Synthetic and structural studies of some thiazene cations

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Synthetic and Structural Studies of Some Thiazene Cations

Aidan Gerard Kendrick

A Thesis submitted for the degree of Ph.D. to the
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To my parents and friends

Si nous ne trouverons pas des choses agréables,
nous trouverons du moins des choses nouvelles

VOLTAIRE, Candide ou l'Optimisme

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MEMORANDUM

The work described in this thesis was carried out by me in the Chemistry Departments of the University of Durham and the University of New Brunswick (Canada) between October 1982 and December 1985. I declare that the work has not been submitted previously for a degree at this or any other University. This thesis is my original work, except where acknowledged by reference. The copyright of this thesis rests with the author. No quotation from it should be published without his written consent and information derived from it should be acknowledged. Material from this thesis has been or will be included in the following publications:

a) "Electrochemical Synthesis of Poly (Sulphur Nitride)", A.J. Banister, Z.V. Hauptman, and A.G. Kendrick, J. Chem. Soc. Chem. Commun., 1983 1016.

b) "Synthesis of Poly (Sulphur Nitride)", A.J. Banister, Z.V. Hauptman, and A.G. Kendrick, UK Pat. Appl. 8420647, May 1985; U.S. Pat. 4,555,316, November 1985.

c) "A Convenient Synthesis of Thiazyl Hexafluoroarsenate(V), $SN^+AsF_6^-$, and Small Quantities of Thiazyl Fluoride, NSF", A. Apblett, A.J. Banister, D. Biron, A.G. Kendrick, J. Passmore, M. Schriver, and M. Stojanac, Inorg. Chem., submitted for publication.

d) "Some Investigations of $S_5N_5^+$ Compounds: the Crystal Structure of S_5N_5Cl" A.J. Banister, Z.V. Hauptman, A.G. Kendrick, and R.W.H. Small, in preparation.

e) "A Convenient Preparation of $S_2N^+SbCl_6^-$", A.J. Banister and A.G. Kendrick, in preparation.

f) "The Crystal Structure of $S_2N^+AsF_6^-$", A.J. Banister, J. Johnson, A.G. Kendrick, and J. Passmore, in preparation.

Synthetic and Structural Studies of Some Thiazene Cations

A.G. Kendrick

ABSTRACT

S_5N_5Cl has been produced by a new route and is much more stable than previously reported owing to greater purity. Its chemical reduction to $(SN)_x$ and reactions with SO_2 and BF_3 were studied. An X-ray structure analysis (R.W.H. Small) revealed secondary cation-anion interactions; the resulting strain in the cation ring could be detected both by bond angle-bond length correlations and MNDO calculations.

Electro-reduction of S_5N_5Cl in liquid SO_2 produced finely powdered $(SN)_x$ which could be used to form good quality vapour deposited films. Cyclic voltammograms in liquid SO_2 (obtained after spending much time developing an improved procedure) indicated possible solvent participation in the reduction process and so electrocrystallization of $(SN)_x$ by electro-reduction of $S_5N_5BF_4$ (prepared from S_5N_5Cl) in acetonitrile was investigated. Cyclic voltammetric evidence was used to propose a mechanism of reduction and bulk electrolyis experiments using bright platinum and $(SN)_x$ film cathodes showed the influence of the cathode on the nature of the $(SN)_x$ deposit.

Small quantities of NSF were produced in ca. 80% yield by the solid state reaction of $SN^+AsF_6^-$ and excess CsF; an unoptimised larger scale preparation indicated the usefulness of this route. Various gas phase reactions of NSF were studied using infrared spectroscopy. Attempts to prepare the simple fluoride S_4N_3F by metathesis from $S_4N_3BF_4$ and CsF were only partially successful owing to reaction with solvent.

Reaction of $S_3N_2^{2+}(AsF_6^-)_2$ with CsF (1:1) produced $S_3N_2F^+AsF_6^-$ but further conversion to $S_3N_2F_2$ was not possible owing to reaction with solvent. Attempted crystal growth experiments indicated that the $S_3N_2^{2+}$ ion existed in an equilibrium mixture containing S_2N^+ and SN^+; this hypothesis was confirmed by its reactions with sulphur and hexafluorobut-2-yne. These solution equilibria were exploited by designing more convenient preparations of $S_3N_2^{2+}(AsF_6^-)_2$ and $S_2N^+SbCl_6^-$. The chemical reactions of $SN^+AsF_6^-$ were studied with a view to the preparation of new compounds. Although no such species were isolated, the results usefully indicated future experiments and the oxidising properties of the SN^+ cation.

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CHAPTER 1

General Introduction

1.1 Historical Development:

The first binary sulphur-nitrogen compound to be reported was S_4N_4, in 1835(1) and sporadic development continued during the nineteenth century. Impure $S_3N_2Cl_2$ was prepared in 1851 and was properly characterized in the 1880s by Demarçay, who also described $(NSCl)_3$, S_4N_3Cl, and $S_6N_4Cl_2$.(2) The following decades saw a gradual recognition of the cyclic structure of such inorganic compounds as the phosphazenes, but little progress was made in the field of sulphur-nitrogen chemistry until after the Second World War. The advent of modern diffraction techniques resulted in the elucidation of the cyclic, pseudo-cluster structure of S_4N_4(3) (more than a hundred years after its first preparation) whilst the development of more sophisticated techniques such as infrared spectroscopy, vacuum line and inert atmosphere manipulation, and the use of aprotic reaction media, resulted in a rapid acceleration in the pace of discovery.

A significant development was the publication by Becke-Goehring of the monograph 'Ergebnisse und Probleme der Chemie der Schwefel-Stickstoffverbindungen'(4) in 1957 and since that date the literature of sulphur-nitrogen chemistry has grown steadily. The most recent texts are by Haiduc(5) and Heal(2) whilst several authors have published review articles, for example Becke-Goehring and Fluck

(1966),(6) Heal (1972),(7) Banister (1975),(8) Roesky (1979),(9) and Chivers (1982, 1983)(10,11). A definitive review of cyclic sulphur-nitrogen compounds has been published by the Gmelin Institute(12) and this book will be of immense use to future workers. The derivative field of sulphur-nitrogen-fluorine chemistry also developed in the post-war period, being largely the work of Glemser and co-workers at Göttingen.

The discovery that the polymer $(SN)_x$ exhibits metallic properties and becomes a super-conductor below 0.3K(13) has stimulated tremendous interest in sulphur-nitrogen chemistry and it is this impetus which has made it one of the most active areas of current inorganic research.(2)

1.2 Current Trends in Sulphur-Nitrogen Chemistry; A Personal View:

This section is an attempt to illustrate some areas of current interest in sulphur-nitrogen chemistry and to show how these areas are related, both amongst themselves and to the wider body of developing chemical knowledge; in short it is an attempt to convey something of the flavour of contemporary sulphur-nitrogen research. Inevitably, the result is a highly subjective view and in no way is this summary intended to be a comprehensive assessment of recent developments in the field.

The current expansion of interest in sulphur-nitrogen chemistry began with the discovery, in 1975, that the polymer $(SN)_x$ is a quasi-one dimensional metal which becomes superconducting below 0.3K.(13) Considerable effort has been spent in devising improved methods of synthesis of the polymer and in particular it has been found that to obtain polymer with reproducible physical properties, extreme care in preparation and manipulation is required.(14) $(SN)_x$ has been used in the fabrication of blue light-emitting diodes which are thought to be of potential commercial significance(15) and has also been used in the fabrication of batteries.(16)

The search for new materials which may have more desirable properties than $(SN)_x$ (for example, a degree of solubility or a higher temperature transition to a super-conducting state) and the consequent search for suitable precursors has provided a major stimulus, particularly to the field of carbon-sulphur-nitrogen chemistry. Many papers have been published recently, interesting examples includ~~e~~ing the synthesis of 1,3,5,2,4-trithiadiazepine(17) and the reactions of the small 'building block' species S_2N^+ with unsaturated species to give dithiazolium cations; these cationic heterocycles may be reduced to free radicals.(18,19) Further synthetic and theoretical studies of sulphur-nitrogen radicals have been published.(20) Although the preparation of new materials with useful properties is a research goal in sulphur-nitrogen chemistry, it remains true that most published work is primarily of fundamental academic interest. At the present stage of development it is the synthetic chemistry which is advancing most rapidly. Old problems are being re-scrutinized (for example the reaction between S_4N_4 and acetylenes)(21) and new synthetic strategies are being used to produce quite startling new compounds (for example the very recent preparation of the azulene analogue $S_4N_4C_2$).(22)

As new species are produced, so interest in the modes of bonding in sulphur-nitrogen compounds increases. The discovery of the 14-π $S_5N_5^+$ cation(23) and the recognition of $S_4N_3^+$ and S_2N_2 as Hückel-aromatic species was a key development. The extent to which sulphur-nitrogen heterocycles are stabilized by this aromaticity and hence which heterocylces are likely to be preparable is still a point of debate. Over the past decade, Chivers and co-workers have prepared a number of new binary sulphur-nitrides (most notably $S_3N_3^-$)(24) and sulphur-nitrogen-phosphorus compounds and have extensively investigated the electron-accepting properties of these electron-rich species, both from the synthetic and theoretical point of view.(10,11) Similarly, the advent of modern, more sophisticated theoretical techniques has resulted in a re-examination of old problems in sulphur-nitrogen chemistry (for example the bonding(25) and pyrolysis products of S_4N_4(26)) and it seems likely that this trend will continue.

Other areas of current interest include the extensive field of metal-sulphur-nitrogen compounds,(27) whilst topics such as sulphur-nitrogen-oxygen(2) and sulphur-nitrogen-boron(28) chemistry seem ripe for more systematic investigation; longer established fields such as sulphur-nitrogen-phosphorus(11) and sulphur-nitrogen-fluorine(29) chemistry continue to yield important results.

Finally, it is worth emphasizing that advances in synthesis have resulted from advances in technique. Increasingly, spectroscopic methods such as e.s.r.(18) and ^{15}N n.m.r.(30) together with electrochemical investigations(31) and the ever-improving methods of X-ray structural analysis, seem likely to result in further rapid advances in this fascinating topic.

1.3 A Brief Overview of this Thesis:

In the following section, the relevance of this thesis to various themes mentioned in Section 1.2 is discussed. Chapter 3 describes various synthetic and structural studies of the compound S_5N_5Cl which were undertaken in order to investigate the new routes to the conducting polymer $(SN)_x$ and to investigate the structural chemistry of the $S_5N_5^+$ cation. A brief MNDO(32) study of the cation is included.

Chapter 4 deals with the preparation of $(SN)_x$ from $S_5N_5^+$ compounds, firstly by electro-reduction of a solution of S_5N_5Cl in liquid SO_2 (either constant current or floating current and floating potential modes) and secondly by controlled potential reduction of a solution of $S_5N_5BF_4$ in acetonitrile. The characteristics of the $(SN)_x$ deposit produced by these two methods are discussed and cyclic voltammetric studies of the two systems are used to elucidate the mechanism of reduction.

Recently, new routes to the potential 'building block' species $SN^+AsF_6^-$(33) and $S_2N^+AsF_6^-$(34) have been described. The use of $SNAsF_6$ in a convenient preparation of the reactive gas NSF, previously accessible only by more complex and expensive routes, is described in Chapter 5. Several gas phase reactions were investigated with the intention of producing new heterocycles, but unfortunately without success although an addition reaction with CF_3OF appeared to yield a species of the type $RNSF_2$ as the primary product. Other attempts to prepare the simple fluoride $S_4N_3^+F^-$ did not proceed simply.

The reaction of S_2NAsF_6 and $SNAsF_6$ had been reported to produce the cyclic compound $S_3N_2(AsF_6)_2$,(35) which was characterized by elemental analysis and vibrational spectroscopy. Chapter 6 describes attempts to prepare the compound $S_3N_2F_2$, previously reported as an obscure volatile crystalline solid,(36) by stepwise reaction of $S_3N_2(AsF_6)_2$ with CsF. The intermediate compound $S_3N_2FAsF_6$ was isolated but conversion to $S_3N_2F_2$ was not achieved owing to reaction with solvent. Crystal growth experiments on $S_3N_2(AsF_6)_2$ indicated that an equilibrium between the S_2N^+, SN^+, and $S_3N_2{}^{2+}$ ions existed in solution and subsequent reactions of SN^+ and $S_3N_2{}^{2+}$ with elemental sulphur together with MNDO calculations, substantiate this hypothesis. The principles discovered in this study of equilibria were used to design a new preparative route to S_2NSbCl_6, which is anticipated to be an increasingly useful precursor in sulphur-nitrogen chemistry.

Finally, Chapter 7 contains an investigation of the chemistry of the reactive SN^+ ion, undertaken with the aim of producing new species from this simple precursor. Although no new species were isolated, useful pointers to future experiments were obtained.

1.4 Some Practical Aspects:

Two factors which above all else determine the experimental procedures in sulphur-nitrogen chemistry are the lability of sulphur-nitrogen rings and cages and their moisture sensitivity. Unlike molecular frameworks constructed of carbon or phosphorus and nitrogen atoms, the sulphur-nitrogen framework will not necessarily persist unchanged through sequential reactions, but will often tend to cleave and rearrange, sometimes in most unexpected ways. This lability is one reason why most of the reactions investigated in this thesis were performed at room temperature or below. More specific examples of lability are discussed in Chapters 3 and 6.

The general moisture sensitivity of sulphur-nitrogen compounds has several implications for work in the area. In the case of the extremely sensitive gas NSF, elaborate precautions must be taken to avoid massive hydrolysis, whilst small amounts of impurities, especially hydrolysis products, exert a profound effect on the properties of $(SN)_x$ (see Chapter 4). For successful preparative work to be undertaken, then, extreme care is necessary in the purification of starting materials and solvents, cleaning of reaction vessels, and manipulation of reaction mixtures and solvents. These constraints can hinder the application of techniques which are routine in other areas of chemistry, a good example being the application of electrochemical techniques to the reduction of the $S_5N_5^+$ ion (see Chapter 4). Similarly, the relatively inert and easily purified solvent of choice for many applications in sulphur-nitrogen chemistry, SO_2, is not always convenient for otherwise routine techniques such as N.M.R. spectroscopy or electrochemistry. Surmounting these and similar difficulties presents one of the enduring challenges in sulphur-nitrogen chemistry; it is also one of the limiting factors in the rate of progress.

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CHAPTER 2

General Experimental Procedures

2.1 General Techniques:

a) Manipulation of moisture-sensitive materials. All manipulations of moisture-sensitive or hygroscopic materials and all purifications or distillations of solvents were performed under an atmosphere of dry nitrogen or in vacuo. For manipulation at the bench, nitrogen from the Departmental supply line was purified by passage through a heated copper tower (to remove oxygen) and through a P_4O_{10} tower (to remove moisture) before use. Other manipulations were conveniently performed under an atmosphere of dry nitrogen in a Vacuum Atmospheres glove box (Type HE43-2) equipped with a recirculating pump and molecular sieve drying column (HE493 DRITRAIN). The pressure in the glove box was regulated with a Pedatrol HE-63-P regulating unit and the nitrogen was supplied from a high pressure cylinder (B.O.C. White Spot grade).

b) Infrared spectra. Infrared spectra were recorded on Perkin-Elmer grating spectrophotometers (Type 477 or 577). Spectra of solids were recorded as nujol mulls on KBr plates unless otherwise stated. Gas phase spectra of non-fluorinated compounds were recorded using a Pyrex cell (10cm) fitted with KBr windows whilst gas phase infrared spectra of fluorinated or highly moisture-sensitive substances were recorded using a passivated stainless steel cell fitted with AgCl windows.

c) **Raman spectra.** Raman spectra were recorded on either a Cary 82 spectrophotometer (Spectra Physics 125 laser , 6328 Å exciting line or Spectra Physics 164 laser, 5145 Å exciting line), or a Ramanlab spectrophotometer (Spectra Physics 125 laser, 5145 Å exciting line). Solid samples were sealed under dry nitrogen in glass capillaries before recording the spectra.

d) **Nuclear magnetic resonance spectra.** Nuclear magnetic resonance spectra of ^{19}F species were recorded using a Varian XL200 200MHZ pulsed Fourier transform spectrometer unless otherwise stated. Spectra of SO_2 solutions were recorded in 10 mm tubes at -70°C

e) **Mass spectra.** Mass spectra were recorded on an A.E.I. (MS9) spectrometer at 120-180°C and 70eV with an accelerating potential of 8 KV. Samples were introduced by direct insertion into the ion source.

f) **X-ray powder diagrams.** X-ray powder diagrams were obtained using a Debye-Scherrer camera and Cu-K_α radiation (nickel filter). The image was recorded on Kodak No-Screen film (Type NS-292T). The samples were ground to a powder (if necessary) and sealed in thin walled capillaries (0.3 mm O.D., Lindemann glass or quartz).

g) **Elemental analyses.** Except where stated otherwise, elemental analyses were performed in this Department by Mr R. Coult (S, N, As, B, Cl, Fe) or by Mrs M. Cocks (C, H). Carbon and hydrogen analyses were obtained using a Perkin-Elmer 240 Elemental Analyser. Sulphur and chlorine were determined by oxygen flask combustion followed by visual or potentiometric titration of sulphate and chloride ions respectively. Nitrogen was determined by the micro-Kjeldhal method whilst boron, arsenic, and iron were determined by atomic absorption spectroscopy using a Perkin-Elmer 403 Atomic Absorption Spectrometer.

f) Glassware. Pyrex flasks and sinters fitted with conical ground-glass joints were either placed in an oven (ca. 100°C) for 30min, or gently flamed with a hand-torch (ca 500°C) in a flow of nitrogen before use. The procedures for using more specialized glassware are described below.

g) Vacuum lines. For general purpose manipulation of solvents, a Pyrex vacuum manifold fitted with greased high vacuum ground-glass taps was adequate and a vacuum as good as to 10^{-2} torr could be achieved; connection to reaction vessels was via tap adaptors and rubber tubing.

For high-vacuum sublimations, a good vacuum was essential to lower the temperature of sublimation and hence to avoid the thermal decomposition of compounds under investigation. The high-vacuum manifold was constructed of Pyrex and had been designed and built by Z.V. Hauptman. Using a silicone oil diffusion pump and rotary backing pump, with J. Young's Teflon-stemmed valves and Viton rubber 'O' ring joints, a vacuum as good as 6×10^{-7} torr was achieved; slight greasing (Apiezon 'N') of the valve stems and 'O' rings was necessary for the best results.

For manipulation of SO_2 and of reactive fluorine compounds, it was found convenient to use a vacuum manifold made of monel, equipped with stainless steel Whitey valves (1KS4). Attachment of vessels to the manifold was via Swagelok Teflon compression fittings (¼" O.D.). Vacuums of 10^{-2} torr were regularly achieved; if SO_2 only was being manipulated, a mercury diffusion pump could be used which achieved vacuums of 10^{-4} torr. The monel line had the added advantage that it could be dried by flaming with a hand-torch whilst under dynamic vacuum; a detailed description of the procedure for conditioning the monel vacuum line to a standard suitable for work with thiazyl fluoride (NSF) is given in Chapter 5.

h) Temperature control. Heating could be achieved by use of a silicone oil bath and stirrer hot-plate or by use of electrical heating tapes and a variable transformer. On the high vacuum line it was possible to control sublimation temperatures to the nearest 1°C by use of a Eurotherm thermostat and either a resistive wire electric furnace (designed and built by Z.V. Hauptman) or a silicone-oil bath and stirrer hot-plate.

Cooling as low as -15°C could be achieved by use of an alcohol-filled Haake bath circulator; the temperature could be adjusted to 1°C.

i) Differential scanning calorimetry (D.S.C.). D.S.C. traces were recorded using a Mettler FP80 control unit coupled to a Mettler FP85 TA thermal analysis cell and a Fisons y-t chart recorder. Samples were hermetically sealed in aluminium capsules by cold welding.

2.2 More Specialized Techniques:

a) **Two-bulbed reaction vessels.** These have been described previously.(1) In this work, each bulb (ca. 10 ml) was surmounted by a J. Young's or Rotaflo Teflon-stemmed valve and the two bulbs were separated by a medium porosity sintered glass frit. A typical vessel is illustrated in Figure 2.1. For some larger scale reactions it was found convenient to use a vessel with 200 ml bulbs and a 2 cm diameter sintered glass frit whilst for reactions involving very fine precipitates, a fine porosity frit was used. The two-bulbed vessels could be attached to the monel vacuum line via their ¼" O.D. ground glass fittings.

These two-bulbed vessels had several distinct advantages for the investigation of moisture-sensitive materials. Firstly, the vessels could be rigorously dried by flaming whilst being kept under dynamic vacuum. Secondly, since the vessels were relatively small they could be weighed accurately and thus losses from or additions to the system under investigation could be detected. Finally, since the vessel is a closed system, solvents with vapour pressures greater than 1 atmosphere could be used (eg SO_2 ca. 3 atm, Cl_2 ca. 6 atm); similarly, accurately weighed aliquots of gaseous reagents could be introduced into reaction mixtures.

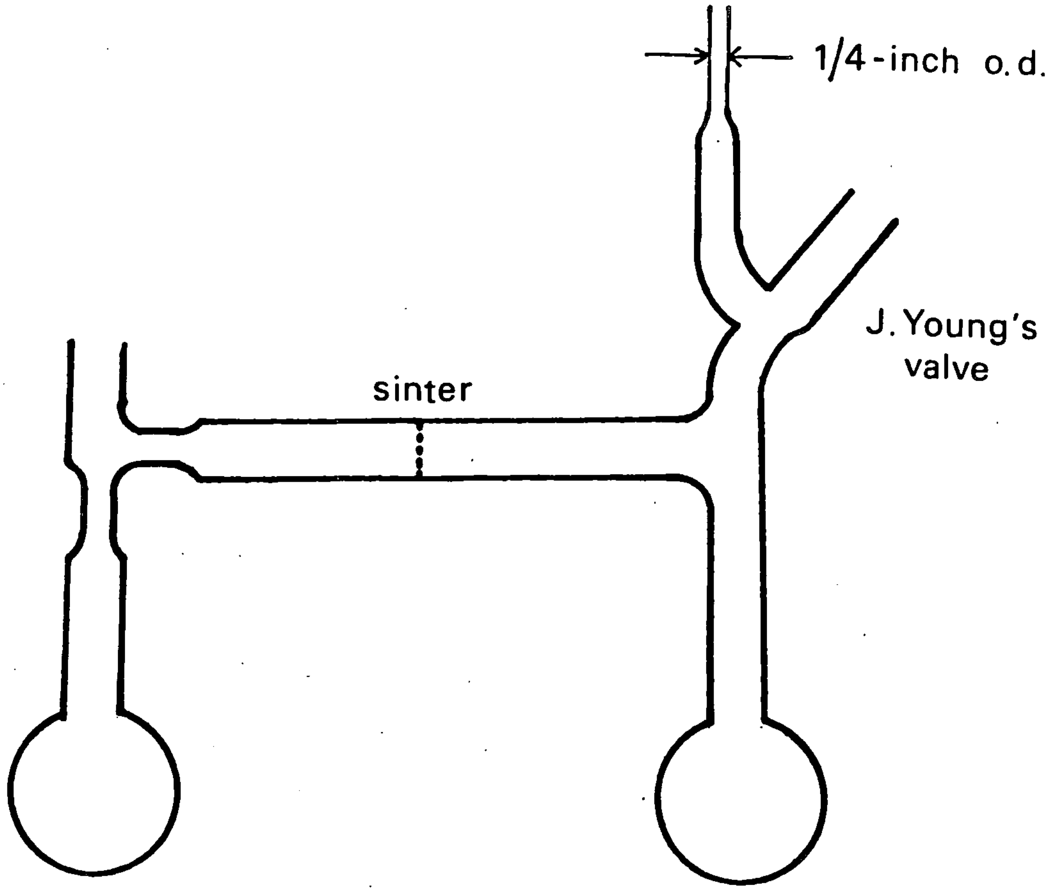

Figure 2.1. A typical two-bulbed reaction vessel

Many reactions discussed in this thesis were between a solid soluble in SO_2 and a solid sparingly soluble in SO_2. In such cases it was possible to place the sparingly soluble solid in one bulb (the reaction bulb) together with a Teflon coated magnetic stirring bar and place the soluble solid in the other bulb. Condensation of SO_2 into both bulbs gave a solution in one bulb and a mixture of solution and solid in the reaction bulb; the soluble reagent could then be added to the reaction bulb. Slight cooling of the empty bulb caused a little SO_2 to distil back and this solvent was returned to the reaction bulb; several repetitions of this procedure enabled complete transfer of the soluble reagent to be achieved. Separation of a soluble from an insoluble product was achieved by a combination of filtration and washing with back-distilled solvent. Products were conveniently recovered after removal of solvent by cutting the bulbs off with a glass-knife; the vessel could be re-used after re-attachment of the bulbs, (using a gas-oxygen torch) and annealing in an oven up to 565°C.

b) NMR tubes. It was found that some reactions could be conveniently monitored by nuclear magnetic resonance spectroscopy. Ten millimetre Pyrex tubes were used and these were fitted with J. Young's Teflon stemmed bleed valves. The tubes could be connected to a monel vacuum manifold by short lengths of Pyrex tube, of an appropriate diameter, which were pushed into the top of the bleed-valve; this joint was protected with Apiezon 'Q' sealing compound. Volatile solvents or reagents were condensed into the tubes from the vacuum manifold. Since the tubes could be weighed on an analytical balance, an accurate record of the amounts of reagents and reference used could be kept, which enabled the yield of products to be estimated.

c) Closed extractors. Exhaustive extractions of moisture-sensitive materials with relatively volatile solvents (e.g. SO_2 or CCl_4) could be conveniently performed in a closed extractor (designed by Z.V. Hauptman). A description of this type of extractor has appeared in the literature.(2)

d) Monel reaction vessels. The monel cans used in the thiazyl fluoride experiments discussed in Chapter 5 have been described previously.(1)

2.3 Electrochemical Techniques:

a) Current supply. Two modes of current supply were used in the bulk electrolysis experiments described in Chapter 4. Constant current (galvanostatic) supply was maintained by a stabilised d.c. source designed and built by A. Royston (University of Durham). This device was capable of delivering constant currents ranging from 0-10mA; the maximum allowable potential drop across the terminals was 40 V.

Constant potential (potentiostatic) current supply was maintained by a Ministat Precision Potentiostat supplied by H.G. Thomson and Associates (Newcastle-upon-Tyne).

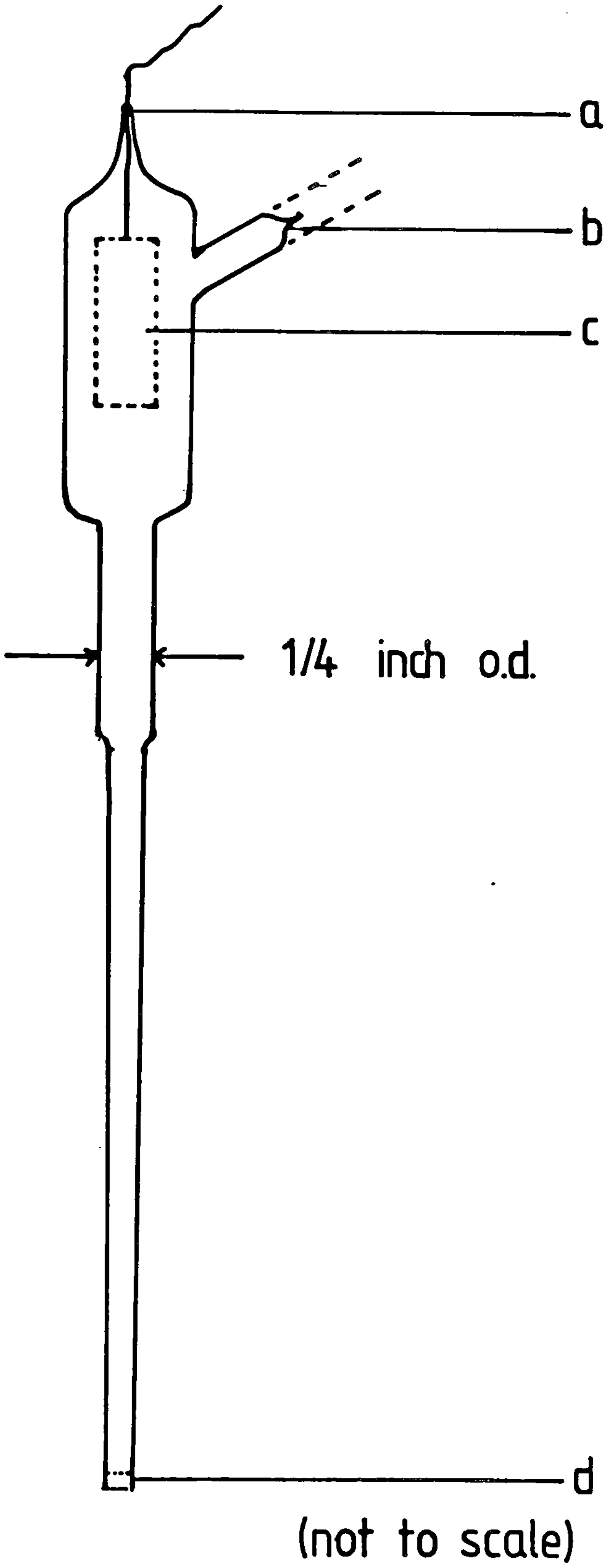

Figure 2.2. The Ag^+/Ag reference electrode.
a) silver wire-in-glass seal, capped with Araldite;
b) sealable side-arm;
c) cylindrical silver gauze;
d) glass sinter

b) Reference electrodes. Although the saturated calomel electrode (S.C.E.) electrode was used in some preliminary experiments, it was found convenient to use a 0.1M Ag^+/Ag electrode, made up in anhydrous acetonitrile, as the reference electrode for both acetonitrile and sulphur dioxide solutions. The reference electrode is illustrated in Figure 2.2. The ¼"O.D. section facilitated a vacuum-tight seal when passed through either a reamed-out Swagelok compression fitting (½" to ¼" reduction) or a Quickfit thermometer screw compression fitting. The electrode was filled by sealing it, via a Quickfit thermometer screw fitting, in a Pyrex bulb and then evacuating it through the side-arm. 'A'. After exhaustive evacuation to remove absorbed gases from the electrode, the side-arm was sealed with a gas-oxygen torch. A thoroughly degassed solution of 0.1M $AgBF_4$ in acetonitrile was transferred to the bulb containing the electrode from another bulb, which was joined to it via a Teflon-stemmed valve. As the porous tip of the electrode was immersed in this solution, the electrode body filled completely with solution. The electrode was stored with the tip sealed under nitrogen in a bulb containing a 0.1M solution of $AgBF_4$ in acetonitrile.

When freshly prepared, the electrode had a potential of +0.26 V vs S.C.E. but after storage for several months, the potential was found to be +0.33V vs S.C.E. During any experiment, the electrode was stable to within ± 5 mV; this compares with ± 50 mV reported for a quasi-reference electrode used by Bard et al for recent work in liquid SO_2.(3)

The fact that the electrode was completely filled with acetonitrile enabled it to be used in pressurised systems such as SO_2 solutions. Although some diffusion across the porous plug occurred causing precipitation of a fine white solid (possibly Ag_2SO_4), the potential of the electrode was not affected. After several experiments in liquid SO_2, a bubble formed in the electrode which necessitated its refilling.

c) **Other electrodes.** For bulk electrolyses, platinum sheet or coiled platinum wire electrodes were used. The use of specially constructed $(SN)_x$-coated electrodes is described in Chapter 4. For cyclic voltammetry, a working electrode consisting of a platinum disc (area = 1.47 mm^2) mounted in Pyrex was used. This type of electrode has been described in the literature.(3) The stem was constructed from ¼" O.D. Pyrex tubing which enabled the electrode to be used, in the same way as the reference electrode, in pressurised and evacuated systems. Platinum cathodes were ground in a slurry of alumina and concentrated nitric acid before use.

d) **Electrochemical cells.** A prototype cell is illustrated in Figure 2.3. Two- or three- limbed versions were used as appropriate; the electrodes could be introduced via either reamed-out Swagelok compression fittings or Quickfit thermometer screw fittings and J. Young's B19 cone-and-socket joints. In later models, the working and reference electrodes could be separated from the counter electrode by means of a medium porosity Pyrex sinter.

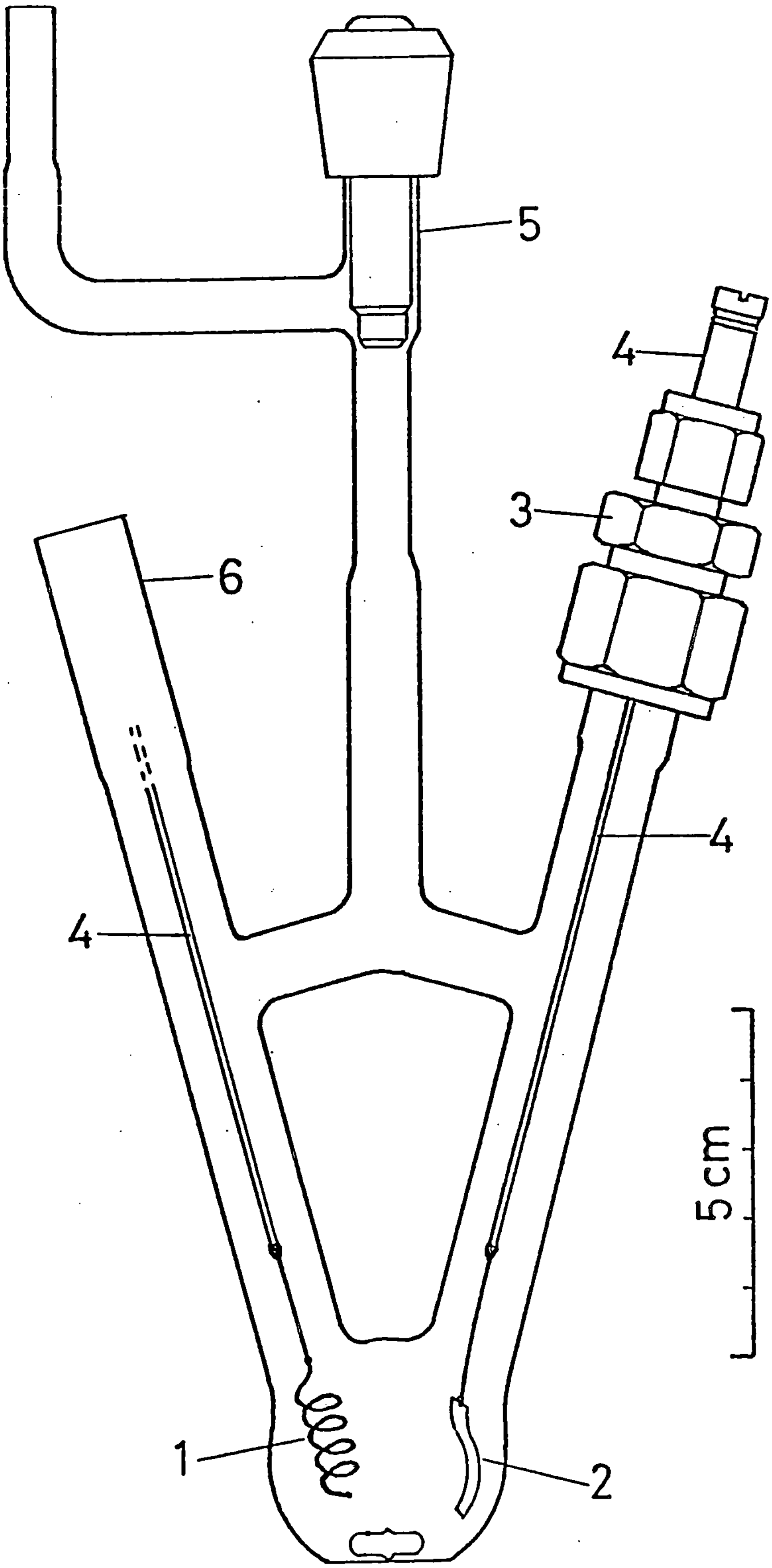

Figure 2.3. A prototype two-limbed electrochemical cell; 1) auxiliary electrode, 2) working electrode, 3) Swagelok ½ to ¼" reduction union, 4) monel leads, 5) Rotaflo valve, 6) ½" O.D. precision tubing

e) Cyclic voltammetry. Cyclic voltammograms were recorded using a BioAnalytical Systems potential wave generator (Type CV-1B) and a Linseis x-y chart recorder.

2.4 Sulphur-Nitrogen Starting Materials:

a) Chlorothiodithiazyl chloride, $S_3N_2Cl_2$. This was prepared by a modification (developed by Z.V. Hauptman) of the procedure of Jolly and Maguire.(4) Ammonium chloride (100g, oven dried), powdered sulphur (20g), and S_2Cl_2 (100 ml) were placed in a 500 ml round-bottomed flanged flask fitted with two air condensers (50 x 3 cm) placed one on top of the other and protected from the atmosphere by a $CaCl_2$ drying tube. All joints were sealed with Teflon sleeves and the flange top was lubricated with Kel-F grease. The mixture was refluxed, the reflux point being initially set close to the top of the first air condenser, which had been scratched on the inside. After a short time, red-brown crystals of $S_3N_2Cl_2$ formed on the inside of the condenser. After the formation of a crystalline ring inside the condenser, the reflux point was gradually lowered by means of a jet of compressed air, thus leaving behind a substantial crystalline deposit of $S_3N_2Cl_2$. After ca. 6h, the reaction was stopped and the lower air condenser was removed and attached to a twin-necked round-bottomed flask fitted with a tap adaptor; stoppers were placed at the top end of the condenser and in the flanged flask. After pumping on the crude $S_3N_2Cl_2$ to remove volatile impurities (S_2Cl_2, SCl_2), the crystals were scraped into the flask against a counter-flow of dry nitrogen and stored under nitrogen in a sealed container in the glove box. Up to 20g of $S_3N_2Cl_2$ could be obtained by this method, and the reaction pot could be re-used up to five times simply by recharging with further 100 ml aliquots of S_2Cl_2. Infrared spectrum, ν_{max} 1010s, 933vs, 826w, 710s, 579s, 459s, 403vs, 381ms cm^{-1}. Raman spectrum (6328 Å), 930vw, 725vw, 580vw, 405w, 370vw, 350vw, 265m, 205w, 180vs, 175m, sh, 140s, 120m, 110m, 90m, 60m, 40w cm^{-1}.

b) Trithiazyltrichloride, $(NSCl)_3$. This material was prepared according to the method of Jolly and Maguire(4) by the chlorination of $S_3N_2Cl_2$. The chlorine was passed through a P_4O_{10} drying column before reaction with the $S_3N_2Cl_2$ which had been placed in a round-bottomed flask. It was found that removal of SCl_2 and breaking up of the crystalline product two or three times during the chlorination helped to ensure complete conversion. The literature recrystallization from hot carbon tetrachloride was found to result in substantial losses as a result of dechlorination, even if performed under an atmosphere of dry chlorine. A better alternative was found to be exhaustive extraction with cold carbon tetrachloride in a scaled-up model of the closed extractor described earlier; $(NSCl)_3$ dissolved to form a bright yellow solution leaving a small amount of a white residual solid (probably NH_4Cl/NH_4SO_4). Virtually quantitative conversion from $S_3N_2Cl_2$ was obtained. Infrared spectrum (CsI plates) ν_{max} 1020vs, br, 835sh, 701s, 622w, 498vs, 441w, 390vs, 360vw, 347sh, 320sh cm^{-1}. Raman spectrum (5145 Å) ν_{max} 1010vw, 695w, 685w, sh, 610w, 485m, 430w, 380s, 340vs, 320m, 185s, 180s, 110s, 80vs, 45w, 25w cm^{-1}.

c) **Thiotrithiazyl Chloride, S_4N_3Cl.** This was prepared by the literature method(4) from $S_3N_2Cl_2$ and excess S_2Cl_2 in dry carbon tetrachloride. The mixture was refluxed for 5h, after which time the $S_3N_2Cl_2$ had been consumed and a canary-yellow precipitate of S_4N_3Cl had formed. The S_4N_3Cl was removed by filtration and after pumping was extracted with dry pentane to remove residual impurities. A relatively low yield of 50% was obtained. Infrared spectrum (CsI plates) ν_{max} 1165s, 1128w, sh, 1000s, 680m, 602vw, 575m, 470s, 455m, sh 330m cm^{-1}. Raman spectrum (5145 Å) ν_{max} 610w, 567w, 477m, 250w, 210w, 165vw, 150vw, 110m, 100m, 80m, 45s cm^{-1}.

d) **Pentathiazyl tetrachloroferrate, $S_5N_5FeCl_4$.** This was prepared by the method of Banister and Clarke(5) from $(NSCl)_3$, $FeCl_3$, and S_4N_4 in $SOCl_2$. Yields of 70% were obtained. Recrystallization of the crude material was from $SOCl_2$(5) if required. Infrared spectrum (CsCl disc) ν_{max} 1138vs, br, 1042w, 925w, 728w, 690m, br, 608m, 528vs, 490sh, 375vs, 328m, 307w, 295w, 283w cm^{-1}.

e) **Thiazyl hexafluoroarsenate, $SNAsF_6$.** This was prepared by an earlier version of the literature procedure.(6) The modified procedure described in the literature was designed to minimize the losses suffered during the sublimation of $NSAsF_6$ from the reaction mixture. Owing to the constraints under which this work was performed, lower percentage yields were accepted in return for higher absolute yields of $SNAsF_6$; higher percentage yields would be obtained by using a higher mole ratio of $AgAsF_6$:$(NSCl)_3$.

In this method, for a typical reaction, $AgAsF_6$ (16.1g, 54.25 mmol) was placed together with $(NSCl)_3$ (3.8g, 15.69 mmol) in a reaction vessel which consisted of a long Pyrex tube (400mm long, 18 mm O.D.), closed at one end and equipped with a J. Young's Teflon stemmed valve and ¼"O.D. fitting at the other. SO_2 (8.05g) was condensed onto the mixture which was left to stand at room temperature. The mixture had a murky green appearance but became a bright yellow slurry after 12h. After removal of solvent the vessel was attached to a vacuum line and placed under dynamic vacuum. The solid reaction residue was heated to 70°C by an electric furnace and a jet of compressed air was directed at the upper part of the reaction vessel. After 16h, a waxy white solid ($SNAsF_6$) had collected on the cooled surface and the sublimation was stopped. The $SNAsF_6$ was removed by breaking open the vessel and scraping; it was stored in sealed ampoules under an atmosphere of dry nitrogen. Yield, 5.5g (50%). Raman spectrum (5145 Å), ν_{max} 1437vs, 683s, 557m cm^{-1}.

f) Preparation of $S_3N_2^{2+}(AsF_6^-)_2$.

$S_3N_2^{2+}(AsF_6^-)_2$ was prepared according to the method of Apblett.(10) $S_2N^+AsF_6^-$ (1.530g, 5.731 mmol) and $SN^+AsF_6^-$ (1.6951g, 7.21mmol) were loaded into separate bulbs of a pre-weighed reaction vessel. SO_2 (5.1055g, 78.4mmol) was condensed onto the solids in approximately equal proportions. After warming to room temperature the pale brown solution of $SN^+AsF_6^-$ was added to the pale yellow solution of $S_2N^+AsF_6^-$.

Immediate reaction occurred to give a brown solution. SO_2 was slowly condensed back to the empty bulb (10°C). Over 36h, yellow crystals formed in the reaction bulb and when only a small amount of SO_2 was left in the reaction bulb, the supernatant liquor was decanted off. Complete removal of SO_2 from the vessel yielded yellow crystals in the reaction bulb; these disintegrated on prolonged pumping.

Yield of yellow crystals, 2.503g (87%); Infrared spectrum, ν_{max} = 1150w, 1045m, 1011m, 971m, 800w, 695s (AsF_6^-), 578m, 562m, 500w, 480m, 441m, 385s(AsF_6^-)cm^{-1}; Raman spectrum(8) (5154 Å), 1054 (17), 971(8), 781(631, 682(67,AsF_6^-), 561(51), 490(34), 394(100), 375(55,AsF_6^-), 561 (51), 490(34), 394(100), 375(55,AsF_6^-)cm^{-1}; Analysis(8) found, S, 19.37; N, 5.51; As, 30.01; F, 45.3; $S_3N_2^{2+}(AsF_6^-)_2$ requires S, 19.16; N, 5.58; As, 29.85; F, 45.41%.

2.5 Other starting materials:

a) Arsenic pentafluoride, AsF_5. It was not possible to obtain commercial supplies of AsF_5 in Britain. It was therefore necessary to prepare this material from available reagents, which in this case were arsenic and fluorine; the fluorine was supplied from an electrochemical cell, maximum cell current 10 A corresponding to 6.7 g/h of fluorine. The apparatus consisted of a flow system in which gaseous fluorine was passed over powdered arsenic and then AsF_5 produced was swept into the first of two cold traps which could be independently isolated by means of J. Young's Teflon stemmed valves. A short manifold, to which a stainless steel cylinder could be attached, was connected to the cold traps. The end of the manifold was arranged such that either a stream of dry nitrogen could be blown across (to disperse unreacted fluorine), or a vacuum applied (to manipulate the volatile AsF_5). The reaction chamber was connected to the traps by a Whitey valve (1KS4) and consisted of a short, wide Pyrex tube fitted with a B34 cone-and-socket joint; a nickel boat containing arsenic could be placed inside. All cold traps were cooled by liquid air (to avoid condensing fluorine) and all connections between metal and glass parts of the apparatus were via ¼" Swagelok Teflon compression fittings and ¼" O.D. copper tubing.

In a typical reaction, arsenic (17g) was placed in the nickel boat and put into the reaction chamber. The whole apparatus was connected together and purged with dry nitrogen. Fluorine from the cell (8 A, 5.4g/h) was passed first through a metal cold trap to remove HF and then into the reaction chamber; a stream of dry nitrogen was passed across the open end of the manifold. Vigorous exothermic reaction occurred almost immediately and a white volatile solid was isolated in the first cold trap; a small amount of a white volatile was isolated in the second cold trap. After approximately 4h, reaction ceased and after the apparatus had been disconnected from the fluorine cell, it was purged with dry nitrogen (10 min). The traps, manifold and stainless steel cylinder were isolated from the rest of the apparatus and evacuated. The second trap was isolated from the first and the small amount of white volatile solid it contained was pumped away. The white volatile material remaining in the first trap (AsF_5) was then transferred to the stainless steel cylinder and stored there before use.

b) Silver hexafluoroarsenate, $AgAsF_6$. This material was prepared by reaction of powdered silver and AsF_5 according to Equation 2.1.

$$2Ag + 3AsF_5 \longrightarrow 2AgAsF_6 + AsF_3 \qquad \text{Equ. 2.1}$$

Powdered silver (5.99g, 55.53 mmol) was placed in a pre-weighed glass bulb (ca. 250 ml) fitted with a J. Young's Teflon stemmed valve. SO_2 (8.7g) was condensed on top and after re-weighing the bulb, AsF_5 (15g) was condensed into the bulb. The vessel was allowed to warm slowly to room temperature and an exothermic reaction occurred to give a light tan solution above the unreacted silver powder. This process was repeated until a total of 15.24g (89.7 mmol) of AsF_5 had been added. After standing and shaking, all the silver powder dissolved to give a lighter brown solution. Removal of the reaction volatiles (excess AsF_5, SO_2, AsF_3) yielded a white microcrystalline solid ($AgAsF_6$). Yield, 16.1g (98%). Infrared spectrum, ν_{max} 690vs, 385s cm^{-1}.

c) Potassium thiocarbonate, K_2CS_3. This was prepared according to the procedure of Deskin.(7)

ν_{max} = 3140m, 1580vw, 1150w, 1010vw, 920m, sh, 885s, 815w, sh, 515w, cm^{-1}. Found; K, 42.9; S, 50.0; K_2CS_3 requires K, 41.9; S, 51.6%.

2.6 Miscellaneous Reagents:

a) Sulphur tetrafluoride, SF_4. This gas was supplied by Matheson and used directly from the cylinder.

b) Arsenic pentafluoride, AsF_5. For work performed in Canada (in particular the preparation of NSF described in Chapter 5), it was possible to use AsF_5 commercially supplied by Ozark-Mahoning. This was used directly from the cylinder.

c) Fluorine F_2. For the passivation of vacuum line and reaction cans described in Chapter 5, elemental fluorine supplied by Matheson was used, direct from the cylinder.

d) Arsenic trifluoride, AsF_3. This material was supplied by Ozark-Mahoning and was stored in a Pyrex bulb over NaF, being distilled therefrom before use.

e) Trifluoroacetonitrile, CF_3CN. Supplied by Ozark-Mahoning, this was used directly from the cylinder.

f) Trifluormethyl hypofluorite, CF_3OF. Supplied by P.C.R., this was used directly from the cylinder.

g) Hexafluorobut-2-yne, CF_3CCCF_3. Supplied by P.C.R., this was used directly from the cylinder.

h) Cyanogen, $(CN)_2$. Supplied by Matheson, this was used directly from the cylinder.

i) **Phosphorus trifluoride, PF_3.** Supplied by Ozark-Mahoning, this was used directly from the cylinder.

j) **Chlorine, Cl_2.** Supplied by Matheson, for large-scale experiments this was used from the cylinder and passed through a P_4O_{10} column prior to reaction. For the experiments described in Chapter 7 small amounts of chlorine were condensed on P_4O_{10} and stored in thick-walled Pyrex bulbs, equipped with J. Young's Teflon stemmed valves, before use.

k) **Silver, Ag.** Silver powder was supplied by B.D.H. and used directly from the bottle.

l) **Silver tetrafluoroborate, $AgBF_4$.** Supplied by B.D.H., this material was stored in its black polythene container, in a glove box.

m) **Boron trifluoride, BF_3.** Supplied by B.D.H., this was used directly from the cylinder.

n) **Fluoroboric acid, HBF_4 (aq).** Supplied by Koch-Light, this 50% solution was used directly from the bottle.

o) **Caesium fluoride, CsF.** It was found that the powdered microcrystalline form supplied by Alpha was most suitable for the reactions discussed in this thesis. Fresh CsF was heated in vacuo to 200°C for 4h before use and was stored under dry nitrogen in a sealed container, in a glove box.

p) Other alkali metal fluorides. Lithium, sodium, potassium, and rubidium fluorides from various supplies were dried by heating in vacuo before use.

q) Ammonium chloride, NH_4Cl. Supplied by Hopkin and Williams, this was dried at 100°C in an oven before use.

r) Sulphur. Supplied by B.D.H., this was dried in vacuo before use.

s) Di-sulphur di-chloride, S_2Cl_2. Supplied by B.D.H. this was used directly from the bottle.

t) Iron (III) Chloride, $FeCl_3$. Supplied by B.D.H., this was refluxed in thionyl chloride before use.

u) Lithium perchlorate, $LiClO_4$. Supplied by B.D.H., this was dried by fusing it under an atmosphere of dry nitrogen; it was stored in a sealed container in a glove box

v) Tetrabutyl ammonium tetrafluorborate, Bu_4NBF_4. Supplied by Aldrich, this was dried by heating in vacuo (3h, 100°C, 10^{-6} torr).

w) Antimony pentachloride, $SbCl_5$. Supplied by B.D.H., this was distilled before use (68°C/14 torr).

2.7 Purification of Solvents:

a) Sulphur dioxide, SO_2. Sulphur dioxide, supplied by B.D.H., was distilled from P_4O_{10} and stored over CaH_2 before use. The distillation and storage were conveniently performed using stainless steel bombs (designed by Z.V. Hauptman) which could accommodate 500 ml batches of SO_2.

b) Acetonitrile, CH_3CN. Two grades of acetonitrile were used. For electrochemical use, a lengthy purification according to the method of Walter and Ramaley(8) was necessary; this consisted of distillation from $AlCl_3$ (to remove acrylonitrile), distillation from $Li_2CO_3/KMnO_4$ (to remove acidic and aromatic impurities), distillation from $KHSO_4$ (to remove amines), and finally distillation from CaH_2. The purified acetonitrile was stored under dry nitrogen in a Pyrex bulb fitted with a J. Young's Teflon stemmed valve and its purity was confirmed by UV spectroscopy and gas-liquid chromatography. It was found that satisfactory results could only be obtained if high-purity acetonitrile (e.g. Fisons H.P.L.C. grade) was used to begin with.

For general purpose use as a solvent, H.P.L.C. grade acetonitrile was distilled from P_4O_{10} and stored in a Pyrex bulb fitted with a J. Young's Teflon-stemmed valve.

c) Solvents dried with sodium wire. These were diethyl ether, toluene, n-pentane.

d) Solvents dried by distillation from P_4O_{10}. These were nitromethane, carbon tetrachloride, methylene chloride.

e) Thionyl Chloride, $SOCl_2$. This was distilled from triphenyl phosphite (10% by weight)$^{(9)}$ in an apparatus fitted with Teflon sleeves. It was stored in the dark in a Pyrex bulb fitted with a J. Young's Teflon stemmed valve.

f) Sulphuryl chloride fluoride, SO_2ClF. Supplied by Aldrich, this solvent was stored over activated molecular sieve in a Pyrex bulb equipped with a J. Young's Teflon stemmed value before use.

g) Freon 11, CCl_3F. Supplied by P.C.R., this was stored over activated molecular sieve in a Pyrex bulb equipped with a J. Young's Teflon stemmed valve before use.

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CHAPTER 3

THE PREPARATION, CHEMICAL REACTIONS AND STRUCTURE OF S_5N_5Cl

3.1 INTRODUCTION

The cyclopentathiazenium ion ($S_5N_5^+$) was first reported by Banister and Dainty.(1) It is the largest known binary sulphur nitrogen ring and is recognised to be a 14-π member of the series of Hückel-aromatic thiazenes (c.f. S_2N_2 and $S_4N_4^{2+}$).(2,3)

Little was and is known of the chemistry of $S_5N_5^+$ salts although their 1:1 sulphur:nitrogen ratio made them likely precursors to the superconducting polymer, $(SN)_x$.(4) Several reports of the structure of the $S_5N_5^+$ ion exist; an early determination(5) describes a heart-shaped conformation whereas more recent papers,(6,7) describe an azulene-type structure. The discrepancy has been explained in terms of cation disorder in the crystal;(8) this theory has the advantage of being able to account for the 'intermediate' structures which have also been found in $S_5N_5^+$ compounds (see, for example, reference 28). Recent theoretical calculations,(9) however, predict similar energies for the two structures and thus genuine isomerism remains a possibility.

Most known $S_5N_5^+$ salts contain large, stabilising counter-ions such as $S_3N_3O_4^-$,(6) $SnCl_5OPCl_3^-$,(7) and $AlCl_4^-$;(5) this is not so for the chloride, $S_5N_5^+Cl^-$, first prepared in an unstable form by

Zbořilová and Gebauer.(10) This compound when prepared in a stable form (see Section 3.2.1) therefore afforded an opportunity to study the chemistry of the $S_5N_5^+$ ion without possible interference from metallic species or other complex anions. The scarlet-red colour of the chloride compared to the usual pale yellow colour of $S_5N_5^+$ compounds (containing colourless counter-ions), indicated either significant cation-anion interactions in the solid state or a different cation conformation; hence a crystal of the pure, stable compound was submitted for structural analysis. Further, the original preparation of S_5N_5Cl from a mixed melt of $(NSCl)_3$ and S_4N_4(10) indicated that the thermochemistry of S_5N_5Cl itself would be of interest. This chapter describes studies of the synthesis, chemistry, and thermochemistry of S_5N_5Cl together with a discussion of both its crystal and electronic structures.

3.2 RESULTS AND DISCUSSION

3.2.1 The Preparation of S_5N_5Cl from $S_5N_5FeCl_4$:

The original report of S_5N_5Cl(10) described it as a thermally unstable solid which could be stored only at low temperature (-20°C). The significance of the new route to S_5N_5Cl, described below, lies in the stability of the product; it can be stored for several months at room temperature in a dry nitrogen atmosphere without decomposition. This, together with the accessibility of the starting materials, makes S_5N_5Cl a useful reagent with which to investigate the chemistry of the $S_5N_5^+$ ion in the absence of other large or Lewis-acidic counterions;

it is also a potentially useful starting material for the preparation of other $S_5N_5^+$ salts by metathesis.

The overall reaction in the preparation from $S_5N_5FeCl_4$ is shown in Equation 3.1.

$$S_5N_5FeCl_4 + 3CsF \longrightarrow S_5N_5Cl + 3CsCl + FeF_3 \qquad \text{Equ. 3.1}$$

Unlike the original route (Equation 3.2, Reference 10),

$$S_4N_4 + \tfrac{1}{3}(NSCl)_3 \longrightarrow S_5N_5Cl \qquad \text{Equ. 3.2}$$

it requires prior formation of the $S_5N_5^+$ ring. The difference in stability of the product prepared by these two routes probably arises from the presence of other, more reactive S-N-Cl compounds produced in Equation 3.2. These may either be formed in the melt or in the subsequent recrystallization from formic acid - a procedure which has been found to adversely affect the stability of S_5N_5Cl.(11) In attempted repetitions of the preparation of S_5N_5Cl from S_4N_4 and $(NSCl)_3$, the purity of starting materials was found to have a critical effect on the formation of the melt and of the yield of product; very pure starting materials did not melt homogenously and produced only low yields of S_5N_5Cl, whereas less pure starting materials melted more easily to produce the crude, unstable material.(11)

The successful preparation of S_5N_5Cl using the heavier alkali metal fluorides (K, Rb, Cs) compared with the failure of the reaction using NaF and LiF, reflects a general trend in the reactivity of alkali metal fluorides in halogen exchange reactions.(12) A more quantitative view may be obtained by considering the prototype reaction.-

$$3MF + FeCl_3 \longrightarrow 3MCl + FeF_3 \qquad \text{Equ. 3.3}$$

The change in free energy ΔG_{298} for the reaction, using different M, can be calculated from published values of ΔG_{298}.(13) The results are summarised in Table 3.1 (all values in Kcal/mol).

Table 3.1

M	ΔG_{298} MCl	ΔG_{298}MF	ΔG_{298} reaction
Li	91.786	128.515	26.903
Na	91.788	129.866	22.866
K	97.506	139.746	44.063
Cs	99.038	125.571	57.084
Fe	81.9	219.0	

which clearly shows the thermodynamic advantage of the heavier alkali metal fluorides. Note that notwithstanding thermodynamic arguments, the insolubility of NaF and LiF in SO_2 may be responsible for their failure to react.

The synthesis of S_5N_5Cl using alkali metal fluorides essentially consists of a chemical removal of $FeCl_3$ from $S_5N_5FeCl_4$. This strategy has been extended by the group in Durham(14) who have developed an alternative route to pure, stable S_5N_5Cl by removal of $AlCl_3$ from $S_5N_5AlCl_4$ by reaction with tetrahydrofuran (THF):

$$S_5N_5AlCl_4 + THF \longrightarrow S_5N_5Cl + AlCl_3.THF \qquad \text{Equ. 3.4}$$

3.2.2 The Preparation of $S_5N_5BF_4$:

As mentioned in the introduction, the $S_5N_5^+$ ion has a favourable stoichiometry for reduction to the super-conducting polymer $(SN)_x$. Electrochemical investigations (Chapter 4) showed that solutions of S_5N_5Cl in SO_2 could be reduced to give good quality $(SN)_x$ at a platinum cathode. This route suffered from the disadvantage of using SO_2 as solvent, which is not convenient for electrochemistry; other media such as anhydrous acetonitrile are much more desirable. The almost total insolubility of S_5N_5Cl in acetonitrile meant that other, soluble, $S_5N_5^+$ salts had to be used, subject to the restriction that the counterion should be electrochemically inactive and should contain no metallic species to contaminate the polymer. The BF_4^- ion fulfills these criteria and the solubility of the $S_4N_3^+$ salt suggested that $S_5N_5BF_4$ would be suitable.

The synthesis of $S_5N_5BF_4$ was achieved by reaction of S_5N_5Cl with aqueous HBF_4 at low temperature (-15°C):

$$S_5N_5Cl + HBF_4(aq) \xrightarrow{-15°C} S_5N_5BF_4 + HCl(aq) \qquad \text{Equ. 3.5}$$

The preparation relies on the remarkable stability of the $S_5N_5^+$ cation in strongly acidic media; the solvation of HCl probably provides a strong driving force for the reaction. The failure of a similar metathesis reaction:

$$S_5N_5Cl + KBF_4 \xrightarrow{SO_2} S_5N_5BF_4 + KCl \qquad \text{Equ. 3.6}$$

is probably a result of the insolubility of KBF_4 in liquid SO_2.

3.2.3 Chemical Reactions of S_5N_5Cl:

a) Reduction by Me_3SiN_3. The production of $(SN)_x$ from this reaction is directly analogous to the chemical synthesis of $(SN)_x$ from azides and sulphur-nitrogen chlorides.(15) The highly reflective nature of the golden flakes isolated from the reaction was taken to be an indication of the good quality of the $(SN)_x$ produced; these flakes were probably formed by the mechanical beating of finely divided, malleable $(SN)_x$ by the magnetic stirrer. The amorphous SiO_2 impurity probably originated from impurities in the Me_3SiN_3.

b) Reaction with K_2CS_3. The original aim of this reaction was the synthesis of an $S_5N_5^+$ salt with a carbon-containing counter-ion which could be a possible precursor to a carbon-containing conductive polymer. Such a polymer might be amenable to modification, for example by the addition of functional groups to the polymer back-bone, thus producing changes in the physical properties of the polymer (e.g. solubility, super-conducting transition temperature). In fact, the reaction with K_2CS_3 is vigorous even at low temperature and produces a

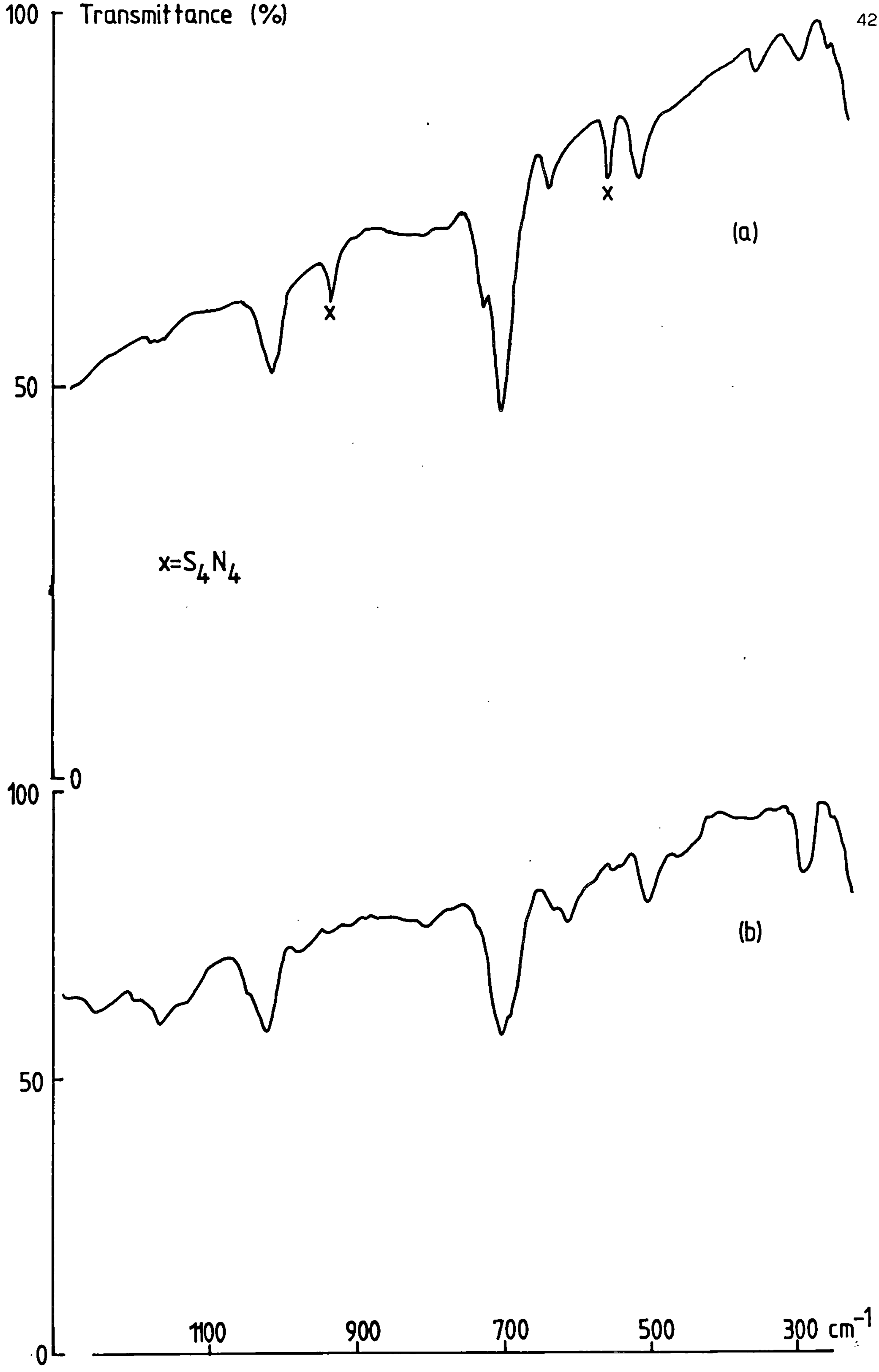


Figure 3.1. Infrared spectra of $(SN)_x$ (nujol mull, CsI plates).
a) Classical $(SN)_x$ contaminated with a little S_4N_4 (supplied by Dr Z.V. Hauptman)
b) Product from the reaction between S_5N_5Cl and K_2CS_3

polymer directly. Exhaustive extraction with SO_2 failed to remove all traces of carbon and so it is quite possible that the product from this reaction contains carbon incorporated in the chain; slight modification in the infrared spectrum compared with $(SN)_x$ (Fig.3.1) suggests that this may be the case. However, the essentially uncontrollable nature of the reaction and the difficulties experienced in obtaining reproducable results from other chemical syntheses of $(SN)_x$,(15) indicated that this route did not merit further attention.

c) Reaction with gaseous BF_3. The aim of the reaction was to prepare $S_5N_5BF_4$:

$$3S_5N_5Cl \xrightarrow{xsBF_3} 3S_5N_5ClBF_3 \xrightarrow{xsBF_3} 3S_5N_5BF_4 + BCl_3 \quad \text{Equ. 3.7}$$

The solid products of the reaction were, however, identified by infrared spectroscopy as a mixture of S_4N_4 and $S_4N_4.BF_3$. Evidently, cleavage of the $S_5N_5^+$ ring had occurred, presumably with liberation of a gaseous species which would account for the bubbling of the solid during reaction:

$$S_5N_5Cl \xrightarrow{BF_3} S_5N_5Cl.BF_3 \longrightarrow S_4N_4.BF_3\ (s) + \text{"NSCl"}$$

$$3\ \text{"NSCl"} \xrightarrow{BF_3} 3NSCl.BF_3 \xrightarrow{BF_3} NSF(g) + BCl_3 + BF_3$$

Scheme 3.1

The adduct $S_4N_4.BF_3$ easily loses BF_3(16) which explains the presence of S_4N_4. Although NSF and BF_3 or BCl_3 may reasonably be expected to form a solid adduct, the BF_3 adduct is reported to be stable only at low temperature (-60°C) and dissociates completely at room temperature.(17)

d) Reaction with $BF_3.Me_2O$. Apart from a small amount of decomposition, no reaction took place. Presumably Me_2O is a stronger base than Cl^-ion in S_5N_5Cl, thereby preventing the initial step of coordination. In terms of bond energies:

$$\sum(Cl^- \rightarrow S_5N_5{}^+) + (Me_2O \rightarrow BF_3) > \sum(Cl^- \rightarrow BF_3) + (Me_2O \rightarrow S_5N_5{}^+)$$

e) Reaction with MeI. The original aim of this reaction was to prepare a methylated derivative of the $S_5N_5{}^+$ ring as a precursor to a methylated S-N polymer. The products isolated, however, were mostly $S_5N_5{}^+I_2Cl^-$ (insoluble) and S_4N_4. The I_2Cl^- compound undoubtedly arises from the reaction of molecular iodine with S_5N_5Cl;(18) the S_4N_4 is probably a result of decomposition during the course of the reaction. The ultimate fate of the methyl groups is unknown but they may be lost as hexane, though reaction with either S_4N_4 or liquid SO_2 is a possibility; these side reactions may explain the unassigned bands in the infrared. The reaction scheme may be represented:-

$$2MeI \longrightarrow 2Me. + I_2 \qquad \text{Equ. 3.8}$$

$$S_5N_5Cl + I_2 \longrightarrow S_5N_5I_2Cl \qquad \text{Equ. 3.9}$$

f) Reaction with AgCN. Again, the desired product, S_5N_5CN, was intended to be a precursor to a carbon-sulphur-nitrogen polymer. The metathetical reaction of S_5N_5Cl with AgCN, however, produced mostly S_4N_4 as the soluble product. The insoluble product, a brown-purple material which showed only the presence of CN^- in the infrared, was probably undissolved AgCN; the dark colour was probably produced by decomposition of $S_5N_5^+$ on the surface of the AgCN granules. There are some unassigned bands in the infrared spectrum of the soluble products; these may originate from the reaction of CN^- with the S_4N_4 produced in situ, since S_4N_4 and KCN are known to form a mixture of products, which include $S_4N_5^-$, SCN^-, and an unidentified CN^- containing species.(18)

g) Hydrolysis of S_5N_5Cl in air. S_5N_5Cl decomposes slowly in moist air to give S_4N_4 and $(NH_4)_2SO_4$ as the major products. These are typical hydrolysis products of sulphur-nitrogen compounds.

Table 3.2 Tensimetric data for the S_5N_5Cl/SO_2 system

Wt of SO_2 in system/g	Mole ratio $SO_2:S_5N_5Cl$	Pressure/mmHg
0.0321	0.6901	5.08
0.0372	0.8004	11.91
0.0382	0.8219	16.88
0.0403	0.8671	27.68
0.0445	0.9575	156.33
0.0446	0.9596	200.13

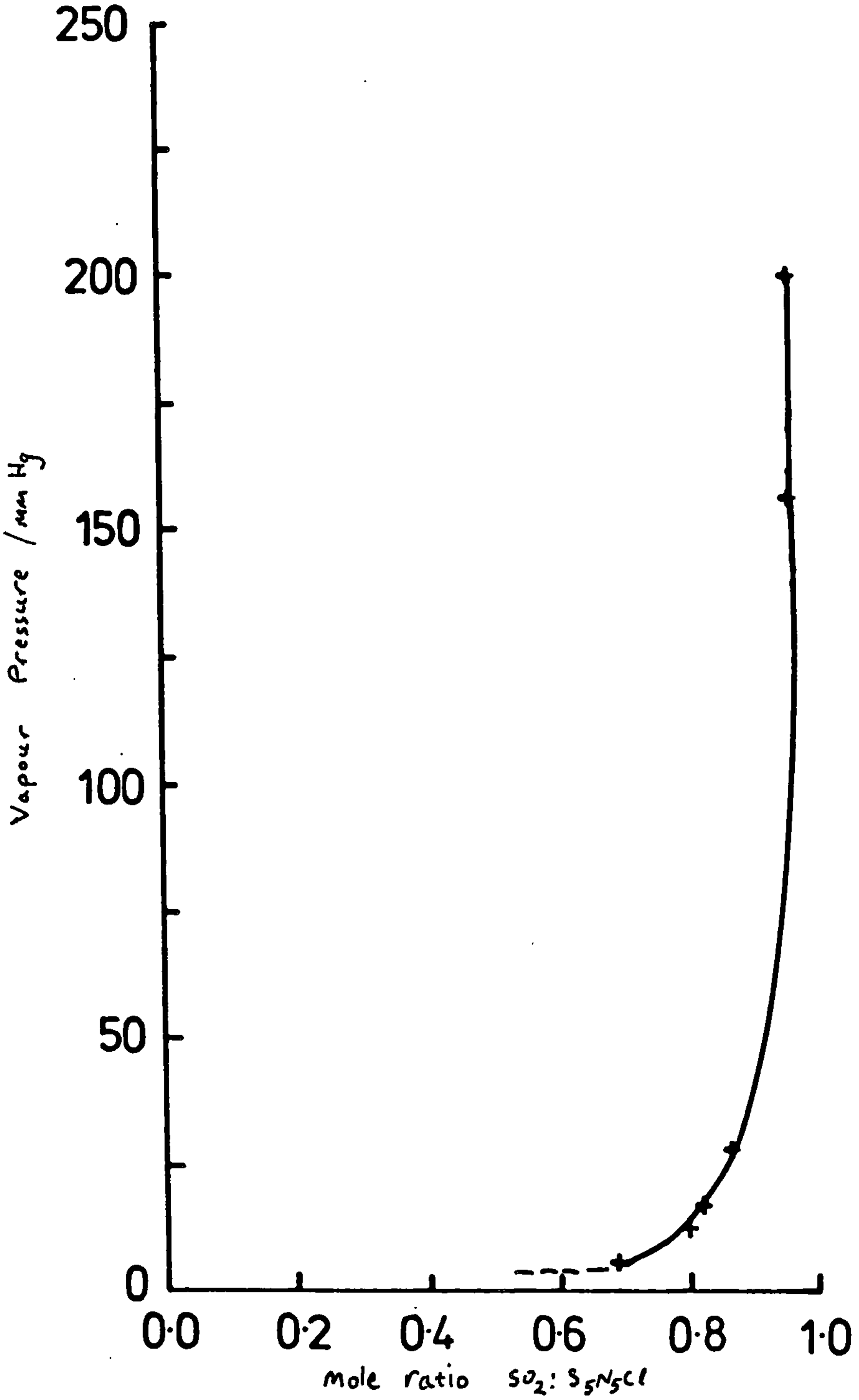


Figure 3.2. Variation of vapour pressure with composition for the S_5N_5Cl/SO_2 system at 2°C.

3.2.4 The action of SO_2 on S_5N_5Cl:

a) S_5N_5Cl is readily soluble in liquid SO_2 (ca. 3g per 100g of solvent). Other $S_5N_5^+$ salts exhibit a similar behaviour (e.g. $FeCl_4^-$, $AlCl_4^-$, BF_4^-); however, whilst other $S_5N_5^+$ salts are also quite soluble in acetonitrile, S_5N_5Cl is virtually insoluble in this medium. On pumping down solutions of S_5N_5Cl in SO_2, the first solids to precipitate are yellow and only become red on pumping to dryness; similarly if S_5N_5Cl is exposed to an atmosphere (ca. 1 atm) of SO_2, the red solid becomes yellow after a few minutes and furthermore seems to exert an almost constant vapour pressure of SO_2 (ca. 20mm Hg).

These observations can be rationalized by postulating the formation of halosulphinate species (SO_2Cl^-) in solution and of a solvate ($S_5N_5Cl.nSO_2$) in the solid state. Tensimetric measurements clearly show (Fig.3.2, Table 3.2) that although the system:

$$S_5N_5Cl + SO_2 \rightleftharpoons S_5N_5Cl.SO_2 \qquad \text{Equ. 3.10}$$

does not equilibrate on a convenient timescale (and hence quantitative ΔH and E_a data are not available), the stoichiometry of the solvate is 1:1.

b) The products isolated from SO_2/S_5N_5Cl mixtures which had been left standing for several months are an illustration of the lability of sulphur-nitrogen species. Two systems were investigated, a saturated solution of S_5N_5Cl/SO_2 (from which a yellow crystalline solid and an orange crystalline solid were obtained) and a sealed ampoule containing approximately equal weights of S_5N_5Cl and SO_2 (from which a yellow crystalline solid were obtained); see Section 3.4.13. The products from the saturated solution of S_5N_5Cl in SO_2, positively identified by infrared spectroscopy, were $S_4N_4O_2$ (20) and $S_4N_3{}^+SO_3Cl^-$.(21) Scheme 3.2 shows a possible reaction path. The formation of $S_4N_4O_2$ was not observed in the sealed ampoule which initially contained solid S_5N_5Cl and a saturated solution of S_5N_5Cl in SO_2; instead, $S_4N_5{}^+SO_3Cl^-$ was identified as a major product together with $S_4N_3{}^+SO_3Cl^-$ and smaller quantities of $S_6N_4Cl_2$ and $OSCl_2$. These differences may have arisen either from the different initial mole ratios of S_5N_5Cl and SO_2 or from the different temperatures at which the mixtures were kept. Scheme 3.3 shows a possible reaction path to the products. It should be said that $OSCl_2$ may have been a product from the saturated solution, but no gas phase infrared spectrum of this system was recorded. The reactions observed in these experiments were very obscure and the products were completely unpredictable. For example, S_4N_4 would be expected as a major decomposition product of S_5N_5Cl but none was detected whereas $S_4N_4O_2$ and $S_4N_5{}^+SO_3Cl^-$ would seem to be unlikely products from this system. Such obscure reactions are, however, not without precedent in the field of sulphur-nitrogen chemistry, as the temperature-sensitive interconversion of $S_6N_4Cl_2$ and S_4N_3Cl, sealed under liquid SO_2,(22) demonstrates.

SCHEME 3.2

a) $\mathrm{S_5N_5Cl.SO_2 \longrightarrow SNSCl + S_4N_4O_2{*}}$

b) $\mathrm{S_5N_5Cl \longrightarrow S_4N_3Cl + N_2S}$

$\mathrm{S_4N_3Cl \xrightarrow{SO_2} S_4N_3O_2Cl}$

$\mathrm{SNSCl + N_2S \xrightarrow{SO_2} S_4N_3O_2Cl}$

$\mathrm{S_4N_3ClSO_2 \xrightarrow{SO_2} 2\ S_4N_3{}^+SO_3Cl^-{*}}$

* = observed product

SCHEME 3.3

a) $\mathrm{S_5N_5Cl.SO_2 \longrightarrow S_4N_3Cl.SO_2 + N_2S}$

b) $\mathrm{S_5N_5Cl.SO_2 \longrightarrow SNSClSO_2 + S_3N_4}$

$\mathrm{S_3N_4 + SNSClSO_2 \longrightarrow S_4N_5ClSO_2 + S}$

$\mathrm{S_3N_4 + S \longrightarrow S_4N_4}$

$\mathrm{S_4N_4 + 2SNSCl \xrightarrow{SO_2} 2S_4N_3ClSO_2}$

$\mathrm{SNSCl \longrightarrow NSCl + S}$

$\mathrm{2SN_2 \longrightarrow S_2N_4 \xrightarrow{NSCl} S_4N_5O_2Cl}$

$\mathrm{SNSCl + N_2S \xrightarrow{SO_2} S_4N_3O_2Cl}$

$\mathrm{S_4N_3O_2Cl + S_4N_3ClSO_2 \longrightarrow 2S_4N_3{}^+SO_3Cl^-{*}}$

$\mathrm{S_4N_5O_2Cl + S_4N_5ClSO_2 \longrightarrow 2S_4N_5{}^+SO_3Cl^-{*}}$

c) $\mathrm{4SNSClSO_2 \longrightarrow S_6N_4Cl_2{*} + 2SOCl_2{*} + 4S}$

$\mathrm{2SO_2Cl \longrightarrow OSCl_2{*} + 2SO_3}$

$\mathrm{S_4N_3Cl + SO_3 \longrightarrow S_4N_3{}^+SO_3Cl^-{*}}$

$\mathrm{S_4N_3Cl + SO_3 \longrightarrow S_4N_3{}^+SO_3Cl^-{*}}$

* = observed product

Table 3.2a Infrared data and assignments for pale yellow crystals ($S_4N_3^+SO_3Cl^-$)

$S_4N_3^+SO_3Cl^-/cm^{-1}$	$S_4N_3^+FeCl_4^-/cm^{-1(23)}$	$Me_4N^+SO_3Cl^-/cm^{-1(24)}$
1320w,sh		
1286vs,sh		
1260vs		1275
1250vs,sh		
1170m	1178m	
1155m	1138w,1094vw	1150
1055vs		1044
1035s,sh	1032,1020s,sh	
820m		
	751vw	
	723vw	
683m	676s,670m,sh	
	647vw	
625m	616w	
590s	570m	
580s		585
540s	564m,sh	565
530s		535
	517m	
490s	486vs,br	
450w	469s,br	
360m,sh		
323s		

Table 3.3b Infrared data and assignments for orange solid ($S_4N_4O_2/S_4N_3{}^+SO_3Cl^-$)

Orange solid/cm^{-1}	$S_4N_3{}^+SO_3Cl^-$/cm^{-1}	$S_4N_4O_2$/cm^{-1}(20)*
1330s		1330vs
1280vs,sh	1286vs,sh	
1260vs	1260vs	
1250vs,sh	1250vs,sh	
1160m	1170m	1170m
1140s	1155m	1138m
1120s		1117us
1045s	1055vs	1060m
1035m,sh	1035s,sh	
980vw		982m
810m	820m	
720m		719m
705s		704m
680m	683m	*Spectrum not reported
635s	625m	below 700 cm^{-1}
590s	590s	
580s	580s	
555m,sh		?
540m	540s	
530m	530s	
505m		?
490s	490s	
455vw,sh	540w	
450s		?
380s,sh		?
	360m,sh	
	332s	

Table 3.3c **Infrared data and assignments for dark red microcrystalline solid ($S_4N_5^+SO_3Cl^-/S_6N_4Cl_2$)**

Dark red solid/cm^{-1}	$S_4N_5^+AsF_6^-$/cm^{-1}(25)	$Me_4N^+SO_3Cl^-$/cm^{-1}(24)	$S_6N_4Cl_2$(22)
1285vs		1275	
1260vs			
1170s	1165w	1150	
1050s		1044	
1025vw,sh	1025w		1018m
990s	980s		
962w			962s
945w			944s
881w			
825s			
710m	708sh		707vs
700w,sh			698vs
625vs	629m		
580w	587sh	585	585s
560w	577s	565	
542m		535	
525s	495w		
	469m		
431m	423vw		433s
375vw			371s
360w			
340vw			
295w			

Table 3.3d Infrared data and assignments for gas phase from ampoule

gas phase from ampoule/cm^{-1}	$OSCl_2/cm^{-1}$(26)	SO_2/cm^{-1}(26)
1350vs		1359,1354
1255sh	1251	
1245m		
1155vs		1152
1145vs		
528vs		519
500vs		

3.2.5 Thermal studies of S_5N_5Cl:

Since S_5N_5Cl was first prepared from the reaction of S_4N_4 and $(NSCl)_3$ in the melt,(10) the action of heat on S_5N_5Cl is of interest with respect to the mechanism of this reaction. The thermolysis of S_5N_5Cl was studied using Raman spectroscopy and also differential scanning calorimetry (D.S.C.), in sealed containers under dry nitrogen.

For pure S_5N_5Cl in a sealed capillary, partial melting occurred at ~95°C followed by decomposition to S_4N_4, S_4N_3Cl (involatile) and $(NSCl)_3$ (volatile), the products being identified by Raman spectroscopy. This was confirmed by D.S.C. which clearly showed a small endothermic event (melting) followed by a large exothermic event (decomposition). The exact onset and peak temperatures varied slightly (±3°C) with the sample (even from the same batch of S_5N_5Cl) and appeared to depend on factors such as degree of crystallinity and efficiency of thermal contact. A typical D.S.C. trace is shown in Figure 3.3. The products of thermolysis from the D.S.C. experiment consisted of a yellow crystalline mass (involatile) identified by infrared spectroscopy as a mixture of S_4N_4 and S_4N_3Cl, and a very small amount of a sticky orange material (volatile) which coated the inside of the aluminium cap. This orange material could not be identified but was probably a product of reaction between $(NSCl)_3$ and Al, possibly $S_4N_3AlCl_4$ or $S_5N_5AlCl_4$,(27) or a mixture of this with $AlCl_3$ and S_4N_4. On cleaning the aluminium capsule and examining it under a microscope, the portion which had been in contact with S_5N_5Cl was found to be slightly etched, hence the observed ΔH for the thermolysis ($\Delta H = 16$ KJmol^{-1}) is likely to be too high, being distorted by exothermic reaction with aluminium. The D.S.C. also affords an insight into the original preparation of S_5N_5Cl from S_4N_4 and $(NSCl)_3$ Since S_5N_5Cl is thermodynamically unstable with respect to thermolysis products, its formation in the melt is a kinetically controlled process. This accounts for the observed dependence of S_5N_5Cl formation in the melt on purity (high purity of starting materials results in an unfavourably high melting point) and on other factors such as rate of heating, degree of dispersion, and crystallinity of starting materials.

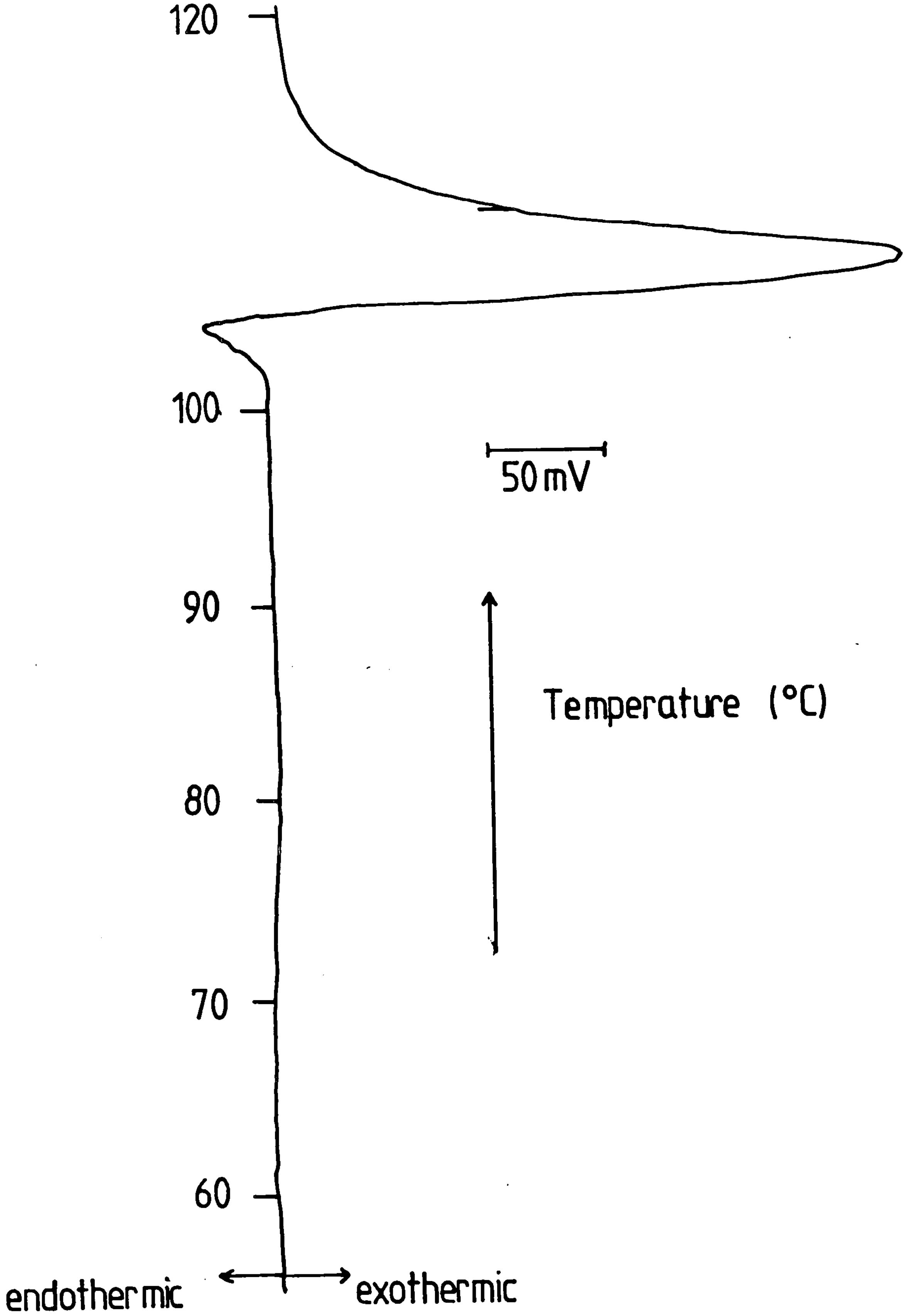


Figure 3.3. A typical D.S.C. trace for S_5N_5Cl in an aluminium capsule

3.2.6 Structure of S_5N_5Cl:

Perhaps the most striking example of $S_5N_5^+$ disorder was described by Gillespie $^{(28)}$ for $S_5N_5SbCl_6$, in which the cation appears as a distorted azulene type ring. In S_5N_5Cl, however, there is no such disorder and in contrast to the approximate non-crystallographic mm symmetry of the $S_5N_5^+$ ion in previous structures,$^{(28)}$ a crystallographic C_2 axis passes through the apical atoms S(1) and N3). Bond distances and angles within the cation are shown in Fig.3.4. The distances of the atoms from the mean plane are also indicated; the ten-membered azulene type ring is almost planar. Three of the five unique S-N distances [S(1)-N(2), S(2)-N(2), and S(3)-N(2)] have the same value within the limits of error whilst S(2)-N(2) and S(3)-N(3) are significantly below and above that value respectively.

The packing of the ions is shown in Figures 3.5, 6, and 7; the cations are disposed in layers approximately parallel to (001), separated by c/2 with the chloride ions interleaved. There are four short S-Cl distances; S(2) makes contacts of 3.277(1) and 3.148(1) Å to Cl at (½, ½, ½) and (½, ½, 0) respectively and S(3), makes contacts to the same Cl of 3.243(1) and 3.279(1) Å. The shortest distance to S(3) is 3.659(1) Å to Cl at (0, 0, 0); this is close to the sum of the van der Waals radii (viz. 3.6 Å). The cation is thus bound to four anions by eight close contacts and it is these interactions which are responsible for the prevention of disorder in S_5N_5Cl.

Recently, correlation functions relating bond angles at nitrogen to adjacent bond lengths have been proposed.$^{(29)}$ The relevant function for cations is:

$$d(NS) = 187.03 - 0.2263\hat{N}$$

where d is in pm and N is in degrees. The correlation can be used to rationalize ring geometries and to detect distortions arising from secondary interactions.(29) For the cation in S_5N_5Cl, the observed mean bond length is 1.582(2) Å [158.2(2)pm] and the observed mean angle at nitrogen is 140.2(2)°. These values deviate from the correlation, the observed bond length being longer than would be anticipated for an angle of 140.2(2)°. The observed mean bond distance is also greater than the calculated value (1.544 Å) obtained by MNDO method (see Section 3.27 below); the calculated mean bond angle at nitrogen is 143.9°. Comparison with the S-N bond lengths found in previously reported, disordered, $S_5N_5^+$ salts is not possible because disordered structure solutions correspond to a statistical model of the solid state structure. The 'real' bond lengths and angles would therefore need to be extracted by a statistical analysis procedure before meaningful comparisons could be made; it has not been possible to devise such a procedure.(30)

The deviations observed in S_5N_5Cl may be ascribed to electron drift from the chloride ion into a low energy unoccupied π^* orbital (see Figure 3.8), which causes a corresponding weakening and lengthening of the bonds. This mechanism may also account for the bright red colour of S_5N_5Cl compared to the usual yellow, since the interaction of the Cl^- ion with the LUMO would perturb the π-system of

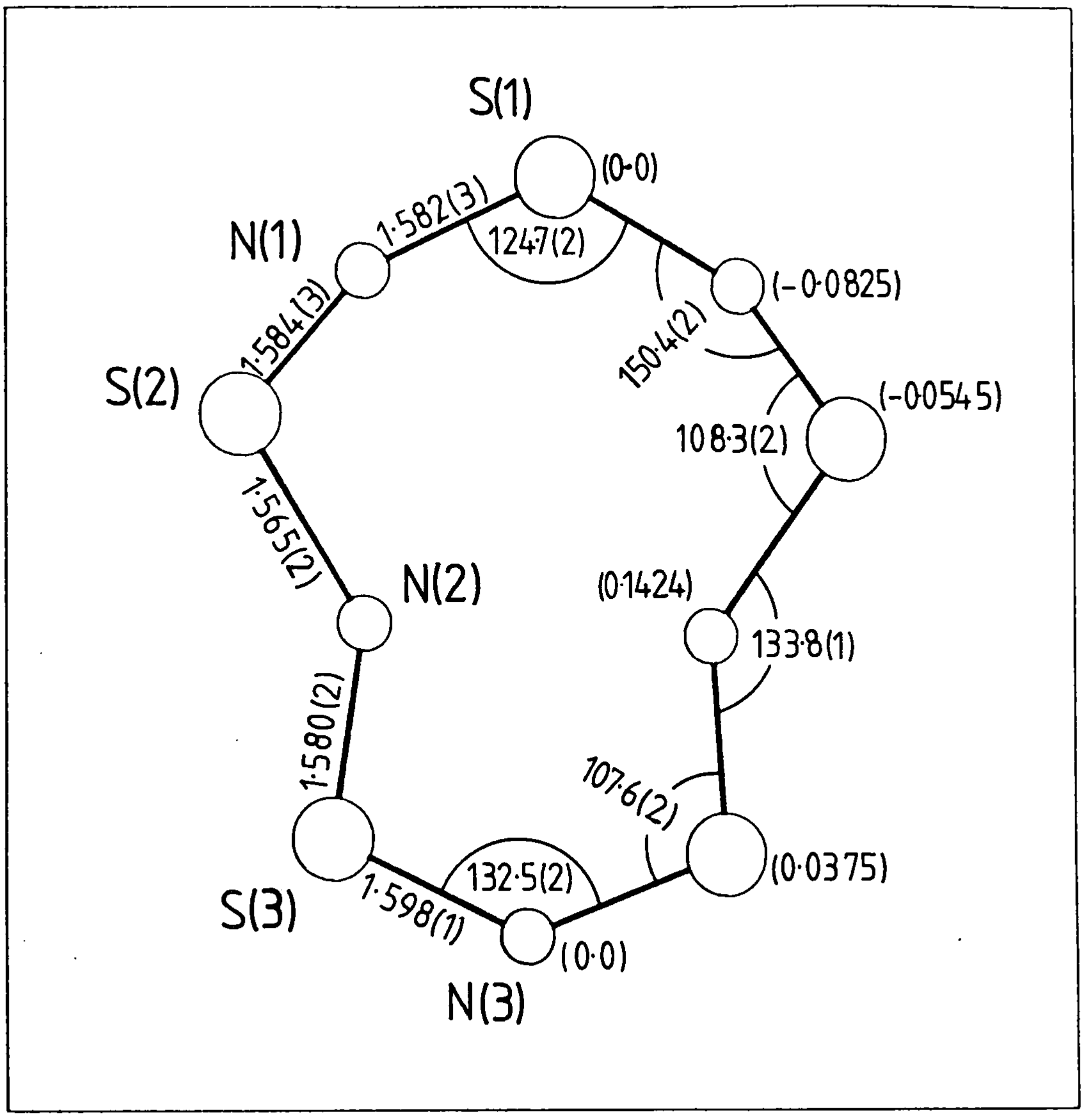


Figure 3.4. The geometry of the $S_5N_5^+$ ion in S_5N_5Cl. Bond lengths (Å) and bond angles (°) are shown with their e.s.d.'s Distances (Å) from the plane 1.38x + 6.690z = 1.745 are also shown

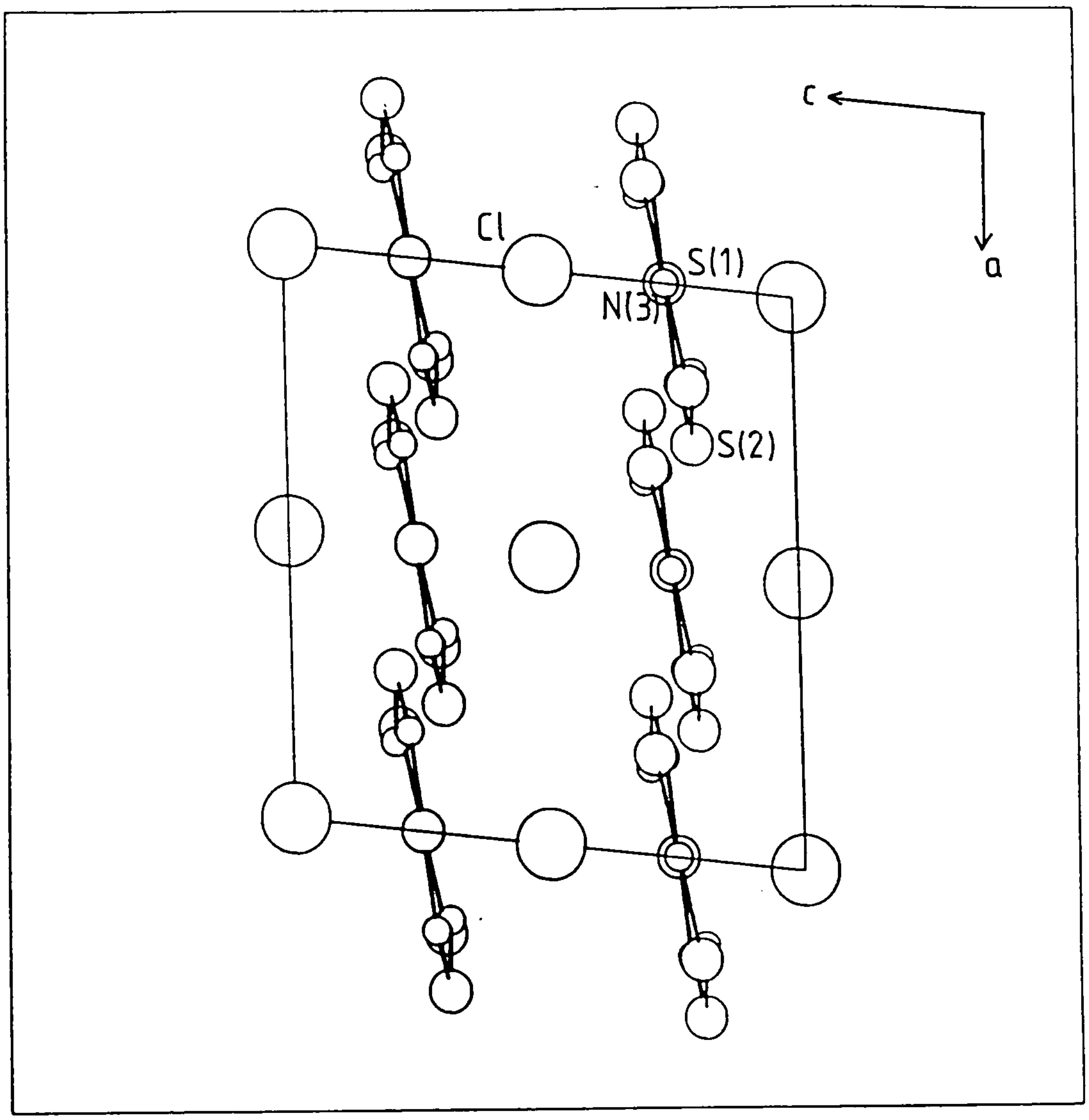
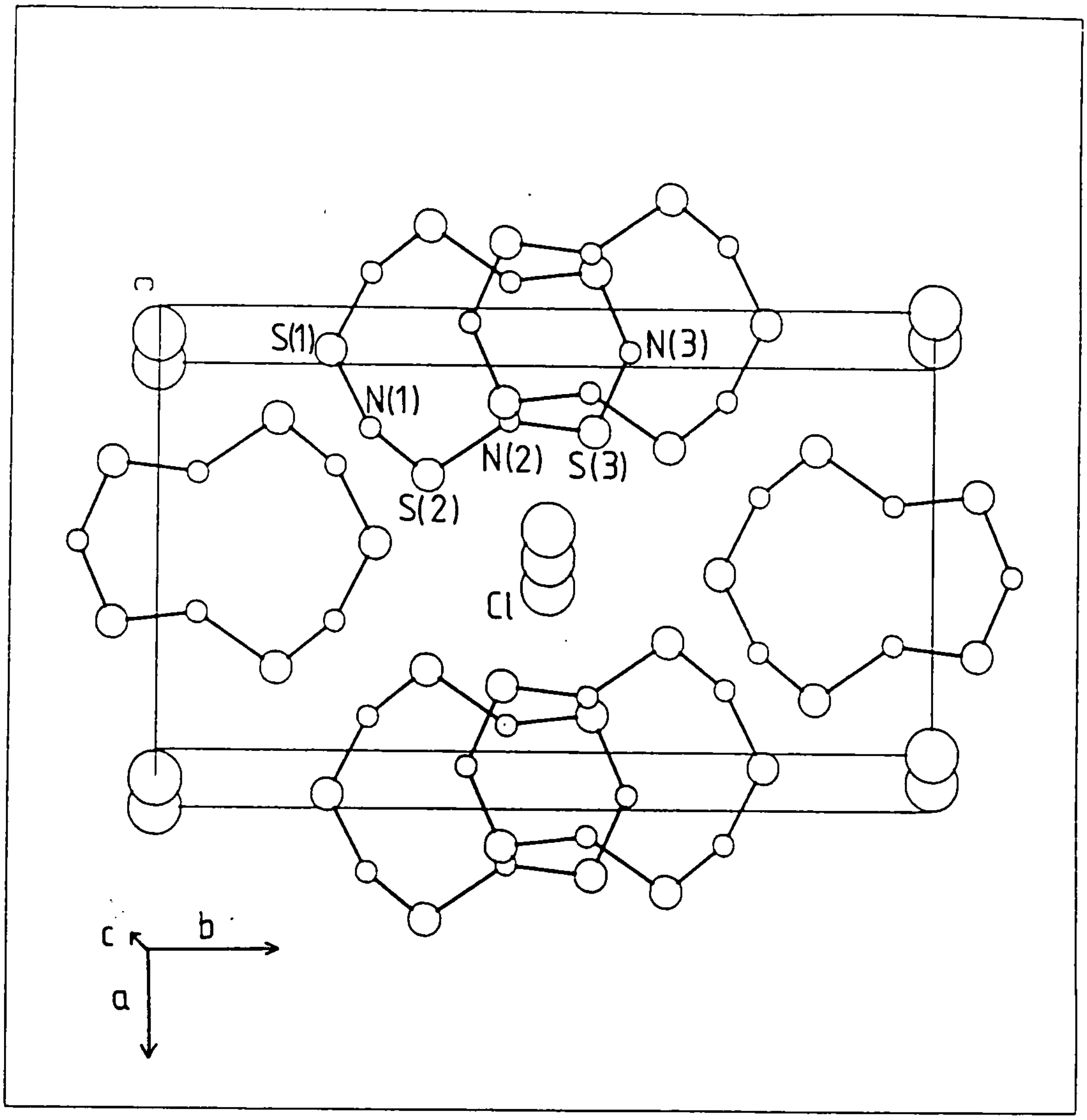


Figure 3.5. Projection of the unit cell of S_5N_5Cl on (010)



3.6

Figure 3.6. Projection of the unit cell of S_5N_5Cl on (001)

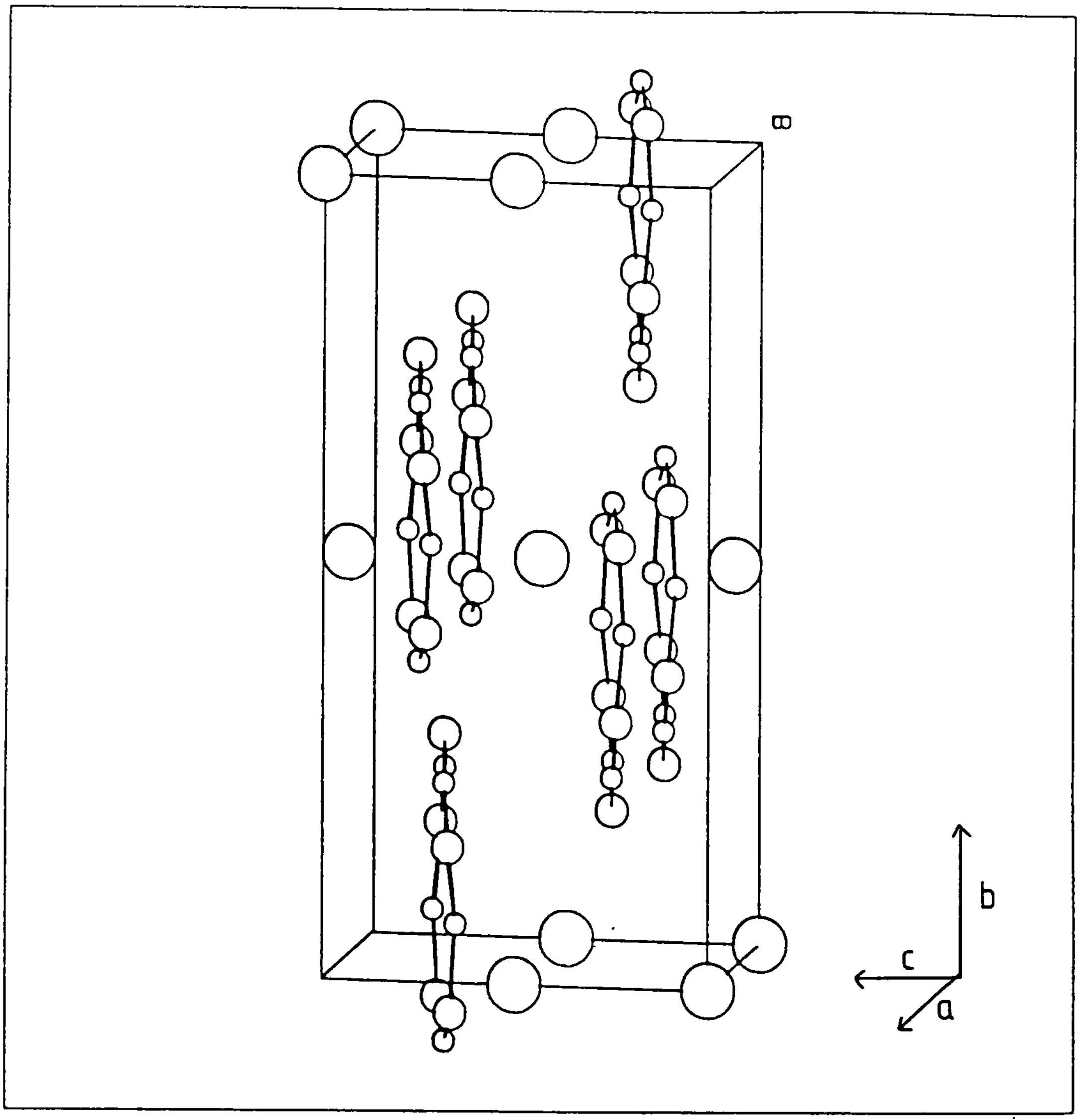


Figure 3.7. Projection of the unit cell of S_5N_5Cl approximately on (100)

Table 3.4 Crystal data and fractional co-ordinates (x 10^4) for S_5N_5Cl

S_5N_5Cl; Monoclinic, space group $C_{2/c}$

a = 7.98(1), b = 14.37(1), c = 7.30(1)Å, β= 97.15(5)

z = 4, D_c = 2.12 g cm^{-3}

	x	y	z
Cl	0	0	5000
S(1)	0	2207(1)	2500
S(2)	2750(1)	3642(1)	2039(1)
S(3)	1751(1)	5576(1)	2103(1)
N(1)	1720(3)	2718(2)	2281(5)
N(2)	1505(3)	4485(2)	2001(4)
N(3)	0	6024(2)	2500

Table 3.5 Thermal parameters for S_5N_5Cl (U_{ii} x 10^4), $Å^2$.

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Cl	284(4)	473(6)	428(4)	-27(4)	65(4)	46(4)
S(1)	343(5)	212(4)	1302(13)	0	270(7)	0
S(2)	205(3)	287(3)	796(5)	-5(3)	149(3)	18(2)
S(3)	242(3)	254(3)	641(5)	-6(3)	85(3)	-50(2)
N(1)	304(11)	294(12)	972(22)	7(14)	179(13)	13(9)
N(2)	225(9)	252(10)	574(13)	-18(10)	103(9)	6(7)
N(3)	292(14)	241(14)	579(18)	0	56(14)	0

the cation. If the HOMO-LUMO gap diminishes as a result, the UV-visible absorption would shift to longer wavelengths and the compound would appear to be more red. This is what seems to be happening in S_5N_5Cl. On addition of SO_2 to the salt, the chloride ion co-ordinates preferentially to it and the yellow colour of the $S_5N_5^+$ ion is restored (see Section 3.2.4a).

The lengthening of sulphur-nitrogen bonds in $S_5N_5^+$ by interaction with halide ions also accounts for the observed lability of S_4N_3F ; (Section 5.2.4) the greater donating power of the fluoride ion probably destabilizes the $S_4N_3^+$ ring sufficiently to render the compound unstable. On this basis it is anticipated that the compound S_5N_5F may be virtually unpreparable at room temperature.

3.2.7 Electronic Structure of S_5N_5Cl:

The electronic spectrum of the $S_5N_5^+$ cation has previously been investigated at the π - electronic PPP level,(31) and the Extended Hückel level.(33) A brief MNDO(32) study of the relative stability of various $S_5N_5^+$ isomers has also been published.(9) The $S_5N_5^+$ ion has been re-examined at the MNDO level in order to calculate its electronic structure and the geometry of the azulene type ring.

Two calculations were performed, (see Figures 3.8 and 9), using the bond lengths and ring angles observed in the structure of S_5N_5Cl, (with the twist angles set to zero), as an initial geometry; in the first calculation the ring was constrained to a plane (C_{2v} symmetry) whilst in the second, the ring was allowed to buckle out of plane. The results from the two calculations were essentially the same. As the largest ring torsion angle calculated in the fully optimised case was only 3.6° and the difference in energy between the two calculations was only 0.155 Kcal mol^{-1}, the discussion will be in terms of the planar (C_{2v}) molecule.

In $S_5N_5^+$, the 54 valance electrons occupy ten σ-bonding orbitals and ten lone-pair orbitals, leaving fourteen electrons to be distributed amongst seven π-orbitals. The π-orbitals are shown in Figure 3.8. The MNDO calculation predicts a slightly different ordering of orbitals than a previous Extended Hückel study;(33) we find that the HOMO of the ion is a π-type orbital, with lone pair molecular orbitals lying at slightly lower energies than the HOMO and HOMO-1 (-15eV compared to -13eV). The MNDO program(32) allows configuration interaction calculations for the excited singlet to be performed; the M.O. energies computed can be used to predict the UV/visible spectrum of the species in question. These calculations for $S_5N_5^+$, however, failed to achieve self-consistence, although substantial agreement with published calculations(28,33) is anticipated since the PPP-CI calculations of Bartetzko and Gleiter(33) predict only minor changes in the electronic spectrum for different conformers of $S_5N_5^+$.

The calculated atomic charges and molecular geometry are shown in Figure 3.9. The calculated mean bond length is 1.544 Å and the calculated mean angle at nitrogen is 143.9°. These values are in strong agreement with the correlation function, since the function predicts a bond length of 1.545 Å for a bond angle of 143.9°. The MNDO values are within 0.2 of an e.s.d. of the correlation function and thus the value of both approaches in predicting minimum energy conformations is confirmed.

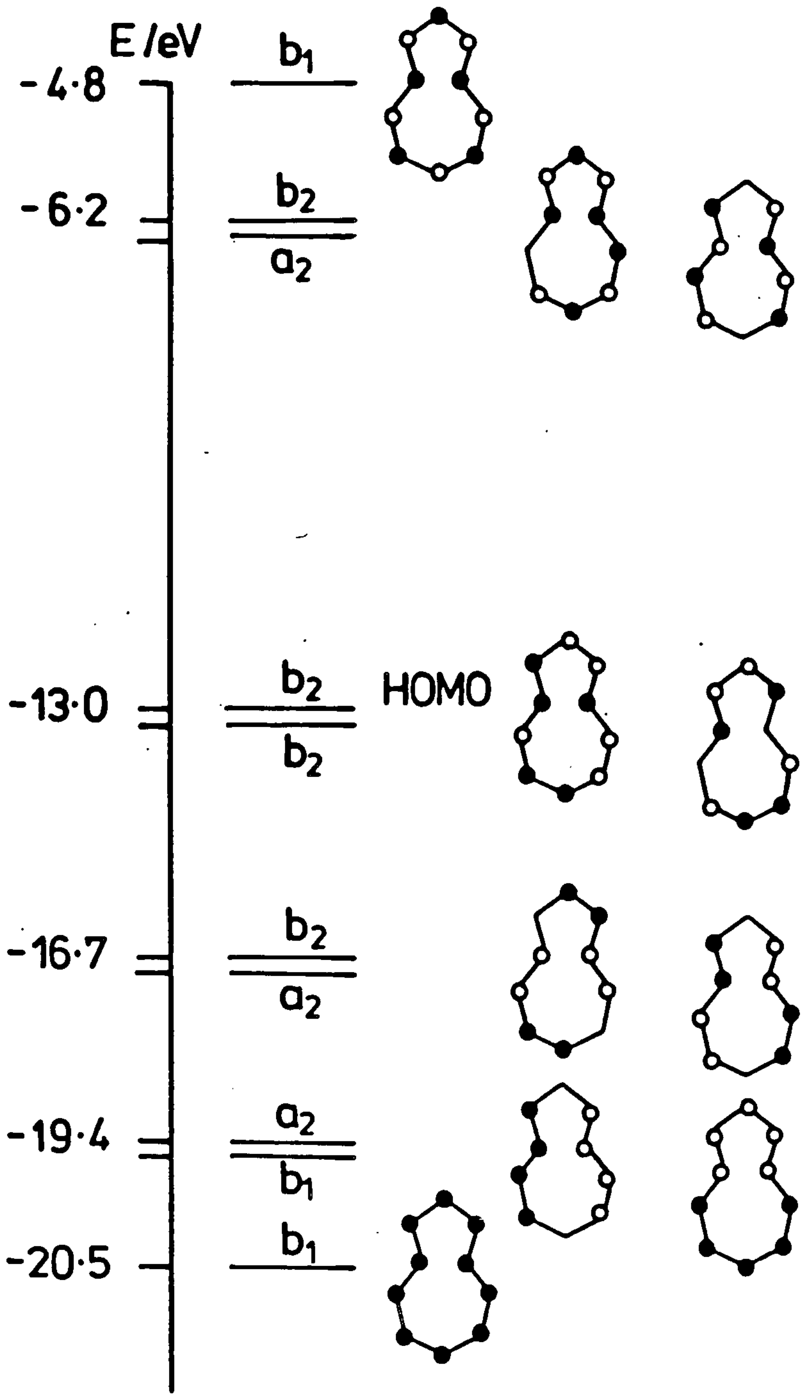


Figure 3.8. MNDO calculated π-orbital energy scheme for $S_5N_5^+$

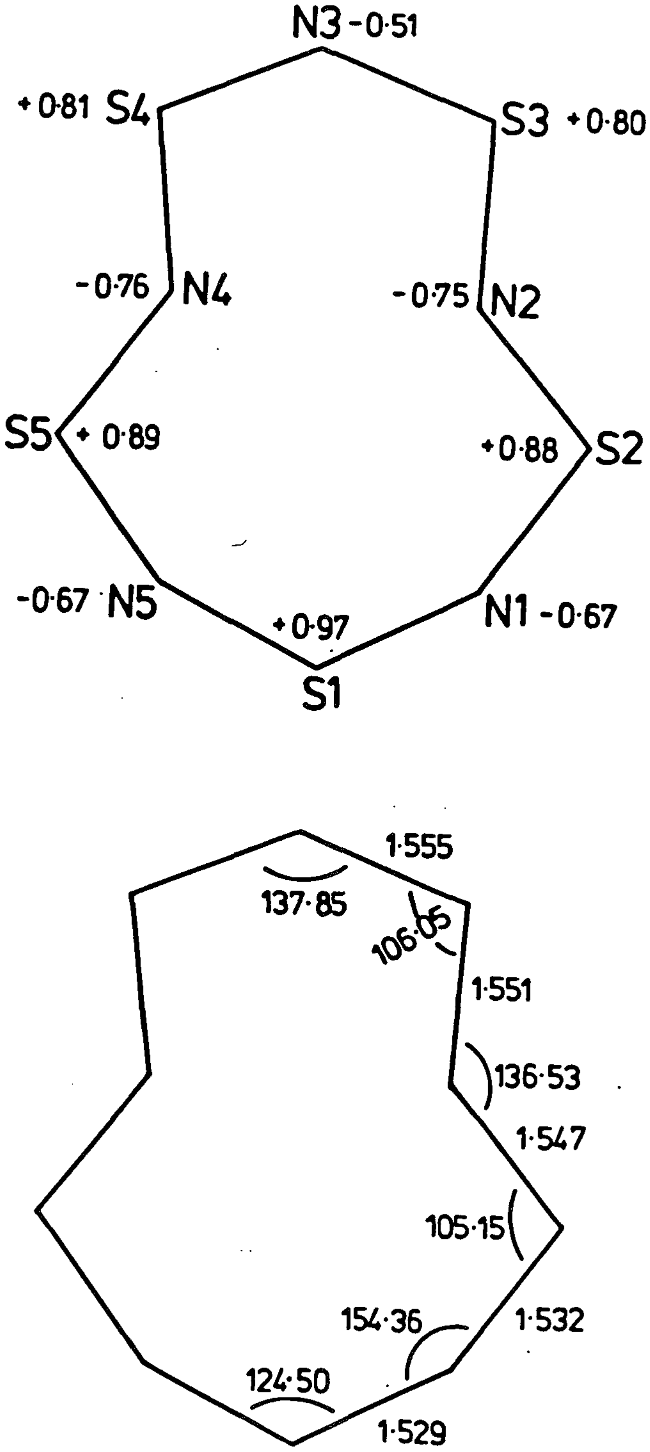


Figure 3.9. MNDO calculated atomic charges and bond lengths (Å) and angles (°) for $S_5N_5^+$

3.3 CONCLUSIONS

A simple synthesis of S_5N_5Cl has been devised and the purity of the product ensured its long term stability; this synthetic strategy has been extended by the group in Durham to produce an even more convenient route. S_5N_5Cl is a versatile starting material for the preparation of other $S_5N_5^+$ salts by metathesis, in particular $S_5N_5BF_4$ which has proved to be useful for the electrosynthesis of $(SN)_x$ layers (see Chapter 4). S_5N_5Cl was also found to be moderately reactive, undergoing an interesting halogen exchange reaction with BF_3 and some intriguing rearrangement reactions with liquid SO_2; this reactivity is undoubtedly the result of its having only a simple chloride counter-ion rather than a larger, more inert species. Chemical reduction of S_5N_5Cl results in the formation of $(SN)_x$. The undertaking of this work coincided with a diminution of interest in chemical preparations of $(SN)_x$ and so the investigations were not pursued. In the event of a resurgence of interest, the chemical reduction of S_5N_5Cl and its reaction with carbon-containing species would merit further attention.

The crystal structure of S_5N_5Cl is highly ordered, in contrast to previously reported structures, owing to appreciable cation-anion secondary interactions. These secondary interactions result in distortions of the cation, which may be detected both by the use of a bond angle - bond length correlation function and by comparison with MNDO calculation. The consequent perturbations of the cation molecular orbitals account for the bright red colour of S_5N_5Cl; these perturbations are removed on exposure of S_5N_5Cl to SO_2 vapours (when the chloride ion preferentially coordinates to SO_2), which accounts for the observed colour change to yellow.

3.4 EXPERIMENTAL SECTION

3.4.1 Preparation of S_5N_5Cl from $S_5N_5FeCl_4$ and Metal Fluorides:

a) Using CsF. $S_5N_5FeCl_4$ (1.0g, 2.3 mmol) was ground together with CsF (1.07g, 7.0 mmol) and the mixture placed, together with a Teflon-coated magnetic stirring bar, in one bulb of a two bulb vessel. SO_2 (approx. 10 ml) was condensed onto the mixture which was stirred at room temperature for 16h. The mixture was filtered and the insolubles were washed with back-distilled SO_2 (2 x 5 ml). The SO_2 was removed to yield yellow-orange crystalline solubles (crude S_5N_5Cl) and grey powdery insolubles (CsCl/FeF_3). The crude S_5N_5Cl was placed in a closed extractor and extracted with acetonitrile (48h) to yield S_5N_5Cl as a scarlet microcrystalline insoluble solid and a mixture of S_4N_4, $S_5N_5FeCl_4$, and CsCl as the soluble impurities extracted by acetonitrile.

Yield, 0.43g (69%). Infrared spectrum of S_5N_5Cl, ν_{max} = 1120s, 1070s,sh, 1045s, 965m, 945m, 735w, 705vw, 670m, 625m, 585vw, 540s, 460m, 410s cm^{-1}. Raman spectrum of S_5N_5Cl (6328 Å), ν_{max} = 730w, 695w, 670w, 645s, 590w, 560vw, 465s, 415vw, 320w, 260m, 220s, 195m, 145s, 100m,sh, 95m, 55vs, 45vs cm^{-1}. Powder pattern (CuK_α), d = 7.04(5), 4.68(3), 3.877 (2), 3.575(10), 3.414 (5), 3.213(3), 3.028(7), 2.951(2), 2.810(4), 2,750(3), 2.647(2), 2.613(7), 2.558(3), 2.527(4), 2.390(17, 2.275(3), 2.242(4), 2.178(1), 2.112(1), 1.964(4), 1.916(3), 1.868(4), 1.783(2), 1.717(2), 1.691(1), 1.601(5), 1.544(1), 1.506(5), 1.491(3), 1.435(1), 1.425(2), 1.337(3), 1.323(2) Å. Analysis: found S, 59.93; N, 26.21; Cl, 13.60; S_5N_5Cl requires, S, 60.32; N, 26.35; Cl, 13.33%.

b) Using KF or RbF. The above experiment was repeated using $S_5N_5FeCl_4$ (0.5g, 1.17mmol) and KF (0.2g, 3.45mmol) or $S_5N_5FeCl_4$ (0.15g, 0.35mmol) and RbF (0.11g, 1.05mmol). In each case S_5N_5Cl was detected as the major soluble product. The RbF product was purified as in a) above whereas the KF product was not purified.

Yields: KF product (crude) approx. 0.3g, RbF product (purified), 0.05g (54%). Infrared spectrum of KF product, ν_{max} = 1115m, br, 1070m, sh, 1040m, sh, 960w, 925m, (S_4N_4), 730m, sh, (S_4N_4), 700m, (S_4N_4) 680, sh, 530m, (S_4N_4) 460w,sh, 375m cm^{-1}. Infrared spectrum of RbF product (CsCl disc), ν_{max} = 1120s, 1070s, sh, 1045s, 965m, 945m, 735w, 705vw, 670m 625m, 585vw, 540s, 510m, 410s cm^{-1}.

c) Attempted reaction using NaF or LiF. The above experiment was repeated using $S_5N_5FeCl_4$ (0.5g, 1.17 mmol) and NaF or LiF (0.2g, 3.96 mmol). The soluble reaction product was identified as $S_5N_5FeCl_4$ i.e. no reaction had taken place. Infrared spectrum of orange-yellow soluble product, ν_{max} = 1160-1120m, br, 1050vw, 610w, 530m, 380vs cm^{-1}.

3.4.2 Preparation of $S_5N_5BF_4$:

S_5N_5Cl (2.2g, 8.28 mmol) was placed in a polythene flask and cold (-15°C) HBF_4 (aq.), (25 ml) was syringed on top. After shaking briefly at room temperature in an ultrasonic bath, the mixture was left overnight at -15°C and subsequently filtered under reduced pressure in a polythene filtration apparatus using ZITEX extrafine Teflon filter membranes. The resulting orange crystalline solid was washed (3 x 1 ml) with cold ether and extracted (closed extractor) with pentane for 24h to remove S_4N_4 (0.1g). The remaining solid was extracted briefly (30 min) with acetonitrile and the soluble fraction was recrystallised from SO_2 to yield orange crystalline $S_5N_5BF_4$.

Yield = 1.6g (61.5%). Infrared spectrum, ν_{max} = 1285w, 1175m, sh, 1060-20vs, vbr, 925m, sh, 765w, 725s, 700w, 680m, 625m, 570m, 540s, 520s, 490s cm^{-1}. Raman spectrum, ν_{max} = 580m, 533vs, 482m, br, 422m, 262s, 238m, 195 vs cm^{-1}, (6328 Å exciting line). Analysis: found S, 50.02; N, 21.4; B, 3.46; $S_5N_5BF_4$ requires S, 50.55; N, 22.08; B, 3.41%.

3.4.3 Preparation of $S_5N_5AsF_6$:

S_5N_5Cl (0.50g, 1.88 mmol) was placed in one bulb of a two bulb vessel together with a Teflon coated stirring bar. $AgAsF_6$ (0.56g, 1.88 mmol) was placed in the other bulb. SO_2 (ca. 10 ml) was condensed in approximately equal quantities in each bulb. After warming to room temperature the solution of $AgAsF_6$ was added to the solution of S_5N_5Cl. Immediate reaction occurred producing a yellow solution and a white precipitate (AgCl). After stirring (2 h) the mixture was filtered and the insolubles were washed with SO_2 distilled back from the solubles bulb (1 x 2 ml). The solvent was removal to yield a yellow crystalline solid ($S_5N_5AsF_6$) and a white powdery insoluble solid which turned grey after exposure to light (AgCl).

Yields: $S_5N_5AsF_6$, 0.7g (88%); AgCl, 0.26g (96%); weight losses a result of losses in manipulation. Infrared spectrum, ν_{max} = 1155s, br, 1070 w, sh, 875 vw, 820w, 700vs, 685vs,sh, 625m, sh, 575m, 545s, 400vs cm^{-1}.

3.4.4 Reduction by Me_3SiN_3:

S_5N_5Cl (0.1g, 0.37 mmol) and a Teflon coated magnetic stirrer were placed in a twin-necked flask fitted with Rotaflo tap adaptors. Acetonitrile (ca. 20 ml) was syringed in against a counterflow of dry nitrogen and the mixture was cooled to -2°C in an alcohol bath. A solution of Me_3SiN_3 (0.25 ml, 0.22g, 1.85 mmol) in acetonitrile (10 ml) in a pressure-equalized dropping funnel fitted with a Teflon needle valve was put in place of one of the top adaptors and the solution was added dropwise (45 min) with stirring. The mixture, initially orange, progressively darkened and a brown heterogenous solid formed in the flask. After stirring for 24h, a dark grey solid identified by i.r. spectroscopy as $(SN)_x$ (34) was separated from the brown solution, which yielded a brown-orange solid (largely S_4N_4) on removal of solvent.

Yields: Brown-orange solid, 0.02g; dark grey solid, $(SN)_x$, 0.08g (92%). Infrared spectrum of dark grey solid, ν_{max} = 1020w, 935vw, 725w, sh, 700m, 635w, 510w cm^{-1}. On examination under a microscope, the $(SN)_x$ was found to contain highly reflective golden flakes and a few amorphous lumps of SiO_2.

3.4.5 Reduction by K_2CS_3:

In a typical experiment, S_5N_5Cl (0.2g 0.75 mmol), K_2CS_3 (0.07g, 0.38 mmol) and a Teflon coated magnetic stirrer were placed in one bulb of a two bulb vessel. SO_2 (10 ml) was condensed on the mixture at liquid nitrogen temperature and as the mixture warmed to -15°C, vigorous reaction occurred producing orange, green and blue colours. After stirring at -15°C for 30 minutes the mixture was filtered yielding a brown solution and a black insoluble solid. Removal of solvent yielded on orange-brown crystalline solid and an insoluble black/purple powder. The powder was extracted exhaustively with SO_2 (72h) in a closed extractor. The black powder was identified as $(SN)_x$ by infrared spectroscopy(34) and x-ray powder diffraction(15,35). The brown-orange solubles were identified by infra-red spectroscopy as a mixture of S_5N_5Cl and S_4N_3Cl.

Yield: $(SN)_x$ 0.08g (46%). Infrared of $(SN)_x$ (CsI plates); ν_{max} = 1250w, br, 1160w, br, 1040 w, sh, 1020m, 800vw, br, 700m, 625vw, sh, 610w, 500m, 290w cm^{-1}. Powder photograph (CuK_α) d = 3.76(5), 3.28 (10), 2.88 (2) Å (all lines diffuse). Analysis; C, 2.49%. Infrared of brown-orange solubles, ν_{max} = 1150m, br (K_2CS_3), 1030sh(?), 1000sh(?), 910vs(K_2CS_3), 755w, 680vs(?) 520vs(K_2CS_3), 370sh cm^{-1}.c.f. K_2CS_3 in Chapter 2.

3.4.6 Reaction with BF_3(g):

S_5N_5Cl (0.1g, 0.38 mmol) was placed in a Pyrex bulb equipped with two vertical limbs each fitted with a J. Young's Teflon stemmed valve and ¼" O.D. ground glass adaptor.

A cylinder of BF_3 gas was connected to one limb <u>via</u> a rubber hose and ¼" O.D. copper tube which in turn was connected to one of the vertical limbs with a Swagelok compression fitting. The other limb was connected <u>via</u> a rubber hose to an exit bubbler. BF_3 was passed over the solid S_5N_5Cl; almost immediately reaction occurred with darkening of the solid. After 10 min the S_5N_5Cl had become a bright scarlet colour and was bubbling slowly. The reaction was stopped after 30 minutes and the system was purged with dry nitrogen. An infrared spectrum of the scarlet product proved it to be a mixture of $S_4N_4.BF_3$ and S_4N_4.

Infrared spectrum, ν_{max} = 1290vw, 1260w, 1180 w, sh, 1150sh, 1040 vbr, 960br, 925*m, sh, 890m, 840vw, 800vw, 770vw, 725s*, 700s*, 650s, 620s, 560w, sh, 545s*, 520s, 500m, 485vw, sh, 420m cm^{-1}. * bands assigned to S_4N_4. C.f. $S_4N_4.BF_3$(16) ν_{max} = 1171m, 1138m, 1117s, 1070s, 1040vs, 1014m, 949s, 908m, 888s, 840mw, 724vw, 697vw, 682vw, 658ms, 623ms, 567w, 552w, 527s, 502m, 490w, sh, 420ms cm^{-1}.

3.4.7 Action of $BF_3.Me_2O$ on S_5N_5Cl:

S_5N_5Cl (0.1g, 0.38 mmol) was placed with a magnetic stirrer in one bulb of a two bulbed vessel and $BF_3.Me_2O$ (0.1 ml, 3x excess) was syringed into the other bulb, the manipulation being performed in a glove box under dry nitrogen. SO_2 (<u>ca</u>.10ml) was condensed onto the etherate and the solution was added to the S_5N_5Cl (-7°C). The reaction mixture was stirred at -7°C, the temperature being maintained by an alcohol bath. After 16h the reaction mixture contained a small amount of a black insoluble material (decomposition product). Filtration and subsequent prolonged pumping yielded red crystalline product which infrared spectroscopy showed to be largely S_5N_5Cl.

Infrared spectrum, ν_{max} = 2100m, br, 1150 w, br, 1120m, 1070m, 1040m, 960m, 940m, 730s 680m, 540s, 460m, 410s, 340vs cm^{-1}. c.f. S_5N_5Cl, ν_{max} = 1120s, 1070s, sh, 1045s, 965m, 945m, 735w, 705vw, 670m, 625m, 585vw, 540s, 460m, 410s cm^{-1}.

3.4.8 Reaction of S_5N_5Cl with MeI in SO_2:

S_5N_5Cl (0.1g, 0.38 mmol) was placed with a magnetic stirrer in one bulb of a two-bulb vessel. MeI (2 ml, 3.08g, 21.7 mmol) was syringed on top of this and SO_2 (ca. 2 ml) was condensed on the mixture. The resulting orange solution was stirred (ca. 16h) by which time a purple-brown solid had formed and the solution had become orange-red. Filtration and removal of solvent yielded a purple-brown insoluble solid and a heterogenous black/orange soluble crystalline fraction. This soluble fraction contained black shiny crystals which sublimed and had a purple vapour, identified as I_2. Infrared spectra showed the soluble fraction to be largely S_4N_4 and the insoluble fraction to be a mixture of $S_5N_5I_2Cl$ and S_4N_4.

Yields: soluble fraction ca. 50 mg, insoluble fraction ca. 50 mg. Infrared spectrum of brown-purple insolubles, ν_{max} = 1230m, br, 1130w, 1070m, 1040 sh, vw, 990w, sh, 955m, 930s*, 860w, sh, 770w , 730s, sh*, 700s*, 665m, 625m, 550s, 460m, 400s cm^{-1}. *assigned to S_4N_4. c.f. $S_5N_5I_2Cl$(18) ν_{max} = 1135s, 1080vs, br, 982m, 954s, 728m, 671m, 628m, 585vs, br 563vs, 541m, 549s, 403s cm^{-1}. Infrared spectrum of black/orange solubles, ν_{max} = 1160vw, 1060vw, 1000w, 920vs, 770w, 760w, 730vs, sh*, 700vs*, 545*, 530s, sh, 465vw cm^{-1}. *assigned to S_4N_4.

3.4.9 Reaction of S_5N_5Cl with AgCN:

S_5N_5Cl (0.1g, 0.38 mmol) was placed together with AgCN (0.3g, 2.2 mmol) and a Teflon coated magnetic stirrer in one bulb of a two-bulb vessel. SO_2 (<u>ca</u>. 8 ml) was condensed on top and the mixture was stirred room temperature (16h). The initial orange solution became olive green after a few minutes and after 16h the reaction mixture consisted of an orange solution and a brown-purple insoluble solid. On filtration and removal of solvent, orange crystals were obtained from the solution.

Yields: Orange crystals 50mg, brown-purple solid 0.3g.
Infrared spectrum of orange crystals, ν_{max} = 2170 vw, 1190m, 1040m, 930m*, 725w, sh*, 700m*, 550m* cm^{-1}. Infrared spectrum of brown purple solid, ν_{max} = 2155 m, br cm^{-1}. *assigned to S_4N_4

3.4.10 Hydrolysis of S_5N_5Cl in Air:

On exposure of a small amount of S_5N_5Cl to moist air (24h), a black solid resulted. Infrared spectrum of black solid, ν_{max} = 3300-3000m], br, 1790-1610 w, br, 1400s], 1200m, 1090s], 1015m, sh, 960w°, 930m*, 725m*, sh*, 700s*, 665w, sh, 615s], 545s*, 460w°, 405m, sh°, 345s, sh cm^{-1}. *assigned to S_4N_4,] assigned to $(NH_4)_2SO_4$, °assigned to residual S_5N_5Cl.

3.4.11 Semi-quantitative Solubility Study of S_5N_5Cl in SO_2:

An accurately weighed amount of S_5N_5Cl was placed in a 50 ml round bottomed flask fitted with a Rotaflo valve, Liquid SO_2 was condensed in until the solid dissolved; small amounts of SO_2 were then removed until a tiny amount of crystalline material was formed which would not dissolve after allowing the system to equilibrate. The final amounts used were 0.1025g S_5N_5Cl in 3.4811g SO_2 or approximately 3g of S_5N_5Cl per 100g of SO_2.

3.4.12 Tensimetric Titration of S_5N_5Cl and SO_2:

A small flask, fitted with a Rotaflo valve, containing S_5N_5Cl (0.1928g, 0.7252 mmol) connected via a T-piece and Whitey valves to a mercury-in-glass manometer and a monel vacuum manifold. The flask was maintained at 2°C in an alcohol bath. A little liquid SO_2 was condensed in. After allowing 5 minutes for the S_5N_5Cl to soak thoroughly, SO_2 was carefully removed until no more liquid was present. The pressure of the system was measured after allowing 15 minutes for equilibration and the flask was detached from the manometer and weighed. On re-attachment, a small amount of SO_2 was removed and the process was repeated. It was found that final equilibration was not achieved even after 4 hours and so a standard time of 15 minutes was allowed for each reading. Solvate formation required initiation by exposure to an excess pressure of SO_2; it was not formed by addition of small aliquots of SO_2 to S_5N_5Cl. See Section 3.2 and Figure 3.2.

3.4.13 Reaction of S_5N_5Cl with liquid SO_2:

a) The saturated solution of S_5N_5Cl in SO_2 prepared in Section 3.3.11 was left standing at room temperature. After several months, pale yellow needle-like crystals formed at the meniscus of the solution and on the walls of the bulb above the solution (which became orange). The crystals continued to grow very slowly. After 2 years, the solvent was removed to yield pale yellow needle-like crystals on the walls of the flask and a slightly sticky, orange, microcrystalline solid from the solution. The crystals and orange solid were removed separately and identified by infrared spectroscopy as $S_4N_3^+ SO_3Cl^-$.

Yields: Pale yellow crystals ca. 50mg, orange solid ca. 50mg. Infrared spectrum of pale yellow crystals (CsI plates), ν_{max} = 1375s, 1320 w, sh, 1286 vs, sh, 1260vs, 1250 vs, sh, 1170m, 1155m, 1055vs, 1035s, sh, 820m, 683m, 642w, 625m, 590s, 580s, 540s, 530s, 490s, 450w, 360m, sh, 332s cm^{-1}. For assignments, see Table 3.3a. Infrared spectrum of orange solid, ν_{max} = 1330s, 1280vs, sh, 1260vs, 1250vs, sh, 1160m, 1140s, 1120s, 1045s, 1035m, sh, 980vw, 810m, 720m, 705s, 680m, 635s, 590s, 580s, 555m, sh, 540m, 530m, 505m, 490s, 455vw, sh, 450s, 380s, sh cm^{-1}. For assignments, see Table 3.3b. For discussion, see Section 3.2.4.

b) In the course of some attempted NQR work, S_5N_5Cl (ca. 1g) was sealed in a Pyrex ampoule with SO_2 (ca. 1g). Initially the red S_5N_5Cl turned yellow on contact with liquid SO_2 but did not all dissolve. After a few weeks, however, the yellow S_5N_5Cl solvate disappeared and was replaced by a dark solution, a dark microcrystalline solid which continued some larger red crystalline features, and some pale yellow rod-like crystals. The ampoule was stored at zero, 0°C in the dark and over a few months the crystalline features slowly grew. After 12 months the ampoule was opened by careful grinding with a carborundum wheel. A gas phase infrared spectrum of the volatiles was recorded and the volatiles were removed to yield pale yellow rod-like crystal ($S_4N_3{}^+SO_3Cl^-$) and a dark microcrystalline mass continuing larger dark red crystalline features, ($S_4N_5{}^+SO_3Cl^-$ and $S_6N_4Cl_2$) both coated with a slightly sticky residue from the solubles.

Yields: Pale yellow crystals ca. 0.2g, dark microcrystalline mass ca. 0.4g.

Infrared spectrum of pale yellow crystals, ν_{max} = 1270 vs, 1180s, 1050m, sh, 1045vs, 1035 vs, sh, 870w, 682s, 652m, 623s, (590, 590)vs, 540s, 530s, 490s, 450vw, sh, 350m, sh, 330s cm^{-1}. c.f. $S_4N_3{}^+SO_3Cl^-$ above. Infrared spectrum of dark microcrystalline solid (CsI plates), ν_{max} = 1285 vs, 1260vs, 1070s, 1050s, 1025vw, sh, 990s, 926w, 945w, 881w, 825s, 710m, 700w, sh, 625vs, 580w, 560w, 542m, 525s, 431m, 375vw, 360w, 340vw, 295w, cm^{-1}. For assignments see Table 3.3c. Infrared spectrum of gas phase from ampoule, ν_{max} = ca. 1350vs, 1255sh, 1245m, 1155vs, 1145vs, 528vs, 500vs cm^{-1}. For assignments, see Table 3.3d.

3.4.14 Thermal Studies of S_5N_5Cl:

a) Raman Studies. A small amount of S_5N_5Cl was sealed under nitrogen in a capillary tube and heated to 95°C for a few minutes. A Raman spectrum was recorded of the red-orange involatile material at the bottom of the tube. The experiment was repeated, (heating to 127°) and Raman spectra were recorded of the resulting yellow involatile solid at the bottom of the tube and the yellow volatile solid which had collected at the top of the tube. Raman spectrum of red-orange melt (95°C), ν_{max} = 465m(?), 350w (S_4N_4), 285m, sh (?), 275m, sh(?), 260m, sh (S_4N_3Cl), 250m, sh (S_4N_3Cl), 220m (S_4N_4), 115s, sh ($(NSCl)_3$, S_4N_3Cl, 70vs ($(NSCl)_3$, S_4N_3Cl), 45vs, sh (S_4N_4, S_4N_3Cl), 35vs (?), 30vs (?), 15vs(?) cm^{-1}. Yellow involatile solid (127°C), ν_{max} = 1000w 720w (S_4N_4), 605m (S_4N_3Cl), 560m (S_4N_3Cl), 450s (S_4N_3Cl), 250m (S_4N_3Cl), 215s (S_4N_4), 200s (S_4N_4), 165vw(S_4N_3Cl), 150m (S_4N_3Cl), 110s, sh (S_4N_3Cl), 100s (S_4N_3Cl), 80s (S_4N_3Cl), 45vs (S_4N_3Cl, S_4N_4), 25w (?) cm^{-1}. Raman spectrum of yellow volatile solid, (After heating to 127°C), ν_{max} = 1125w, 700w, br, 620w, br, 485m, 435w, 375m, 340s, 320m, 195m, 180s, 110s, 80vs, 40w, 25m cm^{-1} [all modes assigned to $(NSCl)_3$].

b) Differential scanning calorimetry (D.S.C.) studies. In a typical experiment, S_5N_5Cl (5.98 mg, 2.33×10^{-2} mmol), was hermetically sealed under dry nitrogen in aluminium capsule by cold welding in a press. The sample was then heated in a thermal analysis cell (rate = 4°C/min, initial temperature = 48°C, final temperature 120°C) and the D.S.C. trace recorded on a y-t chart recorder. Infrared spectra showed that the yellow residue was an S_4N_4 - S_4N_3Cl mixture. Typical weight changes during thermolysis were 0.03 mg.

3.4.15 Crystal Growth of S_5N_5Cl:

A small amount of S_5N_5Cl was placed on the frit of a closed extractor and acetonitrile (10 ml) was distilled into the bulb. The S_5N_5Cl was extracted with acetonitrile (4 days). Small translucent scarlet platelets formed on the side of the solvent bulb and suitable single crystals were selected by hand; they were sealed under nitrogen in quartz capillaries for X-ray examination.

The structure determination was performed by R.W.H. Small (University of Lancaster). Intensity data from a crystal of dimensions 0.25 x 0.2 x 0.15 mm were collected on a Stoe STDI-2 automatic two-circle diffractometer using graphite monochromatised MoKα radiation. Absorbtion and extinction corrections were not applied, 1758 reflexions were measured of which 1629 were unique with an internal agreement of R=0.0086. For refinement of the structure, 1366 reflexions for which $I > \sigma(I)$ were used. All calculations were carried out using the SHELX 76 suite of programs.

The crystal was found to be monoclinic, space group C2/c, a=7.98(1), b=14.37(1), c=7.30(1) Å, β=97.15(5), U=830.6 Å^3, Z=4, D_c=2.12g cm^{-3}, F_{000}=532, λMoK$_\alpha$ =0.7107 Å.

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CHAPTER 4

The Electrochemical Preparation of Poly(Sulphur Nitride)

4.1 INTRODUCTION

The growth of interest in sulphur-nitrogen chemistry in recent years has, in part, been a result of the intense interest in the conducting polymer, poly(sulphur nitride). Poly(sulphur nitride) is a reflective golden crystalline solid and is a metallic conductor ($\sigma = 10^3$ ohm^{-1} cm^{-1}) along the direction of the S-N chains but a poorer conductor ($\sigma =$ ca. 10^2 ohm^{-1} cm^{-1}) perpendicular to the chains; it has been classified as a highly anisotropic 3-dimensional metal and is the best example of this unusual class of materials. The inter-chain interactions are thought to be responsible for preventing a Peierls distortion(1) to a non-conducting state at low temperature and the unique (for a conducting polymer) transition to a super-conducting state below 0.26K. The physical properties of $(SN)_x$ have been well reviewed.(2) $(SN)_x$ is a vacuum - sublimable solid and can be deposited epitaxially on suitable substrates (eg Mylar or Teflon)(3). Thin films (ca. 1μm) of $(SN)_x$ deposited on semi-conducting ZnS have been used to fabricate blue light-emitting diodes, which have a quantum efficiency for the blue, high energy (2.815 eV) emission 100 times that of the corresponding devices fabricated from gold; these devices are considered to be of potential commercial importance.(4)

A major hindrance in the development of this area has been the relative inaccessibility of the pure polymer. Early work(5) reported

$(SN)_x$ as having a 5-10% hydride impurity, but later reports (6,7) disputed this and described $(SN)_x$ as being relatively stable to moist air; similarly, the electrical conductivity of $(SN)_x$ along the chain has been reported as 2-4 x 10^{-3}(8), 600(7), and 10-1730(9) $ohm^{-1}cm^{-1}$. The synthetic route used to prepare these samples of $(SN)_x$ was by solid-state polymerization of S_2N_2,(10) a process which takes up to 8 weeks; trace residues of S_2N_2 or other moisture-sensitive intermediates could account for the variations in reported stability and conductivity of $(SN)_x$.

Clearly, the preparation of analytically pure $(SN)_x$ is a pre-requisite for accurate physical measurements and for any potential applications. Whilst the preparation of $(SN)_x$ via the solid-state polymerization of S_2N_2 can, with care, yield pure crystalline material, the preparation time (ca. 8 weeks) and the laborious nature of the procedure makes this an unattractive synthetic route. Much effort has been spent in developing alternative syntheses, such as the reduction of sulphur-nitrogen chlorides with azides,(11,12) but the products obtained have for the most part been unsuitable for vacuum deposition and hence for device fabrication; co-crystallization of impurities such as elemental sulphur leads to patchiness and instability in the coatings.(13)

S_5N_5Cl was thought to be potentially a particularly suitable starting material for the preparation of $(SN)_x$, since in addition to its favourable S:N ratio, it can be prepared and purified easily on a large scale; this would enable any successful preparation to be scaled up if required. The simple counter-ion ensures that no contamination with metal species (which could affect the physical properties of the polymer) is possible.

4.2 RESULTS AND DISCUSSION

4.2.1 The Electrochemical Reduction of S_5N_5Cl in Liquid SO_2:

Although earlier work using SO_2 as a solvent for electrochemistry indicated that problems arose from low solubility of electrolytes,(14) more recent work(15) showed that using suitable electrolytes, SO_2 is a convenient solvent for the investigation of highly oxidised species. The solubility of S_5N_5Cl in liquid SO_2 and the ease of purification and manipulation of the solvent made the S_5N_5Cl/SO_2 system an attractive one for a first experiment.

The simplest experimental arrangement of a two-electrode (both bright Pt) undivided cell without background electrolyte was chosen to test the viability of $S_5N_5^+$ electroreduction as a synthetic route to $(SN)_x$. Electrolysis of a solution of 4.1×10^{-3} mol dm^{-3} S_5N_5Cl in SO_2 in this cell yielded highly divided microcrystalline $(SN)_x$ as the cathodic product. The polymer formed as a loosely adhering layer on the cathode; S_4N_4 was the major co-product and this could be removed by high vacuum sublimation or by washing with SO_2.

The powdered $(SN)_x$ product was characterized by chemical analysis, X-ray powder diffraction, and infra-red spectroscopy. Each of these techniques showed the product to be of a high quality with none of the bulk chemical impurities (such as SiO_2) which have proved to be a problem in other 'wet' preparations of $(SN)_x$;(11,12) further, the product seemed to be relatively stable to moist air which indicated that the concentration of moisture-sensitive impurities had been reduced to a low level.

Examination of the purified product under an optical microscope (x 40) revealed highly reflective microcrystals of average size 10 μm and a very few needles up to 0.5 mm in length. The microcrystals were stacked in zig-zag chains arranged at right angles with respect to the electrode surface. A scanning electron micrograph (S.E.M.) of the deposit is shown in Figure 4.1; the photograph shows the rounded crystals viewed obliquely down the chain-like stacks. Crystals of 4-5 μm with almost identical growth features were obtained from an experiment performed under slightly different conditions (current density = 7.5 mA cm^{-2} c.f. 1 mA cm^{-2}).

Different electrode materials were tried in the S_5N_5Cl/SO_2 system to see if the nature of the cathode affected the mode of growth of the product. In particular it was hoped that a suitable electrode would be found for the growth of single crystals of $(SN)_x$ from solution; single crystals produced from the solid state polymerization of S_2N_2 have always been found to be disordered multiple twins.(13) Since single crystals of this 'classical' polymer can be obtained as fairly large (ca. 2 x 2 x 2 mm) blocks and since they have a pronounced fibrous texture, it was thought that a suitably oriented classical $(SN)_x$ crystal electrode might be a favourable substrate for electrocrystallization of $(SN)_x$ from S_5N_5Cl in SO_2. However, when a suitable crystal was mounted in platinum jaws the $(SN)_x$ deposited from solution was again in its finely divided form; no preferred growth appeared to have occurred on the crystal. Although indicative that

Figure 4.1 An S.E.M. photograph of the cathodic deposit of $(SN)_x$ from S_5N_5Cl in SO_2; magnification 5000x.

epitaxial growth would be difficult to achieve in this system, the result could have arisen either from using an unfavourable current density or from chemical modifications of the $(SN)_x$ crystal surface (e.g. S=NH end groups). In a similar experiment, an $(SN)_x$-coated platinum wire was inserted as the cathode; the vapour-deposited layer peeled away from the wire on contact with solution.

This problem of mechanical fragility of vapour deposited $(SN)_x$ coatings in solution has been encountered by other workers in the field;(16) presumably stresses induced by the polymer swelling in solution are responsible, since thin compact layers deposited electrochemically from solution (see below) are quite robust whilst immersed in electrolyte.

As the quality of $(SN)_x$ samples is of paramount importance in determining their physical properites such as conductivity (and hence suitability for device fabrication), a test was carried out to see how the electrochemically prepared $(SN)_x$ from SO_2 solution compared with classical $(SN)_x$ as a source material for vacuum deposited films.

A vacuum deposition procedure developed by Z.V. Hauptman(4) was used to deposit thin layers of electrochemically prepared $(SN)_x$ on plane glass substrates. Optical reflective and transmittance spectra of these gold-bronze samples were recorded by R. Friend (Cambridge University) and these were compared with literature data for classical $(SN)_x$. The measured spectra were, within experimental error, identical to those previously reported,(17) which implies that electrochemically prepared $(SN)_x$ would be a suitable source material for the fabrication of electronic devices such as light emitting diodes. This contrasts with the $(SN)_x$ prepared from $(NSCl)_3$ and Me_3SiN_3(11,12) from which it was not even possible to prepare uniformly coated samples.(13)

The failure of the single crystal cathode to initiate preferred growth and the highly divided nature of the cathodic deposit of $(SN)_x$ on both the single crystal and bright platinum cathodes raised the possibility that reduction of the $S_5N_5^+$ cation occurred not on the electrode surface but in the bulk solution. Although sulphur-nitrogen heterocycles are good electron acceptors(18) and sulphur nitrogen cations are expected to be especially so, it is known that SO_2 is also reduced very easily to form the radical anion $SO_2^{\bar{\cdot}}$(19) which can subsequently form $S_2O_4^{\bar{\cdot}}$.(20) Thus, the reduction of $S_5N_5^+$ to $(SN)_x$ may not have occurred on the electrode surface but may have been mediated by SO_2; this would explain the highly divided, loosely adherent nature of the cathodic deposit and also the turbidity of the electrolyte observed during electrolysis. In order to investigate this possibility, the electroreduction process was examined using cyclic voltammetry.

4.2.2 Cyclic Volatammetric Studies of the $S_5N_5^+$ Ion:

a) In liquid SO_2. Although several earlier attempts were made to apply cyclic voltammetry to SO_2 solutions,(14) it was not until recent years that Bard and co-workers developed successful procedures for obtaining cyclic voltammograms in this solvent.(15) They used tertiary butyl ammonium salts as background electrolytes, and a quasi-reference electrode, Ag^+/Ag, which was re-filled each time the cell was filled; the difficulty in reproducing the exact volume of solution in the cell resulted in a reproducibility of only ± 50 mV in the potential of the reference electrode. An additional inconvenience was that the electrochemical cell was constructed with cone and socket joints which necessitated a low (-40°C) experimental temperature in order to reduce the vapour pressure of SO_2.

The experiments described in this Chapter (developed in collaboration with Z.V. Hauptman) have overcome some of the difficulties experienced by other workers. The cell was constructed with Swagelok fittings which enabled it to withstand pressures of up to three atmospheres and thus enabled it to be used at ambient temperatures if required. The reference electrode was completely filled with acetonitrile solution and hence (because of the incompressability of liquids) it could also be used in pressurized solutions; the porous plug helped reduce inter-diffusion of the different solvents. Since the electrode was not re-filled between each experiment, its potential remained remarkably stable (± 5mV) and although some potential drift (vs S.C.E.) over periods of several months was observed (see Chapter 2), measured values could be compared by conversion to the S.C.E. scale. After a considerable time had been spent in solving the above mentioned problems, it was possible to study the system of interest.

A typical cyclic voltammogram of S_5N_5Cl in SO_2 is illustrated in Figure 4.2. In Figure 4.2 and in all subsequent discussions, the potential scale, although measured against the Ag/Ag^+ electrode described in Chapter 2, has been converted to the S.C.E. scale. The major reduction peak at $Ep/2^{red} = 0.34$ V can be assigned to the reduction of the $S_5N_5^+$ ion (c.f. $Ep/2^{red}$ = +0.46 V for $S_5N_5FeCl_4$ in methylene chloride).(21) Unlike the earlier study by Fritz and Bruchhaus(21) of $S_5N_5FeCl_4$ in methylene chloride, however, the reduction of S_5N_5Cl in SO_2 was found to be a reversible process with $Ep/2^{ox}$ = +0.30 V, a half-peak potential difference of 40 mV, compared to the 56 mV allowed for a reversible process.(22) The further large oxidation peak at $Ep/2^{ox}$ = +1.32 V was assigned to oxidation of Cl^- (c.f. +1.3 V vs Ag/AgCl).(19) The very small oxidation peak at $Ep/2^{ox}$ = +1.08 V cannot be unambiguously assigned but may arise from anodic breakdown of a microlayer of $(SN)_x$ formed in the initial reduction process since the anodic breakdown potential of $(SN)_x$ electrodes has been reported as +1 V.(16)

Anodic breakdown on the cyclic voltammogram occurred at ca. +2.5 V and is assigned to the oxidation of the BF_4^- ion, presumably with formation of BF_3 and SO_2F_2 (by reaction with solvent). The anodic breakdown observed in this system is at less positive potentials than have been reported for BF_4^- containing electrolytes in liquid SO_2;(15) it is not clear why this should be the case. The cathodic breakdown occurs at ca. -0.16 V and can be assigned to the reduction of SO_2 to $SO_2^{\cdot-}$.(19,20) The proximity of the $S_5N_5^+$ reduction to the SO_2 reduction implies that, using a non-potentiostatic current source, the bulk electroreduction of $S_5N_5^+$ is probably mediated by $SO_2^{\cdot-}$ or $S_2O_4^{\cdot-}$. In addition to accounting for the powdery nature of the catholic deposit and turbidity of the electrolyte solution, this mechanism would also account for the observed constancy of current and potential, even when a non-galvanostatic current source was used. Since a major research

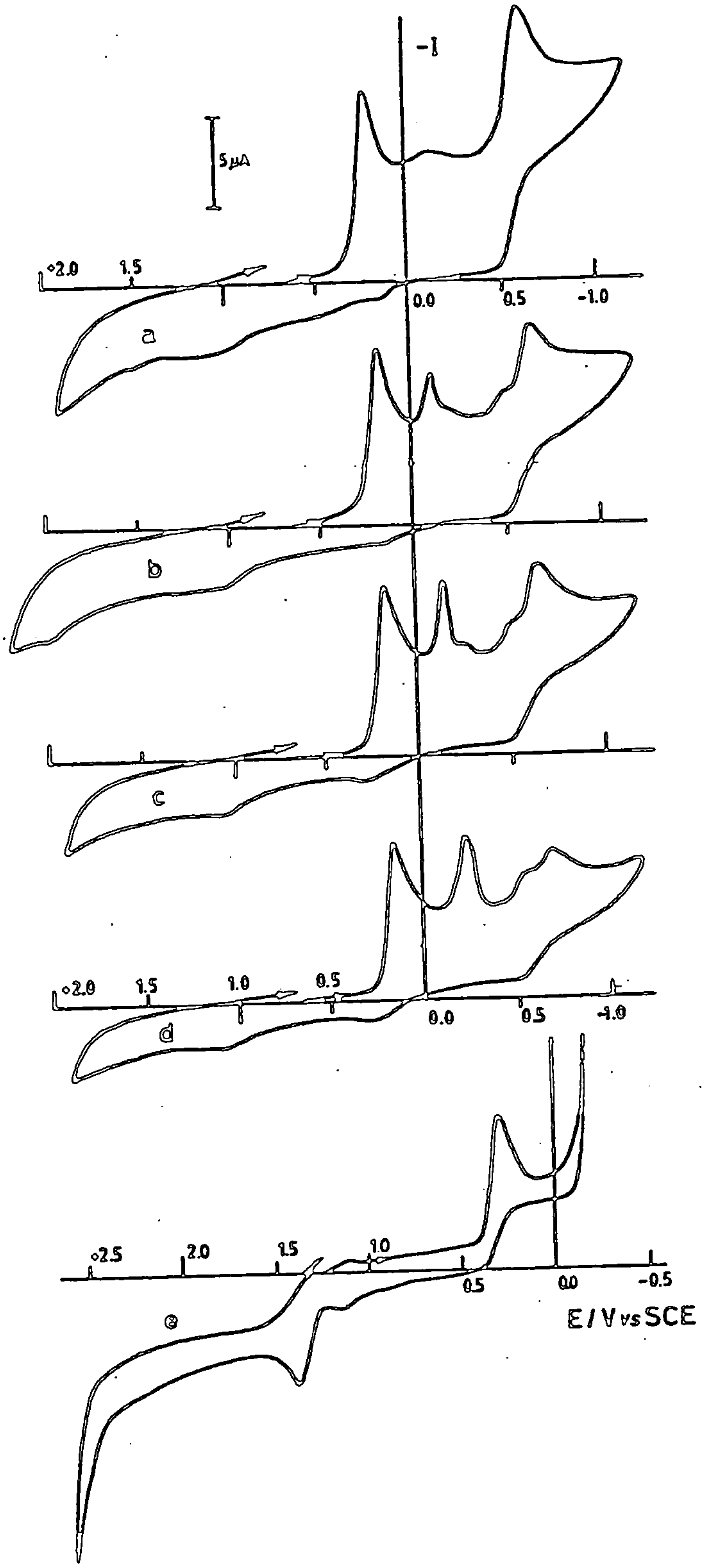


Figure 4.2. Cyclic voltammograms for $S_5N_5^+BF_4^-$ in acetonitrile (a-d) and $S_5N_5^+Cl$ in liquid sulphur dioxide (e) at platinum electrode. Curves (a-d): $S_5N_5^+BF_4^-$, 10^{-3}mol dm^{-3}, Bu_4NBF_4, 0.2mol dm^{-3} in MeCN. (a) 15.5°C, (b) 0°C, (c) -6°C, (d) -18.5°C. Curve (e): $S_5N_5^+Cl^-$, 10^{-3}, Bu_4NBF_4, 0.2mol dm^{-3} in liquid SO_2 at 0°C. Potential sweep rate 100mV s^{-1}.

aim was to achieve electrocrystallization of $(SN)_x$, it was decided to investigate the $S_5N_5^+$ electroreduction in an electro-inert solvent (such as acetonitrile). This would ensure that discharge of the cation occurred at the cathode surface, enabling more precise control of conditions.

b) In acetonitrile. In order to examine the electroreduction of $S_5N_5^+$ to $(SN)_x$ in an electrochemically inert solvent and more especially, to investigate the possibility of electrocrystallization and deposition of compact layers, a cyclic voltammetric study of $S_5N_5BF_4$ in acetonitrile was undertaken as a preliminary to bulk electrolysis. Both acetonitrile and the BF_4^- ion are recognized to be particularly electro-inert.(22) A typical cyclic voltammogram is illustrated in Figure 4.3 and voltammograms recorded at different temperatures are illustrated in Figure 4.2. A mechanism for the electroreduction of $S_5N_5^+$ in acetonitrile is proposed on the basis of the voltammograms obtained and published data; peak numbers referred to in the text correspond to those in Figure 4.3 and the half-peak reduction potentials are summarised in Table 4.1.

The first peak (number 1, $Ep/2^{red} = +0.23$ V) is assigned to the reduction of the $S_5N_5^+$ ion (c.f. $Ep/2^{red} = +0.46$ V for $S_5N_5FeCl_4$ in methylene chloride(21)) although in this system no corresponding oxidation peak is observed and hence the process is irreversible (unlike a) above).

The height of the second peak (number 2, $Ep/2^{red} = -0.08$ V) depends strongly on temperature; at room temperature, it is present

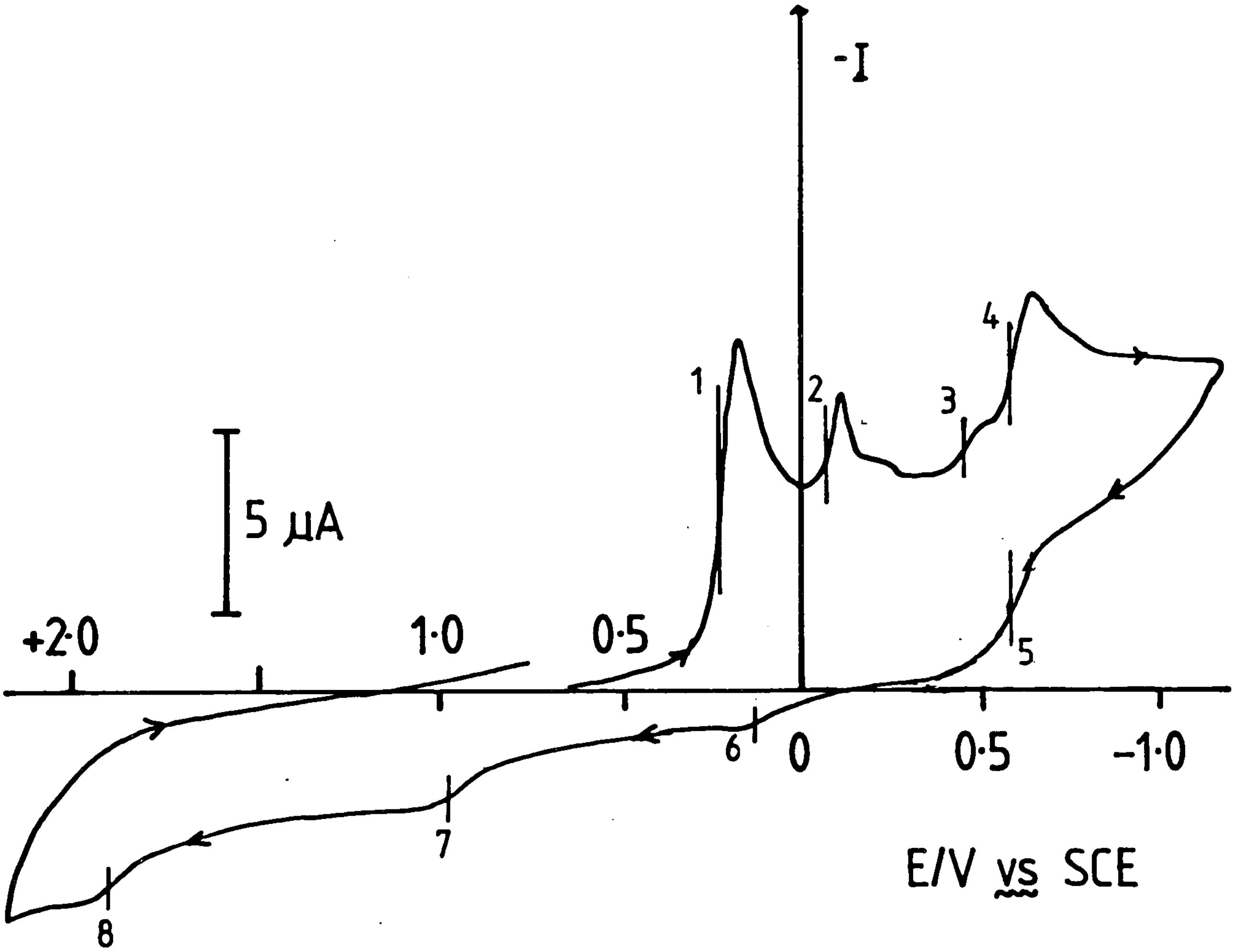


Figure 4.3. A typical cyclic voltammogram for $S_5N_5^+BF_4^-$ in acetonitrile. $S_5N_5^+BF_4^-$, 10^{-3} mol dm^{-3}, Bu_4NBF_4, 0.2 mol dm^{-3}. Temperature = 0°C, scan rate = 100 mVS^{-1}.

Table 4.1 Cyclic voltammetric data for $S_5N_5BF_4$ in 0.1 M $LiClO_4$/ acetonitrile

	Ep/2 / Volts							
	Peak				Number			
Temperature/°C	1	2	3	4	5	6	7	8
15.5	+0.28	-0.06	-	-0.54	-0.55	+0.10	+0.94	-
0.0	+0.23	-0.08	-0.47	-0.59	-0.59	+0.13	+0.94	+1.90
-6.0	+0.21	-0.12	-0.46	-0.58	-0.58	+0.18	+0.96	-
-18.5	+0.19	-0.19	-0.51	-0.59	-0.61	+0.19	+0.98	-

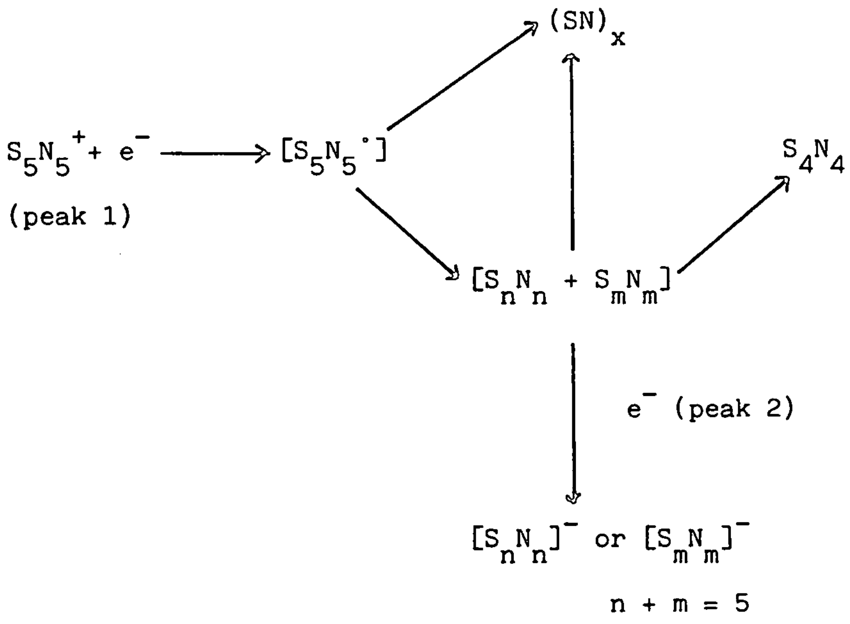
All data recorded at scan rate = 100 mV/S, sensitivity = 20 μA/V

only as a weak, broad feature but at lower temperatures the peak becomes progressively sharper and more intense, until at -18.5°C it is the same height as peak 1. A small shoulder appears on the cathodic side of the peak at 0 and -6°C but is not present at 15.5 and -18.5°C. These observations may be rationalized by assigning peak 2 to the reduction of a short-lived neutral species produced by fragmentation of the $S_5N_5^{\bullet}$ radical (see below). The cathodic shoulder is probably closely related, but since it shows a non-linear dependence on temperature, it is difficult to speculate further on its origin.

The reduction peaks 3 and 4 ($Ep/2^{red}$ = -0.46 and -0.59 V respectively) and the oxidation peak 5 ($Ep/2^{ox}$ = -0.59 V) may all be assigned to the reversible reduction of S_4N_4. Peak 3 corresponds to the pre-wave observed by Chivers and Hojo in their in their polarographic study of S_4N_4.$^{(18)}$ They found that the height of the pre-wave increased at low temperature and depended on the supporting electrolyte, but not on the concentration of S_4N_4 and so concluded that the pre-wave arose from adsorption phenomena. Peaks 4 and 5 correspond to the reduction of S_4N_4 to $S_4N_4^-$ and its re-oxidation respectively.$^{(18)}$ Addition of a small quantity of S_4N_4 to the system resulted in a marked increase in the heights of peaks 4 and 5. The very small oxidation peaks (6,7 and 8) presumably correspond to oxidation of species formed in the reduction processes. As before, peak 7 ($Ep/2^{ox}$ = +0.94 V) may correspond to the anodic breakdown of an $(SN)_x$ microlayer,$^{(16)}$ but more specific assignments are not possible.

These data usefully complement those reported by Fritz and Bruchhaus$^{(21)}$ for the electroreduction of $S_5N_5FeCl_4$, who found reduction peaks at $Ep/2^{red}$ = +0.46 and -0.5 V <u>vs</u> S.C.E. (corresponding to peaks 1 and 4 in the present work). The first, irreversible peak was assigned to the reduction of $S_5N_5^+$ and the second, reversible peak was assigned to the reduction of other, unspecified, sulphur-nitrogen species. Intermediate peaks in that system were masked by the reversible reduction of $FeCl_4^-$.

The overall reaction scheme inferred from the cyclic voltammetric data and subsequent bulk electrolyses (see below) is illustrated in Scheme 4.1.



Scheme 4.1

The $S_5N_5^+$ ion is discharged to form the transient $S_5N_5^{\circ}$ radical. This may either cleave i) to form $(SN)_x$, or ii) cleave to form two neutral species (denoted S_nN_n and S_mN_m); these could be SN° and S_4N_4 (linear) or S_2N_2 (linear or cyclic) and $S_3N_3^-$ (linear or cyclic). One of these species is stabilized at low temperatures and is subsequently reduced to an anion (peak 2); the other may rearrange to form either an $(SN)_x$ deposit or S_4N_4 (cyclic). At higher temperatures, no stabilization occurs and both species rearrange without significant further reduction. Since the observed current yield of $(SN)_x$ in bulk electrolysis experiments in this system is in the region of 40-50% and since $S_3N_3^-$ is a stable species, the cleavage of the $S_5N_5^{\circ}$ radical to linear S_2N_2 and cyclic $S_3N_3^{\circ}$ seems to be the most likely path. Cyclic S_2N_2 does not seem to be an intermediate in the reduction process since no peak corresponding to its reduction ($Ep/2^{red}$ = 0.9 V, $Ep/2^{ox}$ = +0.1 V)(13) is present in the voltammograms. Finally, it is worth noting that processes i), and ii) may occur simultaneously, with temperature determined rate constants. In principle it is possible to confirm the mechanism by in situ e.s.r. experiments but in practice these may be difficult to achieve, since no radical species were detected in the $S_5N_5FeCl_4$/methylene chloride system(21) and no radicals were detectable in an in situ electrolysis of S_5N_5Cl in liquid SO_2.(23)

Since the reduction potential of the $S_5N_5^+$ cation was known, it was then possible to attempt electrocrystallization of $(SN)_x$ by potentiostatic electrolysis.

4.2.3 Potentiostatic Electrolysis of $S_5N_5BF_4$ in Acetonitrile:

Potentiostatic electrolysis of a solution of $S_5N_5BF_4$ in 0.1 M $LiClO_4$/MeCN using bright platinum electrodes at a potential of -0.26 V vs the specially constructed (see Chapter 2) Ag/Ag^+ reference electrode (which in turn had a potential of +0.26 V vs S.C.E) yielded a bronze coloured compact deposit. The cathode was removed after electrolysis, rinsed with acetonitrile and dried in vacuo; during drying, the bronze deposits flaked away from the platium electrode surface. Examination of the flakes under a scanning electron microscope revealed microcrystalline nodules (Figure 4.4). The burst bubble - like structures in the deposit were probably caused by the in vacuo rapid evolution of solvent molecules trapped within the deposit.

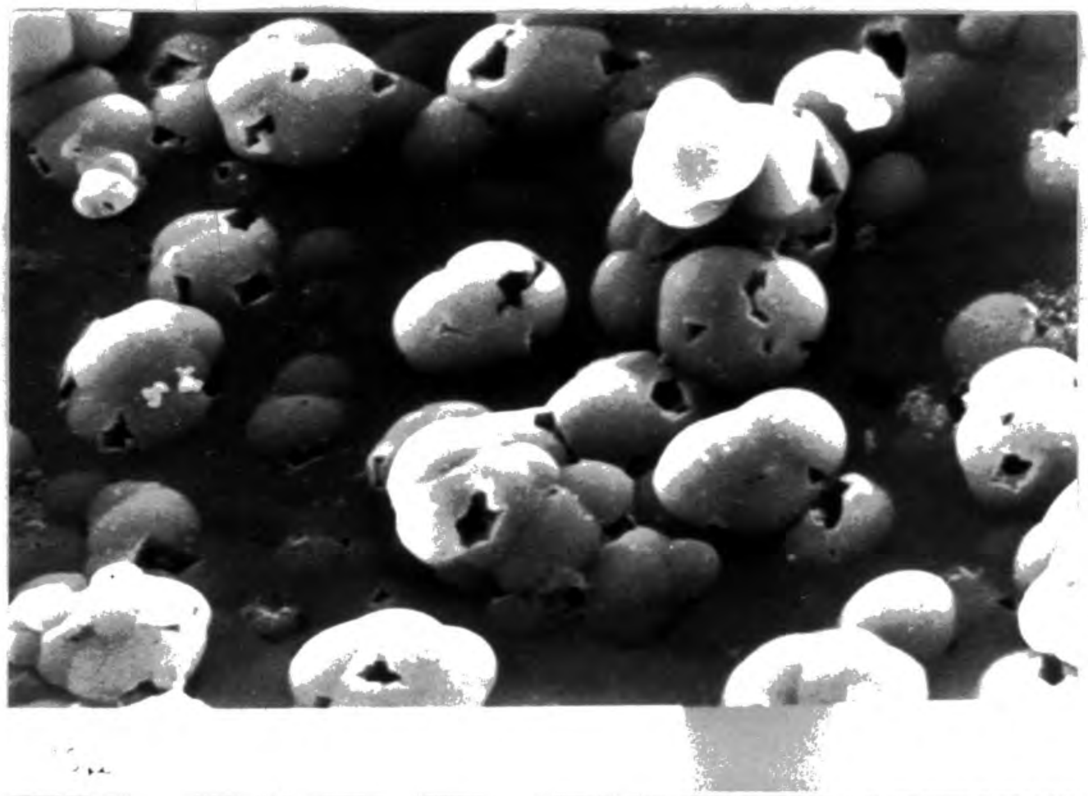


Figure 4.4. $(SN)_x$ deposit on platinum cathode ex $S_5N_5BF_4$ in 0.1M $LiClO_4$/MeCN

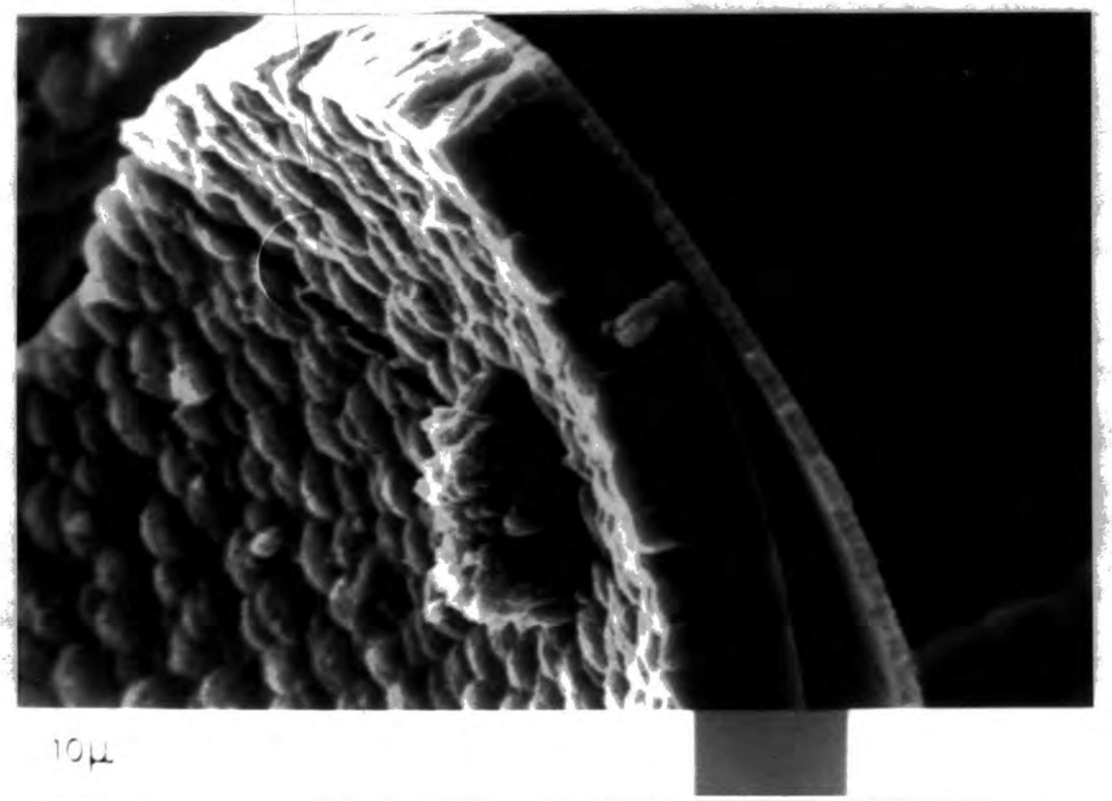


Figure 4.5. $(SN)_x$ deposit on $(SN)_x$ coated cathode ex $S_5N_5BF_4$ in 0.1M $LiClO_4$/MeCN. The thin vapour deposited layer and thick electrodeposited layer have separated

In a further experiment using the same electrolyte and experimental arrangement, the bright platinum cathode was replaced by a sheet of glass, coated with vacuum-deposited $(SN)_x$ (prepared by solid-state polymerization of S_2N_2). The layer was ca. 1.5μm thick and had a bright gold metallic lustre. Examination of the cathode under a polarising microscope (x 400) showed randomly oriented crystallites ca. 5μm average size and reflection electron miscrocopy (RED) produced a distinct arc pattern with periodicities of 3.26 Å (the distance between the $(\bar{1}02)$ planes) and hence confirmed that the crystallites had their $(\bar{1}02)$ planes oriented parallel with the glass surface.(12,13,17)

The $(SN)_x$-coated electrode was used to attempt an epitaxial electrocrystallization. with the potential at the cathode set at 0 V vs S.C.E. the current quickly steadied at 0.22 ± 0.02μmA. For approximately ten minutes the optical appearance of the electrode remained unchanged, indicating that epitaxial growth occurred. However, after this period the electrode surface darkened suddenly presumably due to a secondary nucleation. An alternative explanation could be that the cathode surface was being 'cleaned' by the discharge of $S_5N_5^+$ ions and that growth occurred only after this initiation period. The deposition continued at 0.22 mA for a total of 4½ hours. The final deposit was washed with MeCN and dried in vacuo. Under an optical microscope (x 40) it appeared microcrystalline with a gold-bronze sheen. Portions of the layer were lifted from the glass substrate by gentle heating in vacuum. Once removed, the small fragments buckled whilst the larger ones (several mm) scrolled up.

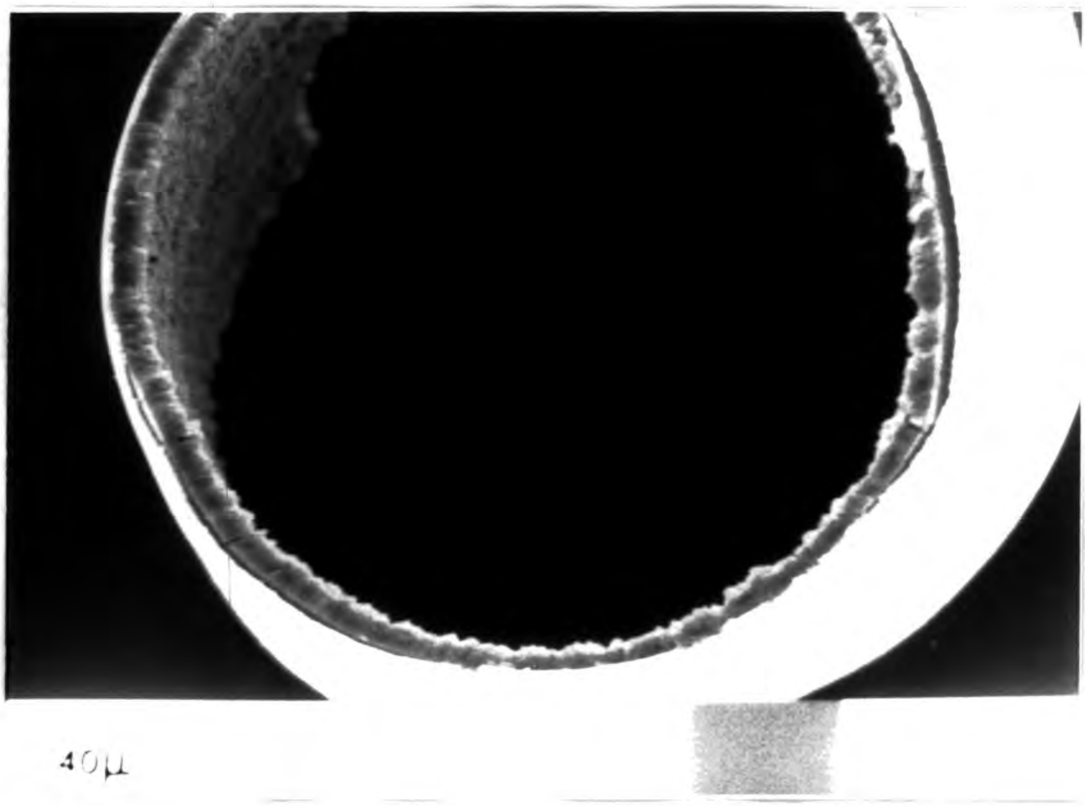


Figure 4.6. (SN)$_x$ deposit on (SN)$_x$-coated cathode ex $S_5N_5BF_4$ in 0.1M $LiClO_4$/MeCN, illustrating the scrolling of the layers.

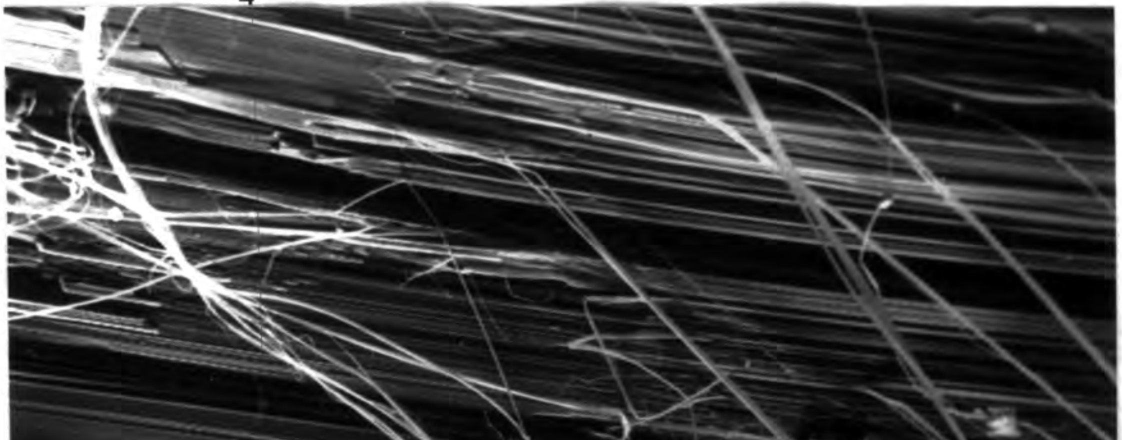


Figure 4.7. Classical (SN)$_x$, illustrating the fibrous nature of the crystal; magnification 150x.

A scanning electron micrograph (Figures 4.5 and 6) shows a fracture face perpendicular across both layers. It is apparent that mechanical stress was responsible for the partial separation of the vacuum-deposited and electro-deposited layers. It seems likely that after a short initial epitaxial growth phase, new nuclei are formed. Those with directions of the polymeric S-N chains (and thus with directions of fastest growth) oriented away from the electrode surface, took over the control of further growth (note the direction of the grain boundaries in Figure 4.5). As a consequence, a lattice mis-match generated mechanical stress. The average thickness of the electrodeposited layer, which was nearly uniform over the total conducting area (ca. 2 cm^2) of the $(SN)_x$ electrode, was 8 μm. A thickness of 16 μm would have corresponded to 100% current yield for the cathode reaction:

$$S_5N_5^+ + e^- \longrightarrow 5/x\ (SN)_x$$

Thus, an approximate 50% current yield was achieved.

The layer deposited on the $(SN)_x$-coated electrode had a higher degree of crystallinity than that deposited on bright platinum; the microcrystals on the coated electrode had dimensions of approximately 8 x 4 μm compared to 5 x 5 μm on the bright platinum. The influence of electrode surface on the polymer crystallinity indicates that with an appropriate choice of electrode material, it should be possible to grow single crystals of $(SN)_x$ electrolytically from this, or a similar, system. The more compact nature of electrochemically deposited $(SN)_x$ is illustrated by comparison with the loosely packed fibrous structure of 'classical' $(SN)_x$ prepared by the solid-state polymerization of S_2N_2. A scanning electron micrograph of the classical material is shown in Figure 4.7.

As an illustration of the suitability of this system for depositing compact layers of $(SN)_x$ a simple one-compartment, two-electrode cell was devised in which the anode was a coiled platinum wire and the cathode was a sheet of glass coated with conductive tin oxide, clamped in platinum jaws; this electrode was optically transparent. Electrolysis of a solution of $S_5N_5BF_4$/MeCN (*ca.* 0.01 M) using a simple d.c. battery source produced a thin dark blue layer of $(SN)_x$ on the cathode. The quality of the layer was indicated by its stability in air and the uniform blue appearance of the deposited film in transmitted light.

4.2.4 The Electrolysis of $S_4N_3BF_4$ in Acetonitrile:

In a preliminary study, $S_4N_3{}^+BF_4{}^-$ in acetonitrile (MeCN) was electrolysed in a divided cell without a reference electrode, using a platinum sheet cathode and an iron rod anode. A current of *ca.* 1 mA (regulated to the nearest 0.05 mA by adjusting the controls of the current source) was passed for 3 h during which time the yellow solution in the cathode compartment became steadily darker until it was a deep red-brown and a bronze layer formed on the cathode. Some bronze deposits were also observed on the iron anode - these dissolved immediately on immersion in aqueous NaOH; this layer could conceivably have been a result of the discharge of some sulphur nitrogen anion (formed by the catalytic action of the silver impurity mentioned below)but was not observed on other occasions. Pumping away the solvent left a dark green sticky solid in the cathode compartment from which a small amount (a few mg) of S_4N_2 could be sublimed; S_4N_4 was the other major co-product. It was discovered that the starting material contained a small amount of silver (from its initial preparation from $AgBF_4$ and S_4N_3Cl) and as silver is known to catalyse reactions involving sulphur-nitrogen compounds and may thus account for the somewhat complicated nature of the products, this system was not studied in further detail. A preliminary study of the electrolysis of $S_4N_3BF_4$ in SO_2 using material prepared from HBF_4(aq) and S_4N_3Cl produced an ill-defined black cathode deposit and $S_6N_4Cl_2$, which again was a result of using impure starting material.

4.3 CONCLUSIONS

Electroreduction of $S_5N_5^+$ compounds proved to be a good method for producing $(SN)_x$ of comparable quality to that obtained by the solid state polymerization of S_2N_2; it is the only alternative route to $(SN)_x$ of this grade since electro-oxidation of $S_3N_3^-$ is reported to produce only S_4N_4.(18) Cyclic voltammetric studies have helped to clarify the mechanism of reduction and thus helped to indicate better approaches to electrocrystallization. Different cathode materials resulted in different characteristics for the deposited layer and it is hoped that a suitable choice of cathode (e.g. an oriented single crystal) will result in the deposition of highly crystalline $(SN)_x$; defect-free single crystals would be of great interest for their physical properties. Finally it is worth remarking that electrochemical techniques, although rarely applied to sulphur-nitrogen chemistry in the past, are becoming increasingly important research tools in this area and throughout synthetic inorganic chemistry; further interesting results are anticipated. A systematic investigation of the electro-reduction of the $S_4N_3^+$ ion should prove worthwhile.

4.4 EXPERIMENTAL SECTION

A general description of electrochemical cells and electrodes is given in Chapter 2.

4.4.1 The Electrochemical Reduction of S_5N_5Cl in Liquid SO_2:

In a typical experiment, a two-limbed undivided cell was used. The cathode was a sheet of platinum foil (area <u>ca</u>. 4 cm^2) and the auxiliary electrode was a coiled platinum wire. S_5N_5Cl (0.160g, 0.60 mmol) was placed in the cell together with a Teflon coated stirring bar. After reassembling the cell, liquid SO_2 (21g) was condensed in, and the mixture was warmed to room temperature to give a yellow solution of <u>ca</u>. 4.1×10^{-3} mol dm^{-3} concentration. The cell was placed in an alcohol bath maintained at -1°C, above a magnetic stirrer and was connected to a galvanostatic (constant current) current source. The cell current was adjusted to 4.0 mA (i.e. a nominal current density of 1.0 mA cm^{-2}); the potential measured across the electrodes was 2.6 V. For the first 10 min the reaction proceeded without stirring and an even black film formed almost immediately on the surface of the cathode which faced the anode (front); a brown turbid cloud appeared in the electrolyte. After 10 min, the stirrer was switched on, the turbidity disappeared and a steady growth ensued. Throughout the electrolysis (4h), the current and potential remained remarkably stable (fluctuation ca. 2%) and no gas evolution occurred. The cell residue was identified by infrared spectroscopy as S_5N_5Cl (major component) and S_4N_4.

The deposit on the front of the cathode was microcrystalline $(SN)_x$ interspersed with minute S_4N_4 crystals. The reverse side of the electrode was coated with a thin continuous blue layer of $(SN)_x$.

The S_4N_4 could be removed from the product by vacuum sublimation (60°C, 10^{-6}torr). Yield, 0.020g, (14.5%). Infrared spectrum (CsI plates), ν_{max} 1010 m, 698m, 627w, 505w, 287s cm^{-1}(24) Found S, 69.17; N, 30.85; $(SN)_x$ requires S, 69.60; N, 30.40%. Powder photograph (CuK_α) 3.6(s), 3.26 (vs), 2.94 1s) Å.(12,25) Identical procedures were followed for experiments in which different cathode materials were used [$(SN)_x$ coated wire, (SN)x single crystal]. These cathodes were clamped in platinum jaws and suspended in the electrolyte.

4.4.2 Preparation of Vapour Deposited Films:

The coated electrodes described in the discussion section were prepared using a method developed in Durham by Z.V. Hauptman.(4) A suitably clean substrate, such as plane glass or platinum wire, was coated with $(SN)_x$ which had been prepared by the 'classical' route(10) to form the electrode surface.

A similar procedure was followed to prepare the samples used for reflectance spectroscopy measurements. A quantity of ca. 80mg of SO_2-washed $(SN)_x$ prepared by the electrochemical reduction of S_5N_5Cl in liquid SO_2 was sublimed at 120-130°C on to clean glass substrates. A uniform $(SN)_x$ coating ca. 1μm thick with a golden bronze colour was obtained after about 16h.

4.4.3 Cyclic Voltammetric Studies:

a) S_5N_5Cl in SO_2. Tertiary butyl ammonium fluoroborate, Bu_4NBF_4 (0.47g) was placed together with S_5N_5Cl (ca. 5mg) in a three-limbed undivided cell equipped with Swagelok compression fittings; a platinum disc microelectrode and a coiled platinum wire counter-electrode were introduced through two of the limbs and the third was sealed with a ¼" O.D. glass plug. SO_2 (18.8g) was condensed into the cell; final concentrations were: S_5N_5Cl, ca. 0.001 M; Bu_4NBF_4, ca. 0.2M. The solution was cooled to 0°C and, against, a counter-flow of dry nitrogen, the specially contructed Ag/Ag^+ reference (see Chapter 2) was inserted in place of the glass plug. Cyclic voltammograms were then obtained using the control box and x-y recorder described in Chapter 2.

b) $S_5N_5BF_4$ in acetonitrile. The procedure described in **a)** above was followed using Bu_4NBF_4 (0.47 g), $S_5N_5BF_4$ (ca. 5 mg), and acetonitrile (15 ml); the resulting concentrations were: $S_5N_5BF_4$, ca. 0.001 M; Bu_4NBF_4, ca. 0.2 M.

4.4.4 Potentiostatic Electrolysis of $S_5N_5BF_4$:

a) At a platinum electrode. A three-electrode cell equipped with Swagelok fittings was used. The reference electrode (specially constructed Ag/Ag^+) and working elecrode (platinum sheet; area, 4.0 cm^2) were separated from the counter-electrode (coiled platinum wire) by a porous glass frit. The potential of the reference electrode was +0.26 V *vs* S.C.E. $S_5N_5BF_4$ (0.25g, 0.79 mmol) was dissolved in 40 ml of 0.1 M $LiClO_4$/acetonitrile and electrodes were inserted against a flow of dry nitrogen. The whole apparatus was maintained under an atmosphere of dry nitrogen at 0°C. The electrodes were connected to the potentiostatic current source and a potential of -0.26 V V *vs* S.C.E) was maintained at the working electrode whilst a current of approximately 0.3 mA passed through the cell. A compact bronze layer was deposited on the cathode. Electrolysis was stopped after 2½h and the deposit was rinsed with acetonitrile and dried *in vacuo*. On drying, the layer flaked away from the electrode and it was not possible to weigh the deposit; a sample was mounted for examination under an electron microscope (see Section 4.2.3).

b) At an $(SN)_x$-coated electrode. Using the same cell and solution as in a) above, but using an $(SN)_x$-coated glass sheet clamped in platinum jaws as the working electrode, a potential of 0 V *vs* S.C.E was maintained for 4½h. The current remained steady at 0.22 0.02 mA throughout. The resultant deposit was rinsed with acetonitrile and mounted for examination under an electron microscope. The current yield was estimated from the layer thickness as 50% (see Section 4.2.3).

4.4.5 Electrolysis of $S_4N_3BF_4$:

a) In acetonitrile. $S_4N_3BF_4$ (*ex* $AgBF_4$ + S_4N_3Cl, 0.2g, 0.8 mmol) was placed in a two-compartment cell and acetonitrile (40 ml) was syringed on top. Two electrodes (iron rod anode and platinum cathode) were introduced into the cell via Quickfit thermometer screw fittings and the cell was cooled to -1°C. A current of 2.0 mA was passed through the cell (nominal cathodic current density, 1.5 mA cm^{-2}) and the potential drop across the cell was 2.5 V. On passing current, the pale yellow cathodic solution became blue-green and a dark layer formed on the anode, later becoming gold; a similar black deposit formed on the anode after 15 min. The beginning of cathodic deposition was accompanied by the return of the original yellow colour of the cathodic solution which, while remaining clear, gradually darkened to orange-brown.

The darkening of the cathodic solution was attributed to the formation of S_4N_2 which was isolated as a volatile red crystalline solid from the residue after electrolysis (and identified by its characterisitc iodine-like smell and its appearance). The gold-coloured coating [presumably of $(SN)_x$] was removed from the anode with alcoholic KOH solution; examination of the iron electrode surface under an optical microscope showed no sign of corrosion. Only milligram quantities of all products were formed.

b) In SO_2. $S_4N_3BF_4$ (ex S_4N_3Cl and aqueous HBF_4, 0.2g 0.8 mmol) was placed in a simple two-limbed cell equipped with Swagelok pressure fittings. The working electrode was a platinum sheet and the counter-electrode was a coiled platinum wire. SO_2 (ca. 20g) was condensed into the cell which was subsequently maintained at -4°C and a current of 5 mA was passed through the cell for a total of 100 min before cell resistance necessitated switching to a cycling mode of operation (2.5 mA, 1 min on, 2 min off). A further increase in cell resistance resulted in the cell being left to stand overnight (unelectrolysed) followed by a further 100 min at 2.5 mA and a final 64 min of cycling mode (2.5 mA, 1 min on, 4 min off). A total of 53.3 coulombs was passed through the cell.

Green crystals precipitated from the electrolyte (which became red-brown) during electrolysis and a black deposit formed on the cathode, but subsequently fell off. The cell was placed in a cycling temperature bath (0 ± 10°C, 1 cycle in 1h) to enlarge the green crystals. After 4 days the solution had become pale brown and the solvent was removed to yield a mixture of crystalline solids. Extraction of these solids with liquid SO_2 yielded a yellow soluble solid (identified by infrared spectroscopy as $S_4N_3BF_4$) and a green insoluble solid (identified by x-ray powder diffraction as $S_6N_4Cl_2$)(25) together with a tiny amount of an insoluble white powdery solid (unidentifiable owing to tiny amount, possibly sulphur). Only a few milligrams of $S_6N_4Cl_2$ were isolated.

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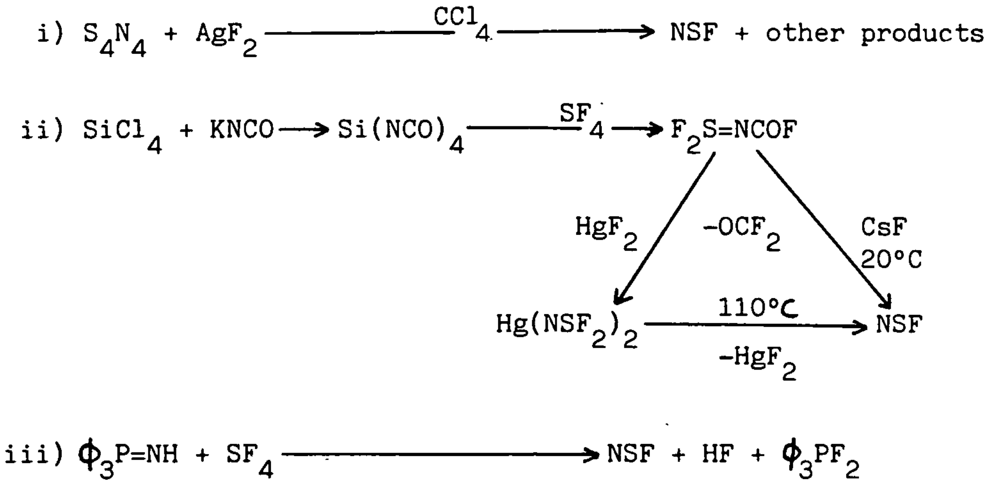
CHAPTER 5

Some Investigations of Sulphur-Nitrogen-Fluorine Compounds: Preparation and Reactions of Thiazyl Fluoride and the Attempted Preparation of S_4N_3F

5.1 INTRODUCTION

The field of sulphur-nitrogen-fluorine chemistry has been developed over the past thirty years, largely by Glemser and co-workers at Göttingen. The first compound to be reported was thiazyl fluoride, NSF, in 1955(1) and this compound together with the S(VI) derivative, NSF_3 has subsequently been of central importance in sulphur-nitrogen fluorine chemistry; nearly all known sulphur-nitrogen fluorine compounds may be derived from NSF or NSF_3. The chemistry of these two key substances has been well reviewed.(2) Many preparative routes to NSF have been described in the literature including the fluorination of a mixture of ammonia and sulphur with AgF_2,(3) the reaction of ammonia with SF_4,(3) and the fluorination of S_4N_4 with AgF_2.(3) These routes are summarised in Scheme 5.1. The major problem with these syntheses is that they produce a mixture of products, including NSF_3, $(NSF)_3$, and $(NSF)_4$. The thermal decomposition of compounds which already contain the N-S-F group e.g. $FCONSF_2$(4) or $Hg(NSF_2)_2$(5) produces NSF as the only sulphur-nitrogen-fluorine containing product in good yield; however, as can be seen from Scheme 5.1 the preparation of starting materials is, in itself, an expensive and arduous procedure.

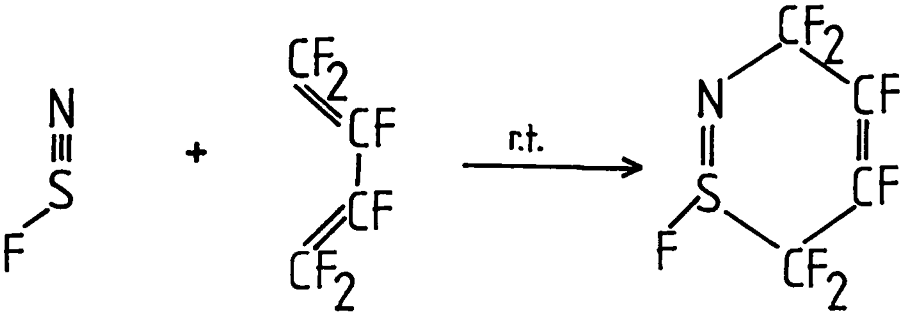

i) $S_4N_4 + AgF_2 \xrightarrow{CCl_4} NSF$ + other products
ii) $SiCl_4 + KNCO \rightarrow Si(NCO)_4 \xrightarrow{SF_4} F_2S{=}NCOF$
HgF_2
$-OCF_2$
CsF
20°C
$Hg(NSF_2)_2$
110°C
$-HgF_2$
NSF
iii) $\phi_3P{=}NH + SF_4 \rightarrow NSF + HF + \phi_3PF_2$

Scheme 5.1

Recent developments in sulphur-nitrogen chemistry have led to the synthesis of small cations and their use as building blocks in further synthesis.(6) The convenient synthesis of the SN^+ cation as its AsF_6^- salt was recently achieved by reaction of the well-known compound $(NSCl)_3$ with $AgAsF_6$;(7) previously the SN^+ cation had been prepared by reaction of NSF with Lewis acids such as AsF_5 to produce $SN^+AsF_6^-$.(8) The facile preparation of $SN^+AsF_6^-$ raised the possibility of conveniently generating NSF by reaction of the SN^+ cation with fluoride ion:

$$SN^+AsF_6^- + CsF \longrightarrow NSF + CsAsF_6 \qquad \text{Equ.5.1}$$

Thiazyl fluoride is a reactive gas and has been used in cyclo-addition reactions as a diene.(9)



Equ. 5.2

Reaction with alkyl butadienes was found to be(2) uncontrollable and results in ignition. The aim of the work described in this section was to devise a convenient method of producing NSF and then react the gas under mild conditions with suitable substrates to produce new heterocycles.

At an early stage it was thought that thermolysis of a sulphur -nitrogen salt containing a suitable fluorinated anion would be a convenient method of preparing sulphur-nitrogen-fluorine compounds and so the preparation and thermoysis of $S_4N_3BF_4$ was studied; it was also thought that $S_4N_3BF_4$ could be used to prepare the compound S_4N_3F which had previously only been reported as its HF solvate.(10) These experiments are described at the end of the chapter.

5.2 RESULTS AND DISCUSSION

5.2.1 Small Scale Preparation of NSF:

a) Solution preparations. It was found that the reaction between CsF and $SN^+AsF_6^-$ in liquid SO_2 could be followed conveniently by monitoring the ^{19}F nmr spectrum. By making up reaction mixtures of known mole-ratios containing known weights of reactants and adding a known amount of Freon 11 as an internal standard, it was possible to estimate an approximate yield for Equation 5.1 in SO_2. Working on a ca. 1 mmol scale, approximately 50% conversion to NSF was achieved, and the NSF in solution appeared to be stable for up to 36h; detected decomposition products were OSF_2 (identified by ^{19}F nmr and gas phase infrared spectroscopy) and $(NSF)_3$ (identified by ^{19}F nmr spectroscopy). The $(NSF)_3$ signal was only observed for the system containing 1:1 mole ratio of $SNAsF_6$:CsF. Although the partial conversion to NSF could have been a result of performing the reactions in situ in a 10mm nmr tube where stirring was impossible, it was decided that, from a synthetic point of view, it would be more useful to produce quantities of gaseous NSF rather that NSF in solution. Since the nmr experiments proved that the reaction between CsF and $SNAsF_6$ in SO_2 did indeed produce NSF, the solid state reaction between these two compounds was chosen for study.

b) Solid state preparation. The extremely hygroscopic nature of NSF is well-documented(2) and experience gained during the nmr experiments indicated that great care in handling procedures was essential for a successful preparation. Thus initial small-scale experiments were performed using a stainless steel gas cell, fitted with a side-arm and AgCl windows, which could be rigorously dried using a combination of heat and scrubbing with SF_4. The generation of NSF could be induced in the side-arm and the gaseous products could be monitored immediately by infrared spectroscopy. The dryness of the system was gauged by the amount of OSF_2 present when an atmosphere of SF_4 (ca. 1 atm) was allowed to sit in the apparatus; less than 5% OSF_2 was considered to be sufficiently dry. At least three cycles of scrubbing with SF_4 were required to achieve this level and a gas phase spectrum illustrating the acceptable standard is illustrated in Figure 5.1a.

A molar ratio of 5:1 CsF:$SNAsF_6$ was chosen to ensure complete conversion to NSF. Moderate heating of this intimately ground mixture resulted in the steady evolution of NSF (monitored by observing the 655 cm^{-1} S-F stretching mode in the gas phase infrared spectrum) and a gas-phase infrared spectrum of the products showed NSF to have been the major product.

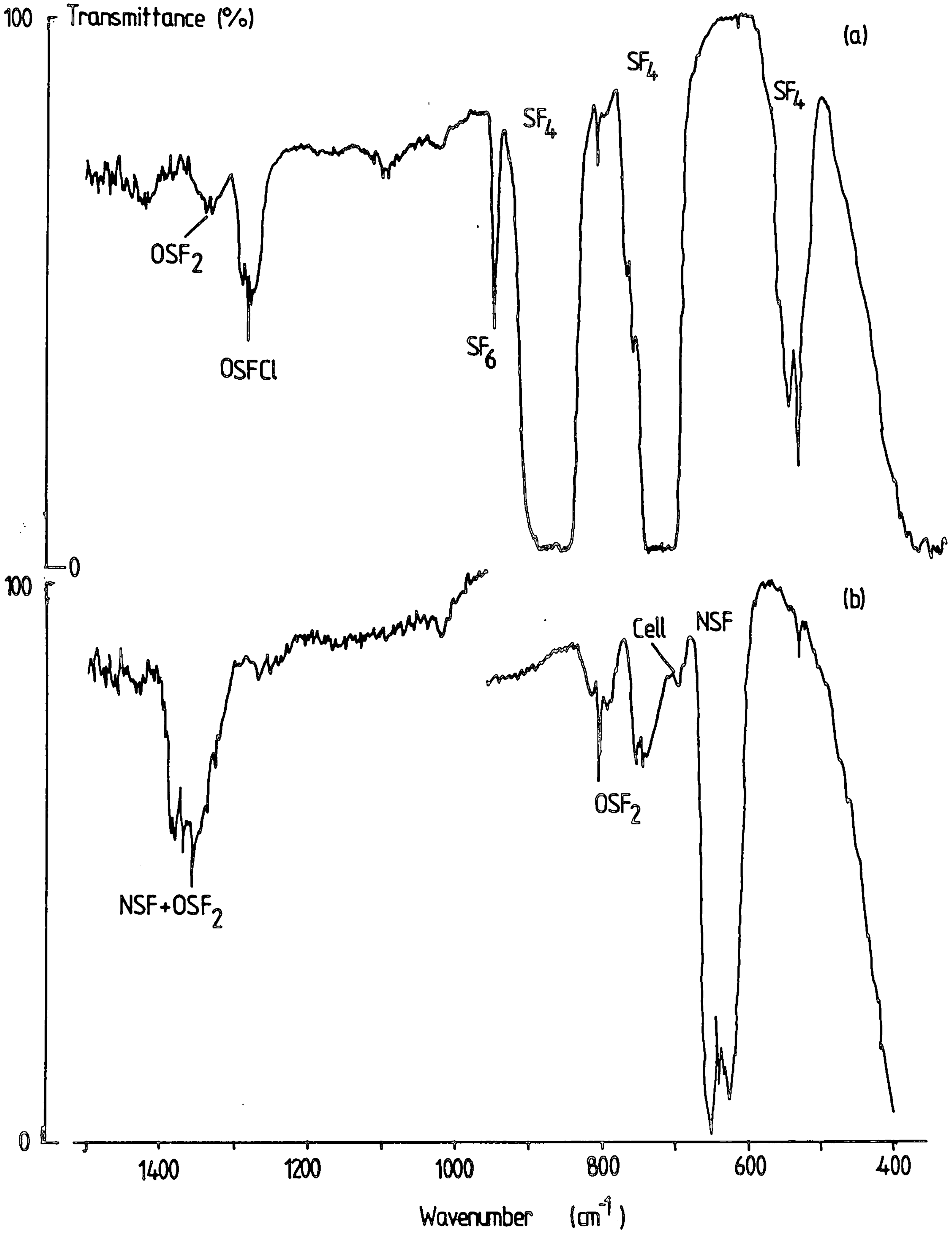


Figure 5.1. (a) Gas phase, infrared spectrum of ca. 1 atm SF_4 in an acceptably dry gas cell.
(b) Gas phase infrared spectrum of NSF generated *in situ*.

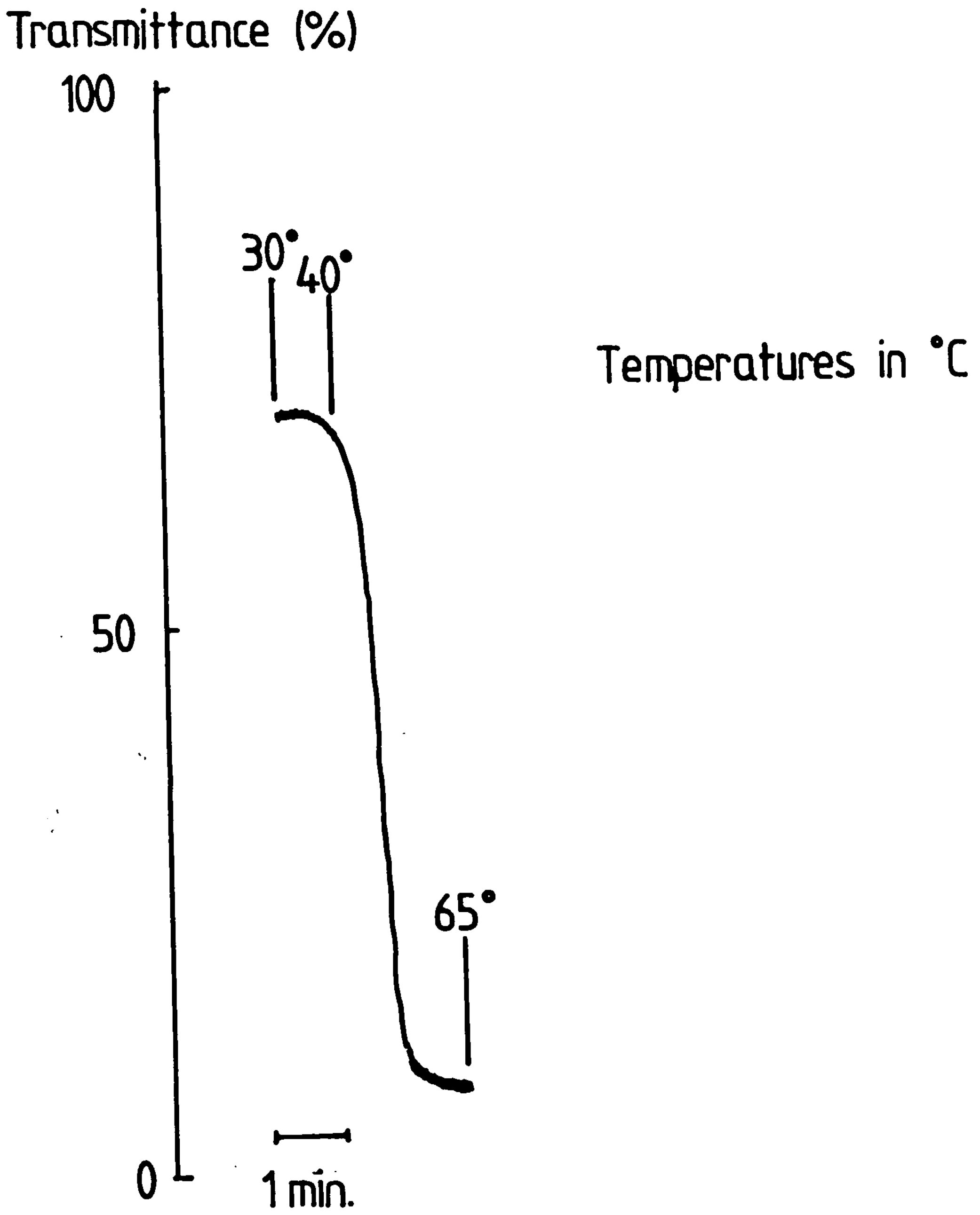


Figure 5.2. Evolution of NSF with increasing temperature.

Comparison with published spectra showed that the relative amounts of products in the gas phase were NSF, 95±5%(11) and OSF_2, 5 ± 2.5%(12) corresponding to an 80% yield of NSF. An infrared trace of the evolution of NSF with temperature is shown in Figure 5.2 and an infrared spectrum of the gas phase products is shown in Figure 16.

5.2.2 Larger scale preparation of NSF:

Since the small-scale reaction proved successful in producing good quality NSF under mild conditions, a larger scale reaction designed to produce ca. 1g of NSF was tried. The reaction vessel was a monel can and the apparatus was carefully scrubbed with F_2 and SF_4 to remove traces of moisture. This time a temperature of 110°C was required to induce production of NSF which was monitored on a pressure gauge. Comparison of the gas phase infrared spectrum of the products with published spectra showed the products to be approximately 80% NSF,(11) 10% SF_4(13) and 10% OSF_2.(12) Co-condensation of the gas phase products with AsF_5 enabled the NSF to be recovered as $SN^+AsF_6^-$ and from the weight of $SN^+AsF_6^-$ recovered, an approximate yield of 50% NSF was deduced.

$$4NSF \longrightarrow 2N_2 + SF_4 + \tfrac{3}{8}S_8$$

$$SF_4 + H_2O \longrightarrow 2HF + OSF_2$$

Scheme 5.2

The lower yield of NSF in the larger scale reaction can be accounted for by Scheme 5.2. Weight measurements on the reaction and product cans indicated that 0.85g was lost from the reaction can, but only 0.67g of volatiles were condensed into the product can. Gas phase infrared showed the volatiles to be a mixture of NSF (80 ± 10%), SF_4 (10 ± 5%), and OSF_2 (10 ± 5%). Assuming the OSF_2 detected was largely a product of SF_4 hydrolysis, 0.16 ± 0.07g (1.5 mmol) of SF_4 was produced by thermal decomposition of NSF. According to Scheme 5.2, 0.16 ± 0.07g of SF_4 would be produced by 0.39 ± 0.04g (6 mmol) of NSF and thus the expected yield of NSF is:

$$(0.85 - (0.39 \pm 0.04)) = 0.46 \pm 0.04\text{g } (7.0 \text{ mmol})$$

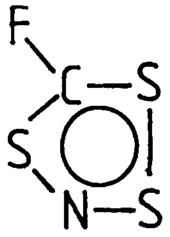
Within experimental error, this is the weight of NSF isolated in the preparation, based on its recovery as $SN^+AsF_6^-$ and so Scheme 5.2 provides a valid explanation of the modest yield of NSF observed in the scale-up experiment. The weight loss of 0.18g between reaction and product cans is accounted for in terms of loss of N_2 from the system and deposition of elemental sulphur in the vacuum manifold.

A comparison of the high yield small scale experiment and the lower yield scale-up experiment usefully pointed to the factors affecting the yield of NSF in this route. Most importantly, the degree of mixing of the starting materials seems to determine the temperature at which NSF generation commences; in the more intimately mixed small scale experiment reaction proceeded at 40-55°C whereas the larger scale experiment required a temperature of 110°, with possible local super-heating and consequent decomposition of product. It should be added that the temperature of the electric furnace (as measured by a mercury-in-glass thermometer) did not necessarily indicate the temperature of the reactants inside the apparatus, since heat-flow through the metal walls and solid reactants will not have been 100% efficient. Nevertheless, it seems fair to say that the larger-scale experiment required a substantially higher temperature for reaction than did the small-scale experiment. The compact waxy nature of $SN^+AsF_6^-$ makes effective grinding difficult; recrystallization from SO_2 improves the ease of grinding and hence should improve the yield. Similarly, optimisation of heating rates and heat transfer in the reaction vessel in larger scale reactions should improve the yield of NSF to the 80% attainable in small scale reactions.

5.2.3 Gas Phase Reactions of NSF:

In spite of the difficulties encountered in devising a gram-scale preparation of NSF, it was found possible to investigate reactions in the gas phase using the small-scale procedure to generate NSF in a gas cell; a suitable amount of a gaseous reagent could then be injected via a vacuum manifold and the course of reaction could be followed by monitoring the gas phase infrared spectrum. Several such experiments were performed and the results are discussed below.

a) Reaction with CS_2. It was hoped that NSF would react with an unsaturated species like CS_2 to produce heterocyclic species such as I which would be a formally 8-π system. In fact, only NSF, OSF_2 and SF_4 (which were all present initially) were detected in the gas phase infrared together with the CS_2 which had been injected. Over a period of 10h the NSF peaks lost intensity whilst the OSF_2 peaks gained intensity, indicating that slow decomposition took place.



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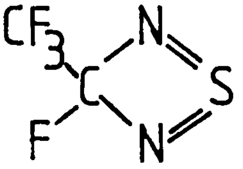
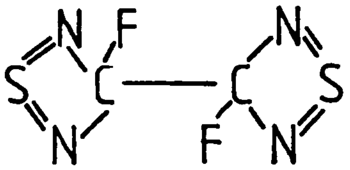


II



III

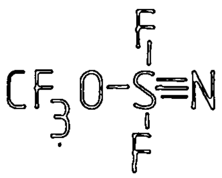
b) Reaction with CF_3CN. It was hoped that NSF would react with CF_3CN to produce a species such as **II**. Again, monitoring the gas infrared showed no significant diminution of the NSF modes on introduction of CF_3CN and no significant changes even after 24h. Evidently NSF and CF_3CN do not react under these conditions.

c) Reaction of NSF with $(CN)_2$. It was hoped that species of the type III would be formed in this reaction; however, as before no reaction was observed on monitoring the gas phase infrared spectrum.

d) Reaction of NSF with CF_3OF. The preceding experiments which were designed to study reactions involving substitution or reactions involving the π-system of NSF all failed; evidently these types of reactions are not favoured under such mild conditions. In a further attempt to achieve room temperature reaction of NSF, an addition reaction with CF_3OF was tried.

Changes in the gas phase infrared spectrum occurred almost immediately on introduction of CF_3OF to the system containing NSF. In general, the spectra indicated the appearance and gradual increase of peaks belonging to SF_4 and OCF_2 and the gradual decrease in intensity of peaks belonging to NSF and CF_3OF. Whilst the presence of so many species in the gas phase obscured a fairly large proportion of the infrared spectrum and gave rise to some coincidences of bands, some peaks which were not assignable to NSF, CF_3OF, SF_4, or OCF_2 were also detected.

These unassigned peaks were observed at 1468, 1280, 1165, and 825 cm^{-1} and reached maximum relative intensity after 6h. The band at 1468 cm^{-1} is in the correct region for the SN stretching vibration (c.f. NSF_3, S≡N 1515cm^{-1},$^{(11)}$ NSF, S≡N = 1372 cm$^{-1(11)}$) and the band at 1280 cm^{-1} is in the C-F stretching region. Since the unknown species appears to contain both an S≡N triple bond and a C-F containing group, its probable structure is proposed to be that of IV.

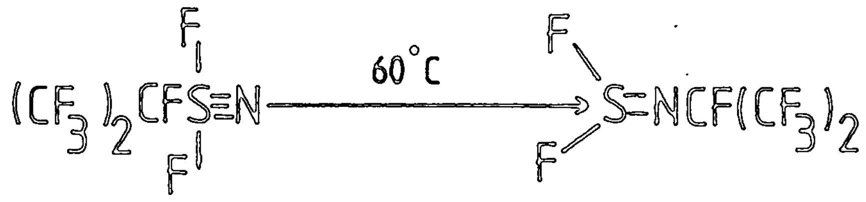


$CF_3O-\overset{\displaystyle F}{\underset{\displaystyle F}{S}}\equiv N$

IV

Derivatives of the type RSF_2N and $RR'SFN$(2,14) have been reported previously and spectral data are summarised in Table 5.1. Thus, the band at 825 cm^{-1} may be assigned either to ν_{as} S-F or to νC-O (c.f. CF_3OF, νC-O = 882 cm^{-1})(15)

The band at 1165 cm^{-1} is more difficult to assign since, although it is in the C-F stretching region, molecules containing a simple CF_3 group e.g. CF_3OF(15) do not exhibit strong absorbtions in this region; the 1165 cm^{-1} band may therefore belong to another, unidentified C-F containing species. Since the compound $(CF_3)_2CFSF_2N$ is known to isomerise at 60°C according to Equation 5.3.(16)



$$(CF_3)_2CF\overset{F}{\underset{F}{S}}{\equiv}N \xrightarrow{60^\circ C} F_2S{=}NCF(CF_3)_2$$

Equ. 5.3

It is possible that CF_3OSF_2N undergoes a similar rearrangement to produce $F_2S{=}NOCF_3$ at room temperature; the 1165 cm^{-1} band could then be assigned to the N=S band of $F_2S{=}NOCF_3$. The reported N=S mode of compound VI is, however, reported as being 1300 cm^{-1}(14) which is appreciably higher than 1165cm^{-1}. It was not possible to extract any further information from the infrared data since so much of the spectrum was obscured by SF_4 and OCF_2; the only unassignable absorptions were two very weak bands at 2050 and 2070 cm^{-1}. A suggested reaction sequence is shown in Scheme 5.3.

Table 5.1 Infrared spectra of RSF_2N and R_2SFN compounds

a) COMPOUND	SN/cm^{-1}	S-F/cm^{-1}	REFERENCE
$(CF_3)_3CSF_2N$	1516,1488	755,722	(2)
$(CF_3)_2CFSF_2N$	1504,1479	746,719	(14)
$(\phi_2N)_2SFN$	1500	795,701	(14)
ϕ_2NSF_2N	1475	750,700	(14)
ϕSF_2N	1468	750,690	(14)
$p\text{-}FC_6H_4SF_2N$	1461	728,688	(14)
ϕ_2SFN	1428	740,600	(14)

b) $(CF_3)_2CFSF_2N/cm^{-1}$	$(CF_3)_3CSF_2N/cm^{-1}$	CF_3OSF_2N/cm^{-1} and Tentative Assignment
1504mw (νSN)	1516m	
1479mw (νSN)	1488m	1468m (νSN)
1279s (νC-F)	1340s	
1263vs (νC-F)	1280vs	1280s (νC-F)
1194mw (νC-F)	1216vs	
1158mw (νC-F)	1179m	1165, (νC-F)
977m (νC-C)	976s	
950mw (νC-C)	926s	
764m,sh (νC-F)	769m	
746m (νas S-F)	755s	ν_{as} S-F 825s or ν C-O
719s (νas S-F)	727s	
624w (deformation)	572s	
542w (deformation)	541m	
520m (deformation)		
502mw,sh (deformation)	493s	

$$NSF + CF_3OF \longrightarrow N{\equiv}SF_2OCF_3 \xrightarrow{\Delta} \tfrac{1}{2}N_2 + SF_4 + 2OCF_2$$

Scheme 5.3

Although this reaction is interesting in that it proceeds under very mild conditions, the fact that RSF_2N derivatives may be prepared from the more easily handled NSF_3 and organo-lithium reagents$^{(14)}$ makes it of limited synthetic interest and so no further investigation was undertaken.

5.2.4 The Preparation and Thermolysis of $S_4N_3^+BF_4^-$; the Attempted Preparation of $S_4N_3^+F^-$:

It is well known that various $S_4N_3^+$ salts may be prepared from S_4N_3Cl by metathesis with a suitable acid such as $HNO_3$$^{(17)}$ or HSO_3F.$^{(18)}$ It was thought that an $S_4N_3^+$ salt with a suitable fluorine containing counter-ion might serve as a convenient starting material for sulphur-nitrogen-fluorine compounds which could be generated by thermolysis. Accordingly, $S_4N_3^+BF_4^-$ was synthesized first by metathesis of S_4N_3Cl with $AgBF_4$ Equation (5.4) and secondly by metathesis of S_4N_3Cl with aqueous HBF_4 Equation (5.5) :

$$S_4N_3Cl + AgBF_4 \longrightarrow S_4N_3BF_4 + AgCl \qquad \text{Equ.5.4}$$

$$S_4N_3Cl + HBF_4\ (aq) \longrightarrow S_4N_3BF_4 + HCl\ (aq) \qquad \text{Equ.5.5}$$

When thermolysed in vacuo, $S_4N_3BF_4$ (prepared from $AgBF_4$) darkens;

at 80°C a small amount of volatile material (SO_2, BF_3 and an unidentified species) was evolved and further heating to 180°C resulted in the formation of a uniform highly reflective coating of $(SN)_x$ on the cool part of the vacuum line. Subsequent elemental analysis found a silver impurity of 0.5% in the starting material and examination of the sublimation residue (largely $S_4N_3BF_4$) under an optical microscope revealed tiny black spots on the crystals. These black spots were presumably Ag_2S, which, like Ag_2Se, is known to catalyse the splitting of sulphur-nitrogen rings.(19) A repeat reaction using $S_4N_3BF_4$ free of silver did not produce an $(SN)_x$ layer. Since pyrolysis of sulphur-nitrogen cations has previously been found to offer no significant advantage over other methods of making $(SN)_x$ and since the reaction of $SNAsF_6$ and CsF had been found to be a convenient method of preparing NSF, no further work was done on this system.

$S_4N_3BF_4$ produced according to Equation (5.5) was used for the preliminary electrochemical studies described in Chapter 4. It was found that most of the chloride impurity (arising from incomplete conversion of S_4N_3Cl to $S_4N_3BF_4$) could be eliminated by brief extraction with SO_2; the more soluble $S_4N_3BF_4$ dissolved whilst the less soluble S_4N_3Cl remained behind. This purified $S_4N_3BF_4$ was used in the attempted synthesis of S_4N_3F.

The strategy adopted was that of ionic displacement:

$$S_4N_3BF_4 + CsF \longrightarrow CsBF_4 + S_4N_3F \qquad \text{Equ.5.6}$$

This approach has been tried successfully in the synthesis of S_4N_5F from $S_4N_5AsF_6$ using SO_2 as solvent.(20) Preliminary nmr tube experiments, monitoring the ^{19}F spectrum of a 1:1 mixture of CsF and $S_4N_3BF_4$ in SO_2 detected after 48h only signals belonging to BF_4^- and a very weak signal assignable to $(NSF)_3$. As a thin blue layer of $(SN)_x$ was also formed on the walls of the tube, it was decided to investigate this reaction on a preparative scale, but with a short reaction time to minimise decomposition. When $S_4N_3BF_4$ and CsF were reacted in SO_2 (1:1 mole ratio) on a preparative scale, an ionic displacement occurred precipitating the expected stoichiometric weight of $CsBF_4$. The soluble product was crystalline but sticky; infrared spectroscopy indicated the presence of $S_4N_3^+$ and S_4N_4 but did not indicate the presence of the BF_4^- ion. The precipitation of the correct stoichiometric amount of $CsBF_4$, combined with the detection of $S_4N_3^+$ and non-detection of BF_4^- in the infrared spectrum of the soluble product, suggested that the soluble product was impure S_4N_3F

Attempts to purify the crude S_4N_3F by first removing the S_4N_4 with pentane and then recrystallyzing the remainder from SO_2 did not succeed; massive decomposition to S_4N_4 occurred on redissolving the S_4N_3F in SO_2. This behaviour recalls that of S_4N_3Cl in SO_2 which has been found to decompose to give a whitish product of unknown composition.(19) It should be added that decomposition probably also occurs during the initial reaction since a thin transluscent layer of $(SN)_x$ was deposited on the walls of the reaction bulb. A further attempt to remove the S_4N_4 impurity from crude S_4N_3F by high vacuum sublimation resulted in decomposition and reaction of S_4N_3F with the residual SO_2; $S_4N_3SO_3F$ was isolated as the major involatile product whilst SO_2, OSF_2, NSF, SiF_4, and a minute quantity of another unidentified species were detected as volatile products. In addition a small quantity of highly coloured volatile material containing S_4N_4 was evolved. A possible reaction scheme is shown in Scheme 5.4; the SiF_4 was presumably a result of hydrolysis, causing the formation of HF which subsequently attacked the Pyrex apparatus.

$$3S_4N_3F + 2SO_2 \xrightarrow{\Delta} S_4N_3SO_3F + OSF_2 + 3/2S_4N_4 + 1/4S_8$$

$$S_4N_3F \xrightarrow{\Delta} NSF + 1/2S_4N_4 + 1/8S_8$$

Scheme 5.4

Attempts to avoid reaction with solvent by using acetonitrile did not succeed as infrared spectra of the products indicated decomposition and incomplete reaction; a thin layer of $(SN)_x$ also formed in the reaction vessel. Since these apparently facile reactions were not proceeding in a simple way, attempts to prepare S_4N_3F were discontinued.

5.3 CONCLUSIONS

The initial aim of devising a more convenient route to NSF was achieved, although further optimization is required for large scale preparations. The gas phase reactions of NSF were disappointing and evidently either more severe reaction conditions must be applied which may result in the formation of complex mixtures(2) or different substrates must be chosen. Since many of the obviously suitable reagents have already been studied,(2) it seemed more interesting to explore the chemistry of the SN^+ or S_2N^+ ions rather than NSF; the use of thiazene cations as 'building blocks' in synthesis has already been demonstrated.(6)

Although S_4N_3F was not isolated in a pure state, it seems likely that it was the primary product from the reaction of $S_4N_3BF_4$ and CsF. Evidently it is a reactive material which, although somewhat stabilized in SO_2 solution, decomposes readily on precipitation. As anticipated, thermolysis of S_4N_3F yielded NSF but a mixture of other products was also detected.

5.4 EXPERIMENTAL SECTION

5.4.1 Solution Preparation of NSF in an NMR Tube:

CsF (0.120g, 0.792 mmol) and $SNAsF_6$ (0.186g, 0.792 mmol) were placed together in a 10mm nmr tube fitted with a J. Young's Teflon stemmed bleed valve. Freon 11 (CCl_3F, 0.3273g, 2.383 mmol) was condensed in followed by SO_2 (ca. 5g). The mixture was allowed to warm to room temperature and shaken vigorously; after standing at room temperature for 2h the ^{19}F nmr spectrum at -75°C was recorded. The sample was kept at room temperature for a further 12h and then cooled to -80° for 20h; the ^{19}F spectrum was re-recorded, again at -75°C. For a 100% reaction, the mole ratio of CCl_3F:NSF would be 3.01:1 and the integrated peak intensities of the ^{19}F nmr spectrum would be expected to be in the same ratio. The actual integrated peak intensities were in the ratio CCl_3F:NSF, 9.56:1.35 indicating a 42.5% yield of NSF. After 12h at room temperature followed by 20h at -80° the ratio was 1:6 indicating a 50.2% yield of NSF. NMR spectrum after 2h, δF (200 MHz, solvent SO_2, reference CCl_3F) 230.6 [1F, s, NSF], 0 [1F, s, CCl_3F], and -60 [6F, vbr s, AsF_6^-]. NMR spectrum after 36h, δF (200MHZ, solvent SO_2, reference CCl_3F), 233.72 [1F, s, NSF], 0 [1F, s, CCl_3F], and -50 [6F, vbr s, AsF_6^-]. In similar (but non-quantitative) experiments, molar ratios of 1:1 and 2:1 CsF:$SNAsF_6$ were used. After being kept at -70°C for 6 days, the samples were allowed to warm to room temperature for several hours before recording the ^{19}F nmr spectrum at -75°C. NMR spectrum of 1:1 mixture, δF (200MHZ, solvent SO_2, reference CCl_3F) 231.1[1F,s,NSF(2)] 70.7 [2F,s, OSF_2(21)], 41.21 [3F, s,vw, $(NSF)_3$ (22)], and -65 [6F, s,br, AsF_6^-(21)]. NMR spectrum of 2:1 mixture, δF (200 MHz, solvent SO_2, reference CCl_3F) 233.4 [1F, s, NSF], 72.4 [2F, S, OSF_2], and -60 [6F, s,br, AsF_6^-].

5.4.2 Preparation of NSF by Solid State Reaction of $SNAF_6$ and CsF:

a) Small Scale Preparation. In a typical experiment, a right-angled closed tube (O.D. ¼ inch, wall approximately 1mm, length approximately 25 cm) was coupled to a stainless steel gas cell, fitted with AgCl windows, <u>via</u> a Teflon Swagelok compression fitting and Whitey valve; the total volume of the system was 190 cm^3. The apparatus was evacuated and SF_4 was carefully admitted (1 atm). The apparatus was then isolated from the gas cell and flamed for a few minutes. After cooling, the SF_4 was pumped away. This process was repeated (3-4 times) until a gas phase infrared spectrum of SF_4 in the apparatus showed 5% OSF_2.

The apparatus was taken into the glove box and, whilst keeping the gas cell under vacuum, the side-arm was uncoupled and loaded with an intimately ground mixture of $SNAsF_6$ (0.123g, 0.523 mmol) and CsF (0.237g, 1.56 mmol) (slight discolouration occurred on grinding the mixture). After re-connection of the side-arm and re-evacuation, the side-arm was heated in on electric furnace to 65°C at a rate of 14°C/min. The steady evolution of NSF between 40 and 50°C, monitored by observing the 655 cm^{-1} S-F mode in the gas phase infrared spectrum, ceased after ca. 3 min. The partial pressures of the products (NSF, OSF_2) were estimated from the final infrared spectrum by comparing infrared intensities with published spectra. Infrared spectrum, ν_{max} 1382m (NSF), 1372m (NSF), 1360s (NSF), 1340m (OSF_2), 1330m (OSF_2), 1270w (NSF), 810m (OSF_2), 760m (OSF_2), 750m (OSF_2), 655vs (NSF), 645vs (NSF), 630vs (NSF), 535w (OSF_2)cm^{-1}. From published spectra of OSF_2(12) and NSF(11) the pressures of NSF and OSF_2 were estimated as 40 torr (95±5)% v/v and 2 torr (5±2.5)% v/v respectively.

b) Larger scale preparation. Two Monel cans and the gas cell used in a) above were connected via Swagelok Teflon compression fittings and Whitey valves to a monel vacuum manifold. Elemental fluorine (1 atm) was carefully passed into the evacuated apparatus, and after flaming and re-evacuation, SF_4 (1 atm.) was enclosed in the apparatus overnight. Spent SF_4 was removed and fresh SF_4 was condensed into the cans with flaming until a gas phase infrared spectrum showed 5% OSF_2.

One of the cans was detached and taken, under vacuum, into the glove box where an intimately ground mixture of CsF (7.0g, 46.08 mmol) and $SNAsF_6$ (3.6g, 15.32 mmol) was packed into the bottom. A further charge of CsF (2.94g, 19.35 mmol) was packed on top of the mixture. After re-attachment to the vacuum manifold and re-evacuation, the can containing the reactants was heated in an electric furnace to 110°C (1.5°C/min). Reaction occurred at 110°C when a rapid evolution of gas was observed. Gas phase infrared spectroscopy showed the products to be NSF (80±10)%, 0.54 ± 0.07g , SF_4 (10±5)%, 0.07±0.03g , and OSF_2 (10±5)%, 0.07 ± 0.03g , the relative amount of each product being estimated from the published spectra of NSF,(11) SF_4,(13) and OSF_2.(12) The reaction volatiles were condensed into the empty can and AsF_5 (3.8g, 22.4 mmol) was condensed on top. Some non-condensible gases (N_2) were pumped away. Weight measurements on the reaction and product cans showed that 0.85g was lost from the reaction can and 0.67g was condensed into the product can. After standing overnight, the volatiles (OSF_2, AsF_5) were removed from the product can and the $SNAsF_6$ produced (1.76g) was identified by Raman spectroscopy. A Raman spectrum of the reaction can residues showed only the presence of AsF_6^-. The 1.76g of $SNAsF_6$ (from the reaction between NSF and AsF_5) corresponds to an NSF yield of 0.48g (48%) which matches the estimate (see above) of 0.54 ± 0.07g. Raman spectra (5145 Å): $SNAsF_6$ recovered, ν_{max} 1434 vs (NS^+), 1062w, vbr (?), 679 vs (AsF_6^-), 558m, br (AsF_6^-) cm^{-1}. Reaction residue, ν_{max} 682m (AsF_6^-), 578w, br (AsF_6^-)cm^{-1}. Infrared spectrum of gas phase products, ν_{max} 2220w (?), 1380m (NSF), 1365m (NSF), 1352s (NSF), 1342s (OSF_2), 1332s (OSF_2), 895m, sh (SF_4), 885s, sh (SF_4), 870s, sh (SF_4), 860vs (SF_4), 802s (OSF_2), 750s, sh (OSF_2, SF_4), 730vs (OSF_2, SF_4), 650vs (NSF, SF_4), 640vs (NSF, SF_4), 625vs (NSF, SF_4), 530s (OSF_2) cm^{-1}.

5.4.3 Gas Phase Reactions of NSF

a) With CS_2. A small quantity (ca. 0.5 mmol) of NSF was generated in a stainless steel gas cell, fitted with AgCl windows, using the procedure described above. In this case a small contamination of the NSF with SF_4 was observed, possibly because insufficient grinding of the reactants necessitated a high reaction temperature (70°C) with resulting thermolysis of NSF. Approximately two line-inches (corresponding to 0.3 mmol) of CS_2 was introduced into the gas cell by cooling the side-arm. The infrared spectrum of the gas cell contents was recorded after 5 min, 40 min, and 10h; only peaks belonging to SF_4, OSF_2, NSF, and CS_2 were observed. The NSF peaks lost a little of their intensity over 10h whilst the OSF_2 peaks gained a little.

b) Reaction with CF_3CN. The procedure described in a) was followed and approximately 0.5 mmol of NSF was generated; OSF_2 was the only containment. Approximately 3.5 line-inches (corresponding to 0.5 mmol) of CF_3CN was injected into the gas cell via the vacuum manifold. Gas phase infrared spectra were recorded after 5 min, 5h, and 24h. The spectra simply showed a mixture of OSF_2, NSF, and CF_3CN although again the NSF peaks lost a little of their intensity whilst the OSF_2 peaks gained a little. Infrared spectrum after 10h, ν_{max} 2460 m, sh (CF_3CN), 2420m (CF_3CN), 2270vs (CF_3CN), 2020m (CF_3CN), 2010w, sh (CF_3CN), 1420m, br (CF_3CN), 1385m, sh (NSF), 1370s (NSF), 1361s (NSF), 1340vs (OSF_2, CF_3CN), 1330vs (OSF_2, CF_3CN), 1320s (OSF_2, CF_3CN), 1225vs (CF_3CN), 1140vw (CF_3CN), 1080vw (CF_3CN), 920vw (CF_3CN), 865vw (CF_3CN), 805vs (OSF_2, CF_3CN), 795vs (OSF_2, CF_3CN), 755s (OSF_2), 745s (OSF_2), 650vs (NSF), 640vs (NSF), 630vs (NSF) cm^{-1}.

c) **Reaction with $(CN)_2$.** Following the procedures described above, approximately 0.15 mmol of NSF, contaminated slightly with OSF_2, was generated in the gas cell. Approximately 1 line-inch of cyanogen (corresponding to 0.15 mmol) was injected into the gas cell. Infrared spectra were recorded after 10 min, 12h, and 20h. No new bands were observed but since so little NSF was generated initially, complete decomposition of NSF to OSF_2 and a trace of SO_2 occurred. Infrared spectrum after 20h, ν_{max} 2160w $(CN)_2$, 2140w, sh $(CN)_2$, 1370m (SO_2), 1360m, sh (SO_2), 1340s (OSF_2), 1330m, sh (OSF_2), 805s (OSF_2), 755m, sh (OSF_2), 740s OSF_2, $(CN)_2$, 725m, sh OSF, $(CN)_2$, 530w (OSF_2) cm^{-1}.

d) **Reaction with CF_3OF.** The procedure described above was used to generate approximately 0.5 mmol of NSF, contaminated with a little OSF_2, in the gas cell. Approximately 0.5 mmol CF_3OF was injected into the cell <u>via</u> the vacuum manifold and infrared spectra of the mixture were recorded after 10min, 6h, 16h and 40h. The gas cell pressure was reduced to approximately 30 torr before recording the 40h spectrum.

The spectra and assignments are listed below; the new bands observed are discussed in the first part of the chapter. Infrared spectrum after 10 mins, ν_{max} 2510w (CF_3OF), 2490w (OCF_2), 1955vs (OCF_2), 1840vs (OCF_2), 1935 (OCF_2), 1550vw, br (OCF_2), 1470m (new species), 1380m sh (NSF), 1370m, sh (NSF), 1360s (NSF), 1340m, sh (OSF_2), 1250v.vs (CF_3OF, OCF_2), 1170m, sh (new species), 975m (OCF_2), 945s (CF_3OF), 890m, (CF_3OF, SF_4), 880m (CF_3OF, SF_4), 868m (SF_4), 825m (new species), 808, (OSF_2), 795m (OSF_2), 775m (OCF_2), 760m, sh (OCF_2, SF_4), 739s (SF_4), 729s (SF_4), 720m, sh (SF_4), 690m, sh (CF_3OF), 680m (CF_3OF), 655vs (NSF), 641vs (NSF), 630vs (NSF), 590vw (CF_3OF, OCF_2), 532w (OSF_2)cm^{-1}. Infrared spectrum after 6h, ν_{max} 2940w (OCF_2), 2920w (OCF_2), 2485w, sh (OCF_2), 2350vw (OCF_2), 2210w (OCF_2), 2180w (OCF_2), 1930v.vs (OCF_2), 1560w, br (OCF_2), 1475m, sh (new species), 1468s (new species), 1385w (NSF), 1340m, sh (OSF_2), 1330m, sh (OSF_2), 1250 v.vs (CF_3OF + OCF_2), 1165m (new species), 975vs (OCF_2), 960vs (OCF_2), 948vs (OCF_2, CF_3OF), 890s (SF_4, CF_3OF), 875vs (SF_4, CF_3OF), 865vs (SF_4), 825s (new species), 820s (OSF_2), 808vs (OSF_2), 798s, sh (OCF_2, OSF_2), 775s (OCF_2), 755s, sh (OCF_2, SF_4), 725vs (SF_4), 655vs (NSF), 638vs (NSF), 630vs (NSF), 535m (OSF_2), 480m, sh (?)cm^{-1}. Infrared spectrum after 16h, ν_{max} 2940w (OCF_2), 2920w (OCF_2), 2205w (OCF_2), 2180w (OCF_2), 2070vw (?), 2040vw (?), 1930v.vs (OCF_2), 1560w, br (OCF_2), 1480m, sh (new species), 1470s (new species), 1455m, sh (new species), 1380w, sh (NSF, CF_3OF,SO_2) 1370w, sh (NSF, CF_3OF,SO_2), 1240m (OSF_2), 1330m (OSF_2), 1280vs (new species), 1240v.vs (CF_3OF, OCF_2), 1165m (new species), 975vs (OCF_2), 960m (OCF_2), 945vs (OCF_2), 900w, sh (SF_4), 890m, sh (CF_3OF, SF_4), 875m, sh (CF_3OF, SF_4), 865s (SF_4), 825s (new species), 808, (OSF_2), 796m, sh (OSF_2, OCF_2), 774m (OCF_2), 755m, sh (OCF_2, SF_4), 747vs (SF_4, OSF_2), 727vs (SF_4), 655m (NSF), 640m (NSF,OCF_2), 630s (NSF, OCF_2), 595vw (OCF_2, CF_3OF), 531m (OSF_2)cm^{-1}. Infrared spectrum after 40h, pressure reduced to 30 torr, ν_{max} 2490 vw (OCF_2), 2210vw (OCF_2), 2070w (?), 2050vw(?), 1955vs (OCF_2), 1942vs (OCF_2), 1925vs (OCF_2), 1470w (new species), 1370w (SO_2), 1360m, sh (SO_2), 1340m (OSF_2), 1330m (OSF_2), 1280s (new species), 1240 (OCF_2), 1165w (new species), 975s (OCF_2), 960s (OCF_2), 950s (OCF_2), 890w (SF_4), 875w, sh (SF_4), 865w (SF_4), 820m, sh (SF_4), 808s (OSF_2), 795m, sh (OSF_2, OCF_2), 774m (OCF_2), 755m, sh (OCF_2, SF_4), 740s (SF_4, OSF_2), 728s (SF_4, OSF_2), 655w (NSF), 645m (NSF, OCF_2), 630m (NSF, OCF_2), 532w (OSF_2) cm^{-1}.

5.4.4 The Preparation of $S_4N_3BF_4$ from S_4N_3Cl and $AgBF_4$:

S_4N_3Cl (0.5g, 2.4 mmol), $AgBF_4$ (0.47g, 2.4 mmol) was placed with a Teflon-coated magnetic stirring bar in one bulb of a two-bulb vessel. Acetonitrile (9 ml) was syringed into the other bulb; after degassing by successive freezing and pumping, the solvent was transferred to the reaction bulb and the mixture was stirred at room temperature (16h). A black polythene sheet was placed over the reaction vessel to prevent photodecomposition. A white solid (AgCl) precipitated and the mixture was filtered to give a clear yellow solution; removal of solvent yielded yellow tabular crystals.

Yield, 0.47g (69%); Infrared spectrum, ν_{max} 1300w, 1200w, 1060vbr, vs (BF_4^-), 780w, 687m, 580m, 530m (BF_4^-), 500s, 345s, 247w cm^{-1}. Raman spectrum (5145 Å), ν_{max} 1190w, 1150vw, 1020w, 720w, 620m, 575w, 430s, 265, 200s, 105m, 60w, 25vw cm^{-1}. δF, (90MHZ, CD_3CN solvent, CCl_3F reference) -150.3 [4F, brvs, BF_4^- reference (23)], m.p. (sealed tube under N_2), 245°C (decomp.); found: N, 16.30; B, 4.3; $S_4N_3BF_4$ requires N, 16.35; B,4.2%. Subsequent analysis found Ag, 0.5%.

5.4.5 Preparation of $S_4N_3BF_4$ from S_4N_3Cl and HBF_4(aq):

An identical procedure to Section 3.4.2 was followed using $S4N_3Cl$ (8.8 g; 43 mmol) and aqueous HBF_4 (342 ml). The crude product (8.04 g) was extracted with liquid SO_2 to give an intermediate product as the soluble fraction (8.04 g) and a portion of this (0.6g) was extracted again with acetonitrile to give purified $S_4N_3BF_4$ as the soluble product (0.44g) and S_4N_3Cl as the insoluble product (0.13g).

Yield; since 0.6g of the intermediate product gave 0.44g of $S_4N_3BF_4$, the overall yield was 48%. Infrared spectrum of $S_4N_3BF_4$, ν_{max} = 1300w, 1200w, 1060vbr, vs, 780w, 687m, 580m, 530m, 500s, 345s, 247w, cm^{-1}. Analysis of soluble product, found: S, 51.2; N, 15.97; B, 4.99; Cl, $<$ 0.5; $S_4N_3BF_4$ requires S, 49.8; N, 16.3; B, 4.21%. Analysis of insoluble product: S, 61.5; N, 19.9; Cl, 16.7; S_4N_3Cl requires S, 62.4; N, 20.42; Cl 17.3%.

5.4.6 Thermolysis of $S_4N_3BF_4$(ex $S_4N_3Cl/AgBF_4$):

A few hundred milligrams of $S_4N_3BF_4$ were heated in vacuo (10^{-6} torr) 60-80°C in an electric furnace. The yellow crystals became olive coloured and a small amount of a colourless volatile material was evolved, being trapped at liquid nitrogen temperature. Gas phase infrared spectra (10 cm Pyrex cell, KBr windows, 70 torr) showed the presence of traces of SO_2, BF_3, and an unidentified species (ν_{max}, 1450, 1445m, 690w cm^{-1}). The cell windows become coated with BF_4^- ion after 70h.

On further heating to 180°C, a highly reflective coating of $(SN)_x$ was deposited on the cooler part of the vacuum manifold. Coloured volatile materials, which polymerised on warming to room temperature, collected in the cold trap. A Raman spectrum of the olive-green residue from the thermolysis proved it to be largely $S_4N_3BF_4$. Examination of the residue under an optical microscope showed that the olive-green crystals were dotted with black specks (presumably Ag_2S).

5.4.7 Thermolysis of $S_4N_3BF_4$ (ex S_4N_3Cl/HBF_4):

$S_4N_3BF_4$ (0.1420g, 0.6 mmol) was placed in a small vessel equipped with a Rotaflo Teflon stemmed valve and was heated in vacuo (10^{-4}torr) to 180° by an electric furnace. A very thin grey-brown film formed on the cool part of the reaction vessel; a gas-phase infrared spectrum of the volatiles evolved showed only the presence of SO_2. An infrared spectrum of the solid residue showed only $S_4N_3BF_4$ whilst an infrared spectrum of the thin grey-brown film proved it to be a mixture of $S_4N_3BF_4$ $\longrightarrow$ and S_4N_4 with extra bands at ν_{max} 970s, sh, 870m, br, and 375s, sh cm^{-1}. The total weight loss from the reaction vessel was 0.0030g (0.2%).

5.4.8 The Reaction Between $S_4N_3BF_4$ and CsF in SO_2:

a) NMR tube reaction. CsF (0.089g, 0.6 mmol) and $S_4N_3BF_4$ (0.150g, 0.6 mmol) were placed together in a 10mm nmr tube equipped with a J.

Young's Teflon-stemmed bleed valve. SO_2 (ca. 5 ml) was condensed in and after allowing the mixture to warm to room temperature with shaking, the ^{19}F nmr spectrum was recorded at -70°C. δF (200MHZ; solvent SO_2; reference CCl_3F) 41.6 [3F, s, $N_3S_3F_3$ (22)] and -137.0 [4F, s, BF_4^-] Note: the BF_4^- signal is shifted slightly downfield compared to a solution containing BF_4^- ions as the only fluorinated species; this effect may be a result of exchange phenomena.

b) Preparative scale reaction. $S_4N_3BF_4$ (0.38g, 1.48 mmol) was placed in one bulb of a two-bulb vessel, equipped with Teflon stemmed valves and a No.4 porosity frit. CsF (0.23g, 1.48 mmol) was placed together with a Teflon-coated stirring bar in the other bulb; SO_2 (10.903g) was condensed, in approximately equal quantities, into both bulbs. On warming to room temperature, the yellow solution of $S_4N_3BF_4$ was added to the CsF/SO_2 mixture. The solution immediately became orange and the mixture was stirred at room temperature for 5h. Filtering and washing with back-distilled SO_2 yielded an orange-brown solution and grey powdery insolubles ($CsBF_4$). Removal of SO_2 yielded a sticky yellow/orange crystalline solid, which could not be completely removed from the reaction vessel. A gas phase infrared spectrum of the reaction mixture showed only SO_2. Yields: yellow/orange solid, 0.23g (expected for a 1:1 reaction. 0.28g); grey powdery insolubles ($CsBF_4$), 0.31g (expected for a 1:1 reaction, 0.33g). The reaction products contained 0.036g of absorbed SO_2.

The yellow/orange solubles were placed in a sublimation tube and heated (65°C/ 6x10^{-7}torr) for 3 days. Orange crystalline S_4N_4 sublimed out and a mixture of highly coloured volatiles collected in the cold traps (liquid N_2). When the sublimation had finished a gas-phase infrared of the cold-trap volatiles was recorded. The yellow crystalline residue from the sublimation was identified (i.r.) as $S_4N_3^+SO_3F^-$ Wt of S_4N_4 sublimed out, 0.067g; wt. of residue, 0.12g; therefore wt. of volatiles in trap, 0.04g. Infrared spectrum of grey powdery insolubles from reaction, ν_{max} 1285m (BF_4^-), 1050vs, br (BF_4^-), 920w, sh (S_4N_4), 762vw, sh (?), 720w (S_4N_4), 570w, br (?), 540w (S_4N_4), 515s (BF_4^-), 485w, br (?) cm^{-1}. Infrared spectrum of residue from sublimation, ν_{max} 1290vs (SO_3F^-), 1260vs, sh (SO_3F^-), 1182m ($S_4N_3^+$), 1090sh (SO_3F^-), 1070vs (SO_3F^-), 1035s (S_4N^+), 930vw, sh, (?), 740vs (SO_3F^-), 700vs ($S_4N_3^+$), 685sh, 660m, sh ($S_4N_3^+$), 620vw, 578s ($S_4N_3^+$, SO_3F^-), 560sh (SO_3F^-), 520w, 490s ($S_4N_3^+$) cm^{-1} c.f. KSO_3F,(24) ν_{max} 1280s, 1080s, 750s, 580s, 570sh cm^{-1}. Gas phase infrared spectrum of volatiles in cold trap, ν_{max} 2500m (SO_2), 2230vw (?), 1350vs (SO_2, NSF), 1265vw (?), 1165vs (SO_2), 1145vs (SO_2), 1025vs (SiF_4), 908vw(?), 809s (OSF_2), 760s (OSF_2), 750s, sh (OSF_2), 712m (?), 655vs (NSF), 630vs (NSF), 530vs (SO_2) 500vs (SO_2) cm^{-1}. Infrared spectrum of solid residue in cold trap, ν_{max} 1165 w, br (?), 1030w, br (?), 920m (S_4N_4), 790vw(?), 720m (S_4N_4), 690m (S_4N_4), 540m (S_4N_4) cm^{-1}.

5.4.9 The Reaction of $S_4N_3BF_4$ and CsF in MeCN:

The procedure detailed above was followed using $S_4N_3BF_4$ (0.5g, 1.85 mmol), CsF (0.3g, 1.95 mmol), and acetonitrile (10 ml). The mixture was stirred at room temperature for 16h; filtration and removal of solvent yielded yellow/orange sticky soluble crystals and a powdery grey insoluble solid ($CsBF_4$). A weight loss of 0.103g was incurred during removal of solvent and a reflective bronze film formed on the vessel wall during the reaction. Yields: yellow/orange solubles, 0.17g (expected for a 1:1 reaction, 0.37g); $CsBF_4$, 0.44g (expected for a 1:1 reaction, 0.43g). Gas phase infrared spectrum of reaction mixture, ν_{max} 1370m (SO_2), 1345m (SO_2), 1160vw, br (SO_2), 810w (OSF_2), 740w, br (OSF_2) 525vw (SO_2) cm^{-1}. Infrared spectrum of grey powdery insolubles (mostly $CsBF_4$), ν_{max} 1285w (BF_4^-), 1050vs, vbr (BF_4^-), 920m, sh (S_4N_4), 800vw(?), 760vw(?), 720m (S_4N_4), 700m (S_4N_4), 540m (S_4N_4), 520s (BF_4^-)cm^{-1}. Infrared spectrum of red-brown solubles, ν_{max} 1290m (BF_4^-), 1270w, 1185w, sh ($S_4N_3^+$), 1000vs, v.bvr (BF_4^-), 930m, sh (S_4N_4), 770m(?), 720m (S_4N_4), 700m, sh (S_4N_4), 675s ($S_4N_3^+$), 630w, sh (?), 570m ($S_4N_3^+$), 540m (S_4N_4), 520m (?), 485s ($S_4N_3^+$), 380vs, sh (?) cm^{-1}.

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CHAPTER 6

Chemical Reactions of $S_3N_2^{2+}(AsF_6^-)_2$ and Synthetic Applications of Lability in Sulphur-Nitrogen Rings

6.1 INTRODUCTION

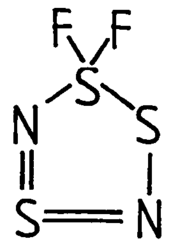
The S_3N_2 ring is a familiar structural unit in sulphur-nitrogen chemistry. It is present in both neutral compounds such as S_3N_2O(1) and cationic species such as $S_3N_2Cl^+$.(2) Although the neutral molecule S_3N_2 has never been prepared, the cation $S_3N_2^{+\cdot}$ is known,(3) being a 7-π radical species, present in $S_6N_4^{2+}$ salts (solid and in solution) and is a member of the series of binary monocyclic thiazenes which also contains the formally Hückel-aromatic species $S_4N_3^+$,(4) $S_5N_5^+$,(5) and $S_3N_3^-$.(6) Although an early report of the preparation and infrared spectrum of the missing 6-π cation $S_3N_2^{2+}$ existed in the literature(7) more recent results(8) indicated that a virtually quantitative preparation of the compound $S_3N_2^{2+}(AsF_6^-)_2$ had been achieved via the symmetry allowed cyclo-addition of SN^+(9) and S_2N^+;(10) the compound was characterized by infrared and Raman spectroscopy and elemental analysis.(8)

This chapter describes some investigations of the chemistry of $S_3N_2^{2+}(AsF_6^-)_2$ which illustrate the labile nature of the ring, the reaction of $S_3N_2^{2+}(AsF_6^-)_2$ with fluoride ion to produce the new derivative $S_3N_2F^+(AsF_6^-)$, and MNDO studies of this reaction and ring cleavage/closure in $S_3N_2^{2+}$. During attempted crystal growth experiments on $S_3N_2^{2+}(AsF_6^-)_2$, a crystal of $S_2N^+AsF_6^-$ was isolated. Its structure, determined by J. Johnson (University of New Brunswick) is reported here. The insight gained into the solution equilibria of sulphur-nitrogen systems was used to devise a more convenient synthesis of $S_3N_2^{2+}(AsF_6^-)_2$ and a new and more convenient synthesis of $S_2N^+SbCl_6^-$.

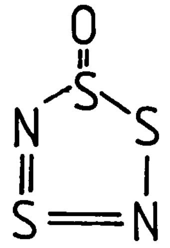
6.2 RESULTS AND DISCUSSION

6.2.1 Reaction of $S_3N_2^{2+}(AsF_6^-)_2$ with Fluoride Ion:

The preparation of $S_3N_2^{2+}(AsF_6^-)_2$ mentioned above makes the $S_3N_2^{2+}$ ion an accessible starting material for further chemical investigation of this ring system. In particular, the preparation of the fluorine derivatives of the ring, $S_3N_2F^+$ and $S_3N_2F_2$ were thought to be of special interest since $S_3N_2F^+$, the analogue of the well known $S_3N_2Cl^+$(2) had not been reported in the literature and $S_3N_2F_2$(11) had been reported as a volatile green crystalline solid which formed in very low yield during the decomposition of NSF in a glass flask. An ultraviolet/visible spectrum and elemental analyses had been reported(11) but no structural data were available; it should be noted that whilst both linear and cyclic structures are possible for $S_3N_2F_2$, the cyclic structure I is more likely, by analogy with the known covalent liquid S_3N_2O, II.(1)



I



II

A likely synthetic strategy to both $S_3N_2F^+$ and $S_3N_2F_2$ seemed to be:

$$S_3N_2^{2+}(AsF_6^-)_2 + CsF \longrightarrow S_3N_2F^+AsF_6^- + CsAsF_6 \qquad \text{Equ.6.1}$$

$$S_3N_2F^+AsF_6^- + CsF \longrightarrow S_3N_2F_2 + CsAsF_6 \qquad \text{Equ.6.2}$$

In order to test this hypothesis, small scale reactions were performed in 10mm nmr tubes using SO_2 as solvent. For a 1:1 mole ratio of CsF:$S_3N_2^{2+}(AsF_6^-)_2$, the ^{19}F nmr spectrum showed the immediate formation of a singlet at $\delta = 38.5$ppm, together with a broad signal at $\delta = -58$ppm assigned to the AsF_6^- ion. The singlet was assigned to the $S_3N_2F^+$ ion [c.f. $(NSF)_3$, $\delta = 44.5$ and $(NSF)_4$, $\delta = 32.8$ ppm]. After a week at room temperature, the $S_3N_2F^+$ signal had diminished whilst the growth of a signal at 71.6 ppm indicated the formation of OSF_2, presumably as a hydrolysis product. Thus the first stage of the stepwise strategy seemed likely to succeed and in order to pursue the synthetic strategy further, preparative reactions were undertaken.

The 1:1 reaction, using both AsF_3 and SO_2 as solvent, produced a brown crystalline product identified by infrared spectroscopy, nmr spectroscopy, and elemental analysis as $S_3N_2F^+AsF_6^-$. The weights of $S_3N_2F^+AsF_6^-$ and $CsAsF_6$ isolated from the reactions corresponded closely to the expected weights from a 1:1 reaction (Equation 6.1), thus $S_3N_2F^+AsF_6^-$ is prepared quantitatively from $S_3N_2^{2+}(AsF_6^-)_2$ and CsF in a 1:1 mole ratio, with only slight <u>in situ</u> hydrolysis (indicated by traces of OSF_2 in the reaction volatiles).

A compound identified crystallographically as $S_3N_2F^+AsF_6^-$ has been isolated from a reaction between $S_2N^+AsF_6^-$ and CsF.(13) The infrared spectrum of this material is compared with that of the $S_3N_2F^+AsF_6^-$ prepared from $S_3N_2(AsF_6)_2$ in Figure 6.1a; the two spectra are essentially the same. The crystallographic investigation shows the $S_3N_2F^+$ ion to have the expected cyclic structure, analogous to $S_3N_2Cl^+$,(2) but cation disorder prevented satisfactory structural refinement.(14) Crystals of $S_3N_2F^+AsF_6^-$ prepared from $S_3N_2(AsF_6)_2$ were grown from SO_2 solution and sent for structural analysis; although these crystals were shown to belong to a different space-group and were thought to be a more ordered form, crystal twinning prevented a structure determination.(14)

The further reaction of $S_3N_2F^+AsF_6^-$ with fluoride ion yielded only decomposition products. These were $S_4N_3^+AsF_6^-$ and OSF_2 (identified by infrared spectroscopy), S_4N_4, and an unidentified red volatile material which was tentatively supposed to be a decomposition product of $S_3N_2O_2$(13) by comparison with the products reported from the reaction of $S_2N^+AsF_6^-$ and CsF ($S_4N_3^+AsF_6^-$, OSF_2, and $S_3N_2O_2$, reference 13). The formation of $CsAsF_6$ during the course of the reaction indicates that at least initially, $S_3N_2F_2$ is formed; a possible route by which $S_3N_2F_2$ reacts with SO_2 to give the observed products is indicated in Scheme 6.1. The use of AsF_3 as an alternative solvent for the preparation of $S_3N_2F_2$ was thought to be inappropriate because of the almost certain reaction with solvent to give $S_3N_2F^+AsF_4^-$:

$$S_3N_2F_2 + AsF_3 \longrightarrow S_3N_2F^+AsF_4^- \qquad \text{Equ.6.3}$$

$$S_3N_2F^+AsF_6^- + CsF \longrightarrow CsAsF_6 + S_3N_2F_2$$

$$S_3N_2F_2 \longrightarrow NSF + S_2NF$$

$$2S_2NF + SO_2 \longrightarrow S_3N_2 + SO + OSF_2$$

$$NSF + SO \longrightarrow OSNSF$$

$$NSF + S_3N_2 \longrightarrow S_4N_3F$$

$$S_3N_2 \longrightarrow \tfrac{1}{2}S_4N_4 + S$$

$$S_3N_2 + SO_2 \longrightarrow S_3N_2O_2 + S$$

$$NSF + S \longrightarrow S_2NF$$

$$OSNSF + S_2NF \longrightarrow S_3N_2 + OSF_2{*}$$

$$S_4N_3{}^+F^- + S_3N_2F^+AsF_6^- \longrightarrow S_3N_2F_2 + S_4N_3{}^+AsF_6^-{*}$$

* = observed product

Scheme 6.1

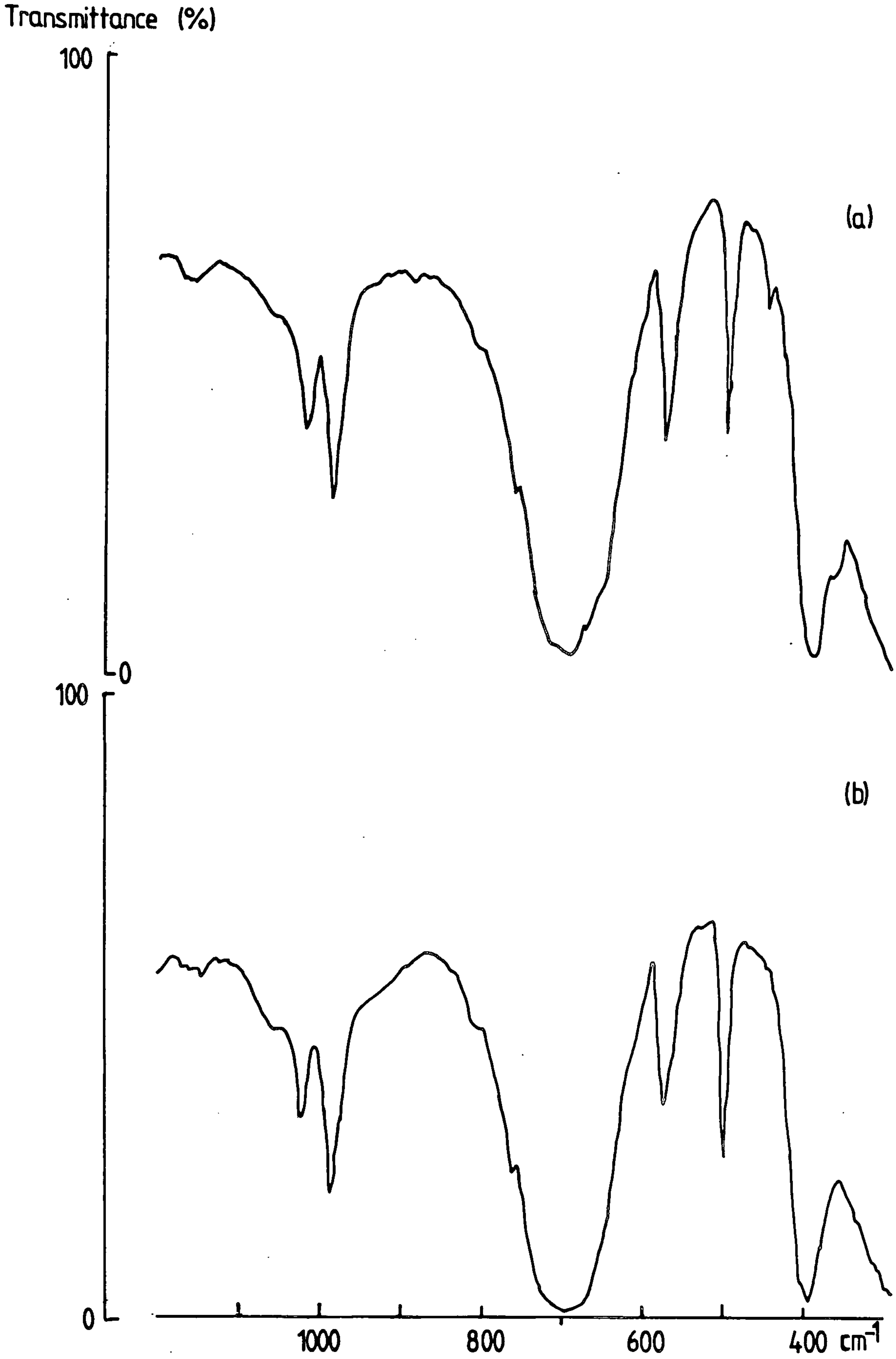


Figure 6.1a. Infrared spectra of $S_3N_2F^+AsF_6^-$ a) prepared from $S_2N^+AsF_6^-$ and CsF; b) prepared from $S_3N_2^{2+}(AsF_6^-)_2$ and CsF.

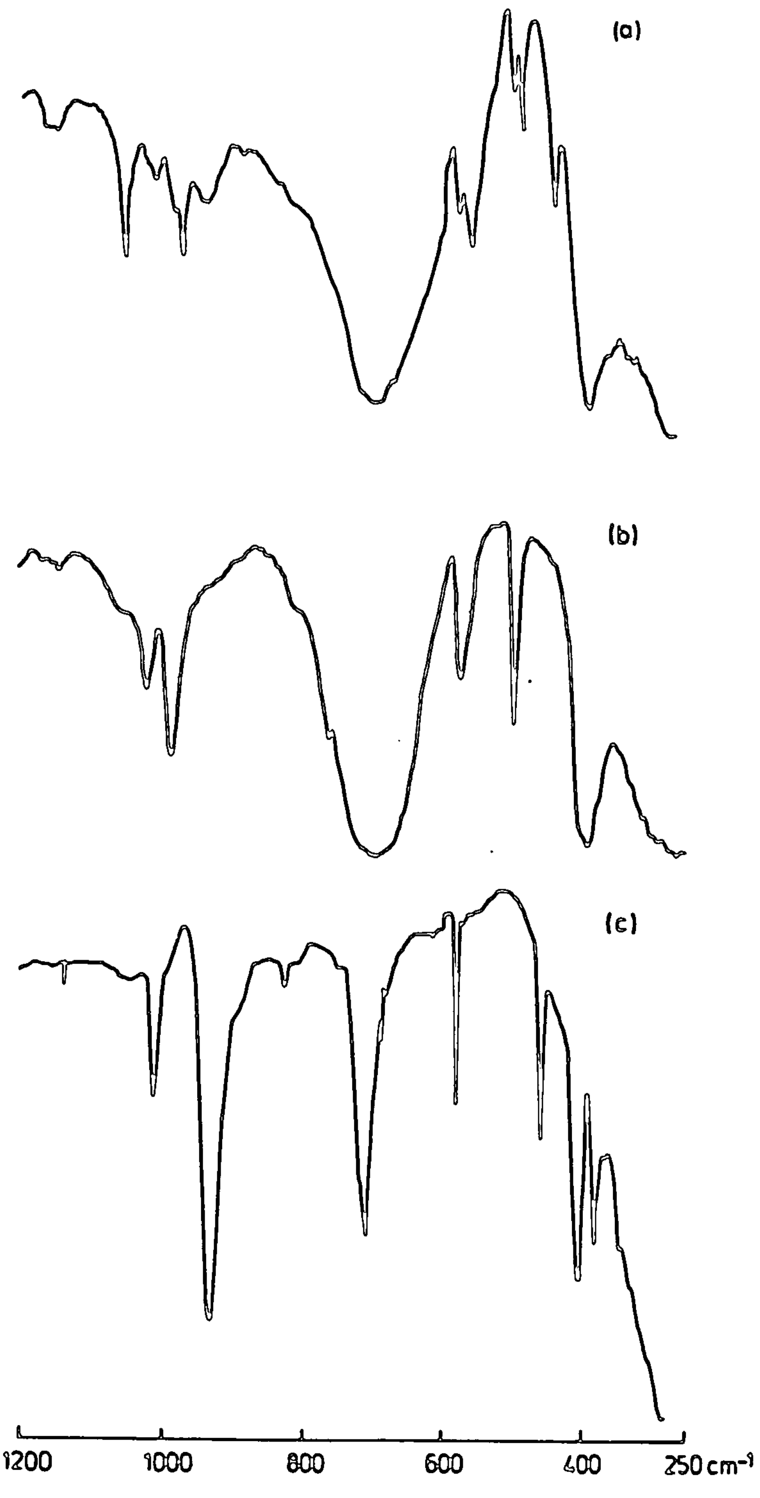


Figure 6.1b. Infrared spectra (nujol mulls) of a) $S_3N_2^{2+}(AsF_6^-)_2$; b) $S_3N_2F^+AsF_6^-$. c) $S_3N_2Cl^+Cl^-$.

The infrared spectra of $S_3N_2^{2+}(AsF_6^-)_2$, $S_3N_2F^+AsF_6^-$, and $S_3N_2Cl^+Cl^-$ are illustrated in Figure 6.1b and clearly show the structural similarity of these three compounds, especially absorptions in the S-N bending region (400-600 cm^{-1}). The S-N stretching and bending modes (900-1050 cm^{-1}) have been shifted to higher wavenumber in $S_3N_2F^+$ compared to $S_3N_2Cl^+$, an effect which may be attributed to the greater electron withdrawing power of fluorine which achieves a stabilisation of the sulphur valency orbitals.

These similarities in infrared spectra strongly suggest that $S_3N_2^{2+}$, $S_3N_2F^+$, and $S_3N_2Cl^+$ share a five-membered S_3N_2 ring as their main structural feature.

6.2.2 Attempted Crystal Growth of $S_3N_2^{2+}(AsF_6^-)_2$:

Attempts were made to grow suitable single crystals of $S_3N_2^{2+}(AsF_6^-)_2$ for X-ray structure analysis. Earlier attempts to grow single crystals by slow evaporation of SO_2 solutions(8) had resulted only in the isolation of a few crystals the structure of which could not be determined unambiguously, but which were thought to be of $SN^+AsF_6^-$(14). An alternative approach was tried using a temperature ripple (± 10°C) applied to a cold (-5°C) saturated solution of $S_3N_2^{2+}(AsF_6^-)_2$. After several days, one or two small crystals had formed in the solution and after manipulation to free these from the solution a crystal, embedded in a microcrystalline matrix, was isolated. X-ray photography and a subsequent structure determination (performed by J. Johnson, University of New Brunswick) showed this crystal to be $S_2N^+AsF_6^-$. its structure is discussed in Section 6.2.6.

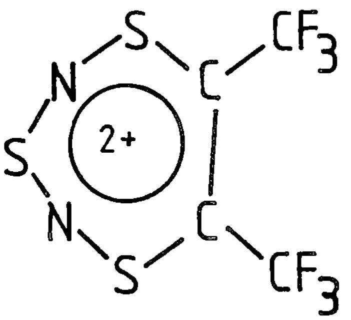
Since the spectra of $SN^+AsF_6^-$ and $S_2N^+AsF_6^-$ are quite distinct from that of $S_3N_2^{2+}(AsF_6^-)_2$, it seemed likely that, in solution, an equilibrium existed between the the two species:-

$$S_3N_2^{2+} \rightleftharpoons S_2N^+ + SN^+ \qquad \text{Equ.6.4}$$

Consequently, no further attempts to grow crystals of $S_3N_2^{2+}(AsF_6^-)_2$ were made.

6.2.3 Reaction between $S_3N_2^{2+}(AsF_6^-)_2$ and Hexafluorobut-2-yne:

Since it is known that S_2N^+ reacts with suitable unsaturated substrates ($CF_3C{\equiv}CCF_3$ or $CF_3C{\equiv}N$, for example) and since the $S_3N_2^{2+}$ ring would be expected to be a highly strained system, it was thought that reaction between $S_3N_2^{2+}$ and an unsaturated species such as hexafluorobut -2-yne ($CF_3C{\equiv}CCF_3$) might occur to give a larger, less strained ring system such as III:



III

The new ring system would be a formally 8-π system and as such would be a possible precursor to a 9-π radical cation and a 10-π neutral species.

In fact, the observed products of the reaction were identified by infrared spectroscopy as a mixture of $SN^+AsF_6^-$, $S_2N^+AsF_6^-$, and the infrared spectroscopy as a mixture of $SN^+AsF_6^-$, $S_2N^+AsF_6^-$, and the heterocycle $(CF_3\overset{+}{\overline{CSNSC}}CF_3)\ AsF_6^-$, which is known to be produced in the reaction between $S_2N^+AsF_6^-$ and $CF_3C{\equiv}CCF_3$.(15) Thus the reaction may be represented in Scheme 6.2:

$$S_3N_2^{2+} \rightleftharpoons SN^+ + S_2N^+$$

$$S_2N^+ + CF_3C\ CCF_3 \longrightarrow CF_3CSNSCCF_3AsF_6^-$$

Scheme 6.2

The result confirmed the hypothesis that in solution, the $S_3N_2^{2+}$ ion was in equilibrium with S_2N^+ and SN^+, so a more systematic investigation of this equilibrium was undertaken.

6.2.4 Chemical Lability of the $S_3N_2^{2+}$ Ring:

a) Reaction of $S_3N_2^{2+}(AsF_6^-)_2$ with sulphur. Hey(16) found that $S_2N^+Cl_6^-$ was the major product from the reaction between $SN^+SbCl_6^-$ and excess elemental sulphur, co-products being $S_3N_2Cl^+SbCl_6^-$ and $N(SCl)_2^+SbCl_6^-$. Subsequent work at the University of New Brunswick(9) showed that $SN^+AsF_6^-$ reacted with excess or a stoichiometric amount of sulphur to form $S_2N^+AsF_6^-$. If the equilibrium postulated in Equation 6.4 actually occurs in solution, addition of a stoichiometric amount of elemental sulphur to a solution of $S_3N_2^{2+}(AsF_6^-)_2$ in liquid SO_2 should result in the formation of $S_2N^+AsF_6^-$ in almost quantitative yield:

$$S_3N_2^{2+}(AsF_6^-)_2 + ⅛S_8 \longrightarrow 2S_2N^+AsF_6^- \qquad \text{Equ.6.5}$$

This reaction was indeed found to proceed easily at room temperature, the reaction products being identified by Raman and infrared spectroscopy. The colour changes observed during reaction [(pale brown, deep blue (instantly), black (5 min), brown (24h)] indicated that sulphur polycations could be present as intermediates (S_8^{2+} is dark blue).

b) Reaction of $SN^+AsF_6^-$ with sulphur in molar ratio 2:1. The preparation of $S_3N_2^+(AsF_6^-)_2$ was first achieved by reaction of $S_2N^+AsF_6$ with $SN^+AsF_6^{-(8)}$. Consideration of the equilibia above, however, suggested that it should be possible to prepare $S_3N_2^{2+}(AsF_6^-)_2$ directly by reaction of an appropriate (2:1) molar ratio of $SN^+AsF_6^-$ and sulphur.

$$SN^+ + \tfrac{1}{8}S_8 \longrightarrow S_2N^+$$

$$S_2N^+ + NS^+ \rightleftharpoons S_3N_2^{2+}$$

overall:

$$2SN^+AsF_6^- + \tfrac{1}{8}S_8 \longrightarrow S_3N_2^{2+}(AsF_6^-)_2$$

Scheme 6.3

$S_3N_2^{2+}(AsF_6^-)_2$ was the product isolated from the reaction, identified by infrared spectroscopy and elemental analyses (N and As). Again, the observed colour changes [pale brown, dark red (instantly), black (1 min), deep red (1h), pale yellow-brown(48h)] indicated the possible presence of sulphur polycation intermediates (S_{19}^{+} is red). As both the reaction and the recrystallization of the product can be performed in a single vessel, using a single sulphur-nitrogen starting material and elemental sulphur, this procedure represents a particularly convenient method of preparing $S_3N_2^{2+}(AsF_6^{-})_2$. Further work on optimisation of the recrystallization procedure should enable almost quantitative yields to be obtained.

c) MNDO calculations. Because of the lability of the $S_3N_2^{2+}$ ring discussed in the preceeding sections and its preparation by the cyclo-addition of SN^{+} and S_2N^{+}, we examined the energetics of the ring opening and closure of $S_3N_2^{2+}$. The MNDO method$^{(15)}$ has been used successfully to rationalize the major structural features of thiazenes.$^{(16)}$

The MNDO optimized geometry of $S_3N_2^{2+}$ is shown in Figure 6.2. To model ring opening, the S-S bond distance was varied whilst optimising all other bond lengths and angles for the planar ion. The planar constraint was relaxed for one calculation (dSS = 3.3 Å) but since the largest resulting ring tension angle was only 0.25° (corresponding to an energy difference of 0.5 Kcal mol^{-1}, the planar calculations were considered to be a valid model. The S-S bond was chosen as the site for ring cleavage (rather than an S-N bond) since i) this is expected to be the weakest bond in the ring - close to an S-S single bond and ii) on electrostatic grounds the S-S bond should be the last formed in the cyclo addition of S_2N^{+} and SN^{+}. Ring cleavage at this position should, therefore, model the ring closure reaction in reverse.

The variation in ΔH_f with S-S bond distance is illustrated in Figure 6.3, the equilibrium planar geometry corresponding to a clear energy minimum. The calculated heat of formation of the ring is, however, considerably higher than the sum of the heats of formation of SN^+ and S_2N^+ (by 101 Kcal Mol^{-1}); this difference in ΔH_f probably corresponds to a much smaller difference in ΔG, an effect which may be ascribed to i) the interactions of SN^+ and $S_3N_2^{2+}$ with solvent SO_2 molecules and ii) considerable lattice energy stabilization of the dication in the solid state. It should be emphasized that the MNDO method calculates equilibrium gas phase geometries whereas for this system both solvent and solid-state interactions will be important in determining stability. The changes in other bond lengths and angles in the ring as a result of S-S bond clearage are summarised in Table 6.1. The major features are an opening out of the angle at N5 to 153°, a shortening of the bonds S1N5, S4N5, and S2N3 and a lengthening of the bond S4N3. Thus, the open molecule begins to approximate to a nucleophilic attack on S_2N^+ at a sulphur position and the assumption, that ring opening at the S-S bond should mimic the ring closure reaction, is vindicated. The calculated energy barrier to ring opening is only 11.5 Kcal mol^{-1} and so equilibrium between the three species is quite feasible at room temperature.

Table 6.1 Variation in ring geometry of $S_3N_2^{2+}$

a/Å	b/Å	c/Å	d/Å	c/Å	/°
1.80	1.56	1.59	1.59	1.56	122.3
2.00	1.53	1.59	1.59	1.53	125.8
2.10	1.52	1.60	1.59	1.52	127.8
2.20	1.50	1.60	1.59	1.50	129.3
2.40	1.48	1.60	1.60	1.48	132.8
2.60	1.47	1.60	1.59	1.47	136.4
2.80	1.45	1.60	1.60	1.45	139.2
3.00	1.45	1.61	1.58	1.45	143.2
3.20	1.45	1.69	1.54	1.44	156.2
3.30	1.44	1.66	1.54	1.44	153.2

In a further series of calculations the effect on the stability of the $S_3N_2^{2+}$ ring of nucleophilic attack by fluoride ion was examined. Attack at one of the S-S bond sulphur atoms was considered (S1S2) since the LUMO of $S_3N_2^{2+}$ has a node at S4 which would therefore be a less favoured postion for attack by nucleophiles.(19) By fixing the S-F distance and allowing the rest of the molecule to optimise, an energy profile of S-F distance with ΔH_f was obtained (Fig.6.4). It can be seen that the resulting $S_3N_2F^+$ ion is strongly stabilised with respect to $S_3N_2^{2+}$. The sharp singlet observed in the ^{19}F nmr at +38 ppm indicated that the $S_3N_2F^+$ ion does not display the same lability as the dication, since dissociation (for example into S_2N^+ and NSF) would show clearly. Indeed, it might be expected that S_2N^+ and NSF would undergo a cyclo-addition reaction to form the $S_3N_2F^+$

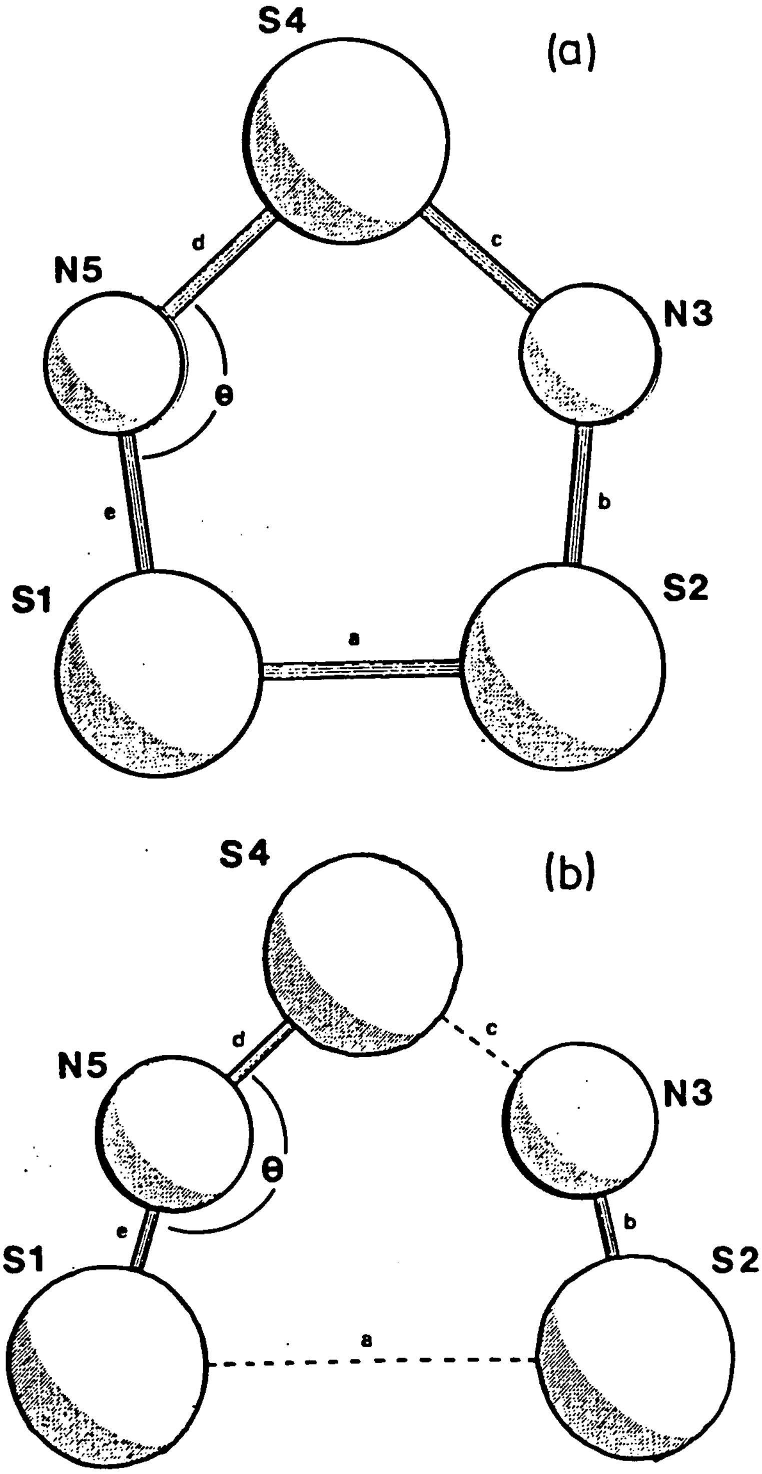


Figure 6.2. MNDO optimised geometry of the $S_3N_2^{2+}$ ring.
a) equilibrium geometry; b) calculated geometry for d S-S = 3.3 Å.

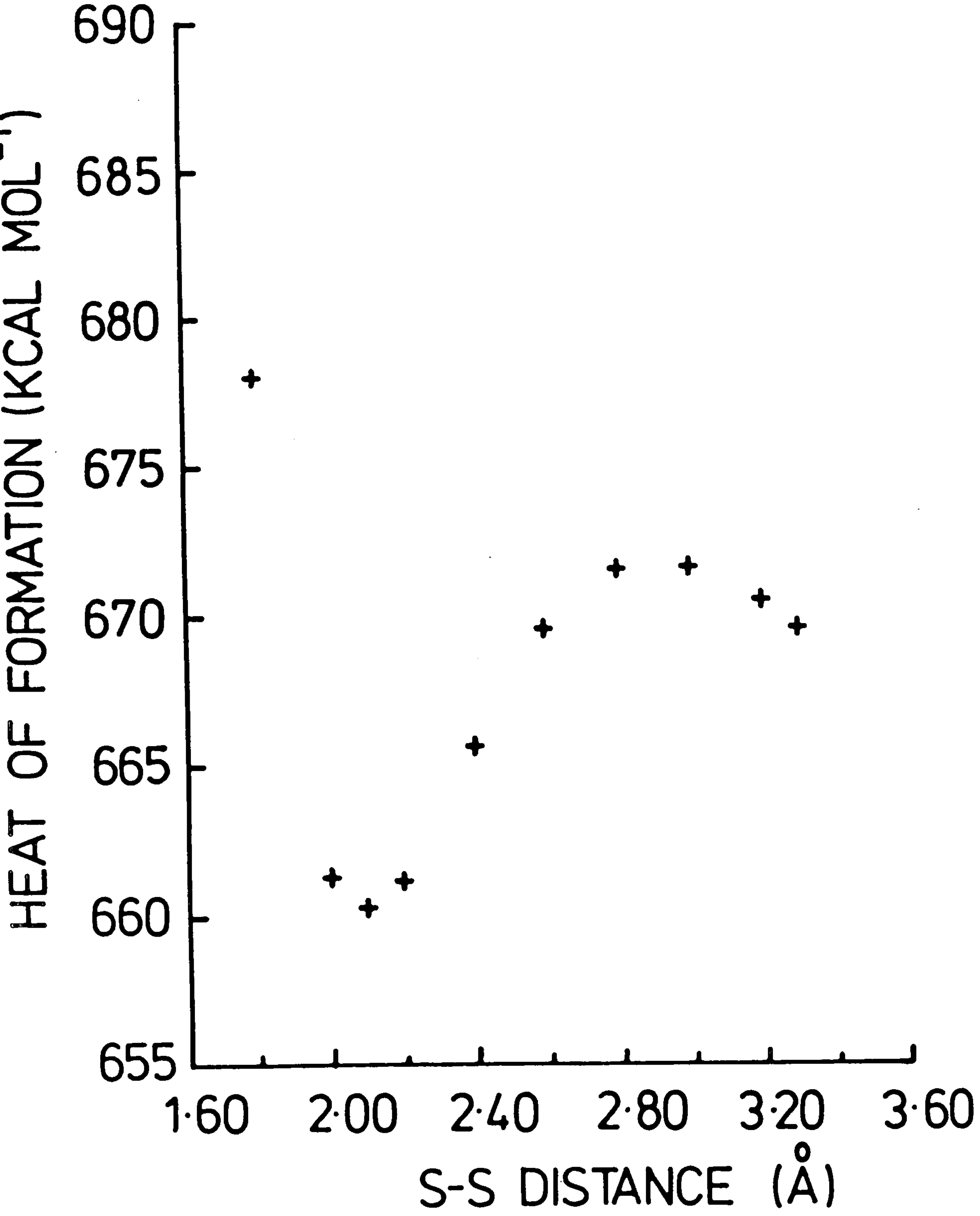


Figure 6.3. Variation of heat of formation of the $S_3N_2^{2+}$ ring with S-S distance

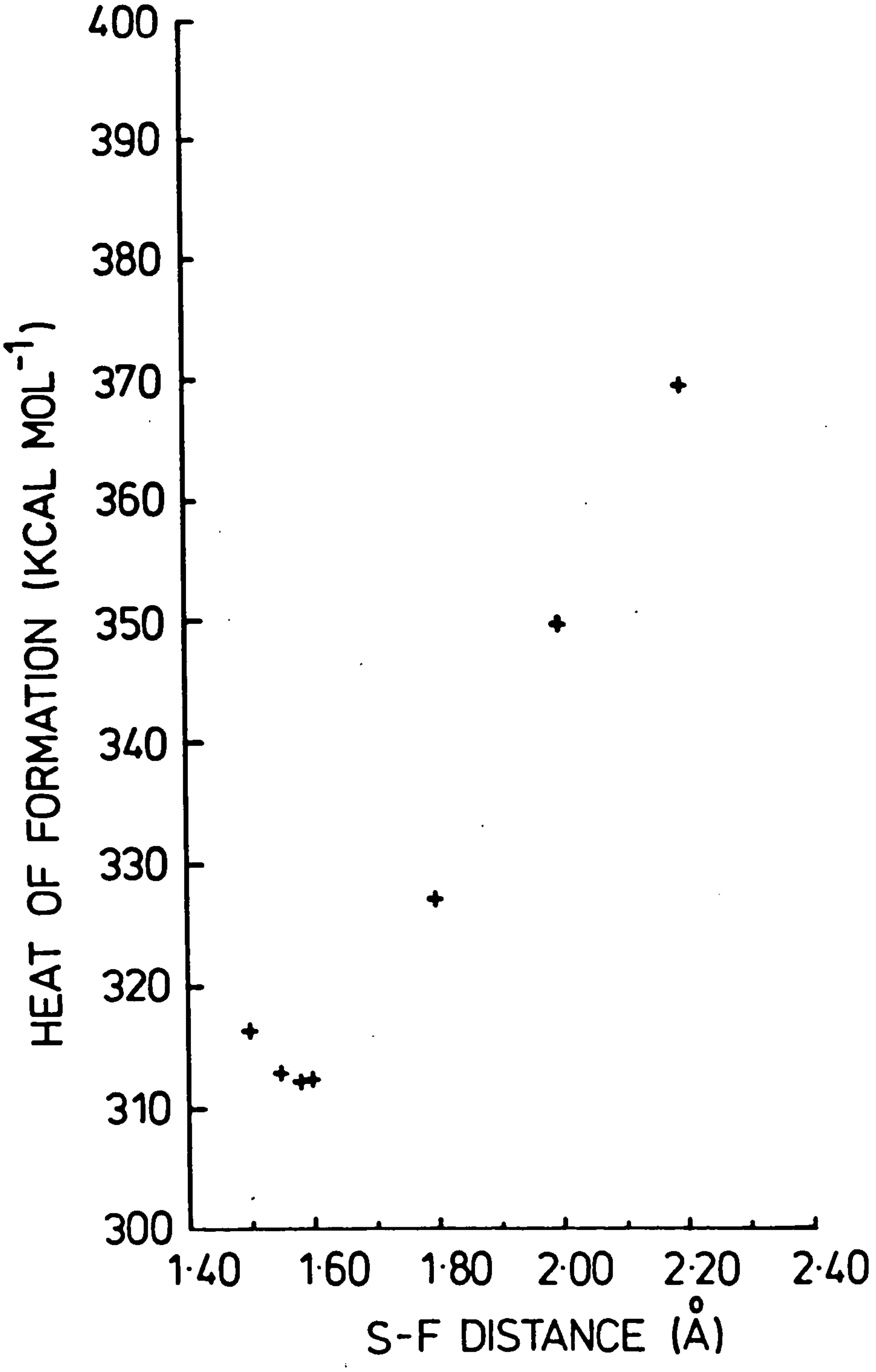


Figure 6.4. Variation of heat of formation of $S_3N_2F^+$ with S-F distance

ion; whilst this work was being undertaken, a brief report of the cyclo-addition reaction of S_2N^+ and NSF to give $S_3N_2F^+$ appeared$^{(20)}$. Although no experimental details were given, it appears that this reaction occurs readily.

6.2.5 A Convenient Preparation of $S_2N^+SbCl_6^-$:

The reaction of the S_2N^+ ion with unsaturated organic species affords a convenient entry to carbon-sulphur-nitrogen chemistry, which is a field of considerable current interest (see Section 1.2). $S_2N^+SbCl_6^-$ was originally prepared in unspecified yield by the reaction of S_7NH, S_7NBCl_2, or 1,4-$S_6N_2H_2$ with $SbCl_5$ in liquid $SO_2$$^{(21)}$ and S_2NAlCl_4 has been isolated in unspecified yield from S_4N_4 and $AlCl_3$ in methylene chloride.$^{(22)}$ Later work$^{(10)}$ has shown that $S_2N^+AsF_6^-$ may be prepared according to Equations 6.6 and 7 in liquid SO_2. The yields were 20 and 77% respectively, though in the absence of traces of bromine, the yield for Equation 6.7 was only ca. 30%.

$$S_8(AsF_6)_2 + NaN_3 \longrightarrow S_2NAsF_6 + NaAsF_6 + N_2 + \tfrac{3}{4}S_8 \qquad \text{Equ.6.6}$$

$$\tfrac{1}{2}S_8 + S_4N_4 + 6AsF_5 \longrightarrow 4S_2NAsF_6 + 2AsF_3 \qquad \text{Equ.6.7}$$

$$SN^+AsF_6^- + S \longrightarrow S_2N^+AsF_6^- \qquad \text{Equ.6.8}$$

Very recently,$^{(9)}$ Equation 6.8 has been found to produce $S_2N^+AsF_6^-$ in 50% yield, but has the disadvantage of requiring the prior preparation and isolation of $SN^+AsF_6^-$ and the consequent use of $AgAsF_6$ which is expensive to buy and both expensive and hazardous to make (requires the use of AsF_5); both Equations 6.6 and 7 also entail the use of AsF_5. A more convenient method of S_2N^+ preparation would therefore be of considerable use in developing its chemistry.

Consideration of the reaction(9,16) between sulphur and SN^+ to form S_2N^+, suggested that addition of a stoichiometric amount of sulphur to an in situ source of SN^+ would result in the facile formation of S_2N^+. The principle of using such a source of SN^+ has been exploited in the preparation of $S_5N_5^+$ (23) and $N(SCl)_2^+$ (24) salts (see Scheme 6.4); the participation of the SN^+ ion in these reactions is confirmed by the isolation of $S_5N_5AsF_6$ and $N(SCl)_2AsF_6$ from the reactions of $SNAsF_6$ with S_4N_4 and SCl_2 (25) respectively.

$$(NSCl)_3 + 3MCl_3 \longrightarrow 3\text{"}NSCl.MCl_3\text{"}$$

$$\text{"}NSCl.MCl_3\text{"} + S_4N_4 \longrightarrow S_5N_5MCl_4$$

M = Fe, Al(23)

$$(NSCl)_3 + 3MCl_3 \longrightarrow 3\text{"}NSCl.MCl_3\text{"}$$

$$\text{"}NSCl.MCl_3\text{"} + SCl_2 \longrightarrow N(SCl)_2\ MCl_4$$

M = Fe, Al,(24) B(26)

$SbCl_6^-$ also prepared(24)

Scheme 6.4

The Lewis acid chosen to investigate the proposed route to S_2N^+ (Scheme 6.5) was $SbCl_5$ since, because it is a liquid miscible with $SOCl_2$, rapid formation of the intermediate adduct should occur.

$$(NSCl)_3 + 3SbCl_5 \longrightarrow 3\text{"}NSCl.SbCl_5\text{"}$$

$$\text{"}NSCl.SbCl_5\text{"} + S \longrightarrow S_2N^+SbCl_6^-$$

Scheme 6.5

The products isolated from the reaction mixture were $S_2N^+SbCl_6^-$, and $S_3N_2Cl^+SbCl_6^-$ (identified by infrared spectroscopy); $S_2N^+SbCl_6^-$ was further characterized by Raman spectroscopy and elemental analysis (S,N,Cl). The product mixture could be easily resolved, since the $S_3N_2Cl^+SbCl_6^-$ remained mostly in solution in the reaction mixture and $N(SCl)_2^+SbCl_6^-$ could be separated from $S_2N^+SbCl_6^-$ by exhaustive extraction with SO_2. The overall yield of $S_2N^+SbCl_6^-$ was 28%. The other reaction products can be accounted for in terms of chlorination of S_2N^+ by solvent (to give $N(SCl)_2^+SbCl_6^-$) and reaction of S_2N^+ with NSCl monomer units (to give $S_3N_2Cl^+SbCl_6^-$). It should be noted, however, that the intermediate adduct "$NSCl.SbCl_5$" is not well characterized and may well be a mixture of different components, since $S_3N_3Cl_2^+SbCl_6^-$, $S_4N_4^{2+}(SbCl_6^-)_2$, $S_5N_5^+SbCl_6^-$, and $S_4N_4.SbCl_5$ have all been isolated from mixtures of $SbCl_5$ and $(NSCl)_3$ in different mole ratios and different solvents;(27) the precise reaction path to the observed products in this system may, therefore, be more complex.

In conclusion, $S_2N^+SbCl_6^-$ is produced according to Scheme 6.5 in 28% yield and the co-products are easily separated by SO_2 extraction. Although the overall yield is low, the accessibility of the starting materials, the facility of reaction, and the ease of purification makes this route an attractive alternative to those previously published; it is likely that modifications of the reaction procedure will result in improved yields. Another attractive feature of this route is that it should allow the preparation of other S_2N^+ salts (e.g. $AlCl_4^-$, $FeCl_4^-$, BCl_4^-) and further, reactions using cyclo-octa selenium instead of sulphur may well provide a facile route to sulphur-nitrogen-selenium compounds. These possibilities are being actively pursued by workers at Durham.

6.2.6 The Crystal Structure of $S_2N^+AsF_6^-$:

The crystal structure of $S_2N^+AsF_6^-$ was determined by J. Johnson (University of New Brunswick) and consists of linear S_2N^+ cations and octahedral AsF_6^- anions with weak cation-anion interactions; the structural data are summarised in Table 6.2 and the thermal ellipsoids are given in Table 6.3. The S-N bond length was found to be 1.480(3) Å [c.f. 1.462(3) in $S_2N^+SbCl_6^-$(21) and 1.464(5), 1.472(5) Å in $S_2N^+AlCl_4$(22)]. The apparently longer bond length in $S_2N^+AsF_6^-$ may arise from thermal effects in the crystal, since the average S-N stretching frequencies in the $SbCl_6^-$ and AsF_6^- salts are 1093 and 1095 cm^{-1} respectively,(10) which indicates that the bond strength in the two compounds is essentially the same. A further analysis of this problem is currently in progress.

Table 6.2 Crystal data for $S_2N^+AsF_6^-$

monoclinic space group $C_{2/m}$

a = 9.5542(13), b = 6.5968(14), c= 5.3017(11) Å, β = 91.159(15)°

U = 334.08 $Å^3$ Z = 2

F(0, 0, 0) = 252 λ MoK_α = 0.7013 Å

R = 0.037

Bond distance (Å)		Bond angle (°)	
S-N	1.480(3) x 2	F(1)-As-F(2)	89.1(2) x 4
As-F(1)	1.696(6) x 2	F(1)-As-F(2)	90.9(2) x 4
As-F(2)	1.705(5) x 4	F(2)-As-F(2)	89.4(2) x 2
		F(2)-As-F(2)	90.6(2) x 2

Fractional atomic co-ordinates

	x/a	y/b	z/c
S	0.6420(3)	0.0000	0.6169(6)
N	0.5000	0.0000	0.5000
As	0.0000	0.0000	0.0000
F(1)	0.1064(7)	0.0000	-0.2523(13)
F(2)	0.1021(5)	0.1837(9)	0.1352(8)

Table 6.3 Anisotropic thermal parameters for $S_2N^+AsF_6^-$

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
S	49(2)	65(3)	73(2)	0	-6(2)	0
N	50(7)	47(8)	40(6)	0	10(5)	0
As	42(1)	41(1)	38(1)	0	3(1)	0
F(1)	72(4)	83(6)	62(4)	0	22(3)	0
F(2)	63(2)	67(4)	80(3)	-8(3)	-7(2)	-11(3)

It is interesting to compare the crystal packing in $S_2N^+AsF_6^-$ and $S_2N^+SbCl_6^-$. It has been reported(28) that all known compounds of the type ABX_6 crystallize in lattices derived from the NaCl or CsCl structures. A review of ABF_6 compounds concluded(29) that the lattice type adopted depends primarily on the size of A and only weakly on the nature of B. A stereo pair drawing of the unit cell of $S_2N^+AsF_6^-$ and projections of the unit cell are shown in Figures 6.5 and 6 respectively. Each cation site is surrounded by eight anion sites at the corners of a highly distorted cube; the lattice is thus derived from the CsCl type.

The packing in $S_2N^+SbCl_6^-$ has been discussed in terms of a distorted close packed array of S and Cl atoms.(21) Inspection of the stereo pair drawing of the unit cell (Figure 6.5) shows that each cation site is surrounded by six anion sites at the vertices of a distorted octahedron and therefore an alternative view of the lattice of $S_2N^+SbCl_6^-$ is that it is derived from the NaCl lattice.

Although the difference in lattice type adopted by ABF_6 compounds (where A is a simple unipositive cation) has been accounted for in terms of relative ion size,(29) in these S_2N^+ salts, the secondary cation anion interactions seem to be more important (even though they are weak - about 90% of the sum of van der Waals radii). In $S_2N^+AsF_6^-$, each sulphur atom makes three short contacts with fluorine atoms (1 x 3.12 and 2 x 3.01 Å) making a total of six interactions per cation. Each sulphur in $S_2N^+SbCl_6^-$ makes contact with four chlorine atoms (4 x 3.54 Å) making a total of eight interactions per cation. The S_2N^+ cation thus has a higher co-ordination number (and probably higher

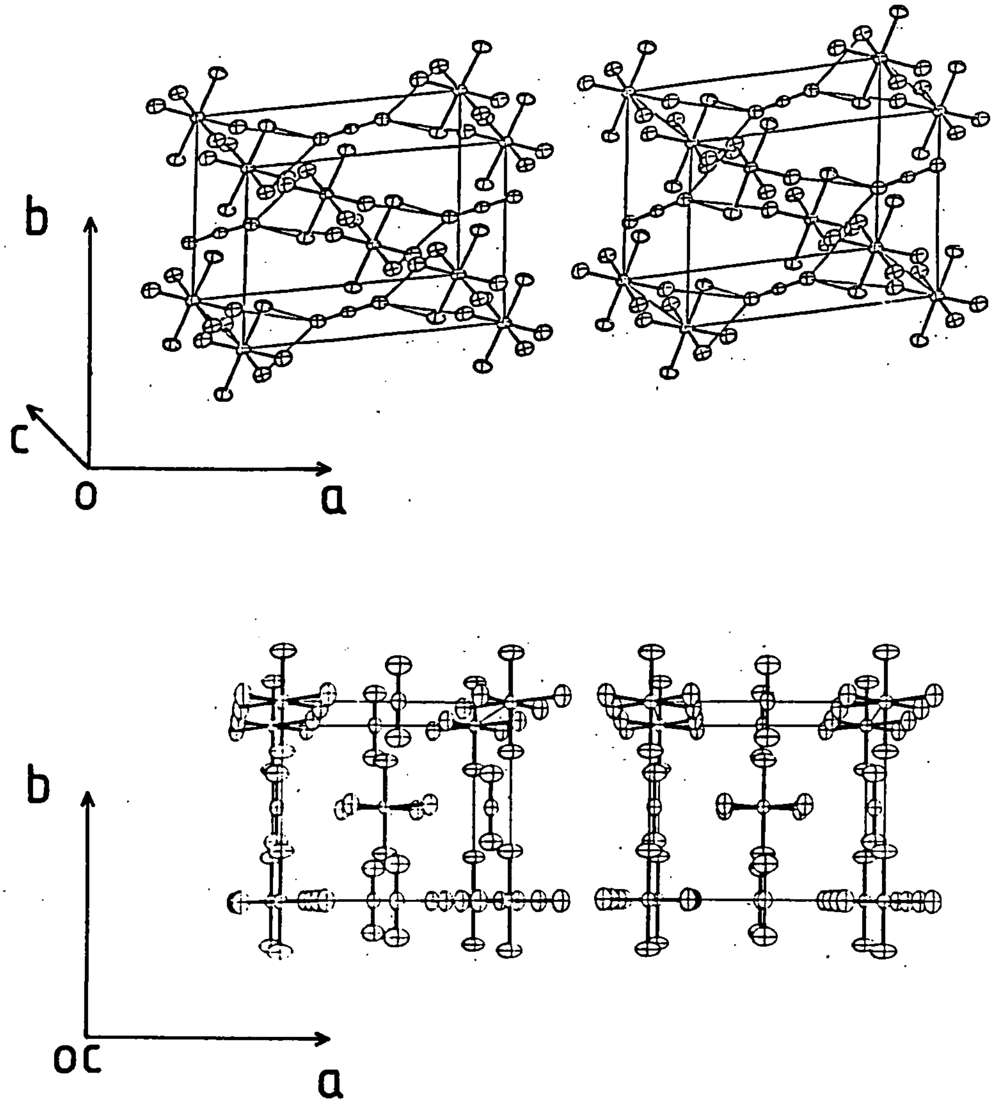


Figure 6.5. Stereo pair drawings of the unit cells of $S_2N^+AsF_6^-$ (upper) and $S_2N^+SbCl_6^-$(21) (lower)

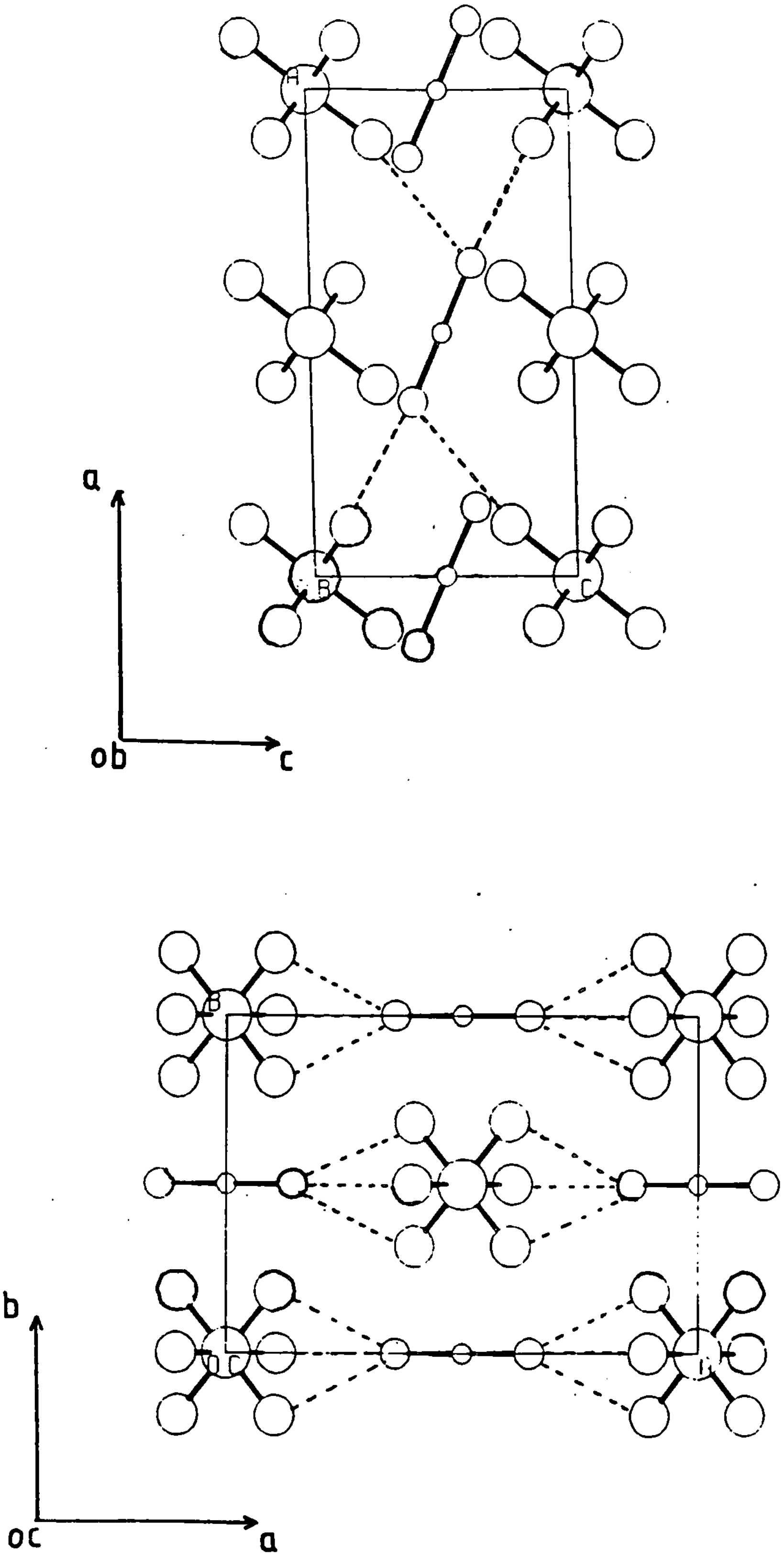


Figure 6.6. Unit cell projections of $S_2N^+AsF_6^-$ showing cation-anion interactions (dotted lines). Upper, (010); lower (001).

bond energy) with the $SbCl_6^-$ ion than with the smaller AsF_6^- ion, a trend which would be consistent with the expected greater Lewis basicity of $SbCl_6^-$. Since lower co-ordination numbers are favoured by lower electronegativity differences between cation and anion,(30) it is logical that the NaCl type lattice is adopted by $S_2N^+SbCl_6^-$ and the CsCl type lattice is adopted by $S_2N^+AsF_6^-$.

6.3 CONCLUSIONS

Reaction of $S_3N_2^{2+}(AsF_6^-)_2$ with CsF in a 1:1 mole ratio results in the quantitative formation of $S_3N_2F^+AsF_6^-$ (identified by infrared and ^{19}F nmr spectroscopy, elemental analysis and the reaction mass balance), which is the fluorine analogue of the $S_3N_2Cl^+$ ion.(2) Further reaction to give $S_3N_2F_2$ was not possible owing to reaction with the solvent (SO_2).

Although $S_3N_2^+(AsF_6^-)_2$ has been characterized in the solid state by infrared and Raman spectroscopy and by elemental analysis, cation dissociation prevented growth of single crystals from SO_2 solutions; nevertheless, a few $S_2N^+AsF_6$ crystals were isolated from the solutions and their structure was determined (J. Johnson). The hypothesis that $S_3N_2^{2+}(AsF_6^-)_2$ existed as an equilibrium mixture containing SN^+ and S_2N^+ was confirmed by its chemical reactions with elemental sulphur and hexafluorobut-2-yne and by MNDO calculations. Furthermore addition of a stoichiometric amount of sulphur to $SN^+AsF_6^-$ leads to the formation of $S_3N_2^{2+}(AsF_6^-)_2$ in 57% yield according to Scheme 6.3.

Consideration of the equilibria observed in these systems suggested a new synthetic route to $S_2N^+SbCl_6^-$. Although this reaction proceeds in only low yield (ca. 28%) the accessibility of the starting materials and ease of purification make it an attractive alternative to published routes.(9,10,21) The possibility of preparing other S_2N^+ salts and related mixed sulphur-nitrogen-selenium systems via this route is being investigated by workers at Durham.

6.4 EXPERIMENTAL SECTION

6.4.1 Reaction of $S_3N_2^{2+}(AsF_6^-)_2$ with CsF; NMR Tube Experiments:-

In a typical experiment, $S_3N_2^{2+}(AsF_6^-)_2$ (0.3g, 0.6 mmol) and CsF (0.091g, 0.6 mmol) were placed in a 10mm nmr tube fitted with a J. Young's Teflon bleed valve. SO_2 (ca. 5 ml) and CCl_3F (a small amount) were condensed in and the mixture was warmed briefly to room temperature. The ^{19}F nmr spectrum was recorded at -70°C and after leaving the mixture at room temparature for 1 week, the spectrum was re-recorded. δ F(200MHZ; solvent SO_2; standard CCl_3F; 30 min) 38.51 [1F,s,$S_3N_2F^+$] and -58 [6F, br, s, AsF_6^-]. δ F(200MHZ; solvent SO_2; standard CCl_3F; 1 week)76.60 [2F, s, OSF_2], 37.35 [1F, s, $S_3N_2F^+$] and -58 [6F, br, s, AsF_6^-].

6.4.2 Reaction of $S_3N_2^{2+}(AsF_6^-)_2$ with CsF; Preparative Scale Experiments:

a)In SO_2. In a typical experiment, $S_3N_2^{2+}(AsF_6^-)_2$ (1.90g, 3.78 mmol) was placed in one bulb of a two-bulbed reaction vessel. CsF (0.58g, 3.78 mmol) was placed together with a Teflon coated stirring bar in the other bulb and SO_2 (12.338g) was condensed in approximately equal quantities into the two bulbs. The pale brown solution of $S_3N_2^{2+}(AsF_6^-)_2$ was added to the CsF and the mixture was stirred at room temperature (6h). The reaction mixture changed colour from brown to deep red/brown and a fine white powder precipitated. The mixture was filtered and the insolubles were washed with SO_2 distilled back from the other bulb. Removal of volatiles SO_2 plus trace amounts of OSF_2 and SiF_4 (i.r.) yielded a dark brown crystalline solid ($S_3N_2F^+AsF_6^-$) and a white powdery insoluble solid ($CsAsF_6$). The brown crystals were slightly sticky but could be cleaned by brief washing with dry methylene chloride.

Yields: Brown crystals ($S_3N_2F^+AsF_6^-$), 1.24g (98%); white insolubles ($CsAsF_6$), 1.22g (expected weight for a 1:1 reaction = 1.22g). Infrared spectrum of $S_3N_2F^+AsF_6^-$, ν_{max} = 1205vw, br, 1145vvw, 1050w,sh, 1021m, 988s, 819w,sh 755s,sh, 700vs, br, (AsF_6^-), 575s, 500s, 390vs, (AsF_6^-) cm^{-1}; δF (200MHZ; solvent SO_2; standard CCl_3F) 38.51 [1F, s, $S_3N_2F^+$] and -58 [6F, s, br, AsF_6^-]. Infrared spectrum of white insolubles ($CsAsF_6$) ν_{max} = 1300vw, br, 700vs, br, (AsF_6^-) 390vs, (AsF_6^-) cm^{-1}.

b) In AsF_3. i) $S_3N_2^{2+}(AsF_6^-)_2$ (0.77g, 1.53 mmol) was placed in one bulb of a two-bulb vessel. CsF (0.26g, 1.68 mmol) was placed in the other bulb together with a Teflon coated stirring bar. AsF_3 (8.329g, 63.1 mmol) was condensed in approximately equal portions into both bulbs. The solutions were allowed to warm to room temperature and the pale brown solution of $S_3N_2^{2+}(AsF_6^-)_2$ was transferred to the bulb containing CsF. Reaction occurred almost immediately giving a red-brown solution which gradually darkened until after 5h stirring it was an intense red-brown. The mixture was filtered and the insoluble solids were washed with back-distilled AsF_3 until white (3 x 1 ml). An infrared spectrum of the reaction volatiles was recorded and the AsF_3 was removed to yield a dark brown slightly tarry crystalline solid and a white isoluble powder. Further prolonged pumping (12h) removed residual AsF_3 to give a brown microcrystalline solid as the soluble product. Yields: brown microcrystalline solid, 0.800g, white insoluble, 0.28g.

ii) Purification of the brown microcrystalline solid was achieved by brief extraction with SO_2. 0.650g of crude material was placed in a closed extractor; after brief extraction by SO_2 and removal of solvent, a brown crystalline material ($S_3N_2F^+AsF_6^-$) was obtained as the soluble product and a white insoluble powder remained on the frit ($CsAsF_6$). The product was characterised by infrared spectroscopy and elemental analysis. Yields: Total recovery, 0.606g; $S_3N_2F^+AsF_6^-$, 0.386g (63.7%). For a 1:1 reaction in the original mixture, the expected yield would be 0.508g, but 0.800g was isolated so that only 63.5% of the crude product could be $S_3N_2F^+AsF_6^-$. Since the recovery of $S_3N_2F^+AsF_6^-$ from the crude product was 63.7%, the original reaction appears to have been quantitative. $CsAsF_6$, 0.22g (36.3%) by a similar argument, this would be the expected recovery of $CsAsF_6$ from a 1:1 reaction. Infrared spectrum of $S_3N_2F^+AsF_6^-$, ν_{max} = 1205vw*, 1150vw*, 1060sh, 1040sh, 1015s, 990s, 925w*, 815sh, 700vs, br, 575s, 500s, 445sh*, 395vs, 365sh, cm^{-1}. *peaks possibly result of hydrolysis on plates, * peaks possibly belong to a contaminant; they are not present in material prepared in SO_2. Infrared spectrum of white isolubles ($CsAsF_6$), ν_{max} = 3310 s, br#, 1300w, br#, 1150w, br#, 815w, sh, 700vvs, vbr, 390 vvs, br cm^{-1} * peaks result of hydrolysis on plates. Raman spectrum of white insolubles ($CsAsF_6$), ν_{max} = 684s, 373m,sh cm^{-1}. Infrared spectrum of reaction volatiles. ν_{max} = 1365s, 1355s, 1340s (all SO_2 plus OSF_2), 1155vw, br (SO_2), 805m (OSF_2), 735s (OSF_2), 700vs (AsF_6^-), 535w (OSF_2) cm^{-1}. Analysis, found S, 29.86; N, 8.83; As 23.56; calculated for $S_3N_2F^+AsF_6^-$; S, 28.96; N. 8.43; As, 22.56%.

6.4.3 Reaction of $S_3N_2F^+AsF_6^-$ with CsF:

i) In a typical experiment $S_3N_2F^+AsF_6^-$ (0.98g, 2.86 mmol) was placed in one bulb of a two-bulb vessel CsF (0.435g, 2.86 mmol) and a Teflon coated magnetic stirrer were placed in the other bulb; SO_2 (17.977g) was condensed in approximately equal quantities into both bulbs. The dark red-brown solution of $S_3N_2F^+AsF_6^-$ was added to the CsF bulb and the mixture was stirred at room temperature (4h). The resulting red solution was filtered and the insolubles were washed with back-distilled SO_2 to yield a red solution and pale biscuit-coloured powdery insolubles. Removal of SO_2 and prolonged pumping yielded a sticky red material, which contained crystals from the soluble fraction.

Yields: Sticky red crystalliferous material, 0.334g (expected for a 1:1 reaction = 0.46g); pale insolubles, 0.90g (expected for a 1:1 reaction = 0.92g) A weight loss of 0.09g was recorded from the system during the pump down.

ii) Purification of the red sticky soluble fraction was achieved by high vacuum sublimation. 0.28g of the soluble fraction was placed in a sublimation tube and attached to a high vacuum line (7 x 10^{-6} torr). The solids were warmed to 65°C and left for 24 h during which time orange crystals of S_4N_4 (infrared) sublimed out together with some more volatile red/yellow material; a pale yellow powdery solid containing crystals was left as the residue and identified by infrared spectroscopy as being largely $S_4N_3^+AsF_6^-$.

Yields: $S_4N_3^+AsF_6^-$ = 0.14 g, S_4N_4, 0.95g. Infrared spectrum of initial reaction volatiles, ν_{max} = 1350vs (SO_2), 1165vs (SO_2), 1145vs (SO_2), 810s (OSF_2), 745s (OSF_2), 530vs (SO_2) 500vs (SO_2) cm^{-1}. Infrared of intial reaction insolubles ($CsAsF_6$), ν_{max} = 1210vw, 1150vw, 700vvs, br, (AsF_6^-). 390vs, (AsF_6^-) cm^{-1}. Infrared spectrum of $S_4N_3^+AsF_6^-$ ν_{max} = 1170m, br, ($S_4N_3^+$), 1010m, ($S_4N_3^+$), 980vvw, 945vvw, 925vvw, 900vvw, 725s (AsF_6^-), 565m (S_4N_3+), 540vw, 480m ($S_4N_3^+$), 400s (AsF_6^-)cm^{-1}. δ F (200MHZ; solvent SO_2; CCl_3F standard), - 42.3 [singlet, unknown origin], and -58.6 [6F, quartet, J = 923 Hz, AsF_6^-].

6.4.4 Reaction of $S_3N_2^{2+}(AsF_6^-)_2$ with Hexafluorobut-2-yne:

i) $S_3N_2^{2+}(AsF_6^-)_2$ (0.4727g, 0.942 mmol) was placed in one bulb of a two-bulb vessel. A Teflon coated stirring bar was placed in the other bulb, and vessel was evacuated. The $S_3N_2^{2+}(AsF_6^-)_2$ was isolated and hexafluorobut-2-yne (0.1544g, 1.02 mmol) was condensed on top of the Teflon stirrer at liquid nitrogen temperature. After degassing the vessel, SO_2 (ca. 4g) was condensed on top of the hexafluorobut-2-yne.

When the vessel had warmed to room temperature, the liquid SO_2/hexafluorobut-2-yne mixture was transferred to the $S_3N_2^{2+}(AsF_6^-)_2$ bulb; when all the solid had dissolved, the mixture was tranferred back to the bulb containing the stirrer and the clear orange-brown solution was stirred for 6 days at room temperature. A gas phase infrared spectrum of the reaction volatiles was recorded and the volatiles were removed to yield a red-brown solid. A weight gain of 0.0712g (corresponding to 0.48 mmol of hexafluorobut-2-yne) was observed during the course of reaction.

Yield: red-brown solid, 0.5439g. Infrared spectrum of red-brown solid (powder), ν_{max} = 1495m(S_2N^+), 1425w(SN^+), 1395vw, 1285s,sh, 1245s,sh, 1185vs, br, 1070s, 1020vw, 985m, 950w,sh, 870vw, 800vw, br, 770m, 700vs, br (AsF_6^-), 575m,sh, 500m, 440w, 390vs (AsF_6^-) cm^{-1}. c.f. ($CF_3\overset{+}{\overline{CSNSC}}CF_3$) ($AsF_6^-$)$^{(17)}$ 1290s, sh, 1250vs, sh, 1200vs, br, 1070s, 990w, 955w, 879vw, 800m, sh, 770s, 700vs, br, 580w, 485vw, 390vs, cm^{-1}.

Infrared spectrum of reaction volatiles, ν_{max} = 2500w (SO_2), 1365vs (SO_2), 1340vs, (SO_2), 1285vs ($CF_3C{\equiv}CCF_3$), 1190vs, (CF_3C CCF_3), 1155m, br, (SO_2), 1125m,br, (SO_2), 895vw ($CF_3C{\equiv}CCF_3$), 635w ($CF_3C{\equiv}CCF_3$), 530s(SO_2), 500s (SO_2) cm^{-1}.

ii) In an nmr-tube experiment, using $S_3N_2^{2+}(AsF_6^-)_2$ (0.1237g, 0.25 mmol) and hexafluorobut-2-yne (0.0767g, 0.47 mmol) in SO_2 (<u>ca</u>. 5g) using CCl_3F (0.331g) as an internal standard, a single ^{19}F nmr signal at -52.8ppm was observed at -70° after the mixture had been standing at room temperature for 3h. The singlet is observed since the ^{19}F chemical shift of hexafluorobut-2-yne (-52 ppm) is the same as that observed in the heterocycle $CF_3\overset{+}{\overline{CSNSC}}CF_3$(15). An infrared spectrum of the sticky yellow material recovered from the nmr tube after removal of volatiles was largely similar to that observed in (i) above; ν_{max} = 1500w, 1435vw, 1190s, br, 1075s, 1015w, 990w, 940s, 875vw, 810w,sh 775m,sh, 755s, sh, 695vs,br, 605m,sh, 570s, 530vw, 505m 475s, 445s, 390vs, cm^{-1}.

6.4.5 Reaction of $S_3N_2^{2+}(AsF_6^-)_2$ with Sulphur:

Elemental sulphur (0.020g, 0.577 mmol) was placed in one bulb of a reaction vessel together with a Teflon coated magnetic stirring bar. $S_3N_2^{2+}(AsF_6^-)_2$ (0.290g, 0.577 mmol) was placed in the other bulb and SO_2 (10.560g) was condensed in approximately equal quantities into both bulbs. After warming to room temperature, the brown solution of $S_3N_2^{2+}(AsF_6^-)_2$ was added to the bulb containing elemental sulphur; immediate reaction occurred producing an intense dark blue colour. The elemental sulphur dissolved and the mixture was stirred; after 24h at room temperature it was brown and after 72h the solution was pale yellow-brown and contained no precipitate. The solution was transferred to the other bulb and the SO_2 was slowly distilled into the empty bulb by application of a small thermal gradient. Yellow crystals formed in the solution bulb and when the solution was reduced to low volume the brown supernatant liquor was decanted off. The yellow crystals were washed briefly with back-distilled SO_2 and the reaction volatiles [SO_2 only (infrared)] were removed to yield pale yellow crystals in one bulb and a brown crystalliferous solid in the other. The yellow crystals were identified as $S_2N^+AsF_6^-$ by infrared and Raman spectroscopy whilst the brown solid was shown to be largely $S_2N^+AsF_6^-$ by infrared spectroscopy.

Yields: Yellow crystals = 0.08g (26%); brown solid, 0.23g Infrared spectrum of yellow crystals, ν_{max} = 2175vw ($\nu_1+\nu_3$ S_2N^+?), 1480s (S_2N^+), 690vs (AsF_6^-), 385vs (AsF_6^-) cm^{-1}. Raman spectrum of yellow crystals (5154 Å) ν_{max} = 788w, br (S_2N^+), 699s (S_2N^+), 685m, sh (AsF_6^-?, 579w (AsF_6^-), 475w(?), 373w (AsF_6^-), 83vs, sh (lattice mode?), 71vs (lattice mode?) cm^{-1}. Infrared spectrum of brown solid, (run on NaCl plates, consequently no 385 cm^{-1} band for AsF_6^-), ν_{max} = 2180vw ($\nu_1+\nu_3$ S_2N^+?), 1480s (S_2N^+), 690vs (AsF_6^-) cm^{-1}.

6.4.6 Reaction of $SN^+AsF_6^-$ with Sulphur:

Elemental sulphur (0.027g, 0.84 mmol) was placed together with a Teflon coated magnetic stirring bar in one bulb of a reaction vessel. $SN^+AsF_6^-$ (0.38g, 1.6 mmol) was placed in the other bulb and SO_2 (8.804g) was condensed in, with approximately equal quantities in both bulbs. After warming to room temperature the pale brown solution of $SN^+AsF_6^-$ was added to the colourless SO_2 mixture; immediate reaction occurred producing on intense red colour and the sulphur dissolved. The following colour sequence was observed whilst stirring at room temperature; red (1min), black (3min) deep red (10min), pale brown (48h), pale yellow-brown (96h). No solids were present in the reaction mixture after about 1 minute. The mixture was transferred to the other bulb and the SO_2 was slowly distilled into the empty bulb by application of a small temperature gradient. Pale yellow-brown crystals formed in the product bulb and when the solution had been reduced to low volume the supernatant liquid was decanted away. The crystals were washed with a small amount of back-distilled SO_2 and the reaction volatiles [SO_2 plus trace amounts of SiF_4 and OSF_2 (infrared)]were pumped away to yield a yellow-brown crystalline solid identified by infrared spectroscopy as $S_3N_2^{2+}(AsF_6^-)_2$ and a brown, more soluble, solid [mostly $S_3N_2^{2+}(AsF_6^-)_2$] from the supernatant fraction.

Yields: Yellow-brown crystals $S_3N_2^{2+}(AsF_6^-)_2$, 0.24g, (57%); more soluble brown residue, 0.16g. Infrared spectrum of yellow-brown crystals, ν_{max} = 1150m, br, 1040m, sh, 1010m, 970m, 930*vw, sh, 890*vw, 810vw, 715vs, vbr (AsF_6^-), 570w, sh, 550m, 485vw, 485vw, 440s, sh, 385vs, (AsF_6^-) cm^{-1}. * due to hydrolysis on plates. Analysis: found N, 5.97; As, 29.76; $S_3N_2^{2+}(AsF_6^-)_2$ requires N, 5.58; As, 29.85%. Infrared spectrum of more soluble brown residue, ν_{max} = 1150* w, br, 1050w, 1010m, 980 vw, 720sh, 700s, 570m, 555m, 495w, 485vw, 440m cm^{-1}. * due to hydrolysis on plates.

6.4.7 Preparation of $S_2N^+SbCl_6^-$:

$(NSCl)_3$ (1.22g, 5 mmol) was placed together with a Teflon coated stirring bar in a 50ml twin necked round bottom flask. $SOCl_2$ (30 ml) was syringed in against a counter-flow of dry nitrogen and after all the solid had dissolved to give a yellow solution, $SbCl_5$ (3.42g, 1.46ml, 15 mmol) was also syringed in. Immediate reaction occurred to give a thick, pale orange precipitate which was stirred at room temperature for a further 30 min. On addition of sulphur (0.48g, 15 mmol), the mixture became black, turning slowly to a very dark green colour and after three hours of vigorous stirring, a pale yellow microcrystalline precipitate had formed. The mixture was stirred for a further 21 h (a total of 24 h) and then filtered to yield a pale yellow green insoluble solid, containing a few large orange crystals, (3.95g) and a dark green solution. No further precipitation from the solution occurred on cooling to -15°C. Complete removal of solvent yielded a brown-green, slightly sticky solid containing cystals (mostly $S_3N_2Cl^+SbCl_6^-$ containing some $S_2N^+SbCl_6^-$, 0.95g). Extraction of the insoluble solid (2.5g) with SO_2 gave a soluble brown crystalline solid [mostly $N(SCl)_2{}^+SbCl_6^-$, 1.4 g] and a pale yellow insoluble solid ($S_2N^+SbCl_6^-$, 1.1 g). The products were identified by infrared and Raman spectroscopy. The discrepancy between the total weight of reactants (5.12g) and the total weight of crude products (4.9g) may be accounted for by the loss of unreacted $SbCl_5$ from the system.

Yields: $S_2N^+SbCl_6^-$, 2.5g of crude product yielded 1.1 g $S_2N^+SbCl_6^-$, therefore 3.95 g of crude product contained 1.74 g (28%); $N(SCl)_2{}^+SbCl_6^-$, by a similar argument, the total amount of $N(SCl)_2{}^+SbCl_6^-$, produced was 2.2 g; $S_3N_2Cl^+SbCl_6^-$, 0.95g. Infrared spectrum of $S_2N^+SbCl_6^-$, ν_{max} = 1485 vs, 372 vs, 340 vs. c.f. reference 21, 1498 m, 374 m, 320s cm^{-1} Raman spectrum of $S_2N^+SbCl_6^-$ (5145 Å) ν_{max} = 770vw, 708vw, sh, 692w, 333s, 298w, 190sh, 180m, 80s, 68sh, 58vs, 28s, c.f. reference 21, 766w, 747vw, 688m, 680vw, 333s, 293w, 283vw, 180m, 175s, 167vw, 78vs, 62s, cm^{-1}. Infrared spectrum of brown SO_2 soluble crystals [mostly $N(SCl)_2{}^+SbCl_6^-$], ν_{max} = 1130m, 1000w, 940vw, 748vw, 720vw, 690m, 652m, 570w, 515vs, 492vs, 451vw, 442w, c.f. reference 24, 1130m, 735sh, 721m, 645s, 521s, 520s, 494s

cm^{-1}. Infrared spectrum of reaction solubles after removal of solvent (mostly $S_3N_2Cl^+SbCl_6^-$ with some $S_2N^+SbCl_6^-$), ν_{max} = 1490m (S_2N^+), 1005vw, 940m, 749m, 715m, 695vs, 575s, 470w, 445m, sh, 420m, sh c.f. $S_3N_2Cl^+FeCl_4^-$(31) 1156vw, 1110w, 1017w, 997w, 938vs, 891vw, 759w, 742s, 717s, 574s, 463s, 458s, 418vs, 379vs, 331m, 324m, 304s cm^{-1}. Analysis for $S_2N^+SbCl_6^-$; found S, 16.01; N, 3.60; Cl, 51.85; $S_2N^+SbCl_6^-$ requires S, 15.5; N, 3.4; Cl, 51.58%.

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CHAPTER 7

Some Attempted Synthetic Studies of the Thionitrosyl Cation

7.1 INTRODUCTION

The thionitrosyl cation (SN^+) was first prepared in 1971$^{(1)}$ by the gas phase reaction of SbF_5 or AsF_5 with NSF, the products being $SN^+SbF_6^-$ and $SN^+AsF_6^-$ respectively; a more convenient preparation in SO_2 solution was subsequently described.$^{(2)}$ Other preparative routes are the reaction between Lewis acids and $(NSF)_3$$^{(3)}$ (AsF_5, SbF_5, and SO_3 produce the AsF_6^-, $Sb_2F_{11}^-$, and SO_3F^- salts respectively) and the reaction between $(NSCl)_3$ and $AgPF_6$, though the latter route produced only an <u>in situ</u> nitromethane solution from which $SN^+PF_6^-$ was not isolated.$^{(4)}$

Because of the difficulty in preparing SN^+ salts, little chemistry of the ion has been reported. The modes of reaction so far discovered$^{(2)}$ may be classed as anion exchange, reaction with nucleophiles, and reaction with polar bonds. These are illustrated in Equations 7.1-4.

$$SN^+AsF_6^- + NO^+CF_3SO_3^- \longrightarrow SN^+CF_3SO_3^- \qquad \text{Equ.7.1}$$

$$'' + S_4N_4 \longrightarrow (S_5N_5AsF_6)_x \qquad \text{Equ.7.2}$$

$$'' + S_4N_4 \longrightarrow S_5N_5^+(AsF_6^-) \qquad \text{Equ.7.3}$$

$$'' + SCl_2 \longrightarrow NS_2Cl_2^+AsF_6^- \qquad \text{Equ.7.4}$$

The transition-metal complex $[Cr(NS)(NCMe)_5][PF_6]_2$ has also been reported(4) and reaction of $SN^+AsF_6^-$ with $[Re(CO)_5X]$ produces $Re(CO)_5NSX$.(5) A review of thionitrosyl chemistry has been published.(6)

Recently, collaborative work performed at the University of New Brunswick and the University of Durham(7) indicated that the reaction between $(NSCl)_3$ and $SbCl_5$ produced $SN^+SbCl_6^-$, although the experimental and purification procedures were somewhat laborious. Further work at the University of New Brunswick,(8) however, resulted in the development of a very convenient synthesis of $SN^+AsF_6^-$ from $(NSCl)_3$ and $AgAsF_6$.(9) $SN^+AsF_6^-$ is an extremely moisture-sensitive waxy white crystalline solid, very soluble in SO_2. This chapter describes attempts to use $SN^+AsF_6^-$ as a precursor to new sulphur-nitrogen compounds; its reactions with CsF and with elemental sulphur have been described in Chapters 5 and 6 respectively.

7.2 RESULTS AND DISCUSSION

7.2.1 The Reaction of $SN^+AsF_6^-$ with Chlorine:

Whilst investigating the reaction of $(NSCl)_3$ with SbF_5, Hey(7) isolated a white compound which he proposed on the evidence of Raman spectra to be $NSCl_2^+SbF_6^-$:

$$2/3\ (NSCl)_3 + 3SbF_5 \longrightarrow SN^+SbF_6^- + NSCl_2^- + SbF_3 \qquad \text{Equ. 7.5}$$

In an attempt to synthesize the cation by a direct route, he reacted $SN^+SbCl_6^-$ with elemental chlorine at room temperature and at 80°C in sealed tubes. No reaction occurred at room temperature whereas at elevated temperature, the product was $NS_2Cl_2^+SbCl_6^-$.(7)

With the relative accessibility of $SN^+AsF_6^-$, it was thought worthwhile to re-investigate the reaction between the thionitrosyl cation and chlorine; with this aim, two experiments were performed.

In order to use the mildest possible reaction conditions $SN^+AsF_6^-$ was soaked in liquid chlorine at room temperature but as before,(7) no reaction was detected.

One reason for the lack of reaction could have been the extreme insolubility of $SN^+AsF_6^-$ in liquid chlorine and so it was decided to repeat the experiment with a little SO_2 added to act as a solvent. The yellow solid isolated from this reaction mixture was shown by Raman spectroscopy to be mostly $SN^+AsF_6^-$; however both the colour of the product and some weak bands observed in the vibrational spectra indicate that another species was present. Further evidence of some reaction was provided by the detection of a high concentration of SO_2ClF in the gas phase infrared spectrum. The extent of reaction is difficult to estimate, but the total weight gain of only 30 mg and the strength of the $SN^+AsF_6^-$ bands in the Raman spectrum suggest that it was only slight. The detection of SO_2ClF as a reaction product may indicate some kind of halogen exchange process, but the vibrational spectra of the solid products did not enable identification of the yellow component. The Raman spectrum, although dominated by $SN^+AsF_6^-$ also contained some weak bands at 385, 370, and 340 cm^{-1} which may correspond to $(NSCl)_3$ (see Chapter 2) which has absorptions at 380(s) and 340 (vs); the other absorbtions of $(NSCl)_3$ are less intense or occur below 200 cm^{-1}, a region which was inaccessible in this experiment owing to sample fluorescence. The infrared spectrum contains more new bands, but also indicates considerable hydrolysis, which almost certainly occurred on the plates. Thus, although the infrared spectrum contains a band at 1205 cm^{-1} which may have corresponded to the band at 1208 cm^{-1} in the Raman spectrum reported by Hey, the absence of such a band in the Raman spectrum recorded during this experiment suggests that the new bands in the infrared spectrum may be products of hydrolysis. No evidence in either the Raman or infrared spectra was found for the absorbtions reported by Hey at 499 and 266 cm^{-1}. A possible reaction scheme is illustrated in Scheme 7.1:

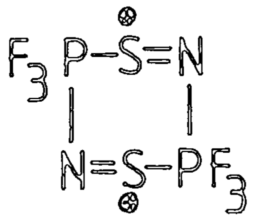
$$SN^+AsF_6 + Cl_2 \rightleftharpoons \text{"}Cl_2SNAsF_6\text{"}$$

$$\text{"}Cl_2SNAsF_6\text{"} + SO_2 \longrightarrow 1/3(NSCl)_3 + SO_2ClF + AsF_5$$

Scheme 7.1

7.2.2 Reaction of $SN^+AsF_6^-$ with PF_3:

a) It was thought that the thionitrosyl cation was a particularly suitable moiety from which to build more complicated species. In particular, it was thought that reaction with phosphorus (III) compounds might afford a route to compounds of the type **I**.



I

Initially, $(Ph)_3P$ was chosen as a reagent, but subsequent investigation showed that this material reacted with SO_2. The next choice was PF_3, since it was found to be unreactive towards SO_2 and because reactions could, in principle, be monitored using ^{19}F nmr spectroscopy.

In fact, rather than addition compounds of the type I, it was found that a redox reaction occurred. The gas phase produces were identified by infrared spectoscopy as PF_5(10) and OPF_3(11) (neither of which was present in the PF_3(12) reagent), together with some unreacted PF_3; OPF_3 was probably a hydrolysis product of the very moisture-sensitive PF_5. The sulphur-nitrogen containing products were a pale crystalline solid (major component) and a bright red crystalline solid (minor component). A significant weight loss (0.135g) was observed on removing the volatile materials from the reaction vessel.

The solid products were found to be difficult to characterize, owing to the extremely moisture-sensitive nature of the pale crystalline produce; even exposure in a freshly regenerated glove-box resulted in decomposition (blackening) after only a few minutes, whilst each transfer to a fresh vessel was also accompanied by surface decomposition. Eventually, authentic samples of both the pale and the red crystalline products were isolated and characterised by a combination of x-ray diffraction,(13,14) infrared spectroscopy, and elemental analysis. The pale product was found to be the known compound $S_4N_4^{2+}(AsF_6^-)_2 . SO_2$(15) and the red product was found to be the known adduct $S_4N_4 . AsF_5$.(16,17) A possible mechanism for the formation of these products is shown in Scheme 7.2. Although AsF_5 was not observed directly in the gas phase spectrum (it forms an adduct with SO_2), the removal of AsF_5 with the reaction volatiles would account for the observed weight loss.

$$2SN^+AsF_6^- + PF_3 \longrightarrow 2SN^\circ + PF_5 + 2AsF_5$$

$$4SN^\circ + AsF_5 \longrightarrow S_4N_4 . AsF_5$$

$$2SN^\bullet + 2SN^+AsF_6^- + SO_2 \longrightarrow S_4N_4^{2+}(AsF_6^-)_2 . SO_2$$

<u>Scheme 7.2</u>

This reaction is very similar to that observed between I_2 and $SN^+AsF_6^-$, in which the oxidised product was found to be $I_5^+AsF_6^-$ and the reduced product $S_4N_4^{2+}(AsF_6^-)_2 . SO_2$.(18) The oxidising properties of the thionitrosyl cation are thus analogous to the better known oxidising properties of the nitrosyl cation, NO^+.(19)

b) The preparation, by the above reaction, of the $S_4N_4^{2+}$ cation was thought to be a good opportunity to attempt the characterization of the $S_4N_4^+$ radical cation by electron spin resonance (esr) spectroscopy. The $S_4N_4^+$ cation has been reported and characterized by X-ray diffraction in the crystalline compound $S_4N_4^+(FeCl_4^-)$,(20) but an esr spectrum was not reported. Two methods of reduction were tried by L.H. Sutcliffe (University of Liverpool; present address, Royal Holloway College, University of London). The first attempt was made by dissolving a solid sample of $S_4N_4^{2+}(AsF_6^-)_2 \cdot SO_2$ in tetrahydrofuran and then adding Et_4NCl followed by $(Ph)_3Sb$; this method of reduction has been used successfully in the generation of carbon- sulphur-nitrogen radicals.(21) The second attempt was made by dissolving a sample of $S_4N_4^{2+}(AsF_6^-)_2 \cdot SO_2$ in acetonitrile and then adding silver powder. In both cases, only weak signals were detected which were uninterpretable and which were probably a result of a mixture of species.(22)

It is interesting that the $S_4N_4^+$ cation should be described crystallographically [the possibility of "$S_4N_4^+(FeCl_4^-)$" actually being $S_4N_4^{2+}(FeCl_4^{2-})$ was specifically discounted by the authors of the paper] and yet the $S_4N_4^+$ cation cannot be formed easily in solution by the reduction of $S_4N_4^{2+}$. Electrochemical studies, especially cyclic voltammetry measurements, would be of great help in elucidating this problem. At present, although several studies have been published on the polarographic reduction of S_4N_4,(23) only one paper has appeared which considers the oxidation of S_4N_4.(24) The oxidation (at +2 V vs Ag/Ag^+) is a 4-electron process and the major product was thought to be SN^+. Further work seems necessary in order to clarify the relationships between $S_4N_4^{2+}$, $S_4N_4^+$, and S_4N_4.

7.2.3 Reaction of $SN^+AsF_6^-$ with $S_5N_5AsF_6$:

There are several conflicting reports in the literature of the preparation of the compound S_3N_3Cl which was believed to contain the $S_3N_3^+$ cation.(25) Although recent calculations (26) indicate that planar $S_3N_3^+$ would be a diradical (and therefore probably unstable), it has been pointed out that a lower symmetry configuration might remove the orbital degeneracy and so result in a stable species.(25) It was therefore thought worthwhile to attempt the preparation of $S_3N_3^+AsF_6^-$ according to Equation 7.6; the relatively large AsF_6^- counter-ion would be expected to help stabilise a reactive cation.

$$SN^+AsF_6^- + S_5N_5^+AsF_6 \longrightarrow 2S_3N_3^+AsF_6^- \qquad \text{Equ.7.6}$$

In fact the results were disappointing, since no new bands were detected by infrared spectroscopy in the reaction products and hence it was concluded that no reaction had occurred. Since $S_3N_3^+$ was not isolated as an oxidation product of $S_3N_3^-$,(25) its existence as a stable species seems doubtful.

7.2.4 Reaction of $SN^+AsF_6^-$ with KCN:

As has been stated in Chapters 1 and 3, the preparation of carbon-sulphur-nitrogen polymers which may have interesting physical properties is an important research goal in sulphur-nitrogen chemistry. perhaps the simplest reaction which could be expected to yield such a polymer is that between the thionitrosyl cation and the cyanide anion:

$$SN^{+}AsF_6^{-} + KCN \longrightarrow \text{"}(SNCN)_x\text{"} + KAsF_6 \qquad \text{Equ.7.7}$$

Two products were obtained, a dark purple-brown insoluble solid and a black soluble tar. Infrared spectroscopy showed that the insoluble material contained unreacted CN^{-} together with a band at 2170 cm^{-1} which probably belonged to some type of chemically bonded -CN group. No N-H hydrolysis bands were observed above 3000 cm^{-1} and so the very broad absorption between 1600 and 1300 cm^{-1} probably belongs to some kind of C=N group; the other weak absorbtions are typical of polymeric materials whilst the AsF_6^{-} bands probably arise from the presence of $KAsF_6$. The infrared spectrum of the soluble tar also contains the absorbtions at 2170 and 1600-1250 cm^{-1}, but in addition, contains N-H hydrolysis bands at 3280 cm^{-1} and hence the other weak bands in the spectrum may well have arisen from hydrolysis; the AsF_6^{-} bands are probably unreacted $SN^{+}AsF_6^{-}$.

This reaction seems to produce an insoluble polymer which contains CN and CN functional groups and may merit further attention. The soluble tar may well be a hydrolysis product arising from incompletely dried KCN. Although a crushed sample of the insoluble polymer was found to be non-conductive, this could be a result of the presence of $KAsF_6$ crystals; extraction with an ionising solvent such as acetonitrile would enable a more meaningful measurement to be made.

If the reaction were to be repeated, an arrangement which allowed KCN to be washed into a bulb containing a solution of $SN^+AsF_6^-$ should be used. This would ensure that complete reaction occurred, without the possibility of surface decomposition on solid KCN.

7.3 CONCLUSIONS

The reactions of $SN^+AsF_6^-$ investigated in this chapter did not result in the isolation of any new compounds; however, some insight was gained into the reactivity of the thionitrosyl cation. Like the nitrosyl (NO^+) cation,(19) it is an oxidising agent and this behaviour distinguishes it from other thiazene cations. Its reactions with the halogens remain an interesting topic for investigation, especially the reaction with chlorine; this should be re-investigated using a salt with a chlorinated anion to prevent halogen exchange. Finally, its reactions with simple anions to produce polymers seem to merit further attention.

The failure to detect the $\dot{S}_4N_4^+$ radical in reduced solutions of $S_4N_4^{2+}$ raises some interesting questions. Although a brown solid, $S_4N_4^+FeCl_4^-$, was characterized crystallographically and spectroscopically, no direct confirmation of the radical nature of the ion was obtained.(20) The reported infrared data seem to be incomplete as no S-N modes are reported above 952 or below 715 cm^{-1}; all hitherto known thiazene cations exhibit bands above 1000 and below $700 cm^{-1}$. Since other sulphur-nitrogen radicals are more highly coloured metallic green or purple solids, an esr spectrum or magnetic susceptibility measurement of $S_4N_4^+FeCl_4^-$ and more complete infrared data would be useful in confirming its identity.

7.4 EXPERIMENTAL SECTION

7.4.1 The Reaction of $SN^+AsF_6^-$ with Chlorine:

a) $SN^+AsF_6^-$ (0.3428g, 1.46 mmol) was placed in a glass bulb fitted with a J. Young's Teflon stemmed valve. Cl_2 (1.0681g, 15.04mmol) was condensed in and the mixture was allowed to stand at room temperature (with occasional shaking) for 48h. The $SN^+AsF_6^-$ did not dissolve. The Cl_2 was then pumped away and an <u>in situ</u> Raman spectrum of the residual white solid ($SN^+AsF_6^-$) was recorded.

Raman spectrum of white solid (5145 Å), ν_{max} = 1435vs (SN^+), 680vs (AsF_6^-), 557s (AsF_6^-), 370s (AsF_6^-)cm.$^{-1}$

b) $SN^+AsF_6^-$ (0.4165g, 17.7 mmol) was placed in a glass bulb, fitted with a J. Young's Teflon stemmed valve, together with a Teflon coated magnetic stirring bar. SO_2 (1.7748g) was condensed into the bulb, followed by Cl_2(3.3787g, 47.6 mmol). The mixture was warmed to room temperature and stirred. The reaction mixture divided into two phases. Initially, the lower phase was brown ($SN^+AsF_6^-/SO_2$) and the upper phase was orange (SO_2/Cl_2) but after stirring for 12h, the lower phase had become a dark orange colour. The mixture was stirred for a further 60h with no further changes in colour. The gas phase infrared spectrum of the reaction mixture was recorded. After removal of volatile materials, a waxy yellow solid was obtained which was characterized by infrared and Raman spectroscopy and found to be mostly $SN^+AsF_6^-$. A total weight gain of 0.030g occurred during the course of reaction.

Yield of yellow solid, 0.4465g. Gas phase infrared spectrum of reaction mixture, ν_{max} = 1465vs (SO_2ClF),(27) 1375m (SO_2), 1360m (SO_2), 1225vs (SO_2ClF), 820vs (SO_2ClF), 630vs (SO_2ClF), 500vs (SO_2Cl) $cm.^{-1}$ Infrared spectrum of yellow solid (powder spectrum), ν_{max} = 3250m,br (hydrolysis), 1435s (SN^+), 1280w, br, 1205m, 1120m, br, 950w, br, 835m, br, 700vs, br (AsF_6^-), 390vs (AsF_6^-) cm^{-1}. Raman spectrum (5145 Å), ν_{max} = 1435vs (SN^+), 682vs (AsF_6^-), 556s, br (AsF_6^-), 385 vw, sh $(NSCl)_3$?, 370w $(NSCl)_3$?, 360m (AsF_6^-), 340 vw, sh $(NSCl)_3$? $cm.^{-1}$

7.4.2 The Reaction of $SN^+AsF_6^-$ with PF_3:

a) In a typical experiment, $SN^+AsF_6^-$ (0.425g, 1.81 mmol) was placed together with a Teflon coated stirring bar in one bulb of a two-bulbed vessel. SO_2 (7.761g) was condensed on top of the $SN^+AsF_6^-$ and that bulb (the reaction bulb) was isolated from the rest of the vessel. After re-evacuating the rest of the vessel, PF_3 was condensed into the empty bulb and degassed; the final weight of PF_3 added to the vessel was 0.174g, 1.98 mmol. After warming to room temperature, the valve isolating the two reagents was opened, and the mixture was stirred. To ensure effective mixing, the SO_2 solution was transferred from one bulb to the other and back again. Reaction occurred almost immediately, the pale brown solution turning orange (5 min), olive (10 min), red (29 min). A pale crystalline solid began to be precipitated after about 30 minutes and the mixture was stirred for a further 96h after which time a gas phase infrared spectrum of the reaction volatiles was recorded. The reaction mixture was cooled (-10°C) in order to precipitate more of the pale product and the red solution was carefully decanted away; the residual pale product was washed (3 x 1ml) with back distilled SO_2 to remove traces of the red product. Complete removal of reaction volatiles yielded a white microcrystalline solid $S_4N_4^{2+}(AsF_6^-)_2.SO_2$ in the reaction bulb and a mixture of the white product and a red microcrystalline solid ($S_4N_4.AsF_5$) in the other bulb.

Yields: white solid, 0.130g; red mixture, 0.155g. A weight loss of 0.135g was observed during the reaction. Gas phase infrared spectrum of reaction mixture, ν_{max} = 2500w(SO_2), 1410s(OPF_3), 1370vs(SO_2), 1350vs(SO_2), 1160m(SO)$_2$), 1140m(SO_2), 1026s(PF_5), 980vs(OPF_3), 940vs(PF_5), 890m, sh (PF_3), 870m (OPF_3), 860m sh (PF_3), 570m (PF_5), 530s (PF_5), 490m(PF_3), 470m (OPF_3) cm^{-1}. Literature spectra for PF_5 and OPF_3 are given in References 10 and 11 respectively. Infrared spectrum of white product $S_4N_4^{2+}(AsF_6^-)_2$, ν_{max} = 1325vs, 1149s, 1030s, br, 850m, 817w, 700v.vs, 570m, 524m, 440s, sh, 390 v.v.s cm^{-1}. C.f. Reference 15, ν_{max} = 1054s, 1040s, 1015s cm^{-1}. Infrared spectrum of red mixture, ν_{max} = 1325m, 1150m, 1070m, 990vw, 925vw, 865m, 845vw, 700vs, br, 570w, sh, 525m, 440w, sh, 395vs cm^{-1}. Analysis for white solid, (O. Beller, Göttingen, FRG) found S, 25.20; N, 9.27; As, 25.0; F, 37.4; O (by difference), 3.13; $S_4N_4^{2+}(AsF_6^-)_2.SO_2$ requires, S, 25.60; N, 8.95; As, 23.9; F, 36.4; O, 5.1%.

b) Separation of the $S_4N_4.AsF_5$ in trace quantities could be achieved by placing the mixed fraction from part a) in another two-bulbed vessel and slowly evaporating an SO_2 solution thereof.

Small crystals of $S_4N_4 . AsF_5$ grew on the walls of the bulb and a suitable crystal was picked and identified by P.S. White (University of New Brunswick). Subsequently, it was found that $S_4N_4 . AsF_5$ could be separated from $S_4N_4^{2+}(AsF_6^-)_2 . SO_2$ by extraction with SO_2ClF. It should be mentioned that in each of the procedures described, extensive decomposition of the $S_4N_4^{2+}(AsF_6^-)_2 . SO_2$ occurred during manipulation. Approximately 0.020g of $S_4N_4 . AsF_5$ was isolated in this way from 0.145g of red mixture and its identity was confirmed by infrared spectroscopy. Infrared spectrum of purified red product, ν_{max} = 1065m, 985m, 862m, 840w, 720m, sh, 680s, 620w, sh, 519m, 430m, 387s, sh cm^{-1}. c.f. Mews et al(16) 1070s, 1015vw, 980m, 925w, 867m, 845w, 693sh, 685vs, 668m, 625m, 551w, 547w, 432m, 388vs, 363m, 349s cm^{-1}.

No Raman spectra of the white compound could be obtained owing to decomposition of the sample in the beam, but a crystal was grown from SO_2 solution and identified by W. Clegg (University of Newcastle upon Tyne) as $S_4N_4^{2+}$ $(AsF_6^-)_2 . SO_2$; the parameters determined (no final refinement) were, monoclinic $C_{2/c}$ or C_c, a = 13.467, b = 7.993, c = 15.386 Å, β = 100.14° which compare well with the parameters given in Reference 15 of monoclinic $C_{2/c}$ or C_c, a = 13.404(2), b = 7.958(1), c = 15.341(3) Å, β = 100.05(1)°.

7.4.3 The Reaction of SN^+AsF_6 with $S_5N_5AsF_6$:

$S_5N_5AsF_6$ (0.40g, 0.95 mmol) was placed together with a Teflon coated stirring bar in one bulb of a two-bulbed vessel. $SN^+AsF_6^-$ (0.22g, 0.95 mmol) was placed in the other bulb and SO_2 (ca. 10 ml in total) was condensed into both bulbs. The pale brown solution of

$SN^+AsF_6^-$ was added to the pale yellow solution of $S_5N_5AsF_6$, which darkened slightly and the mixture was stirred at room temperature for 24h. No further colour changes were observed and a gas phase infrared spectrum of the reaction mixture showed only SO_2. Complete removal of solvent yielded a yellow crystalline solid with a slight greenish cast.

Yield 0.62g. Infrared spectrum of yellow solid, ν_{max} = 1150m, br, 820vw, 700vs, vbr, 575m, 535m, 400vs cm^{-1}. All bands assigned to $S_5N_5AsF_6$ (see Chapter 3); presumably, the SN^+ band at 1435 cm^{-1} was masked by nujol.

7.4.4 Reaction of $SN^+AsF_6^-$ with KCN:

$SN^+AsF_6^-$ (0.2g, 0.85 mmol) was placed in one bulb of a two-bulbed vessel and isolated from the remainder of the vessel. KCN (0.042g, 0.85 mmol) was placed together with a Teflon coated stirring bar in the other bulb and was flamed gently in vacuo to remove traces of moisture (20 min); care was taken to avoid fusing the solid. SO_2 (a total of ca. 4 ml) was condensed into each bulb and after warming to room temperature, the solution of $SN^+AsF_6^-$ was added to the KCN. A reaction occurred immediately to give a black solution and a black insoluble solid. The mixture was stirred at room temperature for 24h; a gas phase infrared spectrum was recorded which showed only the presence of SO_2. The mixture was filtered and the solvent was pumped away to yield a brown purple insoluble solid and a black soluble tar.

Yields: solid, 0.1g; tar, ca. 0.1g. Infrared spectrum of solid, ν_{max} = 2170m, 2080m (CN^-), 1600-1300vv.br, m, 1170br, m, 1070br, w, 970br, m, 830w, sh, 710vs, br, (AsF_6^-), 400vs (AsF_6^-)cm^{-1}. Infrared spectrum of tar (smear), ν_{max} = 3280vbr, m (hydrolysis), 2175w, 1600-1250 v.v.br, s, 1200 br, w, 1080 br, w, 925 br, w, 780 br, sh, 700 vs (AsF_6^-), 525w, 470vw, 445w, 395 vs (AsF_6^-) cm^{-1}.

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APPENDIX

DEPARTMENTAL COLLOQUIA AND DURHAM UNIVERSITY CHEMICAL SOCIETY (D.U.C.S.) LECTURES

13.10.82	Dr W.J. Feast (University of Durham), "Approaches to the synthesis of conjugated polymers".
14.10.82	Prof. H. Suhr (University of Tübingen, FRG), "Preparative Chemistry in Non-equilibrium plasmas".
14.10.82	Mr F. Shenton (County Analyst, Durham), "There is death in the pot". (D.U.C.S.)
27.10.82	Dr C.E. Housecroft (Oxford High School/Notre Dame University, USA), "Bonding capabilities of butterfly-shaped Fe_4 units; implications for C-H bond activation in hydrocarbon complexes".
28.10.82	Prof. M.F. Lappert, F.R.S., (University of Sussex), "Approaches to asymmetric synthesis and catalyses using electron-rich olefins and some of their metal complexes".
	"The Chemistry of some Unusual Subvalent Compounds of the Main Group IV and V Elements". (D.U.C.S.)
4.11.82	Dr D.H. Williams (University of Cambridge), "Studies on the Structures and Modes of action of antibiotics". (D.U.C.S.)
11.11.82	Dr J. Cramp (I.C.I. Ltd), "Lasers in Industry". (D.U.C.S.)
15.11.82	Dr G. Bertrand (University of Toulouse, France), "Curtius rearrangement in organo-metallic series. A route for hybridised species".

24.11.82	Prof. G.G. Roberts (Applied Physics, University of Durham), "Langmuir-Blodgett films: solid state polymerisation of diacetylenes".
25.11.82	Dr D.H. Richards (P.E.R.M.E., Ministry of Defence), "Terminally functional polymers; their synthesis and uses". (D.U.C.S.)
2.12.82	Dr G.M. Brook (University of Durham), "The fate of the ortho-fluorine in 3,3-sigmatropic reactions involving polyfluoraryl and -heteroaryl systems".
8.12.82	Dr G. Wooley (Trent Polytechnic), "Bonds in transition metal cluster compounds".
12.1.83	Prof. D.W.A. Sharp (University of Glasgow), "Some redox reactions in fluorine chemistry". (D.U.C.S.)
3.2.83	Dr R. Manning (Department of Zoology, University of Durham), "Molecular mechanisms of hormone action". (D.U.C.S.)
9.2.83	Dr P. Moore (University of Warwick), "Mechanistic studies in solution by stopped flow F.T.-N.M.R. and high pressure N.M.R. line broadenine".
10.2.83	Sir Geoffrey Allen, F.R.S. (Unilever Ltd), "U.K. Research Ltd". (D.U.C.S.)
17.2.83	Prof. A.G. MacDiarmid (University of Pennsylvania, (USA), "Metallic Covalent Polymers: $(SN)_x$ and (CH)x and their derivatives". (D.U.C.S., R.S.C. Centenary Lecture)
21 2 83	Dr R. Lynden-Bell (University of Cambridge), "Molecular Motion in the cubic phase of NaCN".
2.3.83	Dr D. Bloor (Queen Mary College, University of London), "The solid state chemistry of diacetylene monomers and polymers".

3.3.83	Prof. A.C.T. North (University of Leeds), "The use of a computer display system in studying molecular structures and interactions". (D.U.C.S.)
8.3.83	Prof. D.C. Bradley, F.R.S. (Queen Mary College, University of London), "Recent developments in organo-imido-transition metal chemistry".
9.3.83	Dr D.M.J. Lilley (University of Dundee), "DNA, sequence, symmetry, structure and supercooling".
11.3.83	Prof. H.G. Viehe (University of Louvain, Belgium), "Oxidations on sulphur", "Fluorine substitutions in radicals". (Musgrave lecture).
16.3.83	Dr I. Gosney (University of Edinburgh), "New extrusion reactions: organic synthesis in a hot tube".
25.3.83	Prof. F.G. Baglin (University of Nevada, USA), "Interaction induced Raman spectroscopy in supra-critical ethane".
21.4.83	Prof. J. Passmore (University of New Brunswick, Canada), "Novel selenium-iodine cations".
4.5.83	Prof. P.H. Plesh (University of Keele), "Binary ionisation equilibria between two ions and two molecules. What Ostwald never thought of".
10.5.83	Prof. K. Burger (Technical University of Munich, FRG), "New reaction pathways from trifluoromethyl substituted heterodienes to partially fluorinated heterocyclic compounds".
11.5.83	Dr N. Isaacs (University of Reading), "The application of high pressures to the theory and practice of organic chemistry".

13.5.83	Dr R. de Koch (Caloin College, Michigan, USA/Free University, Amsterdam, Netherlands), "Electronic structural calculations in organo-metallic cobalt cluster molecules. Implications for metal surfaces".
16.5.83	Prof. R.J. Lagow (University of Texas, USA), "The chemistry of polylithium organic compounds. An unusual class of matter".
18.5.83	Dr D.M. Adams (University of Leicester), "Spectroscopy at very high pressures".
25.5.83	Dr J.M. Vernon (University of York), "New heterocyclic chemistry involving lead tetraacetate".
15.6.83	Dr A. Pietrzykowski (Technical University of Warsqs, Poland/University of Strathclyde), "Synthesis, structure and properties of aluminoxanes".
22.6.83	Prof. J. Miller (University of Camfinas, Brazil), "Reactivity in nucleophilic substitution reactions".
5.10.83	Prof. J.P. Maier (University of Basel, Switzerland), "Recent approaches to spectroscopic characterisation of cations".
12.10.83	Dr C.W. McLeland (University of Port Elizabeth, Australia), "Cyclisation of aryl alcohols through the intermediacy of alkoxy and aryl radical cations".
19.10.83	Dr N.W. Alcock (University of Warwick), "Aryl tellurium (IV) compounds, patterns of primary and secondary bonding".
20.10.83	Prof. R.B. Cundall (University of Salford), "Explosives", (D.U.C.S.)

26.10.83	Dr R.H. Friend (Cavendish Laboratory, University of Cambridge), "Electronic properties of conjugated polymers".
3.11.83	Dr G. Richards (University of Oxford), "Quantum pharmacology". (D.U.C.S.)
10.11.83	Dr J. Harrison (Stirling Organic Ltd), "Applied chemistry and the pharmaceutical industry". (D.U.C.S.)
24.11.83	Prof. D.A. King (University of Liverpool), "Chemistry in two dimensions". (D.U.C.S.)
30.11.83	Prof. I. Cowie (University of Stirling), "Molecular interpretation of non-relaxation processes in polymer glasses".
1.12.83	Dr J.D. Coyle (The Open University), "The problem with sunshine". (D.U.C.S.)
14.12.83	Prof. R.J. Donovan (University of Edinburgh), "Chemical and physical processes involving the ion-pair states of the halogen molecules".
10.1.84	Prof. R. Hester (University of York), "Nanosecond laser spectroscopy of reaction intermediates".
18.1.84	Prof. R.K. Harris (University of East Anglia), "Multinuclear solid state magnetic resonance".
26.1.84	Prof. T.L. Blundell (Birbeck College, University of London), "Biological recognition: Interactions of macromolecular surfaces". (D.U.C.S.)
2.2.84	Prof. N.B.H. Jonathan (University of Southampton), "Photoelectron spectroscopy- a radical approach". (D.U.C.S.)

8.2.84	Dr B.T. Heaton (University of Kent), "Multi-nuclear n.m.r. studies".
15.2.84	Dr R.M. Paton (University of Edinburgh), "Heterocyclic syntheses using nitrile sulphides".
16.2.84	Prof. D. Phillips (The Royal Institution), "Luminescence and photochemistry- a light entertainment". (D.U.C.S.)
23.2.84	Prof. F.G.A. Stone, F.R.S. (University of Bristol), "The use of carbene and carbyne groups to synthesise metal clusters" (D.U.C.S. The Waddington Memorial Lecture)
1.3.84	Prof. A.J. Leadbetter (Rutherford Appleton Laboratory), "Liquid crystals". (D.U.C.S.)
7.3.84	Dr R.T. Walker (University of Birmingham), "Synthesis and biological properties of some 5-substituted uracil derivatives; yet another example of serendipity in antiviral chemotherapy".
8.3.84	Prof. D. Chapman (Royal Free Hospital School of Medicine, University of London), "Phospholipids and biomembranes: basic structure and future techniques". (D.U.C.S.)
21.3.84	Dr P. Sherwood (University of Newcastle), "X-ray photoelectron spectroscopic studies of electrode and other surfaces".
23.3.84	Dr A. Ceulemans (Catholic University of Leuvan, Belgium), "The development of field-type models of the bonding in molecular clusters".
28.3.84	Prof. H. Schmidbaur (Technical University of Munich, FRG), "Ylides in coordination sphere of metals: synthetic, structural and theoretical aspects". (D.U.C.S., R.S.C. Centenary Lecture).

2.4.84 Prof. K. O'Driscoll (University of Waterloo, Canada), "Chain ending reactions in free radical polymerisation".

3.4.84 Prof. C.H. Rochester (University of Dundee), "Infra-red studies of absorption at the solid-liquid interface".

25.4.84 Dr R.M. Acheson (Department of Biochemistry, University of Oxford), "Some heterocyclic detective stories".

27.4.84 Dr T. Albright (University of Houston, USA), "Sigmatropic rearrangements in organometallic chemistry".

14.5.84 Prof. W.R. Dolbier, Jr (University of Florida, USA), "Cycloaddition reactions of fluorinated allenes".

16.5.84 Dr P.J. Garratt (University College, London), "Syntheses with dilithiated vicinal diesters and carboximides".

22.5.84 Prof. F.C. De Schryver (Catholic University of Leuven, Netherlands), "Configurational and conformational control in excited state complex formation".

"The use of luminescence in the study of micellar aggregates".

23.5.84 Prof. M. Tada (Waseda University, Japan), "Photochemistry of dicyanopyrazine derivatives".

29.5.84 Dr A. Haaland (University of Oslo, Norway), "Electron diffraction studies of some organo-metallic compounds".

11.6.84 Dr G.B. Street (I.B.M. San Jose, USA). "Conducting polymers derived from pyrroles".

19.9.84 Dr C. Brown (IBM San Jose), "New Superbase Reactions - Organic Compounds".

21.9.84	Dr H.W. Gibson (Signal UOP Research Centre, Des Plaines, Illinois), "Isomerization of Polyacetylene".
18.10.84	Dr N. Logan (University of Nottingham), "N_2O_4 and Rocket Fuels". (D.U.C.S.)
19.10.84	Dr A. Germain (Universite du Languedoc, Montpellier), "Anodic Oxidation of Perfluoro Organic Compounds in Perfluoralkane Sulphonic Acids".
24.10.84	Prof. R.K. Harris (University of Durham), "NMR of Solid Polymers".
25.10.84	Dr W.J. Feast (University of Durham), "Syntheses of Conjugated Polymers. Why and How?". (D.U.C.S.)
1.11.84	Prof. B.J. Aylett (Queen Mary College, University of London), "Silicon - Dead Common or Refined". (D.U.C.S.)
7.11.84	Prof. W.W. Porterfield (Hampden-Sydney College, USA), "There is No Borane Chemistry (Only Geometry)".
7.11.84	Dr H.S. Munro (University of Durham), "New Information from ESCA Data".
15.11.84	Dr H.S. Munro (University of Durham), "New Information from ESCA Data".
21.11.84	Mr N. Everall (University of Durham), "Picosecon Pulsed Laser Raman Spectroscopy".
22.11.84	Prof. D.T. Clark (ICI New Science Group), "Structure, Bonding, Reactivity and Synthesis as Revealed by ESCA". (D.U.C.S.)

27.11.84	Dr W.J. Feast (University of Durham), "A Plain Man's Guide to Polymeric Organic Metals".
28.11.84	Dr T.A. Stephenson (University of Edinburgh), "Some Recent Studies in Platinum Metals Chemistry".
29.11.84	Prof. C.J.M. Stirling (University College of North Wales), "Molecules Taking the Strain". (D.U.C.S.)
5.12.84	Mr P.J. Lux (University of Durham), "IR and GC Studies of the Interaction of CH_3OH with High Silica Zeolites".
6.12.84	Prof. R.D. Chambers (University of Durham), "The Unusual World of Fluorine". (D.U.C.S.)
12.12. 84	Dr K.B. Dillon (University of Durham, "31P NMR Studies of Some Anionic Phosphorus Complexes".
11.1.85	Prof. Emeritus H. Suschitzky (University of Salford), "Fruitful Fissions of Benzofuroxanes and Isobenzimadazoles (umpolung of O-phenylenediamine)".
24.1.85	Dr A.K. Covington, (University of Newcastle-upon-Tyne), "Chemistry with Chips". (D.U.C.S.)
31.1.85	Dr M.L. H. Green (University of Oxford), "Naked Atoms and Negligee Ligands". (D.U.C.S.)
7.2.85	Prof. A. Ledwith (Pilkington Bros), "Glass as a High Technology Material". (D.U.C.S.)
13.2.85	Dr G.W.J. Fleet (University of Oxford), "Syntheses of some Alkaloids from Carbohydrates".
14.2.85	Dr J.A. Salthouse (University of Manchester), "Son et Lumiere" (A Chemical Energy Show) (D.U.C.S.)

19.2.85	Dr D.J. Mincher (University of Durham), "Stereoselective Syntheses of Some Novel Anthracyclinones Related to the Anti-Cancer. Drug Adriamycin and to the Steffimycin Antibiotics".
21.1.85	Prof. P.M. Maitlis, FRS (University of Sheffield), "What Use is Rhodium?" (D.U.C.S.)
27.2.85	Dr R.E. Mulvey (University of Durham), "Some Unusual Lithium Complexes".
7.3.85	Dr P.W. Atkins (University of Oxford), "Magnetic Reactions". (D.U.C.S.)
7.3.85	Dr P.J. Rodgers (ICI plc. Agricultural Division, Billingham), "Industrial Polymers from Bacteria".
12.3.85	Prof. K.J. Packer (B.P. Research Centre), "NMR Investigations of the Structure of Solid Polymers".
14.3.85	Prof. A.R. Katritzky, FRS (University of Florida), "Some Adventures in Heterocyclic Chemistry".
21.3.85	Dr M. Poliakoff (University of Nottingham), "New Methods for Detecting Organometallic Intermediates in Solution".
28.3.85	Prof. H. Ringsdorf (Organic Chemistry Institute, University of Mainz), "Polymeric Liposomes as Models for Biomembranes and Cells?"
24.4.85	Dr M.C. Grossel (Bedford College, University of London), "Hydroxypyridone Dyes - Bleachable One-Dimensional Metals?"
1.5.85	Dr D. Parker (ICI plc, Petrochemical & Plastics Division, Wilton), "Applications of Radioisotopes in Industrial Research".

7.5.85	Prof. G.E. Coates (formerly of University of Wyoming, USA), "Chemical Education in Britain and America: Successes and Deficiencies".
8.5.85	Prof. D. Tuck (University of Windsor, Ontario), "Lower Oxidation State Chemistry of Indium".
9.5.85	Prof. R.K. Harris (University of Durham), "Chemistry in a Spin: Nuclear Magnetic Resonance".
14.5.85	Prof. J. Passmore (University of New Brunswick), "The Synthesis and Characterisation of some Novel Selenium-Iodine Cations, Aided by ^{77}Se NMR Spectroscopy".
15.5.85	Dr J.E. Packer (University of Auckland, New Zealand), "Studies of Free Radical Reactions in Aqueous Solution Using Ionising Radiation".
17.5.85	Prof. I.D. Brown (Institute of Materials Research, McMaster University, Canada), "Bond Valence as a Model for Inorganic Chemistry".
21.5.85	Dr R. Grimmett (University of Otago, Dunedin, New Zealand), "Some Aspects of Nucleophilic Substitution in Imidazoles".
22.5.85	Dr M. Hudlicky (Virginia State University, Blacksburg), "Preferential Elimination of Hydrogen Fluoride from Vicinal Bromofluorocompounds".
4.6. 85	Dr P.S. Belton (Food Research Institute, Norwich), "Analytical Photoacoustic Spectroscopy".
13.6.85	Dr D. Woollins (Imperial College, University of London), "Metal-Sulphur-Nitrogen Complexes".

14.6.85 Prof. Z. Rappoport (The Hebrew University, Jerusalem), "The Rich Mechanistic World of Nucleophilic Vinylic Substitution".

19.6.85 Dr T.N. Mitchell (University of Dortmund), "Some Synthetic and NMR-Spectroscopic Studies of Organotin Compounds".

26.6.85 Prof. G. Shaw (University of Bradford), "Synthetic Studies on Imidazole Nucleosides and the Antibiotic Coformycin".

12.7.85 Dr K. Laali (Hydrocarbon Research Institute, University of Southern California), "Recent Developments in Superacid Chemistry and Mechanistic Considerations in Electrophilic Aromatic Substitutions; A Progress Report".

First Year Induction Course

i) Departmental organization
ii) Safety matters
iii) Electrical appliances
iv) Chromatography and microanalysis
v) Library facilities
vi) Atomic absorption and inorganic analysis
vii) Mass spectrometry
viii) NMR spectroscopy
ix) Glassblowing technique