Properties of tetrasulphur tetranitride in some reactive solvents

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PROPERTIES OF TETRASULPHUR TETRANITRIDE
IN SOME REACTIVE SOLVENTS

by

P.J. DAINTY, B.Sc.

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Not least, thanks are due to Mrs. D.M. Armstrong, for coping with the author's manuscript.

Memorandum

The work described in this thesis was carried out in the University of Durham between October 1966 and July 1969. This work has not been submitted for any other degree and is the original work of the author except where acknowledged by reference.

"Double, double, toil and trouble;
Fire burn and cauldron bubble."

Wm. Shakespeare, "Macbeth."

Abstract

This thesis describes -

1. The completion of the preliminary investigation of $S_4N_4/SOCl_2/MCl_x$ systems commenced by Dr. J.S. Padley (Ph.D. Thesis, University of Durham, July 1967).

2. The carrying out of a more detailed study of the $S_4N_4/SOCl_2/AlCl_3$ and $S_4N_4/SOCl_2/FeCl_3$ systems (which the above noted preliminary investigation indicated would be the most satisfactory systems for more detailed study).

3. The investigation of some S_4N_4/(constant metal chloride)/(varying solvent related to $SOCl_2$) systems; since $SOCl_2$ plays an active role in the $S_4N_4/SOCl_2/MCl_x$ systems, the effect of varying the solvent used repays study.

It has been found that most of the products obtained from the $S_4N_4/SOCl_2/MCl_x$ system could be grouped into only five categories, by the criterion of near infrared spectrum: it is believed that this correlation will be of particular value as more structural data become available.
In the case of most of the compounds prepared, the group of near infrared spectra into which the product obtained from MCl_x falls can be tentatively correlated with the efficiency of MCl_x as a chlorination catalyst.

It is shown that the systems $S_4N_4/MCl_x/SO_2Cl_2$, and $S_4N_4/MCl_x/SCl_2$, are likely to justify an extensive investigation on the scale of that made into $S_4N_4/MCl_x/SOCl_2$ systems.

Results are discussed generally with a view to assisting the understanding and systematisation of (metal-)sulphur-nitrogen(-chlorine) chemistry as a whole, and particularly with reference to the likely structures of the products obtained, which products are believed to include a number of compounds novel to sulphur-nitrogen chemistry.

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INTRODUCTION

Introduction

This introduction is divided into the following sections:

(i) An introduction to tetrasulphur tetranitride, S_4N_4.

(ii) A survey of those aspects of the chemistry of S_4N_4 related to the contents of this thesis.

The chemistry of S_4N_4 with Lewis acids (a) leading to metalliferous compounds, (1) in non-participating solvents and (2) in participating solvents. (Adducts with the non-metal Lewis acids BX_3, SO_3 and $TeBr_4$ are conveniently dealt with at (1).)

The chemistry of S_4N_4 with Lewis acids (b) leading to certain halogenated non-metalliferous compounds.

The chemistry of S_4N_4 (c) leading to other halogenated non-metalliferous sulphur-nitrogen compounds.

(iii) Significant recent developments in sulphur-nitrogen chemistry.

(iv) References to further reviews of areas of sulphur-nitrogen chemistry.

Introduction

(i) Tetrasulphur tetranitride, S_4N_4

Of the various compounds which are strategic in sulphur-nitrogen chemistry as a whole, tetrasulphur tetranitride is one of the most important.

General properties

S_4N_4 is an air-stable, orange crystalline solid; as commonly prepared, it melts at 178°.[1] It has been found that purification by repeated column chromatography sequences raises the melting point to 187-187·5°, but since the tendency of such samples to explode increases substantially as the melting point is raised beyond 179° (samples with melting points further and further below 177° show the same tendency), there is a powerful disincentive to prepare such pure material.[16] S_4N_4 is in fact highly endothermic - about +115 kcal.mole^{-1}; the exact value is uncertain[2] - and can detonate violently on mechanical or thermal shock.

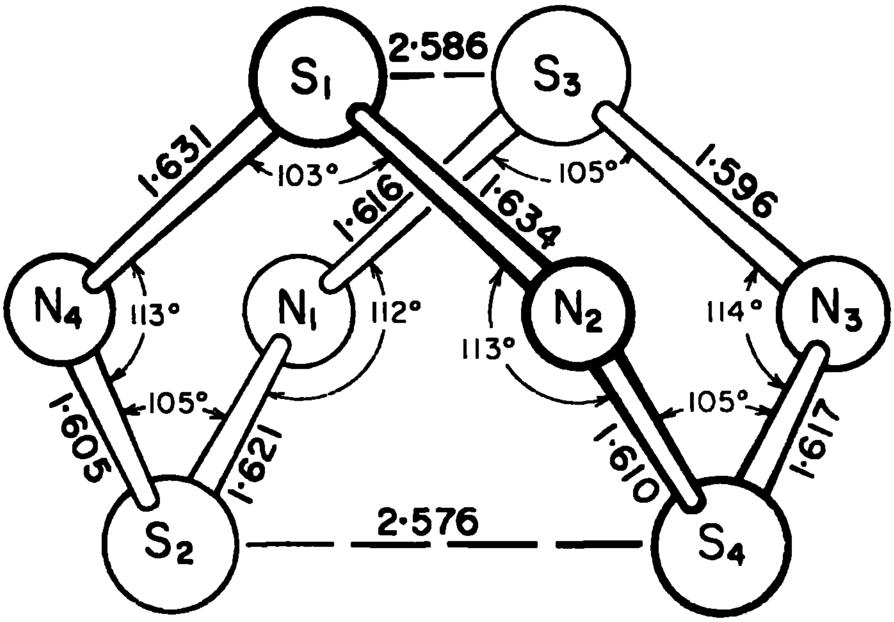
It is readily soluble in benzene[3] and carbon disulphide[3] (without solvolysis) and in liquid ammonia[4] and thionyl chloride[31] (with solvolysis). It is soluble (with or without solvolysis) to a lesser extent in a wide variety of other solvents such as carbon tetrachloride,[5] methylene dichloride,[5] ethanol,[3] sulphuryl chloride and sulphur dichloride.

Molecular and electronic structures

The structure of S_4N_4 was for a long time open to doubt, but is now definitely established for both the crystalline solid,[6,8] and for its vapour.[7] The structure is shown in Fig.1.

Figure 1.

Bond distances and angles in S_4N_4.[8]



The main points to note regarding S_4N_4's structure are (1) the cage conformation of the ring (containing a bisphenoid of sulphur atoms and a square planar arrangement of nitrogen atoms) and (2) the identical lengths of all S-N bonds. Further, the separation of adjacent sulphur atoms (2·58 Å, see Fig.1) is less than the sum (3·7 Å) of van der Waal's radii: this suggests that there is bonding between adjacent sulphur atoms, and in fact the results of an analysis of the visible and ultra-violet spectra[9] require the existence of a weak S-S bonding interaction. Molecular orbital calculations[10] indicate that this interaction results in a bond order of just less than 0·5.

It is now generally accepted that S_4N_4 (in common with other sulphur-nitrogen compounds such as S_4N_3Cl and $N_3S_3Cl_3$, see later) contains a π-delocalised system of electrons which may be understood as derived from overlap of nitrogen pπ and sulphur dπ orbitals.[11]

Preparation

S_4N_4 is formed as a minor product in many reactions,[12] and various synthetic routes have been used on a preparative scale.[13,14] The preparative routes most commonly used at the present time are variants[15,16] of the reaction between chlorinated solutions of S_2Cl_2 in carbon tetrachloride, and ammonia. (The method used in this work is another minor variant of this route, and is described on p.28.). No particular one of these variants is indisputably any better or worse than the others, as regards yield and convenience.

Studies have been made[17] on the interaction of ammonia with sulphur chlorides, with a view to gaining a better understanding of the reaction(s) leading to S_4N_4 (amongst other possible products of this system), and speculation has been made[17] regarding the mechanisms of the reactions involved. The complexity of this system is such that little has been sufficiently reliably established to be of any great value in really <u>understanding</u> the system, but a critical investigation has been made[18] of the exact effect of variables (such as ammonia flow rate) on the final yield of S_4N_4.

(ii) A survey of those aspects of the chemistry of S_4N_4 related to the contents of this thesis

Preliminary remarks

One of the most notable characteristics of S_4N_4 is its ability to react in a variety of ways with a very wide range of Lewis acids to give metalliferous products. The exact product of such reactions depends critically upon the experimental conditions. In this context, solvents (when employed) may be crudely grouped into two categories - non-participating, and participating. The products of reactions in non-participating solvents are quite straightforward, and are best understood as being simple σ-donor/acceptor complexes between an $(SN)_4$ ring and the relevant Lewis acid, with a lattice of discrete molecules. Such a structure has been established for a few of these compounds, by X-ray analysis. Variety is shown by this group of compounds to the extent that stoichiometries (S_4N_4:Lewis acid) vary from 2:1 to 1:4. Examples of the non-participating solvents for such reactions are methylene dichloride and carbon tetrachloride. (The products of solvent-free reactions are analogous to those of reactions in non-participating solvents.) As may be expected, the products of reactions in participating solvents are, in contrast, very diverse - they can contain one or more of a wide range of sulphur-nitrogen moieties. Examples of participating solvents are ethanol and liquid ammonia. The new compounds described in this work are best understood as being derived via participating solvents. A couple of reactions are known (see p. 13) in which S_4N_4 reacts with a metal halide to give - in contrast to the two previous general cases - non-metalliferous, (halogenated) sulphur-nitrogen compounds. Finally, there exists the range of reactions (see p. 14) in which S_4N_4 is halogenated either by the halogen itself, or by a sulphur-halogen compound.

These general points are now considered in more detail.

The chemistry of S_4N_4 with Lewis acids (a) leading to metalliferous compounds

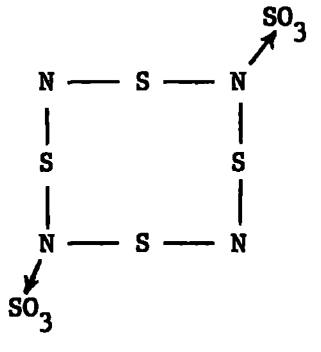
(1) In non-participating solvents. (Adducts with the non-metal Lewis acids BX_3, SO_3 and $TeBr_4$ are conveniently dealt with here)

The most thoroughly investigated example of this aspect of S_4N_4's chemistry is given by the Lewis acids BF_3, BCl_3 and $SbCl_5$.[19] Reaction of S_4N_4 with BCl_3 in CH_2Cl_2 gives $S_4N_4 \cdot BCl_3$; reaction of this adduct with $SbCl_5$ yields the yellow $S_4N_4 \cdot BCl_3 \cdot SbCl_5$. This reaction is particularly interesting since (i) it provides the first case known of a mixed S_4N_4 di-adduct, and (ii) no di-adducts were found when excess BCl_3 or $SbCl_5$ was reacted with S_4N_4. The same workers found that $S_4N_4 \cdot BF_3$ (resulting from the reaction of S_4N_4 and BF_3 in CH_2Cl_2) dissociated reversibly on heating, and was decomposed by BCl_3 and $SbCl_5$ to give, respectively, $S_4N_4 \cdot BCl_3$ and $S_4N_4 \cdot SbCl_5$. In contrast, $S_4N_4 \cdot BCl_3$ could be sublimed with only trace decomposition; its remarkable behaviour with $SbCl_5$ has been noted. It was however found that $S_4N_4 \cdot BCl_3$ could be converted to $S_4N_4 \cdot SbCl_5$ by forming the mixed di-adduct $S_4N_4 \cdot BCl_3 \cdot SbCl_5$, and heating this at 90°

in vacuo, when BCl_3 was lost.

The structures of $S_4N_4{\cdot}SbCl_5$[20] and $S_4N_4{\cdot}BF_3$[21] have been determined by X-ray analysis. They are closely analogous, both involving co-ordination of the $(SN)_4$ ring to the antimony or boron via nitrogen: in either case, the $(SN)_4$ ring is flattened out from the cage conformation of S_4N_4, so that a plane of sulphur atoms, with nitrogen atoms alternately above and below this square (cf. p. 3) results. The structure of $S_4N_4{\cdot}SbCl_5$ is shown in Fig. 2. The structure of the unique adduct $S_4N_4{\cdot}BCl_3{\cdot}SbCl_5$ is uncertain; the workers who prepared it were unable to decide between $[S_4N_4{\cdot}BCl_2]^+$ $[SbCl_6]^-$ and $Cl_3B \leftarrow S_4N_4 \rightarrow SbCl_5$ (B-N and Sb-N bonds).

The chemistry of the adducts $S_4N_4{\cdot}2$ and 4 SO_3 - so far as known[25] - is similar: reaction of S_4N_4 with SO_3 vapour diluted with nitrogen yields $S_4N_4{\cdot}4SO_3$; this adduct can be decomposed to $S_4N_4{\cdot}2SO_3$. It is believed that formation of the tetra-adduct proceeds via the di-adduct. Structures proposed by the workers for these compounds are:



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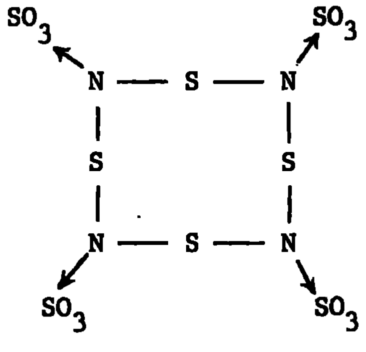


The chemistry of the many other compounds believed by the workers who prepared them to be σ-adducts of S_4N_4 is less thoroughly established, and their structures are unknown - although sometimes speculation has been made regarding the latter property.

Figure 2.

The structure of $S_4N_4 \cdot SbCl_5$.[20]

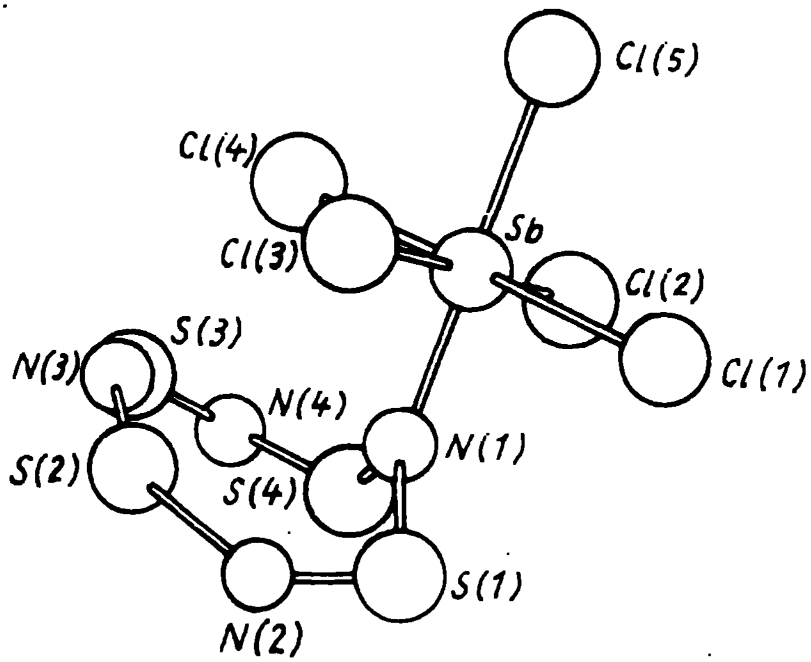


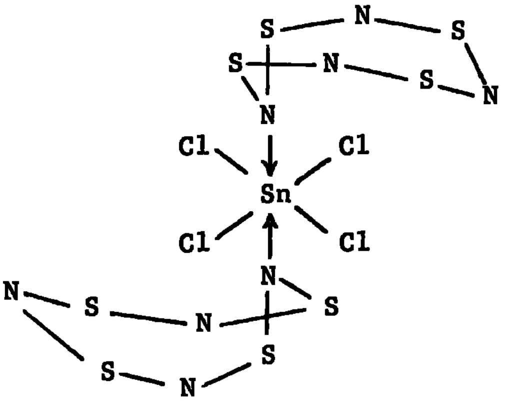
Abb. 2. Strukturmodell von $SbCl_5 \cdot S_4N_4$

The following adducts are reliably established (although little further can usefully be said about them):

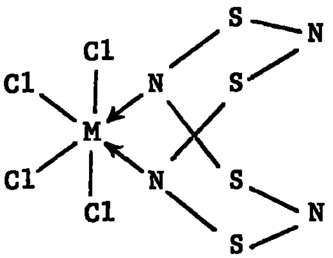
$S_4N_4 \cdot BBr_3$,[19] $2S_4N_4 \cdot SnCl_4$,[22] $S_4N_4 \cdot 2SbF_5$,[23] $S_4N_4 \cdot 4SbF_5$,[24] $S_4N_4 \cdot 2SbBr_3$,[23] $S_4N_4 \cdot 2SbI_3$,[23] $S_4N_4 \cdot TeBr_4$,[26] $S_4N_4 \cdot TiCl_4$,[27] $S_4N_4 \cdot VCl_4$,[28] and $S_4N_4 \cdot WCl_4$.[22,23]

The $SOCl_2$-solvolyses of $S_4N_4 \cdot TiCl_4$, $S_4N_4 \cdot SbCl_5$, $2S_4N_4 \cdot SnCl_4$ and other new S_4N_4-adducts recently prepared[29] in these laboratories are discussed in this work and elsewhere.[31]

Structures which have been proposed[20] for some of these compounds are:



($2S_4N_4 \cdot SnCl_4$)



($S_4N_4 \cdot MCl_4$; M = Ti, V, W)

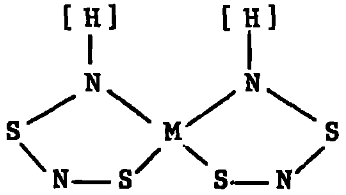
The whole field of S_4N_4 adducts has been the subject of general[30] and detailed[29] reviews.

(2) In participating solvents

This field of sulphur-nitrogen chemistry is notable for first, its diversity, and second, its small degree of systematisation. It was partly for these reasons that an extensive survey of the system $S_4N_4/SOCl_2/MCl_x$ was undertaken in these laboratories (this work, and ref.31). With the completion of this latter work, the understanding of the chemistry of systems involving M-S-N(-Cl) compounds has been increased to such an extent that it is highly likely that if a comparably extensive study of the systems to be surveyed here were to be undertaken, it would transform the information at present available on such systems from mere fragmentary data, to meaningful information forming part of a coherent topic in sulphur-nitrogen chemistry.

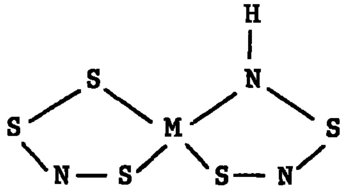
A number of closely related compounds of the group VIII transition metals are known, which are (with one exception) derived from the ethanol-based solvent system. This group of compounds is of particular importance since (i) compounds of three different stoichiometries are involved, (ii) the structures of a number of these compounds have been definitely established, and (iii) an extensive range of structurally characterised organic derivatives has been established for one of these compounds. Consequently, this particular range of compounds represents a usefully developed aspect of sulphur-nitrogen chemistry.

Thus compounds of empirical formula $M(S_2N_2H)_2$ (M = Co, Ni, Pd) are readily prepared by reaction of MX_2 with S_4N_4 in ethanol,[36-38] and $Pt(S_2N_2H)_2$ results from reaction of S_4N_4 and H_2PtCl_6 in dimethylformamide.[37] Compounds of empirical formula MS_5N_3H and MS_6N_2 are trace co-products of $M(S_2N_2H)_2$ (M = Co, Ni, Pd) and are obtained by chromatography of the appropriate reaction mixture.[30,34] The structures of the compounds $M(S_2N_2H)_2$ have been shown to be analogous by X-ray analysis (M = Ni,[32] Pd,[32] Pt[33]), and are:



(The locations of the imino-hydrogen atoms are inferred by analogy with the structure found for a dimethylated derivative, see main section (iii).)

The structures proposed[30,34] for the compounds MS_5N_3H and MS_6N_2 (M = Co, Ni, Pd) are:



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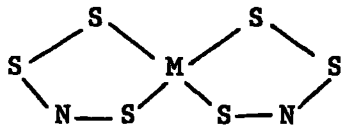


(MS_5N_3H) (MS_6N_2)

One other S_4N_4/Lewis acid/participating-solvent system is known from the literature to be at a comparably useful stage of development, and is that based on liquid ammonia.

There has been uncertainty as to the exact nature of the species present in solutions of S_4N_4 in liquid ammonia, but recent spectroscopic studies on solutions of S, S_4N_4, and H_2S and S_4N_4 in this solvent have established[39] certain points. First, the equilibrium

$$10S + 4NH_3 \rightleftharpoons S_4N_4 + 6H_2S$$

(previously believed to be involved in the preparation of S_4N_4 from sulphur in liquid ammonia[40]) has been shown not to exist to any appreciable extent, and second, the spectrum of S_4N_4 in this solvent has been found to change with time, this observation being interpreted in terms of a reaction of the type:

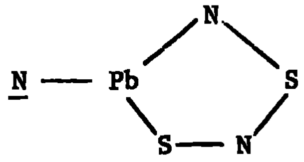
$$S_4N_4 + \text{liquid ammonia} \longrightarrow 2S_2N_2 \text{ (ammonated)}$$

In fact, a red, unstable solid of empirical formula $S_2N_3H_3$ can be isolated from S_4N_4/liquid ammonia solutions[41]; it has been formulated as $S_4N_4 \cdot 2NH_3$,[42] but is now generally formulated as $S_2N_2 \cdot NH_3$ or the more explicit $H{-}N{=}S{=}N{-}S{-}NH_2$.[41]

The compounds $PbS_2N_2 \cdot NH_3$, $2TlS_3N_3 \cdot NH_3$ and $HgN_2S \cdot NH_3$ have been obtained by treatment of S_4N_4/liquid ammonia solutions with PbI_2 or $Pb(NO_3)_2$,[42,43] $TlNO_3$[30,43] and HgI_2,[42] respectively. (All three products can be deammonated by heating in vacuo.[42,43]) It is thus believed[78] that $S_2N_2 \cdot NH_3$ can dissociate according to

$$H{-}N{=}S{=}N{-}S{-}NH_2 \rightleftharpoons H{-}N{=}S + H{-}N{=}S{=}N{-}H$$

The structure of $PbS_2N_2{\cdot}NH_3$ has been found by X-ray analysis[44] to be



probably with all three hydrogen atoms on N, although this is not yet established.

It is convenient to note here that just as the solvent system based on dimethylformamide gave $Pt(S_2N_2H)_2$ from H_2PtCl_6 and S_4N_4,[37] it has been claimed[47] that $CuCl_2$ and $CuBr_2$ react with S_4N_4 in this solvent to give respectively $S_2N_2CuCl_2$ and $S_2N_2CuBr_2$. However, an attempt to repeat the former preparation in these laboratories has been unsuccessful.[48]

Finally, carbonyls have been investigated on occasion (see also main section (iii)): $Fe(CO)_5$,[45] $Co_2(CO)_8$,[37] and $Ni(CO)_4$[46] have been found to react with S_4N_4 in hydrocarbon solvents to give materials of empirical formula $M(SN)_4$, whose constitution is uncertain.

The chemistry of S_4N_4 with Lewis acids (b) leading to certain halogenated non-metalliferous compounds

The reaction of S_4N_4 with HgF_2 in refluxing carbon tetrachloride leads[49] to the formation of the gas thiazyl fluoride, NSF. If, however, the fluorination conditions are slightly altered, the product is changed: if the carbon tetrachloride solution of S_4N_4 is slowly warmed to reflux in the presence of AgF_2, and the mixture is then allowed to cool, tetrathiazyl tetrafluoride, $N_4S_4F_4$, crystallises out.[49] The result of this mild fluorination may be compared with the result of a chlorination studied in this work, see p.125. The reaction involving AgF_2 also yields some SN_2F_2;[50] further, SN_2F_2 is formed when $N_4S_4F_4$ is refluxed in carbon tetrachloride for long periods.[50]

The chemistry of S_4N_4 (c), leading to other halogenated non-metalliferous sulphur-nitrogen compounds.

In common with $N_4S_4F_4$, noted in the preceding subsection, there are two sulphur-nitrogen chlorides of particular interest in terms of this thesis, namely trithiazyl trichloride, $N_3S_3Cl_3$, and thiotrithiazyl chloride, S_4N_3Cl.

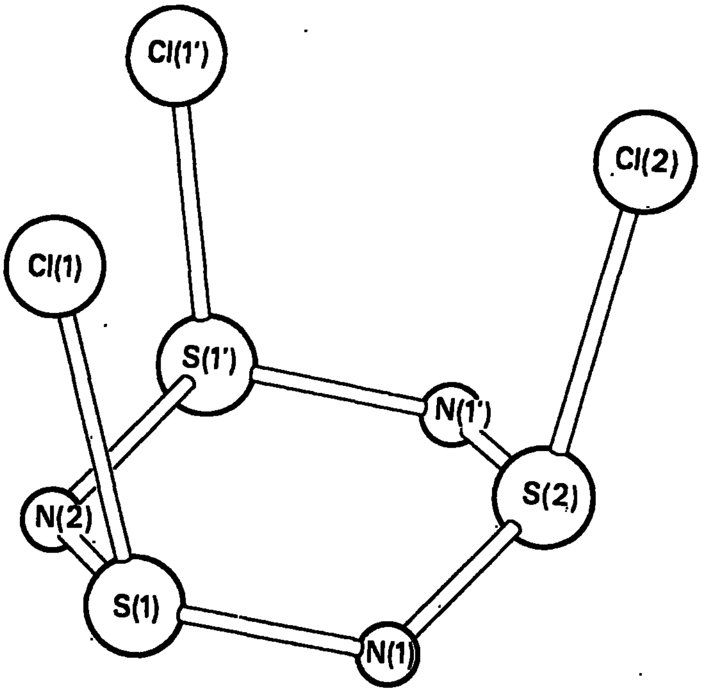
A material characterised as $N_3S_3Cl_3$ results when S_4N_4 is chlorinated by chlorine in carbon tetrachloride;[51] this material shows a complex and distinct near infrared spectrum,[29] and is reported to melt at 77-78°,[81a] 95-96°,[81b,29] 162·5°[51]: the melting point is very sensitive to purification procedure.[29,79] ($N_3S_3Cl_3$ prepared[60] from $S_3N_2Cl_2 + Cl_2$ shows[29] the same near infrared spectrum as $N_3S_3Cl_3$ prepared[60] from $S_4N_4 + Cl_2$.) Chlorination of S_4N_4 by stirring at room temperature in sulphuryl chloride also leads to a material characterised[29] as $N_3S_3Cl_3$; this latter material shows a near infrared spectrum[29] which is much simpler than (and quite distinct from) that of the former preparation, and melts at 90-91° (crude material)[29] and 93-94° (on recrystallisation from SO_2Cl_2).[29] However if the latter variety of $N_3S_3Cl_3$ is heated in benzene at 50-60° for 30 hours, it changes to the former variety.[29] (This behaviour may be compared with that of a compound $(NSCl)_x$ prepared in this work by chlorination of S_4N_4, see p.125.) It has thus been concluded[52] that the product of the former preparative method may be a mixture of isomers of $N_3S_3Cl_3$, while the latter product is probably only one isomer, or a mixture of a much smaller number of isomers.

X-ray analysis of a crystal of $N_3S_3Cl_3$ prepared by the former preparative route revealed[53] the structure shown in Fig.3. The identity of the S-N bond lengths has been taken to indicate the presence of a π-electron system delocalised over all these bonds.[51]

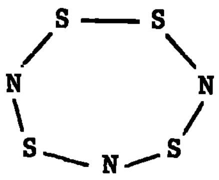
S_4N_3Cl is readily obtained by the chlorination of S_4N_4; a variety of methods have been described.[57-59] (It may be noted however that one involves the use of S_2Cl_2 in carbon tetrachloride,[56] see p.17.) Recently, an alternative preparation involving thiodithiazyl dichloride, $S_3N_2Cl_2$ (more conveniently and more readily obtained than S_4N_4) as starting material, has been described.[60] S_4N_3Cl is simply one example of a range of salts of the $S_4N_3^+$ ion: it is however probably the most readily obtained, and the most studied member of the series. Appropriate metathetical reactions permit other members of the series to be obtained.[61]

Figure 3

The structure of one isomer of trithiazyl trichloride, $N_3S_3Cl_3$[53]



The main point of interest (see p. 98) is that S_4N_3Cl has a characteristic pattern of infrared absorptions, and that the structure of the $S_4N_3^+$ ion has been determined[62,63] by X-ray analysis of its nitrate. The structure is



The ring is planar; the S-S bond is 2·06 Å; and all of the S-N bonds are 1·54 Å, within ± 0·04 Å. An analysis of the electronic spectra of this ion has led to the postulate that the bonding involves a ten-electron π-system delocalised over all the S-N bonds.[64]

The change in product resulting from a small change in the conditions of fluorination of S_4N_4 has already been noted. Similarly, if S_4N_4 is chlorinated by neat S_2Cl_2, or S_2Cl_2 in nitromethane, (rather than S_2Cl_2 in carbon tetrachloride, which leads to S_4N_3Cl, as already noted) the product is thiodithiazyl monochloride, S_3N_2Cl.[65] This last reaction, although of some interest for the reason just noted, and as being part of the chemistry of S_4N_4, is now mainly of academic interest, having been recently superseded by a more convenient preparation.[66]

Finally, note can be made of two halogenations of S_4N_4 involving elemental halogen. First, the preparation of trithiazyl monochloride, S_3N_3Cl, by the action of chlorine on a hot solution of S_4N_4 in chloroform has been described[65] - although attempts to reproduce the preparation have only once been successful.[56] Second, interaction of S_4N_4 and bromine in carbon disulphide leads[54] to a compound formulated as $(NSBr)_x$. This compound appears to be generally insoluble - thus precluding a molecular weight determination - and this property, together with its bronze-metallic colour, is taken to indicate that it is a high polymer.[55] As may be expected, these two compounds have been little studied.

It must be emphasised that it is not possible, within the scope of this Introduction, to do justice to the range, diversity and interest of sulphur-nitrogen-halogen chemistry: references to more exhaustive studies of this topic are given on p.23.

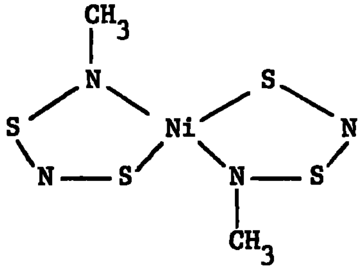
(iii) Significant recent developments in sulphur-nitrogen chemistry

Lines of work that seem promising as a result of work described in this thesis are noted at appropriate points in the Discussion. Other possibly fruitful lines of development may be inferred from the more recent publications of other workers in related fields.

Jolly and co-workers (Berkeley) have notably been preparing new M-N-S-Cl compounds. They have found[74] that reaction of $N_3S_3Cl_3$ (prepared by the "Cl_2 in CCl_4" route) with $Mo(CO)_6$ in CH_2Cl_2 leads to a material $MoS_3N_3Cl_3$, which is insoluble in solvents with which it does not react. (The analogous reaction with $Cr(CO)_6$ and $W(CO)_6$ gave materials of uncertain nature.) In the same work, they report that S_4N_4 and $Mo(CO)_6$ react in refluxing benzene to give an explosive material of composition

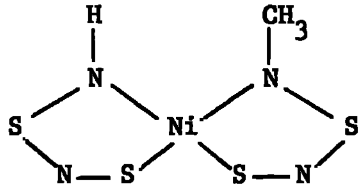
MoS_5N_5CO. Further, they have very recently prepared the adduct $S_2N_2 \cdot 2SbCl_5$,[79] and its structure has been determined by X-ray analysis.[75]

Weiss and co-workers (Heidelberg) have been developing the chemistry of organic derivatives of $Ni(S_2N_2H)_2$, and determining the structures of some of the more interesting derivatives. They have prepared[68] mono- and di-methylated, and mono-ethylated derivatives of $Ni(S_2N_2H)_2$ and have shown[68] the structure of $Ni(S_2N_2CH_3)_2$ to be

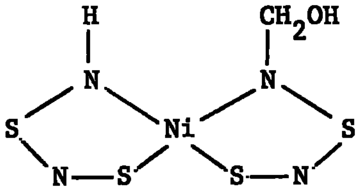


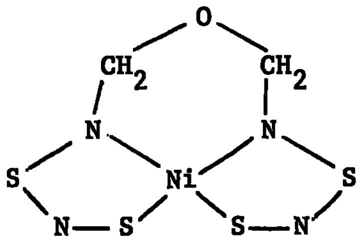
(i.e. trans: this result is in contrast to the structure found[70] for $Pt(S_2N_2H)_2$, which is cis.)

They have also established[80] that the structure of $Ni(S_2N_2H)(S_2N_2CH_3)$ is cis,

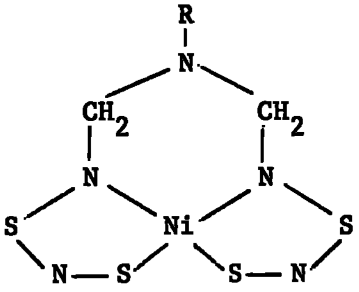


They have shown[69] that reaction of $Ni(S_2N_2H)_2$ with formaldehyde in acetone or methanol solution leads to compounds formulated as, respectively,

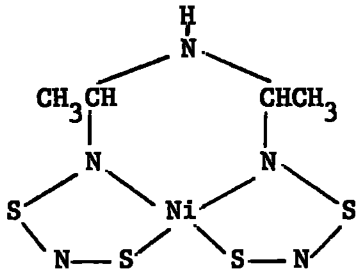




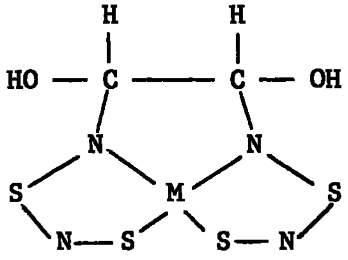
Presence of amines, RNH_2, as well as the formaldehyde led to compounds formulated as



The use of acetaldehyde and ammonia led to

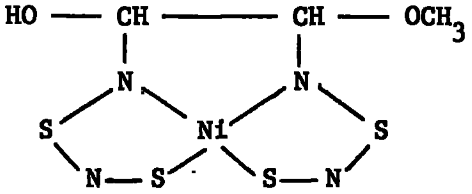


The action of glyoxal on $Ni(S_2N_2H)_2$ and its Co analogue led to

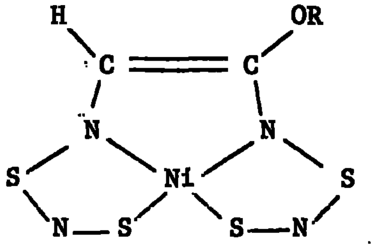


(M = Co, Ni)

Even more highly substituted compounds result when $Ni(S_2N_2H)_2$ and glyoxal react in the presence of alcohols:[71] products which may be obtained include mono-methyl and -ethyl ethers, and optically active di-ethers. The structure of one such mono-ethyl ether has been shown[72] to be



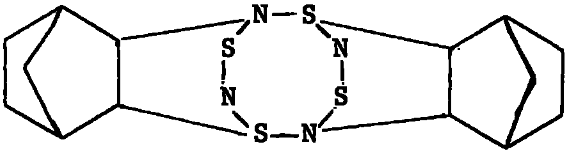
During chromatography on alumina, the di-ethers decompose (by elimination of methanol or ethanol) to the compounds



(The structure of the methyl derivative has been established by X-ray analysis.[73])

Becke-Goehring (Heidelberg) and co-workers have investigated the reactions of S_4N_4 with various olefins:[67] they have shown that S_4N_4 can behave as a diene, reacting as it does with bicycloheptene, bicycloheptadiene and cyclopentadiene to give the crystalline materials characterised as $S_4N_4 \cdot 2C_7H_{10}$, $S_4N_4 \cdot 2C_7H_8$ and $S_4N_4 \cdot 4C_5H_6$ respectively.

The structures they have proposed for these compounds are, respectively,



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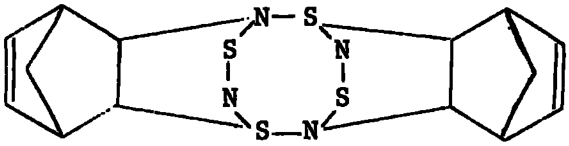

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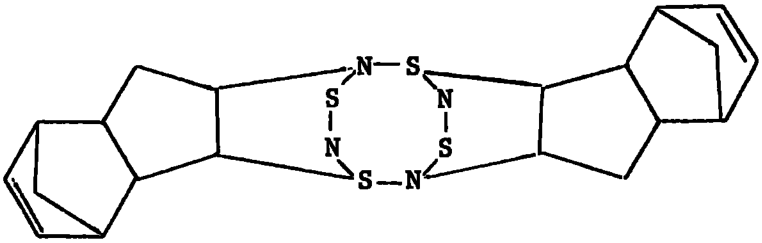

3

(iv) References to further reviews of areas of sulphur-nitrogen chemistry

The chemistry of sulphur nitrides, sulphur-nitrogen hydrides, sulphur-nitrogen oxides, sulphur-nitrogen halides and sulphur-nitrogen metal compounds has been exhaustively reviewed up to May 1967. Ref.31.

The chemistry of sulphur-nitrogen oxide-halides has been exhaustively reviewed up to July 1967. Ref.76.

A review covering important work on sulphur nitrides (including the $S_4N_3^+$ ion), sulphur-nitrogen halides, sulphur-nitrogen imides and their derivatives, amides of sulphur and their condensation products, conjugated sulphur-nitrogen chains and ligands, and special techniques for studying the constitution of sulphur-nitrogen compounds, has been made up to the end of 1966. Ref.77.

EXPERIMENTAL

Experimental

Handling techniques

Nearly all of the compounds dealt with were sensitive to oxygen and water to a greater or lesser degree, and consequently were handled either in a vacuum system or under an atmosphere of dry nitrogen. Traces of oxygen were removed from the nitrogen by passing over copper at 300°, and traces of water vapour by passing first through two traps cooled in liquid nitrogen, then over phosphorus pentoxide. Operations which were inconvenient or impractical under counter-current nitrogen were carried out in a glove box.

Analyses

Analyses were carried out either in the Department, or by Drs. Weiler and Strauss (Analysts), of Oxford.

Melting/Decomposition points

These were determined in sealed tubes.

Infrared spectra

Infrared spectra were recorded on Grubb-Parsons prism grating spectrophotometers; the Spectromaster and the GS2A were used for the range 4000-400 cm^{-1}, and the DM2/DB3 was used for the range 475-200 cm^{-1}. Samples of solids were prepared as Nujol mulls; liquids (both pure substances and solutions) were investigated either as contact films, or as samples of specific thickness in solution cells. The mull or liquid was supported between plates of sodium chloride, potassium bromide, or caesium iodide, whichever was appropriate. When excessive halogen exchange between sample and plates was likely, the sample was placed between thin polythene sheets which were then supported between the plates as usual.

The following symbols are used to denote the relative intensities of infrared absorptions: vs - very strong; s - strong; m - medium; w - weak; vw - very weak; also, sh - shoulder.

Mass spectra

Mass spectra were obtained with an A.E.I. MS9 mass spectrometer, from samples which were mounted on an inert support and were introduced by means of a direct insertion probe. An accelerating potential of 8 kV, 70 eV, was employed.

For brevity,relative intensities of peaks are referred to explicitly only when necessary for discussion.

Molecular weights

Molecular weights were determined cryoscopically in nitrobenzene. A conventional apparatus was used, designed to accommodate oxygen- and water-sensitive compounds under an atmosphere of dry nitrogen; this atmosphere was maintained by a steady counter-current flow of dry nitrogen.

Purification of solvents most frequently employed.

(Others are dealt with at the appropriate points in the main text).

Thionyl chloride.[83] Triphenyl phosphite (40 ml.) was added dropwise over 30 minutes to technical grade thionyl chloride (250 ml.), with vigorous stirring. The resulting mixture was fractionated up a twelve inch column packed with glass helices and connected to a reflux distillation head. The receiver was protected by a calcium chloride drying tube. Up to 60% of the thionyl chloride was distilled over, the first 10 ml. of distillate being discarded.

Thionyl chloride is not a particularly common solvent, so it is perhaps desirable to mention explicitly a few points regarding the techniques of handling it and its solutions.

The solvent has a substantial vapour pressure[84] at room temperature, and so since its vapour is harmful it is handled either in a fume chamber or in sealed containers. It is corrosive in general and it should particularly be borne in mind that both mercury and rotary pump oils are chlorinated by it; that silicone high vacuum grease - although still attacked by it - is generally more satisfactory than apiezon high vacuum grease; that stainless steel - frequently employed for syringe needles, etc. - is corroded by it; and finally that rubber tubing is steadily vulcanised by it. These damaging effects are displayed by both the vapour and the liquid, although they are naturally more rapid and severe with the neat liquid. When anything more than the most infrequent use of this compound is contemplated, techniques should be carefully designed to make due allowance for all of these points.

In addition, these notes are also generally applicable to related solvents containing S-Cl bonds, such as sulphuryl chloride, chlorosulphonic acid, sulphur dichloride and disulphur dichloride.

Nitrobenzene. AnalaR grade nitrobenzene (300 ml.) was fractionated at 1•5 mm. from a flask charged with glass wool, and fitted with a 24 inch column packed with glass helices. When the liquid refluxing at the head of the column ceased to become paler with time, the distillate thus far was discarded, and the bulk of the nitrobenzene distilling over subsequently at 68° was collected. Provision was made in the column head assembly for changing receivers under nitrogen, without disturbing the equilibrium of the column more than slightly. About 250 ml. of the distillate was collected, and redistilled exactly as before. The distillate finally resulting was stored in the dark over calcium chloride, under an atmosphere of dry nitrogen.

Hydrocarbons and diethyl ether. Technical or AnalaR grades (as appropriate) were dried by standing over excess sodium wire for at least one week before use.

Carbon tetrachloride and methylene dichloride. Technical or AnalaR grades (as appropriate) were dried over excess phosphorus pentoxide for at least 48 hours before use.

Reagent proportions

Reactions between tetrasulphur tetranitride and metal/metalloid/non-metal chlorides were carried out using one mole of tetrasulphur tetranitride per mole of metal/metalloid/non-metal, except in the preparation of Compound Two, p. 52. (cf. Discussion, p.134).

Reagent solutions

Thionyl chloride solutions of tetrasulphur tetranitride were always used as soon as they were prepared, unless otherwise stated. 40 ml. of thionyl chloride dissolves 1 gm. of tetrasulphur tetranitride at room temperature.

Secondary products of reactions

In reactions which yielded an insoluble main product, the supernatant liquid always yielded a quantity of a tar when pumped dry; reactions which yielded a soluble main product (or mixture of products) always yielded the appearance of a mixture of a tar and the solid product (or mixture of products) when the mother liquor was pumped dry. These tars and product-tar mixtures were always ignored, except where contrary comment is made; their yields tended to be about 10% by weight of the total.

Preparation of starting materials

Tetrasulphur tetranitride.[85]

Dry carbon tetrachloride (2 l.) was placed in a reaction vessel (5 l.) and disulphur dichloride (75 ml.) was added. The solution was stirred vigorously with a paddle-blade unit and dry chlorine was bubbled through briskly until there was a distinct colour of chlorine above the solution. (This occurred after about 40 min.). The reaction vessel was then cooled to about -5° in an ice-salt bath, and a slow stream of dry ammonia was cautiously passed. Initially, considerable quantities of ammonium chloride were generated by exothermic reaction, and several large vents from the reaction vessel were employed to ensure that outlets from the reaction vessel did not become completely blocked with the ammonium chloride. In order to ensure as high a yield of tetrasulphur tetranitride as possible, care was taken not to let the reaction vessel's temperature rise much above 5^{o}. The rate of formation of ammonium chloride decreased steadily with time, and the solution slowly changed (over one or two hours) to a thick suspension usually coloured yellow to reddish-brown. Passage of ammonia was stopped when the reaction mixture tended to have a colour something like salmon pink (usually after about two to six hours; normally after about four hours). Quantities of solvent were added intermittently to compensate for evaporation losses. When reaction was complete, the contents of the reaction vessel were slurried with water (1·5 l.) until no further decrease in the quantity of the suspension occurred. The residual solid was filtered off, and allowed to dry in the air. The dried solid (usually coloured brown, orange, or green) was agitated with dry diethyl ether (500 ml.) for ten minutes to extract heptasulphur imide. The resulting crude tetrasulphur tetranitride was extracted with dry benzene in a Soxhlet assembly, and was finally recrystallised from dry benzene. The overall yield of this preparation is notoriously variable, but a typically good figure is 30 gm. M.p. = 179^{o}.

Tetrasulphur tetranitride is a very endothermic compound (127·6 kcal. $mole^{-1}$; [2] which can detonate unpredictably, and with considerable violence; consequently it is advisable to take various safety precautions, as follows. The crude compound should never be kept about longer than necessary;

explosions seem to be most frequent with impure material. Storage of the compound should be avoided as far as possible; when storage is necessary, the time involved should not exceed a few months, as the compound slowly decomposes with time. Batches of not more than 10 gm. should be used for storage, and storage should always be in a screw-top container, since grinding (e.g. between ground glass surfaces, or between a cork and the neck of a container) is hazardous. The compound should not be touched with anything metal, since a spark of static electricity could occur, causing detonation. Heating above 100° is undesirable.

Tetra-aquoiron dichloride

Electrolytic grade iron powder (10 gm.) was dissolved cautiously in analysis grade concentrated hydrochloric acid, under an atmosphere of nitrogen. After dissolution was completed, crystallisation from the solution between 12·3° and 72·6°[86,87] yielded the tetra-aquoiron dichloride. Yield about 25 gm. The salt was stored under nitrogen.

Copper(I) chloride[88]

AnalaR grade diaquocopper dichloride (2 gm.) was dissolved in water (2 ml.), and to the stirred solution was added at room temperature a solution of anhydrous sodium sulphite (1·52 gm.) in water (10 ml.). The copper(II) chloride solution turned a dark brown colour, and then white copper(I) chloride slowly precipitated: the supernatant liquid retained a faint green colour. This mixture was poured into a solution of anhydrous sodium sulphite (0·2 gm.) and concentrated hydrochloric acid (0·4 ml.) in water

(200 ml.); the resulting mixture was stirred well, and allowed to stand until the copper(I) chloride had completely settled out. The supernatant liquid was decanted, and the precipitate quickly washed onto a sintered glass filter with a dilute solution of sulphurous acid. Care was taken that a layer of liquid covered the salt at all times. Finally the salt was washed successively with five portions of glacial acetic acid, three of absolute alcohol, and six of anhydrous ether: 10 ml. of solvent was used for each washing. After most of the last portion of ether had been sucked off, the salt was quickly transferred to an oven, and dried for 25 minutes at 90°. The salt was stored under nitrogen. Yield 1 gm.

Tetrasulphur tetranitridoaluminium trichloride[29,89]

Solid tetrasulphur tetranitride (2·76 gm.) was added at room temperature to finely ground aluminium trichloride (2·00 gm.), suspended by vigorous stirring in carbon tetrachloride (25 ml.). A dark red precipitate immediately started to form in the mixture. After 24 hours the precipitate was filtered off, washed with carbon tetrachloride, and pumped dry. Yield 4·7 gm. (Theory, 4·76 gm.).

Tetrasulphur tetranitridotantalum pentachloride[29,89]

Solid tetrasulphur tetranitride (1·54 gm.) was added at room temperature to tantalum pentachloride powder (supplied by Koch-Light) (3·00 gm.), suspended by vigorous stirring in carbon tetrachloride (or methylene dichloride) (25 ml.). A dark red-brown precipitate immediately started to form in the mixture. After 24 hours the precipitate was filtered off, washed with carbon tetrachloride (or methylene dichloride), pumped dry, and recrystallised from methylene dichloride (in which it is sparingly soluble). Overall yield 4·3 gm. (Theory, 4·54 gm.).

Reactions Investigated

Reaction between Tetrasulphur tetranitride and Magnesium chloride in Thionyl chloride

Finely ground hexa-aquomagnesium chloride (0•54 gm.) and thionyl chloride (20 ml.) were stirred at room temperature for two hours, then at reflux for one hour, to dehydrate the salt. The mixture was allowed to cool to room temperature, and more thionyl chloride (20 ml.) was added, followed by tetrasulphur tetranitride (0•49 gm.). The resulting mixture was subsequently held at 40° for 48 hours, with stirring; during this time its appearance (an off-white suspension in a clear orange solution) did not change. The solid was filtered off, washed with thionyl chloride and pentane, and finally pumped dry. Its near infrared spectrum showed only two absorptions,of medium intensity, attributable to H_2O and NH_4^+: on this basis the solid was presumed to be essentially unreacted magnesium chloride, and the reaction was not investigated further.

Reaction between Tetrasulphur tetranitride and Cadmium(II) chloride in Thionyl chloride

Finely ground $CdCl_2.2{\cdot}5H_2O$ (0•57 gm.) and thionyl chloride (20 ml.) were stirred at room temperature for half an hour, then more thionyl chloride (20 ml.) was added and the mixture was refluxed for one hour. A solution of tetrasulphur tetranitride (0•46 gm.) in thionyl chloride (15 ml.) was added to the suspension of anhydrous cadmium(II) chloride, whereupon the latter (which had changed from white at room temperature to dirty pink on refluxing) rapidly turned blue-green: the solution was pale orange-red. The stirred mixture was maintained at 42° for 48 hours, after which time the off-white to pale-green solid was filtered off, washed with thionyl chloride and pentane, and pumped dry. A near infrared spectrum of the solid showed two moderately strong bands, attributable to H_2O and NH_4^+, and a number of weak broad absorptions which could not be assigned. On this basis the solid was presumed to be essentially unreacted cadmium(II) chloride, and the reaction was not investigated further.

Reaction between Tetrasulphur tetranitride and Germanium tetrachloride in Thionyl chloride

Tetrasulphur tetranitride (0·49 gm.) was dissolved in a vigorously stirred solution of germanium tetrachloride (0·30 ml., 0·55 gm.) in thionyl chloride (25 ml.). The appearance of the resulting pale orange solution was only that of a dilute solution of tetrasulphur tetranitride in thionyl chloride. Precipitation of a yellow solid soon commenced, and a moderate quantity formed over the 70 hours for which the mixture was held at 42°. This solid was filtered off, and an additional quantity of yellow solid was subsequently crystallised from the supernatant liquid after pumping off some solvent. The quantities of solid were too small to risk any loss by washing. Near infrared spectra of the yellow solids established that both were thiotrithiazyl chloride, S_4N_3Cl. It was therefore presumed that there had been little if any reaction between the germanium tetrachloride and the tetrasulphur tetranitride; the germanium tetrachloride had probably been lost unnoticed when the supernatant liquid was concentrated down; the tetrasulphur tetranitride apparently reacted in isolation with the thionyl chloride in the well-established manner[57] to yield thiotrithiazyl chloride.

Near infrared spectrum of the yellow solid, thiotrithiazyl chloride: 1167s, 1131vw, 1002vs, 802w, 722w, 684s, 640w, 609w, 566s, 523vw, 474s(sh), 468vs, 453m. Previously reported spectrum, see ref.57.

Reaction between Tetrasulphur tetranitride and Lead dichloride in Thionyl chloride

A mixture of lead dichloride powder (0·70 gm.) and thionyl chloride (20 ml.) was refluxed for one hour, then cooled to 25°. A solution of tetrasulphur tetranitride (0·46 gm.) in thionyl chloride (20 ml.) was added: there was no sign of reaction then, or during the subsequent 71 hours for which the stirred mixture was kept at 45°. After this time the solid was filtered off, washed with thionyl chloride and pentane, and pumped dry. A near infrared spectrum of the pale yellow solid showed only medium intensity absorptions attributable to H_2O and NH_4^+: on this basis the solid was presumed to be essentially unreacted lead dichloride, and the reaction was not investigated further.

Reaction between Tetrasulphur tetranitride and "Titanium trichloride"* in Thionyl chloride

A mixture of titanium trichloride (0·60 gm.) and thionyl chloride (10 ml.) was stirred at room temperature; after about 15 minutes, the violet solid had dissolved to yield a pale yellow, slightly cloudy solution. More thionyl chloride (10 ml.) was added and a trace of insoluble material was filtered off (a number 4 sinter was required). A solution of tetrasulphur tetranitride (0·63 gm.) in thionyl chloride (30 ml.) was added to the filtered solution, resulting in the instant formation of a deep blue-green colour. Over the next few hours a yellow solid was precipitated, while the intensity of the solution's colour decreased considerably. The mixture was held at 43° for 42 hours, after which time the solid was filtered off, washed with thionyl chloride and pentane, and pumped dry.

Properties of the yellow solid:

(a) Analysis - S = 25·85; N = 11·20; Cl = 43·25%. $S_2N_2TiCl_3$ requires S = 26·03; N = 11·37; Cl = 43·17%.

(b) Commenced darkening at 238°, finally melting sharply at 252° to a clear red-orange liquid.

(c) Infrared spectrum: 1259vw, 1179w, 1087vw, 1018m, 939vw, 848vs(sh), 840vs, 818s, 737w, 722w, 678w, 573w, 480s, 475s, 472s(sh), 467m(sh), 417s(sh), 392vs, 339m, 315m, 304w(sh), 279vw, 253vw, 248vw, 222w, 208vw, 200w.

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* cf. "Discussion", p.120.

(d) Mass spectrum: nothing below 120°; at 120°, 140°, 160°, 180°, 200° - S, Cl, SN, Ti, S_2, S_2N, TiCl, S_2N_2, $TiCl_2$, $TiCl_3$, $TiCl_4$. Additionally S_4N_2 was present at 180° and 200°, and S_3N was present at 200°. The spectrum faded out almost completely at 240°.

Reaction between Tetrasulphur tetranitride and Hafnium tetrachloride in Thionyl chloride

Hafnium tetrachloride (0•88 gm.) (supplied by Koch-Light) was dissolved in thionyl chloride (20 ml.) at 60°, and a solution of tetrasulphur tetranitride (0•51 gm.) in thionyl chloride (20 ml.) was added, with the immediate formation of an intense blue-green colour. Precipitation of black tarry globules, and shortly afterwards of a yellow solid as well, rapidly commenced; then over about four hours the tar disappeared, and the yellow solid gained considerably in bulk. The reaction mixture was maintained at 60° for 20 hours then the solid was filtered off, washed with thionyl chloride, and pumped dry.

Properties of the yellow solid:

(a) Analysis - S = 15•80; N = 7•29; Cl = 35•50%. $S_2N_2HfCl_4$ requires S = 15•54; N = 6•79; Cl = 34•37%.

(b) Melted at 135-136°, with apparent decomposition.

(c) Infrared spectrum: 1124vw, 1020w, 1003w, 940vs, 854s, 836m(sh), 827w(sh), 780vw(sh), 771w(sh), 759m(sh), 756m(sh), 746s, 740s(sh), 722s(sh), 717s, 694w(sh), 678vw(sh), 617vw, 572s, 565vw(sh), 477m, 464s, 458w(sh), 417s, 374w, 337m, 318m(sh), 299s, 279s(sh), 248m, 222w, 200w.

(d) Mass spectrum: nothing below 130°; at 135° - S, Cl, SN, S_2, S_2N, S_2N_2, S_3N, S_3N_2, S_3N_3, S_4N_2, S_4N_4; at 160° - S, Cl, SN, S_2, S_2N, SNCl, S_2N_2, S_3N, S_3N_2, S_3N_3, S_4N_2; at 220° - S, Cl, SN, S_2, S_2N, S_2N_2, S_3N_2, S_4N_2, Hf, HfCl, $HfCl_2$, $HfCl_3$, $HfCl_4$; at 265° - S, Cl, SN, S_2, S_2N, S_2N_2, S_3N, S_4N_2. The spectrum had faded out almost completely at 315°.

Reaction between Tetrasulphur tetranitride and Vanadium trichloride in Thionyl chloride

A stirred mixture of vanadium trichloride (0•95 gm.) (supplied by Koch-Light) and thionyl chloride (10 ml.) was refluxed for five minutes, then cooled to 40°. A solution of tetrasulphur tetranitride (1•13 gm.) in thionyl chloride (50 ml.) was added, whereupon the initial appearance of a violet suspension in a colourless liquid rapidly began to change to that of a very dark (almost black) solid in a dark olive-green solution; after half an hour these colours were very pronounced. The reaction mixture was maintained at 41° for 79 hours, then the dark violet solid was filtered off, washed with thionyl chloride and pentane, and pumped dry. The colour of the supernatant liquid at this stage was light green, but had such an intensity as to appear almost black; on standing for some tens of hours at room temperature a quantity of orange-brown crystals was deposited from it, and its colour became red. An attempt was made to improve the apparent quality of these crystals by redissolving them, and allowing the solution to cool in a water-bath, so that crystallisation could be more slow. Small crystals started to deposit between 70° and 60°; on further cooling they slowly disappeared, until at 37°, none were to be seen; the still cooling solution was allowed to stand overnight, when crystals reappeared. These crystals were filtered off, washed with thionyl chloride and pentane, and pumped dry.

Properties of the insoluble solid:

(a) Analysis - S = 10·85; N = 5·05; Cl = 48·90%. SNV_2Cl_4 requires S = 11·07; N = 4·83; Cl = 48·94%.

(b) Between about 120° and about 140° its colour changed to dark green; above 250°, a green liquid sublimed on to the cooler parts of the melting-point tube. Since the solid had presumably decomposed, heating was not continued beyond 260°; there had been no true melting-point below this temperature.

(c) Infrared spectrum: 1263w, 1199w, 1096w, 1020w(sh), 1008m, 852s, 838vs, 802m, 733vw(sh), 721w, 683w, 569w, 473s, 463m, 457vw(sh), 385w, 357w(sh), 345vw(sh), 299vs, 259vw, 255vw, 248vw, 240w, 227vw, 222vw, 212w, 203vw(sh).

(d) Mass spectrum: nothing below 140°; at 145° - S, Cl, SN, V, S_2, S_2N, VCl, S_2N_2, S_3N, VCl_2, S_3N_2, V_2Cl, (? - tentative assignment), S_4N_2, $SNVCl_2$ (? - tentative assignment), V_2Cl_2 (? - tentative assignment); additionally, at 170° the peaks SNCl and SNVCl (? - tentative assignment) are present, and at 200° SNCl and SNVCl (? - tentative assignment) are again present and S_4N_2 and $SNVCl_2$ (? - tentative assignment) are absent. The peaks V_2Cl, V_2Cl_2, SNVCl and $SNVCl_2$ are all of moderate intensity; the assignments are tentative in the absence of accurate masses.

Properties of the soluble solid:

(a) Analysis (cf. "Discussion", p. 92) - S = 41·40; N = 21·70; Cl = 18·25%. S_4N_3Cl requires 62·34; N = 20·43; Cl = 17·23%.

(b) Darkened from about 120°, then melted very sharply at 183° (in a "burst", as if boiling from a superheated condition); thiotrithiazyl chloride decomposes at 170° *in vacuo*.

(c) Infrared spectrum: 1261vw, 1167s, 1131vw, 1095w(sh), 1002vs, 802w, 722w, 684s, 639w, 609w, 566s, 524vw, 474s(sh), 468vs, 453m, 328vs, 303w(sh), 290vw, 279w, 248s, 222vw(sh), 210w, 200vw, i.e. that of thiotrithiazyl chloride (Previously reported spectrum, see 57).

(d) Mass spectrum: not recorded, as the compound was sufficiently identified by its infrared spectrum.

Reaction between Tetrasulphur tetranitride and Molybdenum pentachloride in Thionyl chloride

A solution of tetrasulphur tetranitride (1·40 gm.) in thionyl chloride (60 ml.) was added to molybdenum pentachloride (2·03 gm.) (supplied by Koch-Light), with stirring. The green colour immediately produced rapidly changed to a bright orange-red, then more slowly to the appearance of a red/green dichroic solution. After 30 minutes, the reaction mixture consisted of a dark solid in a red-orange solution. After 4·5 hours, the colour of the supernatant liquid was pale yellow-orange, and after 7 hours the colour of the solid was definitely red-brown. The reaction mixture was held at 45° for 92 hours (although reaction was probably complete by 44 hours, and almost certainly so by 68 hours), when the solid was filtered off, washed with thionyl chloride, and pumped dry.

Properties of the insoluble, red-brown, solid:

(a) Analysis - S = 16•35; N = 14•35; Cl = 35•20%. $S_2N_4MoO_2Cl_4$ requires S = 16•45; N = 14•37; Cl = 36•37%. $S_2N_4MoO_3Cl_4$ requires S = 15•80; N = 13•80; Cl = 34•94%. The formulation $S_2N_4MoO_2Cl_4$ has been tentatively adopted.

(b) Darkened to black at 245°-250°, then turned pasty at 270°-275°, without melting: it was presumed that the compound was by then substantially decomposed, and so it was not studied beyond 285°.

(c) Infrared spectrum: 1259vw, 1089vw, 1028vw, 951vs, 942vs(sh), 810vw, 784m, 738vw, 721vw, 692vw, 671w(sh), 662vs, 639w, 555s, 552s, 546s, 410vs, 357vs, 345vs(sh), 338vs, 322s, 305w(sh), 291vw, 275s, 244vw, 220vw.

(d) Mass spectrum: nothing below 180°; at 190° - S, Cl, SN, SO, S_2, S_2N (weak spectrum); at 270° - S, Cl, SN, SO, S_2, S_2N, S_2N_2, S_3N, S_3N_2, S_4N_2.

Reaction between Tetrasulphur tetranitride and Tungsten hexachloride in Thionyl chloride

A solution of tetrasulphur tetranitride (0•62 gm.) in thionyl chloride (40 ml.) was added with stirring to tungsten hexachloride (1•30 gm.) (supplied by Koch-Light). The tungsten hexachloride rapidly dissolved, and simultaneously a transient orange-red-brown colour was formed. After 1•5 hours the reaction mixture consisted of a very dark solid suspended in an intensely dark, deep red solution. The reaction mixture was maintained at 43° for 70 hours, then the purple-violet solid was filtered out of the still deep red supernatant liquid, washed with thionyl chloride, and pumped dry.

Properties of the insoluble solid:

(a) Analysis (cf. "Discussion") - S = 19•00; N = 11•21; Cl = 28•70%. $S_2N_4WO_2Cl_4$ requires S = 13•42; N = 11•73; Cl = 29•68%.

(b) Blackened at about $200-220^{\circ}$, then abruptly melted to a black tar at 268°.

(c) Infrared spectrum: 1339vw, 1300vw, 1157vw, 1126vw, 1068vw, 1053vw(sh), 1020w(sh), 1003vs, 984m(sh), 964s, 824w, 797s, 792s(sh), 781s, 767w(sh), 739vw, 719vw, 701m, 694m, 666w(sh), 655m, 643w(sh), 552m, 524w(sh), 519m(sh), 516m, 514m(sh), 507w(sh), 405m, 341vs, 333vs, 315s, 296s, 282vw(sh), 279vw, 264w, 254vw, 246vw, 226vw.

(d) Mass spectrum: nothing below 170°; at 180° - S, Cl, SN, SO, S_2, SNCl, S_2N_2 (very weak spectrum); at 240° - S, Cl, SN, SO, S_2, SNCl, S_2N_2; at 300° - S, Cl, SN, S_2, S_2N, SNCl, S_2N_2.

Reaction between Tetrasulphur tetranitride and Cobalt(II) chloride in Thionyl chloride

A mixture of finely ground hexa-aquocobalt(II) chloride (0•60 gm.) and thionyl chloride (20 ml.) was stirred at room temperature for 45 minutes, then at reflux for one hour, by which time the colour of the hydrated Co^{+2} ion had been replaced by the bright azure of the anhydrous ion. The mixture was cooled to room temperature, and a solution of tetrasulphur tetranitride (0·46 gm.) in thionyl chloride (20 ml.) was added; the solid rapidly turned a very dark green, then over about 1·5 hours became paler in colour; the supernatant liquid had a pale orange-brown colour. The reaction mixture was maintained at 40^{o} for 43 hours, then the pale blue-green solid was filtered off, washed with thionyl chloride and pentane, and pumped dry.

Properties of the solid:

(a) Near infrared spectrum: 1261vw, 1186w(sh), 1179m, 1144vw, 1135vw(sh), 1089w, 1025s, 1013w(sh), 803w, 733vw, 722vw, 682m, 670w, 562m, 468m.

(b) Mass spectrum: at 215^{o} - S, Cl, SN, Co (? - tentative assignment), S_2, CoN (? - tentative assignment), S_2N, SNCl, S_2N_2, CoCl (? - tentative assignment), S_3N, S_3N_2, S_3N_3, S_4N_2, S_4N_4. The peaks Co, CoN, and CoCl are all of very low intensity; the assignments cannot safely be more than tentative in the absence of accurate masses.

On the basis of the apparent course of the reaction, and of the two spectra, the blue-green solid appeared to be essentially identical with the previously characterised[31] compound $SNCoCl_2$, and so the reaction was taken to be reproducible.

Some attempts were made to find a suitable solvent for the compound. Diethyl ether did not appear to either dissolve or decompose it, either at room temperature or at reflux. Tetrahydrofuran (freshly distilled from lithium aluminium hydride, and kept under dry nitrogen) appeared to dissolve the compound at room temperature, although not to any useful extent; at reflux, the compound appeared to dissolve with decomposition. Pyridine (distilled onto sodium hydroxide pellets, dried over them for a week before use, and kept under dry nitrogen) appeared to decompose the compound immediately at room temperature, giving a black tar.

Reaction between Tetrasulphur tetranitride and Copper(I) chloride[88] in Thionyl chloride

A mixture of copper(I) chloride (0•32 gm.) and thionyl chloride (20 ml.) was refluxed for 1•5 hours, then allowed to cool to room temperature, when a solution of tetrasulphur tetranitride (0•59 gm.) in thionyl chloride (20 ml.) was added. There was no immediate sign of reaction, but over about 15 hours the colour of the suspension changed from its initial dirty brown, through a green-khaki, to a rich umber; similarly, over the first half hour the supernatant liquid paled from red to orange. The reaction mixture was held at 42° for 91 hours, then the solid was filtered off, washed with thionyl chloride and pentane, and pumped dry. During this last operation, the solid became olive in colour. The infrared spectrum of the residue from pumping down the mother liquor was tentatively interpreted as that of impure $S_3N_2O_2$, thiodithiazyl dioxide.

Properties of the olive solid:

(a) Analysis (cf. "Discussion", p.119) - S = 14•69; N = 6•27; Cl = 38•55%. $S_2N_2Cu_3Cl_5$ requires S = 13•94; N = 6•09; Cl = 38•53%.

(b) Melting/decomposition point not determined, in view of (a).

(c) Infrared spectrum: 1309vw, 1261vw, 1192vw(sh), 1181w, 1143vw, 1027m, 891vw, 869m, 850w(sh), 800vw, 722vw, 684w, 674vw(sh), 641vw, 615vw, 570w, 468m, 394w, 357vw(sh), 298s, 267vw, 256vw, 247vw, 226vw.

(d) Mass spectrum: at 300° - S, Cl, SN, Cu (? - tentative assignment), S_2, S_2N_2, S_4N_2 (weak spectrum). The peak Cu is of low intensity; the assignment is tentative in the absence of an accurate mass.

Reaction between Tetrasulphur tetranitride and Mercury(I) chloride in Thionyl chloride

A mixture of mercury(I) chloride (0•59 gm.) and thionyl chloride (20 ml.) at 43° was stirred for half an hour, then a solution of tetrasulphur tetranitride (0•47 gm.) in thionyl chloride (20 ml.) was added. The initially granular white solid rapidly flocculated to a considerable extent, and appeared to turn pale yellow; the supernatant liquid rapidly became pale orange-brown in colour. The stirred reaction mixture was maintained at 43° for 70 hours, then the lemon yellow solid was filtered off, washed with thionyl chloride and pentane, and pumped dry. A small quantity of bright yellow, well formed, cube shaped single crystals was sublimed (over a couple of hours at room temperature and 0•001 mm. pressure) out of the residue from pumping the supernatant liquid to dryness.

Properties of the insoluble solid:

(a) Analysis - S = 16·91; N = 7·10; Cl = 20·65%. $S_2N_2HgCl_2$ requires S = 17·63; N = 7·71; Cl = 19·50%.

(b) Darkened from 159°, melted at 169°.

(c) Infrared spectrum: 1261vw, 1192w, 1176m, 1156vw(sh), 1134vw, 1089vw, 1028m(sh), 1017s, 816vw(sh), 800w, 721vw, 686vw(sh), 681m(sh), 677m, 644vw, 611vw, 579vw(sh), 573w(sh), 563m, 524vw, 491w(sh), 475s, 444w, 426vw, 350m, 326vs, 308s, 282vw, 276vw, 257m, 224vw, 213vw.

(d) Mass spectrum: at 115° - S_2N_2, Hg (doubly charged), S_3N_2, $HgCl_2$ (doubly charged), S_3N_3, Hg, HgCl, $HgCl_2$, $SNHgCl_2$, $S_2N_2HgCl_2$ (spectrum not scanned below mass 90); at 135° - S, Cl, SN, S_2, S_2N, SNCl, S_2N_2, Hg (doubly charged), S_3N, S_3N_2, $HgCl_2$ (doubly charged), S_3N_3, S_4N_2, Hg, HgCl, $HgCl_2$, $SNHgCl_2$, $S_2N_2HgCl_2$; at 240° - S, Cl, SN, S_2, S_2N, S_2N_2, Hg (doubly charged), S_3N_2, Hg, $HgCl_2$, $SNHgCl_2$, $S_2N_2HgCl_2$, $S_3N_3HgCl_2$, $S_4N_4HgCl_2$ (rather weak spectrum, except for the two Hg peaks).

Properties of the volatile solid:

(a) Near infrared spectrum: 1277vw, 1235w(sh), 1176vs, 1093m(sh), 1042vs, 1018w, 997m, 752vw, 733vw(sh), 718m, 685vs, 656s, 555s, 503s, i.e. that of thiodithiazyl dioxide (previously reported spectrum, see (90)).

(b) Mass spectrum: at 205° - N, O, S, SN, S_2, S_2N, S_2N_2, S_2NO, S_2N_2O, S_2NO_2, S_3N_2, S_3N_3, $S_3N_2O_2$, S_4N_4. Note - the peaks N and O could be of atmospheric origin, rather than from the compound; S_2NO_2 is not distinguishable from S_3N in the absence of an accurate mass; and finally S_3N_2, S_3N_3 and

S_4N_4 are attributable to thermal decomposition of the compound. After allowance is made for the last of these points, the spectrum becomes the same as that previously reported[31] for thiodithiazyl dioxide.

Some attempts were made to find a suitable solvent for the compound $S_2N_2HgCl_2$. Refluxing pentane apparently neither dissolved nor decomposed it. Refluxing methylene dichloride dissolved it slightly, without any sign of decomposition, but the solubility was not of a useful extent. Refluxing benzene appeared to dissolve it to a significant extent, but only with decomposition. Diglyme (freshly distilled from an excess of phosphorus pentoxide, and stored under dry nitrogen) appeared to dissolve it fairly readily at room temperature, and more readily still at reflux, but in both cases only with decomposition.

The solubility in nitrobenzene was studied in a little more detail (cf. "Discussion"). An estimated 0·2 gm. of $S_2N_2HgCl_2$ was stirred at room temperature with 5 ml. of nitrobenzene; the solvent rapidly developed a greenish colour. Over about 15 minutes this colour intensified until the solvent was sky-blue by light transmitted through a few millimetres, and intensely blue-green when viewed in bulk. The extent of dissolution of the $S_2N_2HgCl_2$ was too small to be detectable by eye, even when another 5 ml. of solvent was added. A near infrared spectrum of this solution (0·1 mm. path length) showed no band capable of being correlated with a band at 555 cm^{-1} shown by solutions of tetrasulphur tetranitride in the same solvent.

A sample of $S_2N_2HgCl_2$ was exposed to air for 24 hours, then its near infrared spectrum was recorded: this spectrum was essentially identical to that tabulated above for a sample of the compound handled under rigorously oxygen- and water-free conditions. The only differences between the two spectra are that in the case of the sample exposed to air the band 1261vw is absent; the band 1192w is decreased in intensity to "vw"; the bands 1089vw, 816vw(sh), and 800w are absent; a band 734vw(sh) appears; and the band 721vw is increased in intensity to "w". The bands 1261vw, 1089vw, 816vw(sh) and 800w can be fairly confidently attributed to trace contamination by silicone grease, and so almost certainly do not themselves reflect any deterioration of the $S_2N_2HgCl_2$; less certainly, the new and the intensified bands could be attributed to silicone grease decomposition products; finally the band 1192w/vw could be tentatively attributed to silicone grease or some other trace contaminant already partly degraded in some way. On this basis $S_2N_2HgCl_2$ appears to be almost completely (if not totally) air-stable and is hence unique* among the new compounds described in this "Experimental" section; the other compounds dealt with all deteriorate visibly in air, many within seconds, most within minutes, and all within a few hours at most. (cf. "Discussion", p.113).

* But see pp.154, 155 re. later discovery.

Reactions between Tetrasulphur tetranitride and Aluminium trichloride in Thionyl chloride

One

Aluminium trichloride (2·00 gm.) was dissolved in thionyl chloride (30 ml.), and any traces of insoluble material were filtered off. The resulting solution was refluxed for one hour, allowed to cool to 65-70°, and then a solution of tetrasulphur tetranitride (2·80 gm.) in thionyl chloride (120 ml.) was added. A red-brown colour was immediately produced, then during a few minutes this disappeared as the solution developed an intensely dark, red/green dichroic colouring. No deep blue colour was noticed between these two conditions (contrast with Reaction Two). The reaction mixture was maintained at 60° for 21 hours, although no change was noticed after half an hour's reaction time. The volume of solution was then reduced to about 10 ml. by pumping off solvent, precipitated solute was redissolved at reflux, and the solute was allowed to recrystallise from the solution. The resulting yellow to yellow-brown crystals were filtered off, washed with thionyl chloride, and pumped dry. Finally they were recrystallised to constant melting point.

The resulting pale yellow, glistening plates of Aluminium Compound One were exceedingly soluble in refluxing thionyl chloride (solubility was estimated to be roughly 2·5 gm. per 10 ml.) and were very soluble even at room temperature (solubility was estimated to be roughly 1 gm. per 10 ml.). The solutions were intensely dark, and red/green dichroic. Crystallisation from very concentrated solutions was not easy: such solutions could apparently exist for at least several days at room temperature without crystallising, although they were (nominally at any rate) considerably supersaturated. Seeding induced crystallisation in such solutions without any trouble, but crystallisation still tended to proceed with surprising slowness. Mechanical shock (such as vigorous stirring) could usually induce crystallisation, but under these conditions the solute would come out as an unmanageable sludge. This tendency to ready supersaturation could be tentatively attributed (in part at least) to the relatively high viscosity (compared with the pure solvent) possessed by these strong solutions. Recrystallisation from only moderately concentrated solutions was generally straightforward. For the reasons just noted, crystallising solutions were always left at least overnight, and whenever possible for one or two full days, before being handled. (These characteristics and remarks apply also to any thionyl chloride solutions of Compound Two which contain significant quantities of Aluminium Compound One).

If desired the overall yield of Aluminium Compound One can be increased somewhat by appropriately modifying the fractionation process to be described in Reaction Two, but experience suggests that the returns do not justify the effort involved: it is probably simpler, and certainly far less tedious, to repeat the process described earlier. The final yield of constant melting crystals of Aluminium Compound One was estimated to be about one gram.

Properties of Aluminium Compound One (cf. "Discussion", p.128):

(a) Analysis - S = 20·65, 28·97; N = 8·24, 8·59; Cl = 50·50, 54·61, 58·1; Al = ?. $S_2N_2AlCl_5$ requires S = 21·64; N = 9·45; Cl = 59·80; Al = 9·10%.

(b) Softened from 80^{o}; slowly started to melt locally at 85^{o}; melted relatively sharply and in bulk at $88\text{-}89^{o}$, to a black liquid.

(c) Infrared spectrum: 1239vw, 1170vw, 1059vw(sh), 1033w, 1012w, 988vw, 967w, 942vs, 784vw(sh), 765m, 745s, 716s, 695w, 685w, 574m, 571m, 529s(sh), 508vs(sh), 489vs, 477vs, 461vs, 423s, 381s, 319m, 306s. Any weak absorptions occurring below 227 cm^{-1} may conceivably have been obscured by a rising base-line.

(d) Mass spectrum: nothing below 70^{o}; at 80^{o} - S, Cl, SN, S_2, SCl, S_2N, SNCl, S_2N_2, S_2Cl, SCl_2, S_2Cl_2 (weak spectrum); at 115^{o} - S, Cl, SN, S_2, SCl, S_2N, SNCl, S_2N_2, S_2Cl, SCl_2, S_3N, S_3N_2, S_2Cl_2, S_4N_2.

(e) Molecular weight: 161, 161.

A sample of the compound (estimated 0·1-0·2 gm.) was dissolved in nitrobenzene (10 ml.). The near infrared spectrum of the resulting solution (0·1 mm. path length) showed a weak absorption at 554 cm^{-1} which corresponded to an absorption at 555 cm^{-1} shown by solutions of tetrasulphur tetranitride in the same solvent.

This particular compound was exceedingly sensitive to oxygen and/or water; despite all precautions it appeared to be impossible to avoid deterioration of crystal surfaces during handling.

Two. Preparation of the raw mixture containing Compound Two

Aluminium trichloride (1·40 gm.) was dissolved in thionyl chloride (80 ml.), and any traces of insoluble material were filtered off. The resulting solution was refluxed for one hour, cooled to 30-35°, and then solid tetrasulphur tetranitride (2·00 gm.) was added with stirring. Initially reddish streaks trailed off the tetrasulphur tetranitride, subsequently to colour the whole reaction mixture. Over the succeeding few minutes the colour of the mixture gradually altered from red-brown to purple, before rapidly changing to a deep blue; this blue colour lasted for some two hours. At about four hours reaction time the solution was blue-green, then it finally went through an olive colour (at about eight hours reaction time) to a red/green dichroic condition. With the exception of the initial red-brown, all of the colours were intense. The reaction mixture was maintained at 35° for 48 hours. After this time the reaction mixture was pumped down to about 10 ml., precipitated solute was redissolved at reflux, and then the solution was allowed to stand overnight at room temperature. The resulting crystals were filtered out of the mother liquor, washed with more thionyl chloride, and pumped dry. The residue from pumping the mother liquor to dryness was redissolved at reflux in about 5 ml. of solvent, and the crystallisation and extraction process was repeated. Finally the same sequence was repeated with a recrystallisation from about 2 ml. of solvent. The crystallised batches of solute were then combined, and fractionated according to the process outlined below.

The crystallisate

Two compounds could be isolated in substantial yield from the crystallisate, (a) the major product (Compound Two) which was the subject of this reaction (obtained in estimated 60-70% proportion of total compound yield), and (b) the minor product (Aluminium Compound One) which was the subject of Reaction One (obtained in estimated 30-40% proportion of total compound yield).

The composition of any crystal or clump of crystals obtained as earlier was readily established by scanning its infrared spectrum from 1250 to 900 cm^{-1}; Compound Two showed a distinctive, somewhat broad, medium intensity absorption at 1144 cm^{-1}; Aluminium Compound One showed a sharp, very intense absorption at 942 cm^{-1}.

The combined yield of crystals obtained from the reaction mixture tended to consist of essentially two types: the first was fairly pure Compound Two, present as clear, bright glassy-orange crystals which did not change in appearance when exposed for several days to an atmosphere of nitrogen containing both oxygen and water in the proportions of about 10-20 p.p.m.; the second contained both Compound Two and Aluminium Compound One in comparable amounts, and was present as opaque brownish crystals which slowly turned a rather darker shade of brown when exposed similarly to a slightly impure nitrogen atmosphere. Solutions containing a moderate excess of Compound Two over Aluminium Compound One (as was the case with the reaction mixture) always tended to crystallise in this way.

Crystallisation of solutions containing Aluminium Compound One, and Compound Two

A. Crystallisation of solutions containing a large excess of Compound Two over Aluminium Compound One, particularly under such conditions that little (if any) of the latter was deposited, tended to yield the former as rather orange-brown, matted feathery chunks. These crystals did not deteriorate in a slightly impure nitrogen atmosphere.

B. Crystallisation of solutions containing closely similar quanties of Compound Two and Aluminium Compound One tended to yield a little of the glassy orange crystals, much of the brownish chunky crystals, and in addition a small quantity of slightly opaque yellowish crystals which blackened in a matter of hours in a slightly impure nitrogen atmosphere. These last were fairly pure Aluminium Compound One.

C. Crystallisation of solutions containing a moderate excess of Aluminium Compound One over Compound Two tended to yield much of the brownish chunky crystals, and rather less of the slightly opaque yellowish crystals of Aluminium Compound One.

D. Crystallisation of solutions containing a large excess of Aluminium Compound One over Compound Two, particularly under such conditions that little (if any) of the latter was deposited, tended to yield the former as pale yellow, opaque, well-formed plates.

The fractionation process

By utilising the above observations in conjunction with numerous crystallisation sequences and laborious hand-picking of individual crystals in a glove-box, an estimated 1-1•5 gm. of fairly pure Compound Two was obtained. This was recrystallised to constant melting point, the final yield of constant melting compound being estimated to be about 0•5 gm.

If only relatively restricted quantities of tetrasulphur tetranitride are available, the fractionation process described can be employed to extract an estimated 80-90% of the total quantity of Compound Two present in the raw reaction mixture, and in addition to yield an estimated 5-15% (based on total compound yield) of Aluminium Compound One if desired. However, if sufficient quantities of tetrasulphur tetranitride are available, experience has indicated that useful quantities of Compound Two are more readily obtained by using scaled-up- or multiple-preparations, and only one or two crystallisation sequences, in conjunction with the discarding of relatively large quantities of mixtures of Compound Two and Aluminium Compound One, from which useful quantities of Compound Two could still be extracted.

<u>Pure Compound Two</u> was finally obtained as pale yellow to pale orange needles which tended to crystallise in slightly matted chunks, giving an appearance somewhat similar to that of chopped straw. Its solutions in thionyl chloride were clear, and bright orange in colour, and from these solutions it could be recrystallised quite readily. Its solubility was estimated to be of the order of 1 gm. per 10 ml. at reflux, and of the order of 0•1-0•2 gm. per 10 ml. at room temperature.

Properties of Compound Two:

(a) Analysis - N = 17·09; S = 39·47; Cl = 42·90%. $(NSCl)_x$ requires N = 17·18; S = 39·33; Cl = 43·49%. (But, cf. "Discussion", p.92 , the following results also were obtained - S = 37·70; Cl = 34·10, 38·90%.)

(b) Melted sharply to a clear orange liquid at 181°.

(c) Infrared spectrum: 1144s, 1048w, 1023w(sh), 976vw(sh), 733m, 722m(sh), 687w, 613w, 529s, 497vs(sh), 483vs, 327m. A possible very weak absorption at 225 cm^{-1} was ambiguous owing to a high and unsteady base-line.

(d) Mass spectrum: nothing below 90°; at 105° - S, Cl, SN, S_2, S_2N, SNCl, S_2N_2, S_3N, S_3N_3, S_4N_2, S_4N_4; at 135° SNCl is absent, and at 170° S_3N additionally is absent.

(e) Molecular weight: 235.

Minor products of the reaction

When the fractionation process leading to pure Compound Two was conducted in such a way that any species other than Compound Two and Aluminium Compound One tended to accumulate in one batch or at one stage; recrystallisation of this residual material frequently yielded significant quantities of clear, very pale yellow needles. These needles had a near infrared spectrum which was blank except for an intense, broad absorption centred around 500 cm^{-1}; the needles' mass spectra at 185° and 250° (particularly the former) consisted essentially of strong peaks assignable to Al, Cl, AlCl, and $AlCl_2$, with a weak pattern at $AlCl_3$: on these grounds the needles were presumed to be fairly pure, unreacted aluminium trichloride (cf. "Discussion", p.134).

At apparently unpredictable stages during the fractionation, very small quantities of clear, bright glassy-yellow, chip-like crystals were sometimes obtained; these crystals did not deteriorate over several days in a slightly impure nitrogen atmosphere. In one particular experiment, the reaction leading to a mixture of Compound Two and Aluminium Compound One was carried out as described for Reaction Two, except that the solution of aluminium trichloride in thionyl chloride was added to solid tetrasulphur tetranitride at -196^{o}, and then the resulting mixture was warmed to 40^{o}. Apart from other points regarding the nature and proportion of the various products (discussed on p.132) it was noticeable that there was a considerably increased yield of the glassy yellow chips, to the extent that an estimated 30-40 mgm. of them were accumulated; this just sufficed for a near infrared spectrum. The spectrum obtained was - 1183m(sh), 1174m, 1139w, 1040s(sh), 1034s, 744vw(sh), 721w, 676m, 616vw, 570m, 562vw(sh), 522s(sh), 490vs. This spectrum is discussed on p.131. For reference, these crystals will be referred to as Aluminium Compound Three.

Reactions between Tetrasulphur tetranitride and Iron trichloride in Thionyl chloride

Note. Although the compound used as the source of iron in these reactions was tetra-aquoiron(II) chloride, it was established that the purple solid formed from it during the dehydration process had a chlorine content of 65•1%, and hence could confidently be taken to be iron trichloride (required Cl = 65•6%). Tetra-aquoiron(II) chloride was used because it could be handled conveniently in air (unlike anhydrous iron trichloride), and because it also had a precisely known water content (unlike the most readily available hydrated varieties of iron trichloride).

One. Preparation of Iron Compound One, using a solution of tetrasulphur tetranitride in thionyl chloride, at a reaction temperature of 60°

Finely ground tetra-aquoiron(II) chloride (4•27 gm.) was stirred with thionyl chloride (40 ml.) first at room temperature for half an hour, then at reflux for 1•5 hours, to dehydrate and oxidise the salt. A solution of tetrasulphur tetranitride (3•96 gm.) in thionyl chloride (160 ml.) was then added (at 60°) to the purple suspension. Within about half an hour the solution had become red/green dichroic, and intensely dark in colour. The reaction mixture was held at 60° for 17 hours, then the volume of the dichroic solution was reduced to about 15 ml. by pumping off solvent, precipitated solid was redissolved at reflux, and the solute was allowed to recrystallise from the solution, by standing at room temperature. The resulting yellow to yellow-brown crystals were filtered off, washed quickly with thionyl chloride, and pumped dry. Lastly, they were recrystallised to constant melting point, from more thionyl chloride. The crystals of Iron Compound One thus obtained were pale yellow when finely divided, and yellow-brown when relatively bulky. The final yield of compound was estimated to be 2-2•5 gm. The points noted on p. 50 regarding properties of solutions of Aluminium Compound One in thionyl chloride, and the possibility/desirability of increasing its yield from the raw reaction mixture, are all generally applicable to Iron Compound One.

Properties of the compound (cf. p.129):

(a) Analysis - S = 20·40, 26·22; N = 7·92, 8·10, 8·57; Cl = 52·30, 51·13, 55·50; Fe = 16·4%.*

(b) Softened a little from 76°, also darkened a little from 79°; turned pasty at 82° and melted to a black liquid at 83°.

(c) Infrared spectrum: 1156vw, 1091vw, 1037vw, 1008vw, 938vs, 891vw, 759w, 742s, 717s, 574s, 463s, 458m(sh), 418vs, 379vs, 331m, 324m, 304s.

(d) Mass spectrum: nothing below 75°; at 80° - S, Cl, SN, S_2, S_2N, SNCl, S_2N_2; at 180° - S, Cl, SN, S_2, S_2N, SNCl (weak spectrum).

(e) Molecular weight: 202, 183.

A sample of the compound (estimated 0·15 gm.) was dissolved in nitrobenzene (10 ml.) to yield a solution which was yellow-green by transmitted light and yellow-brown by reflected light. The near infrared spectrum of this solution (0·1 mm. path length) was recorded 1·5 hours after the solution had been prepared, and showed a weak absorption at 554 cm^{-1} which corresponds to an absorption at the same frequency shown by solutions of tetrasulphur tetranitride in the same solvent.

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* $S_2N_2FeCl_5$ requires S = 19·72; N = 8·60; Cl = 54·50; Fe = 17·17%.

Two. Preparation of Iron Compound Two, using solid tetrasulphur tetranitride, at a reaction temperature of about -15°

Finely ground tetra-aquoiron(II) chloride (4·09 gm.) was stirred with thionyl chloride (80 ml.) first at room temperature for 45 minutes, then at reflux for one hour, to dehydrate and oxidise the salt. More thionyl chloride (80 ml.) was added, and the mixture was cooled for 20 minutes in an acetone/solid carbon dioxide bath. The bath was then removed, and solid tetrasulphur tetranitride (3·79 gm.) was added to the vigorously stirred cold suspension of iron trichloride. The reaction mixture was slowly warmed up by the intermittent application of a tepid waterbath, until the tetrasulphur tetranitride started to dissolve; the temperature of the reaction mixture had been raised to a little below 0° after about 10 minutes, and reaction had appeared to commence at an estimated -20 to -10°. The slow warming was continued so that after about 30 minutes the reaction mixture was at about 15°, and rich blue-green in colour; a solid phase which appeared to be red in colour was present. Finally the mixture was allowed to reach room temperature. Over the succeeding 10 hours or so, the colour of the solution altered to olive green, and a check showed that no solid was then visible. By 17 hours of reaction time, the solution was red/green dichroic, and a considerable quantity of solid was present. After 24 hours, this rust-coloured solid [A] was filtered off, washed with thionyl chloride, and pumped dry: it was fairly pure Iron Compound Two (see below for purification). It is worth remarking that in the earliest stages of other experiments involving the same reactants under varied but similar conditions, a transient,intense red-orange colour has occasionally been observed.

The residue from pumping the filtrate to dryness was dissolved at reflux in 20 ml. of thionyl chloride, and the solute was allowed to recrystallise overnight; these crystals were then filtered off, washed with fresh solvent, and pumped dry. This sequence of operations was repeated three or four times; the volume of solvent used for each repeat sequence was about half that employed for the previous recrystallisation. The crystallised batches of solute resulting were combined [B].

Extraction of crude Iron Compound Two from [B]; purification of the crude Iron Compound Two so obtained, and purification of the precipitated crude Iron Compound Two [A]

Preliminary observations

The major product,which is the subject of this reaction (Iron Compound Two), and the minor co-product (Iron Compound One) are readily distinguished. As obtained, "raw" from the reaction mixture, they appear as follows:

(i) The sample of crude Iron Compound Two which precipitates out of the reaction mixture [A] is a dull, red-brown coloured powder. This powder does not deteriorate significantly on several days exposure to nitrogen atmospheres slightly contaminated by oxygen and water.

(ii) Crystallised samples of crude Iron Compound Two, as obtained from [B], appear as clear, glistening, blackberry coloured cubes and blocks.

These crystals also do not deteriorate significantly on several days exposure to nitrogen atmospheres slightly contaminated by oxygen and water.

(iii) Crystallised samples of crude Iron Compound One, as obtained from [B], appear as dull, somewhat opaque (almost milky) yellow needles and plates. These crystals tended to darken slightly towards brown on several days exposure to nitrogen atmospheres slightly contaminated by oxygen and water.

In addition -

(iv) Crystallisation of solutions containing a large excess of Iron Compound Two over Iron Compound One, particularly when carried out under such conditions that little (if any) of the latter was deposited, tended to yield the former as rather matted, feathery clumps of red-brown crystals. Any Iron Compound One which crystallised out simultaneously tended to appear as described above in (iii).

(v) Crystallisation of solutions containing roughly comparable quantities of Iron Compounds One and Two tended to yield the two compounds in the manner described above in (ii) and (iii) respectively.

The fractionation process

In the light of the above observations, it was possible to isolate pure Iron Compound Two by the following process:

(a) A batch of crude crystals of Iron Compounds Two and One ([B], for example) was sorted out by hand in a glove-box, to yield an enriched fraction consisting essentially of crystals of crude Iron Compound Two [C]. The residual Iron Compound One was discarded.

This batch of crystals [C] was recrystallised from thionyl chloride.

(b) The sequence (a) was repeated, still using observations (i) to (v) above, until an accumulated sample of crystals [D] visibly contained no Iron Compound One. [A] was then added to [D], and [A] + [D] was then recrystallised to constant melting point.

The final yield of constant melting compound was estimated to be about 1-1•5 gm.

The remarks made earlier (p. 55) with regard to the extraction of Compound Two from the relevant reaction mixture are also generally applicable to Iron Compound Two. Thus increased quantities of the latter are probably obtained most simply, and with the least effort, by using scaled-up- or multiple-preparations, and only one or two crystallisation sequences, in conjunction with the discarding of relatively large quantities of mixtures of Iron Compounds One and Two, from which useful quantities of the latter could still be extracted. This course of action is certainly to be recommended if sufficient quantities of tetrasulphur tetranitride are available. However, if only relatively restricted quantities of tetrasulphur tetranitride are available, then there is a substantial incentive to pursue the fractionation process as far as it can be made to go; ultimately, an estimated 90-95% of the total quantity of Iron Compound Two present in a raw reaction mixture could probably be extracted.

Pure Iron Compound Two was finally obtained as mahogany coloured platelets. It dissolved slowly in thionyl chloride to give clear solutions from which it could be recrystallised quite readily. When the compound was dissolved at reflux, the resulting solution's colour was initially orange; on cooling however, this colour always appeared to darken and intensify somewhat, tending towards brown; when crystallisation was complete, the colour of the mother liquor was a paler version of this brown (cf. "Discussion", p.138). The compound's solubility was estimated to be of the order of 1 gm. per 10 ml. at reflux, and of the order of 0·2 gm. per 10 ml. at room temperature.

Properties of Iron Compound Two (cf. "Discussion", p.127):

(a) Analysis - S = 34·93; 36·61; N = 15·85, 17·43; Cl = 33·03, 37·60; Fe = 14·20%.*

(b) Melted sharply to a clear red liquid at 181°.

(c) Infrared spectrum: 1143s, 1047w, 1017vw(sh), 731m, 721m(sh), 685m, 608m, 528s, 370vs, 327s. Characteristics of the absorption curve which could be described as bands 256m, 224s, 211s, were probably better attributed to a poor base-line.

(d) Mass spectrum: nothing below 140°; at 150° - S, Cl, SN, S_2, S_2N, SNCl, S_2N_2 (weak spectrum); at 170°, 185° - S, Cl, SN, S_2, S_2N, SNCl, S_2N_2, S_3N_2, S_3N_3, S_4N_4.

(e) Molecular weight: 259, 296.

* $S_3N_3FeCl_3$ requires S = 32·02; N = 13·99; Cl = 35·40; Fe = 18·59%.
$S_4N_4FeCl_4$ requires S = 33·58; N = 14·67; Cl = 37·13; Fe = 14·62%.

Three. Preparation of Iron Compound Three, using a solution of tetrasulphur tetranitride in thionyl chloride (which had stood at room temperature for 20 minutes), at a reaction temperature of 40°

Approach to the extraction of pure Iron Compound Three.

The investigations of the iron trichloride/tetrasulphur tetranitride system which were directed to obtaining pure samples of Iron Compounds One and Two, showed incidentally that a further compound, Iron Compound Three, was produced under certain reaction conditions. Trial experiments were conducted to determine optimum reaction conditions (maximum yield of Iron Compound Three, and minimum contamination by Iron Compound One, which has a similar appearance) but after a few experiments it was decided that the effort involved was not worthwhile.

Separation of Iron Compound Three from co-products

The relative proportions of Iron Compounds One, Two and Three (in any combination, in any crystal or clump of crystals) was inferred from the infrared spectrum (between 1250 and 900 cm^{-1}) of the sample in question. Iron Compound One shows a sharp, very strong absorption at 938 cm^{-1}; Iron Compound Two shows a strong, distinctly broad absorption at 1143 cm^{-1}; and Iron Compound Three shows a moderately strong absorption at 1168 cm^{-1} together with a strong absorption at 1030 cm^{-1}.

Preparation of the mixture to lead to pure Iron Compound Three

In the preparation to be described, the proportion of Iron Compound

Three yielded was such that the intensity of its absorption at 1168 cm^{-1} was identical with that of Iron Compound Two's absorption at 1143 cm^{-1}; this was tentatively interpreted as representing a roughly 3:2 proportion of the former to the latter, on the basis of previous comparisons, first by eye of the proportions of the two compounds present in a well crystallised sample, and second of the relative intensities of the two diagnostic infrared absorptions shown by a powdered sample (sufficiently large to be representative) of the crystallised mixture. No Iron Compound One was detected in the reaction mixture.

Finely ground tetra-aquoiron(II) chloride (0•76 gm.) was stirred with thionyl chloride (20 ml.) first at room temperature for half an hour, then at reflux for one hour, to dehydrate and oxidise the salt; the mixture was then cooled to 45°. A solution of tetrasulphur tetranitride (0•71 gm.) in thionyl chloride (40 ml.) was prepared, allowed to stand at room temperature for 20 minutes, then added to the stirred suspension of iron trichloride. A rich yellow-green colour was immediately generated. After 3 hours of reaction time, the resulting solution was red/green dichroic, and so intensely coloured as to be almost black; additionally, a small quantity of pale yellow precipitate was present, and over the succeeding 13 or so hours, this precipitate increased substantially in quantity. After 40 hours reaction time at 42°, the solid was filtered off, washed with thionyl chloride, and pumped dry. The residue from pumping the filtrate to dryness was recrystallised from thionyl chloride (2 ml.). The crystals so obtained were filtered off, washed with more thionyl chloride, and pumped dry. A bright, glassy yellow crystal of Iron Compound Three was taken from the crystallisate, and its near infrared spectrum was recorded. The remainder of the crystallisate was refluxed with thionyl chloride (10 ml.); it slowly dissolved to give a clear orange solution. After one hour at reflux, this solution was quickly cooled to 35° to precipitate solute in a finely divided form. This powder was the sample employed to infer the relative proportions of Iron Compounds Two and Three present, as noted earlier.

Properties of the insoluble, pale yellow powder filtered out of the raw reaction mixture:

(a) Infrared spectrum: 400s(sh), 380s.

(b) Analysis: Cl = 56•2%; $FeCl_2$ requires Cl = 55•94%.

On these grounds, the insoluble solid was presumed to be iron dichloride.

Near infrared spectrum of the bright, glassy yellow crystal of fairly pure Iron Compound Three: 1168m, 1136w(sh), 1094vw(sh), 1038s(sh), 971s, 962vw, 747vw(sh), 733w(sh), 723m, 674s, 646vw, 614vw, 569s, 517m, 485vs, 466m(sh).

It must be noted however that the chemistry of systems designed to lead to substantial quantities of Iron Compound Three appears not to be on a firm foundation as yet; when the above preparation was repeated, exactly as described (except that it was on a four times larger scale) no iron dichloride was precipitated, and significant amounts of Iron Compound One were detected, in contrast to the "pilot scale" experiment.

Reaction between Tetrasulphur tetranitride and Tantalum pentachloride in Thionyl chloride

Tantalum pentachloride (2•30 gm.) (supplied by Koch-Light) was dissolved in thionyl chloride (20 ml.), and any traces of insoluble material were filtered off. To the resulting solution was added at room temperature a solution of tetrasulphur tetranitride (1•18 gm.) in thionyl chloride (50 ml.), with the immediate generation of an intense deep blue-green colour; the mixture was then brought to 40°. After about 15 minutes the colour had altered to olive green, then over the succeeding few hours it finally changed to red/green dichroic. Deposition of yellowish crystals commenced after about 5 hours of reaction time. After 45 hours, these crystals were filtered out of the mother liquor, washed with thionyl chloride, and pumped dry. An additional quantity of these crystals was obtained from the mother liquor by pumping off about half of the solvent, redissolving the precipitated solid at reflux, and allowing the intensely dark, red/green dichroic solution to crystallise. These latter crystals also were filtered off, washed with thionyl chloride, and pumped dry. The two batches were combined, and recrystallised once from thionyl chloride.

Properties of the yellow-brown crystals:

(a) Analysis - S = 14•93; N = 6•19; Cl = 40•45%. $S_4N_4 \cdot 2TaCl_5$ requires S = 14•24; N = 6•22; Cl = 39•36%.

(b) Softened a little from about 90°, melted sharply at 102°.

(c) Infrared spectrum: 1259vw, 1156w, 1111w, 1017w, 998w, 941vs, 762w, 746m(sh), 742m, 720s(sh), 715s, 569s, 534vw, 521w, 466m, 459w(sh), 432vs(sh), 418vs, 376m, 316vs, 279s(sh), 253w, 246vw, 224w. Additional bands may conceivably be present below 240 cm^{-1}, but obscured by a rising base-line.

(d) Mass spectrum: nothing below 75°; at 85° and 110° - S, Cl, SN, S_2, S_2N; at 155° - S, Cl, SN, S_2, S_2N, SNCl, S_2Cl, SCl_2, S_2Cl_2, Ta, TaCl, $TaCl_2$, $TaCl_3$, $TaCl_4$; at 170°, S_2N_2 additionally is present.

Reaction between Tetrasulphur tetranitride and Gallium trichloride in Thionyl chloride

Gallium trichloride (0•73 gm.) (supplied by Koch-Light) was dissolved in thionyl chloride (10 ml.), and the resulting solution was treated with a solution of tetrasulphur tetranitride (0•77 gm.) in thionyl chloride (30 ml.); the mixture was brought to 45°. The intense blue colour which was immediately generated slowly altered through blue-green (after about 1•5 hours reaction time) and olive green (after about 5 hours reaction time) to a red/green dichroic condition (within 24 hours). After 46 hours, all of the solvent was pumped off except for an estimated 10 ml., precipitated solid was redissolved at reflux, and the solution was allowed to stand at room temperature overnight. The resulting crystals were filtered off, washed with thionyl chloride and hexane, and pumped dry. It appeared to be impossible to remove (by washing) small quantities of tarry material which were adhering to these crystals. The residue from pumping the mother liquor of the recrystallisation to dryness was dissolved at room temperature in thionyl chloride (20 ml.), and a few mls. of pentane were very slowly added to the vigorously stirred dark red/green dichroic solution, to precipitate a quantity of the solute for examination. Addition of pentane was stopped well before either the intensity or the colour of the mother liquor had been significantly reduced. The precipitate was filtered off, washed with a 3:1 mixture of thionyl chloride and pentane, and pumped dry.

(The following results are discussed on p.143).

A sample of the tar-contaminated crystallisate, exactly as isolated, had the following properties:

(a) Analysis - S = 16•08; N = 11•51; Cl = 37•60%.

(b) Melted at 170-171^{o} to a clear red-orange liquid.

(c) Infrared spectrum: 1144s, 1047w, 992vw, 950w, 938m, 744w(sh), 736m, 723m, 715m, 696w, 670vw, 606vw, 573vw, 524m, 369m.

(d) Mass spectrum: nothing below 70^{o}; at 80^{o} and 115^{o} - S, Cl, SN, S_2, S_2N, S_2N_2 (weak spectrum); at 155^{o} - S, Cl, SN, S_2, S_2N, S_2N_2, S_3, S_4, S_5, S_6, S_7, S_8; at 175^{o} - S, Cl, SN, S_2, Ga, S_2N, S_2N_2, S_3, GaCl, S_4, $GaCl_2$, S_5, $GaCl_3$, S_6, S_7, S_8.

A single crystal (Gallium Compound Two), selected from the crystallisate as being apparently free from traces of tar, showed the following near infrared spectrum: 1146s, 1049w, 1020w(sh), 988vw(sh), 733w, 722w, 712w(sh), 687w, 608w, 529s.

The precipitate obtained (Gallium Mixture) had the following properties:

(a) Analysis: S = 30·61; N = 9·75; Cl = 33·40%.

(b) Slowly darkened from about 70°; softened from about 85°; melted at 91-92°.

(c) Infrared spectrum: 1147s(sh), 1139s, 1042s(sh), 1033s, 990vw(sh), 940m, 744w, 733w, 718m, 695vw, 676w, 615vw, 607vw(sh), 574w, 569w, 524s, 485s, 463w, 422m, 382s(sh), 365s, 325m(sh), 304m, 260vw, 223m, 214m. These last two absorptions may in fact only represent an erratic base-line.

(d) Mass spectrum: nothing below 150°; at 160° and 190° - S, Cl, SN, S_2, S_2N_2 (weak spectra); at 200° and 210° - S, Cl, SN, S_2, Ga, SNCl, S_2N_2, GaCl, S_3N_2, S_3N_3, $GaCl_2$, $GaCl_3$, S_4N_4.

Reaction between Tetrasulphur tetranitride and Indium trichloride in Thionyl chloride

Finely ground Indium trichloride (1·04 gm.) (supplied by Koch-Light) was suspended in thionyl chloride (15 ml.) by vigorous stirring, first at room temperature for 15 minutes, then at reflux for 4·5 hours. A solution of tetrasulphur tetranitride (0·87 gm.) in thionyl chloride (40 ml.) was added to the suspension at about 45°; an intense blue colour was rapidly generated, and the indium trichloride dissolved. Within a few minutes this colour had altered to blue-green, then over the succeeding few hours the colour finally changed through olive green, to red/green dichroic. The temperature of the reaction mixture was maintained at 45°. By about 40 hours of reaction time, the colour of the solution was less intense, and a quantity of pale yellow precipitate was present. After 113 hours, the solid was filtered off, washed with thionyl chloride and pentane, and pumped dry. The residue from pumping the mother liquor to dryness was refluxed with thionyl chloride (35 ml.), when it slowly dissolved to give a clear, pale orange-red solution; on allowing this solution to cool, a substantial yield of a yellow solid was obtained. This solid also was filtered off, washed with thionyl chloride and pentane, and pumped dry. These two samples of solid had the same near infrared spectrum. Further, but less pure, samples of this solid could be recovered by repeating the process employed to obtain the second batch.

Properties of the first yield of pale yellow powder:

(a) Analysis (cf. p. 92) - S = 9•60, 12•15, 12•32; N = 8•26, 8•81, 10•36; Cl = 40•70, 41•78, 42•75%.

(b) Darkened from about 170°; softened from about 230°; melted at 320°, and immediately resolidified. Sample tube burst at 352°, and the sample promptly melted to a cherry-red liquid.

(c) Infrared spectrum: 1179m, 1139w, 1042s(sh), 1033vs, 752vw, 723vw, 676s, 648vw, 615vw, 571m, 520m, 487vs, 424vw, 331s, 296m. Any peaks which may be present below 280 cm^{-1} are obscured by a high base-line.

(d) Mass spectrum: nothing below 150°; at 160° - S, Cl, SN, S_2, S_2N, S_2N_2, S_3N, In, S_3N_2, S_3N_3, InCl, S_4N_2, $InCl_2$, $InCl_3$. At 180° and 240°, SNCl additionally is present; at 300° the spectrum consisted essentially of In, InCl, $InCl_2$ and $InCl_3$, with a few weak S- and N- derived peaks. The spectrum faded almost completely out at 320°.

Reaction between Tetrasulphur tetranitridotantalum pentachloride and Thionyl chloride

Thionyl chloride (40 ml.) was added at room temperature to tetrasulphur tetranitridotantalum pentachloride (3·00 gm.)[89] and the mixture was stirred. Initially the adduct appeared simply to dissolve a little, giving a pale orange-red solution, but over a few minutes the mixture gradually changed to an almost black suspension in a dark solution. The mixture then rapidly developed an intense blue colour, and all the solid present appeared to dissolve. Over the succeeding hours the colour slowly altered through blue-green and olive green to red/green dichroic. After 65 hours, the mixture was refluxed for 4 hours to ensure completion of reaction, and to dissolve a small quantity of yellow precipitate that was present. The solution was then allowed to stand at room temperature for 24 hours to crystallise. A small quantity of well-formed, yellow-brown needles was obtained, which were filtered off, carefully washed with thionyl chloride, and pumped dry. Additional quantities of the product could be obtained by successively recrystallising the residue from pumping the mother liquor to dryness. The first stages of the reaction were conducted at room temperature with a view to minimising formation of tarry by-products, but subsequent experience suggests that it is likely to be perfectly satisfactory to conduct the reaction at about 40°, with a proportionately shorter reaction time.

Properties of the resulting yellow-brown crystals:

(a) Near infrared spectrum: 1260vw, 1156w, 1110w, 1017w, 997w, 941vs, 762w, 746m(sh), 742m, 721m(sh), 715m, 570m, 534w, 522w, 466m, 460w(sh), 432s(sh), 418s. This spectrum is indistinguishable from that of the product of the reaction between tetrasulphur tetranitride and tantalum pentachloride in thionyl chloride.

(b) Softened from about 90°, melted at 105°-107°. A recrystallised sample of the substance softened from 102°, then appeared to melt locally at about 109°, shortly after which it resolidified; it finally melted in bulk at 137°.

(c) Analysis: (discussion p.140) - S = 14•71; N = 6•20; Cl = 31•90, 33•80%. $S_4N_4.2TaCl_5$ requires S = 14•24; N = 6•22; Cl = 39•36%.

Reaction between Tetrasulphur tetranitridoaluminium trichloride and Thionyl chloride

(with a note regarding solutions of this adduct in nitrobenzene)

Tetrasulphur tetranitridoaluminium trichloride (0•80 gm.)[89] was stirred at 40° with thionyl chloride (10 ml.). The initial appearance of the mixture was that of a red-brown solid suspended within a similarly coloured solution, but within a few minutes the mixture darkened considerably, to become almost black. After about 10 minutes of reaction time, more thionyl chloride (20 ml.) was added and most of the solid still present dissolved; additionally, the colour of the solution had become an intense blue-green.

By about 5 hours of reaction time, the colour had altered to olive green, and by 16 hours reaction time the solution was red/green dichroic. After 41 hours, the reaction mixture was pumped down to an estimated 5 ml., precipitated solid was redissolved at reflux, and the solution was allowed to stand overnight at room temperature. The resulting small yield of crystals was filtered off, washed with thionyl chloride and pentane, and pumped dry. The residue from pumping the mother liquor to dryness was redissolved (by warming slightly) in more thionyl chloride (40 ml.) to give an intensely dark, red/green dichroic solution. A few tens of mls. of pentane were slowly added to the vigorously stirred thionyl chloride solution, to precipitate a sample of solute for examination: precipitation was stopped before either the intensity or the colour of the solution had been significantly reduced. The yellow-brown precipitate resulting was filtered off, washed with a 4:3 mixture of thionyl chloride and pentane, and pumped dry.

Properties of the yellow-brown crystals (discussed on p.132):

(a) Near infrared spectrum: 966vw, 941s, 763vw, 744w, 739w(sh), 722m(sh), 715m, 571w, 527w(sh), 504vs, 492vs(sh), 473s, 462s, 423m. This spectrum is essentially the same as that of the product from Reaction One of tetrasulphur tetranitride and aluminium trichloride, in thionyl chloride. The sample available was not sufficient for a far infrared spectrum.

(b) Melted at 67-69° to a black liquid.

(c) Analysis: S = 20·10; N = 9·21; Cl = 43·50%.

(d) Mass spectrum: at 100° - S, Cl, SN, S_2, S_2N, SNCl, S_2N_2, SCl, S_3N, S_2Cl_2, S_4N_2, S_4N_4; at 165° - S, Cl, SN, S_2, S_2N, SNCl, S_2N_2, S_4N_2; at 180° and 200° - S, Cl, SN, AlCl, S_2, S_2N, SNCl, S_2N_2, $AlCl_2$, S_3N, S_3N_2, $AlCl_3$, S_4N_2.

The yellow brown precipitate showed the following infrared spectrum: 1143m, 1031w, 1013w(sh), 966w, 940s, 763w, 743m, 722s(sh), 715s, 687w, 610vw, 570w, 525s(sh), 501vs(sh), 483vs, 462s(sh), 417s, 376w, 324w, 304w, 280vw. Any absorptions which may have been present below 270 cm^{-1} were obscured by a rising base-line. This spectrum is discussed on p.132.

A sample of tetrasulphur tetranitridoaluminium trichloride (estimated 0·2 gm. sample) was stirred at room temperature with nitrobenzene (5 ml.), when a little slowly dissolved to give (after about 10 minutes) an orange solution in which some green solid remained suspended. The solid was allowed to settle out, and the near infrared spectrum of the solution (0·1 mm. path length) was recorded. This solution showed a weak absorption at 555 cm^{-1} which corresponded to an absorption at the same frequency shown by solutions of tetrasulphur tetranitride in nitrobenzene. The solution also showed a medium intensity absorption at 589 cm^{-1} which was not assigned. On continuing the stirring of the green solid/orange solution, the solution's colour gradually changed to an intense brown-orange, and simultaneously the solid slowly dissolved. After about 4 hours the intensity of colour of the solution started to decrease. After 6 hours, a near infrared spectrum (0·1 mm. path length) of this solution showed the absorption at 555 cm^{-1} was still present, while the absorption at 589 cm^{-1} had disappeared.

Reaction between Tetrasulphur tetranitride and Iron trichloride in Sulphuryl chloride

A solution of tetrasulphur tetranitride (1·44 gm.) in sulphuryl chloride (100 ml., technical grade) was added to a stirred suspension of iron trichloride (1·25 gm.) in more sulphuryl chloride (20 ml., technical grade), at 40°. The initial purple colour of the mixture immediately started to alter towards rust. After about 10 minutes, no iron trichloride was visible, but a substantial quantity of bright red solid was suspended in the red solution. The intensity of colour of the solution tended to decrease slowly with time. After 44 hours the solid was filtered off, washed with sulphuryl chloride (technical grade), and pumped dry.

Properties of the scarlet solid:

(a) Analysis (cf. p.148) - S = 20·80, 24·43, 25·74; N = 9·46, 11·43; Cl = 49·30, 49·49, 54·6; Fe = 14·5%.

(b) Melted at 80°-81° to a black liquid.

(c) Infrared spectrum: 1170vw, 1133m(sh), 1116s, 1099s(sh), 1071m(sh), 1050m, 857vw, 735vw(sh), 721vw, 657w(sh), 654m, 645w(sh), 623w, 516vs, 504vs(sh), 495vs, 463s, 377vs, 330s, 311m(sh), 242vw, 226w.

(d) Mass spectrum: nothing at 75°; at 100° - S, Cl, SN, S_2, SCl, SNCl, S_2N_2, SCl_2, S_3N, S_3N_2, S_3N_3, S_4N_2, S_4N_4; at 110° the spectrum is a weak version of that at 100°.

The compound was exceedingly sensitive to oxygen and/or water vapour; despite all precautions, it did not appear to be possible to handle the compound without it deteriorating. This deterioration was manifested as a tendency for its bright scarlet colour to fade towards a more sombre red-brown.

Reaction of the product with thionyl chloride

A sample of the compound (estimated about 0•5 gm.) was stirred at room temperature for several minutes with thionyl chloride (8•5 ml.) without any obvious reaction. The mixture was quickly brought to 40°, and after about 15 minutes appeared to consist of unaltered solid suspended in a red-brown solution. After about 45 minutes, the solution had a very dark, red-brown colour, and only an estimated 0•1 gm. of the solid remained undissolved. By 18 hours of reaction time no solid remained, and the solution was an intensely dark red. The solution was then pumped down to an estimated 1•5 ml., precipitated solid was dissolved at reflux, and the solution was allowed to cool down to room temperature overnight. The resulting yellow-brown crystals were filtered off, washed with thionyl chloride, and pumped dry. Their near infrared spectrum was 1042vw, 1011vw, 937vs, 785vw, 759w, 741s, 716s, 682vw, 574s, 516vw, 505vw, 493vw, 463s, 419vs. This spectrum is essentially the same as that of the product from Reaction One of tetrasulphur tetranitride and iron trichloride in thionyl chloride. The near infrared spectrum of the residue from pumping the mother liquor from the crystallisation to dryness was established to be only a less "clean" version of the spectrum just noted.

A sample of the compound (estimated 0•05 gm.) was stirred with nitrobenzene (3 ml.), when it readily dissolved to give a dark, intensely red-orange-brown solution. The near infrared spectrum (0•1 mm. path length) of this solution showed a weak absorption at 554 cm^{-1} which could correspond to that at 555 cm^{-1} shown by solutions of tetrasulphur tetranitride in nitrobenzene.

Reaction between Tetrasulphur tetranitride and Iron trichloride in Sulphur dichloride

Technical grade sulphur dichloride (80 ml.) was freed from dissolved chlorine by degassing at the rotary pump, and added at room temperature to a stirred mixture of tetrasulphur tetranitride (1•05 gm.) and iron trichloride (0•93 gm.). For several hours there was no sign of reaction, but by 16 hours of reaction time much yellow solid was present, and only a little unreacted iron trichloride remained. Stirring was continued until no unreacted iron trichloride was visible (by about 65 hours). The yellow solid was then filtered off, washed with hexane, and pumped dry. (While pumping down, it was noticeable that the mother liquor contained about 10 ml. of a liquid which was far less volatile than sulphur dichloride.)

Recrystallisation from thionyl chloride

The yellow solid (estimated about 1•5 gm.) was refluxed with thionyl chloride (80 ml.), when it dissolved readily to give a clear, pale yellow-brown solution: traces of insoluble material were filtered off, any solute precipitated during this operation was redissolved, and the hot solution was left to stand at room temperature. By about 3 hours, a small quantity of material had crystallised out as small, very fine plates, and after this time the main quantity of solute slowly crystallised as well-formed, yellow-brown needles. The crystals were filtered off, washed with thionyl chloride, and pumped dry.

The small quantity of fine plates which crystallised first was believed to be trace impurity (cf. p.154). Attempts to achieve a substantial separation of this impurity in one crystallisation sequence were not successful; it appeared that although the impurity crystallised out well in advance of the major product, separation from the supernatant liquid was not practical, since any disturbance of the solution after the impurity had finished crystallising seemed always to induce rapid crystallisation of the major solute as fine platelets. Various experiments conducted with both very concentrated and very dilute solutions always encountered this difficulty. The crystals involved were also of such a shape, colour and size as not to lend themselves readily to separation by hand. It was presumed that the only way this small quantity of impurity could be satisfactorily removed was by an extended fractional crystallisation process.

Additional quantities of solute could be crystallised from the residue from the above recrystallisation if required.

Properties of the slightly contaminated yellow-brown needles:

(a) Analysis (cf. p. 92) - S = 15•95, 17•21; N = 4•27, 4•90; Cl = 67•44, 67•80; Fe = 16•1, 18•1%.

(b) Darkened a little from 77°, softened somewhat at 88-92°, then melted to a clear orange liquid at 99-101°.

(c) Infrared spectrum: 1159vw, 1130m, 1115w(sh), 735vw(sh), 722w, 705vw(sh), 655s, 647m(sh), 517vs, 506vs, 494vs, 383vs, 373vs, 352w(sh), 329vw.

(d) Mass spectrum: attempts to obtain a mass spectrum at less than 100°, at 105°, and 145°, all gave only an essentially blank spectrum.

In addition to the small quantity of by-product already referred to which could not be removed by the one crystallisation, rather larger quantities of another by-product were also found to be formed in this reaction, which apparently could be successfully removed from the major reaction product, using only the one crystallisation. The near infrared spectrum of a quantity of material considerably enriched in this latter by-product showed that it was almost certainly Iron Compound One, i.e. the product from Reaction One of tetrasulphur tetranitride and iron trichloride in thionyl chloride.

The possible modes of formation of these by-products are discussed on p. 152.

Reaction between Tetrasulphur tetranitride and Iron trichloride in Disulphur dichloride

Disulphur dichloride (100 ml., technical grade) was added at room temperature to a stirred mixture of tetrasulphur tetranitride (1·14 gm.) and iron trichloride (1·00 gm.). A substantial quantity of dark brown solid [A] was immediately formed and kept in suspension in the clear orange-brown solution, along with much unreacted iron trichloride. After 2 hours the colour of the solution had reverted to that of the pure solvent, i.e. pale yellow-orange. By about 9 hours of reaction time, the suspended solid was noticeably turning a paler colour, and no unreacted iron trichloride was visible. By 19 hours the suspended solid appeared to be a pale green-brown, and a small number of lumps of dark material were visible. Stirring at room temperature for a total time of 140 hours did not appear to reduce the quantity of this dark material, and so after this time the solids were filtered off and washed with pentane; the finely divided pale green-brown solid turned bright yellow on washing. The pentane was then pumped off, the bulk of the disulphur dichloride was decanted, and the solids were pumped dry. The few lumps of dark material were then removed from the yellow powder, and discarded.

Properties of the yellow powder: (cf. p. 153):

(a) Analysis: S = 38·39; N = 7·98; 12·79; Cl = 32·37; Fe = 6·77%.

(b) Softened to an orange paste at 140°, then melted to a clear orange-red liquid at 142-145°.

(c) Infrared spectrum: 1191w(sh), 1181s, 1031m(sh), 1016vs, 721vw, 678m, 676m(sh), 645vw, 613vw, 568w(sh), 563m, 516vw, 490w(sh), 466vs, 439m(sh), 379vs, 325vs, 254m.

(d) Mass spectrum: Attempts to obtain a mass spectrum, between room temperature and 200°, were all unsuccessful.

A sample of the yellow solid was recrystallised (as fine platelets) from thionyl chloride, in which it was sparingly soluble. The crystals so obtained started to melt locally at 169°, softened at 176°, and finally melted in bulk at 178-179° to a clear orange-red liquid. They showed the following near infrared spectrum: 1179m, 1139w, 1033vs, 957vw, 749vw, 721vw, 675s, 646vw, 615w, 570s, 519m, 487vs, 434w.

The possible relationship between the above two compounds is discussed on p.153.

Reaction between Tetrasulphur tetranitride and Iron trichloride in Chlorsulphonic acid

Chlorsulphonic acid (60 ml., technical grade) was added at room temperature to a stirred mixture of tetrasulphur tetranitride (0·74 gm.) and iron trichloride (0·65 gm.); a red-black mixture was immediately generated. Over the succeeding few minutes, the mixture's appearance altered: initially it became that of a pale brown, finely divided solid in suspension, then it soon changed to that of a pale green-brown solid mixed with a few small pieces of a black solid, all still being held in suspension.

After 18 hours, the quantity of this black solid was noticeably reduced, and after 42 hours none could be seen at all. The pale green-brown solid was too finely divided to be filtered out using slight suction across a no.3 sinter. Filtration under gravity removed the solid, but even after 4 days about 10 ml. of liquid still had not filtered through, and the paste of liquid and solid still remaining on the upper side of the sinter appeared to be too viscous to filter, with the small hydrostatic head that remained. The filtrate that had been obtained was pale yellow. An attempt to coagulate the solid into a more readily filtered form, by addition of hexane to a sample of the suspension,appeared to be unsuccessful: the initially pale green solid immediately turned chocolate brown, and little if any of the hexane dissolved in the chlorsulphonic acid. The hexane layer became very slightly cloudy, but the suspension in the acid layer did not coagulate. Over the succeeding few days, this hexane/chlorsulphonic acid/ chocolate brown suspension decomposed to a black oil. Attempts to pump off the chlorsulphonic acid from another sample of the suspension were defeated by the low volatility of the acid; pumping for 40 hours yielded several mls. of a pale grey-brown glue from about 10 ml. of the green suspension. A near infrared spectrum of this glue was recorded on a contact film between polythene discs, which had been prepared with limited access of air (a rigorously air-free manipulation was not practical); except for a medium intensity absorption at 559 cm^{-1}, this spectrum was almost identical to that shown by chlorsulphonic acid under the same conditions.

Reaction between Tetrasulphur tetranitride and Iron trichloride in Benzenesulphonyl chloride

Benzenesulphonyl chloride (60 ml., technical grade) was added at room temperature to a stirred mixture of tetrasulphur tetranitride (1•35 gm.) and iron trichloride (1•18 gm.). An intensely dark solution was immediately formed, which in thin film appeared to be red-brown by transmitted light; a small quantity of iron trichloride and a trace of tetrasulphur tetranitride still remained out of solution after a few minutes reaction time. The mixture was quickly brought to 40°. After one hour, the solution (again by light transmitted through a thin film) was more orange in colour, and no solid was detectable. After 43 hours, attempts were made to precipitate a sample of the solute for examination (none had precipitated spontaneously, and the solvent was not sufficiently volatile to be easily removed by pumping). Addition of hexane (20 ml.) gave no sign of precipitation; addition of benzene (20 ml.) to the hexane/benzenesulphonyl chloride mixture similarly gave no sign of precipitation; addition of 80-100° petroleum ether (20 ml.) to the hexane/benzene/benzenesulphonyl chloride mixture (giving mixture [M]) just started to cause precipitation: on stirring [M] for 45 minutes at room temperature substantial quantities of a fairly granular, orange precipitate were obtained. Addition of 0•5 parts of 80-100° petroleum ether to one part of [M] apparently caused only additional precipitation of the orange solid; addition of 0•75 parts of the hydrocarbon to one part of [M] appeared to cause precipitation of a darker chocolate-brown coloured solid. Consequently the sample of orange solid resulting from the addition of 0•5 parts of 80-100° petroleum ether to one part of [M] was filtered off, and washed with more of the hydrocarbon, whereupon it changed to the chocolate-brown colour. The bulk of the liquid was then decanted, and the solid was pumped dry.

Properties of the chocolate-brown solid (cf. p.157):

(a) Analysis: C = 18•60; H = 1•30; N = 10•42; S = 27•74; Cl = 31•90; Fe = 8•4%.

(b) Blackened at 90°, then melted to a black liquid at 102°.

(c) Near infrared spectrum: 1575vw, 1312w, 1295w, 1174s, 1149m(sh), 1070vs, 1040m(sh), 1020w(sh), 1004m, 928vw, 891vw, 839w, 778vs, 756vs, 724vs, 682vs, 623m(sh), 606vs, 578w, 569vw(sh), 555vs, 546vs, 516vs, 462w.

(d) Mass spectrum: nothing below 70°; at 80° and 100° - S, C_6H_5, $C_6H_5SO_2$, $C_6H_5SO_2Cl$ (weak spectra).

Appendix to Experimental

Appendix

Analytical techniques found to be generally satisfactory.[82]

Nitrogen analysis

Method used - Standard Kjeldahl (Micro)

Air sensitive compounds were handled in small glass phials with closely fitting walls, the phials being filled in a glove box, and weighed before and after filling,on a standard micro balance. The phials were broken under concentrated sulphuric acid, in the presence of Se catalyst,and heated in the usual manner.

The Dumas Combustion Method was found to be unreliable and unsatisfactory for air-sensitive compounds.

Sulphur analysis

Method used

Between 25 and 50 mg. of sample was loaded in a gelatine capsule in the manner described for the nitrogen analysis, and combusted in a 21. dropping funnel of oxygen, containing 20 ml. of dilute hydrogen peroxide solution. The contents of the flask were washed out, and SO_4^{2-} ions were determined gravimetrically as barium sulphate in the standard manner.

Two modified oxygen flask methods tried were found to be unsatisfactory (1) Budesinsky, Anal. Chem., 37 (1965) 1159 and (2) McGillivray and Woodger, Analyst, 91 (1966) 611.

Chlorine analysis

Method used

12-15 mg. of sample loaded in a gelatine capsule (as described for the sulphur analysis) was combusted in a 21. dropping funnel of oxygen containing 20 ml. of dilute alkaline hydrogen peroxide solution. The contents of the flask were made up to 100 ml. and suitable aliquots were titrated potentiometrically against N/100 silver nitrate solution using Ag/AgCl electrodes in acetone medium.

Iron analysis

Method used

A sample of the compound loaded in a gelatine capsule (as described for the sulphur analysis) was heated with concentrated sulphuric acid until decomposed. The residue was diluted with water (the pH was adjusted to 4•8 to 5•0) and made up to 100 ml. A suitable aliquot was transferred to a 50 ml. graduated flask, dipyridyl reagent was added, and the optical density of the ferrous dipyridyl complex was measured at 522 mμ.

DISCUSSION

Discussion

This discussion is divided into eight main sections:

(i) Résumé of the origin and development of this work.

(ii) Discussion of analytical difficulties.

(iii) Discussion of sources of structural information.

(iv) Consideration of those $S_4N_4/SOCl_2/MCl_x$ systems which can usefully be discussed without reference to the $S_4N_4/SOCl_2/AlCl_3$, and $S_4N_4/SOCl_2/FeCl_3$ systems, i.e. (a) systems in which the metal halide did not react (MCl_x = $MgCl_2$, $CdCl_2$, $GeCl_4$ and $PbCl_2$) and (b) systems involving Hg_2Cl_2, $CoCl_2$, CuCl, $TiCl_3$, VCl_3, $HfCl_4$, $MoCl_5$ and WCl_6 (in which there was partial or complete reaction of the metal chloride).

(v) Consideration of the systems $S_4N_4/SOCl_2/AlCl_3$ and $S_4N_4/SOCl_2/FeCl_3$, which were studied in some detail.

(vi) Consideration of those systems which are most easily understood in the light of findings made in the systems $S_4N_4/SOCl_2/AlCl_3$ and $S_4N_4/SOCl_2/FeCl_3$, i.e. the $S_4N_4/SOCl_2$ systems involving $TaCl_5$, $GaCl_3$ and $InCl_3$.

(vii) Consideration of the $S_4N_4/FeCl_3$ systems in which SO_2Cl_2, SCl_2, S_2Cl_2, $Cl{\cdot}SO_2{\cdot}OH$ and $C_6H_5{\cdot}SO_2{\cdot}Cl$ are the solvents.

(viii) Miscellaneous:

(a) Organically substituted metal-sulphur-nitrogen compounds.

(b) Studies on the $S_4N_4/SOCl_2$ system, and on the early stages of some reactions in $S_4N_4/SOCl_2/MCl_x$ systems.

(c) Nitrobenzene solutions of various metal-sulphur-nitrogen-chlorine compounds.

These subdivisions have been made purely to serve as introductory guide-lines: not infrequently the results and topics which are to be discussed cross one or more of these arbitrary divisions.

Discussion

(i) Résumé of the origin and development of this work

This work is a continuation of that by J.S. Padley[31] on $S_4N_4/SOCl_2/MCl_x$ systems. Dr. Padley briefly investigated some of the properties of a large number of specific systems of this type; his work enabled tentative conclusions to be drawn regarding which systems would be the most promising for more detailed study.

The initial stage of this work consisted of completion of the wide-ranging (but cursory) investigation of specific systems in the $S_4N_4/SOCl_2/MCl_x$ family. When this stage of the work had been completed, it seemed clear that the $S_4N_4/SOCl_2/AlCl_3$ and $S_4N_4/SOCl_2/FeCl_3$ systems would be the most rewarding for a more detailed study.

These studies of the $SOCl_2$-based system indicated that the $SOCl_2$ participated also as a reactant, and so when the more detailed study of the above two systems was completed, systems involving S_4N_4, a constant metal chloride, and solvents related to $SOCl_2$ were investigated. The chloride selected was $FeCl_3$, largely on the grounds that since it had been found to yield no less than three compounds from the system $S_4N_4/FeCl_3/SOCl_2$, all of which were soluble in $SOCl_2$, it was as promising a metal chloride as any with which to investigate the systems S_4N_4/MCl_x/(solvent related to $SOCl_2$). An additional factor favouring the choice of $FeCl_3$ was that Mössbauer studies could then be carried out on any products which might be obtained, thus providing useful access to structural information. The value of any definite structural information, and the difficulty often experienced in obtaining such information,is indicated in main section (iii).

Future developments of this work are given detailed consideration whenever appropriate, at the relevant points elsewhere in this Discussion.

(ii) Discussion of analytical difficulties

The analytical procedures which appeared to be generally satisfactory are given in the Appendix to the Experimental Section.

Difficulties have frequently been encountered in attempts to obtain reliable analyses for many of the compounds described in this work, consequently efforts to arrive at one of the most fundamental properties of a compound, namely its empirical formula, have often been seriously hindered. These difficulties broadly fall into two categories:

(a) Samples submitted for analysis from the same batch of product, or even from batches which had been recrystallised to constant melting point, often failed to give reproducible analyses. Variation of 2% or so were common; variations of 5-10% were not infrequent. The reasons for such inconsistencies are not clear.

In illustration of this difficulty, the case of the pale yellow solid [1] precipitating from the $S_4N_4/SOCl_2/InCl_3$ system is typical. There is no reason to doubt the precipitate's homogeneity, but three samples of it gave the following sets of analyses:

First: S = 12•15; N = 10•36; Cl = 42•75 %.
Second: S = 12•32; N = 8•81; Cl = 41•78 %.
Third: S = 9•60; N = 8•26; Cl = 40•70 %.

(b) Analyses of a product sometimes gave results which were fairly consistent in themselves, but which did not appear to represent reasonably straightforward, intelligible empirical formulae. Such results could be obtained even when the product was unlikely to be a mixture (by the criterion of near infrared spectrum, see succeeding main section).

To illustrate this difficulty, two cases may be considered. The first is again that of the pale yellow solid [1] referred to above: no combination of the analyses obtained on it (see above) is a good fit to a plausible empirical formula. [1] may be a mixture, but there is no positive evidence to support such a possibility. The analyses tabulated above are of the order of those required for the empirical formulae N_2SInCl_3 (requires S = 11•40; N = 9•96; Cl = 37•82%) or N_2SInCl_4 (requires S = 10•12; N = 8•85; Cl = 44•78%), and it is just as reasonable to suppose that [1] does in fact have one of these empirical forumulae (but that inexplicably erratic analysis results are obscuring this fact), as to suppose that it is a mixture. It is impossible to draw any positive conclusions from such indeterminate data.

The second case is that of the main product obtained from the S_4N_4/$FeCl_3$/SCl_2 system. This product has given the analyses S = 15•95, 17•21;

N = 4•27, 4•90; Cl = 67•44, 67•80; Fe = 16•1, 18•1%. These results suggest an empirical formula close to $S_3N_2Fe_2Cl_{12}$ (requires S = 14•54; N = 4•24; Cl = 64•33; Fe = 16•89%). Attempts to arrive at an empirical formula with which the analyses found would be in better agreement have been unsuccessful.

Lastly, the initial stages of attempts to obtain the analyses of a new product often encountered another difficulty: analyses did not add up to 100%. Results summing to 98-102% were not uncommon; exceptionally, results would sum to as low as 90%, or as high as 105%. Fortunately, repetition of analyses usually led to their sum approaching 100% more closely. The reasons for such results are not clear.

Two examples may be quoted to illustrate this difficulty. For the first instance, the first set of analyses obtained on the constant-melting-point sample of Compound Two, $(NSCl)_{3\text{ or }4}$, were S = 37•70; N = 17•09; Cl = 34•10%: total found percentage = 88•89. In the second instance, the first set of analyses the main product of the $S_4N_4/FeCl_3/SCl_2$ system gave was S = 15•95; N = 4•90; Cl = 67•8; Fe = 18•1%: total found percentage = 106•75.

These points have already been made implicitly in the Experimental section, when analyses of the product(s) of a reaction have been recorded.

(iii) Discussion of sources of structural information

The following sources are considered:

(a) Elemental analysis.

(b) Mass spectrometry.

(c) Molecular weight determinations in solution.

(d) Infrared spectroscopy.

(e) X-ray analysis.

(f) Mössbauer spectroscopy.

(a) Elemental analysis

In many fields of inorganic chemistry, much structural information about a new compound is inferred from its analysis. Ideally the compound's analysis leads to its empirical formula, and thus to a small number of possible structures which will be not merely compatible with this empirical formula, but also plausible when all other available data have been considered as well.

As noted in the preceding main section of this Discussion, the situation was frequently less than ideal in the cases of many of the new compounds described in this work. The proportion of these new compounds whose analyses are believed to be confidently established is small. Further, such analyses often come out to $S_2N_2MCl_x$ (where M represents a metal, and x is generally a common oxidation state of that metal): the compounds having this empirical formula show between them no less than four well-defined patterns of near infrared spectrum - probably representing about as many different types of molecular structure (cf. subsection (d) of this main section). Consequently the overall usefulness of elemental analysis as a source of structural information is reduced even more.

(b) Mass spectrometry

In general, a compound's mass spectrum often provides useful structural information. If the mass spectrum does not actually show the parent ion, and hence the compound's molecular weight directly (an item of information complementary to an empirical formula inferred from elemental analysis), then it frequently reveals the presence of various structural sub-units. Any ambiguities such as whether the species at a particular mass number contains two oxygens or one sulphur can sometimes be resolved by an accurate mass determination. Not infrequently a compound can be completely characterised from its mass spectrum, if sufficient data in the form of a parent ion, metastable peaks, and breakdown patterns are present.

A number of complications restricted the utility of mass spectra in this particular work. In general it was possible to obtain suitably strong mass spectra of the compounds studied only above their melting/decomposition points. Further, these mass spectra were usually broadly similar: thus the spectra obtained normally consisted of some or all of the fragments S, Cl, SN, S_2, S_2N, SNCl, S_2N_2, S_3N, S_3N_2, S_3N_3, S_4N_2,

S_4N_4, sometimes with MCl_x fragments as well. When the structures of a number of these compounds have been unambiguously established, correlation of the patterns of fragments in their mass spectra with the patterns of fragments in the mass spectra of other compounds, may permit useful conclusions to be drawn.

The relationships between sulphur-nitrogen compounds and their mass spectra may appear to be more complex and subtle than a cursory survey of the field would suggest: for instance $\overset{+}{S_4N_3}$ is a well-established moiety giving rise to a whole series of stable salts, yet its relative peak height (SN = 100) in the mass spectrum of $\overset{+}{S_4N_3}\overset{-}{Cl}$ is only 0·45 ± 0·04,[31] and the case of the $\overset{+}{S_3N_2Cl}$ cation and the mass spectrum of its chloride, $\overset{+}{S_3N_2Cl}\overset{-}{Cl}$, is similar - no mass at S_3N_2Cl could be detected at all.[90] Such behaviour is however to be expected when substantial numbers of hetero-atoms with lone pairs (S,N) are present in the relevant compounds.

(c) Molecular weight determinations in solution

The commonest sources of molecular weight data alternative to mass spectrometry, i.e. cryoscopic and ebullioscopic molecular weight determinations, were normally not applicable to the compounds discussed in this work. The majority of these compounds were insoluble in the solvent in which they were prepared, and were also insoluble in all other solvents studied, except when they dissolved with decomposition (see pp.43 , 47).

However, four compounds (isolated from the $S_4N_4/SOCl_2/AlCl_3$ and $S_4N_4/SOCl_2/FeCl_3$ systems) were found to be sufficiently soluble in nitrobenzene to permit determination of cryoscopic molecular weights. (It is probably significant that these four compounds were also very readily soluble in $SOCl_2$.) It was hoped that nitrobenzene was sufficiently inert to eliminate the possibility of any reaction with the solutes: however, the molecular weight results were never entirely consistent with other data, and the most reasonable interpretation of the results obtained is that in all cases the solute fragmented, often substantially, under the determination conditions. This conclusion is supported by the infrared studies made on the nitrobenzene solutions of some of these (and other closely related) compounds: see main section (viii), subsection (c).

The results for all four compounds studied cryoscopically are considered at the appropriate points in main section (v).

(d) Infrared spectroscopy

Structural information about the compounds prepared in this work has so far been inferred most frequently, and also most rewardingly, from a combined assessment of the elemental analysis and the near infrared spectrum of these compounds. The use of elemental analysis has already been discussed; infrared spectroscopy is now considered.

As a general rule, it is inadvisable to deduce structures from unassigned vibrational spectra, but in the present work there is a combination of circumstances which allows this to a limited extent:

One - the near infrared spectra of more than 25 compounds isolated from the $S_4N_4/SOCl_2/MCl_x$ reaction systems are of only five different types [see Tables 1 (this work) and 2 (previous work, ref. 31)].

Two - in each of these groups the individual spectra are closely similar, and are quite distinct from those of the other groups.

Three - the spectra of two groups (T1 and T3) are remarkably similar to those of two well-established sulphur-nitrogen compounds - S_4N_4 and S_4N_3Cl respectively. Further, despite the large number of spectra, none are at all similar to those of other simple sulphur-nitrogen compounds of known structure [viz. S_3N_2Cl, $S_3N_2Cl_2$, $(NSCl)_3$ (both varieties, see p.14), $(NSF)_3$ and $(NSF)_4$].

Four - it has been established[91] that for all sulphur-nitrogen compounds where the S-N bond distance is known, and the S-N stretching mode has been assigned, there is a straight-line correlation between the S-N distance, and the stretching mode's absorption wavelength.

We therefore concluded that for the sulphur-nitrogen portion of each compound, within any given group, there were likely to be close similarities in S-N bond distance, and possibly also in symmetry. Allocation of a compound to one group not only implies similarity to the other members of the group (including the "parent"), but also probable dissimilarity to other compounds not within the group. Any further structural inferences are probably unjustified. These structural conclusions seem reasonable, despite the fact that (at present) it often

TABLE 1

Group of near infrared spectra	"Parent" compound of group	Members of group other than any parent	Preparation on page
Type One (T1)	S_4N_4	Iron Compound One Aluminium Compound One $S_4N_4 \cdot 2TaCl_5$ One component of "Gallium mixture"	
Type Two (T2)	Compound Two	Iron Compound Two Gallium Compound Two	
Type Three (T3)	S_4N_3Cl	$S_2N_2HgCl_2$ $SNCoCl_2$ Product from Indium reaction Iron Compound Three Aluminium Compound Three Second component of "Gallium mixture" • Product from copper(I) reaction (Note that the products of the S_4N_4/$FeCl_3$/S_2Cl_2 system fit in this group.)	

• (See Table 2)

TABLE 1 (contd.)

Group of near infrared spectra	"Parent" compound of group	Members of group other than any parent	Preparation on page
Type Four (T4)	No "parent" known at present	$S_2N_2TiCl_3$ Product from vanadium reaction	
Type Five (T5)	No "parent" known at present	$S_2N_2HfCl_4$ (other member of group is $S_2N_2ZrCl_4$, see ref.)	

TABLE 2 (derived from ref. 31)

Group of near infrared spectra	Material		Preparation on page - in ref.31
	System of origin	Characterised as	
Type One (T1)	$S_4N_4/SOCl_2/BCl_3$	? $S_2N_3Cl_4B_{24}$	See ref.92
	$S_4N_4/SOCl_2/NbCl_5$	Uncertain	See ref.92
	$S_4N_4/SOCl_2/SbCl_5$	$S_3N_3SbCl_6$	73
	$S_4N_4/SOCl_2/SnCl_4$	$S_2N_3SnCl_4$	72
† (See below)	† $S_4N_4/SOCl_2/TeCl_4$	Uncharacterised	61
Type Three (T3)	$S_4N_4/SOCl_2/ZnCl_2$	$S_2N_2ZnCl_2$	68
† (See above)	† $S_4N_4/SOCl_2/TeCl_4$	Uncharacterised	61
	* $S_4N_4/SOCl_2/SeCl_2$	$S_2N_2SeCl_2$	60
	* $S_4N_4/SOCl_2/CuCl_2$	$S_2N_3Cu_2Cl_4$	67
	* $S_4N_4/SOCl_2/CrCl_3$	$S_2N_2CrCl_3$	64
Type Five (T5)	$S_4N_4/SOCl_2ZrCl_4$	$S_2N_2ZrCl_4$	63
	(other member of group is $S_2N_2HfCl_4$, prepared in this work)		

*The systems so qualified give products showing the appropriate pattern of absorptions, but in addition an absorption at about 870 cm^{-1}.

appears to be impossible to reconcile such conclusions with other data (such as molecular weight determinations), and despite the obvious weaknesses of the approach, which are:

One - the λ_{SN} vs. d_{SN} plot noted in Four, above, holds well for relatively simple sulphur-nitrogen compounds with few S-N stretching modes, not so well for cyclic systems, e.g. 1,4-$S_6(NH)_2$ - where mixed vibrations are to be expected - and not at all for complex molecules with so many S-N stretching modes that one cannot be sure of the appropriate λ_{SN} for the λ_{SN} vs. d_{SN} plot (e.g. S_4N_4). However, it still remains true that for all molecules, the infrared spectrum depends solely on structural parameters. The (M-)N-S-Cl compounds discussed in this work are probably complex molecules; however, such a situation would be expected to <u>reduce</u> structural similarities.

Two - the λ_{SN} vs. d_{SN} plot will not apply for compounds with infrared inactive S-N stretching modes.

Three - spectral similarities may arise from similarities in the structure of only small sub-units of each molecule. Larger-scale similarities are nevertheless still a possibility.

There is however at least one instance known where the structure indicated by near infrared spectra has been confirmed by X-ray analysis, viz. the case of the adduct $S_2N_2.2SbCl_5$.[75]

The products obtained from the systems $S_4N_4/SOCl_2/MoCl_5$ and $S_4N_4/SOCl_2/$

FIGURE ONE T1 NEAR INFRARED SPECTRA

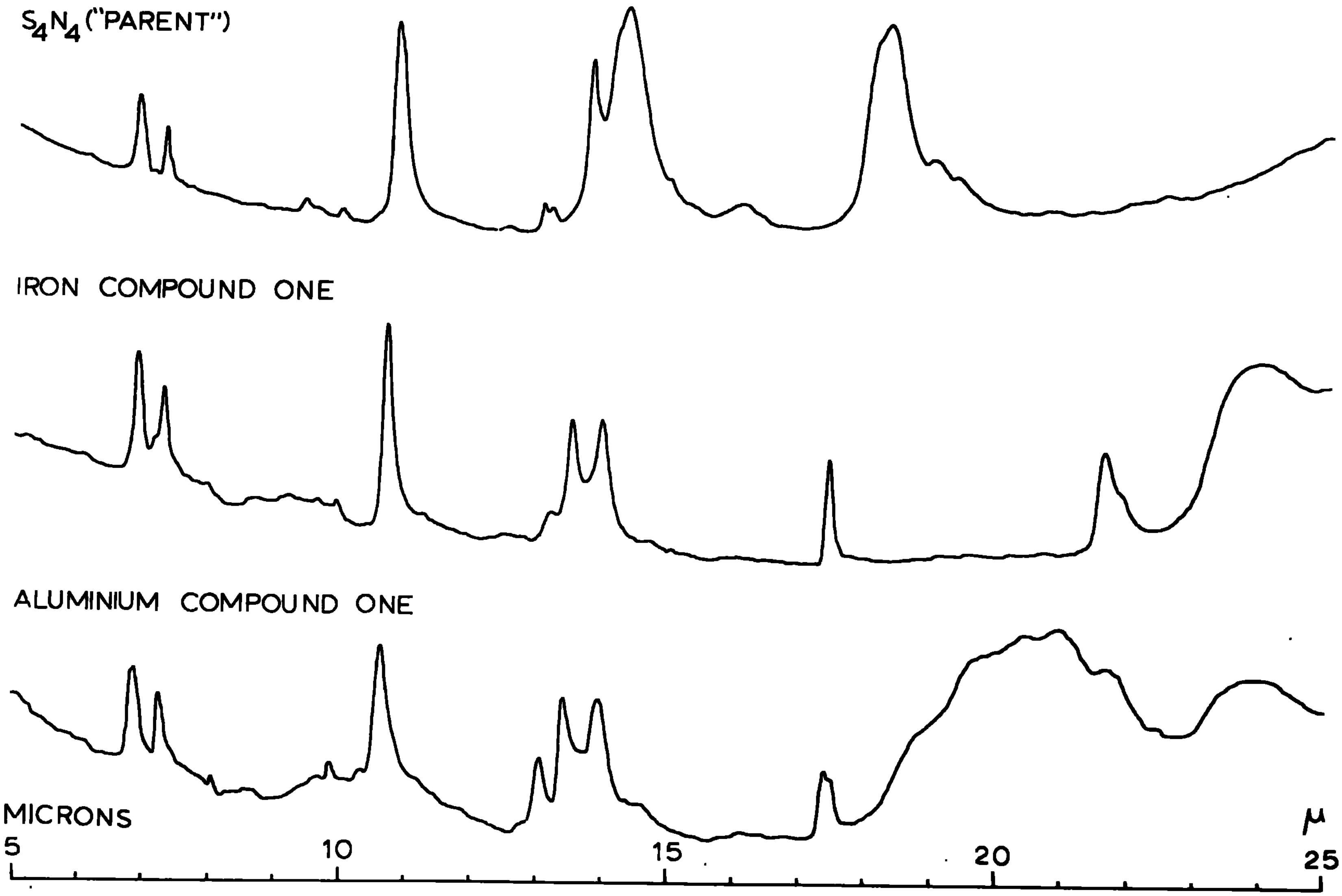


FIGURE 2

T2 NEAR INFRARED SPECTRA

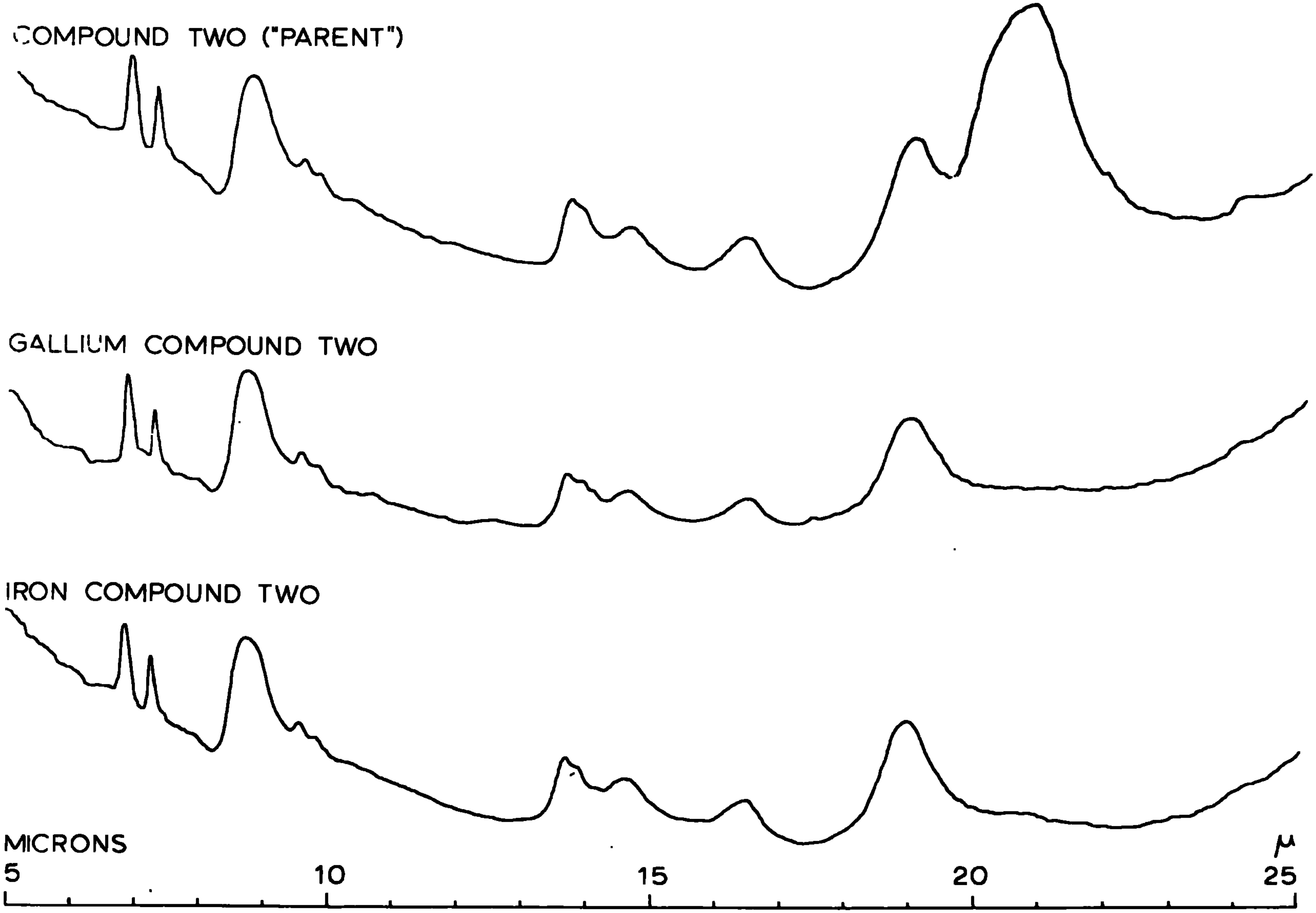


FIGURE 3 T3. NEAR INFRARED SPECTRA

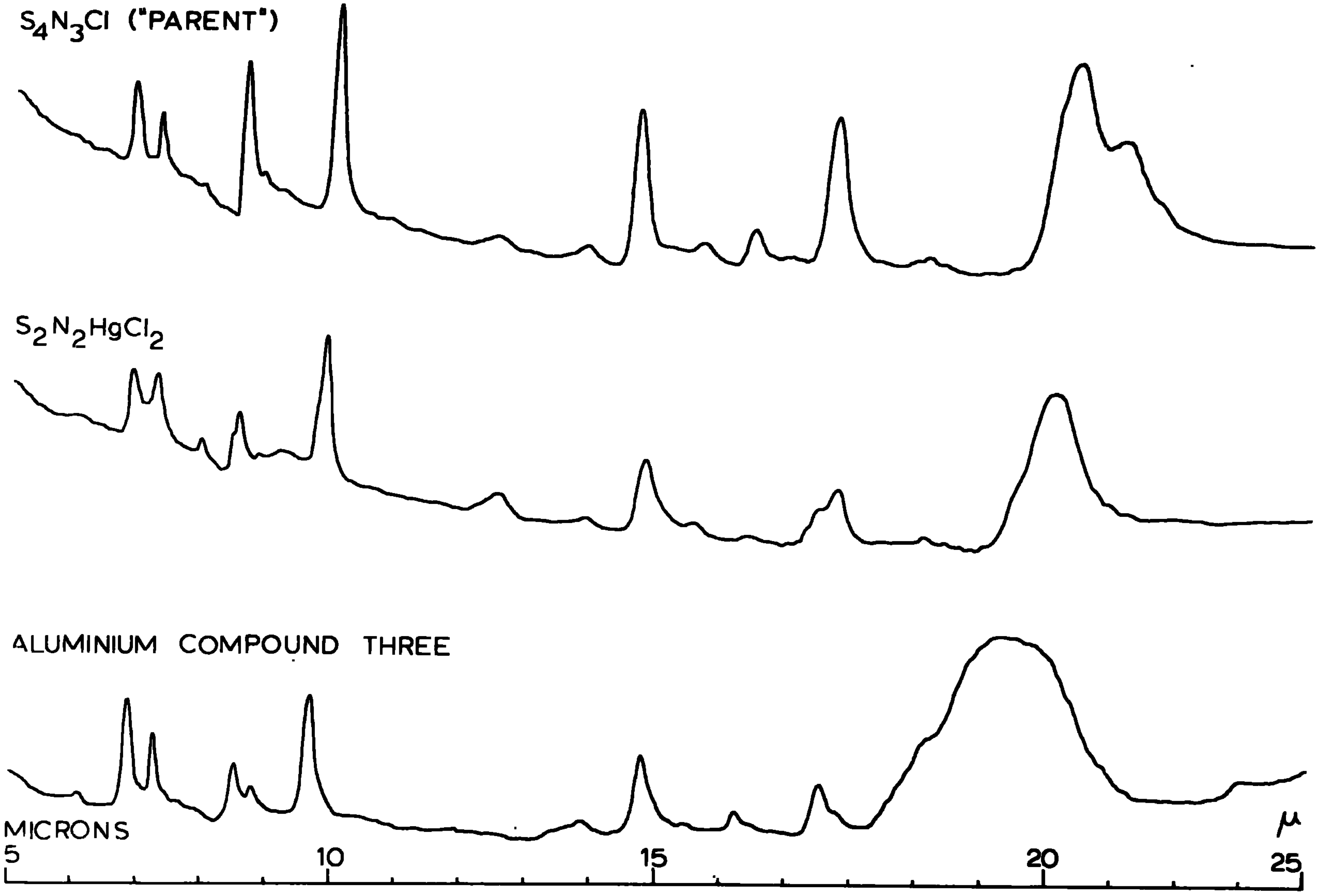


FIGURE 4 T4 NEAR INFRARED SPECTRA

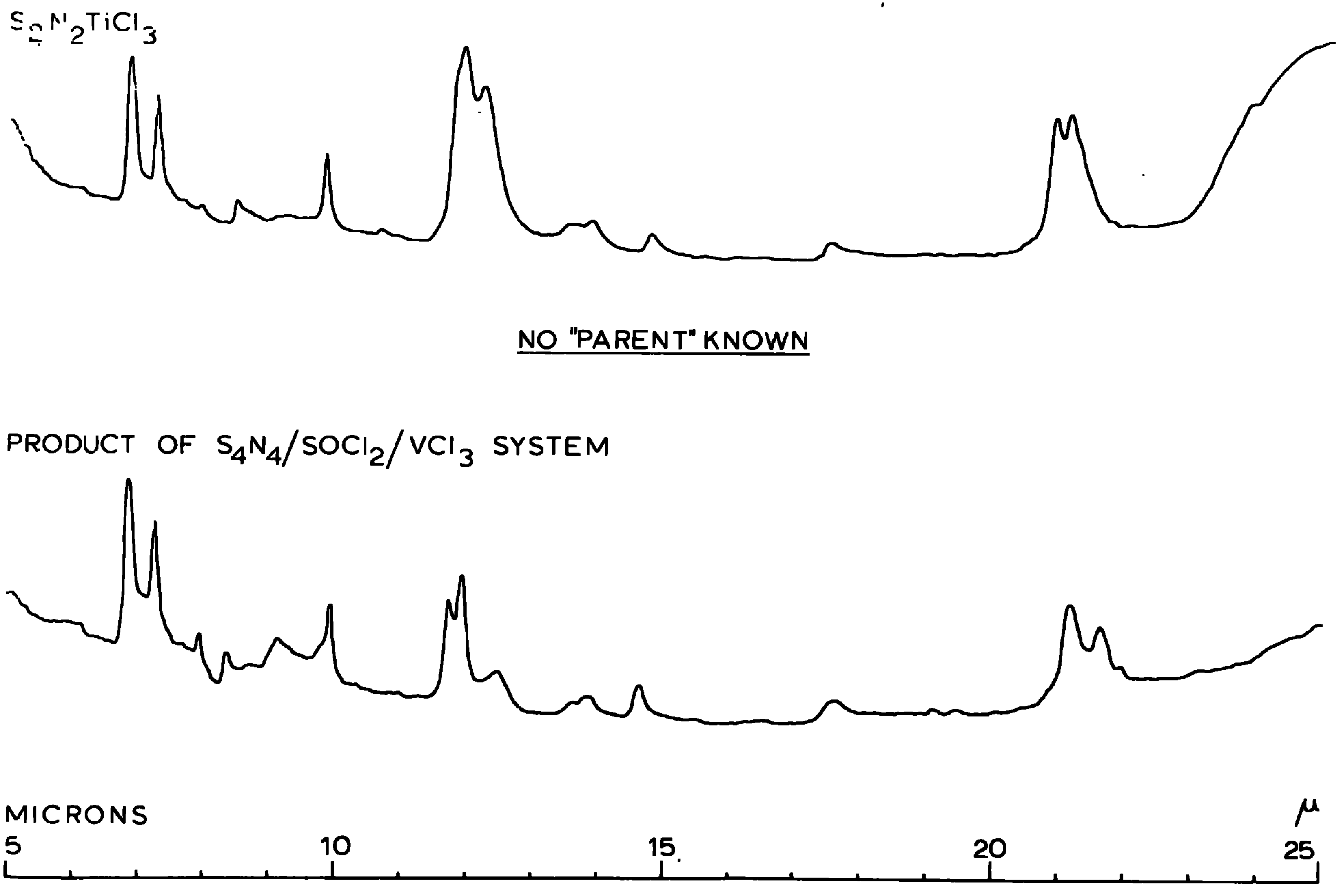


FIGURE 5

T5 NEAR INFRARED SPECTRA

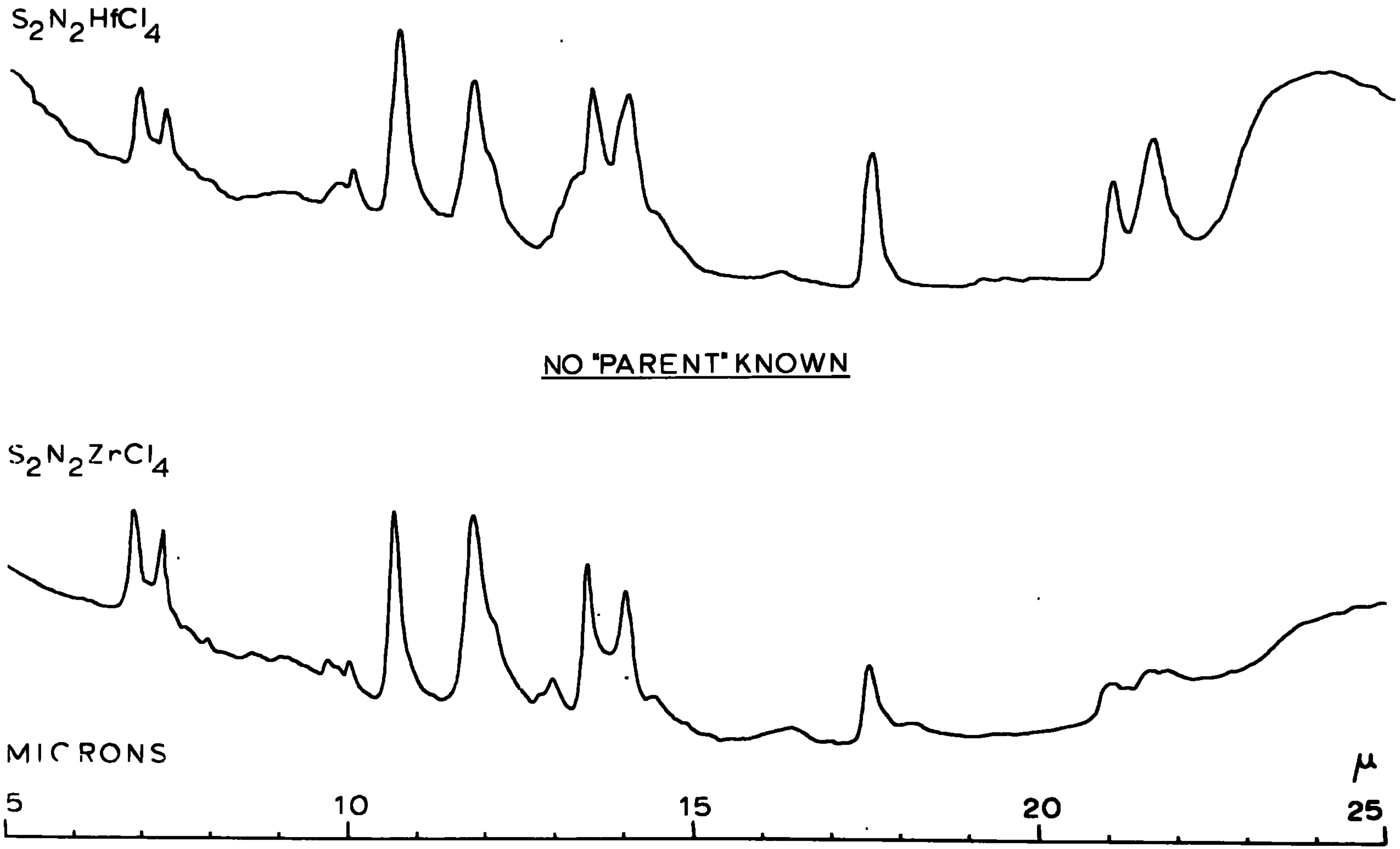
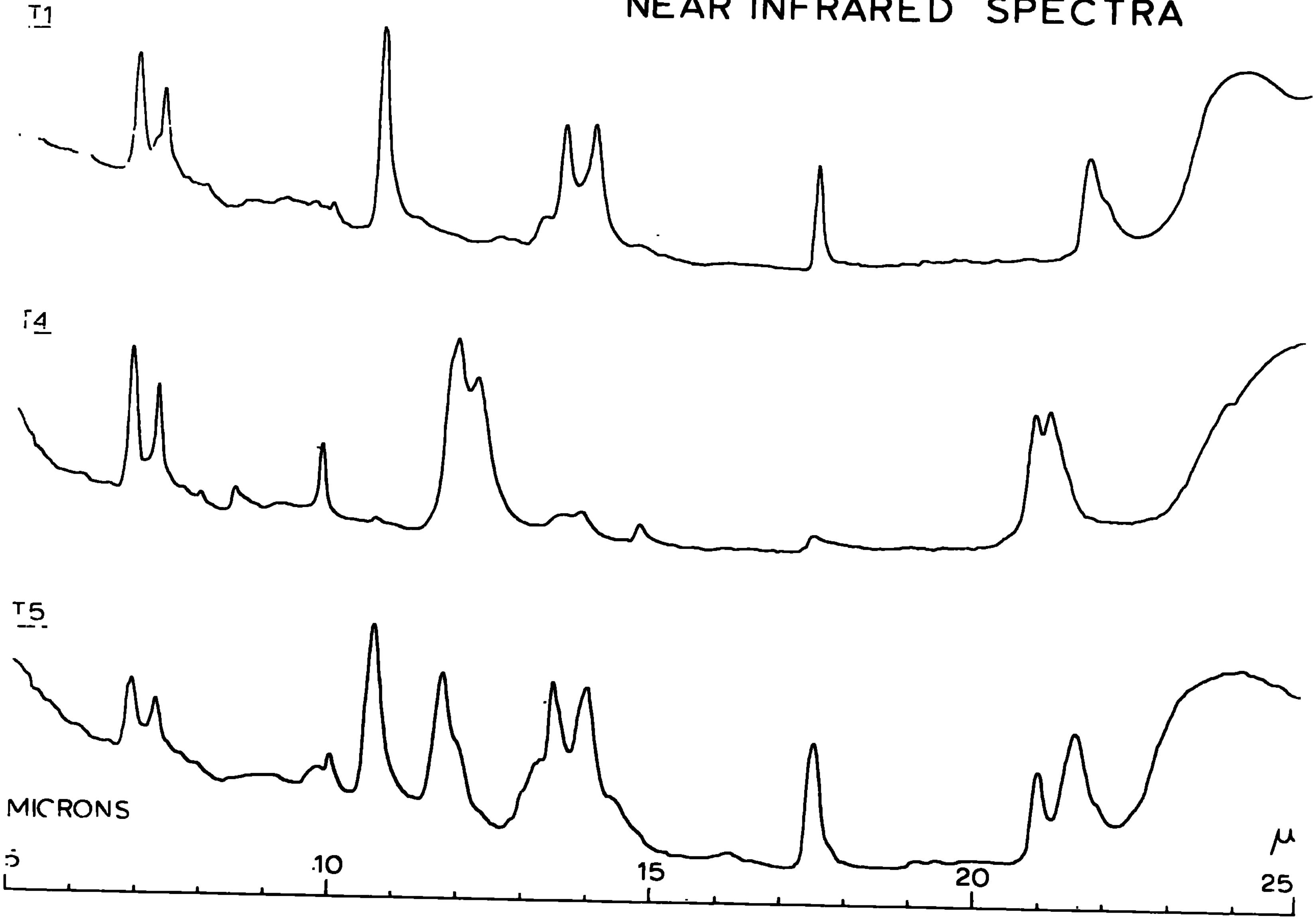


FIGURE 6

COMPARISON OF (T1 + T4) AND (T5)
NEAR INFRARED SPECTRA



WCl_6 have near infrared spectra which cannot be correlated with themselves, or with the products obtained from other $S_4N_4/SOCl_2/MCl_x$ systems described in this work, or with the products obtained from the $S_4N_4/SOCl_2/MCl_x$ systems previously described.[31]

Near infrared spectra typical of each of the five groups are shown in Figs. 1- 5. It is convenient to remark here that the T5 spectrum is, to a good approximation, the sum of T1 and T4 spectra (see Fig. 6).

(e) X-ray analysis

Alone among the various sources of structural information which could be employed in this work, X-ray analysis can effectively establish a compound's structure both fully and unambiguously. The application of the technique is only limited by its need of suitable single crystals.

Pure crystalline samples of Aluminium Compound One and Iron Compound One (both showing T1 spectra), and of Compound Two and Iron Compound Two (both showing T2 spectra) have been prepared, and there is no obvious reason why similar samples of Iron Compound Three and the product obtained from the $S_4N_4/SOCl_2/InCl_3$ system (both showing T3 spectra) should not be prepared. Thus X-ray analyses could be carried out on two compounds of each of the T1, T2 and T3 spectral types; further, if desired, the system $S_4N_4/SOCl_2/GaCl_3$ appears to be capable of yielding an additional compound in each of the T2 and T3 groups, while the $S_4N_4/SOCl_2/TaCl_5$ system will readily yield an additional compound of the T1 group. Also, a crystalline sample of the main product of the $S_4N_4/FeCl_3/SCl_2$ system has been obtained, so that overall, a reasonably useful range of compounds could be studied.

Finally it is possible that further studies on the other M-N-S-Cl compounds for which suitable solvents are not yet known will lead to further samples suitable for X-ray analysis.

(f) Mössbauer spectroscopy

Mössbauer spectroscopy is a ready source of information about the electronic environment(s) (and hence implicitly the stereochemical environment(s) also) of an element showing the Mössbauer effect. The greatest possible amount of such information is obtainable when a series of related compounds of one appropriate element is studied. Iron is one of the elements displaying the Mössbauer effect, and it was partly for this reason that $FeCl_3$ was chosen for the investigation of the systems S_4N_4/constant metal chloride/varying solvent related to $SOCl_2$ (see p.91).

The advantages of the technique are quite remarkable. For instance the exact physical state of the sample being studied is unimportant - it can be crystalline, microcrystalline, or amorphous. Purity of the sample is unimportant within wide limits; contamination of a sample with as much as 10% of other material (which can itself be Mössbauer active) does not affect the reliability or the extent of the results obtainable. Finally, the information which is sought is available in a matter of days, in contrast to the weeks and months required for a full X-ray analysis.

It is hoped that Mössbauer studies will shortly be commenced on the iron compounds which have been prepared in this work.

(iv) Consideration of those $S_4N_4/SOCl_2/MCl_x$ systems which can usefully be discussed without reference to the $S_4N_4/SOCl_2/AlCl_3$ and $S_4N_4/SOCl_2/FeCl_3$ systems

i.e. (1) the systems involving $MgCl_2$, $CdCl_2$, $GeCl_4$ and $PbCl_2$ (in which systems the metal chloride did not react), and (2) the systems involving Hg_2Cl_2, $CoCl_2$, CuCl, $TiCl_3$, VCl_3, $HFCl_4$, $MoCl_5$ and WCl_6 (in which systems there was partial or complete reaction of the metal chloride).

(1) The systems derived from $MgCl_2$, $CdCl_2$, $GeCl_4$ and $PbCl_2$

It appeared that none of the above chlorides reacted significantly with S_4N_4, in $SOCl_2$. It has been established that $ZnCl_2$ and $HgCl_2$ both react readily[31] with S_4N_4 in $SOCl_2$, giving products characterised as $S_2N_2ZnCl_2$ and $S_4N_4HgCl_6$ (but see p.117 regarding the latter). Consequently, $CdCl_2$ was anticipated to react in some way. The near infrared spectrum of the solid material obtained from the $S_4N_4/SOCl_2/CdCl_2$ system, together with the colour changes this material went through, suggest that a slight interaction of S_4N_4 and $CdCl_2$ had in fact occurred. It is possible that a very slow reaction does take place.

The apparent failure of the $S_4N_4/SOCl_2/MgCl_2$ system to yield a product occasions no surprise. Generally, compounds seem to be most readily obtained from the system $S_4N_4/SOCl_2/MCl_x$ when M is of intermediate, rather than very high or very low, electronegativity. The $MgCl_2$ reaction was carried out to try to establish how low the electronegativity of a metal had to be before its chloride failed to react. It is necessary to remember however, that many other properties of the metal and/or its chloride will be involved in facilitating or suppressing any reaction. Finally, although reaction was not in fact expected, sulphur-nitrogen derivatives of metals of very low electronegativity (Na and K) are known[93,94] from other solvent systems.

The possible reaction of S_4N_4 and $PbCl_2$ in $SOCl_2$ solution was investigated because a number of lead-sulphur-nitrogen compounds are known from another solvent system. Since $PbCl_2$ does not hydrate, and is stable to water, it would possibly be worth making persistent attempts to prepare a lead-sulphur-nitrogen-chlorine compound either from the $S_4N_4/SOCl_2/PbCl_2$ system, or from a system closely related to it. This is because alone among the chlorides studied in the $S_4N_4/SOCl_2/MCl_x$ systems, $HgCl_2$ or Hg_2Cl_2 (oxidation state of Hg uncertain, see p.117) - both of which chlorides, like $PbCl_2$, neither hydrate nor are unstable to water - gave a product which appeared to be virtually (if not fully) air-stable. Consequently it is suspected that the prerequisite to air-stability of most M-S-N-Cl compounds is a parent MCl_x that neither hydrates nor hydrolyses. (It is believed that the stability to air of the material obtained from the $S_4N_4/FeCl_3/S_2Cl_2$ system may have a slightly different origin. See p.155)

The reasons why $MgCl_2$, $CdCl_2$ and $PbCl_2$ (particularly the last two) failed to interact with the $S_4N_4/SOCl_2$ system have not yet been established. The salts $MnCl_2$, $CoCl_2$, $ZnCl_2$ (whose metal atoms all have generally similar electronegativites, and which are also all in the (II) oxidation state, and which probably all have the same very low solubility in $SOCl_2$) gave reasonably reliably characterised products[31]: $FeCl_2$ is a special case, being oxidised to $FeCl_3$ by $SOCl_2$. Similarly, the salts $NiCl_2$ and $CuCl_2$, and CuCl appeared to react at least partially with the $S_4N_4/SOCl_2$ system, although the materials obtained from these last three systems are not so reliably characterised.[31] Probably the energy which could be released by formation of any Mg-, Cd-, or Pb-N-S-Cl compound in the $SOCl_2$ system is simply not enough to counterbalance the energy necessary to break down the $MgCl_2$, $CdCl_2$ or $PbCl_2$ lattices in the first place.

The case of the $S_4N_4/SOCl_2/GeCl_4$ system is rather different. It has been established[31] that S_4N_4 and $SnCl_4$ react in $SOCl_2$ solution to give a product which (although retrospectively the analysis obtained on it must be regarded as suspect) has a near infrared spectrum clearly belonging with the Tl group. Further, $GeCl_4$ is known to form adducts quite readily with species co-ordinating through sulphur or nitrogen atoms.[95] Thus there was reason to expect an interaction of some description between $GeCl_4$ and S_4N_4, particularly since (unlike the case of the $MgCl_2$, $CdCl_2$ and $PbCl_2$ systems) both potential reactants were present in solution.

To attempt to explain this apparent absence of any reaction, one may speculate that (for instance) the activation energy for interaction of $GeCl_4$ (or any species derived from it) with S_4N_4 (or any species derived from it) may be higher than the activation energy for the reaction of S_4N_4 with $SOCl_2$ (leading to S_4N_3Cl).

(2) The systems derived from Hg_2Cl_2, $CoCl_2$, CuCl, $TiCl_3$, VCl_3, $HfCl_4$, $MoCl_5$ and WCl_6

Hg_2Cl_2, $CoCl_2$, CuCl. The products respectively obtained from the reaction of these chlorides with S_4N_4, in $SOCl_2$, showed T3 near infrared spectra. The three systems are thus considered together, since comment on any one compound's structure based upon the compound's near infrared spectrum, is tentatively applicable to the other two compounds.

(a) Hg_2Cl_2

The following points have been established regarding the product obtained from the system $S_4N_4/SOCl_2/Hg_2Cl_2$:

1. - Analyses suggest the empirical formula $S_2N_2HgCl_2$, or a close approximation to this.

2. - Its mass spectrum below its melting/decomposition point shows the parent ion $S_2N_2HgCl_2$, and a clear breakdown pattern derived from this parent.

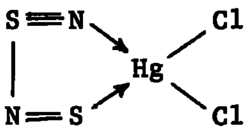
3. - The product either does not dissolve, or dissolves only with apparent decomposition in such solvents as have been investigated (p. 47).

4. - Its near infrared spectrum closely resembles that of S_4N_3Cl. (Both are T3).

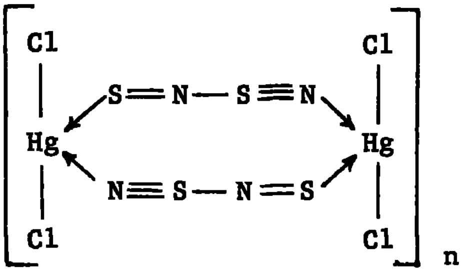
5. - Melting point = 169°.

Points 1 and 2 together make it virtually certain that the compound's empirical formula is $S_2N_2HgCl_2$. Insufficient evidence is available for reliable conclusions as to the compound's state of aggregation or structural nature. Nothing can be inferred from its general insolubility (point 3):

it may be polymeric, or ionic, or a particularly compact lattice of polar covalent molecules. The intermediate melting-point (point 5) and mass spectrum (which shows $S_2N_2HgCl_2$ as parent ion, and no higher mass fragments) (point 2) favour a polar covalent, or readily degraded polymeric, structure. Possible structures for the compound are -

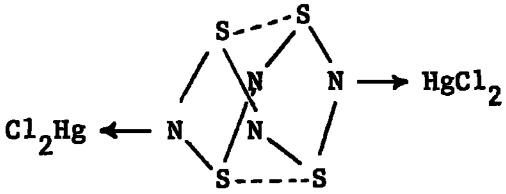


1



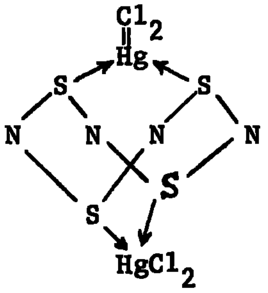
(could be polymerised through Cl-bridges at octahedral mercury)

2



(probably polymerised through Cl-bridges at tetrahedral mercury)

3



(could be polymerised through Cl-bridges at octahedral mercury)

4

Other structures are plausible, which are essentially only variations of structures such as 1 - 4.

The least likely of the above structures may be 3: the compound $(S_2N_2HgCl_2)_n$ is unaffected by boiling $SOCl_2$ and no S_4N_4 adducts are known which are stable to $SOCl_2$ - but $(S_2N_2HgCl_2)_n$ could be an exception.

As implied in the structures suggested, the compound may be a derivative of Hg(II) although the source of mercury used was Hg_2Cl_2. (It is established that $SOCl_2$ oxidises $FeCl_2$ to $FeCl_3$ (p. 57) and it is almost certain that it oxidises $TiCl_3$ to $TiCl_4$ p.120; oxidation of Hg_2Cl_2 to $HgCl_2$ is thus quite possible.) However, the near infrared spectrum of $S_2N_2HgCl_2$ is extremely similar to that of a material derived from the $S_4N_4/SOCl_2/HgCl_2$ system and characterised as $S_4N_4HgCl_6$.[31] No melting point or mass spectrum was recorded for the latter, and it seems likely that the latter also is $S_2N_2HgCl_2$, and that poor analyses (see main section (ii)) concealed the fact. A re-investigation of the systems $S_4N_4/SOCl_2/Hg_2Cl_2$ and $S_4N_4/SOCl_2/HgCl_2$ should clarify matters.

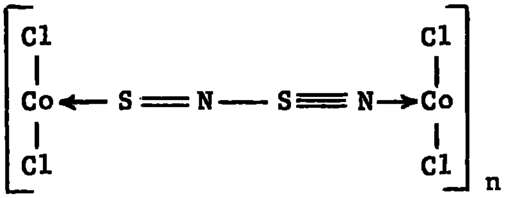
The exceptional stability of $S_2N_2HgCl_2$ to air is discussed on p.113; the reasoning employed is equally valid whether $S_2N_2HgCl_2$ is derived from $HgCl_2$ or Hg_2Cl_2.

The mass spectrum of $S_2N_2HgCl_2$ is especially interesting. When recorded at 240°, i.e. at a temperature well in excess of the temperature (169°) at which the compound melts (and probably decomposes), the spectrum is weak, and based upon fragmentation from a parent ion $S_4N_4HgCl_2$. This spectrum is quite different from the strong ones recorded at temperatures (115° and 135°) chosen well below the compound's melting (and decomposition?) point.

Two explanations for the appearance of this ion seem reasonable. First, a species $S_4N_4 \cdot HgCl_2$ (of uncertain nature) results from pyrolysis of $S_2N_2HgCl_2$, or second, a species $S_4N_4 \cdot HgCl_2$ is a minor co-product of $S_2N_2HgCl_2$. If the latter case, $S_4N_4 \cdot HgCl_2$ must be much less volatile than $S_2N_2HgCl_2$. Of the two possibilities, the former is perhaps the more likely since (a) no adduct $S_4N_4 \cdot MCl_x$ has yet been found stable to $SOCl_2$ (this work, and ref.31) (but see earlier comments re. structure <u>3</u>) and (b) attempts to prepare an adduct of S_4N_4 and $HgCl_2$ have been unsuccessful.[29]

(b) <u>$CoCl_2$</u>

The product obtained from the $S_4N_4/SOCl_2/CoCl_2$ system has already been characterised,[31] and the structure



polymerised through chlorine bridges, has been proposed for it. (In this context, it may be noted that it shows a T3 spectrum - as does $S_2N_2HgCl_2$ - and the proposed/suggested structures for $SNCoCl_2$ and $S_2N_2HgCl_2$ may be compared.)

The melting-point[31] (>360°) and the failure of the compound to dissolve in any of the solvents studied, except with decomposition, could be taken to support the polymeric constitution proposed for $SNCoCl_2$.

This repeat study of the $S_4N_4/SOCl_2/CoCl_2$ system was made to discover whether or not a particular system picked at random from the general group $S_4N_4/SOCl_2/MCl_x$ would show reproducible behaviour. Such was found to be the case, by the criteria of near infrared and mass spectra.

(c) CuCl

The material obtained from the $S_4N_4/SOCl_2/CuCl$ system analysed to the empirical composition $S_2N_2Cu_3Cl_5$, which probably represents a mixture of a compound $S_2N_2Cu_xCl_y$ and unreacted copper chloride. For this reason, no thorough study was made of the compound's properties.

It was however established that the compound showed a T3 infrared spectrum which was closely similar to that of the material derived from the $S_4N_4/SOCl_2/CuCl_2$ system,[31] while being still fundamentally distinct from it. Nothing positive regarding the identity or otherwise of these two compounds can be inferred from their mass spectra, but it is noticeable that at any temperature, the CuCl-derived material shows a weaker spectrum than does the $CuCl_2$-derived material. It is thus believed that $SOCl_2$ does not oxidise Cu(I) to Cu(II)(in contrast to Fe(II) → Fe(III); Ti(III) → Ti(IV); Hg(I) → Hg(II)), and that the material obtained contains a Cu(I)-N-S-Cl compound. There is insufficient information available at the present time to speculate usefully on the structure of the supposed

$S_2N_2Cu_xCl_y$, especially as the analysis figures leading to the assumed empirical formula may be erroneous (see main section (ii)).

It seems reasonable to suppose that the lattice energy of CuCl is too high to permit its ready reaction in the $S_4N_4/SOCl_2$ system; it may therefore be worth attempting to complete the conversion of CuCl to the supposed $S_2N_2Cu_xCl_y$, to test this theory.

$TiCl_3$,VCl_3 The materials obtained from the reaction of these chlorides with S_4N_4, in $SOCl_2$, both showed T4 near infrared spectra, and so the two systems are considered together.

(a) **$TiCl_3$**

The product obtained from the $S_4N_4/SOCl_2/TiCl_3$ system is believed to be in fact derived from Ti(IV), since $TiCl_3$ is an established strong reducing agent, and $SOCl_2$ is known to oxidise $FeCl_2$ to $FeCl_3$ (p.57) and believed to oxidise Hg_2Cl_2 to $HgCl_2$ (p.117). Further, the near infrared spectra of the products of the systems $S_4N_4/SOCl_2/TiCl_3$ and $S_4N_4/SOCl_2/TiCl_4$[31] are indistinguishable, and the mass spectrum of the $TiCl_3$-derived material showed a breakdown pattern derived from $TiCl_4$, at temperatures below the product's melting (and decomposition?) point.

Points established for the product of the $TiCl_3$-derived system are:

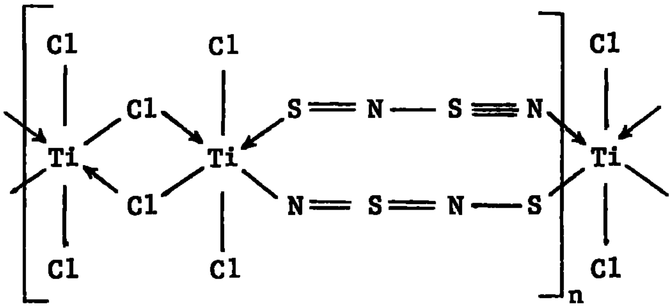
1. - Analyses indicate the empirical formula $S_2N_2TiCl_3$.

2. - As noted earlier, mass spectra at temperatures below the melting(/decomposition?) point show a $TiCl_4$-derived breakdown pattern.

3\. - Melting point = 252°.

4\. - The compound slowly precipitated from $SOCl_2$ solution.

Point 3 suggests that $S_2N_2TiCl_3$ is either ionic or associated: point 4 could be taken to support either of these possibilities. Taking this in conjunction with points 1 and 2, means a structure such as that below is possible for the compound.



Finally, it can be noted that when the $S_4N_4/SOCl_2/TiCl_4$ system was investigated[31] as noted earlier, although the product's infrared spectrum was indistinguishable from that of the product of the $S_4N_4/SOCl_2/TiCl_3$ system, its observed melting point was 142°, and its analyses indicated the empirical formula $S_3N_4Ti_2Cl_6$: in retrospect, it is believed that the current investigation has simply yielded a purer sample of the $S_2N_2TiCl_3$ (derived from Ti(IV)) than did the previous investigation, and that better elemental analyses have been obtained in the current case.

(b) $\underline{VCl}_3$

Of the various confidently characterised compounds obtained from the system $S_4N_4/SOCl_2/MCl_x$, only a very few appear to contain more than two SN units per metal atom, and the great majority contain two such units per metal atom. Only $SNMnCl_2$[31] and $SNCoCl_2$[31] contain one unit per metal atom. Consequently the empirical formula indicated by elemental analyses for the product of the $S_4N_4/SOCl_2/VCl_3$ system, SNV_2Cl_4, must be treated with caution, containing as it does only 0·5 SN units per metal atom.

At the present time, insufficient data are available regarding this product, for useful speculation about its nature. Attempts to devise a plausible structure for the apparent empirical formula have been unsuccessful. It is suspected that the empirical formula SNV_2Cl_4 may represent a mixture of unreacted VCl_3, and a V-N-S-Cl compound of unknown composition. It is possible that this V-N-S-Cl compound is a derivative of VCl_4 (formed by slow oxidation of VCl_3 by $SOCl_2$); this possibility would allow for the fact that the product material may be a mixture, and for the similarity of its near infrared spectrum with that of $S_2N_2TiCl_3$ (which is almost certainly derived from $TiCl_4$). A study of the system $S_4N_4/SOCl_2/VCl_4$ should be helpful in this respect.

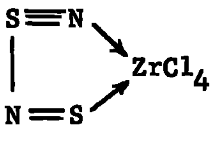
The remarkable behaviour on recrystallisation of what appeared to be a sample of S_4N_3Cl (see p. 38), suggests that the system $S_4N_4/SOCl_2/VCl_3$ is more peculiar and complex than might initially be supposed.

$HfCl_4$

The product of the system $S_4N_4/SOCl_2/HfCl_4$ shows a near infrared spectrum which is quite distinct from those shown by the products of the other systems discussed in this main section; consequently it is discussed independently of these systems. As may be expected, its spectrum is however closely similar to that of the previously characterised[31] product of the $S_4N_4/SOCl_2/ZrCl_4$ system.

At the present time, little can confidently be inferred about the nature of this compound. Analyses suggest the empirical formula $S_2N_2HfCl_4$; the slow precipitation of the compound from the $SOCl_2$ shortly after a black tar was formed may be taken to represent growth of polymer chains of the compound, from $SOCl_2$-soluble oligomers to $SOCl_2$-insoluble polymers. The melting-point (135-6°) is of no diagnostic value. Its near infrared spectrum (T5) is very similar to the sum of a T1 and a T4 spectrum: presumably the structural elements ultimately responsible for the latter two near infrared absorption patterns are present in $S_2N_2HfCl_4$.

The previously characterised $S_2N_2ZrCl_4$ which has generally similar properties is believed[31] to exist as the discrete molecule



or as low oligomers of this unit.

$MoCl_5$ and WCl_6

The analyses obtained on the product of the $S_4N_4/SOCl_2/MoCl_5$ system are in good agreement with those required for the empirical formula $S_2N_4MoO_2Cl_4$: they are in less good agreement with the formula $S_2N_4MoO_3Cl_4$, and in relatively poor agreement with the formula $S_2N_4MoOCl_4$. The ability of $MoCl_5$ and WCl_6 to extract oxygen from various compounds (such as liquid SO_2, dimethyl sulphoxide, or triphenylphosphine oxide) is well-established,[96] hence it is reasonable to accept that these products are likely to contain oxygen (derived in this case from $SOCl_2$). The present non-availability of metal analyses means however that for the time being there is uncertainty as to the exact proportion of oxygen present in these two products.

If it is assumed (see main section (ii)) that the analyses obtained on the WCl_6-derived product include a high sulphur analysis, then this product may be $S_2N_4WO_2Cl_4$ (in tentative analogy with the $MoCl_5$ system).

Such studies as have been made upon the two compounds have given no useful indication of their structures. Their melting points, mass spectra, and insolubility in $SOCl_2$ may all be taken to suggest they are polymeric. The significance of the fragments SO in their mass spectra is not yet established. Their infrared spectra do not resemble each other, and neither has yet been correlated with that of another (M-)N-S(-Cl) compound. Further potentially useful information regarding the nature of these two compounds could possible be obtained from magnetic moment determinations.

(v) Consideration of the systems $S_4N_4/SOCl_2/AlCl_3$ and $S_4N_4/SOCl_2/FeCl_3$

Preparations: Iron Compound One, p.58 ; Iron Compound Two, p.60 ; Iron Compound Three, p.65 ; Aluminium Compound One, p.49 ; Compound Two, p.52 .

These two systems were studied in some detail, with a view to increasing the understanding of the general system $S_4N_4/SOCl_2/MCl_x$. Crystalline, constant-melting samples of Aluminium and Iron Compounds One, and of Compound Two and Iron Compound Two, were prepared so that X-ray analyses of their structures could be undertaken.

The nature of the various products of these two systems is considered first. Their preparative origins and interrelationships are then discussed.

Compound Two

Points established regarding this compound are:

1 - Elemental analyses require the empirical formula NSCl.

2 - Apparent cryoscopic molecular weight in nitrobenzene = 235 ($N_3S_3Cl_3$ would require 245, to nearest integral value).

3 - It is obtained in maximum yield when solid S_4N_4 (rather than an $SOCl_2$ solution of S_4N_4) is reacted with the $SOCl_2$ solution of $AlCl_3$. ($SOCl_2$ rapidly degrades S_4N_4 to species with shorter S-N skeletons.)

4 - In contrast to the behaviour of the two materials established to be $N_3S_3Cl_3$ (see p. 14), it may be recrystallised unaltered from benzene,

after 24 hours at 55°. The variety of $N_3S_3Cl_3$ believed to be a pure isomer is converted into the variety believed to be a mixture of isomers, under the same conditions.[29]

5 - Unlike the same two established $N_3S_3Cl_3$'s,[29] it does not show the patterns for $N_3S_3Cl_3$, $N_3S_3Cl_2$, or N_3S_3Cl, in its mass spectrum.

6 - Its infrared spectrum is quite distinct from those of the materials characterised as $N_3S_3Cl_3$[29] (which are noticeably similar to each other).

7 - Its solubility in $SOCl_2$ (estimated at roughly 0·1-0·2 gm. per 10 ml. at room temperature, and 1 gm. per 10 ml. at reflux) suggests it is neither ionic nor polymeric.

If points 1 and 2 are considered in isolation, then Compound Two is almost certainly a trithiazyl trichloride, $N_3S_3Cl_3$. However, interpretation of the results of cryoscopic molecular weight determinations on the related substances Iron Compound Two, and Iron and Aluminium Compounds One, requires that in every case the solute has fragmented substantially (see later in this main section). Consequently, Compound Two may be a higher oligomer than a trimer, but dissociates or decomposes in the nitrobenzene solution in such a way that its apparent molecular weight is fortuitously that of a trimer.

Points 4-6 show that if it is a trimer (i.e.a trithiazyl trichloride) it is quite distinct from those already known. Point 3 may in fact be taken to indicate that Compound Two's skeleton is $(SN)_4$, i.e. that it is a tetrameric NSCl (and cf. the remarks regarding point 2).

Thus Compound Two appears most likely to be either an entirely new trithiazyl trichloride, $N_3S_3Cl_3$, or (a) tetrathiazyl tetrachloride, $N_4S_4Cl_4$. Its sulphur-nitrogen skeleton is likely to be a ring rather than a chain - no sulphur-nitrogen-halogen compounds are definitely known to have a chain skeleton, and only $(NSBr)_n$ is believed to have one.[55] Consequently, if Compound Two is trimeric, it is likely to be simply a geometric isomer of the established $N_3S_3Cl_3$. An X-ray analysis is in progress.

Two thiazyl fluorides, $N_3S_3F_3$[97] and $N_4S_4F_4$[49] are known. Consequently (despite the likely high insolubility of AlF_3 in SOF_2) an investigation of the $S_4N_4/AlF_3/SOF_2$ system would be worthwhile: if the system were found to lead to one of these oligomers, to the virtual exclusion of the other, Compound Two could be taken to be the corresponding oligomer of thiazyl chloride.

Iron Compound Two

Points established for this compound are:

1 - Elemental analyses lead to the empirical formula $S_4N_4FeCl_4$: the available data are in less good agreement with the formula $S_3N_3FeCl_3$.

2 - Its near infrared spectrum is remarkably similar to that of Compound Two, (one of the products of the $AlCl_3$-derived system).

3 - A cryoscopic molecular weight determination gave the results

259, 296 which are compatible only with those of a solute species whose molecular weight is the same as, or even lower than, that of $S_3N_3FeCl_3$ (requires 300) unless substantial solute fragmentation is postulated.

4 - Its solubility in $SOCl_2$ (estimated at respectively 0·2 and 1 gm. per 10 ml. at room temperature and at reflux) suggests it is neither ionic nor polymeric.

Iron Compound Two appears most likely to be $S_4N_4FeCl_4$ (assuming good analyses, and considerable fragmentation during molecular weight determination, points 1 and 3) or, rather less likely, $S_3N_3FeCl_3$ (assuming less good analyses, and only a little fragmentation during molecular weight determination). The close similarity of the near infrared spectra and preparative origins of Compound Two and Iron Compound Two suggests that they are closely related compounds. When the structure of the former has been established, it should be possible to draw further conclusions about the nature of the latter.

Iron and Aluminium Compounds One

So many properties of these two compounds (such as method of preparation, near infrared and mass spectra, melting points, and solubilities in $SOCl_2$) are so similar that it is certain these two compounds are closely related. The empirical formula of Iron Compound One is established, although analytical difficulties are still frustrating attempts to confirm that of Aluminium Compound One. For these reasons the discussion of these two compounds will be in terms of the iron compound, but is applicable to the aluminium compound.

Points established for Iron Compound One are:

1 - Elemental analyses lead to the empirical formula $S_2N_2FeCl_5$.

2 - It has a low melting point, and a high solubility in $SOCl_2$.

3 - It is stable to prolonged and repeated refluxing in $SOCl_2$.

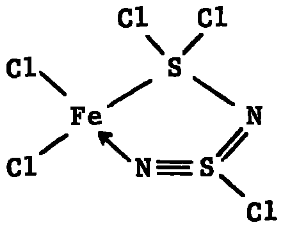
4 - Its near infrared spectrum is closely similar to that of S_4N_4.

5 - Its solution in nitrobenzene shows an infrared absorption corresponding to one shown by solutions of S_4N_4 in nitrobenzene.

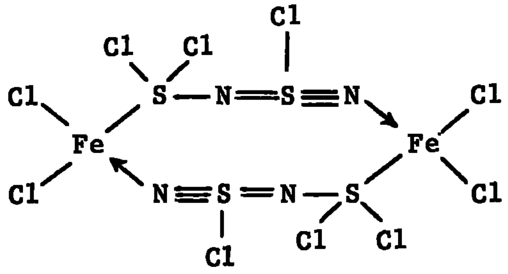
6 - Its cryoscopic molecular weight determination in nitrobenzene gave results (202, 183) compatible only with those of a solute species whose molecular weight is lower even than that of $S_2N_2FeCl_2$ (requires 219), unless substantial solute fragmentation is postulated.

7 - Its $SOCl_2$ solution is dichroic, requiring that at least one solute species has no centre of symmetry.

In terms of points 1 and 2, possible structures are -



1



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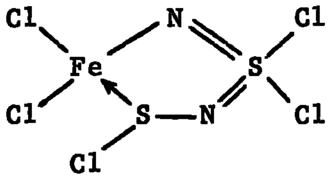

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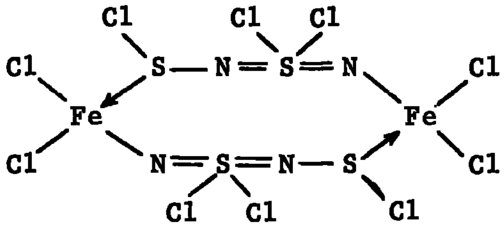

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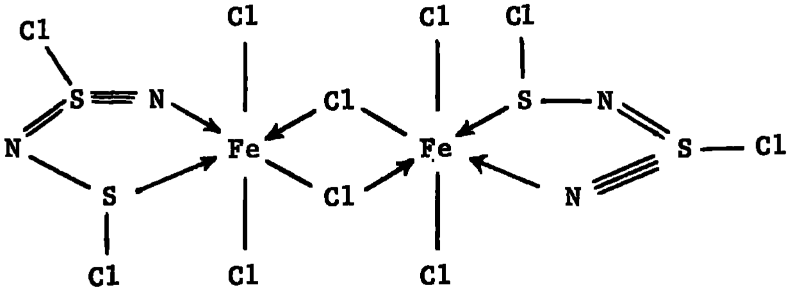


5

Other, closely similar, variations of such structures are possible.

1 and 2 are more likely than 3-5, since a system which oxidises sulphur up to S^{VI} is likely to involve S^{IV} as a lower oxidation state, rather than S^{II}.

1, 3 and 5 are perhaps more likely than 2 and 4 since S_2N_2 chains have so far only been established[32,33] to occur bidentate to a single metal atom, in sulphur-nitrogen-metal compounds.

Points 4 and 5 are most easily understood in terms of structures 2 and 4. These two points are not taken to indicate the presence of a structural unit very closely related to that of S_4N_4, in view of point 3. S_4N_4 is rapidly converted at room temperature to S_4N_3Cl by $SOCl_2$, and there is no reason to suppose that coordination of S_4N_4 to an iron chloride renders it stable to $SOCl_2$, since S_4N_4 adducts with $TeCl_4$, $TiCl_4$, $SnCl_4$ and $SbCl_5$,[31] and with $AlCl_3$ and $TaCl_5$ (this work) are known to be decomposed by $SOCl_2$.

Point 6 emphasises that the absorption relevant to point 5 probably derives from a vibrational sub-unit of S_4N_4 (which may be common to many sulphur-nitrogen compounds), rather than from the S_4N_4 cage. See p.163.

Point 7 favours structures 1 and 3, rather than 2, 4 or 5, at least for the species in solution (which is not necessarily the same as that present in the crystal).

Finally, see the discussion of the product of the $S_4N_4/SOCl_2/TaCl_5$ system.

Iron and Aluminium Compounds Three

These two materials are at the present time characterised by infrared spectrum alone, and the remarks made about the compounds $S_2N_2HgCl_2$, $SNCoCl_2$ and $S_2N_2Cu_xCl_y$ (which also show T3 spectra) are taken to be generally applicable to them.

Aluminium Compound Three appears to be only a trace product of the $S_4N_4/SOCl_2/AlCl_3$ system, but substantial quantities of Iron Compound Three can be obtained from the analogous $FeCl_3$ system. The efforts made to obtain a crystalline, constant-melting sample of Iron Compound Three for an X-ray analysis were abandoned only because the returns in terms of the effort necessary were judged at that time to be too small: there is no reason to suppose that renewed efforts would not be completely successful. See p. 136 regarding further discussion of Iron Compound Three.

The preparative origins and inter-relationships of Aluminium Compound One, Compound Two, and Aluminium Compound Three, and of Iron Compounds One, Two and Three. (For the preparations of these compounds see respectively pp.49, 52, 57, 58, 60,65.

The $S_4N_4/SOCl_2/AlCl_3$ system is considered first.

Aluminium Compound One is formed in varying - but generally large - quantity, whatever the reaction temperature, and whether the reactants (S_4N_4, $AlCl_3$) are both in solution or not: frequently, Compound Two is formed as well. If solid S_4N_4 is reacted with a solution of $AlCl_3$ in $SOCl_2$ at about 30°, the proportion of Compound Two to Aluminium Compound One is at maximum, and estimated at 2:1. Reducing the reaction temperature causes this ratio to steadily alter to an estimated 1:2 at about -40°: raising the reaction temperature causes the ratio to fall rapidly to virtually zero, at about 70°. Use of a solution of S_4N_4 in $SOCl_2$, rather than solid S_4N_4, causes the proportion of Compound Two to Aluminium Compound One to fall, whatever the reaction temperature.

The well-established[29] σ-adduct $S_4N_4{\cdot}AlCl_3$ is known to decompose in $SOCl_2$ to Aluminium Compound One (plus a little Compound Two); it also has the distinctive red-brown colour shown by many $S_4N_4{\cdot}MCl_x$ σ-adducts. Although particularly transient at reaction temperatures close to the boiling point of $SOCl_2$ (78°), just such a colour is seen at the first stage of the interaction of S_4N_4 and $AlCl_3$, in $SOCl_2$. It is thus suspected that the interaction in $SOCl_2$ of S_4N_4 (whether solid or in solution) and $AlCl_3$, leading to Aluminium Compound One, proceeds via $S_4N_4{\cdot}AlCl_3$. A study of this reaction at temperatures at which the red-brown colour is stable for some time (zero and below) may enable the colour to be definitely attributed to this adduct.

The observations regarding the reaction conditions which lead to maximum yields of Compound Two suggest that the geometric and/or stereochemical requirements for the particular interaction of S_4N_4 and $AlCl_3$, leading to Compound Two, are relatively inflexible. Such rigidity of requirements is to be expected, whether Compound Two is a new isomer of trithiazyl trichloride, or the hitherto unknown tetrathiazyl tetrachloride. By comparison, the geometric and/or stereochemical requirements of the interaction leading to $S_4N_4{\cdot}AlCl_3$ would not be expected to be so inflexible, since they probably only require some flattening-out of the S_4N_4 ring.

Consequently, formation of $S_4N_4{\cdot}AlCl_3$ occurs quite readily under all reaction conditions, with proportionate ultimate formation of Aluminium Compound One, while the reaction leading to Compound Two is only a minor side-reaction, except when conditions are precisely correct for this latter reaction.

The $SOCl_2$-solvolysis of $S_4N_4 \cdot AlCl_3$ to Aluminium Compound One has not yet been closely studied, but certainly shows a high percentage conversion: when the reaction was investigated, only a small quantity of Compound Two was detected. The solvolysis of S_4N_4 in $SOCl_2$ leads to S_4N_3Cl (which has a seven-membered sulphur-nitrogen skeleton) and $S_3N_2O_2$ (five-membered skeleton);[62,98] the decomposition of S_4N_4 by $SOCl_2$ in the presence of SO_2, NO or $AsCl_3$,[99] or of a mercury chloride (this work), or of $MnCl_2$ or $CoCl_2$,[31] leads to the formation of $S_3N_2O_2$ (five-membered sulphur-nitrogen skeleton). Thus the $AlCl_3$ is certain to be actively involved in the conversion of $S_4N_4 \cdot AlCl_3$ into $S_2N_2Cl_2 \cdot AlCl_3$ (Aluminium Compound One). The significance of the observation that this $SOCl_2$-solvolysis of $S_4N_4 \cdot AlCl_3$ leads also to small quantities of Compound Two, is not yet established.

Regarding the preparation described for Compound Two (p. 52): this is the only preparation where a reagent proportion (S_4N_4:MCl_x) of other than 1:1 is employed. A ratio of 1·0 S_4N_4 to 0·9 $AlCl_3$ was used, since unreacted $AlCl_3$ had been obtained from 1:1 reaction mixtures, and it was hoped to reduce the yield of the "by-product" Aluminium Compound One (which contains Al) without reducing the ($AlCl_3$-catalysed) yield of Compound Two. As hoped, the proportion of Compound Two did appear to be increased, and reduced quantities of unreacted $AlCl_3$ were present after reaction was completed. Possibly the proportion of $AlCl_3$ could be reduced to 0·7-0·8, without seriously decreasing the absolute quantity of Compound Two obtained.

The chemistry of Aluminium Compound Three is not yet sufficiently established for useful comment to be made regarding its preparative origin, or its relationship with Compound Two and Aluminium Compound One. The comments made (p. 136) regarding Iron Compound Three are however presumed to be generally applicable to it.

The $S_4N_4/SOCl_2/FeCl_3$ system is now considered.

The remarks made concerning the relationships of Aluminium Compound One and Compound Two, in the preceding discussion of the $AlCl_3$-derived system are broadly applicable to the relationships of Iron Compounds One and Two in the analogous $FeCl_3$-derived system. Reactions in this latter system are however complicated by the fact that substantial quantities of the additional product Iron Compound Three can be obtained.

Thus Iron Compound Two is prepared in high yield by the interaction of solid S_4N_4 and $FeCl_3$ suspended in $SOCl_2$, at a reaction temperature of about -15^{o}: its co-product is Iron Compound One (traces of Iron Compound Three have also been detected on occasion). Reducing the reaction temperature causes the proportion of Iron Compound Two to fall somewhat; raising the reaction temperature causes the proportion to fall rapidly to virtually zero (at about 60^{o}).

By analogy with the suspected course of the reaction leading to Aluminium Compound One, the author proposed that the formation of Iron Compound One proceeded via an (at that time unknown) adduct of S_4N_4 and $FeCl_3$: this proposition has been supported by the subsequent isolation of the σ-adduct $S_4N_4 \cdot 2FeCl_3$.[29] The interaction of this adduct and $SOCl_2$ should be investigated as an additional test of the theory: besides the anticipated high conversion to Iron Compound One, significant quantities of Iron Compound Two should be present, and some Iron Compound Three may also be obtained. It must be noted however that $[S_4N_4 + TiCl_4]$ in $SOCl_2$, and $S_4N_4 \cdot TiCl_4$ in $SOCl_2$, do not appear to give the same product.[31]

The reaction of a fresh solution of S_4N_4 with a suspension of $FeCl_3$ in $SOCl_2$ at temperatures in excess of 60° leads to Iron Compound One, with traces of Iron Compounds Two and Three as co-products. Reaction at 50° still yields much Iron Compound One, but Iron Compounds Two and Three are now obtained in substantial quantity. Reaction at 35° leads mostly to Iron Compound Two, with rather less Iron Compound Three and at most only traces of Iron Compound One.

The reaction of an $SOCl_2$ solution of S_4N_4 which has stood at room temperature for between 15 and 30 minutes, with the $SOCl_2$ suspension of $FeCl_3$, at 40°, leads mostly to Iron Compound Three, Iron Compound Two being the co-product. The enhanced yield of Iron Compound Three from "old" $S_4N_4/SOCl_2$ solutions suggests it is more closely related to one or other of the $SOCl_2$-solvolysis fragments of S_4N_4, than are Iron Compounds One and Two. Interpretation in terms of the degradation product $\overset{+}{S_4N_3}\overset{-}{Cl}$ is particularly attractive, since both compounds show T3 spectra. However, the substantial solubility of Iron Compound Three makes an ionic constitution unlikely, except perhaps if the cation $S_4N_3^+$ were to be accompanied by a large anion, e.g. $FeCl_4^-$. Further it is established that the $SOCl_2$ - solvolysis of S_4N_4

in the presence of $AsCl_3$,[99] or $CoCl_2$ or $MnCl_2$,[31] or Hg_2Cl_2 leads to $S_3N_2O_2$ (which is known[98] to have a sulphur-nitrogen skeleton smaller than that of S_4N_3Cl[62]), and that in the presence of the appropriate metal chloride, compounds such as $S_2N_2HgCl_2$ (T3 spectrum), $S_2N_2TiCl_3$ and $S_2N_2HfCl_4$ are obtained, all of which compounds are believed to be derived from S_2N_2 moieties, so that $SOCl_2$-solvolysis in the presence of metal chlorides seems normally to yield fragments with sulphur-nitrogen skeletons substantially smaller than that of S_4N_3Cl. This again points away from the presence of $S_4N_3^+$ in Iron Compound Three. (The quantity of S_4N_3Cl isolated from the $S_4N_4/SOCl_2/VCl_3$ system is believed to reflect the fact that the usual reactant ratio of one S_4N_4 per VCl_3 was used, while the product (SNV_2Cl_4) contains only 0•5 SN per V - unlike the more usual 2SN per metal atom - so that most of the S_4N_4 used could have been solvolysed in isolation, giving the S_4N_3Cl.) This compound is thus likely to contain structural units having S_2N_2 or possible $(N_2S)_x$ skeletons (the product of the $S_4N_4/SOCl_2/InCl_3$ system appears to contain $(N_2S)_x$ units, is soluble in $SOCl_2$, and shows a T3 spectrum). A polymeric constitution is not likely, in view of its solubility.

These remarks are taken to be generally applicable to Aluminium Compound Three, with the reservation that the action of "old" $S_4N_4/SOCl_2$ solutions on $AlCl_3/SOCl_2$ solutions has not yet been studied.

Regarding the $S_4N_4/SOCl_2/FeCl_3$ system in general, it is very interesting to note that substantial quantities of $FeCl_2$ were isolated from this system, which latter is believed to be capable of oxidising sulphur(III) (ex-S_4N_4) to sulphur(IV) or sulphur(VI), by chlorination (see p.130); it is further interesting to note that the one exceptionally large yield of $FeCl_2$ was obtained on the same occasion as the greatest yield of Iron Compound Three was obtained, which latter compound (by analogy with other compounds showing a T3 spectrum) is believed not to contain chlorinated sulphur-nitrogen chains - in contrast to the other M-N-S-Cl products of the $S_4N_4/SOCl_2/FeCl_3$ system.

It appears to be a characteristic of the $S_4N_4/SOCl_2/FeCl_3$ and $S_4N_4/SOCl_2/AlCl_3$ systems that pumping dry the mother liquor from the recrystallisation of a sample of the T1 or T2 products of either system (which samples had previously been recrystallised to constant melting point) always yielded a residue with the appearance of being slightly stained by dark contaminants: this effect was most noticeable with Iron Compound Two. Consequently it is suspected that the four compounds referred to are not quite stable to refluxing $SOCl_2$, but always decompose a little (on recrystallisation, for instance) giving small quantities of tarry and/or polymeric breakdown materials.

(vi) Consideration of those systems which are most easily understood in the light of findings made in the systems $S_4N_4/SOCl_2/AlCl_3$ and $S_4N_4/SOCl_2/FeCl_3$, i.e. the $S_4N_4/SOCl_2$ systems involving $TaCl_5$, $GaCl_3$ and $InCl_3$.

(a) The $S_4N_4/SOCl_2/TaCl_5$ system

The studies made on this system indicate it is a simplified analogue of the $S_4N_4/SOCl_2/AlCl_3$ system (which is itself a simplified analogue of the $S_4N_4/SOCl_2/FeCl_3$ system). Points established about the product of this system are:

1 - A sample of the product (m.pt. 102°) analysed to S = 14•93; N = 6•19; Cl = 40•45%. Another sample (m.pt. 105-107°) analysed to S = 14•71; N = 6•20; Cl = 31•90, 33•80%. $S_2N_2TaCl_5$ requires S = 14•24; N = 6•22; Cl = 39•36%.

2 - The product shows a T1 spectrum.

3 - The product is readily soluble in $SOCl_2$ - estimated solubility 0•5-1•0 gm. per 10 ml. at room temperature, 1•5-2•0 gm. per 10 ml. at reflux (78°).

4 - Mass spectra recorded at 155° and 170°, i.e. above the product's melting(/decomposition?) point, showed in addition to the fragments anticipated, (see main section (iii), subsection (b)) patterns of comparable intensity for the fragments S_2Cl, SCl_2, S_2Cl_2.

5 - The same product is obtained from (S_4N_4 + $TaCl_5$) in $SOCl_2$, as from S_4N_4•$TaCl_5$ in $SOCl_2$.

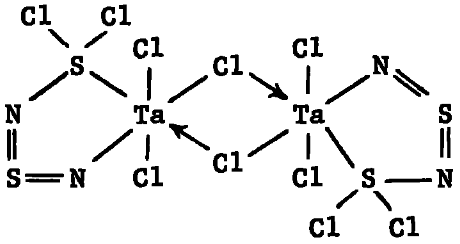
6 - The product is stable to prolonged and repeated refluxing in $SOCl_2$.

Point 1 suggests that the empirical formula for the product is $S_2N_2TaCl_5$: the improvement in the already close sulphur and nitrogen analyses, when a higher melting sample of the product was analysed, supports the conclusion that the later chlorine analyses were in error. (See main section (ii).)

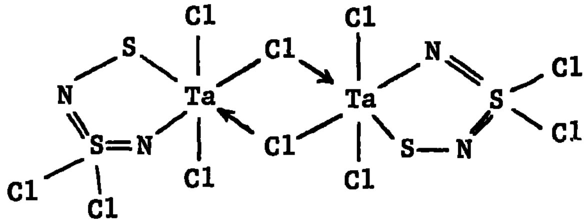
Points 2, 3 and 5 show that the product is closely related to Iron and Aluminium Compounds One.

The fragments noted in point 4 may result from (1) S-Cl bonds in the product, or (2) thermal degradation, or (3) atmospheric decomposition (a direct insertion probe has to be used, see p.25).

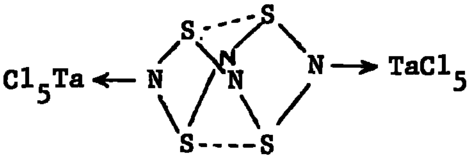
Possible structures for the compound are -



1



2



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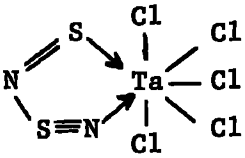
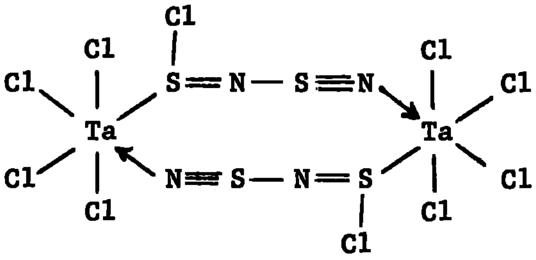


4



5

Other structures are possible, which are simply variants of the above suggestions, involving for instance redistribution of chlorines, or change of tantalum's coordination number..

Structures 1 and 5 are more likely than 2-4, since they contain only S^{IV}, rather than S^{IV} and S^{II}, (the system $SOCl_2/TaCl_5$ is likely to oxidise sulphur by chlorination). Similarly 1, 2 and 5 are more likely than 3 or 4, since the former contain chlorinated sulphur-nitrogen chains. Structure 3 accommodates point 2 (S_4N_4 has a T1 spectrum) very well, but point 6 reduces its likelihood - $SOCl_2$ rapidly decomposes S_4N_4 at room temperature. Also, coordination of S_4N_4 to metal chlorides such as $TiCl_4$, $TaCl_5$, $AlCl_3$, $SnCl_4$, $SbCl_5$ and $TeCl_4$ does not cause the S_4N_4 ring to become stable to $SOCl_2$ (this work, and ref. 31). 1, 2 and 4 are perhaps more likely than 3 or 5 (sulphur-nitrogen chains have so far only been established[32,33] to occur bidentate to a single metal atom, in metal-sulphur-nitrogen compounds). Structures 1, 2 and 5 are those which accommodate most readily the similarity between the product, and Iron and Aluminium Compounds One (points 2, 3 and 5): however it should be noted that the product of the systems $[S_4N_4 + SbCl_5]$ in $SOCl_2$ and $S_4N_4 \cdot SbCl_5 + SOCl_2$ is related to the former three compounds (it shows a T1 spectrum) but is characterised (by elemental analyses) as $S_3N_3SbCl_6$.

At the present time, exactly as with the systems based on $SbCl_5$ and $NbCl_5$[31] no material showing other than a T1 spectrum has been detected in this system: formation of materials showing T2 and T3 spectra in addition to a material showing a T1 spectrum appears to be restricted to those $SOCl_2$ -

based systems derived from $AlCl_3$, $GaCl_3$ and $FeCl_3$. It is possible that use of solid S_4N_4 or of "old" solutions of S_4N_4 in $SOCl_2$ (rather than fresh $S_4N_4/SOCl_2$ solutions), or of lower or higher reaction temperatures than those so far employed, may lead to materials showing T2 and/or T3 spectra; see the preceding main section.

(b) The $S_4N_4/SOCl_2/GaCl_3$ system

The studies made on this system indicate it is fully analogous to the $S_4N_4/SOCl_2/FeCl_3$ system. The latter system being one of those selected from the general $S_4N_4/SOCl_2/MCl_x$ group for more detailed investigation, no attempt was made to isolate pure products from the $GaCl_3$-derived system.

A crude crystallisate was extracted from this system (see p. 70). Its near infrared spectrum was that of a T2 compound (Gallium Compound Two), plus additional weak absorption patterns, some of which were those of a T1 compound (Gallium Compound One). Consequently other properties of the crystallisate cannot be reliably interpreted. A single crystal, selected from this crystallisate as being free from obvious contamination (see p. 70) showed a "clean" T2 spectrum: this spectrum contained no strong absorptions centred around 485 cm^{-1} (Compound Two contains such absorptions; Iron Compound Two does not) hence this crystal was taken to be a fairly pure sample of Gallium Compound Two, and the compound was presumed to be closely analogous to Iron Compound Two.

A sample of solute ("Gallium mixture") was precipitated from the mother liquor remaining from the crystallisation. Its near infrared spectrum was the sum of T1, T2 and T3 patterns. This is interpreted as representing the presence of three appropriate $GaCl_3$-derived compounds; consequently other properties of the precipitate cannot be reliably interpreted.

The preparative conditions used appear to lead mostly to Gallium Compound Two, together with a little Gallium Compound Three, and still less Gallium Compound One.

The remarks made in the preceding main section regarding Iron Compounds One, Two and Three are presumed to be broadly applicable to Gallium Compounds One, Two and Three respectively.

Mass spectra of the crystallisate (the impure Gallium Compound Two), determined at a temperature close to its melting point, showed a complete breakdown pattern derived from S_8: the exact significance of this observation is not yet established.

(c) The $S_4N_4/SOCl_2/InCl_3$ system

Points established for the product of this system are:

1 - Its analysis suggests the empirical formulae N_2SInCl_3 or N_2SInCl_4, or a close approximation to these. (cf. pp.92,93).

2 - It has a T3 spectrum.

3 - It melts at 320^o (then immediately re-solidifies).

4 - It is moderately soluble in refluxing $SOCl_2$ (estimate, 0·5 gm. per 10 ml.).

Since the empirical formula of the product is not yet confidently established, comments must be restricted to generalisations about its likely nature.

The melting point is relatively high for metal-sulphur-nitrogen-chlorine compounds (point 3), suggesting that it is not a monomeric covalent compound. Its moderate solubility in $SOCl_2$ (point 4) suggests that it is not polymeric. Solubilities in $SOCl_2$ of the various metal-sulphur-nitrogen-chlorine materials prepared in this work tend to fall into two sharply defined categories:

(a) Those materials showing negligible solubility, which (in the solid state) are believed to be either strongly associated polar covalent or polymeric compounds (but which may still be ionic), e.g. $S_2N_2HgCl_2$, $S_2N_2TiCl_3$, $S_2N_2HfCl_4$.

(b) Those materials showing remarkably high solubility (of the order of 1 gm. per 10 ml., between room and reflux temperatures), which are believed to consist of discrete molecules - e.g. Iron and Aluminium Compounds One, Compound Two and Iron Compound Two.

The solubility of the $InCl_3$-derived product is intermediate between these two cases. This could be because it is a salt containing a pair of large ions (e.g. $S_3N_2Cl^+$, $S_4N_3^+$ or - cf. point 1 - the hitherto unknown N_2S^+, with $InCl_4^-$ or, less likely, $InCl_6^{3-}$): since a relatively low lattice energy results in such instances, a slight solubility in suitable solvents (e.g. SO_2Cl_2, $SOCl_2$, SCl_2) is to be anticipated. The same solubility characteristics would be expected if the compound consisted of relatively weakly associated polar covalent molecules.

The most interesting discovery regarding the $S_4N_4/SOCl_2/InCl_3$ system is the nature of its relationship with the analogous $AlCl_3$- and $GaCl_3$-

derived systems. Only vanishingly small quantities of T3 material have ever been obtained from the $AlCl_3$-based system; the $GaCl_3$-derived system readily yields significant quantities of T3 material; and no trace of any material other than T3 has yet been detected in the $InCl_3$-derived system.

It is established that both the T1 and T2 products of the $S_4N_4/SOCl_2/AlCl_3$ and $S_4N_4/SOCl_2/FeCl_3$ systems are quite highly chlorinated, compared to the products of (e.g.) the Hg_2Cl_2 system (see preceding two main sections), and that the $S_4N_4/SOCl_2/GaCl_3$ system is closely analogous to the $S_4N_4/SOCl_2/FeCl_3$ system. Further, $AlCl_3$, $FeCl_3$ and $GaCl_3$ are all well-known as powerful chlorination catalysts. It appears that systems derived from less powerful chlorination catalysts (e.g. $TaCl_5$, or $SbCl_5$ [31]) do not yield T2 materials, but only T1 materials which in addition are less highly chlorinated than the T1 materials derived from $FeCl_3$ and $AlCl_3$. Consequently it is reasonable to suppose that systems based upon metal chlorides which are only very poor chlorination catalysts will not show any T2 products, will be unlikely to show any T1 products, and are in fact likely only to show products involving unchlorinated SN chains, such as are proposed for T3 compounds, and shown by $InCl_3$. (In this context it is noteworthy that on the one occasion when large quantities of T3 material were obtained from the $FeCl_3$ system, $FeCl_2$ also was found in quantity (see p.67)).

Alternatively, the shift from T1 and T2, to T3, products could be associated with decrease in acceptor strength of the metal chloride involved.

It is very probable that both T1 and T2 materials result from chlorination of S-N units coordinated to MCl_x. Also, it is reasonable to suppose that chlorination of an S-N moiety reduces its donor ability, and hence it is possible that with increasingly weak acceptors (Al > Ga > In) a point is reached where coordination of chlorinated S-N species, and hence ultimate formation of T1 and T2 compounds, is energetically too unfavourable to occur.

The $S_4N_4/SOCl_2/InCl_3$ system will be better understood when the effect of varying reaction conditions from those already employed has been investigated. Thus solid S_4N_4 and "old" $S_4N_4/SOCl_2$ solutions (rather than fresh $S_4N_4/SOCl_2$ solutions) should be used, and higher and lower reaction temperatures also. The solvolysis of $S_4N_4 \cdot InCl_3$ should also be investigated.

(vii) Consideration of the $S_4N_4/FeCl_3$ systems in which SO_2Cl_2, SCl_2, S_2Cl_2, $Cl \cdot SO_2 \cdot OH$ and $C_6H_5 \cdot SO_2 \cdot Cl$ are the solvents

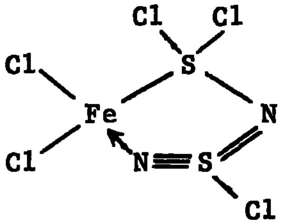
The data discussed below for the $S_4N_4/FeCl_3/SO_2Cl_2$ and $S_4N_4/FeCl_3/SCl_2$ systems indicates that the solvents SO_2Cl_2 and SCl_2 are especially satisfactory for further extensive, detailed study. It is believed at the present time that of all the solvents listed in the heading to this main section, these two are most likely to yield S_4N_4/MCl_x/(solvent related to $SOCl_2$) systems which could readily justify an extensive investigation along the same lines as that carried out (this work, and ref. 31) on $SOCl_2$-based systems, in terms of enhanced understanding of (metal-)sulphur-nitrogen (-chlorine) chemistry.

With the information at present available, it is not possible to decide which of these two systems would be the more satisfactory for further study. However the SO_2Cl_2- and $SOCl_2$-based systems are directly related (see below), consequently since the chemistry of the $S_4N_4/SOCl_2/MCl_x$ system is now believed to be fairly well established, this direct relationship may facilitate the understanding of the SO_2Cl_2-based system. In contrast, the SCl_2-based system appears to be completely unrelated to any other system so far known, and results so far obtained suggest that it will yield pure, crystalline materials more readily than the SO_2Cl_2-based system. As has been made clear in preceding main sections of this Discussion, the nature of the great majority of the materials prepared in this work is likely to be established only by full X-ray analyses: consequently the ability of any system to yield crystalline materials greatly increases the desirability of investigating that particular system.

(a) The SO_2Cl_2-based system

Elemental analyses indicate the empirical formula $S_3N_3FeCl_6$ for the product of this system. (Required - S = 23·65; N = 10·33; Cl = 52·29; Fe = 13·73%. Found - S = 20·80, 24·43, 25·74; N = 9·46, 11·43; Cl = 49·30, 49·49, 54·6; Fe = 14·5%.)

It is established[29] that the reaction of S_4N_4 with SO_2Cl_2 leads to a trithiazyl trichloride, $N_3S_3Cl_3$, and that the adduct $N_3S_3Cl_3 \cdot Hg(C_6H_5)_2$ can be prepared from it: the empirical formula $S_3N_3FeCl_6$ could thus be tentatively interpreted as $N_3S_3Cl_3 \cdot FeCl_3$. The solvolysis by $SOCl_2$ of this product, to Iron Compound One - which is believed to have a structure such as



(see p.129)

- can be readily appreciated in terms of the formula $N_3S_3Cl_3 \cdot FeCl_3$.

$N_3S_3Cl_3$ can theoretically exist in a number of conformations which depend upon whether the six-membered sulphur-nitrogen ring skeleton is in the chair or boat form, or whether some (or all) of the chlorine atoms are in axial or equatorial positions. (In principle, the $N_3S_3Cl_3$ sub-unit could alternatively have a chain (rather than ring) skeleton: since no sulphur-nitrogen halide is yet known to have such a skeleton, this possibility will be ignored here.) Consequently it is not surprising that the near infrared spectrum of the supposed $N_3S_3Cl_3 \cdot FeCl_3$ does not resemble those of the known varieties of $N_3S_3Cl_3$. In terms of already established behaviour of M-S-N-Cl compounds, such an adduct is most likely to σ-monodentate via N-donation.[20,21] Coordination via S, N or π donation (mono-, di-, or tri-dentate) is however possible.

Similarly, the simplicity of its near infrared spectrum (compared with that of the variety of $N_3S_3Cl_3$ which is believed to be a mixture of isomers - see p.15) makes it very likely that only one conformational isomer of $N_3S_3Cl_3$ is involved in the adduct. The likelihood that such is the case is further strengthened by experience in the $SOCl_2$-based system - it seems virtually certain that S_4N_4 interacts with metal chlorides in stereochemically very precise ways (see pp.132-3), and it is similarly certain that the $FeCl_3$ does actively participate in the reaction between the S_4N_4 and the SO_2Cl_2, since reaction in its presence is complete in about 30 minutes, while at least as many hours are necessary in its absence.[29]

More confident and more detailed comment on this product may be possible when further studies have been made on SO_2Cl_2-based systems. Invaluable information on the $S_4N_4/FeCl_3/SO_2Cl_2$ system and its relationship with the $SOCl_2$-based system is likely to result from study of the effect of SO_2Cl_2 on $S_4N_4 \cdot 2FeCl_3$, in analogy with the studies made on - for instance - $[S_4N_4 + AlCl_3]$ in $SOCl_2$, and $[S_4N_4 \cdot AlCl_3 + SOCl_2]$, and on $[N_3S_3Cl_3 \cdot FeCl_3 + SOCl_2]$; the product is tentatively expected to be (an) $N_3S_3Cl_3 \cdot FeCl_3$.

Not enough information is yet available for useful comment on the observation that nitrobenzene solutions of the supposed $N_3S_3Cl_3 \cdot FeCl_3$ show an infrared absorption corresponding to that shown by solutions of S_4N_4 in nitrobenzene (but see main section (viii), sub-section (c).)

(b) The SCl_2-based system

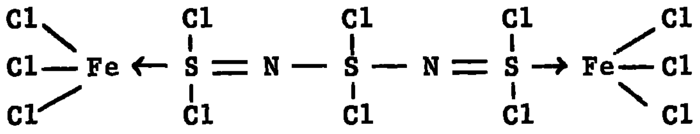
Analyses of the product of this system indicate an empirical formula approximating to $S_3N_2Fe_2Cl_{12}$ (Required - S = 14•54; N = 4•24; Cl = 64•33; Fe = 16•89%. Found - S = 15•95, 17•21; N = 4•27, 4•90; Cl = 67•44, 67•80; Fe = 16•1, 18•1%.) (Note that the sum of the lowest analysis for each element ≡ 103•76%.) Attempts to devise an empirical formula with which the analyses found would be in better agreement have not yet been successful.

At the present time, the best indication of the nature of the supposed $S_3N_2Fe_2Cl_{12}$ is given by the character of its solubility in $SOCl_2$. As noted above in the discussion of the $S_4N_4/SOCl_2/InCl_3$ system, the solubilities of (metal-)sulphur-nitrogen(-chlorine) materials in $SOCl_2$ fall into sharply defined categories: the solubility of the supposed $S_3N_2Fe_2Cl_{12}$ is estimated as of the order of 1•0 gm. per 10 ml. at reflux, and of the order of 0•1 gm. per 10 ml. at room temperature. This is the same order as that of Compound Two and Iron Compound Two; further, like these two compounds, the supposed $S_3N_2Fe_2Cl_{12}$ readily recrystallises from the $SOCl_2$. It is thus supposed that this product is broadly similar to Compound Two and Iron Compound Two. (Compare these points with the behaviour of Iron and Aluminium Compounds One.)

The ready solubility of the product, and its low melting point (99-101°), suggest that it consists of simple discrete molecules: consequently, it is surprising that no mass spectrum could be obtained, when materials either known to be ionic (e.g. $\overset{+}{S_4N_3}\overset{-}{Cl}$) or believed to be polymeric (e.g. $S_2N_2TiCl_3$) give spectra quite readily. Further attempts are to be made to obtain a mass spectrum of the product.

The infrared spectrum of the compound has not yet been matched with that of any other (metal-)sulphur-nitrogen(-chlorine) compound. Experience with the $SOCl_2$-based system indicates that useful information is likely to be obtainable from the infrared spectrum of this product when a wide range of others from the SCl_2-based system are available for comparison.

Structures such as



are compatible with the information at present available on the compound: other closely related variants are possible, which depend only upon redistribution of chlorine atoms, alteration of the bridging units, and so on. Again by analogy with findings in the $SOCl_2$ system, it is likely that a cryoscopic molecular weight determination in nitrobenzene could be performed: this may provide useful information, but the $SOCl_2$-analogy suggests otherwise. The small quantity of Iron Compound One detected may be due to the presence of small quantities of $SOCl_2$ in the technical grade SCl_2 used, or it may be due to a minor side reaction which occurs in SCl_2

anyway. The likely nature and origin of the second trace co-product are discussed in the following subsection.

Examination of the black solid precipitating out of solutions of about 0•7-0•8 gm. of S_4N_4 per 10 ml. of SCl_2 within about 30 min. of their preparation may assist the understanding of the metalliferous products likely to be derived from the SCl_2-based system.

Straightforward experiments which may help to relate the SCl_2 system to the $SOCl_2$ and SO_2Cl_2 systems are:

1 - $S_3N_2Fe_2Cl_{12}$ + SO_2Cl_2

2 - $N_3S_3Cl_3{\cdot}FeCl_3$ + SCl_2 (the converse experiment to 1)

3 - $S_4N_4{\cdot}MCl_x$ + SCl_2 (in analogy with $S_4N_4{\cdot}MCl_x$ + $SOCl_2$)

The S_2Cl_2-based system

The information at present available regarding this system is insufficient to permit any really useful conclusions to be drawn. Remarks are thus restricted to a summary of what is established, and a brief consideration of the few inferences which can be drawn.

The near infrared spectrum of the product of this system is interpreted as being a combination of two slightly different T3 patterns; one, X, is distinctly weaker than the other, Y. Extraction of the mixed product, X + Y, with refluxing $SOCl_2$ enabled a small quantity of pale yellow crystals, sparingly soluble in $SOCl_2$, to be obtained: these showed a T3 pattern which was indistinguishable from that of X alone.

The exact relationship between X and Y is not yet established. The most likely possibilities are (a) Y is insoluble in $SOCl_2$ (and thus likely to be polymeric), while X is sparingly soluble in $SOCl_2$ (and thus likely to be ionic), or (b) refluxing $SOCl_2$ rapidly converts Y into X, as Y slowly dissolves in $SOCl_2$: in this case, comment can only be made on the solubility of X, and is exactly as for case (a). Possibilities (a) and (b) could be distinguished by determining the effect of repeated extractions of X + Y with refluxing $SOCl_2$.

The behaviour of the trace co-product observed in the $S_4N_4/FeCl_3/SCl_2$ system was closely similar to that observed for X; consequently it is suspected that this trace co-product may be either related to, or identical with, X. A fractionation process directed to obtaining a pure sample of this co-product would permit this theory to be tested. This co-product may owe its origin to a trace of S_2Cl_2 in the technical grade SCl_2 used, or it may result from a secondary reaction occurring in SCl_2 anyway, or it may result from trace $SOCl_2$-solvolysis of $S_3N_2Fe_2Cl_{12}$ (the main product of the $S_4N_4/FeCl_3/SCl_2$ system).

The most notable conclusion to be drawn from the present study of the $S_4N_4/FeCl_3/S_2Cl_2$ system is that S_4N_4 and $FeCl_3$ can give no less than three different compounds (X, Y and Z) which all show closely similar, but quite distinct, T3 spectra (Z - Iron Compound Three - results from the $SOCl_2$-based system). It is presumed that X, Y and Z all have related, but distinct, structures. The constitution of Z is discussed on p.136.

Only little less remarkable is the fact that the near infrared spectrum of X + Y is unaltered after three hours exposure to air; such stability is uncharacteristic of (M-)N-S(-Cl) compounds. The reason for this stability is uncertain, but it is known[100] that S_4N_3Br (the $S_4N_3^+$ salt least sensitive to air) is almost indefinitely stable to air, and - for instance - that S_4N_3NCS decomposes only very slowly. It is suspected that this stability reflects an energetically favourable match of ion sizes, and (since all are T3 materials) that X, Y, S_4N_3Br and S_4N_3NCS may all be stable for the same reason(s).

The dark brown solid [A] which precipitated at the beginning of the $S_4N_4/FeCl_3/S_2Cl_2$ reaction is believed to be either closely related to, or identical with, the very dark brown solid which precipitates from solutions of S_4N_4 in S_2Cl_2 within a few minutes of their preparation. Examination of these solids may assist the understanding of the S_2Cl_2-based system.

The failure of X + Y to give a mass spectrum is surprising: further attempts are to be made to obtain a spectrum.

Finally, it can be noted that the analyses so far obtained on X + Y (S = 38•39; N = 7•98, 12•79; Cl = 32•37; Fe = 6•77%) sum to only 90•32% even when the higher nitrogen result is taken.

The next two systems to be discussed, those derived from chlorosulphonic acid and benzenesulphonyl chloride, were investigated with a view to preparation of organically-substituted metal-sulphur-nitrogen (-chlorine) compounds. The interaction of S_4N_4 and MCl_x in solvents which would be expected to play a "passive" role in their reaction (such as

CH_2Cl_2, CCl_4) leads to compounds (σ-adducts, $S_4N_4 \cdot MCl_x$) having distinctive patterns of properties.[29] Use of the same reactants in a series of different solvents (e.g. S_2Cl_2, SCl_2, $SOCl_2$, SO_2Cl_2) leads to products showing quite different patterns of properties. It is thus very probable that these latter solvents play a more "active" role in the interaction of the reactants. It is known[36-8] that simple hydrogenated compounds such as $Ni(S_2N_2H)_2$ can be prepared in EtOH: consequently, it was decided to investigate the interaction of $FeCl_3$ and S_4N_4 with first, a hydroxylated solvent and second an organically substituted solvent, both suitably related to those already studied, with a view to obtaining organically-substituted metal-sulphur-nitrogen-chlorine compounds by solvent interaction with the S_4N_4 and/or $FeCl_3$. (The approach to preparation of organically-substituted compounds is considered in more detail in the following main section.)

The $Cl \cdot SO_2 \cdot OH$-based system

0·1 gm. of S_4N_4 dissolves in 10 ml. of $Cl \cdot SO_2 \cdot OH$ in a few minutes at room temperature to yield an intensely dark, red/green dichroic solution. It is thus certain (as anticipated anyway) that $Cl \cdot SO_2 \cdot OH$ interacts with S_4N_4: since the behaviour of the system is quite different when $FeCl_3$ is present, it seems reasonable to suppose that the S_4N_4, $FeCl_3$, and $Cl \cdot SO_2 \cdot OH$ may all be mutually interacting, hence it is likely that this system (or a closely related one) could yield hydrogenated metal-sulphur-nitrogen-chlorine compounds, as hoped. The properties of $Cl{\cdot}SO_2{\cdot}OH$ itself (it is exceptionally corrosive, and not very volatile, for instance) mean that it is not easy to work with, and compounds of the required kind are likely to be more readily obtained from a related solvent with less extreme properties. Preparation of the required kind of compound is believed to be dependent upon relatively slow and moderate degradation of S_4N_4 by the solvent (see under the appropriate solvents), in the presence of a metal chloride: it has been established[101] that the interaction of S_4N_4 and 100% H_2SO_4 proceeds according to

$$\underbrace{S_4N_4}_{\text{1 mole}} + \underbrace{H_2SO_4}_{\text{excess}} \longrightarrow 2SO_2 + \underbrace{\overset{+}{NH_4}\ \overset{-}{HSO_4}\ \overset{+}{NH_3}\text{—}\overset{-}{SO_3}}_{\text{1 mole}} + \overset{+}{S_2N_2} + \overset{+}{SN_2} + \text{intensely coloured species + radical species (which last two may be the same).}$$

It is thus likely that $Cl{\cdot}SO_2{\cdot}OH$ would similarly degrade the S_4N_4 too far for the required type of reaction to be possible.

The $Ph{\cdot}SO_2{\cdot}Cl$-based system

This system was investigated for the reasons previously outlined, and was found to behave in the manner anticipated and desired.

The material obtained from the system analysed to C = 18·6; H = 1·30; S = 27·74; N = 10·42; Cl = 31·9; Fe = 8·4% (Total = 98·36%). A satisfactory empirical formula has not yet been arrived at for the material. ($C_{10}H_9S_6N_5FeCl_6$ approximates to the situation, but found C:H is in fact almost exactly 6:5 for instance.) However, these analyses are individually in the range broadly anticipated. The material's near infrared spectrum indicates that phenyl groups are almost certainly present. It is thus very probable that this system has yielded an organically-substituted Fe-S-N-Cl compound; the solid isolated may be either a pure compound, or (more probably) a mixture of related compounds. (The material's analyses and possible empirical formulae support the latter possibility.) The sum of the analyses may be taken to indicate that no oxygen is present, but the material may in fact contain several per cent oxygen, with high analyses on other elements obscuring this fact. (See main section (ii).) The mass spectrum obtained gives no reliable information regarding the nature of the material: the peaks observed (C_6H_5, $C_6H_5SO_2$, $C_6H_5SO_2Cl$) could equally be attributed to trace contamination by $Ph{\cdot}SO_2{\cdot}Cl$ as to the presence of appropriate structural units in the material. Further work in this or related systems should resolve these problems.

(viii) Miscellaneous

(a) Organically substituted metal-sulphur-nitrogen(-chlorine) compounds.

(b) Studies of the $S_4N_4/SOCl_2$ system, and of the early stages of reactions in $S_4N_4/SOCl_2/MCl_x$ systems.

(c) Nitrobenzene solutions of various (metal-)sulphur-nitrogen(-chlorine) compounds.

(a) Organically substituted metal-sulphur-nitrogen(-chlorine) systems.

Passing reference has been made in preceding main sections to organically substituted metal-sulphur-nitrogen(-chlorine) compounds. The motivation to prepare such compounds was that additional analytical information (C and H determinations) would be available, and that these analyses might be relatively free from complicating difficulties (such as have plagued S, N, and Cl determinations in M-S-N-Cl compounds).

It was further hoped that more useful information could be obtained from organically substituted compounds than from their "parents", via stabilisation of structural units by aromatic substituents, so that these structural units could be recognised from a mass spectrum.

Finally, it was hoped that suitable addition of organic substituents to M-S-N-Cl compounds would confer air-stability on the latter so that their potential applications would be increased.

Such are the main advantages it is thought could result from shift of emphasis to organic-M-S-N-Cl compounds. Information so far available suggests however that systems designed to lead to such compounds are likely to be at least as intractable as those giving M-S-N-Cl compounds such as have been discussed in this work. Three main approaches may be suggested.

(1) Conversion of M-S-N-Cl compounds already known, to simple organic derivatives.

(2) Use of organometallic chlorides as starting materials, with reaction conditions otherwise generally the same as those so far described for M-S-N-Cl systems.

(3) Use of organically substituted solvents, with reaction conditions otherwise generally the same as those so far described for M-S-N-Cl systems.

Approach 1. A substantial amount of work has been done on the preparation of suitable organic derivatives of $N_3S_3Cl_3$[29] and of $(NSOCl)_3$.[48] This work has shown that satisfactory derivatives (air-stable, crystalline materials) can be obtained from quite "clean" reactions. However, there is so far only one satisfactory synthetic route to derivatives known for a given "parent" sulphur-nitrogen compound ($N_3S_3Cl_3$ or $(NSOCl)_3$). Routes to other derivatives which have been studied have always either failed completely, or given inadequate yields, or given intractable mixtures of products. Consequently it may not be easy to establish suitable synthetic pathways to derivatives of other varieties of sulphur-nitrogen compounds.

For $(NSOCl)_3$ the method established is -

$$(NSOCl)_3 \xrightarrow[\text{in } C_6H_6]{\text{Aryl}_2\text{Hg}} Ar_2(NSO)_3Cl$$

For $(NSCl)_3$ the method established is -

$(NSCl)_3$ + epoxides (particularly epichlorhydrin or cyclohexene oxide) $\longrightarrow$ esters, readily purified by recrystallisation.

These, or closely related, synthetic routes may prove suitable for other varieties of sulphur-nitrogen compounds.

Approach 2. Air-stable organometallic chlorides such as Cp_2TiCl_2 may be useful (for the reasons outlined on p.113 regarding $PbCl_2$ and $Hg_2Cl_2/HgCl_2$). It will however be necessary to choose the exact reactants and solvents with care (since for instance Cp_2TiCl_2 is rapidly decomposed by $SOCl_2$). Experience with the reactions of $PhBCl_2$ and Ph_3AsCl_2 with S_4N_4 in $SOCl_2$ has not been encouraging in this respect.[31]

Approach 3. The difficulty likely to be encountered in this technique is that the product from two reactants will alter drastically with only relatively minor changes of solvent (this effect has been demonstrated for the series S_2Cl_2, SCl_2, $SOCl_2$, SO_2Cl_2, $Cl{\cdot}SO_2{\cdot}OH$, $Cl{\cdot}SO_2{\cdot}Ph$). Experience in the $PhSO_2Cl$ system has shown that general intentions apparently can be achieved, but obtaining and characterising pure compounds in reasonable yield may be less straightforward. Experience of the systems based on S_4N_4 and thiols or disulphides has not been encouraging.[102]

(b) Studies of the $S_4N_4/SOCl_2$ system, and of the early stages of reactions in $S_4N_4/SOCl_2/MCl_x$ systems

Despite the fact that it has been shown (this work and ref. 31) that the presence of metal chlorides greatly modifies the end products obtainable from the interaction of S_4N_4 and $SOCl_2$, understanding of the $S_4N_4/SOCl_2/MCl_x$ systems may still be increased by a detailed study of the system $S_4N_4/SOCl_2$. Establishing the exact nature of the intermediates in the solvolysis of S_4N_4 to S_4N_3Cl would be particularly useful: are they chains or rings? and of what size? are they radical species? are they ionic species?. If the answers to such problems could be established, the likely mode of interaction of these intermediates with MCl_x could be more easily assessed. It is in fact very probable that S_2N_2 chains are present; the presence of $S_2N_2^+$ and N_2S^+ in 100% H_2SO_4 has been inferred;[101] it has been shown that the conductivity of $SOCl_2$ rises rapidly on addition of S_4N_4;[52] but the exact nature of all of the species involved has still to be definitely established.

It has been observed (this work, and ref.31) that the interaction of S_4N_4 and such covalent metal chlorides as give soluble products (for instance $AlCl_3$, $GaCl_3$, $FeCl_3$ and $TaCl_5$) in $SOCl_2$ leads either immediately or rapidly to an intense blue-green colour, which then alters through olive-green to red/green dichroic. Not infrequently this blue-green colour is preceded by an intense deep blue. The $InCl_3$-derived system, although finally giving an insoluble product, also shows each of these colourings, from blue through to red/green dichroic, and the $TiCl_4$- and $HfCl_4$-derived systems (which also give insoluble products) show the blue-green colour as reaction commences.

The consistent behaviour of this colour phenomenon suggests that it corresponds to a common reaction pathway for the systems cited. In the case of the reaction of $S_4N_4 \cdot TaCl_5$ and $SOCl_2$ at least, the transition between the blue and red/green dichroic conditions is relatively slow at room temperature (several tens of hours): thus it is possible that by suitably interrupting the reaction, and precipitating solutes for examination, some idea of the intermediate species involved could be obtained. It must however be remembered that such an experiment may not succeed in "freezing" the intermediates, so that any species which may finally be obtained for study are not necessarily those involved in the reaction. Also, the colours observed may be due to inisolably small traces of materials, or they may be due to by-products of the main reaction, which lead to tars, rather than to the required main product.

With the present state of knowledge regarding the stages intermediate between reactants and products, and regarding the structural nature of products, it still seems worth carrying out some studies of this kind, despite the difficulties involved.

(c) Nitrobenzene solutions of various (M-)S-N(-Cl) compounds

It has been established that nitrobenzene solutions of compounds known or believed to be S_4N_4, $S_4N_4 \cdot AlCl_3$, $S_2N_2FeCl_5$ (Iron Compound One), $S_2N_2AlCl_5$ (Aluminium Compound One), and $N_3S_3Cl_3 \cdot FeCl_3$ all show an absorption at 554 cm^{-1}; solutions of $S_2N_2HgCl_2$ do not. Consequently, study of the nitrobenzene solution spectra of a suitably wide range of (M-)S-N(-Cl) compounds may permit conclusions regarding the structural elements present in such compounds to be drawn. Note however that the widely varying structures the above compounds are known or believed to have suggests that the absorption involved derives from a relatively simple structural subunit common to most, if not all, (M-)S-N(-Cl) compounds (the failure to detect an absorption in the case of $S_2N_2HgCl_2$ may be due to insolubility of the compound in nitrobenzene, rather than to absence from the compound of the relevant structural unit). Difficulties such as these may reduce the utility of the technique.

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