was identified as sulfur (Rf value = 0.95) which composed most of the residue but the second (Rf value = 0.8) corresponded to S_7NH. Some other minor spots were also observed. These were on or near the base line and were therefore probably either support electrolyte or ammonium polysulfides. The ammonium polysulfides are red in colour and were particularly evident when H_2S was added as a support electrolyte.

The S_7NH was in sufficient quantities to enable it to be separated from sulfur and other components by column chromatography (CS_2 elutant). S_7NH was identified by its infrared spectrum. It was estimated (from the appearance of the spots under uv. light and knowing the approximate weight necessary to give a spot of known density) that S_7NH comprised a few percent of the total residue.

No other products (e.g. S_4N_4, S_4N_2 or other imides) were identified.

(E) Discussion

Electrolysis of solutions of sulfur in liquid ammonia was found to produce some S_7NH although in low yield. We have shown that traces of S_7NH are also produced by simply evaporating off the ammonia from such solutions, without using electrolysis. The effect of electrolysis on these solutions seems to be to increase the yields of S_7NH although the exact amount is difficult to determine, the majority of the residue in all cases being sulfur. This is not surprising considering the total current passed although the yields of S_7NH are much less than would have been expected had all the current been used to convert sulfur to S_7NH so that other electrolytic reactions must also occur. If species such as $S_x(NH)_y^-$ are present they may undergo electrolysis to produce sulfur and ammonia and possibly also hydrogen and nitrogen as well as some S_7NH.

The graphs 2 and 3 show that the solution obeys Ohm's law ($V \propto I$) fairly well (up to ca. 20 volts) although at higher voltages there is some "tailing off" (current less than expected) and this is probably due to the decrease in the efficiency of the electrodes, due to the heating effect causing the ammonia solution to boil rapidly.

The effect on the conductivity of the solution through adding sulfur at a fixed potential is interesting (Graph 1). The current passed increases with increasing amount of sulfur added as expected although the increase is not linear and at higher voltages the effect is more pronounced than at lower voltages. Therefore, the same amount of sulfur causes a proportionally greater increase in current at high voltages, than at lower voltages. This may be due to a proportionally larger concentration of ionic species at higher concentrations of sulfur.

(F) Electrolytic Reduction of S_4N_4

Tetrasulfur tetranitride (S_4N_4) has been shown to form anions of the type $S_4N_4^{n-}$ (n = 1 to 4). When S_4N_4 was treated with potassium metal in scrupulously dry dimethoxy ethane[93] colour changes were observed which were interpreted as successive reductions:

$$S_4N_4 \xrightarrow{e-} S_4N_4^{-} \xrightarrow{e-} S_4N_4^{2-} \xrightarrow{e-} S_4N_4^{3-} \xrightarrow{e-} S_4N_4^{4-}$$

An esr. spectrum of the solution showed that the negative charge was delocalised throughout the anion.[191]

The anion $S_4N_4^{4-}$ is also formed when $S_4(NH)_4$ is treated with triphenyl methyl sodium[36] and other anions of the type $S_4N_4^{n-}$ are probably intermediates in its formation. Other sulfur nitrogen anions (e.g. S_7N^-) are also known.[342,343,365]

The basis of the present work was to electrolytically reduce S_4N_4 in solution in a suitable solvent to $S_4(NH)_4$ via the $S_4N_4^{n-}$ anions. These could then be hydrolysed to yield $S_4(NH)_4$. Some preliminary work was also undertaken on solutions of S_4N_4 in liquid ammonia.

1. Experimental

The electrolytic cell was supplied by Dr. O.R. Brown (Newcastle)[197] and all the electrolytic experiments involving the cell were carried out there.

The cell was of a simpler design to that used for liquid ammonia since the solvents were liquids under normal conditions and hence reflux condensers and vacuum jackets were unnecessary. The cell was made of glass with a capacity of about 150 ml. It consisted of a disc rotary platinum cathode and a fixed platinum anode remote from the cathode but in the same single compartment. The cell was maintained under nitrogen and reagents added under a back pressure of nitrogen. Emf. could be varied continuously and current versus emf. recorded as a direct plot on graph paper.

Acetonitrile and pyridine were used as solvents for electrolysis.[395] Since the solutions themselves do not conduct electricity support electrolytes were also added.

(i) Electrolysis of S_4N_4 in Acetonitrile

Tetrasulfur tetranitride (S_4N_4) was dissolved in acetonitrile to form a saturated solution (ca. 0.01M). Tetra tertiary butyl ammonium bromide (Bu_4^tNBr)[396] was used as the support electrolyte. A plot of current against emf. (cyclic voltametry) showed successive oxidations at the cathode. (At least two and probably a third were observed although masked by electrolysis of the support electrolyte). Reduction of Br^- (from the support electrolyte) was observed at the anode.[211]

(ii) Electrolysis of S_4N_4 in Pyridine[197]

S_4N_4 was dissolved in pyridine (S_4N_4 is slightly soluble and stable to pyridine). Tetra tertiary butyl ammonium perchlorate ($Bu_4^t N ClO_4$) was used as the support electrolyte. The solution was electrolysed as before and the solution changed colour during the electrolysis from yellow to green which was taken to indicate the formation of S_4N_4 anions. After ca. 1 hour no further colour changes were observed and the green solution appeared to be stable to storage for a few hours. Addition of ammonium chloride (as protonating agent) gave no reaction with the solution so concentrated hydrochloric acid was added. The green colour was immediately discharged forming a colourless solution which gave a white solid on evaporation. A sample of this solid was washed with water (to remove the ammonium salts and pyridine hydrochloride) and analysed. The infrared spectrum indicated a mixture of products, although S_4N_4 itself was absent and this was confirmed by an ultraviolet spectrum.

TLC (triethylamine elutant) showed a series of six separate components (Rf values: 0.14, 0.22, 0.31, 0.40, 0.48, 0.53) together with "tailing" between Rf. 0.53 to ca. 0.8 and a final spot at Rf. = 0.94. These may represent a whole series of imides or imide-like compounds, and are more fully discussed on page 100.

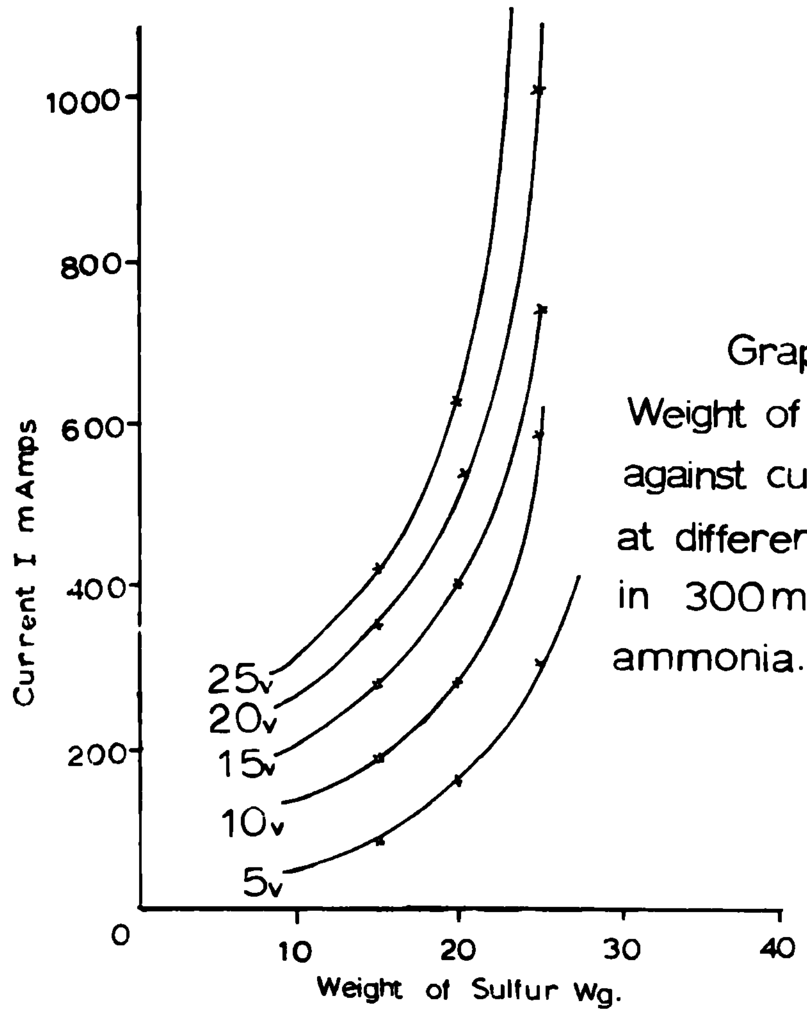
(iii) Electrolysis of S_4N_4 in Liquid Ammonia

Solutions of S_4N_4 in liquid ammonia have been studied by Nelson.[34] The solutions are red and conduct electricity[397] and spectral data indicate that a new species is formed. Ruff has shown that S_4N_4 gives an ammoniate of composition $S_4N_4\cdot 2NH_3$[74] which is identical with the ammoniate $S_2N_2\cdot NH_3$[7]. This species has been formulated as $HNSNSNH_2$[7], and gives conducting solutions in ammonia.[7,32,36,227] All three hydrogens may be replaced by sodium to form salts[37,228] but one is more acidic than the other two. The electrolysis of S_4N_4 in liquid ammonia has not been studied and so a preliminary investigation was undertaken.

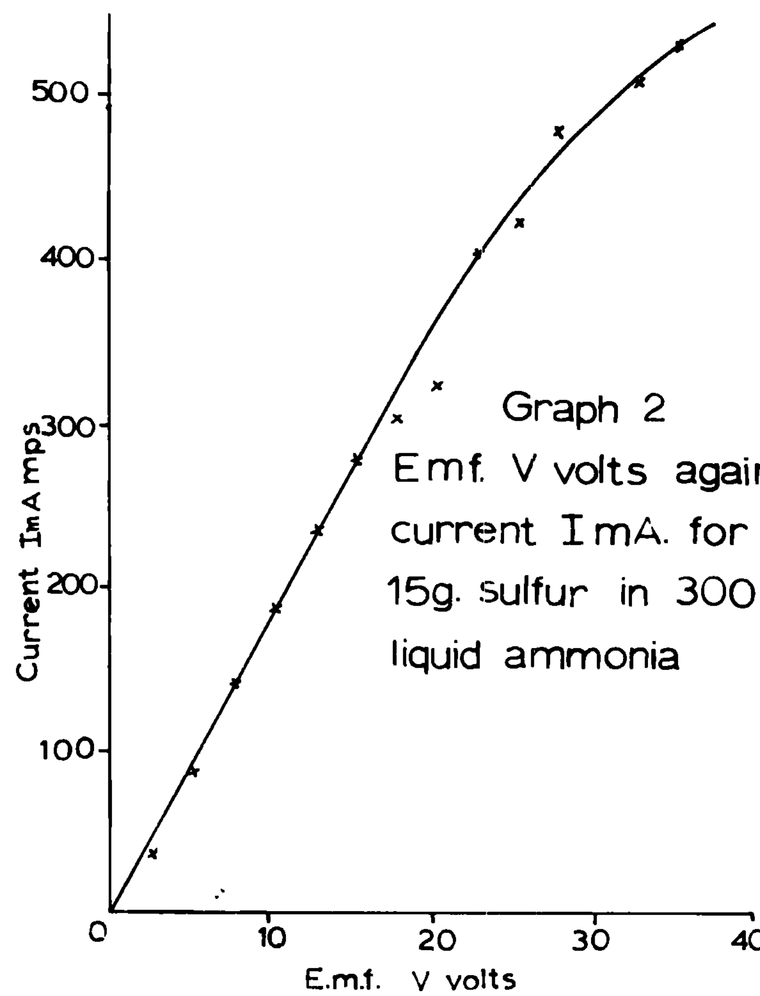
The same cell was used as for the electrolysis of sulfur in liquid ammonia. About 250 ml. of ammonia were condensed into the cell and 1 g. of S_4N_4 was added to the liquid with stirring. This dissolved in ca. ½ hour to give a light orange solution which conducted electricity. A plot of emf. against current gave a linear graph (4) which tended to "tail off" at higher emf's probably due to a decrease in effective surface area of the electrodes due to the boiling of the ammonia from the electrodes as previously noted in the case of sulfur. A further 1 g. of S_4N_4 was dissolved and the solution electrolysed for ca. 2 hours at 15v, during which time the current fell from 130 mA to 110 mA. The solution remained the same colour throughout the electrolysis although a darkening in colour was noticed in the solution around the cathode. After 2 hours the solution was removed from the cell using the syphon and the ammonia allowed to evaporate off leaving a dark yellow solid. Analysis of this solid using TLC (CS_2 elutant) gave three spots. The first two were S_4N_4 and sulfur and the third was S_7NH although present in only small amounts. No other products were detected.

(iv) Selenium in Liquid Ammonia

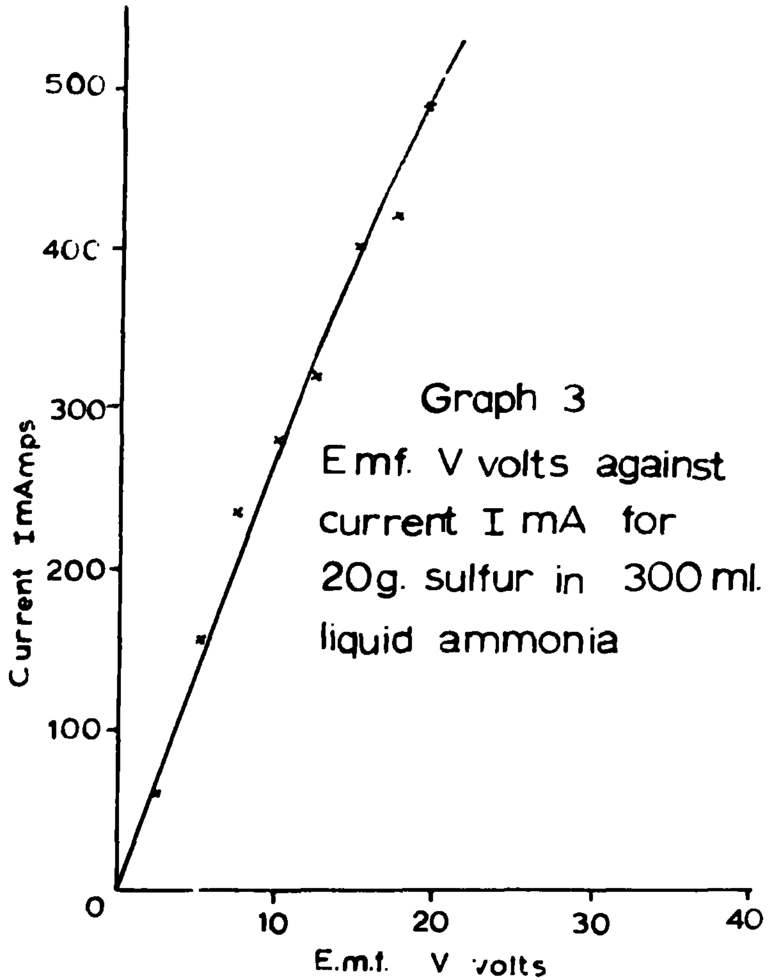
Selenium, unlike sulfur and S_4N_4, is insoluble in liquid ammonia. 1 g of grey selenium was added to 250 mls of liquid ammonia in the cell but remained undissolved after several hours stirring; there was also no detectable change in the conductivity and the selenium was eventually recovered unchanged.

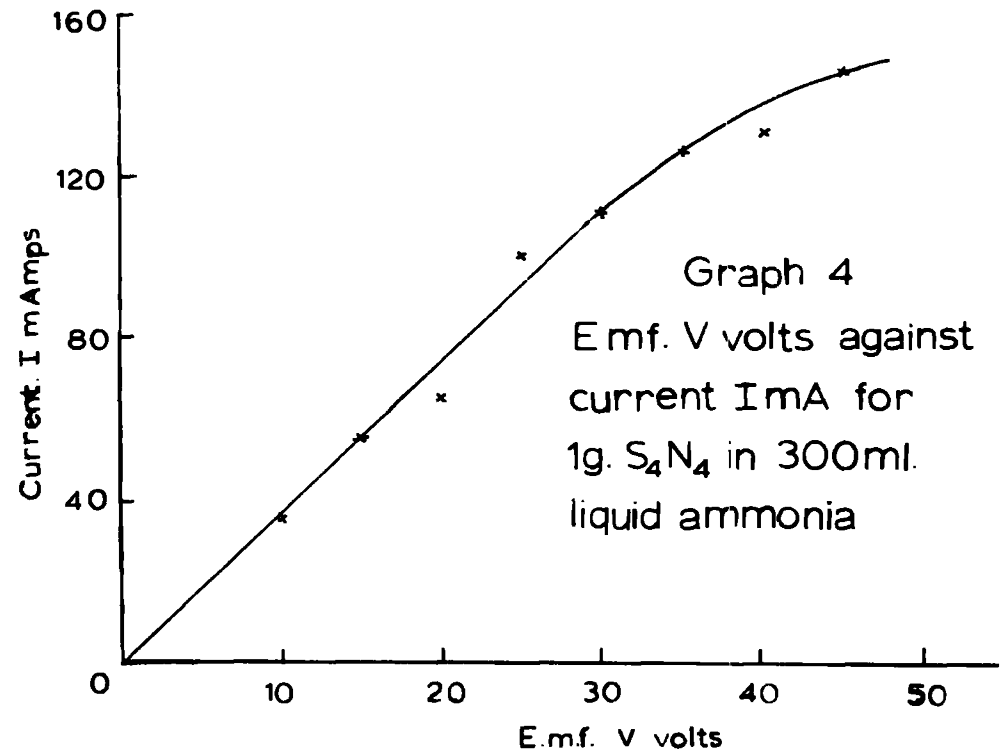


Graph 1
Weight of sulfur Wg against current ImA at different emf.s in 300ml. liquid ammonia.



Graph 2
Emf. V volts against current ImA. for 15g. sulfur in 300ml. liquid ammonia


Graph 3
Emf. V volts against current I mA for 20g. sulfur in 300 ml. liquid ammonia
Current I mAmps
E.m.f. V volts
0
10
20
30
40
100
200
300
400
500


Graph 4
Emf. V volts against current I mA for 1g. S_4N_4 in 300ml. liquid ammonia
Current I mAmps
E.m.f. V volts
0
10
20
30
40
50
40
80
120
160

2. Discussion

The conductivity of S_4N_4 in both acetonitrile and pyridine showed that S_4N_4 can be electrolysed.

The stages of reduction (at least two) observed in acetonitrile very probably correspond to the formation of the $S_4N_4^{n-}$ anions:

i.e. $S_4N_4 \xrightarrow{e-} S_4N_4^{-} \xrightarrow{e-} S_4N_4^{2-} \xrightarrow{e-}$ etc.

as has been observed in other systems.

Although $S_4(NH)_4$ could not be obtained from the solution by hydrolysis (this may be due to the decomposition of the anions on hydrolysis since they are very reactive) the electrolysis shows that it is a possible preparative route for other sulfur-nitrogen compounds, particularly anions.

A similar situation occurred in pyridine, colour changes indicating reaction. The analysis of the final products showed a complex mixture of at least six components and the absence of S_4N_4.

The products may be a mixture of unidentified sulfur imides or other sulfur-nitrogen compounds, but is also possible that the S_4N_4 underwent oxidation by the support electrolyte ($Bu^t{}_4NClO_4$) during electrolysis to form the observed products. In either case it would be useful for further work to be done on these compounds since, as yet, they have not been identified but from their appearance on the TLC plate they are probably closely related.

S_4N_4 in liquid ammonia conducts electricity therefore ionic species from the S_4N_4 must be present, presumably ions from the species: $HNSNSNH_2$. The product from electrolysis was mainly sulfur, although some S_7NH was also detected, showing that some electrolytic reaction had occurred. The darkening in colour of the solution around the cathode during electrolysis also indicates that a reaction may be occurring.

This was only a preliminary investigation and more work is necessary to further rationalise this system.

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THE SULFUR IMIDES

CHAPTER 4

The Sulfur Imides

(A) Introduction

The chemistry of the two sulfur imides: $S_4(NH)_4$ and S_7NH was investigated as these were the two most probable products from the electrolytic reduction of S_4N_4 and sulfur discussed in the previous chapter. The synthesis of new derivatives of these imides was studied in order to prepare new and hopefully useful compounds. $S_4(NH)_4$ and S_7NH are the two most easily prepared sulfur imides so that many reactions could be carried out using imides in quantities of about 1 g. S_7NH is reported to have organic activity as a fungicide and pesticide,[334,374] and its derivatives may also possess similar properties.

The reactions of the two imides are dealt with separately in this chapter.

(B) Reactions of $S_4(NH)_4$

$S_4(NH)_4$, prepared from S_4N_4 by reduction with alcoholic $SnCl_2$, was found (from infrared spectrum and analysis) to be sufficiently pure to be used without further purification. Many of the reactions and properties of this compound were studied by Younger at this University,[398] and therefore the work described in this thesis concentrates on the areas not covered by him.

1. Reaction of $S_4(NH)_4$ with Alkaline Formaldehyde Solution

Since the product $(SN.CH_2OH)_4$ from this reaction, formed the starting material for several other reactions described in this section, the preparation was repeated many times. In a typical reaction: $S_4(NH)_4$ (0.94 g) was slowly heated with ca. 10 ml. of aqueous formaldehyde solution (40%) and ca. 20 ml. of 1 N sodium hydroxide solution, with stirring. The $S_4(NH)_4$ (insoluble in water) gradually dissolved on heating to form a colourless solution (little apparent reaction at 20°C) and when dissolution was complete, the solution was filtered hot, evaporated to low bulk and then allowed to cool to 0°C. White plate-like crystals were formed which were filtered, washed with a little cold water, and dried by pumping in vacuo. The product was recrystallised from dry ether. The volumes of formaldehyde and sodium hydroxide used are not critical, so long as they are in excess.

Yield of recrystallised material = ca. 1 g. = ca. 77%

The above is a modification of the preparation first described by Meuwsen[75] and also later repeated by Arnold.[64]

Analysis:

Found %	$(SN.CH_2OH)_4$ requires %
S = 41.58	S = 41.58
N = 18.40	N = 18.18
C = 16.00	C = 15.58
H = 3.80	H = 3.90
O = 20.22 (by difference)	O = 20.76

Infrared spectrum (as a nujol mull. and as a KBr disc):

3,125 (s), 2,632 (m), 2,532 (w), 1,482 (m), 1,460 (sh), 1,389 (w), 1,282 (m), 1,111 (m), 1,058 (s), 1,038 (vs), 1,013 (m), 862 (m,b), 775 (vs), 730 (m,b), 680 (s), 667 (sh), 448 (m), 435 (m) cm^{-1}

(See Appendix)

Product: White plate-like crystals. M.pt. 160°C (decomp). Very slow recrystallisation yields long needle-like crystals. Soluble in acetone, CCl_4, toluene, ether, alcohol, benzene and most other common organic solvents. Soluble and stable in water. Insoluble in saturated hydrocarbon solvents (e.g.: hexane).

2. Reaction of $S_4(NH)_4$ with other aldehydes

In view of the reaction of $S_4(NH)_4$ with formaldehyde, which readily yielded a crystalline derivative, the reaction of other aldehydes with $S_4(NH)_4$ was investigated. There was no reaction in the absence of alkali and in the presence of alkali, aldehydes with an α-hydrogen readily undergo the aldol condensation,[399] so that the reaction of these aldehydes with $S_4(NH)_4$ fails. Benzaldehyde (C_6H_5CHO) was chosen since there is no α-hydrogen to the aldehyde group.

$S_4(NH)_4$ (ca. 1 g) was suspended in ca. 20 ml. of 1 N sodium hydroxide solution and ca. 5 ml. of benzaldehyde added to the mixture (benxaldehyde is insoluble in water). The mixture was stirred and heated for ca. 2 hours, but no reaction appeared to occur, the infrared spectrum of the reaction products showing only unreacted starting material as identifiable compound.

The reaction was also attempted using furfural in place of benzaldehyde (furfural is soluble in water), but, once again, no apparent reaction occurred.

3. Partial Substitution by Formaldehyde

In $(SN.CH_2OH)_4$, all four positions on the SN ring, are substituted with the $-CH_2OH$ group; therefore investigations were carried out to determine if products could be obtained with only some of these positions substituted.

$S_4(NH)_4$ (1.0 g) was suspended in ca. 20 ml. of 1 N sodium hydroxide solution, as before, and 0.5 ml. of 40% formaldehyde solution added (molar ratio $S_4(NH)_4$: HCHO = 1:2). The mixture was heated as before but very little reaction occurred the unreacted $S_4(NH)_4$ being filtered off and a very small quantity of compound (identified as $(SN.CH_2OH)_4$ by the infrared spectrum) was recovered on evaporating off the solution.

4. Reactions of $(SN.CH_2OH)_4$ with metal chlorides

The reactions of sulfur-nitrogen compounds with metal chlorides has produced a large number of interesting compounds. S_4N_4 forms a large series of adducts with metal halides and other Lewis acids (see also introduction - Pages 22ff), and $(NSCl)_3$ also forms adducts with metal chlorides such as $AlCl_3$, $FeCl_3$ and $SbCl_5$, which are intermediates in the formation of $S_2NCl_2^+$ and $S_5N_5^+$ salts (see Chapters 5 and 6, this thesis). The reactions of $(SN.CH_2OH)_4$ with metal chlorides were therefore investigated as a possible route to new and useful intermediates.

(i) Reaction with Stannic Chloride

$(SN.CH_2OH)_4$ (0.2249 g) was dissolved in ca. 20 ml. of dry benzene and a benzene solution of stannic chloride ($SnCl_4$ is miscible with benzene) was added slowly to the stirred solution. An immediate white precipitate appeared on mixing the solutions, which did not appear to react with excess stannic chloride. No gases (e.g. HCl) were evolved. The precipitate was filtered off, washed with dry benzene, and dried in vacuo. Product: white powder, apparently air and water stable, insoluble in all common solvents, decomposes without melting at ca. 120°C.

Infrared spectrum (nujol mull and KBr disc):

3,125 (s,vb), 1,695 (m), 1,613 (sh), 1,449 (sh), 1,409 (s), 1,266 (w), 1,191 (vw), 1,136 (m), 1,124 (m), 1,070 (s), 1,047 (m), 1,026 (sh), 784 (s), 752 (w), 685 (m) cm^{-1} (See Appendix)

Analysis:

Found % (i)	Found % (ii)	Required: $(SN.CH_2OH)_4$, $SnCl_4$ Requires %	Required: $(SN.CH_2OH)_4$, $2SnCl_4$ Requires %
N = 7.82	N = 8.24	N = 9.85	N = 6.75
C = 13.04	C = 10.8	C = 8.48	C = 5.79
H = 2.54	H = 2.26	H = 2.13	H = 1.46

Since the analysis was inconclusive as to the stoichiometry of the compound (assuming it to be a simple adduct of the form: $(SN.CH_2OH)_4$,n $SnCl_4$), a gravimetric analysis was carried out:

$(SN.CH_2OH)_4$ (0.2249 g) was dissolved in benzene, and excess $SnCl_4$ added, to give the adduct as before. The flask was then pumped dry to constant weight (both benzene and $SnCl_4$ are volatile under these conditions); 0.5787 g of product was formed. This calculates n = 1.84, i.e. a mixture.

(ii) Reaction with $FeCl_3$

$(SN.CH_2OH)_4$ (about 0.5 g) was dissolved in dry benzene as before, excess ferric chloride in dry benzene added and the mixture stirred for ca. 2 hours. A brown precipitate gradually formed and this was filtered, washed several times with dry benzene and pumped dry in vacuo. Product: Brown powder, apparently air and water stable.

Infrared spectrum (KBr disc):

3,226 (s,b), 2,632 (w), 2,532 (vw), 1,626 (w), 1,450 (w), 1,409 (w), 1,390 (w), 1,266 (w), 1,191 (vw), 1,143 (m), 1,099 (s), 1,070 (vs), 1,042 (vs), 1,020 (vs), 926 (w), 833 (sh), 781 (vs), 723 (vw), 680 (m), 526 (w,b) cm^{-1}

This infrared spectrum shows a similarity to that of the $(SN.CH_2OH)_4$, $SnCl_4$ complex, indicating a similar structure.

(iii) Reaction with $TaCl_5$

$(SN.CH_2OH)_4$ (1.0 g) was dissolved in benzene, as before, and 5.0 g (4:1, slight excess) of $TaCl_5$ in benzene added. An immediate reaction occurred, to yield a white microcrystalline solid, which was presumably the $(SN.CH_2OH)_4$, n $TaCl_5$ adduct. It was apparently air and water stable.

Infrared spectrum (nujol mull):

3,125 (s), 2,632 (w), 2,247 (w), 1,640 (w), 1,282 (m), 1,099 (m), 1,064 (s), 1,042 (vs), 1,015 (s), 855 (m,b), 779 (vs), 722 (m,b), 680 (s), 450 (s), 437 (s) cm^{-1}

The analyses were inconclusive so that the value of n in the formula could not be determined.

(iv) Reaction with $SbCl_5$

$(SN.CH_2OH)_4$ (0.0768 g) was dissolved in ca. 10 ml. of dry CCl_4, and ca. 0.15 ml. of $SbCl_5$, (excess), added to the stirred solution. An immediate reaction occurred, a white precipitate forming, and turning light pink on stirring for ca. 5 minutes. The mixture was stirred for ca. 1 hour. No further reaction occurred and the mixture was pumped dry in vacuo ($SbCl_5$ and CCl_4 both pumped off). Product: cream coloured powder, air and moisture sensitive.

Infrared spectrum (nujol mull):

3,200 (s), 1,680 (s), 1,520 (w), 1,280 (m), 1,120 (m,b), 1,030 (m,b), 910 (m), 810 (m), 795 (w) cm^{-1}

Analysis: General formula: $(SN.CH_2OH)_4$, n $SbCl_5$.

Found %	Required for:	n = 1	n = 2	n = 3	n = 4
S = 10.8	S =	21.11	14.15	10.64	8.52
N = 3.99	N =	9.22	6.18	4.65	3.72
Cl = 44.38	Cl =	29.18	39.11	44.12	47.13

Although the analyses are inconclusive, the formula with $n_{av} \approx 3.0$, seems the most probable.

(v) Reaction with $TiCl_4$

$(SN.CH_2OH)_4$ (0.08 g) was dissolved in ca. 10 ml. of dry CCl_4 and 0.15 ml. $TiCl_4$ (excess), added to the stirred mixture. An immediate reaction occurred, a pink (flesh-coloured), precipitate forming rapidly. The mixture was stirred for ca. 1 hour. No further reaction took place and the mixture was pumped dry in vacuo. ($TiCl_4$ and CCl_4 both pumped off). Product: light-pink coloured powder.

Infrared spectrum (nujol mull):

3,150 (m), 1,650 (w,b), 1,310 (w), 1,270 (s), 1,105 (s), 1,030 (m), 810 (s,b) cm^{-1}

Analysis: For general formula: $(SN.CH_2OH)_4$, n $TiCl_4$

Found %	% Required for	n = 1	n = 2	n = 3	n = 4
S = 10.22	S =	25.74	18.64	14.61	12.02
N = 6.44	N =	11.25	8.15	6.38	5.25
Cl = 45.77	Cl =	28.47	41.24	48.48	53.15

Although the analyses are inconclusive, the formula with $n_{av} \approx 3.0$ again seems the most probable.

(vi) Reaction with $AlCl_3$

$(SN.CH_2OH)_4$, (0.0839 g) was dissolved in ca. 20 ml. of CCl_4 and $AlCl_3$ (0.15 g) (1:4 molar ratio) dissolved in ca. 100 ml. CCl_4 and added to the solution. The mixture was stirred for ca. 6 hours at room temperature. A white precipitate gradually formed during this time. The solution was filtered and the precipitate pumped dry in vacuo. The product (cream-coloured powder) was difficult to mull, but an infrared spectrum indicated a similarity to the other $(SN.CH_2OH)_4$/ metal chloride adducts previously prepared.

(vii) Reaction with thallium compounds

$(SN.CH_2OH)_4$ in ethanol solution, reacted immediately with a solution of thallous hydroxide in ethanol to give a white precipitate, which gradually turned black on exposure to air, but which presumably was a thallium derivative.

5. Reaction of $(SN.CH_2OH)_4$ with Isocyanates

(i) Reaction with phenyl isocyanate

$(SN.CH_2OH)_4$ (1.0 g) and phenyl isocyanate (slight excess) were separately dissolved in dry benzene and the solutions mixed and refluxed with stirring. A white precipitate was formed after ca. 10 minutes, which was filtered off, and recrystallised from ethanol. The product, however, was probably dimeric phenyl isocyanate.

Product: White crystalline solid, M.pt. and decomposition point > 250°C.

Infrared spectra (nujol mull), main absorptions:

1,775 (vs), 1,750 (vs), 1,600 (s), 1,500 (vs), 1,420 (vs), 1,260 (s), 1,110 (s), 1,090 (s), 1,040 (m), 1,030 (m), 898 (m), 800 (s), 790 (s), 765 (vs), 745 (vs), 690 (s) cm^{-1}

Analysis:

Found %	$(C_6H_5NCO)_n$ requires %
N = 11.96	N = 11.7
C = 70.67	C = 70.6
H = 4.15	H = 4.24
O = 13.22 (by difference)	O = 13.46

(ii) Reaction with α-naphthyl isocyanate

$(SN.CH_2OH)_4$ (1.0 g) and α-naphthyl isocyanate (slight excess) were refluxed together in dry benzene. A white precipitate was formed after ca. 10 minutes which was filtered and pumped dry in vacuo. The product was, however, found to be probably dimeric α-naphthyl isocyanate.

Infrared spectra (nujol mull):

1,710 (s), 1,630 (m), 1,595 (w), 1,560 (m), 1,410 (m), 1,345 (w), 875 (w), 800 (m), 775 (s), 765 (m), 725 (m) cm^{-1}

Analysis:

Found %	$(C_{10}H_7NCO)_n$ requires %
N = 8.3	N = 8.3
C = 77.0	C = 78.09
H = 4.8	H = 4.16
O = 9.9 (by difference)	O = 9.45

(iii) Reaction with t-butyl isocyanate

$(SN.CH_2OH)_4$ (1.0 g) was refluxed with t-butyl isocyanate in dry benzene for ca. 6 hours; but an infrared spectrum of the products obtained by evaporating off the solvent showed that little reaction had taken place, the product being mainly unreacted $(SN.CH_2OH)_4$.

6. Reactions of $(SN.CH_2OH)_4$ with Acid Chlorides

(i) Reaction with acetyl chloride

The acetyl derivative was prepared, as described by Arnold,[64] i.e. $(SN.CH_2OH)_4$ (0.8 g) was added to 1 g of acetyl chloride and 2 g of potassium carbonate in ethyl acetate as solvent. The reaction mixture was warmed for ca. 15 minutes, filtered to remove the inorganic material, and the ethyl acetate evaporated off, leaving the product in about 10% yield.

This reaction was repeated several times with varying degrees of limited success and was also carried out using pure acetyl chloride as the solvent. A crystalline product was eventually formed which was not starting material; however, the analysis and infrared spectrum were inconclusive as to its identity, the desired product being the ester-type derivative: $(SN.CH_2OCOCH_3)_4$.

Similar observations were made with propionyl chloride in place of acetyl chloride.

(ii) Reaction with p-nitrobenzoyl chloride

This reaction is also described by Arnold.[64] The reaction was carried out on ca. ⅓ scale: i.e. $(SN.CH_2OH)_4$ (0.3 g), p-nitrobenzoyl chloride (0.8 g) and ca. 5 ml. of benzene were refluxed for ca. 15 minutes. A white precipitate was formed, which was washed with hot benzene, dissolved in hot nitrobenzene (ca. 80°C), and precipitated from the evolved solution by excess CCl_4. Recrystallisation was from a nitrobenzene-acetone mixture.

The above preparation was carried out twice. The purification and recrystallisation from a nitrobenzene-acetone mixture was found to be difficult, although no alternative solvent was found. The final yield was small, but consisted of cream-coloured plates (as described by Arnold).[64]

The analysis was inconclusive, but the infrared spectrum appeared consistent with the desired compound; i.e. $(SN.CH_2O.CO.C_6H_4(p\text{-}NO_2))_4$.

(iii) Reaction with 3,5-dinitrobenzoyl chloride

$(SN.CH_2OH)_4$ (1.0 g), 3,5-dinitrobenzoyl chloride (slight excess) and ca. 1 ml. pyridine, were mixed together in benzene solution and the mixture heated to reflux for ca. 45 minutes. The solution was then allowed to cool, and ca. 10 ml. of saturated aqueous sodium bicarbonate solution added. The precipitate was filtered, washed with fresh sodium bicarbonate solution, then with water and recrystallised from a methanol/water mixture. Product: white crystalline solid M.pt. 104°C.

The infrared spectrum was consistent with the desired product, although the analysis was inconclusive, so that the product was not positively identified as the 3,5-dinitrobenzoyl "ester" derivative, i.e. as $(SN.CH_2O.CO.C_6H_4(3,5(NO_2)_2))_4$.

7. Reactions of $S_4(NH)_4$ with Isocyanates

(i) Reaction with phenyl isocyanate

The reaction of $S_4(NH)_4$ with phenyl isocyanate, to form $(SN.CO.NH.C_6H_5)_4$ has been reported by Arnold.[64] The preparation was repeated in approximately 1/10th quantities, i.e. $S_4(NH)_4$ (0.5 g) and phenyl isocyanate (ca. 1.5 g) were refluxed in benzene solution for ca. 4 hours, the mixture cooled and the residue filtered off, washed with benzene, and recrystallised from acetone.

However, the product obtained was found (by its infrared spectra) to consist mainly of starting material, $S_4(NH)_4$, and so little reaction had taken place.

(ii) Reaction with α-naphthyl isocyanate

The above reaction was repeated using α-naphthyl isocyanate in place of phenyl isocyanate and a pink-coloured powder was obtained, but, once again, the infrared spectra showed it to be impure starting material, $S_4(NH)_4$.

8. Reactions of $(SN.CH_2OH)_4$ with Metallic Sodium

Since $(SN.CH_2OH)_4$ contains alcohol (-OH) groups, the hydrogen may be replaceable, forming an anion, with metallic sodium.

$(SN.CH_2OH)_4$ (ca. 1.0 g) was stirred with excess metallic sodium in diethyl ether. The reaction was very slow and little change was observed, although a gas (presumed to be hydrogen) was slowly evolved. After several days, the excess sodium was removed, and ethyl iodide added. No immediate reaction occurred and on evaporation a white solid was produced which turned yellow on exposure to air.

The reaction was repeated using benzene as solvent and the mixture refluxed. The $(SN.CH_2OH)_4$ (white) slowly turned to a green powder which appeared to be fairly air stable, although it decomposed in water. An infrared spectrum, although difficult to prepare, suggested that the S-N ring was still intact. Reaction with ethyl iodide did not produce any identifiable product.

9. Reactions between $(SN.CH_2OH)_4$ and Phosphorus Chlorine Compounds

(i) Reaction with $(PhO)_2POCl$

$(SN.CH_2OH)_4$ (0.2867 g) was dissolved in ca. 20 ml. CCl_4, $(PhO)_2POCl$, (1.0 g) added (1:4 molar ratio, miscible with CCl_4), and the solution stirred at ca. 60°C for ca. 1 hour. HCl was evolved. A white precipitate gradually formed and this was filtered, washed with further CCl_4, and pumped dry in vacuo. Product: white powder, apparently air and water stable.

Infrared spectrum (nujol mull):

1,587 (m), 1,493 (m,obsc), 1,300 (m), 1,190 (m), 1,163 (m), 1,093 (sh), 1,069 (m), 1,026 (s), 971 (s), 930 (m), 909 (sh), 769 (s,b), 752 (sh), 730 (sh), 722 (sh), 685 (s), 615 (w) cm^{-1}

The infrared spectrum shows similarities to those of $(SN.CH_2OH)_4$ (with shifts in the absorptions), and also to $(PhO)_2POCl$. Also the absorption for -OH in $(SN.CH_2OH)_4$ (at 3125 cm^{-1}) is absent. This indicates that the product has substituted the hydrogen on the alcohol group, probably at all four positions, to give "ester-like" compounds of the form $\left[SN.CH_2OP(O)(PhO)_2\right]_4$.

(ii) Reaction with Ph_2PCl

The above reaction was repeated using Ph_2PCl. $(SN.CH_2OH)_4$ (0.3339 g) were dissolved in ca. 15 ml. of CCl_4, and Ph_2PCl (ca. 2 g) (excess) was added slowly. The solution was warmed to ca. 60°C with stirring. Hydrogen chloride was evolved, and a white precipitate gradually formed. The solution was refluxed for ca. 12 hours to ensure completion of reaction, then filtered; the precipitate was washed with CCl_4 and pumped dry in vacuo. Product: white powder, soluble in CS_2 (without decomposition), insoluble CCl_4, fairly soluble in benzene and THF. TLC analysis (CS_2 solvent): product remains on base line, no other spots detected.

Infrared spectrum (nujol mull):

2,941 (s), 2,778 (s,obsc), 1,667 (s), 1,613 (w), 1,587 (vw), 1,460 (s), 1,401 (s), 1,316 (m), 1,266 (w), 1,183 (m), 1,123 (s), 1,105 (sh), 1,070 (sh), 1,042 (w), 1,000 (w), 935 (m), 840 (sh), 833 (m), 787 (m), 751 (m), 722 (s), 694 (s), 548 (m) cm^{-1}

The analyses in both cases were inconclusive.

10. Reactions of $S_4(NH)_4$ with Sulfur

The reactions of $S_4(NH)_4$ with sulfur were studied under a variety of conditions, as a potential route to other sulfur imides.

(i) Reaction of $S_4(NH)_4$ with sulfur in the melt

Tetrasulfur tetraimide $S_4(NH)_4$ (0.381 g) and sulfur (4.086 g) (stoichiometric ratio for formation of S_7NH), were mixed together and heated slowly under dry nitrogen until the mixture melted (ca. 120°C). The mixture became red in colour and the temperature was maintained at 120° for ca. 15 minutes. The mixture was then allowed to cool to room temperature and analysed by TLC chromatography (CS_2 elutant). Five spots were observed:

No.	Rf value	Designation
1	0.0 base line	$S_4(NH)_4$
2	0.4	S_4N_4
3	0.8	S_7NH
4	0.9	Red compound (S_4N_2) ?
5	0.95	Sulfur

$S_4(NH)_4$, S_4N_4, S_7NH and sulfur were identified by comparison with standard samples. S_7NH was also identified by collecting sufficient sample from the TLC plate to run an infrared spectrum. The red compound (4) gradually decomposed on the plate and so was probably S_4N_2.

(ii) Reaction of sulfur and $S_4(NH)_4$ in toluene

$S_4(NH)_4$ (0.3988 g) and sulfur (0.5432 g) (molar ratio $S_4(NH)_4:S_8 = 1:1$), were mixed in ca. 50 ml. toluene and stirred together at room temperature. No apparent reaction occurred, so the mixture was refluxed (110°C) for ca. 6 hours, and then cooled. The toluene was pumped off in vacuo, and the residue analysed by TLC using CS_2 as elutant as before.

S_4N_4 was the main reaction product although some S_7NH was also present, together with the same red compound as before (S_4N_2?). Some starting material was also present, so the residue was refluxed in toluene for a further 12 hours, the same products were formed.

(iii) Decomposition of $S_4(NH)_4$

$S_4(NH)_4$ was heated under dry nitrogen at ca. 110°C alone and in refluxing toluene until complete decomposition had occurred. The only identifiable sulfur-nitrogen product was S_4N_4, which is the main decomposition product, as previously reported.[62] Pyrolysis of other sulfur imides also yields S_4N_4 as the only identifiable sulfur-nitrogen product.[400]

(iv) Reaction of $S_4(NH)_4$ with sulfur in liquid ammonia

Solutions of sulfur in liquid ammonia are a potential source of sulfur imide fragments of the form: $S_x(NH_2)_y^{y-}$ and/or $S_x(NH)_y^{2y-}$,[34] (see discussion in previous chapter) and so, for the results obtained above, liquid ammonia was used as an alternative solvent to toluene.

$S_4(NH)_4$ (0.2263 g) and sulfur (0.9247 g) (molar ratio for formation of S_7NH) were mixed in a Carius tube and dry ammonia condensed into the tube using a vacuum line in the normal way. The tube was sealed in vacuo and allowed to warm up (behind a blast screen) to room temperature.

The solution was the characteristic deep blue colour of sulfur in liquid ammonia. The solution was further heated to ca. 55°C for ca. 1 hour and then cooled to liquid nitrogen temperatures. The Carius tube seal was broken under dry nitrogen, the ammonia evaporated off, and the residue extracted with CS_2. TLC analysis showed the presence of S_4N_4, S_7NH and a red compound (S_4N_2?), as well as starting materials (sulfur and $S_4(NH)_4$). The most intense spot was sulfur, although this is not unexpected since the initial starting material consisted mainly of sulfur. The spots due to S_4N_4 and S_7NH were also clear and of roughly equal intensity.

(C) Properties and Reactions of S_7NH

S_7NH was prepared from the reaction of concentrated aqueous ammonia solution with S_2Cl_2 in CS_2 and purified chromatographically, as previously described.[44,45]

1. Physical Properties

S_7NH and other sulfur-nitrogen compounds could be identified by their position on a TLC plate (Rf values):

	Solvent	
Compound	CCl_4	CS_2
S_7NH	0.75	0.8
S_8	0.94	0.91
S_4N_4	0.57	0.4

S_7NH was observed to melt at 112.5° (literature value = 113.5)[8,333,334] and to decompose immediately after melting. S_7NH sublimes at 10^{-3}mm mercury pressure at 100°C. Some decomposition to sulfur was observed (by analysis using TLC). S_7NH sublimes more slowly at 70°C but less decomposition was observed. Elemental sulfur also sublimes under these conditions.

S_7NH, present in a mixture, can be quantitatively determined, using TLC techniques. A sample of a mixture of sulfur and S_7NH (previously made up from pure compounds) was separated into its components (using CS_2 solvent) and the sulfur and S_7NH recovered and weighed with a 4% overall loss.

2. Reaction with Dimethyl Chloramine - Me_2NCl

(i) In CCl_4 solution

S_7NH (0.3956 g) was dissolved in ca. 50 ml. of CCl_4, and cooled to -20°C. This solution was added to a solution of dimethyl chloramine[389,401] (0.2 g, slight excess) in CCl_4, at -20°C with stirring and the solution allowed to warm slowly to room temperature. A yellow solution and a yellow-orange precipitate were formed. The solution was filtered and evaporated to dryness yielding a yellow solid. The precipitate (yellow-orange) was added to dry dioxane to attempt a recrystallisation but the precipitate turned yellow without dissolving and it was concluded that this precipitate was mainly sulfur although other products may have been formed, before decomposing.

(ii) In CS_2 solution

S_7NH was dissolved in CS_2 at -78^o and some pyridine added (slight excess). A solution of dimethyl chloramine in CS_2 at -78^o was slowly added to the stirred solution. An immediate reaction occurred and a yellow solution was formed. The solution was allowed to gradually warm up to room temperature, the yellow solution gradually turned red, and a white precipitate was also formed. This was filtered off and identified as pyridinium hydrochloride. A black solid was also formed from the red solution, insoluble in CS_2 and dioxane, and only slightly soluble in CCl_4. A TLC analysis (CCl_4 elutant) showed that S_7NH and sulfur were present together with some unidentifiable, insoluble material on the base line, and a small quantity of product just off the base line. The quantities were, however, insufficient to warrant further investigation.

3. Reaction of S_7NH with Sulfuryl Chloride

S_7NH was dissolved in CCl_4 at -20^o, sulfuryl chloride slowly added (slight excess) and the solution allowed to warm up slowly to room temperature. A yellow precipitate was formed (no gas evolved) and the CCl_4 was evaporated yielding a small quantity of yellow solid, insoluble in dioxane. The solid was difficult to chromatograph, but it was concluded that it was decomposition product, probably consisting mainly of sulfur.

4. Reaction of S_7NH with Alkaline Formaldehyde Solution

S_7NH was reacted with an aqueous solution of excess sodium hydroxide and formaldehyde by heating the mixture in the same way as for $S_4(NH)_4$. However, no crystalline or easily identifiable product was obtained, and it was concluded from the infrared spectrum and the analysis of the residue (nitrogen practically absent) that little, if any, of the original S_7NH had been converted into the desired $S_7N.CH_2OH$ derivative.

Elemental sulfur gave similar products under the same conditions so that ring fragmentation of S_7NH probably occurred.

(D) Discussion $S_4(NH)_4$

1. Reactions of $S_4(NH)_4$ to form $(SN.CH_2OH)_4$

The reaction of $S_4(NH)_4$ with aqueous alkaline formaldehyde solution to produce $(SN.CH_2OH)_4$ is probably the most important reaction of this compound. It is very easy to carry out, and gives high yields of pure product even from impure samples of $S_4(NH)_4$. The product is both air and water stable and can be used to form many other derivatives.

The reaction can be summarised:

$$S_4(NH)_4 + 4\ HCHO \xrightarrow{NaOH\ aq} (SN.CH_2OH)_4$$

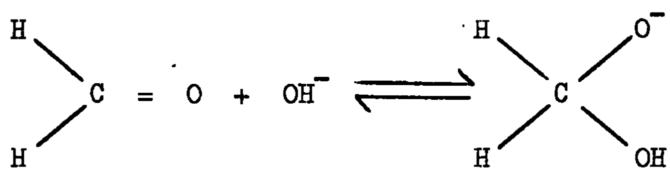
Similar derivatives have been described for $S_5(NH)_3$,[181] and for S_7NH,[344] but in the latter case, the yields are very low.

The reaction does not occur in the absence of alkali so that the OH^- ion must take part in the reaction being eliminated again on the formation of the product.

The first stage in the reaction is, presumably, the reversible addition of hydroxide ion to the carbonyl group of the formaldehyde.[399] (Figure 4.1)

Figure 4.1

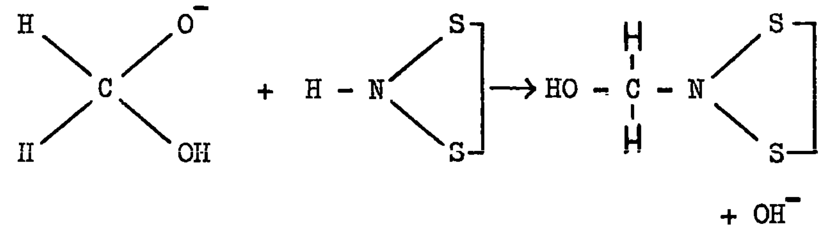
(a)



The hydroxylalkoxide ion so formed may then attack the nitrogen of the imide eliminating OH^- to form the hydroxymethylene derivative. (Figure 4.2)

Figure 4.2

(b)



The above mechanism implies that there is hydrogen exchange between $S_4(NH)_4$ and OH^- during the reaction and deuterium labelling of the imide would show whether this occurs or not.

The partially substituted hydroxymethyl derivatives of $S_4(NH)_4$, i.e. $S_4(NH)_{4-n}(CH_2OH)_n$ (n = 1 to 3), have not been prepared, and so far attempts to prepare them only form $(SN.CH_2OH)_4$. If the addition of formaldehyde to $S_4(NH)_4$ is stepwise, each nitrogen being substituted separately then this implies that the initial substitution is the slowest step, the subsequent substitutions taking place too rapidly for any partially substituted intermediates to be isolated.

Reactions of $S_4(NH)_4$ with other aldehydes, RCHO, to produce derivatives of the type: $(SN.CH(R)OH)_4$, have also so far been unsuccessful. Aldehydes containing an α-hydrogen readily undergo aldol additions and condensations in alkaline conditions,[399] and so are unsuitable but those not containing an α-hydrogen: e.g. formaldehyde, benzaldehyde, furfural, etc., do not, but instead undergo the Cannizzaro reaction:[399] e.g. for formaldehyde:

$$HCHO + NaOH(aq) \xrightarrow{Heat} CH_3OH + HCOONa$$

The Cannizzaro reaction is generally much slower than corresponding aldol reactions and therefore is of only minor importance as a competing reaction.

The failure so far of inducing other aldehydes to react with $S_4(NH)_4$ may suggest that both the hydrogens in formaldehyde are utilised in the reaction mechanism, and that the replacement of one by another group will stop the reaction from taking place. Alternatively, the reaction may be very much slower with other aldehydes so that the Cannizzaro reaction predominates and very little $S_4(NH)_4$ derivative is produced.

The compounds $(SN.CH(R)OH)_4$, if they could be made, would be interesting since they would open up a whole new range of sulfur-nitrogen ring compounds with organic substituents. They would probably be air and water stable and have organic activity. A further point of interest is that the carbon atoms attached to nitrogen are all asymmetrically substituted and therefore the compounds should exhibit a whole range of optical isomers.

The structure of $(SN.CH_2OH)_4$ has not yet been determined although comparing it with the known structure of $S_4(NH)_4$,[299,305] (the parent compound), it should consist of an eight membered puckered ring with the $-CH_2OH$ groups attached, one to each nitrogen. In $S_4(NH)_4$, the group: $\begin{smallmatrix}S\\S\end{smallmatrix}\!>$N-H, is coplanar,[299] and the methyl groups in $S_4(NCH_3)_4$ are only 11° out of the S_2N plane,[357] due to the delocalisation of the lone pair on nitrogen. This may also be the case for $(SN.CH_2OH)_4$ with the $\begin{smallmatrix}S\\S\end{smallmatrix}\!>$N-C- grouping coplanar, although a change in ring conformation to accommodate the larger $-CH_2OH$ groups is also a possibility.

2. Reactions of $(SN.CH_2OH)_4$ with Metal Chlorides

$(SN.CH_2OH)_4$ reacts immediately and apparently quantitatively with respect to the sulfur-nitrogen compound with metal chlorides in inert solvents to produce insoluble compounds. No other products are observed, and the compounds themselves appear to be quite stable.

$(SN.CH_2OH)_4$ has been reacted with: $SnCl_4$, $TiCl_4$, $SbCl_5$, $FeCl_3$, $AlCl_3$, $TaCl_5$, and also with TlOH, forming compounds which are probably representative of a large series of $(SN.CH_2OH)_4$, metal chloride complexes. The stoichiometry of these complexes has not yet been established. This is partly because the calculated analysis figures for the different stoichiometries are not sufficiently different for a distinction to be drawn from the observed analysis figures, and also because a condensation reaction with elimination of HCl is possible. The compounds are therefore probably a mixture of stoichiometries. The infrared spectra of these compounds and of $(SN.CH_2OH)_4$ itself, all show some overall similarities, implying that all have related structures. It is therefore probable that the $(SN.CH_2OH)_4$ molecule remains essentially intact in the compounds although the conformation of the ring may be altered.

Any further discussion on the structure of these compounds is speculative but based on the above observations and on other sulfur-nitrogen, metal halide compounds, there seems to be two main possibilities:

(a) Electron donation from nitrogen to the metal atom forming a nitrogen-metal bond. This is observed in the wide range of S_4N_4, metal halide compounds known, e.g.: S_4N_4,BF_3[141,147] and $S_4N_4,SbCl_5$[138,139,147] where the SN ring is altered in conformation but remains intact and one nitrogen is bonded directly to boron or antimony respectively (see also Chapter 1, Pages 22ff). $S_4(NH)_4$ forms adducts with $AlCl_3$ and $AlBr_3$, in which the imide ring appears to remain intact,[358] the structure probably involving nitrogen donation to the metal. Similar structures may also occur in the $(NSCl)_3$,metal chloride adducts (see later discussion). The negative charge of the oxygen atom in the hydroxyl dipole may cause an electron drift away from the nitrogen lone pair thus affecting possible bonding.

(b) Electron donation from the lone pairs on oxygen to the metal atom. The lone pairs on nitrogen are considerably delocalised into the SN ring in $S_4(NH)_4$ and also probably in $(SN.CH_2OH)_4$. They are also sterically shielded by the $-CH_2OH$ groups, thus, the lone pairs on oxygen may be more likely to bond with the metal than those on nitrogen, to form metal-oxygen bonds. This is observed in compounds such as $ROH.BF_3$, where an alcohol combines with an electron pair acceptor, BF_3.[399]

In the case of the $TiCl_4$ and $SbCl_5$ adducts, analyses suggest that n = 3, full substitution may be difficult for steric reasons; however, a great deal more work would need to be done on these compounds to determine their composition and structure.

3. Reactions of $(SN.CH_2OH)_4$ as a Polyhydric Alcohol

In order to prepare derivatives of $(SN.CH_2OH)_4$, its function as a polyhydric alcohol (i.e. the reactions of the hydroxyl groups) were investigated.

(i) Reactions with isocyanates

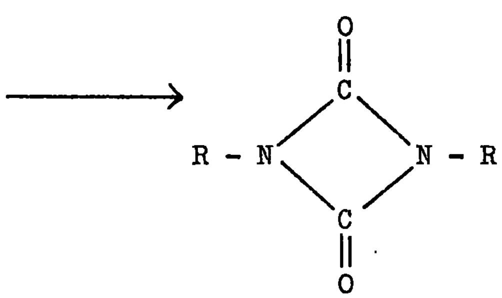
Isocyanates undergo a general reaction with alcohols of the type:[399]

$$RNCO + R'OH \longrightarrow R-\overset{H}{\overset{|}{N}}-\overset{O}{\overset{\|}{C}}-OR'$$

and compounds of the type: $(SN.CH_2OCONHR)_4$, were expected from the reactions.

However, no reaction was observed with phenyl, α-naphthyl and t-butyl isocyanates. In the first two cases the isocyanate simply dimerised to give the observed product.[399]

i.e. 2RNCO



R = phenyl, α-naphthyl

(ii) Reactions with acid chlorides

Acid chlorides undergo general reactions with alcohols to form esters:[399]

$$RCOCl + R'OH \longrightarrow RCOOR' + HCl$$

Reactions of $(SN.CH_2OH)_4$ with acetyl chloride and p-nitrobenzoyl chloride, to give "ester-type" compounds were reported by Arnold.[64] These reactions were repeated and crystalline products were formed, which were assumed to be the desired product although not positively identified as such. The reactions were slow and/or incomplete since $(SN.CH_2OH)_4$ did not seem to be particularly reactive. The reaction with 3,5-dinitrobenzoyl chloride was also carried out to give a crystalline solid and, presumably other "ester-type" compounds could also be similarly prepared.

(iii) Reaction with metallic sodium

Alcohols react with metallic sodium to form the alkoxide ion, and to liberate hydrogen:[399]

i.e. $$ROH + Na \longrightarrow RO^-Na^+ + \tfrac{1}{2} H_2$$

The alkoxide ion can further react with alkyl halides to give an ether:

e.g. $$RO^-Na^+ + R'I \longrightarrow ROR' + NaI$$

The reaction of $(SN.CH_2OH)_4$ with sodium in ether at room temperature was very slow. In refluxing benzene a reaction took place producing a green powder in which the SN ring appeared to be intact. This indicated that at least some of the hydrogen of the -OH groups had been displaced. The route was not, however, investigated further for two reasons. Firstly, because the formation of the "alkoxide" ion appeared to be slow and incomplete, and also because its reaction with ethyl iodide appeared to cause decomposition rather than "ether" formation.

(iv) Reactions with phosphorus chlorine compounds

The reactions of $(SN.CH_2OH)_4$ with the phosphorus acid chlorides $(Ph_2O)_2$ POCl and Ph_2PCl also suggest that "ester like" compounds are formed, in reactions analogous to the reactions with the acid chlorides RCOCl. The products could not be positively identified since the analysis figures were inconclusive, and also since the products remained on the base line on a TLC plate, and so could not be separated from any impurities. Their infrared spectra however showed similarities to $(SN.CH_2OH)_4$; the probable absence of an absorption due to the -OH groups indicating an "ester" linkage.

(v) $(SN.CH_2OH)_4$ Summary of reactions

The reactions of $(SN.CH_2OH)_4$ show that it does behave as a polyhydric alcohol although to an extent limited by the presence of the SN ring. Partial substitution may occur with the phosphorus and chlorides, or in the reaction with sodium since the products have not been fully characterised.

Donor properties from nitrogen or oxygen to a metal atom are probably exhibited in the formation of adducts with metal chlorides.

The foregoing results indicate that the properties of $(SN.CH_2OH)_4$ as an alcohol are probably worth studying further, as a starting material for the synthesis of new derivatives. The reactions of $(SN.CH_2OH)_4$ so far studied have only been of limited success so that reactions with new types of reagents (e.g. with phosphorus halides or thionyl chloride as a possible route to the halide derivative, with sulfonyl chlorides to give the sulfonyl derivative, or with Ketene dimer to form the acetoacetic acid derivative),[399] should be investigated in preference to some of those already studied.

4. Reactions of $S_4(NH)_4$ with Isocyanates

The reaction of $S_4(NH)_4$ with phenyl isocyanate is reported by Arnold to form: $(SN.CONH.C_6H_5)_4$.[64] Organic amines react with isocyanates to form analogous derivatives:[399]

i.e. $$RNCO + R'NH_2 \longrightarrow R-\underset{H}{\underset{|}{N}}-\underset{O}{\underset{\|}{C}}-\underset{H}{\underset{|}{N}}-R'$$

This reaction could not be repeated, the only product being impure starting material, and similarly using α-naphthyl isocyanate and $S_4(NH)_4$.[64] This may throw some doubt on Arnold's work, but it is probable that the reactions are sensitive to conditions, and that these were not adequately duplicated.

This may also explain the difficulties in preparing other organic derivatives of $(SN.CH_2OH)_4$.

5. Reactions of $S_4(NH)_4$ with Sulfur

The thermal decomposition of all the sulfur imides (including $S_4(NH)_4$), yields S_4N_4 as the only sulfur-nitrogen compound.[62,400] It is therefore interesting that the reactions of $S_4(NH)_4$ with sulfur, (in equimolar quantities, or with sulfur in excess) at ca. 110°, (55° in liquid ammonia) yield, not only S_4N_4 (main product), but also S_7NH in quantities sufficient for identification by infrared spectroscopy, and possibly also small amounts of S_4N_2, which appeared as a red spot on the TLC plate. The reactions were carried out in an oxygen-free atmosphere, so that $(OSNH)_4$ was not formed.[368] (When $(HNS)_4$ is heated in an oxygen atmosphere, $(OSNH)_4$ is produced).

The reactions probably involve the fragmentation of both the S_8 and $S_4(NH)_4$ rings, the S_8 fragmenting to sulfur chains, and then "picking up" 'NH' units from the imide, before recyclysing to form S_7NH. Tetrasulfur tetranitride, (S_4N_4), (probably formed by the reaction of S_8 with $S_4(NH)_4$, eliminating H_2S) can react with more sulfur to yield S_4N_2.[222] No other spots were visible on the TLC plate (e.g. other sulfur imides).

The reaction in liquid ammonia probably also involves the solvent, but this has been discussed in the previous chapter.

It would be of future interest to carry out similar reactions using selenium in place of sulfur, as a possible route to produce sulfur-selenium imides analogous to the compounds S_7Se, S_6Se_2 and S_5Se_3, prepared by Schmidt,[322] since these compounds can be prepared by heating mixtures of sulfur and selenium. It is possible therefore, that by heating mixtures of $S_4(NH)_4$ or S_7NH and selenium, (S_7NH has been shown to behave in analogous ways to sulfur (see discussion)), that mixtures of sulfur-selenium imides could be formed.

(E) Discussion S_7NH

The molecular structure of S_7NH is very similar to that of S_8, the only essential difference being the substitution of one sulfur atom for an $>$NH group. This similarity is reflected in its chemical properties, which were based on the reactions of the $>$NH group, but in which S_7NH often behaved as sulfur.

1. Properties

S_7NH is only weakly absorbed on a chromatography column or TLC plate, the Rf values decreasing in the order: $S_8 > S_7NH > S_6(NH)_2 > S_4N_4$. Therefore apparently decreasing in order of increasing nitrogen content. Chromatography is a good method of separating sulfur and S_7NH (sulfur is the most common impurity in S_7NH), and this was demonstrated by the complete and almost quantitative chromatographic separation of a known mixture.

S_7NH can be sublimed under low pressure with little decomposition, ring fragmentation yielding sulfur under these conditions.

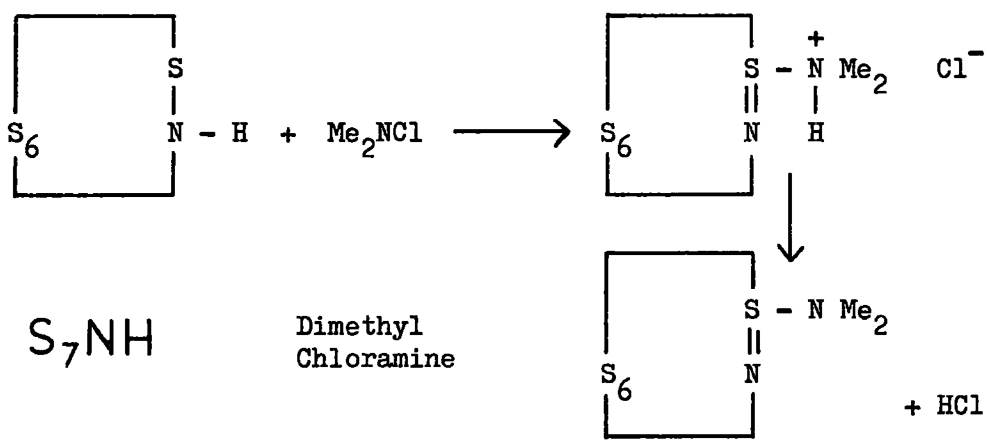
2. Reactions

Whereas $S_4(NH)_4$ gives practically quantitative yields of $(SN.CH_2OH)_4$ with alkaline formaldehyde solution, the analogous reaction with S_7NH yielded no detectable quantities of $S_7N.CH_2OH$. (Meuwsen reports an 8% yield from this reaction).[344] The sulfur containing products were a mixture of sulfur-oxygen anions (sulfite, thiosulfate, etc.) very similar to those obtained from the reaction of sulfur with alkaline formaldehyde, and therefore in this reaction, S_7NH is behaving in a similar way to sulfur.

S_7NH contains six S-S bonds, whereas $S_4(NH)_4$ contains only S-N bonds, thus it appears that the alkaline conditions are such as to cause an S-S bond to break, but not an S-N bond. Although the S-S and S-N single bonds are about the same strength (63 and 59 K.cal/mole respectively[96,140]), more lone pair delocalisation can occur from the nitrogen of an S-N bond making this bond the stronger due to partial multiple bonding.

The reaction of S_7NH with dimethyl chloramine was an attempt at the following reaction (Figure 4.3):

Figure 4.3

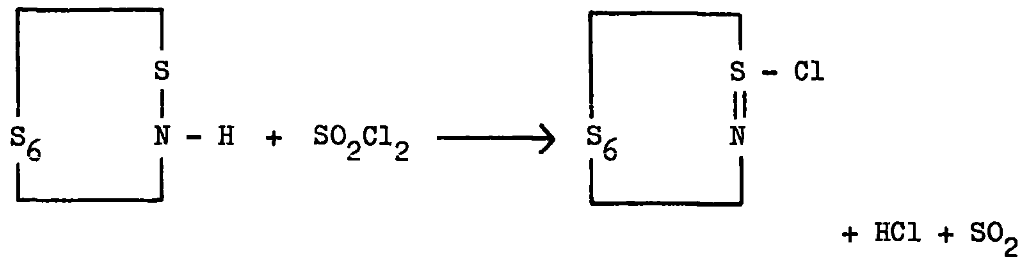


The desired final product is a sulfur nitrogen ring, substituted at sulfur, as distinct from other sulfur imide derivatives, which are substituted at nitrogen.[342]

A reaction appeared to occur in CS_2 solution, since the solution became yellow, and pyridinium hydrochloride was formed. On warming up to room temperature, decomposition to sulfur occurred, and it is probable that the product is stable only at low temperatures. The unidentifiable material on the TLC plate was probably polymeric, rather than a useful reaction product.

The reaction of S_7NH with sulfuryl chloride was an attempt to form an S-Cl bond from S_7NH, from which other derivatives could be made (e.g. using epoxides[51]). (Figure 4.4)

Figure 4.4



S_7NH

This reaction would be analogous to the reaction of $S_4(NH)_4$ with sulfuryl chloride to form $(NSCl)_3$, where N-H bonds are exchanged for S-Cl bonds,[398] although ring contraction also occurs in this case.

However, in this case, decomposition occurred, and sulfur was the only identifiable product.

TRITHIAZYL TRICHLORIDE/LEWIS ACID ADDUCTS AND THEIR REACTIONS

CHAPTER 5

Trithiazyl Trichloride/Lewis Acid Adducts and their Reactions

(A) Introduction

The reactions of trithiazyl trichloride, $(NSCl)_3$, with Lewis acids to form adducts and their subsequent reactions were studied, as it was hoped to be able to convert the imides discussed in the previous chapters, into compounds containing S-Cl bonds; these studies were therefore carried out concurrently with those on $S_4(NH)_4$. $(NSCl)_3$ is a model compound for compounds containing S-Cl bonds, and so a study of its reactions would be of value. $(NSCl)_3$ is also probably the cheapest pure source of SN and NSCl fragments, since it is easily synthesised from $S_3N_2Cl_2$ and sulfuryl chloride.[279] In the form of adducts with metal chlorides, it was found to behave as a potential source of SN^+ which has been found to be an important intermediate in the preparation of other sulfur-nitrogen compounds (e.g. $S_5N_5^+$, (this thesis) and Padley,[148] $S_2N\ Cl_2^+$, (this thesis), and $R\text{-}CN_2S_2^+$.[51,279,402])

(B) Experimental

1. Formation of $(NSCl)_3$/Lewis Acid Adducts

The behaviour of $(NSCl)_3$ as a potential source of NS^+ was investigated by reacting it with various Lewis acids ($FeCl_3$, $AlCl_3$, $SbCl_5$) in thionyl chloride solution, to form a series of adducts.

(i) Reaction of $(NSCl)_3$ with $FeCl_3$

Trithiazyl trichloride, $(NSCl)_3$, (0.3463g), was dissolved in 10 ml. of thionyl chloride in a round bottomed flask, and ferric chloride (0.2296g) was added with stirring, (molar ratio $(NSCl)_3$:$FeCl_3$ = 1:1). A bright, brick-red precipitate was gradually formed over ca. ½ hour, the thionyl chloride solution was red and all the ferric chloride had dissolved. A second batch of $FeCl_3$ (0.2296g) was then added, to give a molar ratio of $(NSCl)_3$:$FeCl_3$ = 1:2, and the solution was stirred. After ca. 2 hours, a rust-brown precipitate had been formed, but some $FeCl_3$ remained undissolved. A third batch of $FeCl_3$ was then added and the solution stirred as before for ca. 12 hours, after which time, the orange precipitate was still present, together with the molar excess of $FeCl_3$. Several repeats of this experiment confirmed that a bright-red compound is formed with $(NSCl)_3$ and $FeCl_3$ in molar ratio 1:1, a rust-brown in molar ratio 1:2, and that, at room temperature, further $FeCl_3$ does not react. On refluxing, the $FeCl_3$ eventually dissolves and $S_2N\ Cl_2\ FeCl_4$ is finally formed (see later discussions, page 138).

(ii) Reaction of $(NSCl)_3$ with $AlCl_3$

Trithiazyl trichloride (0.5849g) was dissolved in 10 ml. of thionyl chloride in a round bottomed flask and $AlCl_3$ (0.3189g) added (molar ratio 1:1). The mixture was stirred for ca. ½ hour, during which time the solution became deep red and a red precipitate was formed. All the $AlCl_3$ appeared to have dissolved. A further batch of $AlCl_3$ (0.3189g) was then added, to give a molar ratio of $(NSCl)_3$:$AlCl_3$ = 1:2, and the solution stirred as before. The red precipitate dissolved, and a yellow-orange precipitate gradually formed, a little more slowly than the corresponding $FeCl_3$ compound. A further batch of $AlCl_3$ (0.3189g) was then added, to give a molar ratio of $(NSCl)_3$:$AlCl_3$ = 1:3, but the $AlCl_3$ remained undissolved after ca. 12 hours stirring, and the precipitate was unchanged. Several repeats of this experiment showed that a red compound is formed with $(NSCl)_3$ and $AlCl_3$ in molar ratio 1:1, a yellow-orange compound in molar ratio 1:2, and that further $AlCl_3$ does not react at room temperature. On refluxing the mixture, similar reactions to those of $FeCl_3$ occur.

(iii) Reaction of $(NSCl)_3$ with $SbCl_5$

Trithiazyl trichloride, $(NSCl)_3$, (0.8730g) was dissolved in ca. 15 ml. of thionyl chloride, and 1.3 ml. of freshly distilled $SbCl_5$ (molar ratio 1:3, $(NSCl)_3$:$SbCl_5$) added via a syringe to the vigorously stirred solution under a back pressure of nitrogen over a period of several minutes. An immediate reaction took place on mixing the two liquids, a dense yellow-green precipitate was immediately formed, and the reaction was noticeably exothermic. All the $SbCl_5$ appeared to react with the $(NSCl)_3$ in solution. After stirring for ca. 6 hours the precipitate became yellow but otherwise remained unchanged. Several repeats of this experiment showed that a yellow, sparingly soluble precipitate is formed when $(NSCl)_3$ and $SbCl_5$ are mixed in thionyl chloride. This compound is probably the 1:3 adduct, which was probably formed via the 1:1 and 1:2 adducts as for $FeCl_3$ and $AlCl_3$. These antimony adducts were not individually isolated because the three adducts of antimony (v) chloride: $(NSCl)_3$, x $SbCl_5$ (x = 1,2 or 3), have already been described.[289]

(iv) Reaction of $(NSCl)_3$, 2 $FeCl_3$ adduct with $(NSCl)_3$

The $(NSCl)_3$, 2 $FeCl_3$ adduct was prepared in thionyl chloride as before, and a molar equivalent of $(NSCl)_3$ added to the solution with stirring, to give an overall molar ratio of $(NSCl)_3$:$FeCl_3$ of 1:1. A bright brick-red precipitate was gradually formed over ca. ½ hour which appeared to be identical with the 1:1 adduct previously described. It also reacted with S_4N_4 to yield S_5N_5 $FeCl_4$. (See Chapter 6).

(v) Reaction of $(NSCl)_3$, 2 $AlCl_3$ adduct with $(NSCl)_3$

The $(NSCl)_3$, 2 $AlCl_3$ adduct was prepared in thionyl chloride as before, and a molar equivalent of $(NSCl)_3$ added to the solution, in a similar way to $FeCl_3$ (above). A red precipitate was gradually formed over ca. ½ hour, which appeared to be identical with the 1:1 adduct previously described. The 1:2 adduct reacts (like the 1:1 adduct) with S_4N_4 to yield S_5N_5 $AlCl_4$. (See Chapter 6).

(vi) Effect of heat on the adducts in solution

The $(NSCl)_3$, $FeCl_3$ adduct (1:1) was prepared as before, and the solution heated to reflux. The brick-red adduct dissolved, and after being allowed to cool slowly, large bright-red needle-like crystals appeared, which underwent the same reactions as the original adduct, and were therefore presumably the recrystallised adduct. The $(NSCl)_3$, $AlCl_3$ adduct behaved similarly, to give large yellow crystals. The 1:2 adducts were also recrystallised in the same way, to yield large needle-like crystals: $(NSCl)_3$, 2 $FeCl_3$ (rust-brown) and $(NSCl)_3$, 2 $AlCl_3$ (yellow-orange).

(vii) Attempted isolation of the adducts

Attempts were made to isolate the pure adducts to determine their structure from spectra and analysis. The adducts were filtered from thionyl chloride using a sintered disc, the final traces of thionyl chloride were removed by pumping dry in vacuo. During this procedure, both the iron and the aluminium adducts darkened noticeably, indicating some decomposition. The dry adducts were then transferred to a dry box for analysis, but any further attempt to isolate them, or to obtain spectra, resulted in complete decomposition, and no further useful data was obtained. It was therefore concluded that all the adducts are extremely moisture sensitive and that thionyl chloride helps to stabilise them. All the adducts are indefinitely stable at room temperature under thionyl chloride.

(viii) Attempted preparation of the adducts in other solvents

Equimolar quantities of $(NSCl)_3$ and $AlCl_3$ were dissolved in separate solutions of dry CCl_4, (both are soluble in this solvent), and the solutions were mixed under dry conditions, in an attempt to prepare the $(NSCl)_3$, $AlCl_3$ adduct. However, on mixing, a black tarry residue was immediately formed which was too viscous to give any satisfactory analysis but which was obviously a decomposition product. A repeat reaction gave the same result, as did a similar reaction using dry benzene as the solvent.

The reaction was also carried out, using liquid SO_2 as the solvent: $(NSCl)_3$ (1.3935g) was partially dissolved in ca. 50 ml. of liquid SO_2. ($(NSCl)_3$ was found to be fairly soluble in liquid SO_2 and more soluble at $-23^\circ C$ than at $-78^\circ C$, since some crystallised out on cooling). $FeCl_3$ (0.6161g) was then added in one batch (molar ratio 1:1) to minimise the amount of moisture introduced. The solution became very dark, as most of the $FeCl_3$ appeared to dissolve, but it was difficult to see whether any precipitate had been formed.

The solution was stirred at $-23^\circ C$ for ca. 1 hour; but the solution remained dark, and the characteristic bright-red colour of the 1:1 adduct was not formed. Some reaction may have occurred, although on pumping off the solvent, mostly starting materials remained. Sulfur dioxide is therefore not such a good solvent as thionyl chloride for the formation of these adducts.

(ix) Reaction of $(NSCl)_3$ with $SnCl_4$ in CCl_4

Trithiazyl trichloride $(NSCl)_3$ (1.0771g) was dissolved in ca. 50 ml. of dry CCl_4 with stirring, and a solution of freshly distilled $SnCl_4$ in dry CCl_4, (0.7731 ml. $SnCl_4$ in ca. 20 ml. CCl_4) added slowly via a syringe. (Molar ratio $(NSCl)_3$:$SnCl_4$ = 1:1.5). An immediate reaction occurred, although not noticeably exothermic, and an orange precipitate formed, which remained unchanged throughout the addition of the $SnCl_4$. The solution was stirred for a further ten minutes, the precipitate darkening slightly during this time. The precipitate formed is probably an $(NSCl)_3$, $SnCl_4$ adduct, which is interesting since both the corresponding $AlCl_3$ and $FeCl_3$ adducts appear to be unstable in CCl_4 (see experiment (viii)). The $(NSCl)_3$, $SnCl_4$ adduct may therefore have a structure different from the other adducts (e.g. the $SnCl_4$ can form the $SnCl_6^{2-}$ anion, and could therefore be co-ordinated to two $(NSCl)_3$ molecules via a six-co-ordinated tin atom instead of only one, as is probably the case with the other adducts).

(x) Reaction of $(NSCl)_3$ with BCl_3 gas

$(NSCl)_3$ (1.111g) was dissolved in ca. 50 ml. of thionyl chloride in a round bottomed flask fitted with a stirrer, a reflux condenser and a gas inlet and outlet. BCl_3 gas, from a cylinder was diluted with dry nitrogen and passed into the stirred solution.

The BCl_3 gas appeared to dissolve since no BCl_3 was evolved from the gas outlet (BCl_3 rapidly fumes in moist air) and the solution changed from light red to dark red. The BCl_3 was passed until the solution was saturated with the gas, and BCl_3 was being evolved at the gas outlet. The solution was dark red in colour but no precipitate formed. It was probable however that the product was an adduct, soluble in thionyl chloride.

(xi) Reactions of $(NSCl)_3$ with metal chlorides in 1:3 molar ratio

(a) With $FeCl_3$

$(NSCl)_3$ (1.03g) and $FeCl_3$ (2.0493g) (1:3 stoichiometric ratio) were dissolved in ca. 100 ml. of thionyl chloride and the mixture refluxed, (78°C). After ca. 2 hours the solution was cooled and rust-brown crystals were precipitated; however, unreacted ferric chloride was also present, so presumably only the 1:2 adduct had been formed. The solution was therefore refluxed for a further 6 hours and then cooled. Yellow, needle-like crystals were formed, and the ferric chloride previously present appeared to have reacted. The solution was filtered cold and the air sensitive crystals (long, dark yellow needles) were pumped dry of solvent. The filtered solution was dark brown, but no ferric chloride could be seen mixed with the crystals. An infrared spectrum showed the product to be $S_2NCl_2\ FeCl_4$ (see page 139), rather than the 1:3 adduct.

(b) With $AlCl_3$

Trithiazyl trichloride $(NSCl)_3$ (0.9867g) and $AlCl_3$ (1.6139g) (molar ratio 1:3) were dissolved together in ca. 50 ml. of thionyl chloride, and stirred at room temperature for about 12 hours to form the 1:2 adduct, (orange powder). The solution was then refluxed for about 6 hours, and allowed to cool slowly to -10°C. Yellow/green needle-like crystals were formed. These were filtered off and pumped dry in vacuo. The filtered solution was very dark in colour.

The green colouration was only a surface effect since the crystals were yellow when powdered. The compound was identified as $S_2NCl_2\ AlCl_4$, from its infrared spectrum. (See page 141 and Appendix).

2. Reactions of the $(NSCl)_3$/Lewis Acid Adducts

(i) Reactions with SCl_2

Glemser has reported the cation $S_2NCl_2^+$ [289,291,403] as a product of various reactions (see discussion, page 157) and this cation could also be formed by the addition of SN^+ to SCl_2, the $(NSCl)_3$/Lewis acid adducts being used as a potential source of NS^+.

(a) $(NSCl)_3$, $FeCl_3$ adduct (SCl_2 + $(NSCl)_3$, 2 $FeCl_3$ + $FeCl_3$)

$(NSCl)_3$ (1.6832g) was dissolved in ca. 50 ml. of thionyl chloride, $FeCl_3$ (3.3492g) added (molar ratio 1:3) and the mixture stirred for about 12 hours to form the 1:2 adduct as before. Sulfur dichloride (SCl_2) (1.4 ml. molar ratio 1:3.6, slight excess of SCl_2 to ensure complete reaction), was then added via a syringe to the vigorously stirred solution over a period of about one minute. There was no immediate colour change on adding the SCl_2, but an orange precipitate gradually formed after about two minutes. After precipitation was complete (ca. 1 hour), the solution was filtered under reduced pressure through a sintered disc, and the precipitate pumped dry in vacuo, to yield a yellow powder. This was recrystallised from thionyl chloride, the product being moderately soluble in the solvent, to give yellow needle-like crystals, which were filtered and pumped dry. Infrared spectrum (nujol mull): 1130 (m), 735 (sh), 721 (m), 704 (sh), 654 (s), 645 (sh), 517 (s), 505 (s), 494 (s) cm^{-1}. Yield: 80% pure product.

The infrared spectrum was identical to that of the initial yellow powder.

Analysis:

Observed %	$S_2NCl_2\ FeCl_4$ requires %
S = 18.37	S = 18.50
N = 4.17	N = 4.04
Cl = 61.89	Cl = 61.36
Fe = 15.57 (by difference)	Fe = 16.11

UV spectrum: (solvent conc. H_2SO_4): λ max. nm. 378, ca. 220. The absorption at ca. 220 nm. was difficult to locate accurately due to low solubility and slow decomposition.

(b) $(NSCl)_3$, $AlCl_3$ adduct (SCl_2 + $(NSCl)_3$, 2 $AlCl_3$ + $AlCl_3$)

$(NSCl)_3$ (0.7939g) was dissolved in ca. 100 ml. of thionyl chloride, $AlCl_3$ (1.2986g) was added, (molar ratio = 1:3) and the solution stirred for ca. ½ hour, until the adduct was formed. (In this instance there was no precipitate, since the adduct dissolved completely in the thionyl chloride). SCl_2 (0.7 ml.) (molar ratio 1:1.2 with $AlCl_3$, slight excess to ensure complete reaction) was added to the stirred solution. An immediate reaction occurred, the solution became a very dark yellow colour, almost black. The solution was stirred for about ½ hour, during which time an orange precipitate gradually formed, the solution being light yellow in colour. The precipitate was recrystallised without filtering, by heating the mixture to reflux temperature (78°C) and then allowing to cool slowly to -10°C. Bright yellow, needle-like crystals were formed. These were filtered off and pumped dry in vacuo. Weight of recrystallised product = 2.4874g = 80.4% yield. Infrared spectrum (nujol mull): 1136 (m), 738 (sh), 721 (m), 658 (s), 649 (sh), 524 (s), 510 (s), 496 (s), 481 (s) cm^{-1}. (Absorptions at ca. 490 cm^{-1}, due to $AlCl_4^-$ [404]). (The infrared spectrum is similar to that of $S_2NCl_2\ FeCl_4$ which shows that the same $S_2NCl_2^+$ species is present).

UV (solvent conc. H_2SO_4): λ max. nm. 374, 206. (The compound dissolved slowly, and also decomposed, therefore accurate molar extinction coefficients could not be determined). (See Appendix for IR and UV spectra). Yield = 85% pure product.

Analysis:

Observed %		S_2NCl_2 $AlCl_4$ requires %	
S	= 20.55	S	= 20.17
N	= 4.37	N	= 4.41
Cl	= 66.80	Cl	= 66.93
Al	= 8.37	Al	= 8.49
Total	= 100.09 %	Total	= 100.00 %

(c) SCl_2+ $(NSCl)_3$, $nBCl_3$ adduct

Trithiazyl trichloride $(NSCl)_3$ (0.7510g) was dissolved in about 50 ml. of thionyl chloride, and BCl_3 gas diluted with dry nitrogen was bubbled through the solution until it was saturated with the gas. The colour of the solution changed slowly from yellow to red during this period, showing that a reaction had probably occurred. There was no precipitate but this was probably because the adduct formed is soluble in thionyl chloride. About 0.6 ml. of SCl_2 was then added to the solution (slight excess) as before, and the solution became lighter, showing that a reaction was again occurring. A yellow precipitate gradually formed over a period of about 10 minutes, and this was filtered off under reduced pressure. However, on pumping the precipitate dry, the yellow compound darkened, and a gas (presumably BCl_3) was evolved, indicating decomposition. It was therefore not possible to obtain any satisfactory physical data on the compound. The compound also appeared to decompose, presumably again with evolution of BCl_3, when heated in thionyl chloride solution to attempt a recrystallisation. This experiment was repeated with the same results.

A lower temperature may therefore be required for the preparation to avoid decomposition and evolution of BCl_3.

(d) SCl_2 + $(NSCl)_3$, 3 $SbCl_5$

Trithiazyl trichloride $(NSCl)_3$ (1.3508g) was dissolved in ca. 100 ml. of thionyl chloride and $SbCl_5$ (0.9 ml, slight excess) was added from a graduated syringe, slowly with stirring. The yellow adduct precipitated out immediately on mixing the two reagents. The mixture was stirred for a further ½ hour, and then SCl_2 (1.1 ml.) was added while stirring vigorously. A rapid reaction occurred, and a yellowish solid was formed (the thionyl chloride solution was dark red). The mixture was stirred for about ½ hour,, heated to reflux temperature, and then allowed to cool to -10°C. A yellow/green powder was formed, the thionyl chloride solution being very dark in colour. The precipitate was filtered off, and pumped dry in vacuo, to yield a bright yellow, microcrystalline powder. Yield: about 80%. UV spectrum (solvent: conc. sulfuric acid): λ max. nm. 374, 205. (The compound dissolves slowly with decomposition, therefore the molar extinction coefficients could not be determined). Infrared spectrum (nujol mull): 1130 (m), 735 (sh), 721 (m), 654 (s), 521 (s), 520 (s), 494 (s) cm^{-1}. (Spectrum very similar to analogous $FeCl_3$ and $AlCl_3$ compounds). Yield = 85% pure product.

Analysis:

Found %	S_2NCl_2 $SbCl_6$ requires %
S = 13.00	S = 13.26
N = 3.11	N = 2.90
Cl = 57.46	Cl = 58.66
Sb = 26.43 (by difference)	Sb = 25.18

(ii) Reactions with $C Cl_3 SCl$

The reactions $(NSCl)_3$ + Lewis acid + $C Cl_3 SCl$ were studied in an attempt to prepare a reagent which could then be used to introduce carbon into a sulfur-nitrogen cation, (e.g. $S_2N_2CR^+$).[51,279,402]

(a) $(NSCl)_3$, $FeCl_3$ adduct

Trithiazyl trichloride $(NSCl)_3$ (1.9619g) was dissolved in ca. 100 ml. of thionyl chloride, $FeCl_3$ (3.9037g) added, (molar ratio 1:3) and the mixture stirred for ca. 2 hours to form the adduct. Trichloromethyl sulfenyl chloride ($C Cl_3 SCl$) was then added to the vigorously stirred solution over ca. 1 minute (molar ratio $FeCl_3$:$C Cl_3 SCl$ = 1:1). The solution turned a dichroic red/green-blue colour immediately, showing that a reaction had taken place, and the solution was stirred vigorously for ca. 2 hours. A brownish precipitate eventually appeared, although the solution was still red/green-blue dichroic in colour. The solution was heated to ca. 50°C, and allowed to cool slowly to -10°C. Needle-like orange crystals, together with some brownish powder, were formed. These were filtered off and pumped dry in vacuo. The crystals were separated from the powder by hand in a dry box, and recrystallised twice from thionyl chloride, to yield small orange needle-like crystals. The powder could not be recrystallised and would not easily mull, and so was not investigated further.

Infrared spectrum of crystalline product (nujol mull):

1493 (m), 1409 (m), 1010 (m), 975 (sh), 971 (s), 940 (s), 787 (sh), 758 (sh), 741 (m), 714 (s), 575 (m), 568 (sh), 463 (m), 447 (w), 422 (m,b) cm^{-1}.

(Spectrum similar to that of $S_3N_2Cl^+$ salts).

Analysis:

Found %			$S_3N_2Cl\ FeCl_4$ requires %		
S	=	24.0	S	=	26.92
N	=	7.28	N	=	7.84
Cl	=	48.8	Cl	=	49.61

UV spectrum (solvent: conc. sulfuric acid) λ max nm: 363, 280 (sh), 230 (cf. UV spectrum of $S_3N_2Cl_2$, recorded in Appendix).

(b) $(NSCl)_3$, $AlCl_3$ adduct

$(NSCl)_3$ (2.4026g) and $AlCl_3$ (3.9299g) (molar ratio 1:3) were dissolved in ca. 100 ml. of thionyl chloride and stirred for ca. 12 hours to form the 1:2 adduct. Trichloromethyl sulfenyl chloride (CCl_3SCl) (3.2 ml) was then added to the vigorously stirred solution (molar ratio $AlCl_3$:CCl_3SCl = 1:1). An immediate reaction occurred, the solution turning red/green-blue dichroic as previously observed. The mixture was vigorously stirred for ca. 12 hours, the solution eventually becoming orange in colour, but there was no precipitate. The solution was reduced to ca. ⅓ bulk by distilling off some thionyl chloride, and then allowed to cool to -10°C. Yellow-orange crystals appeared together with some brown coloured powder, and this was filtered off, pumped dry and recrystallised from thionyl chloride to remove the brown powder and to yield fine yellow needle-like crystals.

Infrared spectrum (nujol mull):

1520 (w), 1430 (w), 1140 (m), 1000 (m), 943 (s), 787 (vw), 769 (m), 746 (s), 730 (vw), 719 (s), 697 (w), 658 (m), 621 (m), 577 (m), 520 to 450 (vs,vb) 424 (sb) cm^{-1}.

(Similar to that of the $FeCl_4^-$ salt, and also to $S_3N_2Cl^+$ salts, since the characteristic $S_3N_2Cl^+$ absorptions are at:

940 (vs), 741 (s), 717 (s), 574 (s), 464 (s) and 418 (b,s) cm^{-1}.)

Analysis:

Found %			$S_3N_2Cl\ AlCl_4$ requires %		
S	=	26.62	S	=	29.28
N	=	9.26	N	=	8.53
Cl	=	55.11	Cl	=	53.97

UV spectrum (solvent: conc. sulfuric acid): λ max. nm: 364, ca. 280 (sh) ca. 235. (Spectrum difficult to obtain, due to sparing solubility and slow decomposition).

(c) $(NSCl)_3$, $SbCl_5$ adduct

$(NSCl)_3$ (1.3306g) was dissolved in ca. 50 ml. of thionyl chloride and $SbCl_5$ (2 ml.) added slowly to the stirred solution to form the adduct. After stirring for ca. 1 hour, CCl_3SCl (1.78 ml) was added slowly to the vigorously stirred mixture. An immediate reaction occurred, the solution becoming noticeably warmer, and the colour changing immediately to red/green-blue dichroic. A greenish precipitate gradually appeared (the solution remained dark in colour) and, after stirring for ca. 24 hours with no further apparent reaction, the precipitate was filtered off and purified by solvent extraction with thionyl chloride, since it was not very soluble in the solvent. (A dark brown precipitate was not observed in this case, although it was observed in the case of the $FeCl_3$ and $AlCl_3$ adducts). Yellow needle-like crystals were formed, which were filtered and pumped dry in vacuo.

IR (same as crude product) (nujol mull):

930 (s), 763 (m), 741 (m), 719 (m), 714 (m), 691 (sh), 654 (w), 568 (s), 521 (s,b), 495 (m), 468 (s), 435 (s,b), 420 (s,b) cm^{-1}

(Similar to $S_2NCl_2^+$ salts).

Analysis:

Found %			$S_2NCl_2^+ SbCl_6^-$ requires %		
S	=	13.25	S	=	13.26
N	=	4.02	N	=	2.90
Cl	=	58.84	Cl	=	58.66
Sb	=	23.89	Sb	=	25.18
(by difference)					

UV spectrum (solvent conc. sulfuric acid) λ max. nm: 363.5, ca. 235 (compound only sparingly soluble).

(iii) Reactions with elemental sulfur

In order to further study the reactions of the $(NSCl)_3$/metal chloride adducts, their reactions with elemental sulfur were investigated in an attempt to prepare the new cation: $S_3N_2^{2+}$ by the reaction:

e.g. $\frac{2}{3}(NSCl)_3 + 2\ MCl_3 + 2S \longrightarrow S_3N_2^{2+}\ 2\ MCl_4^-$

The cation $S_3N_2^{2+}$ would be a member of the "electron rich aromatic" series of sulfur-nitrogen compounds, having 6 π electrons.[106] (See also later discussions on page 193).

(a) $(NSCl)_3$, $FeCl_3$ adduct

$(NSCl)_3$ (1.501g) was mixed with $FeCl_3$ (2.9867g) (1:3 molar ratio) in ca. 50 ml. of thionyl chloride to form the adduct. The mixture was refluxed, (78°C) and elemental sulfur (1.7709g) added to the refluxing mixture.

An immediate reaction occurred, and the colour of the solution changed from the rust brown adduct, to red/green-blue dichroic. The mixture was stirred at reflux temperature for ca. ½ hour, and then allowed to cool slowly to -10°C. Orange crystals and some dark brown powder were formed, the solution being dark red in colour. The precipitate was filtered off, the orange crystals separated from the powder by hand in the dry box, and recrystallised twice to give orange, needle-shaped crystals; the overall yield was small. The powder could not be recrystallised, and was not investigated further.

IR (nujol mull):

1136 (m), 1042 (vw), 1010 (w), 971 (w), 938 (s), 758 (sh), 741 (s), 717 (s), 654 (s), 649 (m), 647 (sh), 575 (s), 517 (s), 504 (s), 494 (s), 464 (s), 423 (s,b) cm^{-1}.

(Corresponding to a mixture of $S_3N_2Cl^+$ and $S_2NCl_2^+$ salts).

(iv) Reactions with elemental Selenium

Following on from the reactions of the $(NSCl)_3$/metal chloride adducts with elemental sulfur (Section (iii)), it was thought probable that some of the elemental sulfur was ending up in the reaction products, so that the corresponding reactions using elemental selenium were studied, in an attempt to prepare selenium analogues of $S_3N_2Cl^+$ and $S_2NCl_2^+$ salts.

(a) $(NSCl)_3$, $FeCl_3$ adduct

$(NSCl)_3$ (1.5657g) and $FeCl_3$ (1.5577g) were stirred in ca. 50 ml. of thionyl chloride to form the adduct. The mixture was then heated to ca. 60°C, and elemental selenium (grey allotrope) (0.7583g) was then added quickly to the mixture. (There was no apparent reaction at room temperature). An immediate reaction occurred, the solution changed from a bright red to a very dark colour, and the stirring was continued with cooling to room temperature for <u>ca.</u> ½ hour, during which time a greenish precipitate was gradually formed. The solution was then heated again to reflux temperature (76°C) and allowed to cool slowly without stirring to -10°C, in order to recrystallise the product. Yellow plate-like crystals were formed, (solution was orange/red), and these were recrystallised from fresh thionyl chloride. A flame test suggested that only traces of selenium were present in the compound.

IR spectrum (nujol mull):

1163 (vw), 1010 (vw), 935 (vs), 913 (sh), 758 (sh), 741 (s), 715 (s), 575 (s), 463 (s), 422 (s,b) cm^{-1}.

(Identical spectrum to $S_3N_2Cl\ FeCl_4$).

Analysis:

Found %		$S_3N_2Cl\ FeCl_4$ requires %	
S =	24.5	S =	26.92
N =	8.06	N =	7.84
Cl =	49.0	Cl =	49.61
Fe =	18.44	Fe =	15.63
(by difference)			

(v) Reactions with disulfur dichloride

Following on from the reactions of $(NSCl)_3$/metal chloride adducts with SCl_2, to form $S_2NCl_2^+$ salts, the reaction of S_2Cl_2 with these adducts was studied in an attempt to produce the analogous $S_3NCl_2^+$ salts.

(a) $(NSCl)_3$, $AlCl_3$ adduct

$(NSCl)_3$ (1.0g) and $AlCl_3$ (1.62g) were mixed in ca. 50 ml. of thionyl chloride to form the adduct and 1.0 ml. of S_2Cl_2 was added to the stirred mixture, as for SCl_2. An immediate reaction occurred and the solution became very dark in colour. Stirring was continued for ca. ½ hour and a yellow precipitate gradually formed, which was filtered off and pumped dry in vacuo to yield a yellow powder which was very moisture sensitive, but stable in a dry atmosphere.

IR (nujol mull):

1163 (vw), 1136 (w), 1117 (sh), 1058 (vw), 1031 (sh), 1020 (m), 735 (sh), 719 (m), 655 (s), 619 (w), ca. 530-440 (s,vb) cm^{-1}.

(Probably a mixture of S_2NCl_2 $AlCl_4$ and some S_3N_2Cl $AlCl_4$). (Absorptions at ca. 530-440 cm^{-1}, due to the $AlCl_4^-$ ion.[404]).

(vi) Reactions with diselenium dichloride

Having investigated the reaction between $(NSCl)_3$/metal chloride adducts and S_2Cl_2, the analogous reaction with Se_2Cl_2 was studied in an attempt to prepare selenium analogues of the corresponding sulfur compounds.

(a) $(NSCl)_3$, $AlCl_3$ adduct

$(NSCl)_3$ (1.0g) and $AlCl_3$ (1.64g) were mixed in ca. 50 ml. of thionyl chloride to form the adduct, and 1.1 ml. of Se_2Cl_2 added to the stirred solution. An immediate reaction occurred, the solution became very dark in colour, and an orange precipitate gradually formed over ca. ½ hour. This was filtered off and pumped dry in vacuo, to give an orange powder. Attempts to recrystallise the product from thionyl chloride were unsatisfactory, since it was only sparingly soluble in the solvent, and heating the solution appeared to cause some decomposition. The product was moisture sensitive, but was stable in a dry atmosphere. A flame test showed the presence of selenium in more than trace amounts.

IR spectrum (nujol mull):

1274 (vs,b), 1111 (w), 1042 (sh), 952 (m,b), 847 (w), 820 (w), 722 (s,b), 617 (m), ca. 520-440 (s,vb) cm^{-1}. (See Appendix)

The spectrum appeared to be different from other sulfur-nitrogen compounds, and the compound itself probably contained selenium, although the analyses were unsatisfactory.

Analyses:

Found %		$SSeNCl_2^+ AlCl_4^-$ requires %	
S	= 4.4	S	= 8.79
N	= 6.7	N	= 3.84
Cl	= 59.2	Cl	= 58.32

A mixture of sulfur-nitrogen selenium compounds is probable.

(vii) Reactions of $(NSCl)_3$/metal chloride adducts with S_4N_4

The reactions of $(NSCl)_3$ adducts with S_4N_4 lead to the formation of $S_5N_5^+$ salts. The synthesis, properties, reactions and structure of these salts occupied a large section of the research work, and so is dealt with in depth in the following chapter. The reactions involved may be summarised:

$$\text{(i)}\quad (NSCl)_3 + 3\,MCl_3 + S_4N_4 \xrightarrow{SOCl_2} S_5N_5^+\,MCl_4^-$$

(M = Fe, Al)

$$\text{(ii)}\quad (NSCl)_3 + 3\,SbCl_5 + S_4N_4 \xrightarrow{SOCl_2} S_5N_5^+\,SbCl_6^-$$

All reactions proceed in two stages via the adduct, as for the other $(NSCl)_3$/Lewis acid adduct reactions.

(viii) Direct preparation of $S_3N_2Cl^+$ salts

Since many of the compounds prepared in these and other reactions appeared to be $S_3N_2Cl^+$ salts (as determined by IR, UV and visible spectra, and by analysis), the corresponding $S_3N_2Cl^+$ salts were prepared by the direct reaction of $S_3N_2Cl_2$ with a chloride ion acceptor in thionyl chloride. The products were compared with the compounds prepared by other reactions.

The S_3N_2Cl and metal chloride (chloride ion acceptor) were mixed in a 1:1 molar ratio in thionyl chloride, stirred for about 6 hours, heated to reflux and then allowed to cool slowly to -10°C, during which time the product crystallised out. The crystals were filtered, recrystallised from thionyl chloride and pumped dry in vacuo. In the case of $SbCl_5$, the reaction occurred immediately on mixing, to give an insoluble yellow powder.

The following compounds were prepared:

$S_3N_2Cl^+ AlCl_4^-$: Orange needles.

$S_3N_2Cl^+ FeCl_4^-$: Dark orange needles.

$S_3N_2Cl^+ SbCl_6^-$: Insoluble yellow powder.

All three compounds appeared to be stable to thionyl chloride. Analysis of the compounds were in agreement with their formulation. The infrared spectra of all the compounds showed the presence of the same ($S_3N_2Cl^+$) cation, and the infrared spectrum was one of the main means of identifying these compounds.

IR spectrum (nujol mull) ($FeCl_4^-$ salt):

2200 (w), 1667 (b,vw), 1412 (w), 1300 (w), 1266 (w), 1163 (w), 1053 (m), 1010 (w), 995 (m), 940 (vs), 893 (vw), 787 (w), 758 (m), 741 (s), 717 (s), 615 (b,w), 574 (s), 515 (m), 464 (s), 418 (b,s) cm^{-1}.

(ix) Direct preparation of $S_4N_3^+$ salts

The $AlCl_4^-$, $FeCl_4^-$ and $SbCl_6^-$ salts of $S_4N_3^+$ were also similarly prepared by mixing S_4N_3Cl with the corresponding metal chloride in 1:1 molar ratio in thionyl chloride as solvent, in order to identify any $S_4N_3^+$ salts which may be formed as reaction products. All three compounds were yellow solids.

Infrared spectrum: ($S_4N_3^+$ cation):

1400 (w), 1160 (s), 1125 (sh), 998 (vs), 682 (s), 637 (w), 606 (w), 565 (s), 466 (vs), 450 (sh) cm^{-1}.

The infrared spectrum of the $S_4N_3^+$ cation, shows a marked susceptibility to distortion by the Christiansen effect.[405]

S_4N_3Cl was also reacted with the metal chlorides: $CoCl_2$, $ZnCl_2$ and $HgCl_2$.

S_4N_3Cl and the metal chloride were mixed together in thionyl chloride in the correct stoichiometric ratios and stirred at room temperature for _ca._ 6 hours. The products were filtered and pumped dry in vacuo. Their infrared spectra showed the characteristic absorptions of the $S_4N_3^+$ cation, with slight shifts due to the change in anion. The analyses were inconclusive, possibly due to incomplete reaction, but it was concluded that the following salts had been formed: $(S_4N_3^+)_2$ $CoCl_4^{2-}$ (green), $(S_4N_3^+)$ $ZnCl_4^{2-}$ (yellow), and $(S_4N_3^+)_2$ $HgCl_4^{2-}$ (yellow).

It was concluded that the $S_4N_3^+$ cation can easily be identified from its characteristic infrared spectrum irrespective of the anion, since the shifts in absorption are small. In particular, the absorptions at: 1160, 998, 682 and 565 cm^{-1} are strong and very characteristic.

(C) Reactions of $(NSCl)_3$/Lewis Acid Adducts

Discussion

1. Structure and Properties of the Adducts

The following $(NSCl)_3$/Lewis acid adducts have been prepared in thionyl chloride solution:

Adduct	Colour of Crystals	Page No.
$(NSCl)_3$, $AlCl_3$	Red	133
$(NSCl)_3$, 2 $AlCl_3$	Yellow-orange	133
$(NSCl)_3$, $FeCl_3$	Brick-red	133
$(NSCl)_3$, 2 $FeCl_3$	Rust-brown	133
$(NSCl)_3$, x $SbCl_5$ (x = 1,2 or 3)	Yellow powder	134
$(NSCl)_3$, n BCl_3 (n = unknown)	Red solution	137
$(NSCl)_3$, n $SnCl_4$ (n = unknown, CCl_4 soln)	Orange powder	137

Many other $(NSCl)_3$/Lewis acid adducts should be preparable in a similar way to the above adducts, and should also undergo analogous reactions with S_4N_4 and SCl_2 to form the corresponding $S_5N_5^+$ and $S_2NCl_2^+$ salts respectively. The 1:3 adducts of $(NSCl)_3$ with $AlCl_3$ and $FeCl_3$ may also be formed when $(NSCl)_3$ is heated with the corresponding metal chloride in thionyl chloride solution in the correct molar ratio, since the reagents dissolve on heating, and the final product, the $S_2NCl_2^+$ salt, is only formed very slowly. The formation of this product is probably due to further reaction of the adduct with the solvent:

i.e. (i) $(NSCl)_3 + 3\ MCl_3 \longrightarrow (NSCl)_3, 3\ MCl_3$

(ii) $2\ SOCl_2 \xrightleftharpoons{heat} SCl_2 + SO_2Cl_2$ [382]

(iii) $(NSCl)_3, 3\ MCl_3 + 3\ SCl_2 \longrightarrow 3\ S_2NCl_2\ MCl_4$

(M = Al,Fe) (See discussions of reactions of adducts with SCl_2).

The $SnCl_4$ adduct of $(NSCl)_3$ may possibly be of use in the synthesis of 2+ sulfur-nitrogen cations since the corresponding $SnCl_6^{2-}$ anion is doubly negative, and is therefore more compatible with a doubly charged cation.

The 1:1 and 1:2 adducts are in equilibrium with each other for M = Al and Fe (as observed in reactions (iv) and (v)).

i.e. $(NSCl)_3, MCl_3 + MCl_3 \xrightleftharpoons{SOCl_2} (NSCl)_3, 2\ MCl_3$

The adduct formed depends upon the molar ratios present. This equilibrium probably also exists for other similar adducts.

The adducts themselves are extremely air and moisture sensitive, much more so than either $(NSCl)_3$ or the metal chloride, but they are stable in thionyl chloride solution. Because of this extreme sensitivity, the adducts themselves have not been isolated free from thionyl chloride solution, and their stability in the solution is probably due to two factors:

(i) Thionyl chloride reacts with water to produce the gases SO_2 and HCl, therefore a solution acts as its own dehydrating agent, protecting the adducts against moisture.

i.e. $SOCl_2 + H_2O \longrightarrow SO_2 + 2\ HCl$ [382]

(ii) The adducts probably form some sort of donor-acceptor complex with the thionyl chloride solvent molecules. They are therefore stabilised by solvent-solute interaction and this type of stabilisation is not present in non-complexing solvents such as CCl_4 and benzene in which the adducts are much less stable.

The adducts decrease in solubility in thionyl chloride with increasing atomic weight of the metal.

i.e. In order of decreasing solubility: Al adduct > Fe adduct > Sb adduct. This trend is also observed in the reaction products of these adducts (e.g. $S_2NCl_2^+$ and $S_5N_5^+$ salts). This is probably due to the trend in anion size, since the lattice energy of the crystal structure increases as anion and cation become more compatible in size (e.g. as the anion increases in size towards the large $S_5N_5^+$ cation). Solvation energies are also probably a contributing factor.

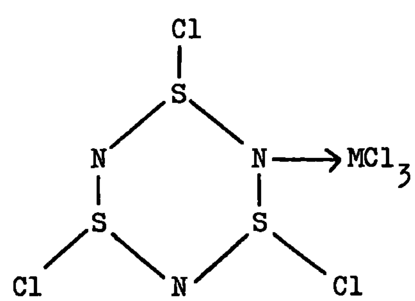
Since the adducts are so moisture sensitive, no structure determination has yet been undertaken, although satisfactory crystals are formed, so that structures for these adducts can only be suggested, and must await confirmation from other physical data.

There seem to be two main possibilities for the structures of the adducts, either:

(i) Nitrogen donation, from one or more nitrogen atoms in the $(NSCl)_3$ ring, to the metal atom of the Lewis acid (Figure 5.1). This occurs in S_4N_4 adducts (e.g. in S_4N_4, $SbCl_5$, where one nitrogen in S_4N_4 is bonded directly to the antimony atom, the S_4N_4 ring being distorted, but remaining intact.

Figure 5.1

i.e.



(1:1 adduct)

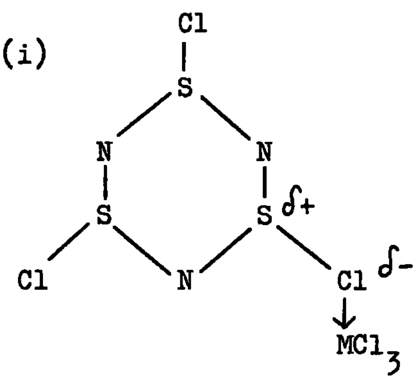
In the $(NSCl)_3$/metal chloride adducts, the ring may alter conformation, but probably remains intact.

(ii) Partial or even complete chloride ion abstraction by the Lewis acid. Ionic compounds such as $NS^+ SbF_6^-$ and $NS^+ AsF_6^-$ have been identified[292,293] where a very strong Lewis acid is used, and halide abstraction by the Lewis acid is complete, ring fragmentation also occurring to produce the NS^+ cation.

The structure of the $(NSCl)_3$/metal chloride adducts may therefore be represented by one of two main structures (Figure 5.2).

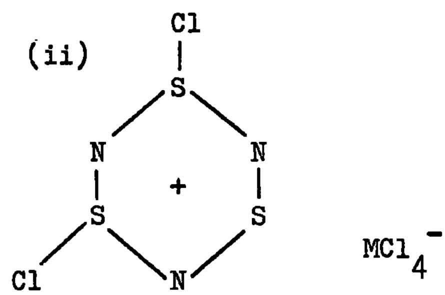
i.e. Figure 5.2

(i)



(M = Al,Fe, 1:1 adducts)

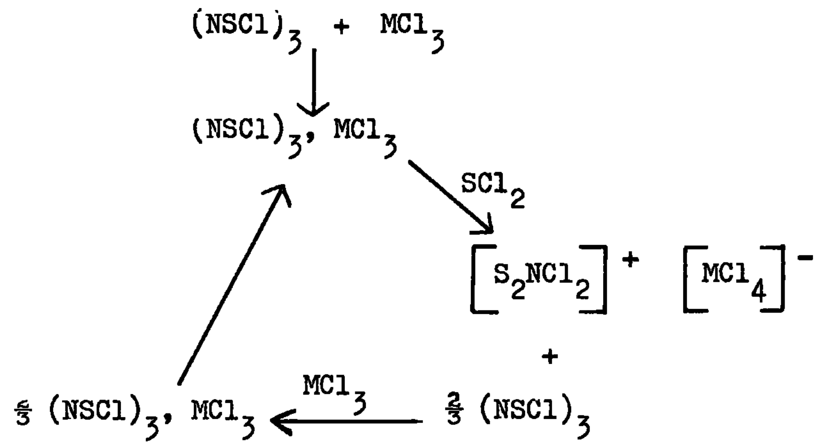
(ii)



The adducts behave in the reactions so far studied, as if they were $NS^+ MCl_4^-$ together with NSCl, although it is unlikely that they actually have this structure, since the 1:1 and 1:2 adducts appear to be distinct compounds, and since $AlCl_3$ and $FeCl_3$ are probably not sufficiently strong Lewis acids for complete chloride ion abstraction to occur.

In all the following reactions of these adducts, it was found that both the 1:1 and the 1:2 adducts, as well as the 1:2 adduct with a molar excess of metal chloride (1:3 ratio), all reacted equally well to give the same product; any excess metal chloride being consumed during the reaction, or excess $(NSCl)_3$ remaining unreacted. This can be explained through a "cyclic" mechanism, by which NSCl is liberated on reaction of the adduct. This may then react with excess metal chloride to form more adduct, which can then react further, and so on until one reagent is completely consumed. (Figure 5.3)

e.g. <u>Figure 5.3</u>



The adducts of $(NSCl)_3$ with $AlCl_3$, $FeCl_3$ and $SbCl_5$ can therefore be conveniently written as $NS^+ \; MCl_4^-$ (M = Al,Fe) or $NS^+ \; SbCl_6^-$, emphasising their role as a source of NS^+.

2. Reactions of $(NSCl)_3$/Lewis Acid Adducts

The $(NSCl)_3$/Lewis acid adducts behave as potential sources of NS^+, as if their structure were $NS^+ \; MCl_4^-$. NS^+ is a good electrophile, and will attack many compounds with lone pairs of electrons to give an intermediate complex (probably of a donor-acceptor form) which then rearranges to give a stable cation.

(i) With SCl_2

SCl_2 contains lone pairs on the sulfur atom; the reaction mechanism may be summarised as:

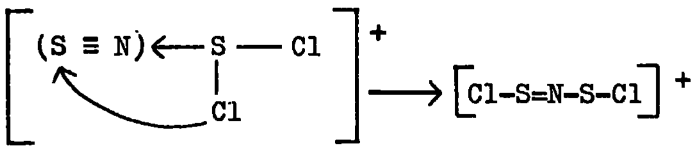
$$\text{(i)} \quad (NSCl)_3 + MCl_3 \xrightarrow{SOCl_2} (NSCl)_3, MCl_3 \text{ adduct}$$

The $(NSCl)_3$, MCl_3 adduct behaves as if it were $NS^+ \; MCl_4^-$, (see previous discussion), therefore:

$$\text{(ii)}\quad NS^{+}\,MCl_4^{-} + SCl_2 \xrightarrow{SOCl_2} \left[(S\equiv N)\leftarrow \underset{\text{complex}}{SCl_2}\right]^{+}\left[MCl_4\right]^{-}$$

The complex then rearranges via chloride ion transfer to give the more stable structure:

(iii)



The chloride ion transfer may be either intra- or inter-molecular (e.g. via a solvent molecule).

(a) <u>The $S_2NCl_2^{+}$ cation</u>

The cation $S_2NCl_2^{+}$ has been reported by Glemser.[289,291,403] It was prepared in two types of reaction:

$$\text{(i)}\quad (NSCl)_3 + 3\,SCl_2 + 3\,BCl_3 \longrightarrow 3\left[N(SCl_2)\right]^{+}\left[BCl_4\right]^{-} \quad ^{403}$$

$$(NSCl)_3 + 3\,SCl_2 + 3\,AlCl_3 \xrightarrow{SCl_2} 3\left[N(SCl)_2\right]^{+}\left[AlCl_4\right]^{-} \quad ^{289}$$

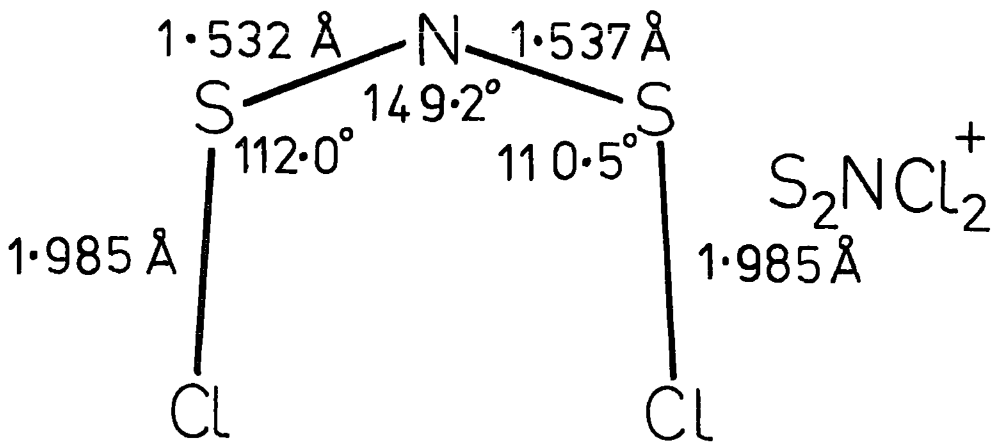
$$\text{(ii)}\quad 2\,NSF_3 + 3\,BCl_3 \xrightarrow{\text{a few days}} \left[NS_2Cl_2\right]^{+}\left[BCl_4\right]^{-} + \tfrac{1}{2}\,N_2 + \tfrac{3}{2}\,Cl_2 + 2\,BF_3 \quad ^{291,403}$$

Conversion of the BCl_4^{-} salt to the $SbCl_6^{-}$ salt:

$$\text{(iii)}\quad N(SCl)_2^{+}\,BCl_4^{-} + SbCl_5 + SbF_3 \xrightarrow[\text{Solvent}]{SbCl_5} \left[N(SCl)_2\right]^{+}\left[SbCl_6\right]^{-} + BF_3 + SbCl_3 \quad ^{289}$$

A crystal structure determination by x-ray structural analysis of $S_2NCl_2^+ BCl_4^-$, showed that the $S_2NCl_2^+$ cation has the structure:[291]

Figure 5.4



The cation is planar, with cis configuration and approximately C_{2v} symmetry:[291]

The compounds described in this chapter prepared by the reaction of $(NSCl)_3/MCl_3$ adducts with SCl_2, analyse closely to $S_2NCl_2^+ MCl_4^-$ (M = Al, Fe) and also to $S_2NCl_2^+ SbCl_6^-$. $S_2NCl_2^+ MCl_4^-$ is also the most reasonable reaction product, since it is formed merely by the addition of "NS^+" to SCl_2; however, the infrared spectral data differ from the spectra of the compounds prepared by Glemser.

i.e.

$S_2NCl_2^+ BCl_4^-$ [291] (Glemser)	$S_2NCl_2^+ AlCl_4^-$ [289] (Glemser)	$S_2NCl_2^+ MCl_4^-$ (M = Al,Fe this thesis)
	1410 (w)	
1380 (s)		
1340 (s)		
1325 (s)		
1265 (m)	1220 (w)	
	1130 (vs)	1130 (m)
		975 (w)
	800 (w)	

$S_2NCl_2^+ BCl_4^-$ [291] (Glemser)	$S_2NCl_2^+ AlCl_4^-$ [289] (Glemser)	$S_2NCl_2^+ MCl_4^-$ (M = Al,Fe this thesis)
		738 (sh)
		722 (m)
705 (w)	695 (s)	704 (sh)
	655 (vs)	654 (s)
		645 (sh)
525 (s)		517 (s)
423 (s)		505 (s)
408 (s)	490 (sh)	494 (s)

The infrared spectra for $S_2NCl_2^+ AlCl_4^-$, $FeCl_4^-$ and $SbCl_6^-$ (this thesis) are the same, apart from the expected small shifts due to changes in anion, and absorptions from the anion itself, thus confirming the presence of the same cation. The infrared spectrum reported by Glemser for $S_2NCl_2^+ AlCl_4^-$ is similar, but not the same, as that recorded for $S_2NCl_2^+ AlCl_4^-$ prepared by ourselves, and is quite different from that of $S_2NCl_2^+ BCl_4^-$, obtained by Glemser. These discrepencies are at first difficult to understand, but the spectrum of $S_2NCl_2^+ AlCl_4^-$ was recorded by Glemser at 80°C between silver chloride plates,[289] whereas our spectrum was recorded using a nujol mull (KBr discs), at room temperature. It is also possible that Glemser's sample of $S_2NCl_2^+ AlCl_4^-$ contained some $(NSCl)_3$, $AlCl_3$ adduct as an unsuspected impurity, rendering it very moisture sensitive, thus requiring the use of an unusual technique to record the spectrum. The presence of this adduct could help to explain the differences in the infrared spectra. The differences between the infrared spectrum of $S_2NCl_2^+ BCl_4^-$, and the other $S_2NCl_2^+$ salts are more difficult to explain. We did not obtain an infrared spectrum of this compound, due to its instability although it was probably formed in solution on reacting SCl_2 with the $(NSCl)_3$, n BCl_3 adduct in thionyl chloride. Glemser also states that this compound is very hygroscopic, and rapidly decomposes, yielding BCl_3,[291] so that the infrared spectrum recorded by him may be that of decomposition products rather than the pure compound. A repeat of this preparation at lower temperatures may be more successful.

Glemser also used different preparative routes from those reported in this thesis, and postulates different reaction mechanisms. For example, for the reaction: $(NSCl)_3 + 3\ SCl_2 + 3\ BCl_3 \longrightarrow 3\ [NS_2Cl_2]^+ [BCl_4]^-$ [403] : he postulates the following mechanism:

$$\text{(i)}\quad SCl_2 + BCl_3 \longrightarrow [SCl]^+ [BCl_4]^-$$

$$\text{(ii)}\quad (NSCl)_3 \rightleftharpoons 3\ NSCl$$

$$\text{(iii)}\quad NSCl + [SCl]^+ [BCl_4]^- \longrightarrow S_2NCl_2^+\ BCl_4^-$$

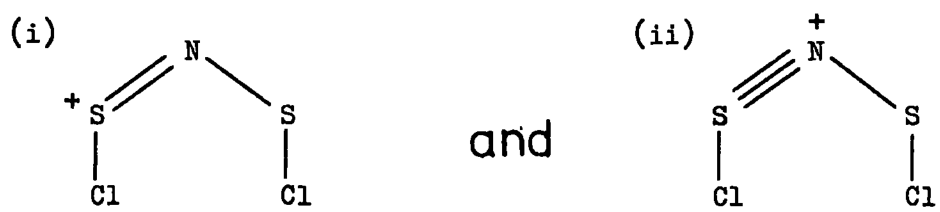
The mechanism, according to Glemser, involves the electrophillic attack of the SCl^+ cation on NSCl, whereas our results indicate that the reaction should proceed via the $(NSCl)_3$, n BCl_3 adduct (at least in thionyl chloride solution), which acts as a source of NS^+ in the electrophillic attack of NS^+ on SCl_2 to yield $S_2NCl_2^+$ and similarly for the $AlCl_3$, $FeCl_3$ and $SbCl_5$ salts (this thesis).

Glemser uses the same mechanism to explain part of the rather more involved mechanism, for the formation of $[NS_2Cl_2]^+ [BCl_4]^-$ from BCl_3 and NSF_3.[403]

The reaction of $(NSCl)_3$ with SCl_2 and $AlCl_3$ in SCl_2 to yield $[NS_2Cl_2]^+ [AlCl_4]^-$ reported by Glemser, most probably also goes via the $(NSCl)_3/AlCl_3$ adduct as an undetected intermediate. The compound $[S_2NCl_2]^+ [FeCl_4]^-$ has not been previously reported.

The observed S-N bond distance (1.53 Å) in $S_2NCl_2^+$ BCl_4^- corresponds to a "Glemser" bond order of 1.7 to 1.8,[403] and is obviously of a bond order greater than one. Glemser suggests[403] that the structure of $S_2NCl_2^+$ can be rationalised as consisting of two canonical forms (Figure 5.5).

i.e. Figure 5.5



From comparison with other cyclic sulfur-nitrogen species: $S_4N_3^+$ and $S_5N_5^+$, where bond orders greater than one are observed, their structures are more easily rationalised in terms of delocalised $p\pi$ and $d\pi$ bonding, rather than by resonance canonicals (which cannot be adequately represented in these cases without trans-annular bonding). The rings are planar, and therefore similar delocalised π bonding probably occurs in $S_2NCl_2^+$, which is also planar.[291] The sulfur atoms in $S_2NCl_2^+$ probably carry most of the positive charge, by analogy with $S_4N_3^+$ and $S_5N_5^+$.[105]

S_2NCl_2 $AlCl_4$ and S_2NCl_2 $FeCl_4$ are sparingly soluble in concentrated sulfuric acid and decompose slowly, as indicated by their UV spectrum in that solvent. It is probable that the absorptions are due to the $S_2NCl_2^+$ cation, rather than the anion, since the UV spectra of both salts are the same, and also by analogy with the corresponding $S_5N_5^+$ salts (see Chapter 6), the $AlCl_4^-$ and $FeCl_4^-$ anions decompose in concentrated sulfuric acid to yield HCl and to leave the cation in solution.

The presence of absorptions in the near UV, shows the existence of low lying vacant orbitals, which is consistent with the presence of the postulated delocalised $p\pi$ - $d\pi$ bonding in the cation.

(ii) With CCl_3SCl

Trichloromethyl sulfenyl chloride (CCl_3SCl) can be regarded as a derivative of SCl_2 previously studied, where CCl_3 replaces Cl. The CCl_3 derivative was chosen as it is stable to chlorinating agents (e.g. thionyl chloride), and it was hoped that new compounds of the type: $[CCl_3SNSCl]^+$ $[MCl_4]^-$ would be formed analogous to the SCl_2 derivatives.

In each of the three cases studied the reaction occurred immediately on adding the CCl_3SCl to the $(NSCl)_3$ adducts of $AlCl_3$, $FeCl_3$ and $SbCl_5$. Reaction products consisted of $S_3N_2Cl^+$ and $S_2NCl_2^+$ which were identified by their infrared spectra and by elemental analysis and insoluble powders which could not be identified. (See discussion).

i.e.	Starting Materials	Identifiable Products
	$(NSCl)_3 + 3\ FeCl_3$	$S_3N_2Cl^+\ FeCl_4^-$ (mainly)
	$(NSCl)_3 + 3\ AlCl_3$	$S_3N_2Cl^+\ AlCl_4^-$ (mainly) and
		$S_2NCl_2^+\ AlCl_4^-$
	$(NSCl)_3 + 3\ SbCl_5$	$S_3N_2Cl^+\ SbCl_6^-$ and
		$S_2NCl_2^+\ SbCl_6^-$ (mainly)

In the first two cases, $S_3N_2Cl^+$ salts were the main product, and in the last case $S_2NCl_2^+\ SbCl_6^-$ was the main product, as indicated in the infrared spectra. The analyses were also consistent with the above being the main products.

The reasons for these products being formed, rather than the expected CCl_3SNSCl^+ derivatives, are not as yet completely clear. In every case, there was an immediate reaction on addition of the CCl_3SCl to the thionyl chloride solution of the adduct, the solution became the characteristic red/green-blue dichroic, indicating that some sort of reaction with the CCl_3SCl was taking place, and that some sort of "$CCl_3SCl.SN^+$" complex was formed. However, this must obviously rearrange to give the observed products, possibly via reaction with thionyl chloride solvent or with excess $(NSCl)_3$. In each reaction the yields were fairly low (about 15%), particularly when compared with the yields obtained in the direct preparations of $S_2NCl_2^+$ salts, and fairly large quantities of unidentified impurities are also present, indicating several side reactions.

The following very tentative reaction mechanisms may help to explain the identifiable products formed.

(a) (i) $(NSCl)_3 + MCl_3 \xrightarrow{SOCl_2} (NSCl)_3, MCl_3$ adduct

(ii) $(NSCl)_3, MCl_3 + CCl_3SCl \xrightarrow{SOCl_2}$

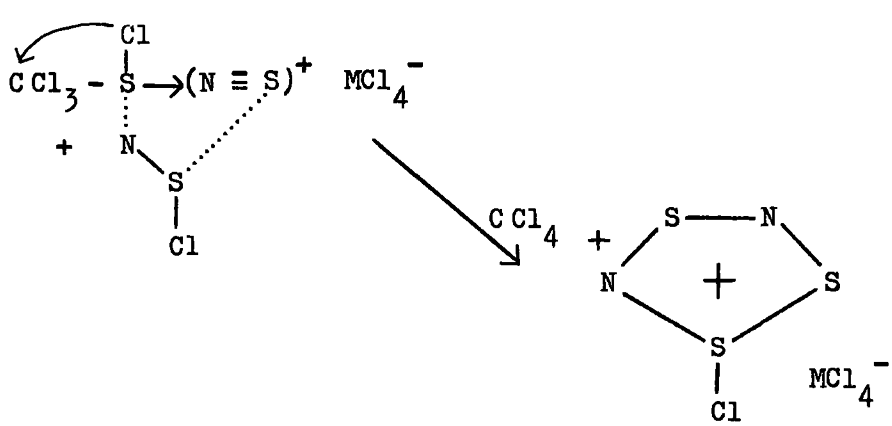
$CCl_3 - S(Cl) \rightarrow (N \equiv S)^+ \; MCl_4^-$ complex

This intermediate complex may then stabilise itself in two ways: by chlorination by the thionyl chloride solvent to yield the $S_2NCl_2^+$ ion and CCl_4, or by chloride ion transfer (either intra or inter-molecular) and reaction with excess NSCl, to yield the $S_3N_2Cl^+$ ion.

i.e. (iii) $CCl_3 - S(Cl) \rightarrow (N \equiv S)^+ \quad MCl_4^- \xrightarrow[SOCl_2]{\text{Chlorination}}$

$CCl_4 + S(Cl) - N - S - Cl^+ \quad MCl_4^-$

and



(b) Alternatively, the reaction may go via a CCl_3S^+ ion, by reaction of the Lewis acid with CCl_3SCl. The CCl_3S^+ ion would be analogous to the S_2Cl^+ ion formed from S_2Cl_2 and Lewis acids,[406] and the SCl^+ ion postulated by Glemser as a reaction intermediate;[403] other RS^+ ions are also known:

$$\text{e.g.} \qquad PhSBr + AgClO_4 \longrightarrow \left[PhS^+ \ ClO_4^-\right] \text{ intermediate}^{407} + AgBr$$

If mechanism (a) is correct, CCl_4 should also be present in solution, although this has not been verified, and several other mechanisms are possible since side reactions also occur.

(iii) With elemental sulfur (attempted preparation of the $S_3N_2^{2+}$ cation)

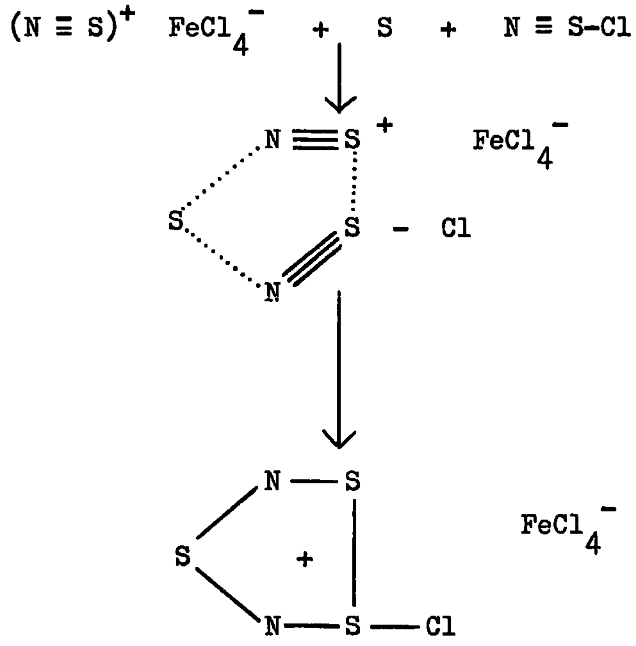
The reaction of elemental sulfur with $(NSCl)_3$ and $FeCl_3$, in the molar ratio: $(NSCl)_3$:$FeCl_3$:S = 1:3:9, produced only a mixture of $S_3N_2Cl^+ \ FeCl_4^-$ and $S_2NCl_2^+ \ FeCl_4^-$ as identifiable products, together with some $FeCl_3$ and excess sulfur. Since an immediate reaction occurred on adding the sulfur to the refluxing solution, the sulfur must take some part in the reaction.

The formation of the products can be explained in the following way:

$$\text{(i)} \quad (NSCl)_3 + 2\ FeCl_3 \xrightarrow{SOCl_2} (NSCl)_3,\ 2\ FeCl_3$$

Formation of the adduct, which can then react as a source of NS^+. It is often useful in describing ring formation, to split the ring into its component parts, and in this case the $S_3N_2Cl^+$ ring can be formed from SN^+, NSCl and S, as component fragments:

i.e. (ii)



The formation of $S_2NCl_2^+$ can also be rationalised:

(iii) $$(N \equiv S)^+ \; FeCl_4^- \; + \; S \longrightarrow S = \overset{+}{N} = S \quad FeCl_4^-$$

$$\downarrow \; SOCl_2 \text{ chlorination}$$

$$Cl - S - N - S - \overset{+}{Cl} \quad FeCl_4^-$$

(iv) With elemental selenium

From the above reaction with sulfur, it was hoped that, by using selenium instead of sulfur, selenium could be inserted into a sulfur-nitrogen ring or chain, to give the selenium analogues of $S_3N_2Cl^+$ or $S_2NCl_2^+$. The selenium analogues of $S_4N_3^+$, i.e. $S_3SeN_3^+$ has been shown to be a possible product from the reaction between S_4N_4 and Se_2Cl_2,[130] and so cations such as $S_2SeN_2Cl^+$ and $SSeNCl_2^+$ should exist. However, when selenium was added to the $(NSCl)_3/FeCl_3$ adduct, although an immediate reaction occurred, the only product to be identified was $S_3N_2Cl^+ \; FeCl_4^-$, and not the selenium analogue. Therefore, although an initial complex may be formed, which contains selenium, this proceeds to eliminate selenium, and to give the more stable sulfur analogue, possibly through some sort of sulfur-selenium exchange with the thionyl chloride solvent, or with $(NSCl)_3$. Due to the complexity of the reaction, and to the impurities present in the reaction products, it was not possible to determine the final fate of the selenium.

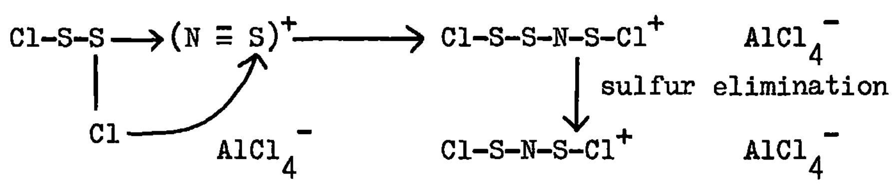
(v) <u>With disulfur dichloride</u>

From the reactions of the $(NSCl)_3$/metal chloride adducts with SCl_2, which gave $S_2NCl_2^+$ salts in good yield, it was hoped that the reactions with S_2Cl_2 would give $S_3NCl_2^+$ salts of probable structure: Cl-S-S-N-S-Cl$^+$. An immediate reaction took place on mixing the reagents showing that some sort of S_2Cl_2 $(NS)^+$ $AlCl_4^-$ complex was initially formed. However, the final product was a mixture of $S_2NCl_2^+$ and $S_3N_2Cl^+$ salts. The reaction is similar to that using CCl_3SCl, and it is probable that the initial complex underwent further reactions to yield the observed products, so a tentative reaction mechanism is proposed to account for the observed products:

(i) $(SN)^+ AlCl_4^-$ (adduct) $+ S_2Cl_2 \xrightarrow{SOCl_2}$ Cl-S-S(Cl)$\rightarrow(N\equiv S)^+$ $AlCl_4^-$ (complex)

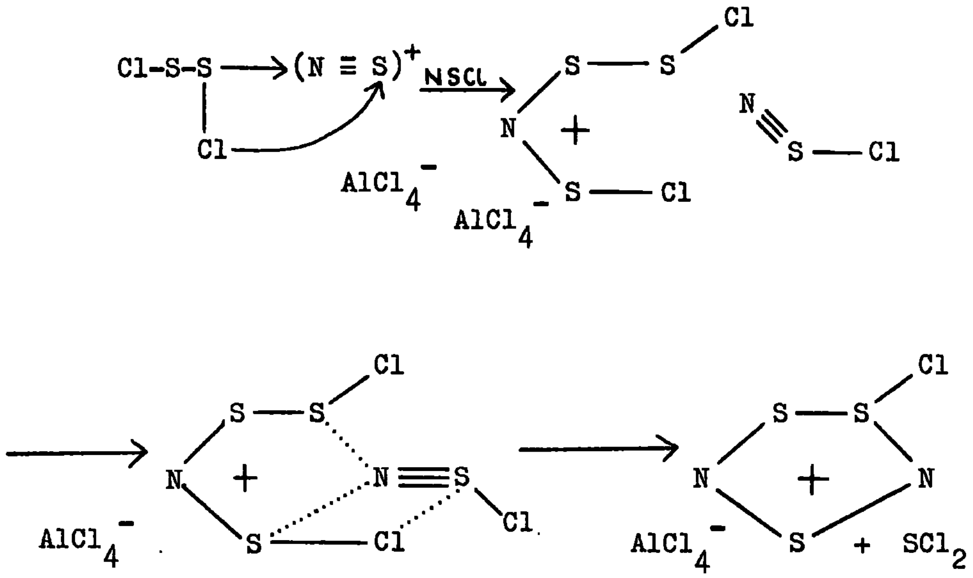
(ii) (a) The intermediate complex may rearrange through chloride ion transfer and sulfur elimination to yield $S_2NCl_2^+$ $AlCl_4^-$:

i.e.



(b) The intermediate complex may also cyclise with excess NSCl to form $S_3N_2Cl^+$ $AlCl_4^-$, with the elimination of SCl_2.

i.e.



From the infrared spectrum, S_2NCl_2 $AlCl_4$ appears to be the main product, although S_3NCl_2 $AlCl_4$, the desired product, is not entirely ruled out, since the product was more air and moisture sensitive than either pure S_2NCl_2 $AlCl_4$ or S_3N_2Cl $AlCl_4$.

(vi) With diselenium dichloride Se_2Cl_2

The selenium analogue of disulfur dichloride (Se_2Cl_2) was also reacted with the $(NSCl)_3$/metal chloride adducts. Once again an immediate reaction occurred, and a product was formed (orange powder), which apparently contained selenium (flame test), and whose infrared spectrum was different from those of any other sulfur-nitrogen compound. Attempts to purify it were unsuccessful, since it is only sparingly soluble in thionyl chloride, and appears to decompose on heating. The analyses were inconclusive, but showed the presence of sulfur, nitrogen and chlorine, (selenium was not analysed for). The product is therefore probably a mixture and by analogy to the reactions with S_2Cl_2, is probably a mixture of the selenium analogues of $S_2NCl_2^+$ and $S_3N_2Cl^+$, although the number of selenium atoms replacing sulfur was not determined. All these selenium compounds are, at present, unknown. (See Appendix for infrared spectrum).

THE PREPARATION, STRUCTURE AND REACTIONS OF $S_5N_5^+$ SALTS

CHAPTER 6

The Preparation, Structure and Reactions of $S_5N_5^+$ Salts

(A) Introduction

The preparation, structure and reactions of the cyclopentathiazenium ($S_5N_5^+$) salts, occupied a large part of the research work, and although they are prepared from $(NSCl)_3$/metal chloride adducts, (see previous Chapter for the other reactions of these adducts), the $S_5N_5^+$ salts are best dealt with in a separate chapter in some detail, with cross references to other chapters.

Through a series of separate preparations of $S_5N_5^+$ salts, the following optimum procedures were established.

(B) Preparation of $S_5N_5^+$ Salts

1. Preparation of $S_5N_5^+ MCl_4^-$ (where M = Al or Fe)

Trithiazyl trichloride $(NSCl)_3$, ferric or aluminium chlorides and S_4N_4 were weighed out in the stoichiometric ratio 1:3:3. The preparation may be scaled as necessary, so that the weights used for a typical preparation are given.[288,408]

$(NSCl)_3$ (5.96g) was dissolved in ca. 100 ml. of thionyl chloride in a round-bottomed flask with stirring, and powdered $AlCl_3$ (6.6g) or $FeCl_3$ (8.08g) then added to the solution, which was stirred for about 1 hour to form the 1:2 adduct. Tetrasulfur tetranitride (S_4N_4) (9.2g) was then added over a period of a few minutes to the vigorously stirred mixture. It was important that the mixture was stirred vigorously, otherwise the yields were considerably reduced. The solution immediately became a very dark red-green/blue dichroic colour, and the stirring was continued for about 2 hours, during which time the $S_5N_5^+$ salt gradually precipitated out: $S_5N_5^+ AlCl_4^-$, orange/yellow; $S_5N_5^+ FeCl_4^-$, rust-brown. The solution was reduced to about half bulk by distillation under reduced pressure, then cooled to -10°C and filtered cold. The precipitate was pumped dry from thionyl chloride in vacuo to yield the crude product, which was rather darker in colour than the final recrystallised product. An infrared spectrum indicated that the main impurity was $S_4N_3\ MCl_4$. Recrystallisation was from thionyl chloride with final cooling to -10°C; the product was filtered and pumped dry in vacuo as before.

Yields: $AlCl_4^-$ salt: 70% crude product; 50% recrystallised.
$FeCl_4^-$ salt: 95% crude product; 90% recrystallised.

Products: (i) $S_5N_5\ AlCl_4$: Orange-yellow needles, similar in appearance to S_4N_4. Melting point (after several recrystallisations) = 181°C (with decomp.).

Infrared spectrum (nujol mull):[184]

1144 (s), 1048 (w), 1023 (w,sh), 976 (vw,sh), 733 (m), 722 (m,sh), 687 (w), 613 (w), 529 (s), 497 (vs,sh), 483 (vs), 327 (m) cm^{-1}.

(Absorptions at ca. 490 (s,vb) cm^{-1} due to $AlCl_4^-$ ion[404]). (See Appendix).

Ultraviolet spectrum: (Solvent conc. sulfuric acid (18.3 M)): (225-700 nm). λ max. 327 nm. ($\varepsilon = 3.5 \times 10^4$); 426 nm ($\varepsilon = 2.5 \times 10^3$). (See Appendix for UV spectrum).

HCl was evolved on dissolution, but this was due to the decomposition of the anion only.

Concentrated nitric and anhydrous formic acid were also used as solvents for the determination of the UV spectrum. Decomposition was more rapid than in concentrated sulfuric acid, but the spectra of the fresh solutions were the same as for S_5N_5 $AlCl_4$ in concentrated sulfuric acid.

Analysis:

Found %		$S_5N_5^+$ $AlCl_4^-$ requires %	
S =	39.7	S =	40.2
N =	17.5	N =	17.5
Cl =	35.3	Cl =	35.5
Al =	6.7	Al =	6.8
Total =	99.2%	Total =	100.0%

A study was undertaken on the optical properties of the $S_5N_5^+$ $AlCl_4^-$ crystal[409]: $S_5N_5^+$ $AlCl_4^-$ is biaxial and of negative sign, the maximum and minimum refractive indices are: $\gamma = 1.810$, $\alpha = 1.750$. The refractive index along the third direction was estimated as $\beta = 1.807$. The crystal is therefore almost uniaxial ($\beta \approx \gamma$) having a birefringence of 0.060. It is also slightly photosensitive, darkening on prolonged exposure to sunlight (several months).

The darkening was only a surface effect, and a control sample stored in darkness for several months did not show this effect, thus confirming that it was light rather than moisture that was responsible.

(ii) $S_5N_5^+ FeCl_4^-$: Dark orange needle-like crystals. Melting point (after several recrystallisations): 181°C (with decomposition).

Infrared spectrum (nujol mull):[184]

1143 (s), 1047 (w), 1017 (vw,sh), 731 (m), 721 (m,sh), 685 (m), 608 (m), 528 (s), 370 (s), 327 (s) cm^{-1}.

The spectrum is essentially the same as for S_5N_5 $AlCl_4$, slight shifts in absorptions can be attributed to the change in anion size. The ultraviolet spectrum of a 3×10^{-5} M soln. in concentrated sulfuric acid (18.3 M) was found to be the same as for S_5N_5 $AlCl_4$.

Analysis:[288]

Found %			S_5N_5 $FeCl_4$ requires %		
S	=	37.3	S	=	37.5
N	=	16.3	N	=	16.4
Cl	=	32.5	Cl	=	33.1
Fe	=	13.6	Fe	=	13.0
Total	=	99.7%	Total	=	100.0%

Both S_5N_5 $AlCl_4$ and S_5N_5 $FeCl_4$ are air and moisture sensitive, S_5N_5 $AlCl_4$ being rather more sensitive than S_5N_5 $FeCl_4$.

2. Preparation of $S_5N_5^+$ $SbCl_6^-$

The preparation of this salt is similar to that of the $AlCl_4^-$ and $FeCl_4^-$ salts (Section 1), but slightly different techniques are used, due to the increased reactivity of $SbCl_5$, and to the sparing solubility of the products. The reagents: $(NSCl)_3$, $SbCl_5$ and S_4N_4 are again used in the molar ratio 1:3:3.

In a typical preparation: $(NSCl)_3$, (0.8730g) was dissolved in <u>ca</u>. 20 ml. of thionyl chloride and freshly distilled $SbCl_5$ (3.2g, 1.37 ml) was slowly added to the vigorously stirred solution, using a graduated syringe. Slow addition with cooling was used since the reaction was fairly exothermic. The $(NSCl)_3$, 3 $SbCl_5$ adduct (yellow) precipitated out almost immediately,[289] but to ensure completion of the reaction, the solution was stirred for about ½ hour. S_4N_4 (1.97g) was then added slowly to the vigorously stirred mixture. The yellow adduct dissolved immediately, and a very dark red-green/blue dichroic solution was formed, which was stirred at room temperature for about 24 hours, during which time a dark yellow precipitate gradually formed, (impure S_5N_5 $SbCl_6$). The solution was filtered and the precipitate washed with fresh cold thionyl chloride solution, yielding a yellow-orange powder. S_5N_5 $SbCl_6$ was only sparingly soluble in thionyl chloride, therefore purification was by solvent extraction using thionyl chloride, to yield S_5N_5 $SbCl_6$ (yellow powder), mp. 188°C (decomp.) Yield = 80%.

IR spectrum (nujol mull):

1258 (w), 1163 (s), 1111 (s), 1026 (sh), 975 (sh), 806 (m), 720 (m), 673 (w), 621 (w,b), 532 (vs) cm^{-1}

(The spectrum is essentially the same as for S_5N_5 $AlCl_4$ and S_5N_5 $FeCl_4$, the slight shifts in absorption can be attributed to the change in anion).

Analysis:[288]

Found %		S_5N_5 $SbCl_6$ requires %	
S	= 28.3	S	= 28.4
N	= 12.3	N	= 12.4
Cl	= 37.6	Cl	= 37.6
Sb	= 21.8 (by difference)	Sb	= 21.6

S_5N_5 $SbCl_6$ is practically air and water stable. Contact with water for ca. 24 hours, caused only slight decomposition, as revealed by an IR spectrum.

3. Preparation of Other $S_5N_5^+$ Salts

(Reinekate, tetraphenyl borate, nitrate and hexachloroantimonate)

(i) Reinekate

S_5N_5 $FeCl_4$ (0.6609g) was suspended in ca. 10 ml. of anhydrous formic acid (S_5N_5 $FeCl_4$ in slightly soluble) and Reineke salt (NH_4^+ $[Cr(NH_3)_2(SCN)_4]^-$), (0.5195g), was added to the stirred mixture. The dark orange colour of the S_5N_5 $FeCl_4$ gradually turned red and the solution was stirred for ca. 24 hours to complete the reaction. The precipitate was then filtered and pumped dry in vacuo. Product: orange powder.

IR spectrum (nujol mull):

2083 (vs), 1724 (w), 1613 (w), 1263 (s), 1163 (m), 1117 (m), 1047 (vw) 1020 (vw), 830 (vw), 719 (sh), 701 (s), 617 (w,b), 532 (m,b) cm^{-1}.

(Spectrum shows the characteristic absorptions of the $S_5N_5^+$ cation and of the Reinekate anion).

Analysis:

Found %			$S_5N_5^+$ $[Cr(NH_3)_2(SCN)_4]^-$ requires %		
N	=	26.86	N	=	28.08
C	=	8.46	C	=	8.76
H	=	1.20	H	=	1.10

$S_5N_5^+$ Reinekate$^-$ is practically air and water stable. The UV spectrum (in CH_2Cl_2 solvent) is also consistent with the presence of the $S_5N_5^+$ ion.

(ii) Tetraphenyl borate

S_5N_5 $FeCl_4$ (0.3257g) was added to ca. 20 ml. of anhydrous formic acid, and the mixture stirred. Dry sodium tetraphenyl borate (NaB $(C_6H_5)_4$) (0.2604g) was then added, and the mixture stirred until no further precipitate was formed, (about two hours). The precipitate (orange powder) was filtered off and pumped dry in vacuo. There was no sign of the other reaction products (e.g. $FeCl_3$) and these may well have dissolved in the formic acid. The final product was a dark yellow powder. The analysis was inconclusive, but a flame test (green) showed the presence of boron. On heating, the colour changed to dark orange at ca. 80°C, and the compound decomposed at ca. 134°C. The infrared spectrum (nujol mull) and electronic spectra (in CH_2Cl_2 solvent) were consistent with the presence of the $S_5N_5^+$ cation.

(iii) Nitrate

S_5N_5 $FeCl_4$ (1.0g) was dissolved in ca. 5 ml. of concentrated nitric acid. A gas (presumably HCl) was evolved, and a white precipitate appeared. This was filtered off and pumped dry in vacuo, but it was found to be very moisture sensitive, as decomposition rapidly occurred on exposure to air or moisture, to yield a red compound. An infrared spectrum, however, indicated the presence of the $S_5N_5^+$ cation, and the product was therefore probably the nitrate, by comparison with $S_4N_3^+$ NO_3^- which is prepared from S_4N_3Cl in an analogous way.[260,261,262,270]

(iv) Hexachloroantimonate from tetrachloroaluminate

S_5N_5 $AlCl_4$ (1.0g) was dissolved in ca. 50 ml. of thionyl chloride at 50°C, and ca. 0.5 ml. of $SbCl_5$ (excess), added to the stirred solution, via a syringe. An orange solid immediately precipitated out, and the solution was stirred and allowed to cool to 20°C, to complete the reaction. The precipitate was filtered, washed with cold thionyl chloride, and dried in vacuo. An infrared spectrum (cf. Page 173) identified the product as S_5N_5 $SbCl_6$.

4. Reaction of the S_4N_4, $SbCl_5$ Adduct with $(NSCl)_3$

Tetrasulfur tetranitride (1.7136g) was added to ca. 10 ml. of CCl_4, and $SbCl_5$ (1.2 ml) was added to the stirred mixture. An immediate reaction occurred, with the production of the adduct S_4N_4, $SbCl_5$.[137,138,139,146,151] $(NSCl)_3$, (0.7581g) was then added, and the mixture stirred for ca. 6 hours at 50°C. No reaction appeared to take place, and an infrared spectrum showed only S_4N_4, $SbCl_5$ and $(NSCl)_3$, without any trace of $S_5N_5^+$ salts. Similar observations were made when thionyl chloride was used as the solvent.

5. Attempted Direct Preparation of $S_5N_5^+$ Salts from S_4N_4

S_4N_4 reacts with sulfuryl chloride (SO_2Cl_2) to form $(NSCl)_3$ and SO_2;[279] and, in the presence of a Lewis acid, this reacts to form an adduct, which would then react with more S_4N_4, to give $S_5N_5^+$ salts; giving an overall reaction:

$$5\ S_4N_4 + 2\ SO_2Cl_2 + 4\ AlCl_3 \longrightarrow 4\ S_5N_5^+\ AlCl_4^- + 2\ SO_2$$

S_4N_4 and $AlCl_3$ were used in the correct molar ratios, firstly in thionyl chloride, with the correct molar quantity of SO_2Cl_2, and then repeated using SO_2Cl_2 as solvent.

In both cases, a large amount of impurity was formed, and the only recognisable product, from the infrared spectrum, was $S_4N_3^+$ probably as the $AlCl_4^-$ salt, no $S_5N_5^+$ salts being detected.

(C) Discussion of the Reaction Mechanism, Properties and Structure of $S_5N_5^+$ Salts

1. Reaction Mechanism

$S_5N_5^+$ salts were first prepared, together with $S_3N_2Cl^+$ and $S_4N_3^+$ salts, from the reaction of S_4N_4 with thionyl chloride, in the presence of metal chlorides.[146,184,410] The proposed[148] mechanism for this preparation can be summarised:

$$S_4N_4 \xrightarrow{SOCl_2} NSCl \xrightarrow{MCl_3} \left[NS^+\ MCl_4^-\right] \xrightarrow{S_4N_4} S_5N_5\ MCl_4$$

The preparations of the $S_5N_5^+$ salts described in this Chapter were devised so as to check this proposal of mechanism and also to simplify the preparation. The various $(NSCl)_3$/metal chloride adducts were prepared in $SOCl_2$ and, in the ratio 1:3 shown to behave as a potential source of NS^+.

The reaction mechanism may be summarised:

(i) $(NSCl)_3 + 2\ MCl_3 \xrightarrow{SOCl_2} (NSCl)_3,\ 2\ MCl_3$ adduct.

The $(NSCl)_3$, 2 MCl_3 reacts as if it were: "$NS^+\ MCl_4^-$", therefore:

(ii) "$NS^+\ MCl_4^-$" + $S_4N_4 \xrightarrow{SOCl_2} S_4N_4,\ (NS)^+\ MCl_4^-$ complex

(iii) "$S_4N_4,\ (NS)^+\ MCl_4^-$" $\xrightarrow[\text{slow}]{\text{rearrangement}} S_5N_5^+\ MCl_4^-$

In the preparation, the $(NSCl)_3$ and metal chloride are mixed in the molar ratio 1:3, and therefore there is free metal chloride present on addition of the S_4N_4, however, as noted in the reaction of the adducts with SCl_2 (Chapter 3, Page 156), it is rapidly consumed during the reaction, via the production of free NSCl from the formation of the complex.

S_4N_4 decomposes slowly in thionyl chloride with the probable formation of various fragments such as NSCl. Other fragments account for the other cations formed, (e.g. $S_3N_2Cl^+$, $S_4N_3^+$), and without the presence of a metal chloride, S_4N_4 in thionyl chloride is eventually converted to S_4N_3Cl.[130,148,183] The preparation involving the $(NSCl)_3$/metal chloride intermediate adducts (this thesis) is a better preparative route since the yields are higher, the reaction is very much quicker and easier to carry out, side reactions are small, and it does not involve the tedious separation of $S_5N_5^+$ salts from the other crystalline salts also prepared.

The reaction of the S_4N_4 with the adduct is so rapid, and the decomposition of S_4N_4 in thionyl chloride to yield S_4N_3Cl so much slower, that $S_4N_3^+$ salts are only produced in small amounts.

The fact that $(NSCl)_3$ does not react with the adduct S_4N_4, $SbCl_5$ to form $S_5N_5^+\ SbCl_6^-$ (Page 173), i.e. that the reaction: $S_4N_4, SbCl_5 + \frac{1}{3}(NSCl)_3 \xrightarrow{SOCl_2} S_5N_5^+\ SbCl_6^-$ does not occur, is also consistent with the proposed mechanism. The $(NSCl)_3$/metal chloride adduct is probably a necessary intermediate.

It seems likely that many other $S_5N_5^+$ salts should be preparable by the reaction of S_4N_4 with other $(NSCl)_3$,metal chloride adducts, e.g. $S_5N_5^+\ GaCl_4^-$ is known,[184] and could probably be prepared from S_4N_4 and the $(NSCl)_3$, $GaCl_3$ adduct; similarly S_4N_4 should react with the $(NSCl)_3$, BCl_3 adduct to form $S_5N_5^+\ BCl_4^-$, so that the salts produced are only representative of the large number of salts that are preparable by this route.

Other $S_5N_5^+$ salts can be prepared from $S_5N_5^+\ FeCl_4^-$ or $AlCl_4^-$, by methasis in anhydrous formic acid. This was concluded after preparing the Reinekate and tetraphenyl borate in anhydrous formic acid. The hexachloroantimonate was prepared from $S_5N_5\ AlCl_4$ in thionyl chloride, and this was an example of a stronger Lewis acid ($SbCl_5$) displacing a weaker Lewis acid from a salt. The sparing solubility of the $SbCl_6^-$ salt probably also helped the reaction to proceed. Initial results also indicate that other liquid metal chlorides (e.g. $TiCl_4$) also react with S_5N_5 $AlCl_4$ in thionyl chloride in a similar way. These reactions too have much wider applications, and many other salts should be preparable by this means.

The Reinekate and tetraphenyl borate derivatives were chosen as representative examples because:

(i) Both anions are air and water stable, and it would be useful to determine the air and water sensitivity of the $S_5N_5^+$ ion. ($S_5N_5^+$ $AlCl_4^-$ and $S_5N_5^+$ $FeCl_4^-$ are both moisture sensitive due to the presence of a sensitive anion).

(ii) Both anions are large and therefore are suitable for stabilising a large cation such as $S_5N_5^+$. The Reinekate anion has been used to stabilise many other large cations.[140]

(iii) Both anions are easy to prepare and to obtain pure.

The preparation of S_5N_5 $SbCl_6$ from S_5N_5 $AlCl_4$ is presumably by the reaction:

$$S_5N_5\ AlCl_4 + SbCl_5 \xrightarrow{SOCl_2} S_5N_5\ SbCl_5 + AlCl_3$$

This illustrates the use of thionyl chloride as an alternative solvent for these reactions.

The air and water stability of the $S_5N_5^+$ Reinekate and tetraphenyl borate (and also the hexachloroantimonate), demonstrates the remarkable stability of the $S_5N_5^+$ cation, which may well be due to its delocalised electronic structure. (See later discussions).

A third route to $S_5N_5^+$ salts is through reaction of $S_5N_5^+ AlCl_4^-$ or $FeCl_4^-$ with the appropriate concentrated liquid acid. $S_5N_5^+ AlCl_4^-$ reacts with concentrated sulfuric acid to evolve HCl, (decomposition of the anion only), and leaves $S_5N_5^+$ in solution, as shown by the UV spectrum, presumably HSO_4^- ions are also present. Similarly, with nitric acid, and, in this case, a possible nitrate derivative: $S_5N_5^+ NO_3^-$ has been prepared, although it was too unstable for any accurate IR or UV measurements to be carried out on it. The nitrate,[140,270] perchlorate[266] and hydrogen sulfate,[256,266] and many other salts of $S_4N_3^+$ have been prepared by reaction of S_4N_3Cl with the appropriate concentrated acid, and the same could apply to $S_5N_5^+$ salts. (See Introduction, Section on $S_4N_3^+$, Page 51).

The direct preparation of $S_5N_5^+ AlCl_4^-$, by the reaction of S_4N_4, $AlCl_3$ and sulfuryl chloride, was unsuccessful, probably due to the slowness of the first step, the formation of $(NSCl)_3$ from S_4N_4 and SO_2Cl_2,[279] which allows other side reactions to take place, including the formation of $S_4N_3^+$ salts.

2. Ultraviolet Spectrum of $S_5N_5^+$

The ultraviolet and visible spectra have only previously been reported for an acetonitrile solution.[184] Measurement of the spectra was difficult since:

(i) $S_5N_5^+$ salts are only slightly soluble.

(ii) Decomposition occurs in the solvent.

(iii) Parts of the ultraviolet range are obscured by the solvent.

Because of these factors, only estimated extinction coefficients and approximate positions of absorption could be determined.[184]

Concentrated (18.3 M) sulfuric acid was found to be a much better solvent for the ultraviolet spectrum since:

(i) The $S_5N_5^+$ salt is readily soluble.

(ii) Decomposition occurs only over a period of days (possibly due to traces of moisture), which does not effect the spectrum determinations. HCl is evolved on dissolution, but this is due to the decomposition of the anion only ($AlCl_4^-$).

(iii) Conc. H_2SO_4 is essentially transparent in range used. (190 to 700 nm).

Several determinations were carried out in concentrated sulfuric acid, all in good agreement with each other, and the following results obtained:[184,411] (See Appendix).

Wavelength λ max. nm	Mean ε molar
327	3.48×10^4
426	2.47×10^3

In addition, a peak was also observed at around 225 nm, although it varied in position and intensity. It was practically absent in fresh solutions, but gradually appeared as the solutions slowly decomposed with time (see Appendix). It was therefore concluded that the peak was probably largely due to decomposition products, although a new, unidentified compound is also a possibility. No other peaks were observed, even in very concentrated solutions.

Anhydrous formic acid and concentrated nitric acid were also used as solvents for the ultraviolet spectrum of S_5N_5 $AlCl_4$.

Although these solvents are not as good as concentrated sulfuric acid, since decomposition is rather more rapid in concentrated nitric acid and anhydrous formic acid interferes with the spectrum below ca. 260 nm, the spectra were essentially the same as those in concentrated sulfuric acid, and consistent extinction coefficients were obtained.

Methylene dichloride (CH_2Cl_2) was used as the solvent, for the measurement of the spectra of S_5N_5 (Reinekate), and of S_5N_5 BPh_4; confirmatory spectra were obtained (with similar extinction coefficients), showing that the $S_5N_5^+$ cation was present.

The fact that the spectra in concentrated nitric and sulfuric acids are essentially identical to those in anhydrous formic acid, acetonitrile, and methylene dichloride, suggests that the $S_5N_5^+$ cation is not protonated in the former, strongly acidic solvents, as might have been expected due to the presence of delocalised lone pairs in the ring. The spectrum would be expected to change on protonation, since the presence of an extra positive charge would tend to contract the d-orbitals on sulfur, and hence perturb the electronic orbitals, changing the spectrum. A stronger acid, (e.g. oleum or possibly "super acid" (HSO_3F (SbF_5)),[412,413] may be needed in order to effect protonation. However, protonation of $S_5N_5^+$ should provide an interesting situation because of the delocalisation of the lone pairs in the ring system to which the proton would be attached. The proton itself could therefore also be delocalised.

Zahradnik has studied the ultraviolet and visible spectrum of $S_5N_5^+$.[411] The spectrum was interpreted using π-electronic LCI-SCF procedures. The calculated π-electron densities and bond orders ($\sim$0.5) were found to be fairly uniform, supporting the idea that $S_5N_5^+$ is aromatic (see later discussion). This was also found to be true for the first and second excited singlet state; however, in the (hypothetical) 16π anion, $S_5N_5^-$, there are very low π-bond orders (∼0.15) at the open S-N bonds (i.e. at the lower point of the 'heart'), and this represents a serious hindrance to electron delocalisation in $S_5N_5^-$,[278,411] which is therefore no longer aromatic.

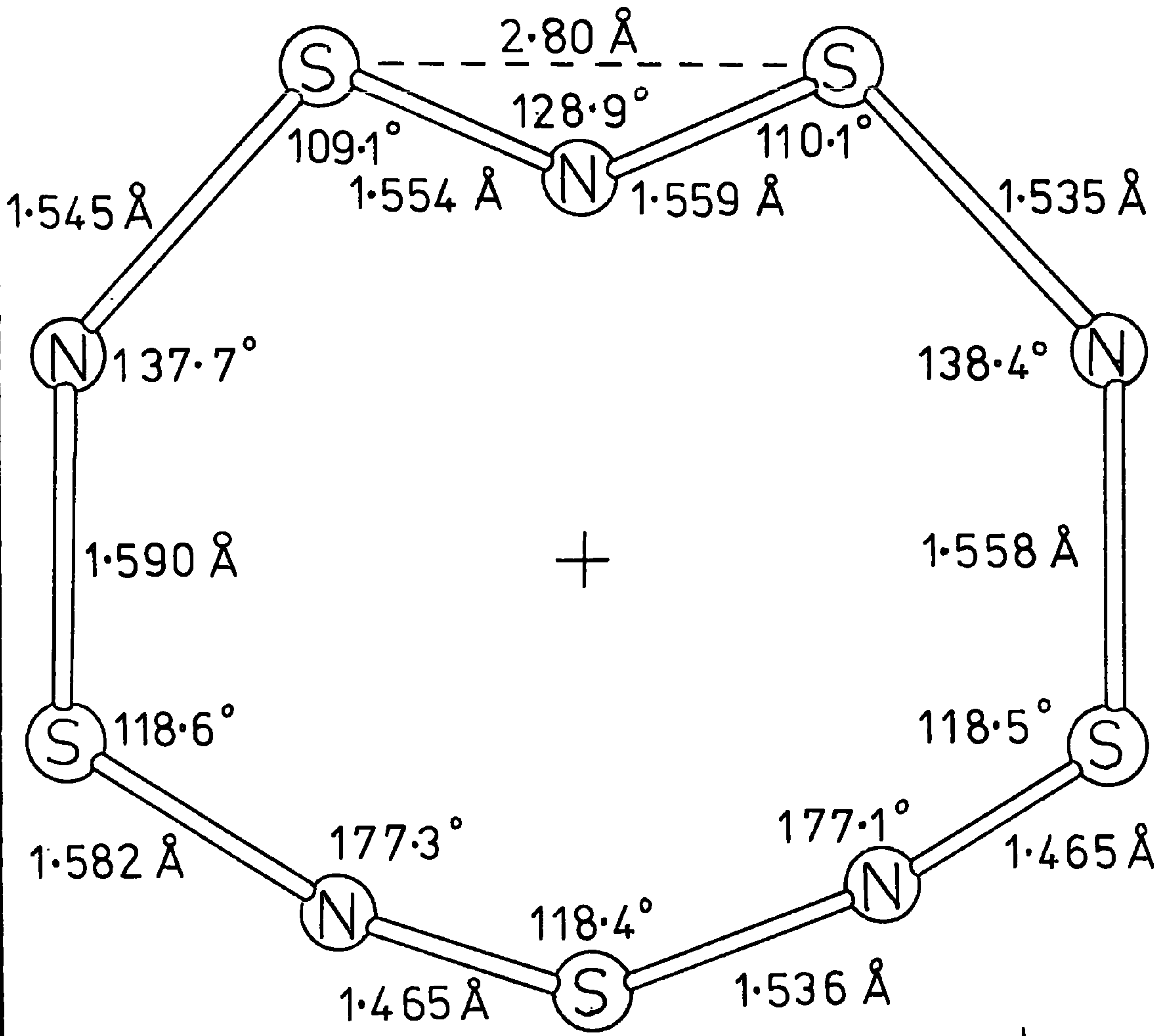
Concentrated sulfuric acid was also similarly used as the solvent to record the ultraviolet and visible spectra of the $S_3N_2Cl_2^+$, $S_4N_3^+$, $S_2NCl_2^+$ salts, and also of S_3N_2Cl. These spectra confirmed that they were all distinct compounds, (See Appendix), but did not identify the decomposition product of $S_5N_5^+$.

Nitrogen NQR work is also being undertaken on S_5N_5 $AlCl_4$.[379]

3. Structure of $S_5N_5^+$

The structure of the $S_5N_5^+$ cation has been determined from an x-ray determination on a single crystal of S_5N_5 $AlCl_4$.[410,414] (Figure 6.1)

Figure 6.1



$S_5N_5^+$

Mean esd.= 0·009 Å

The $S_5N_5^+$ ion is almost planar, with a unique heart-shape, but without a mirror plane perpendicular to the ring. (The S-N distances at the "base" of the heart, 1.536 Å and 1.465 Å, are significantly different).

The $S_5N_5^+$ ion has been shown to be a 14π-electron system[105,411,415] and has been considered as a member of a series of "electron-rich" aromatic sulfur-nitrogen species, together with $S_4N_3^+$ (10π-electron system) and $S_3N_2Cl^+$ (pseudo 6π-electron system).[101,106]

In $S_5N_5^+$, each sulfur atom is considered to provide four bonding electrons from both p- and d-orbitals and each nitrogen three bonding electrons. (Figure 6.2)

<u>Figure 6.2</u>

i.e.

		2s	2p	
N:	He +	↑↓	↑ ↑ ↑	
		lone pair	bonding electrons	

		3s	3p	3d
S:*	Ne +	↑↓	↑ ↑ ↑	↑
		lone pair	bonding electrons	

Each atom utilises two electrons to form the σ-bonds of the ring framework, leaving sulfur with two electrons, and nitrogen with one, to form a delocalised π-system around the ring. In the case of $S_5N_5^+$, the π-electron count is: $5 \times 2 + 5 \times 1 - 1 = 14\pi$, which is a member of the $(4n + 2)$ Huckel series of aromatics. Similarly, for $S_4N_3^+$, the electron count is: $4 \times 2 + 3 \times 1 - 1 = 10\pi$.

In $S_5N_5^+$ and $S_4N_3^+$, each atom also has a "non-bonding" pair of electrons, contributing to the electronic structure.

The structure of $S_5N_5^+$ is unusual in several other ways:[288]

(i) The wide bond angles at the nitrogen atoms (between 137 and 178°) indicate extensive in-plane lone-pair delocalisation, since their stereochemical activity is greatly reduced, enabling the bond angle to open up considerably. This was confirmed by the all valence electron SCFMO treatment of Adams et al,[105] therefore, the 10 "non-bonding" electron pairs are not entirely non-bonding.

(ii) The shortest S-N ring distances known (1.465 Å) are shown by the almost-linearly co-ordinated nitrogen atoms (bond angles 177.1° to 177.3°) in $S_5N_5^+$. Thus, each of these nitrogen atoms has two multiple NS bonds, the distance of one being close to that of 1.446 Å in N ≡ S-F,[416] which has been considered to have a bond order of 2.7.[417]

(iii) The ring distances are so short (average S-N bond length = 1.54 Å) that the sulfur atoms on either side of each nitrogen atom are closer than the Van der Waals diameter for sulfur of ca. 3.70 Å.[140] The shortest "non-bonded" S-S distance (2.80 Å) is at the "top" of the heart, where there is considerable cross-ring S-S interaction. Ring distances are also short in the 10 π system $S_4N_3^+$ (average S-N bond length = 1.55 Å),[266] which is the only other planar SN species known.[262,263,264]

The short ring distances in $S_5N_5^+$ and $S_4N_3^+$ are less surprising when one calculates the average number, n, of σ and π electrons per SN bond. For $S_5N_5^+$, n = 3.40, and for $S_4N_3^+$, n = 3.43. Thus each ring atom in $S_5N_5^+$ exercises an apparent covalency (on average) of 3.40. Alternatively, by considering bond length as an indication of bond order, the maximum apparent covalency of a nitrogen atom, using Glemser's data[417] is about 3.9. (1.465 Å corresponds to a bond order of ca. 2.2 and 1.536 Å to ca. 1.7). This high bond order is particularly remarkable for the nitrogen atoms, which all carry a negative charge.[105]

The covalency of neutral nitrogen is normally limited to 3, and N^+ to 4, so that negatively charged nitrogen should exhibit a covalency of less than 3. This unusually high apparent covalency can be explained by the delocalisation of the lone pairs on the nitrogen atoms into the vacant sulfur d-orbitals, as well as the π bonding perpendicular to the ring. This lone pair delocalisation greatly reduces their stereochemical activity, thus also enabling the bond angles to increase. This is evident throughout the $S_5N_5^+$ ring, particularly at the "pointed" base of the ring, where the S-N-S bonds are almost linear.

The extensive π and lone pair delocalisation, and the high bond orders in $S_5N_5^+$ and $S_4N_3^+$, no doubt contribute to the striking chemical stability (particularly under acid conditions) of the salts. A further consequence is that satisfactory sets of canonical structures cannot be written. This perhaps explains why $S_4N_3^+$ was not earlier recognised as being one member of a potentially large class of sulfur-nitrogen aromatic species, of which $S_5N_5^+$ is also a member. This difficulty is also evident from the numerous unsuccessful attempts by earlier workers to rationalise the structures of other sulfur-nitrogen species such as $S_4N_3^+$ using classical valence theories.

It is because of the apparent excess of electrons over those required for "normal" covalent bonding, and also the impossibility of writing satisfactory canonical structures, that compounds of the series: $S_4N_3^+$ and $S_5N_5^+$ have been termed "electron rich aromatics".[418]

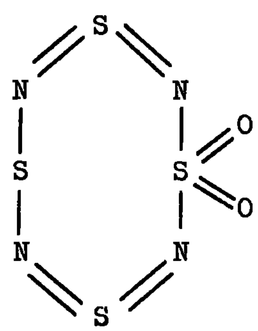
4. Recent Studies of $S_5N_5^+$

Two compounds of the general formula: $S_4N_4O_2$ have recently been prepared.[440,441] They were formed when a solution of $(CH_3)_3$ Si-N=S=N-Si $(CH_3)_3$ (0.2 mole) in 50 ml. of methylene chloride was added with stirring over 5 hours to a solution of FSO_2 N=S=O (0.2 mole) in 250 ml. of methylene chloride, and then refluxed for about 1 hour until the evolution of sulfur dioxide had ceased.

The volatile products: SO_2, $(CH_3)_3$ SiF, $(CH_3)_3$· Si·NSO and the solvent were removed in vacuo, and the liquid residue digested with 30 ml. of methylene chloride. The solid residue was removed by filtration. After several days away from the filtrate, violet-black needles (I) were deposited, which were recovered by filtration. When a few millilitres of solvent were removed from the filtrate, yellow needles (II) were formed.[441]

Compound (II) was shown to be monomeric in the gas phase, and from elemental analysis, infrared and mass spectra, the structure (Figure 6.3) was assigned.[441]

Figure 6.3



$S_4N_4O_2$(II)

Compound (I) was characterised by elemental analysis, infrared spectrum and x-ray analysis. The mass spectrum gave only S_4N_4 as an identifiable decomposition species.

The x-ray crystal structure showed that (I) consisted of an $S_5N_5^+$ cation and an $S_3N_3O_4^-$ anion.[441] (Figures 6.4 and 6.5). The $S_5N_5^+$ cation is planar (implying that it is a 14π electron rich aromatic system), but is of a different shape to the "heart-shaped" $S_5N_5^+$ cation previously described, being a "figure '8' shape" but without transannular bonding (Figure 6.4). This is the first time that an aromatic system has been shown to exist in more than one conformation, and further demonstrates the unique properties of this unusual cation.

The anion also is new and unusual. It consists of an S_3N_3 ring with alternating S and N atoms in a chair conformation, with two pairs of oxygen atoms bonded to two sulfur atoms, the third sulfur atom not being bonded to any exocyclic group (Figure 6.5) This is the first time that this anion has been reported. The structure is somewhat similar to the sulfanuric halides, (e.g. $S_3N_3Cl_3O_3$), and therefore might be considered to be related to these compounds.

The SN bond distances in the $S_5N_5^+$ cation are all almost equal (1.55 to 1.58 Å) which is slightly longer than those observed for "heart-shaped" $S_5N_5^+$ (average bond distances S-N = 1.54 Å) and so corresponds to a short S-N bond distance, once again indicating the existence of electron-rich aromatic bonding in the system.

The reasons why $S_5N_5^+$ should exist in two different conformations are not yet clear, but it may be that both conformations have a very similar energy and that crystal lattice forces or conditions of crystallisation determine the conformation adopted. It would therefore be interesting to see if it is possible to convert one conformational structure of $S_5N_5^+$ into the other; for example, by changing the conditions of crystallisation (e.g. by varying the solvent or by rapid crystallisation), or by changing the anion to vary the crystal forces.

Further work is continuing on these compounds.

Figure 6.4

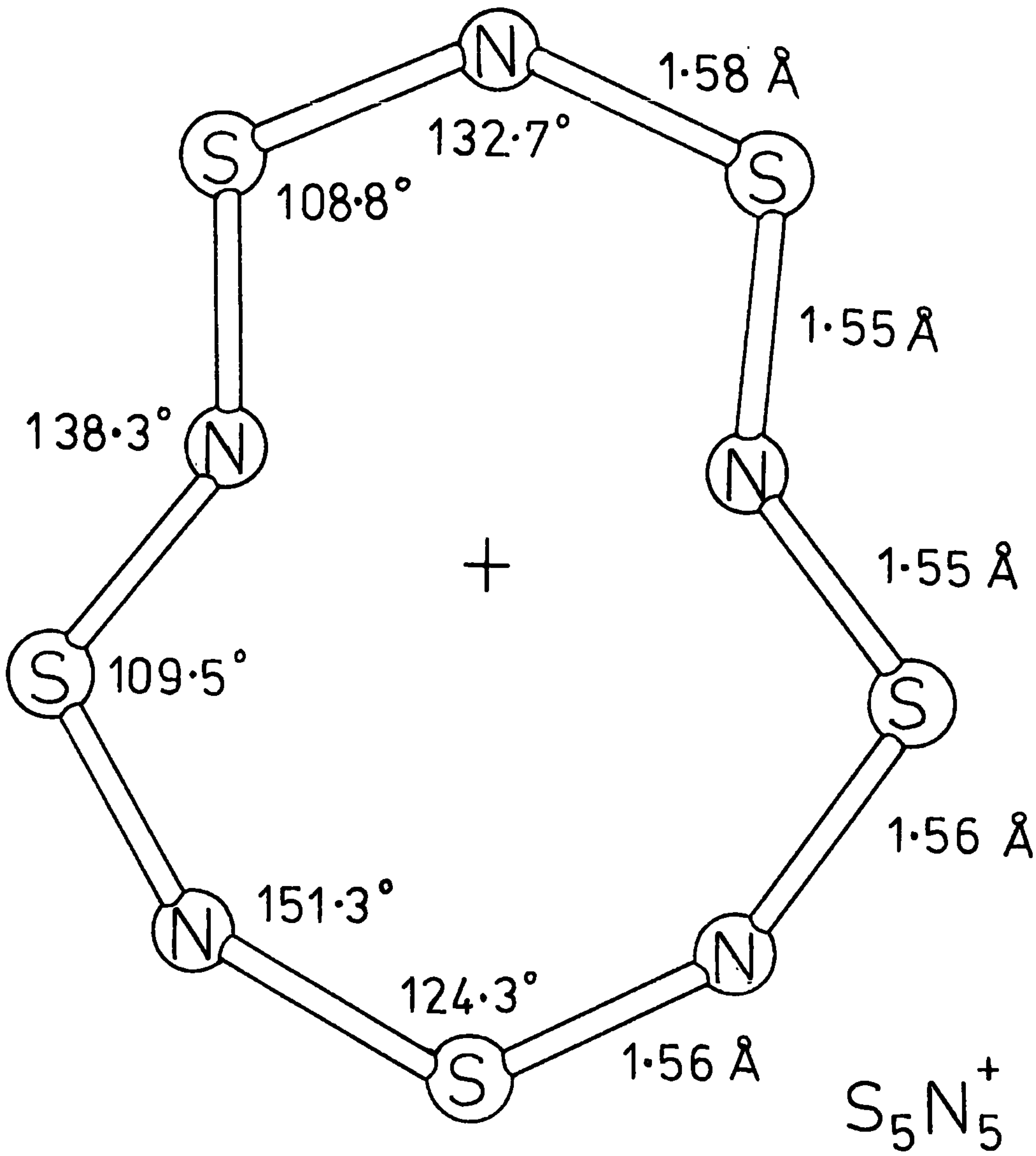
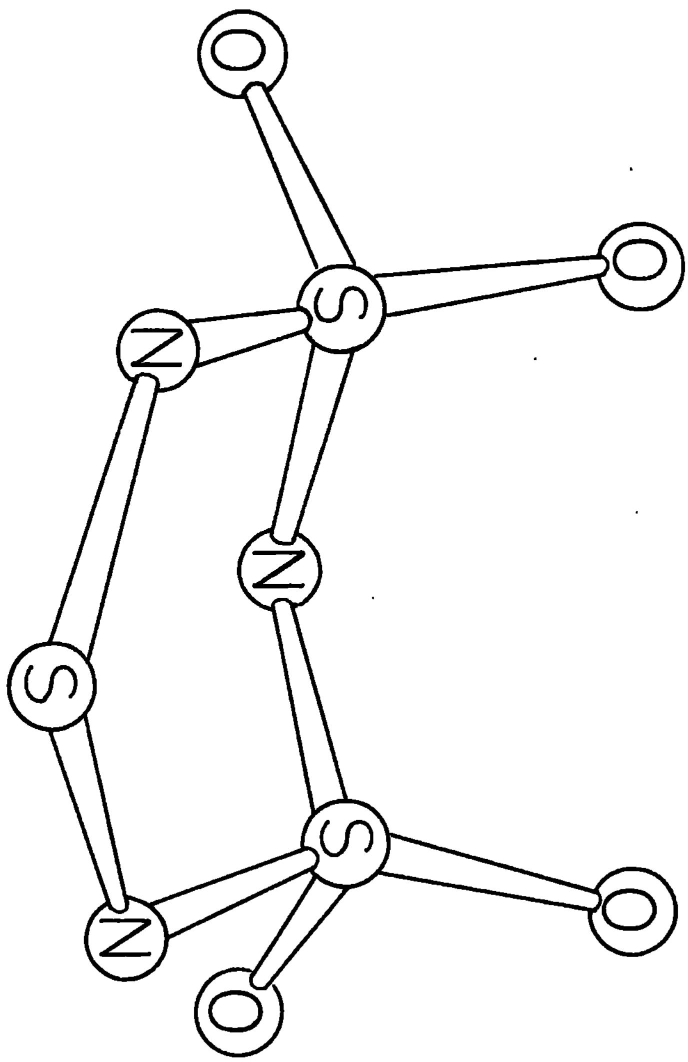


Figure 6.5

$S_3N_3O_4^-$



5. Other Members of the "Electron-Rich Aromatic" Sulfur-Nitrogen Series[418]

The recognition of $S_4N_3^+$ and $S_5N_5^+$, as members of a hitherto unrecognised series of "electron-rich aromatic" sulfur-nitrogen series, implies the existence of other members of this series, yet unprepared. Their existence can be predicted on the basis of there being the correct number of π-electrons in the "aromatic" ring system, the "correct number" being a member of the Huckel series for aromatic compounds, i.e. (4n + 2) where n is integral. The first members of this series being: 2, 6, 10, 14 ..... etc.

Assuming, as before, that sulfur contributes two electrons to the π system, and nitrogen one electron, (in addition to those used for bonding and "lone-pairs"), Tables 6.1 and 6.2 can be constructed, for the number of π-electrons in any sulfur-nitrogen ring system.[106]

Table 6.1

π-electron counts for Neutral SxNy species:[106]

No. of N atoms, y	No. of S atoms, x: 1	2	3	4	5	6
1	3	5	7		Weakly contracted	
2	4	6	8	10	sulfur d	
3		7	9	11	13	orbitals
4		8	10	12	14	16
5	Unstable		11	13	15	17
6				14	16	18
7					17	19

Table 6.2

π-electron counts for unipositive $SxNy^+$ species:

No. of N atoms, y	No. of S atoms, x: 1	2	3	4	5	6
1	2	4	6		Weakly contracted	
2	3	5	7	9	sulfur d	
3		6	8	10	12	orbitals
4	Unstable		9	11	13	15
5				12	14	16
6					15	17

In the tables, those species with the correct number of π-electrons have been underlined once, and the known species underlined twice. (S_4N_4 is not included, since it is an example of cage bonding, rather than electron-rich aromatic bonding).

To achieve maximum stability, as well as having the correct number of π-electrons, the species should also have roughly the same number of sulfur and nitrogen atoms; this is because:

(i) Monocyclic compounds containing more nitrogen than sulfur require the presence of N-N bonds. The N-N single bond is weak (38.4 K.cal/mole),[140,419] but this is due to lone pair-lone pair repulsions between nitrogen atoms which weaken the bond. It has been calculated that, in the absence of these repulsions, the N-N single bond would be considerably stronger (94.7 K.cal/mole[419]). In the case of electron rich aromatic compounds, such as $S_4N_3^+$ and $S_5N_5^+$, the stereochemical activity of the lone pairs on nitrogen is greatly reduced, due to their delocalisation into the vacant d-orbitals of adjacent sulfur atoms. Since a nitrogen atom does not possess d-orbitals, lone pair delocalisation cannot occur along a nitrogen-nitrogen bond, and therefore each nitrogen atom must be directly bonded to at least one sulfur atom for lone pair delocalisation, and the consequent increased stability, to occur. Monocyclic compounds with a large excess of nitrogen would therefore probably be less stable.

Since, however, the N-N single bond is strong in the absence of lone pair repulsions as noted above, electron rich aromatic compounds containing N-N bonds should exist and be stable, although none have so far been prepared. The π delocalisation would further help to strengthen the N-N bond.

(ii) It is a characteristic feature of $S_4N_3^+$ and $S_5N_5^+$, that each sulfur atom carries a positive charge,[105] and this probably assists in stabilising the sulfur d-orbital contributions to the bonding,[107] therefore a combination of sulfur with the more electronegative nitrogen, and the presence of a cation charge favours stability. In S_4N_2, the sulfur atoms are in the 1,3 position,[237] and the compound readily disproportionates to S_4N_4 and sulfur. This suggests that each sulfur atom in a stable aromatic sulfur-nitrogen system requires at least one directly attached nitrogen atom, and that sulfur d-orbital contributions weaken with the reduction of the N/S atomic ratio. Therefore, an area of "maximum stability" (See Tables 6.1 and 6.2, Page 194) can be established in the tables, where there is approximately the same number of sulfur and nitrogen atoms.

All the known "electron rich aromatic" species are included in the tables; these are: S_2N_2 and S_4N_2 (neutral), $S_4N_3^+$ and $S_5N_5^+$ (unipositive) and SN^+ (formally included, although obviously not a ring). $S_4N_3^+$ and $S_5N_5^+$ are planar, and S_2N_2 and S_4N_2 are thought to be planar. (A planar system allows maximum overlap of the π orbitals). No anions have yet been prepared, so the effect of the negative charge in de-stabilising the π-bonding by expanding the d-orbitals on sulfur, is not known. Compounds containing N-N bonds have also not yet been prepared, but may well be preparable. The table allows other yet unprepared members of this series to be predicted. (Table 6.3)

Table 6.3

e.g.	Anionic	Neutral	Cationic
	$S_3N_3^-$ (10π)	S_3N_4 (10π)	$S_2N_3^+$ (6π)
		S_4N_6 (14π)	$S_3N_2^{2+}$ (6π)
		S_5N_4 (14π)	$S_6N_4^{2+}$ (14π)
		S_6N_6 (18π)	$S_6N_7^+$ (18π)
			$S_8N_8^{2+}$ (22π)
			$S_9N_9^+$ (26π)

Most of these species would be unstable with respect to disproportionation or decomposition, e.g. S_6N_6 would probably be unstable, yielding S_4N_4; and S_4N_6 would probably decompose to S_4N_4 and nitrogen; however others, e.g. $S_3N_2^{2+}$, S_5N_4, $S_6N_7^{+}$, $S_5N_6^{2+}$ and $S_6N_4^{2+}$ could be stable and preparable, as could $S_8N_8^{2+}$ and $S_9N_9^{+}$, which are the next members of the series to contain only S-N bonds. These last two, being large rings, may exhibit unusual conformations and bonding, as in $S_5N_5^{+}$.

It would be of importance to be able to synthesise some of these electron rich aromatic systems, particularly those containing N-N bonds, as it would be of great interest to determine the N-N bond lengths which should be short and of high 'bond order', and also as a possible route to nitrogen fixation,[113] since because of this high bond order, the energy required to convert the nitrogen-nitrogen triple bond (in molecular nitrogen) (226 K.cal/mole)[419] into the N-N bond in these compounds, would be relatively small, and should be easily made up by the π-delocalisation energy, on formation of the ring.

Hydrazine (N_2H_4) and azides (N_3^-) may be a useful source of N-N bonds for the synthesis of such compounds, although the use of such reactive compounds as azides may be hazardous.[113] Other possible routes include sulfur abstraction from other sulfur-nitrogen compounds, and the use of organic N-N compounds (triazoles, tetrazoles, etc.)[113]

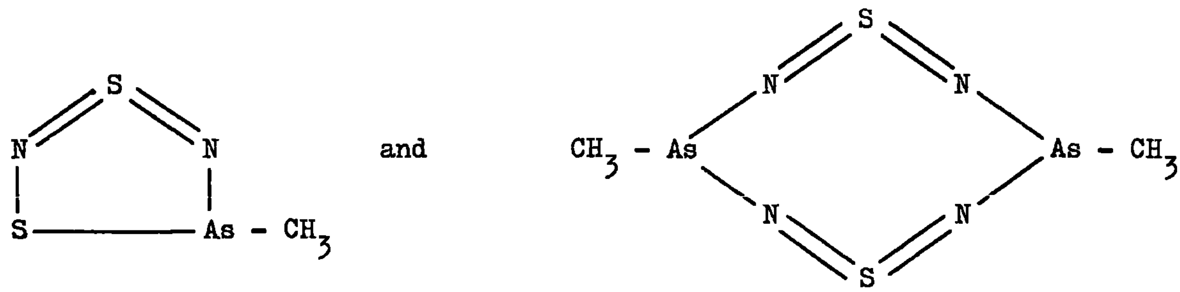
Many more sulfur-nitrogen Huckel structures can be formed by inserting a group which provides no further π electrons, for instance, inserting Cl - S$\langle^{+}$ into S_2N_2, yields $S_3N_2Cl^{+}$ which is known to be a (pseudo) 6 π system,[105] for although not strictly aromatic (since the sulfur bonded to the exocyclic chlorine is out of the plane of the ring,[189] and therefore $\sigma - \pi$ separability does not strictly hold) there is still considerable π delocalisation, with the sulfur atoms having a positive charge.[105] Other similar groups which could also be inserted are: O = S$\langle$, $O_2S\langle$, O = P$\langle$, ClB$\langle$ and PhC$\langle^{+}$

Other Huckel species could be formed by replacing atoms or groups by other atoms or groups which provide the same number of π electrons; for instance, replacing the Cl-S$<$ group in $S_3N_2Cl^+$ by R-C$<$, (R = organic group) yields compounds of the type $S_2N_2CR^+$ A^- (A^- = Cl^- or other anion). These compounds are known where R = C_6H_5, CCl_3 or $(CH_3)_3C$.[418,420] Carbon atoms with exocyclic groups could also replace nitrogen in any inorganic aromatic ring system, giving a whole range of new ring systems: e.g. $RCS_4N_2^+$, $RR'C_2S_4N^+$; $RR''C_3S_4^+$, all formed by replacing N by C-R in $S_4N_3^+$, and similarly for $S_5N_5^+$. The carbon atom would not destroy the planarity of the ring, and since the carbon atom is also bonded to an exocyclic group which can be varied without changing the aromatic character of the ring system (whereas sulfur and nitrogen do not have any exocyclic group bonded to them in such compounds), the variety of compounds that could be prepared is greatly increased.

Electron rich aromatic ring structures with positive charges greater than one, e.g. $S_3N_2^{2+}$, $S_6N_4^{2+}$ and $S_8N_8^{2+}$ should be preparable, and the extra charge may enhance their stability by causing the sulfur d-orbitals to contract even more, thus achieving better overlap with the π system, and could also allow a higher S/N ratio, cf:S_8^{2+}.

Other elements as well as carbon, could also replace sulfur or nitrogen. For example, sulfur could be partly or completely replaced by R-$P^V$$<$ (no phosphorus lone pair, and R preferably electron withdrawing). There are apparently no such phosphorus compounds known. Arsenic could also be similarly used, and the compounds (Figure 6.6) are known.[421]

Figure 6.6



(i) (ii)

One disadvantage with such compounds is that the " π path" may probably be interrupted at the arsenic atom, thus reducing the stabilisation due to π delocalisation, and it is probable that there is little π delocalisation in these compounds.

A further possibility is for selenium to replace sulfur, and the cation $S_3N_3Se^+$ (a selenium analogue of $S_4N_3^+$) may have been formed in the reaction of S_4N_4 with Se_2Cl_2 in thionyl chloride.[130]

(D) Reactions of the $S_5N_5^+$ Cation

The reactions of the $S_5N_5^+$ salts in which one anion is exchanged for another through reaction with concentrated acids, through metathetical reactions in anhydrous formic acid or by displacement reactions in thionyl chloride in which the $S_5N_5^+$ cation remains intact, have already been discussed (this Chapter). A study was therefore made of the reactions of the $S_5N_5^+$ cation to determine its use as a starting material for other sulfur-nitrogen compounds.

1. Reaction between S_5N_5 $AlCl_4$, $(NSCl)_3$ and $AlCl_3$

The reaction of S_5N_5 $AlCl_4$ with $(NSCl)_3$ and $AlCl_3$ was carried out in an attempt to produce $S_6N_6^{2+}$ 2 $AlCl_4^-$. According to Banister,[101,113] $S_6N_6^{2+}$ could be an 8 electron pair cage species rather than a 16π electron system, (since "electron rich aromatic" compounds require 6, 10, 14, 18π electrons etc.). An 8 electron pair cage would have 7 corners, e.g. based on a pentagonal bipyramid,[100] and would be in the same series as S_4N_4, (which with $S_4N_5O^-$ are the only SN cage compounds of this type).

The reaction would be:

$\frac{1}{3}$ $(NSCl)_3$ + $AlCl_3$ + S_5N_5 $AlCl_4$ $\longrightarrow$ $S_6N_6^{2+}$ 2 $AlCl_4^-$, possibly via the $(NSCl)_3$, $AlCl_3$ adduct, which would add NS^+ to the $S_5N_5^+$ ring to give $S_6N_6^{2+}$.

Trichlorocyclotrithiazene $(NSCl)_3$ (0.8021g), S_5N_5 $AlCl_4$ (3.9271g) and $AlCl_3$ (1.312g) (molar ratio 1:3:3) were mixed together in a dry box, transferred to a round bottomed flask and slowly heated while stirring under nitrogen. No apparent reaction occurred until ca. 50°C, when the mixture (orange-yellow) turned a darker colour. The mixture melted at ca. 70° to 80°C (indistinct melting point) and it was allowed to remain molten for ca. 15 minutes at ca. 80°C, and then allowed to cool to room temperature. A dark brown solid was gradually formed on cooling. An infrared spectrum of the solid was complex, and apart from some starting material, no other compounds could be identified, although it showed that a reaction had taken place.

The experiment was continued by again heating the solid to ca. 80°C for ca. 2 hours under dry nitrogen, cooling and then adding thionyl chloride to dissolve any reaction product. On removing some of the thionyl chloride by distillation, and cooling to -10°C, crystals were formed, but an infrared spectrum showed that they consisted of unreacted starting material, the only other identifiable product being $S_4N_3^+$. The remaining products were probably a mixture, since the spectrum was indistinct, but may contain new sulfur-nitrogen species.

The reaction was also carried out in thionyl chloride solution, but S_5N_5 $AlCl_4$ did not react, and only the $(NSCl)_3$, 2 $AlCl_3$ adduct was formed from the $(NSCl)_3$ and $AlCl_3$.

2. Reaction between S_5N_5 $AlCl_4$ and S_4N_4

The reaction between S_5N_5 $AlCl_4$ and S_4N_4 was an attempt to produce the cation $S_9N_9^+$, through the reaction:

$$S_5N_5^+ \ AlCl_4^- + S_4N_4 \longrightarrow S_9N_9^+ \ AlCl_4^-$$

$S_9N_9^+$ could be a 26π member of the "electron rich" aromatic series, previously noted (Page 196), or alternatively could be based on an icosahedral structure.[113] (13 electron pairs).

The reaction may well be thermodynamically favoured, since S_4N_4 is an endothermic compound (standard heat of formation of S_4N_4 (s) = + 110.0 ± 2.0 K.cal/mole[27]), and since $S_9N_9^+$ is expected to be stable due to its aromatic nature. (The reaction of the $(NSCl)_3$/metal chloride adducts with S_4N_4 to product $S_5N_5^+$ salts (see previously), is thermodynamically favoured for similar reasons).

Tetrasulfur tetranitride (S_4N_4) (1.798g) and S_5N_5 $AlCl_4$ (0.830g) were mixed together dry (in 1:1 molar ratio) and gradually heated while stirring (orange powder). There was little reaction until about 140°C, when the mixture began to melt; a dark red liquid was formed and the mixture was maintained at ca. 140°C for about 5 minutes. The mixture was then cooled, and thionyl chloride added to the cooled (dark red) solid. The solid immediately changed colour to a very dark red, showing that an overall reaction had occurred. An infrared spectrum did not show any identifiable products, apart from possible traces of starting material, but presumably other compounds had been formed in the reaction, some of which may have been new and unidentified sulfur-nitrogen species, so that these types of reaction are worth further investigation.

The reaction was also carried out in thionyl chloride solution, but the S_5N_5 $AlCl_4$ did not react, and the S_4N_4 gradually decomposed to eventually form S_4N_3Cl.

3. Attempted Reaction Between S_5N_5 $AlCl_4$ and CCl_3CN

In order to investigate possible routes to carbon containing sulfur-nitrogen ring systems(see Page 198), the reaction between S_5N_5 $AlCl_4$ and CCl_3CN was studied, since a reaction between acetonitrile and S_5N_5 $AlCl_4$ had been observed, but the products could not be identified.[184]

S_5N_5 $AlCl_4$ (2.7825g) was stirred at room temperature with 30 ml. of trichloroacetonitrile (CCl_3CN) for ca. 18 hours, with little apparent reaction. S_5N_5 $AlCl_4$ is only sparingly soluble in CCl_3CN, so that any reaction would be expected to be slow. The mixture was then heated with stirring to ca. 70°C for ca. 4 hours, and then allowed to cool, yielding a yellow precipitate and a yellow solution as before. The yellow precipitate was filtered off and pumped dry in vacuo, yielding a yellow powder which was shown to be starting material

(S_5N_5 $AlCl_4$) by infrared and ultraviolet spectroscopy, with no indication of other compounds present. Evaporation of the yellow solution gave a yellow powder, which was similarly identified to consist mainly of S_5N_5 $AlCl_4$, with a small amount of impurity (possibly containing $S_4N_3^+$) which was probably present initially in the starting material.

(E) Reactions of the $S_5N_5^+$ Cation - Discussion

Neither of the first two reactions studied (S_5N_5 $AlCl_4$, + $(NSCl)_3$ + $AlCl_3$ and S_5N_5 $AlCl_4$ + S_4N_4) both in the melt and in thionyl chloride solution, produced any identifiable new sulfur-nitrogen species, although some new and unidentified species may have been formed. Due to the stability of the $S_5N_5^+$ ring, reaction conditions in thionyl chloride solution were not sufficiently forcing, and so a reaction in the melt was used. Fairly high temperatures had to be used (ca. 140°C for the second reaction), before the mixture melted so that decomposition of possible reaction products could have occurred. The $AlCl_4^-$ anion is perhaps not a very suitable anion, being too small to adequately stabilise the large $S_9N_9^+$ cation, a larger anion, e.g. Ph_4B^- might be better.

The reaction of S_5N_5 $AlCl_4$ with CCl_3CN was carried out as an initial experiment to try to substitute carbon into an aromatic sulfur-nitrogen ring. The reaction may be possible because:

(i) S_5N_5 $AlCl_4$ reacts with acetonitrile[184] (as described on Page 202), and this may be due to the production of a new carbon-containing compound, or by decomposition due to the presence of either the nitrile group, or of the methyl group. The use of CCl_3CN could at least help to distinguish between the last two possibilities.

(ii) Reaction of $S_3N_2Cl_2$ or $(NSCl)_3$ with refluxing CCl_3CN produces good yields of $CCl_3CS_2N_2^+Cl^-$, which, as has been previously discussed (Page 198), is an electron rich sulfur-nitrogen aromatic ring containing carbon,[418,420] and a similar reaction might occur with $S_5N_5^+$ salts.

Although no reaction took place, the experiment demonstrates the use of CCl_3CN as a purifying solvent for $S_5N_5^+$ salts, since some impurity was removed by the CCl_3CN, and it also shows that the decomposition of S_5N_5 $AlCl_4$ in acetonitrile, previously observed was due to the methyl rather than the nitrile group.

Finally, this sequence of reactions further demonstrates the stability of the $S_5N_5^+$ ring, previously discussed.

THE PREPARATION, PROPERTIES AND STRUCTURE OF S_3N_2Cl AND ITS DERIVATIVES

CHAPTER 7

The Preparation, Properties and Structure of S_3N_2Cl and its Derivatives

(A) Introduction

The compound S_3N_2Cl has been known since 1880,[255] as a very dark green powder, formed when $S_3N_2Cl_2$ decomposes in vacuo at 80° to 90°C.[52,249] It analysed to S_3N_2Cl, but its structure was unknown, since it was apparently insoluble in every solvent that it did not react with. No crystals suitable for x-ray analysis have therefore been made.

It was decided to undertake a study of this compound, since very little work had been previously undertaken. The properties and reactions of S_3N_2Cl were studied with particular reference to a determination of its structure by x-ray diffraction methods, either by preparing S_3N_2Cl in crystalline form from a suitable solvent, or by preparing a crystalline derivative. (See also Introduction, Chapter 1, Page 55).

(B) Preparative Routes

S_3N_2Cl was prepared in two ways:

1. Action of Heat on $S_3N_2Cl_2$

Powdered $S_3N_2Cl_2$ was heated at 80° to 90° in vacuo for about ½ hour, gradually forming very dark green S_3N_2Cl,[52,249] (see experimental section). S_3N_2Cl was identified by infrared and ultraviolet spectra, and by analysis.

Infrared spectrum (nujol mull):

1015 (w), 962 (s), 943 (s), 746 (w), 716 (sh), 709 (s), 699 (s), 667 (sh), 584 (s), 570 (w), 500 (w,b), 431 (m) cm^{-1}. (See Appendix)

Ultraviolet spectrum (conc. sulfuric acid solvent) (195-700 nm):

λ max. nm	ε (estimated for fresh soln.)
356	9×10^2
248.5	4.7×10^3
219	ca. 3.5×10^3

HCl gas is evolved on dissolution.

The absorption at 219 nm. becomes more intense on standing and may be due to decomposition (see Appendix) since it has not been identified with any known sulfur-nitrogen species.

Analysis:

	Found %	S_3N_2Cl requires %
S =	59.53	60.24
(by difference) N =	17.91	17.55
Cl =	22.56	22.21

2. Reaction of $S_3N_2Cl_2$ with Anhydrous Formic Acid

$S_3N_2Cl_2$ was found to react with anhydrous formic acid as solvent to yield insoluble S_3N_2Cl.

Powdered $S_3N_2Cl_2$ (4.8936g) was stirred at room temperature with ca. 50 ml. of anhydrous formic acid. The orange $S_3N_2Cl_2$ gradually turned dark green (S_3N_2Cl) and gases were evolved (one was HCl, the other presumably CO_2). After the reaction had been completed (ca. 2 hours) the precipitate (S_3N_2Cl) was filtered off and pumped dry in vacuo. S_3N_2Cl was identified by its infrared and electronic spectra. The reaction was probably:

$$2\ S_3N_2Cl_2 + HCOOH \xrightarrow{HCOOH} 2\ S_3N_2Cl + CO_2 + 2\ HCl$$

The yields of S_3N_2Cl were higher, but the product was not as pure as the S_3N_2Cl obtained by heating $S_3N_2Cl_2$ in vacuo (method (1)), as shown by less satisfactory analysis figures and some $S_3N_2Cl_2$ was probably still present.

(C) Reactions of S_3N_2Cl to Form Crystalline Derivatives for X-Ray Analysis

It was thought probable that S_3N_2Cl was ionic or sufficiently polar to allow the chlorine to be replaced as Cl^- by another anion, and this was thought to be the best method of preparing a crystalline derivative. S_3N_2Cl was found to be slightly soluble in liquid SO_2 (the solution was coloured yellow) and decomposition did not appear to occur on dissolution, but no crystals of S_3N_2Cl could be obtained on cooling and pumping off some solvent.

Two of the many suitable anions for x-ray work are $FeCl_4^-$ and $AlCl_4^-$ [422] since the atoms are easy to locate by x-ray, and so the initial work was concentrated in preparing these derivatives.

1. Reactions of S_3N_2Cl with $AlCl_3$ and $FeCl_3$ in Thionyl Chloride

S_3N_2Cl (0.8898g), and $AlCl_3$ (0.7432g) (1:1 molar ratio), were mixed in ca. 10 mls. of thionyl chloride and stirred for ca. 12 hours. No apparent reaction occurred and S_3N_2Cl, (insoluble in $SOCl_2$) remained. The solution was therefore heated to ca. 50°C for ½ hour, during which time the S_3N_2Cl dissolved and on cooling a crystalline solid precipitated out. The solid was filtered off and recrystallised twice from thionyl chloride. Product: orange needle-like crystals. An infrared spectrum showed that the product was $S_3N_2Cl^+ AlCl_4^-$ (see Chapter 5, Page 151), by comparison with an authentic sample, prepared from $S_3N_2Cl_2$ and $AlCl_3$ in thionyl chloride.

The experiment was repeated, using a 1:1 mixture of S_3N_2Cl and $FeCl_3$ in thionyl chloride. Similar reactions occurred, and a yellow crystalline compound was formed, which was recrystallised from thionyl chloride, and similarly shown to be $S_3N_2Cl^+ FeCl_4^-$.

2. Reactions of S_3N_2Cl with $AlCl_3$ and $FeCl_3$ in CCl_4

$AlCl_3$ (3.0240g) was dissolved in ca. 50 ml. of dry CCl_4, (non-chlorinating solvent), and S_3N_2Cl (3.6206g) added. The mixture was stirred for ca. 12 hours, and then refluxed for a further 12 hours. In both cases, no obvious reaction occurred, only starting materials being observed in an infrared spectrum; similarly no reaction was observed between S_3N_2Cl and $FeCl_3$ in CCl_4.

3. Reaction of S_3N_2Cl with $FeCl_3$ in Nitrobenzene

$FeCl_3$ (3.72g) was added to 50 ml. of nitrobenzene, together with S_3N_2Cl (3.6613g) and the mixture stirred for ca. 60 hours at room temperature. No obvious reaction occurred, although the solution became darker in colour, and the reagents appeared to have dissolved. Petroleum ether was then added to the solution in an attempt to cause precipitation be reducing the solubility, but this was unsuccessful and removing the nitrobenzene in vacuo, produced a very dark viscous oil, which would not crystallise. The reaction was not studied further.

4. Reaction of S_3N_2Cl with $FeCl_3$ in Chlorobenzene

$FeCl_3$ (0.7994g) and S_3N_2Cl (0.8629g) were added to ca. 15 ml. of chlorobenzene, and the mixture stirred at room temperature. As for nitrobenzene, only a dark viscous oil was obtained on evaporating off the solvent, and the reaction was not studied further.

5. Reaction of S_3N_2Cl with $FeCl_3$ in Acetyl Chloride

$FeCl_3$ and S_3N_2Cl were added to ca. 50 ml. of acetyl chloride and the mixture stirred for ca. 24 hours at room temperature. A red, hygroscopic solid was formed, and this was filtered off and pumped dry in vacuo. IR and UV spectra showed that it was not a derivative of S_3N_2Cl and possibly a reaction product of acetyl chloride, (e.g. $CH_3CO^+FeCl_4^-$).[399] The reaction was not studied further.

6. Reactions of S_3N_2Cl with $AlCl_3$ and $FeCl_3$ in Liquid SO_2

S_3N_2Cl (2.0549g) and $AlCl_3$ (1.7163g) were mixed in a schlenk, and dry SO_2 condensed onto the mixture (ca. 50 ml. of liquid SO_2 used) and the mixture stirred at -23°C for ca. 24 hours. ($AlCl_3$ is fairly soluble in liquid SO_2, and S_3N_2Cl slightly soluble). The solution gradually turned a green colour, and a greenish precipitate formed. The SO_2 was allowed to evaporate off to half bulk, and the solution cooled to -78°C to induce crystallisation. However, only powder was formed and eventually the precipitate was filtered and the SO_2 removed in vacuo. The product was a yellow-green powder. The ultraviolet spectrum was similar to that of S_3N_2Cl itself, as was the infrared spectrum. The analysis was inconclusive; however, the product was amorphous rather than crystalline and therefore unsuitable for x-ray determination. Similar results were obtained using $FeCl_3$ instead of $AlCl_3$; the product being a dark sparingly soluble powder.

7. Reaction of S_3N_2Cl with $AlCl_3$ in liquid SO_2 under pressure

The reaction of S_3N_2Cl with $AlCl_3$ was repeated using liquid SO_2 under pressure so that higher temperatures could be used.

$AlCl_3$ (0.6233g) and S_3N_2Cl (0.5206g) were mixed in a Carius tube with a stirrer, and SO_2 condensed onto the mixture via a vacuum line, until the Carius tube was ca. $\frac{2}{3}$ full (ca. 100 ml. SO_2). The tube was then sealed under vacuum (the SO_2 being frozen in liquid nitrogen) then allowed to warm up to room temperature behind a blast screen and then carefully heated to ca. 55°C, (10 atmospheres pressure)[386] in a water bath. Much of the solid dissolved although some powder remained and on cooling the Carius tube slowly to -78°C, a few greenish needle-shaped crystals were formed. The Carius tube was broken under dry nitrogen, at $-78^{o}C$, and the SO_2 slowly pumped off under vacuum; however, the crystals were lost during the removal of the solvent, and a greenish powder remained which appeared to be similar to that obtained in the previous experiment and so not suitable for x-ray work. The experiment was repeated with similar results.

8. Reactions between S_3N_2Cl and HSO_3Cl

This reaction was carried out either in pure HSO_3Cl as solvent or using liquid SO_2 as solvent. The reactions produced a crystalline derivative of S_3N_2Cl, and so were repeated several times to determine optimum conditions for crystal formation.

(i) Reaction in pure HSO_3Cl as solvent

S_3N_2Cl (2.5627g) was added to ca. 50 ml. of freshly distilled HSO_3Cl in a round bottomed flask under nitrogen. A rapid reaction occurred, and a gas was given off. (This was identified as HCl). A very dark brown solution was formed after the initial reaction had been completed, although there was no precipitate. The solution was allowed to stand under nitrogen at room temperature, for several days, occasionally pumping off a little solvent under vacuum, (HSO_3Cl has a b.pt. of $153^{o}C$,[386] so that the vapour pressure at room temperature is small). During this time, very dark plate-like crystals formed at the bottom of the flask, together with a yellowish powder. The solid was filtered, pumped as dry as possible under vacuum, and then washed with a little liquid SO_2. (HSO_3Cl and liquid SO_2 are miscible). The crystals were again pumped dry and hand sorted in a dry box from the yellow powder (which was not further studied). The crystals were again hand sorted for x-ray analysis, and suitable crystals mounted in glass capillary tubes for this purpose. Some crystals were found to be complex or twinned, and others had a fine layer of powder on the surface, but some satisfactory single crystals were eventually found and studied by I. Rayment (this Department).[422]

UV spectra (conc. sulfuric acid solvent) showed absorptions at: λmax = 356 nm and 248.5 nm , (as for S_3N_2Cl). Extinction coefficients: ε approximately 1×10^3 and 5×10^3 respectively.

(The extinction coefficients could not be accurately determined, due to the small quantities available, but the values are approximately correct for a S_3N_2Cl derivative. The analyses were inconclusive for the same reason). Infrared spectra: the crystals were found to be difficult to mull, and hence a satisfactory spectrum was difficult to obtain, however, the absorptions at ca. 960 (s), 940 (s), 700 (s), and 580 (s) cm^{-1}, indicated that the compound was an S_3N_2Cl derivative.

(ii) Reaction of S_3N_2Cl with HSO_3Cl in liquid SO_2 as solvent

S_3N_2Cl (1.345g) was placed in a schlenk and dry SO_2 (ca. 100 ml. liquid) condensed onto it. (S_3N_2Cl is slightly soluble in liquid SO_2). 0.6 ml. (slight excess) of HSO_3Cl was then added to the stirred mixture under a back pressure of nitrogen. The solution rapidly turned a dark brown colour and a gas was evolved (identified as HCl) showing that a reaction had taken place. The reaction mixture was allowed to stir at -23°C for several hours and then filtered into the other limb of the schlenk. The SO_2 solution was dark coloured and a dark precipitate remained. The SO_2 was then distilled back into the first limb of the schlenk, filtered again, and a few dark crystals were formed in the other limb, on evaporation of the SO_2. This was repeated several times, the SO_2 being used to extract the precipitate from the first limb, filtered into the second limb and then evaporated from there back into the first limb, to deposit a few crystals and to repeat the process once again.

Eventually quite a few crystals had been formed, and there was also no other contaminating solid. The SO_2 was then pumped out of the schlenk and the crystals removed from the schlenk in a dry box.

UV and IR spectra indicated that these crystals were the same as those previously obtained, using pure HSO_3Cl as solvent, however, since most of the crystals were twinned or complex, rather than being single crystals, they were less suitable for x-ray analysis, than those previously obtained.[422] However, the experiment showed that this is an alternative method for preparing the S_3N_2Cl derivative and a different recrystallisation procedure should produce suitable crystals for x-ray analysis.

(D) S_3N_2Cl Discussion

1. Preparative Routes

The reaction of $S_3N_2Cl_2$ with anhydrous formic acid to yield S_3N_2Cl has not been previously reported. The reaction is interesting since in the overall mechanism, the S-Cl bond in $S_3N_2Cl_2$ has been reduced to sulfur, (eliminating chlorine as HCl), and this type of reaction may be of importance in removing other acyclic chlorine atoms attached to sulfur, while leaving the rest of the molecule intact.

The other preparative route, by heating $S_3N_2Cl_2$ in vacuo, has already been discussed. (See Introduction, Page 55).

2. Reactions with Metal Chlorides and with HSO_3Cl

The structure of S_3N_2Cl was unknown, but it was thought that the chlorine may be present as ionic chloride or at least as a polar bonded chlorine which may be replaceable by other more suitable anions. Waddington and Lynch[379] (Durham), have studied $S_3N_2Cl_2$ and S_3N_2Cl by measurements of the chlorine NQR frequencies at 77^oK in the region expected for chlorine covalently bonded to sulfur (13.0 to 44.0 MHZ). For $S_3N_2Cl_2$, signals were detected at 29.02 MHZ for ^{35}Cl and at 22.91 MHZ for ^{37}Cl as expected for the known structure of $S_3N_2Cl_2$[189] which contains a covalent chlorine sulfur bond. In contrast to this, no signal was detected in this region for S_3N_2Cl, implying that the chlorine is essentially ionic. (Completely ionic chlorine would give no signal at all).

(i) Reactions with metal chlorides

The first reactions attempted were based on analogous reactions with S_4N_3Cl and $S_3N_2Cl_2$ where the addition of a chloride ion acceptor ($AlCl_3$ or $FeCl_3$), forms $S_4N_3^+$ MCl_4^- and $S_3N_2Cl^+$ MCl_4^- (M = Al,Fe). These anions are very suitable for x-ray work.[422] The main problem, in the case of S_3N_2Cl, was the choice of a suitable solvent. $SOCl_2$ was found to be unsuitable since S_3N_2Cl is chlorinated by the solvent to $S_3N_2Cl_2$, which then reacts with the metal chloride (chloride ion acceptor), in the normal way to give the $S_3N_2Cl^+$ salt.

The organic solvents, nitrobenzene, acetylchloride, chlorobenzene and carbon tetrachloride were also unsuitable since side reactions appeared to take place with the solvent, probably as a result of reactions taking place between the metal chloride and the solvent and no useful product was obtained. In the case of carbon tetrachloride, no reaction at all occurred.

Liquid sulfur dioxide appears to be the best solvent so far found, since it is an inert solvent in which S_3N_2Cl dissolves slightly without apparent decomposition and aluminium chloride is also soluble without decomposition. The products produced from the reaction of S_3N_2Cl with $AlCl_3$ in liquid SO_2, both at low temperatures and under pressure could be the impure tetrachloroaluminate derivative of S_3N_2Cl but unfortunately the product was not crystalline, and so was unsuitable for x-ray structure determination.

(ii) Reactions with HSO_3Cl

The reactions of S_3N_2Cl with HSO_3Cl to prepare a crystalline derivative were based on the reactions of S_4N_3Cl[268,272] and $S_5N_5^+$ salts (this thesis) with concentrated acids, where HCl is eliminated, and the appropriate anion from the acid, replaces the chloride or chloro-metallate ion; and also on the observation that S_3N_2Cl reacts with concentrated sulfuric acid to eliminate HCl, and to form fairly stable solutions (as determined by UV and visible spectroscopy). Sulfuric acid itself is obviously not a very convenient solvent to use for crystallisation, due to its high boiling point, and high viscosity, although $S_4N_3^+ HSO_4^-$ can be prepared from S_4N_3Cl and concentrated sulfuric acid,[256,266] so that initially at least, chloro-sulfonic acid, HSO_3Cl, was chosen since it has a lower boiling point, is less viscous but is still related to sulfuric acid. $S_4N_3^+ SO_3 Cl^-$ can also be prepared by reaction of S_4N_3Cl with HSO_3Cl,[272] (or SO_3)[273] as can $S_3N_2Cl^+ SO_3Cl^-$ from $S_3N_2Cl_2$ and HSO_3Cl,[280] and it was hoped that a similar derivative could be made from S_3N_2Cl.

HCl was evolved on dissolution both in pure HSO_3Cl and in HSO_3Cl dissolved in liquid SO_2 indicating a reaction of the type:

$$S_3N_2Cl + HSO_3Cl \longrightarrow "S_3N_2\ SO_3Cl" + HCl$$

(the derivative having a tentative formulation only).

The crystals obtained from both the reaction with pure HSO_3Cl, and in liquid SO_2, appeared chemically identical, (based on the UV and visible spectra, which was the main method of identification used), but the former crystals were more suitable for the x-ray work, since many were single crystals, whereas in the latter case, they were complex or twinned.[422] This was probably due to the different methods of crystallisation. Liquid SO_2 is a good solvent for washing the crystals free of excess HSO_3Cl. A small quantity of powdered material was observed on the surface of the crystals, but this did not seriously affect the x-ray analysis.[422]

3. Crystal Structure of the S_3N_2Cl/HSO_3Cl Derivative

The crystal structure of the S_3N_2Cl/HSO_3Cl derivative was obtained by I. Rayment and H.M.M. Shearer (Durham) on a single crystal of the compound.[423] Despite the difficulties in preparation, handling, and possible impurities on the crystal itself, good x-ray diffraction patterns were obtained, since sulfur in both the anion and cation, gave a large number of reflections,[422] so that the anion was not wholly unsuitable.

The crystals were triclinic[423] with unit cell dimensions: a = 7.689, b = 10.726, c = 6.614 Å, α = 101.00°, β = 114.43°, γ = 90.35°, space group $P\bar{1}$, with N = 2. The intensity data were collected on a four circle diffractometer using Zr-filtered Mo radiation to a limit of θ = 25°. A total of 1707 reflections were recorded and of these 1337 reflections were considered to be observed having net counts $\geqslant$ 3 esd's. The structure was solved using the Patterson function and refined by full matrix least squares methods. The final R-value was 0.031 for the observed reflections.[422,423]

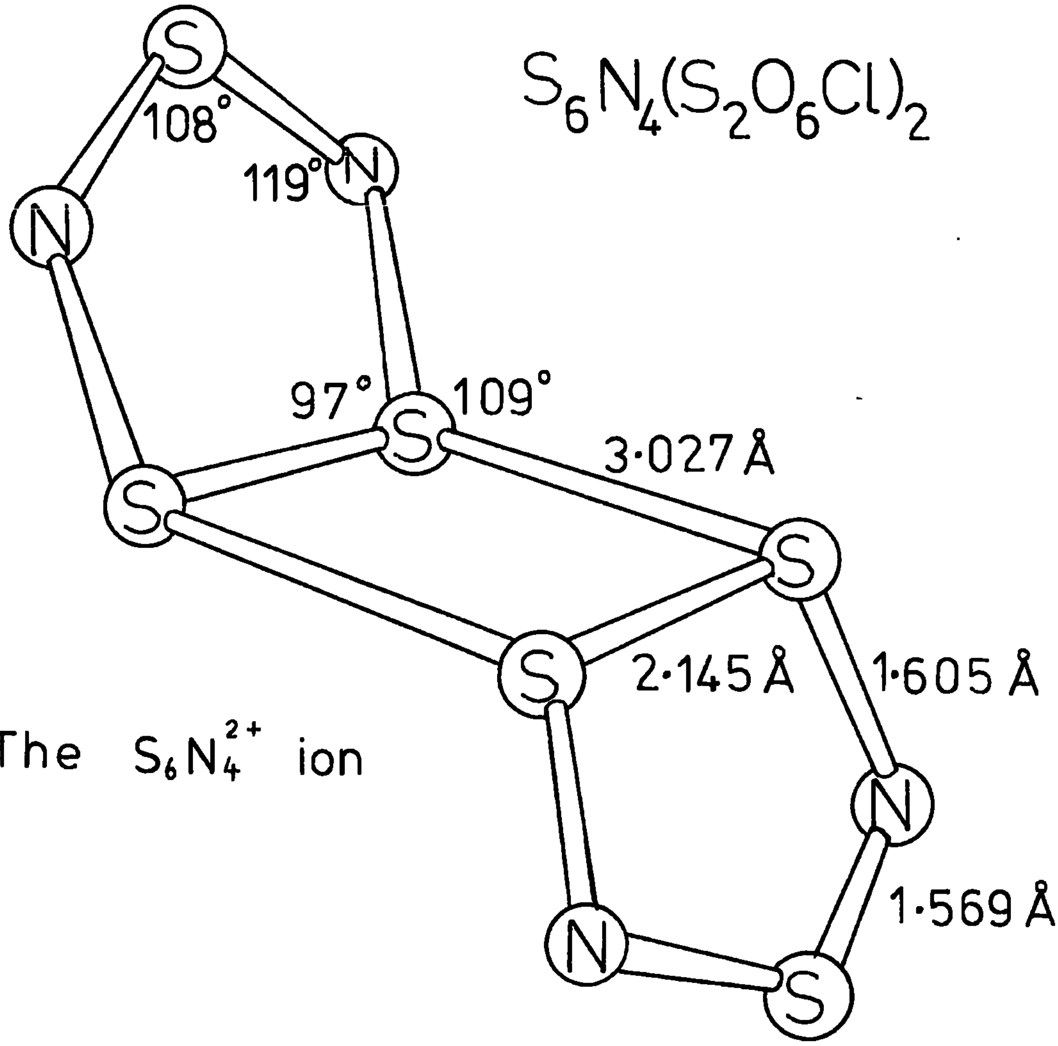
The structure consists of two planar five membered S_3N_2 rings in parallel planes in which the S-S distance (2.145 Å) and the mean SN distance (1.587 Å) are the same as in $S_3N_2Cl_2$,[189] which is a π delocalised SN ring. There are, however, two distinct SN distances (mean values 1.569 Å and 1.605 Å). The S_3N_2 rings which lie in parallel planes 2.884 Å apart are separated from each other by S-S distances of 3.027 Å, which is shorter than the Van der Waal's diameter for sulfur (ca. 3.70 Å)[140] and is in the same region as found for cross ring interactions in S_8^{2+}, [101,103,193] where the short cross-ring distances were interpreted as resulting from multicentre bonding.[101]

Each ring is closely associated with a $ClS_2O_6^-$ ion. (Therefore the anion is $ClS_2O_6^-$ (chlorodisulfate) and not $ClSO_3^-$ (chlorosulfonate) as had been expected).

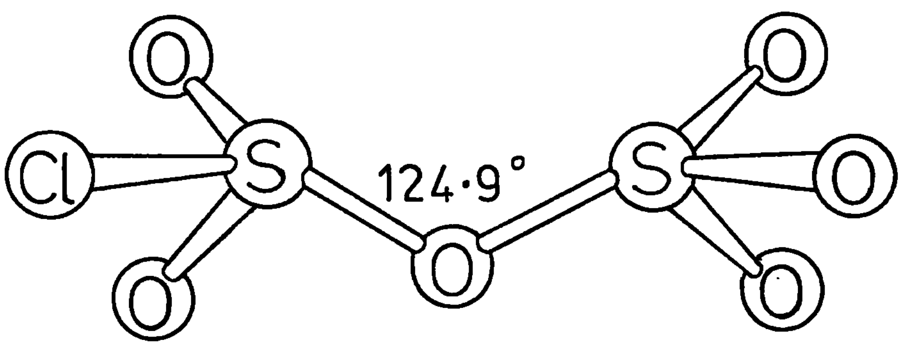
The isolated S_3N_2 rings are of C_{2v} symmetry within the limits of experimental error, and pairs of S_3N_2 rings are related to each other by a centre of symmetry. (Figure 7.1)

In the anion $ClSO_3 \cdot O \cdot SO_3^-$, the S O bridge distances are 1.552 and 1.718 Å, the shorter distance involves the sulfur atom attached to chlorine. The terminal S O distances lie between 1.396 and 1.438 Å, and the S Cl distance is 1.986 Å. All the terminal oxygen atoms approach closely (in the range 2.68 - 3.04 Å) the sulfur atoms of the cations (Figure 7.1) which is within the sum of the Van der Waal's radii for sulfur and oxygen atoms (ca. 3.25 Å [140]), indicating interaction between these atoms.

Figure 7.1



(i) The $S_6N_4^{2+}$ ion



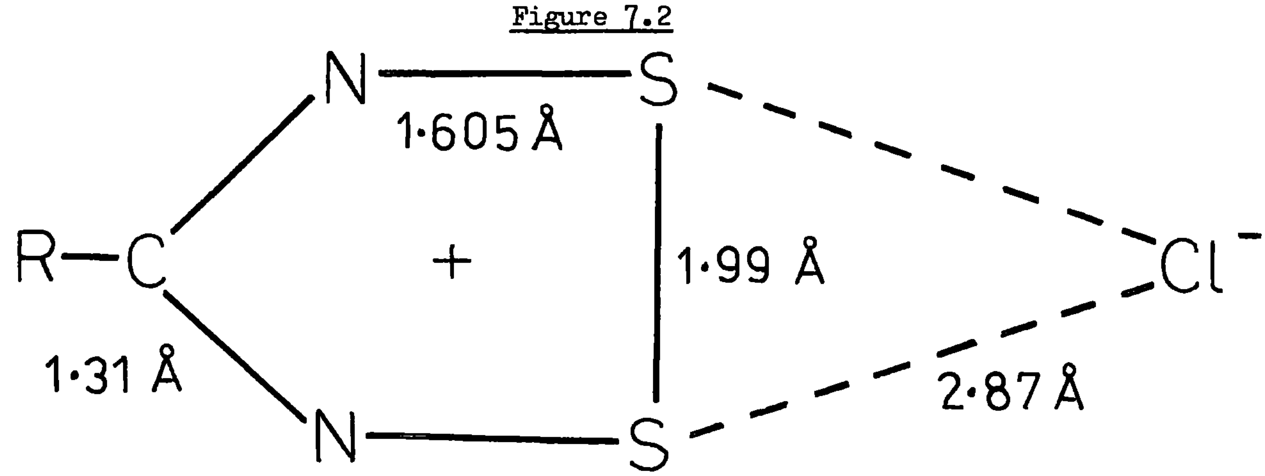
(ii) The $S_2O_6Cl^-$ ion

4. Discussion of Structure

The compound may be formulated either as $S_3N_2S_2O_6Cl$, or as $(S_3N_2^+)_2$ $2\ S_2O_6Cl^-$, emphasising the interaction that exists between pairs of S_3N_2 rings. However, theories that S_3N_2Cl may contain the $S_6N_4^{2+}$ cation and be $S_6N_4^{2+}\ 2\ Cl^-$,[9,113] are now unlikely since S_3N_2Cl probably has a similar structure to the chlorodisulfate derivative. (See later discussion). The $S_6N_4^{2+}$ cation, if cyclic and planar, would be another member of the "electron-rich aromatic" series, being a 14π electron system.

The formation of the $S_2O_6Cl^-$ anion, rather than the SO_3Cl^- ion is understandable when one considers that it is formed merely by the addition of SO_3 to SO_3Cl^-,[424] and that HSO_3Cl (equivalent to SO_3 + HCl) loses HCl on heating;[382] (the chlorodisulfate is presumably less soluble than the chlorosulfate in chlorosulfonic acid). It is the first time that the crystal structure of this anion has been reported. The interaction of anion and cation is characteristic of several other sulfur-nitrogen compounds. For example, in the case of the compounds: $R\text{-}CN_2S_2^+Cl^-$ (R = Bu^t, CCl_3, Ph) which consist of a five membered CN_2S_2 ring, with an exocyclic R group on carbon and carrying a positive charge, there is considerable interaction between the chloride ion and the two sulfur atoms (S-Cl distance =2·87 Å) forming almost a three centre bond.[418,420] (Figure 7.2)

Figure 7.2



RCN_2S_2Cl

The structure of the S_3N_2 cation is particularly interesting:

Because charges must balance, S_3N_2 must carry a single net positive charge, i.e. $S_3N_2^+$. Since the cation is planar and stable, it is reasonable to assume that there is considerable aromatic π-bonding, of the type already observed for electron-rich aromatic species such as $S_4N_3^+$ and $S_5N_5^+$, which are also almost planar. $S_3N_2^+$, as formulated, however, has 7π electrons, and therefore to achieve an aromatic 6π system, a further electron has to be lost from the ring. This could be done, by pairing this odd electron with the corresponding odd electron of an adjacent $S_3N_2^+$ ring, to form a four atom-two electron bond between the two pairs of adjacent sulfur atoms of the rings. Therefore, the observed structure consisting of two planar, interacting rings, may be due to the formation of such a bond between them. Although sulfur-sulfur interactions are fairly common in sulfur-nitrogen chemistry, between sulfur atoms not bonded by a common σ-bond, they are usually lone-pair type interactions, and this would be a unique example of an interaction involving sulfur atoms in adjacent ring systems, and using electrons eliminated from these rings, on their achieving an aromatic (6π) electronic structure. (See Figure 7.3).

Alternatively, the odd electron in each ring may remain unpaired rather than take part in multicentre bonding and in this case the close approach of the rings may merely be due to crystal packing. One obvious way to determine which of these two possible electronic structures is correct, would be to determine whether the crystal was diamagnetic or paramagnetic; diamagnetism would indicate that all the electrons are paired, and hence implying the former electronic structure, whereas paramagnetism would show the presence of unpaired electrons and would support the latter electronic structure. Magnetic moment measurements on S_3N_2Cl show that it is diamagnetic,[422] and this is therefore strong evidence for the former structure being correct. (i.e. Two aromatic 6π S_3N_2 rings, with four centre, two electron bonding between pairs of rings). Although it is possible that S_3N_2Cl and $S_3N_2S_2O_6Cl$ may have different structures, the following physical and chemical properties of S_3N_2Cl and $S_3N_2S_2O_6Cl$ suggest that they are of similar structure:

(i) Both compounds have an essentially identical electronic spectrum when dissolved in concentrated sulfuric acid, suggesting that the same cation is present in both compounds (i.e. $S_6N_4^{2+}$). The fact that an electronic spectrum is observed in the region studied (200 to 700 nm) means the existence of low lying vacant electronic orbitals, which in turn suggests $\pi \longrightarrow \pi^*$ electronic transitions and hence π-bonding.

(ii) S_3N_2Cl is insoluble or reacts with most solvents so far used (except Me_2SO in which it is freely soluble,[422] and liquid SO_2 in which it is only slightly soluble). It is also involatile in not having a melting point but decomposing in vacuo at 120° to 140°.[249] These properties suggest either an ionic or a polymeric structure, and it is possible that, in S_3N_2Cl itself, the S_3N_2 rings are interacting via multi-centre bonds in groups greater than two, and that the rings may be in "ladder formation" with the multi-centre bonding holding them together. (Figure 7.5) The smaller size of the Cl^- ion compared to the $S_2O_6Cl^-$ ion would help the rings to come closer together and it is probable that the Cl^- ions are closely associated with the S_3N_2 rings with sulfur-chlorine interactions.

(iii) Chlorine NQR measurements indicate that the chlorine in S_3N_2Cl is ionic.[379]

(iv) $S_3N_2Cl_2$ and S_3N_2Cl are easily interconvertible and also S_3N_2Cl is easily converted into the $S_2O_6Cl^-$ derivative, (Figure 7.4) and since $S_3N_2Cl_2$[189] and $S_3N_2S_2O_6Cl$ consist of a five membered S_3N_2 rings, it is reasonable to suggest that S_3N_2Cl does also.

Figure 7.3

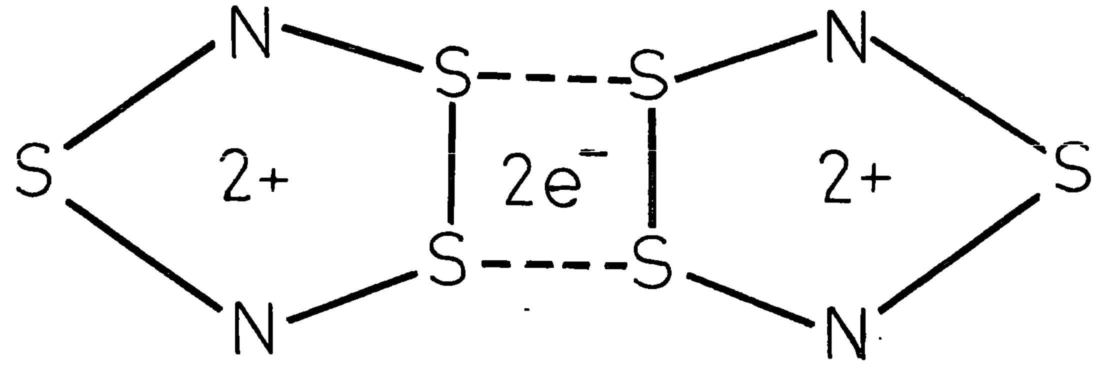


Figure 7.4

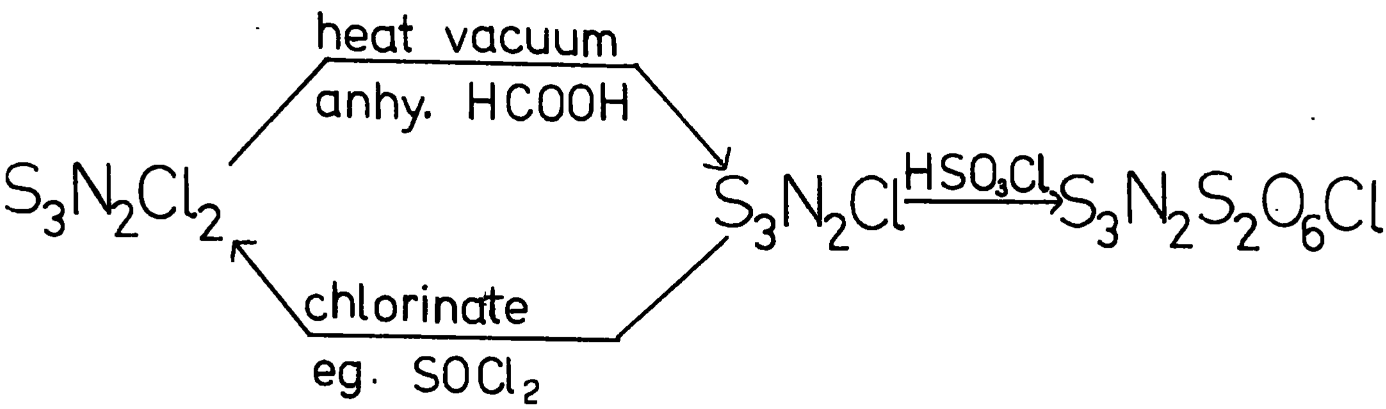
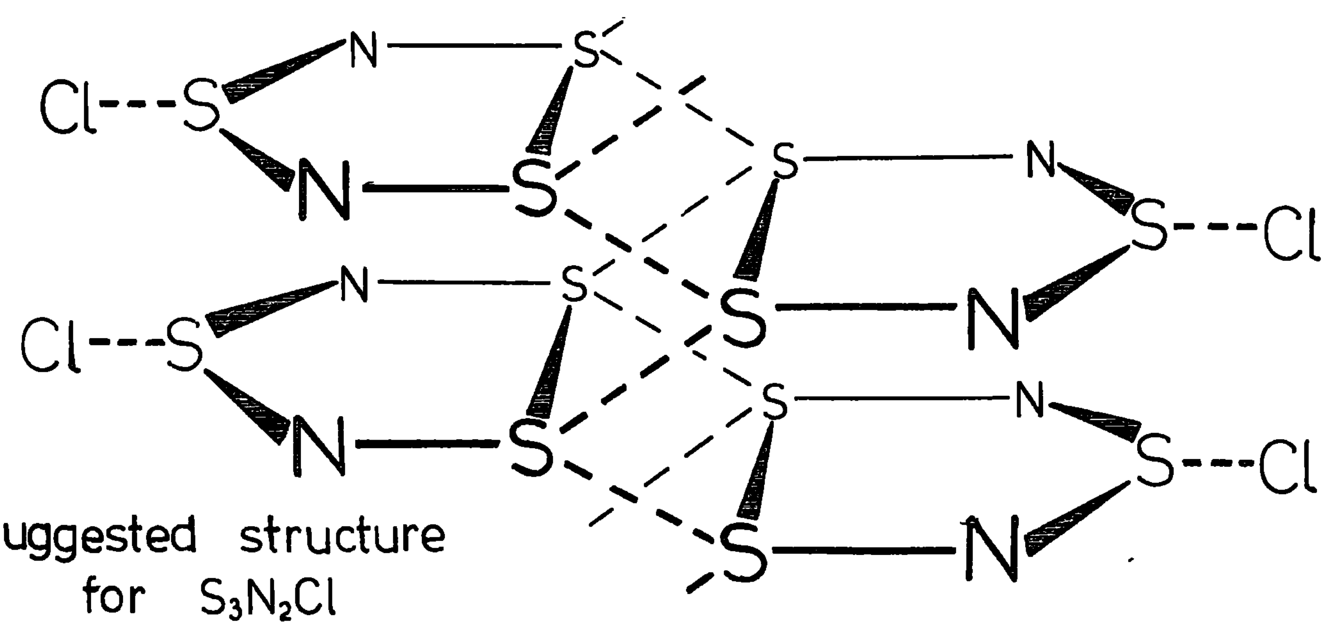


Figure 7.5



Suggested structure for S_3N_2Cl

(v) The $S_2O_6Cl^-$ derivative is easily made from S_3N_2Cl and HSO_3Cl, and by analogy with similar reactions of S_4N_3Cl,[272] this can be regarded as displacement of the chloride ion in S_3N_2Cl, by the SO_3Cl^- anion, evolving HCl, the $S_2O_6Cl^-$ anion being subsequently formed by interaction with further HSO_3Cl.

i.e. (i) $S_3N_2Cl + HSO_3Cl \longrightarrow S_3N_2\ SO_3Cl + HCl$

(ii) $S_3N_2\ SO_3Cl + HSO_3Cl \longrightarrow S_3N_2S_2O_6Cl + HCl$

(HSO_3Cl also loses HCl on heating[382])

This again implies that the S_3N_2 ring remains intact throughout the reactions.

(vi) $S_3N_2Cl_2$ and S_3N_2Cl show close similarities in their infrared spectra, indicating similarities in structure (see spectra in Appendix).

The $S_2O_6Cl^-$ (chlorodisulfate) anion, has only been known since 1962 when it was observed in solutions of SO_3 in chlorosulfonic acid.[424] Alkali metal, aluminium, ammonium, and substituted ammonium salts of $S_2O_6Cl^-$ and related anions, have been prepared, using SO_2 as solvent under vigorously anhydrous conditions.[425] Na S_2O_6Cl has been prepared from NaCl, SO_2 and SO_3 as a white crystalline hygroscopic solid and other metal chlorodisulfates by the action of thionyl chloride on metal sulfates and disulfates.[426]

The decomposition reactions of Na S_2O_6Cl to form mainly Na SO_3Cl and SO_2 and its reactions with $NaNO_3$, N_2O_4 and water to form Na S_2O_7, Na NOS_2O_7 and Na HS_2O_7 respectively, have been studied,[427] as have the reactions of the $S_2O_6Cl^-$ anion as an O^{2-} donor or acceptor.[428] With an O^{2-} donor, $S_2O_6Cl^-$ reacts:

$$S_2O_6Cl^- + O^{2-} \longrightarrow S_2O_7{}^{2-} + Cl^-$$

and with a strong O^{2-} acceptor, in the presence of SO_3:

$$S_2O_6Cl^- \longrightarrow S_2O_5Cl^+ + O^{2-}$$

The $S_2O_6Cl^-$ anion contains an S-O-S bridge[427] as shown by its chemical properties. The characteristic vibrational frequencies of the $S_2O_6Cl^-$ anion have been assigned.[429,430]

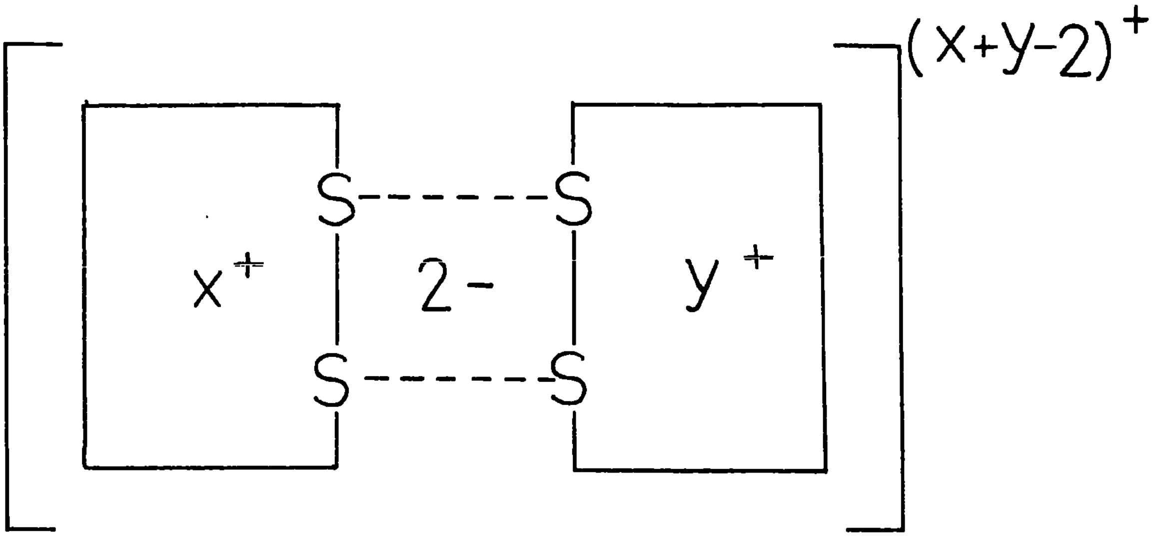
The crystal structure of the anion shows that this oxygen bridge is assymmetric. The bridge S-O distance involving the sulfur atom attached to oxygen only, is also unusual, being remarkably long (1.718 Å). It is a rare example of an SO bond longer than the "single bond" distance calculated from either Pauling's covalent radii (1.70 Å)[431] or from the Schomaker-Stevenson rule (1.69 Å).[432] The other S-O bridge distance (1.552 Å) can be compared with that in $HO-SO_3^-$ (1.56 Å in $KHSO_4$[433]) and $CH_3O-SO_3^-$ (1.58 Å)[434]. The terminal SO distances (1.396-1.438 Å) are close to those in the disulfate ion $S_2O_7^{2-}$ (mean SO = 1.437 Å).[435] The SCl distance (1.986 Å) is similar to those in S_2Cl_2 (1.99 Å)[436] and SO_2Cl_2 (2.011 Å),[437] so that these last bond distances are normal for the types of bonds involved.

The $S_2O_6Cl^-$ anion is closely packed around the S_3N_2 cation with the chlorine atom in the same plane as the S_3N_2 ring, and several of the oxygen atoms sufficiently close to the sulfur atoms of the ring, for interactions to occur.

$S_3N_2S_2O_6Cl$ is the first derivative of S_3N_2Cl to have been prepared and characterised and it is also the first time that the structure of the $S_2O_6Cl^-$ anion has been determined by x-ray diffraction and the first time that this anion has been paired with a cation other than a metal, ammonium or substituted ammonium. This is particularly unusual, since the cation S_3N_2 was previously unknown.

Another important aspect of the x-ray results is that it indicates that other 1,2-dithiolium cations could link up through multicentre bonds. The $S_6N_4^{2+}$ cation may be the archetype for a whole series of new compounds, of the type:[113] (Figure 7.6)

Figure 7.6



WORK CARRIED OUT AT STAVELEY CHEMICALS LIMITED

CHAPTER 8

Work Carried out at Staveley Chemicals Limited

(A) Introduction

As part of the research (CAPS) award, three months between the 3rd July and 29th September, 1972, were spent in full-time employment at Staveley Chemicals Limited. The work undertaken was an investigation into the mercury emission on the Chlor-Alkali Plant and included recommendations of methods of reducing mercury losses.

The following section is a summary of the work carried out on the plant during this period. The results obtained formed the basis of the Staveley Chemicals Limited reply to the questionnaire on mercury emission issued by the Bureau International Technique du Chlore to its member companies, and also constituted an internal report to Staveley Chemicals Limited.

The Chlor-Alkali Plant produces caustic soda, chlorine and hydrogen from the electrolysis of brine, using a moving mercury cathode (Hoechst-Uhde mercury cell). The project was concerned with the losses of this mercury to the environment in various forms.[438,439]

The results obtained showed that the mercury lost in the products (chlorine, sodium hydroxide and hydrogen), the brine solution and the cell itself, was approximately a quarter of the total loss of the plant. A similar quantity of mercury was recovered from catchpots within the cell room. Small quantities of mercury (3-4% of total loss) were found in the effluent from the plant. It was estimated that the major mercury emission arose from mechanical losses associated with spillages, etc. in the plant.

(B) Experimental

The mercury losses were determined experimentally using various techniques according to the nature of the material under examination. These were typified by:

1. Air Sampling

Air was sampled for mercury content by passing it through a Hendry Relay meter. The metal concentration was continuously determined through its absorption in the ultraviolet and directly recorded on a dial. This relay meter would not function in the presence of large quantities of water vapour, (e.g. in the brine saturation pit), and for such determinations other methods had to be used.

2. Hydrogen Sampling

The hydrogen produced by the cell contains mercury vapour, most of which is retrieved in catchpots situated in the hydrogen line and returned to the cells. The amount of mercury remaining in the product hydrogen was determined by passage of the gas through acidified potassium permanganate solution. The mercury content of the latter solution was determined by atomic absorption spectrophotometry. After passing through the potassium permanganate solution the gas was dried using concentrated sulfuric acid and the volume measured using a flow meter. (The flow meter required dry gas for reliable readings).

3. Sodium Hydroxide Sampling

The sodium hydroxide produced in the cell runs over the surface of hot mercury agitated by hydrogen evolution, and therefore contains some dissolved and suspended mercury. Some of this mercury is trapped out in catchpots, but the remainder contaminates the product. The mercury content of this product sodium hydroxide solution was determined using atomic absorption spectrophotometry.

4. Chlorine Sampling

The chlorine gas was initially passed through a chlorine flow meter, and then through two Dreschel bottles containing sodium hydroxide solution. The chlorine was absorbed and the solution analysed as before for mercury content.

5. Sampling in Brine Saturation Pit

The method used was similar to that used for the sampling on the hydrogen line, since the Hendry relay meter could not be used. The apparatus was set up at various points in and around the brine saturation pit and a known volume of air was pulled, by use of a calibrated aspirator, through a series of three Dreschel bottles containing acidified potassium permanganate solution. The mercury content of the resulting permanganate solution was determined as previously indicated.

6. Brine Sampling

Samples of brine were taken at various points along the brine circuit, and their mercury content determined by atomic absorption spectrophotometry.

7. Graphite Anode Sampling

The graphite anodes tend to absorb mercury from the cell although they are not in direct contact with the metal. The anodes gradually wear away, through the action of electrolysis and the resulting graphite particles are filtered off in the brine filtration tanks. The mercury content from this and other sources in the brine filter residues were estimated by allowing the filter residues to form a homogeneous suspension with the water in the tank (a suspension was obtained by agitation using compressed air) and then scooping out a sample. The mercury content of this sample, after addition of potassium permanganate solution was determined by atomic absorption spectrophotometry.

The used graphite anodes themselves were also sampled for mercury content.

8. Waste Water Sampling

The waste water effluent from the plant, before treatment, was sampled at hourly intervals on various days, the mercury content again being estimated by atomic absorption spectrophotometry.

9. Accidental Losses

Various catchpots on the plant are used to recover mercury either lost by accidental spillage or contained in the crude product lines. The mercury in these pots was recovered and weighed, and the losses through accidental spillages estimated. The mercury recovered can be re-used after purification. The losses of mercury through waste scrap were also estimated.

(C) Results

The mercury losses from products, brine, graphite anodes and air, accounted for approximately a quarter of the total loss of the plant, whereas the major source of mercury emission arose from mechanical losses associated with spillages, etc., in the plant, and accounted for a little over half the total loss of mercury.

The losses of mercury through waste effluent were estimated to be between three and four per cent of the total mercury loss. This result was rather lower than expected, and may be due to sampling errors, dilution effects, or from the fact that the average flow rate of waste water from the plant was an estimate, and not an absolute determination.

The remaining mercury loss (the difference between known usage and mercury losses which were experimentally determined as above) amounted to about 16% of the total loss. It is believed that this discrepancy can be accounted for by:

(i) Errors in estimating mercury losses from the various sources, particularly those relating to mechanical losses, spillage, etc. in the plant, which are large, and very difficult to determine accurately, since the mercury is lost in the defects in the building or is trapped in the piping and machinery of the plant, or becomes contaminated with oil and dust and hence is unrecognisable as the metal.

(ii) Unidentified losses not yet characterised.

(iii) Random fluctuations on the plant increasing the error in the determination of mercury losses, since results were averaged out on a weekly basis.

(iv) Total loss is based on the "make-up" value. (Amount added to cells to maintain their mercury content), rather than the mercury actually known to be lost.

(D) Conclusion

It was felt that the main sources of loss were identified, and the results obtained were valid within the limits of the experimental methods which could be used. The overall results obtained were used both by Staveley Chemicals Limited in their reply to the questionnaire on mercury emission issued by the Bureau International Technique du Chlore to its member companies, and as an indication of areas in which improvements could be made to decrease future mercury emissions on the plant.

APPENDIX

CHAPTER 9

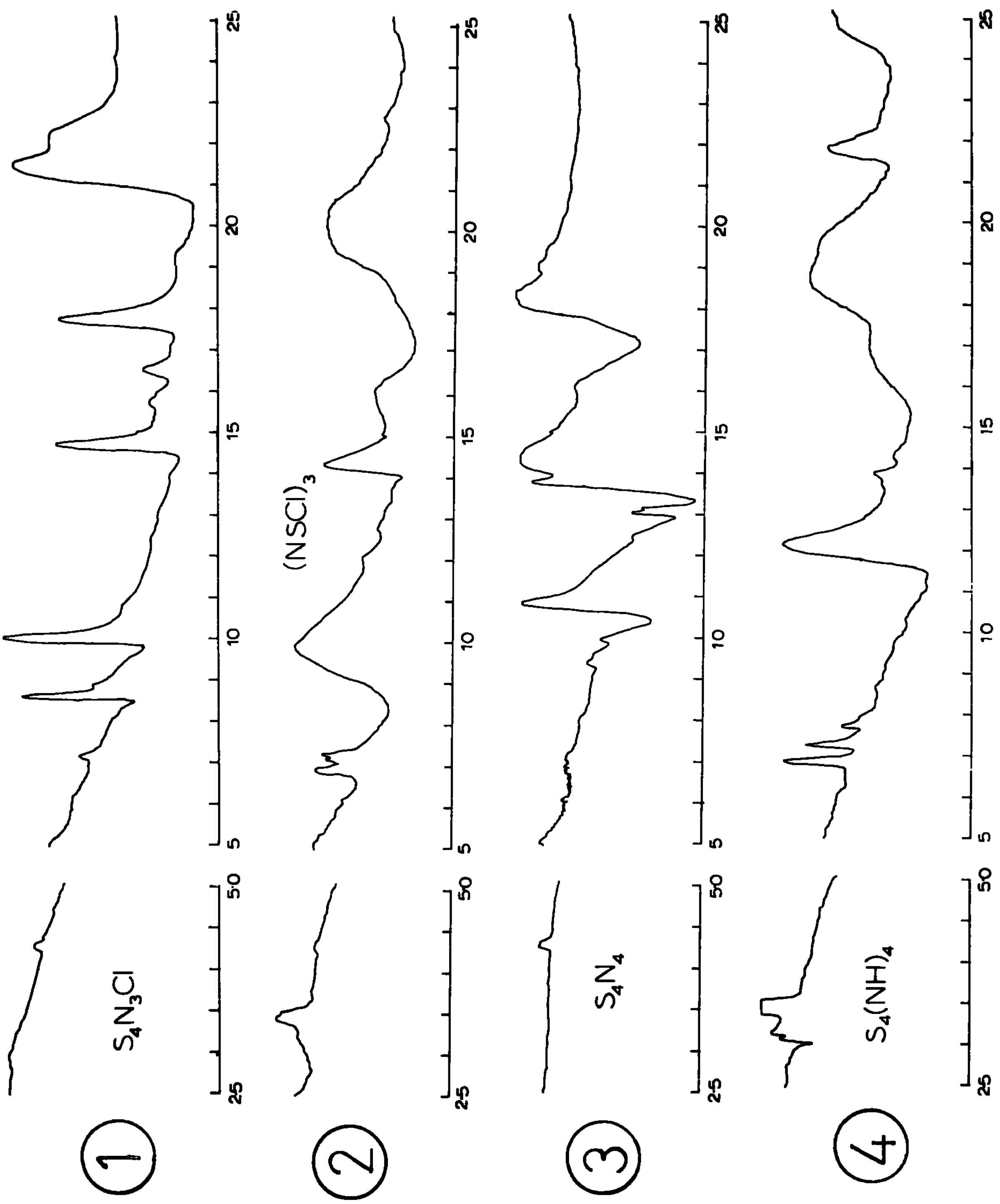
APPENDIX

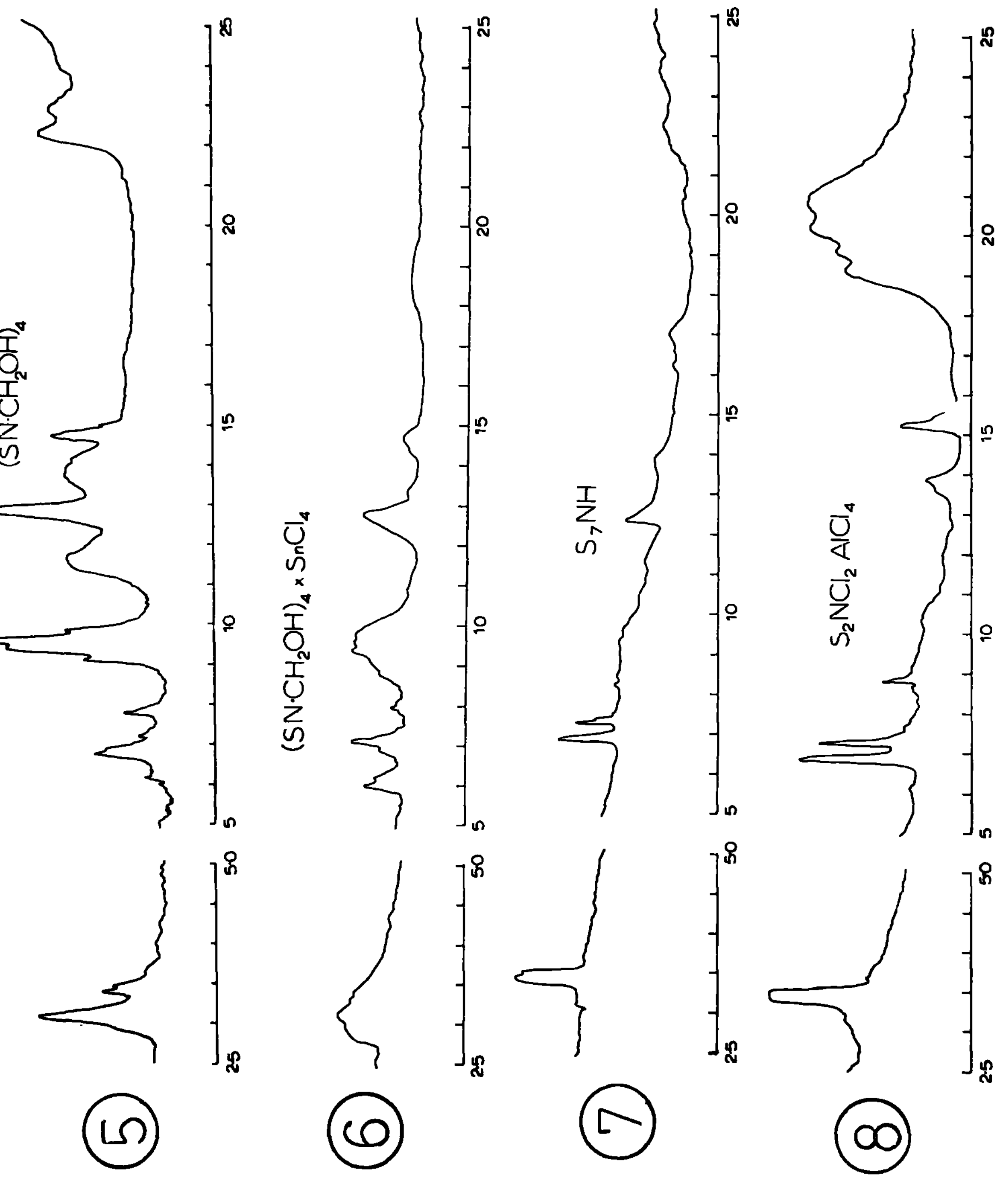
(A) Spectra

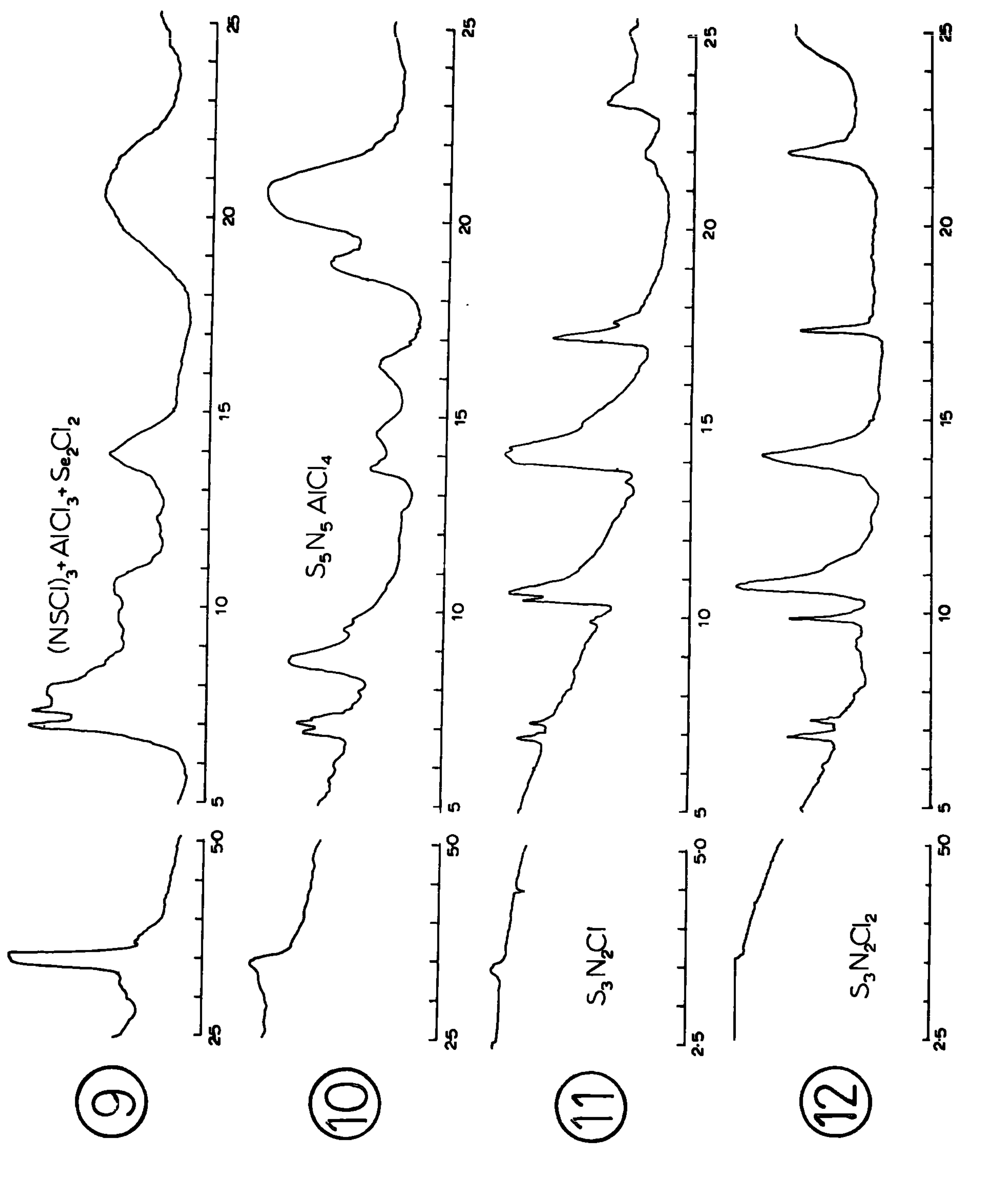
1. Infrared Spectra

Some of the infrared spectra of compounds referred to in this thesis are reproduced here. All the spectra were recorded with samples in the form of nujol mulls (apart from those of S_4N_3Cl, S_4N_4, $(SN.CH_2OH)_4$ and $(SN.CH_2OH)_4$,x $SnCl_4$, which were made up as KBr discs). The main absorptions of nujol being: 2900 (vs), 2857 (sh), 1471 (s), 1389 (s) cm^{-1}. 3.45 (vs), 3.5 (sh), 6.8 (s), 7.2 (s) microns (μ). The wavelengths of the spectra are calibrated in microns. (Microns and cm^{-1} are inversely proportional to each other: x microns = $^{10^4}/x\ cm^{-1}$). 1 micron = 10^{-6}m = 10^{-4} cm.

Index of Infrared Spectra


1
S$_4$N$_3$Cl
2
(NSCl)$_3$
3
S$_4$N$_4$
4
S$_4$(NH)$_4$
2·5
5·0
5
10
15
20
25

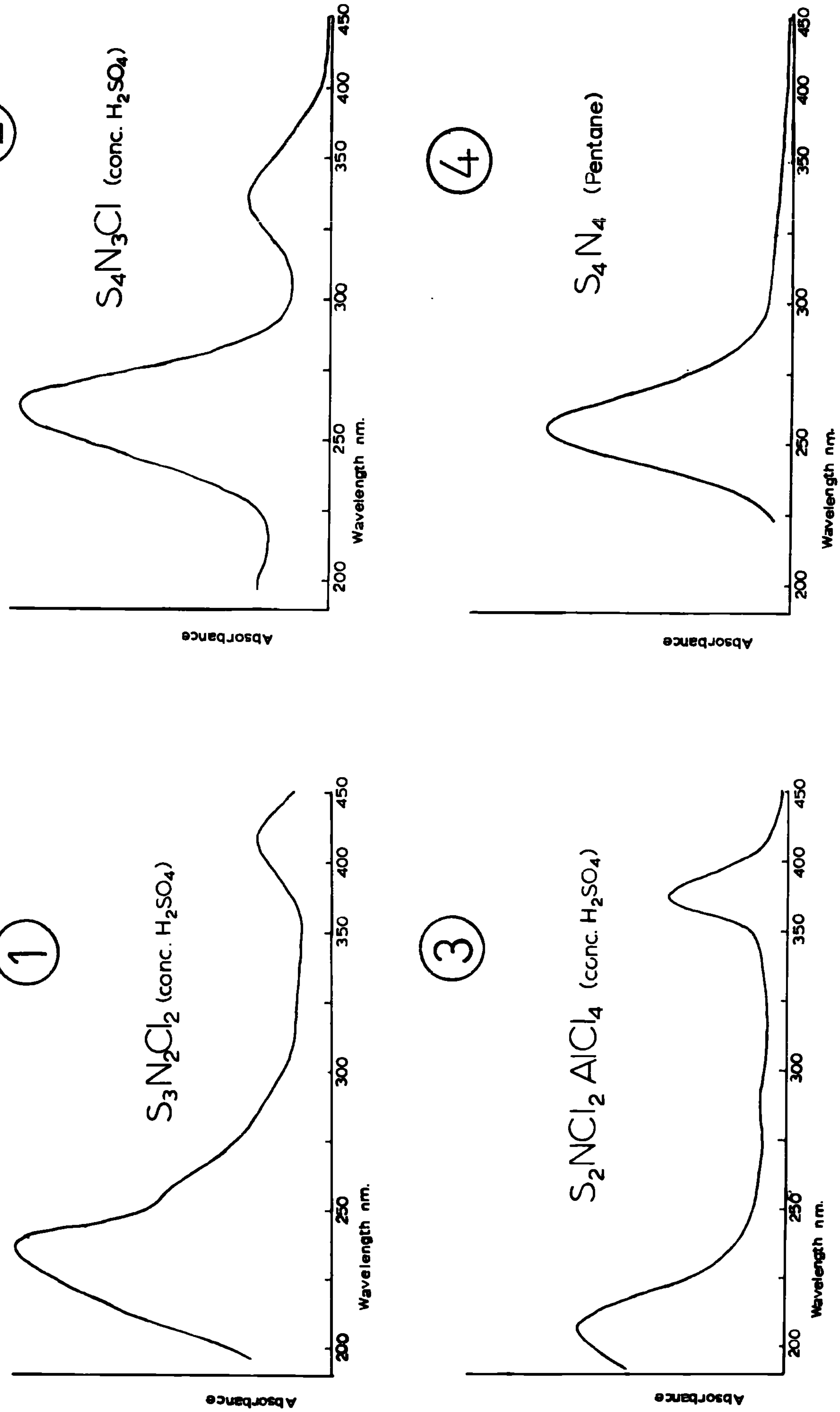

5
$(SN \cdot CH_2OH)_4$
6
$(SN \cdot CH_2OH)_4 \times SnCl_4$
7
S_7NH
8
$S_2NCl_2 AlCl_4$
2·5
50
5
10
15
20
25

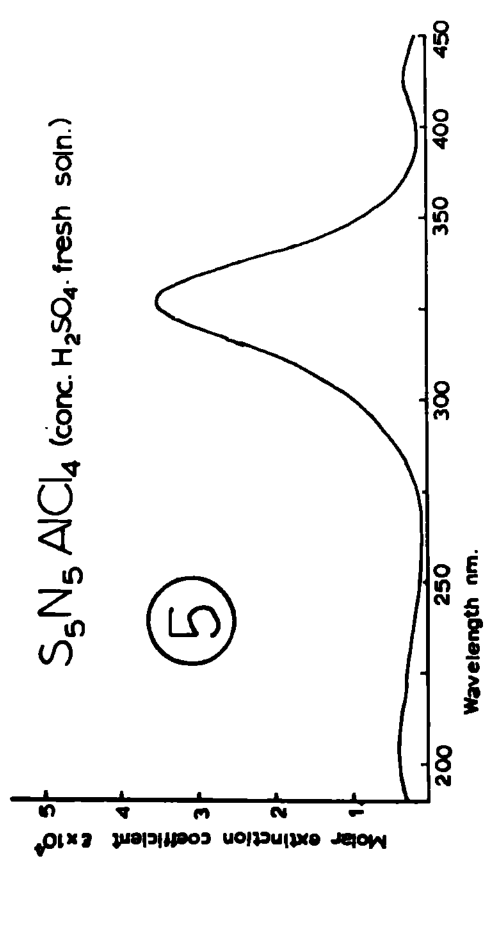

9
(NSCl)3 + AlCl3 + Se2Cl2
10
S5N5 AlCl4
11
S3N2Cl
12
S3N2Cl2

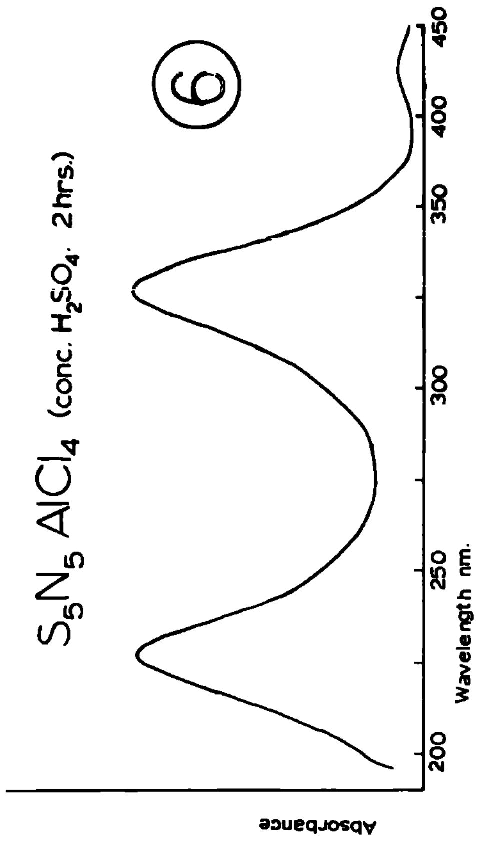
2. Ultraviolet Spectra

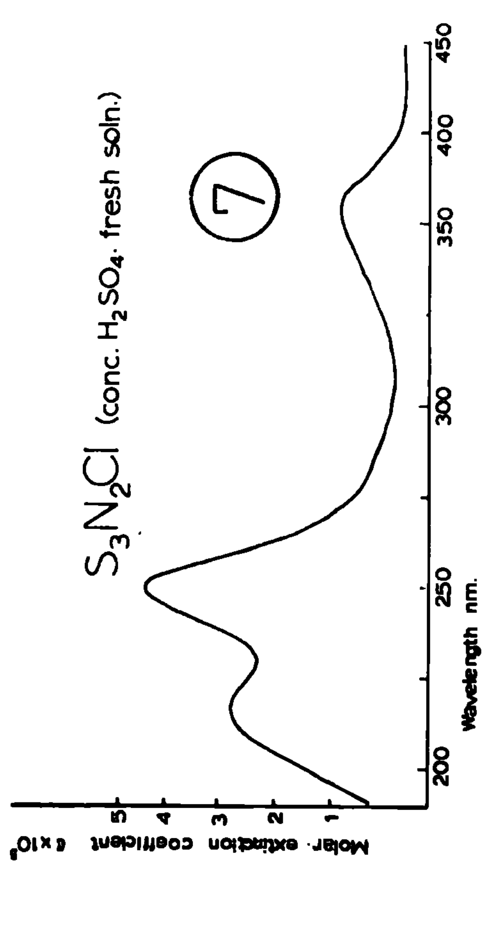
All spectra were recorded as described in the experimental section and except for S_4N_4, the spectra were recorded using concentrated sulfuric acid as the solvent. The spectra were recorded between the wavelengths 190 to 700 nm, but in every case there were no absorptions above 450 nm, so that this part of the spectra was omitted. The vertical (y) axis is calibrated in molar extinction coefficient (ε) in some cases, but in others this is not possible due to the slow decomposition or sparing solubility of the compound used. In these cases absorbance (directly proportional to molar extinction coefficient) is used.

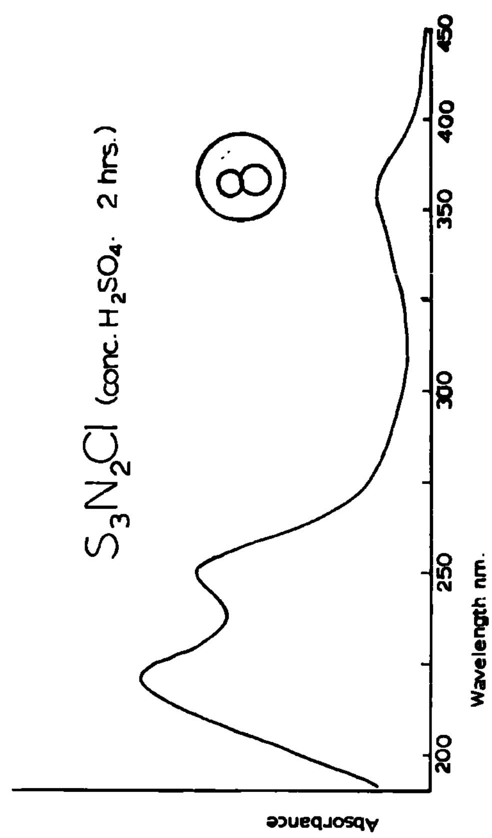
Index of Ultraviolet Spectra


1
$S_3N_2Cl_2$ (conc. H_2SO_4)
2
S_4N_3Cl (conc. H_2SO_4)
3
$S_2NCl_2\,AlCl_4$ (conc. H_2SO_4)
4
S_4N_4 (Pentane)
Absorbance
Wavelength nm.
200
250
300
350
400
450


$S_5N_5\,AlCl_4$ (conc. H_2SO_4· fresh soln.)
5
Molar extinction coefficient ε x10⁴
Wavelength nm.
200 250 300 350 400 450
1 2 3 4 5


$S_5N_5\,AlCl_4$ (conc. H_2SO_4· 2hrs.)
6
Absorbance
Wavelength nm.
200 250 300 350 400 450


S_3N_2Cl (conc. H_2SO_4· fresh soln.)
7
Molar extinction coefficient ε x10⁴
Wavelength nm.
200 250 300 350 400 450
1 2 3 4 5


S_3N_2Cl (conc. H_2SO_4· 2 hrs.)
8
Absorbance
Wavelength nm.
200 250 300 350 400 450

3. Mass Spectra

The mass spectra of many of the compounds prepared were recorded. Normally, the compounds had to be heated above their decomposition points to obtain a sufficiently high vapour pressure, and so parent peaks are either weak or absent.

The peak due to SN^+ (mass = 46) was generally very strong, and is characteristic of sulfur-nitrogen compounds in general,[132] and so intensities were measured relative to SN = 100%.

Peaks of intensity greater than 10% were recorded, unless they were known to be definitely spurious, and peaks less than 10% were ignored, unless their probable designation was known. The reason for this was that spurious peaks are often caused by contamination of the probe by the residues of compounds from other workers, for instance, a peak of mass 69 (impossible for N and S only) was often noted. This was due to CF_3 fragments from the fluorocarbons of other workers, and was therefore ignored. In general such peaks were less than 10% of the intensity of the SN peak.

All designations are for unipositive ions unless otherwise indicated.

(i) Electron rich aromatic rings

(a) $S_3N_2Cl_2$

Mass of Peak	Designation	Relative Intensity
32	S and O_2	154
35	^{35}Cl	21
36	$H^{35}Cl$	23
37	^{37}Cl	9.0
38	$H^{37}Cl$	7.6
46	SN	100
48	?	40

Mass of Peak	Designation	Relative Intensity
62	$S_3N_2^{2+}$?	10
63	?	80
64	S_2 and SO_2	47
78	S_2N	27
80	?	15
92	S_2N_2	87
124	S_3N_2 ?	1.3

(b) $S_3N_2Cl^+ AlCl_4^-$

Mass of Peak	Designation	Relative Intensity
32	S and O_2	20
35	^{35}Cl	45
36	$H^{35}Cl$	236
37	^{37}Cl	10
38	$H^{37}Cl$	100
46	SN	100
48	?	75
63	?	45
64	S_2 and SO_2	170
76	$S_3N_4^{2+}$?	25
78	S_2N	38
94	?	20
113	S_2NCl^{35}	36
115	S_2NCl^{37}	12
140	?	45

(c) S_4N_3Cl

Mass of Peak	Designation	Relative Intensity
32	S and O_2	50
35	^{35}Cl	20
36	$H^{35}Cl$	70
37	^{37}Cl	5
38	$H^{37}Cl$	25
44	?	10
46	SN	100
64	S_2 and SO_2	30
76	$S_3N_4^{2+}$?	20
78	S_2N	10
92	S_2N_2	20
124	S_3N_2	10
170	S_4N_3	3

(d) $S_5N_5\ AlCl_4$

Mass of Peak	Designation	Relative Intensity
32	S and O_2	95
35	^{35}Cl	43
36	$H^{35}Cl$	195
37	^{37}Cl	15
38	$H^{37}Cl$	70
46	SN	100
48	?	40
62	$S_3N_2^{2+}$?	20
63	?	70
64	S_2?, SO_2	40
76	$S_3N_4^{2+}$?	24

Mass of Peak	Designation	Relative Intensity
78	S_2N	30
92	S_2N_2, $S_4N_4^{2+}$?	100
124	S_3N_2 ?	5
138	?	85
184	S_4N_4	28
230	S_5N_5 ?	6.5

(e) $S_5N_5\ FeCl_4$

Mass of Peak	Designation	Relative Intensity
32	S and O_2	15
35	^{35}Cl	8.5
36	$H^{35}Cl$	50
37	^{37}Cl	3.0
38	$H^{37}Cl$	17
46	SN	100
48	?	10
76	$S_3N_4^{2+}$?	15
78	S_2N	26
81	NS ^{35}Cl	10
84	?	20
92	S_2N_2, $S_4N_4^{2+}$?	100
124	S_3N_2	12
138	?	30
140	?	10
184	S_4N_4	7.5
230	S_5N_5	7.5

(f) S_5N_5 $SbCl_6$

Mass of Peak	Designation	Relative Intensity
32	S and O_2	20
35	^{35}Cl	27
36	$H^{35}Cl$	128
37	^{37}Cl	9
38	$H^{37}Cl$	43
46	SN	100
76	?	10
78	S_2N	10
81	$NS^{35}Cl$?	10
92	S_2N_2, $S_4N_4^{2+}$?	50
121	?	10
138	?	20
184	S_4N_4	8
191	?	65
193	?	90

(ii) S_3N_2Cl

Mass of Peak	Designation	Relative Intensity
32	S and O_2	225
35	^{35}Cl	23
36	$H^{35}Cl$	155
37	^{37}Cl	9
38	$H^{37}Cl$	54
46	SN	100
62	$S_3N_2^{2+}$	30
64	S_2 and SO_2	25
78	S_2N	25
92	S_2N_2, $S_4N_4^{2+}$?	132

Mass of Peak	Designation	Relative Intensity
124	S_3N_2	5

(iii) $(NSCl)_3$

Mass of Peak	Designation	Relative Intensity
32	S and O_2	35
35	^{35}Cl	45
36	$H^{35}Cl$	330
37	^{37}Cl	17
38	$H^{37}Cl$	110
46	SN	100
63	?	15
64	S_2 ? SO_2	20
78	S_2N	28
81	$NS^{35}Cl$	10
83	$NS^{37}Cl$	3.5
92	S_2N_2	78
124	S_3N_2	16
138	S_3N_3	24
156	?	10

(iv) S_4N_4

Mass of Peak	Designation	Relative Intensity
32	S and O_2	45
46	SN	100
62	${S_3N_2}^{2+}$?	10
78	S_2N	30
64	S_2 ?, SO_2	8
76	${S_3N_4}^{2+}$?	32

Mass of Peak	Designation	Relative Intensity
92	S_2N_2	126
124	S_3N_2	26
138	S_3N_3	120
184	S_4N_4	40

(v) $S_2NCl_2^+$ Salts

(a) $S_2NCl_2\ AlCl_4$

Mass of Peak	Designation	Relative Intensity
32	S and O_2	286
35	^{35}Cl	242
36	$H^{35}Cl$	2000
37	^{37}Cl	100
38	$H^{37}Cl$	665
46	SN	100
64	S_2 ?, SO_2	230
67	SCl^{35}	143
69	SCl^{37}	57
76	?	100
102	?	110
104	?	80
123	?	60

(b) $S_2NCl_2\ FeCl_4$

Mass of Peak	Designation	Relative Intensity
32	S and O_2	37
35	^{35}Cl	60
36	$H^{35}Cl$	350
37	^{37}Cl	20

Mass of Peak	Designation	Relative Intensity
38	$H^{37}Cl$	144
46	SN	100
48	?	95
63	?	150
64	S_2 ?, SO_2	160
67	$S^{35}Cl$	20
69	$S^{37}Cl$	8
76	?	45
78	S_2N	10
80	?	20
83	?	22
94	?	32
129	?	130
131	?	60

(vi) Sulfur Imides

(a) $S_4(NH)_4$

Mass of Peak	Designation	Relative Intensity
32	S and O_2	16
46	SN	100
47	SNH	68
48	?	23
62	SN_2H_2	81
63	?	55
64	S_2 ?, SO_2	14
78	S_2N	33
80	?	25
92	S_2N_2	11

Mass of Peak	Designation	Relative Intensity
93	S_2N_2H	10
94	$S_2N_2H_2$	7
110	?	20
123	?	25
125	S_3N_2H	40
139	S_3N_3H	20
186	$S_4N_4H_2$	54
188	$S_4N_4H_4$	12

(b) S_7NH

Mass of Peak	Designation	Relative Intensity
32	S and O_2	65
36	?	90
38	?	30
46	SN	100
47	SNH	40
64	S_2 and SO_2	390
66	?	40
78	S_2N	39
79	S_2NH	35
92	S_2N_2 ?	40
96	S_3	10
128	S_4, S_8^{2+} ?	10
160	S_5	22
192	S_6	24
224	S_7 ?	5
256	S_8 ?	3

(B) Mass Spectra, Discussion

1. Electron Rich Aromatics

The fragmentation patten of the electron rich aromatic compounds, gives SN^+ as the principal fragment, $S_2N_2^+$ being the next most intense peak in most cases. The remainder are also formed by simple ring fragmentation, although no peaks have been definitely assigned to fragments with more nitrogen than sulfur. The parent peaks are weak for the $S_4N_3^+$ [148] and $S_5N_5^+$ salts, and are absent for the $S_3N_2Cl^+$ salts, since the $S_3N_2Cl^+$ ring has less aromatic stabilisation energy than $S_4N_3^+$ and $S_5N_5^+$, due to the non-planarity of the ring. Anion fragments are not observed, apart from Cl^+ (identified by isotopic ratio), but this is formed from hydrolysis of the anion by traces of moisture to HCl (which is observed as a very strong peak), which can then split to yield Cl, rather than being formed directly from the anion. This is observed in all chlorine-containing sulfur-nitrogen compounds.

A few unidentified peaks were observed. Some were tentatively assigned, e.g. mass 76 as $S_3N_4^{2+}$, which could be an eight-electron cage species, and mass 62 as $S_3N_2^{2+}$ which, if cyclic, could be a 6π electron rich aromatic species. These factors would increase the stability of these fragments, making them observable. A peak at mass 64 was observed for S_5N_5 $AlCl_4$. This could be S_2 (and SO_2) indicating the existence of the S-S interaction at the 'top' of the heart-structure, although the peak was weak in the $S_5N_5^+$ spectra with other anions.

Further peaks, including persistent peaks at masses 48 and 63 could not be assigned, and may be due to impurities on the probe.

2. S_3N_2Cl

The mass spectrum of S_3N_2Cl is consistent with its postulated structure (this thesis), the fragmentation patten corresponding to the breakdown of the five-membered S_3N_2 ring, the most prominent peaks being SN^+ and $S_2N_2^+$.

The peak assigned to $S_3N_2^{2+}$ is more intense than that assigned to $S_3N_2^+$ (which is technically the parent peak). This is probably due, as previously noted, to the aromatic character of the $S_3N_2^{2+}$ ion.

3. $(NSCl)_3$

The mass spectrum shows the fragmentation patten of an SN ring, with SN^+ and $S_2N_2^+$ being the principal fragments. Chlorine-containing fragments are weak or absent, the only observed peaks being those due to NSCl, which are expected to be strong since $(NSCl)_3$ dissociates into NSCl in the vapour phase. The electronegative chlorine, however, destabilises the positive NSCl ion, causing it to split, yielding NS^+. The peaks at masses 63 and 156 are weak, and probably due to impurities on the probe.

4. S_4N_4

The mass spectrum of S_4N_4 is consistent with its known structure, showing all combinations of S and N atoms (apart from S_4N_3) of the type S_xN_y (y = 1 to 4) where y = x or x - 1. Fragments with more nitrogen than sulfur (apart from $S_3N_4^{2+}$, see below), are not observed. The peak at 64 is assigned to S_2 (and SO_2) indicating transannular S-S interactions in S_4N_4, and tentative assignments are also made for $S_3N_2^{2+}$ (mass 62) and $S_3N_4^{2+}$ (mass 76).

5. $S_2NCl_2^+$ Salts

The $S_2NCl_2^+$ ion yields SN and SCl as identifiable fragments, S_2N being weak and the assignment therefore only tentative, however, the SN peak is not particularly strong, and this inevitably means the inclusion in the analysis of many other peaks (due to the "10% rule", see Introduction) which could well be due to impurities and would have been ignored, had the SN peak been stronger. Anion fragments (other than Cl) are not observed, although Glemser reports aluminium containing anion fragments from $S_2NCl_2^+$ $AlCl_4^-$.[289]

6. Sulfur Imides

The inclusion of hydrogen in sulfur-nitrogen compounds causes the peaks to appear in groups, separated by a unit mass (hydrogen atom) making them more easily identified. SN^+ is the strongest peak in $S_4(NH)_4$, the other peaks (apart from S_2N) being of the form $(SN)_x$ ($x = 1$ to 3) with one or more hydrogen atoms. Some combinations are weak or absent, and several unassigned (and probably spurious) peaks are observed. A weak peak at mass 64 (S_2 and SO_2) is also observed, indicating a rearrangement of the ring in the ionising chamber.

In the case of S_7NH, S_2^+ is more abundant than SN^+, due to the greater number of ways that S_2 can be formed, and the whole series, from S_2 to S_7 (and possibly S_8) was identified.

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The abbreviations of the following references are in accordance with the recommendations of the Journal of the American Chemical Society. Reference citations in American Chemical Abstracts (abbreviation: CA) are given where available.

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