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Chapter 6

ELEMENTS OF GROUP 6

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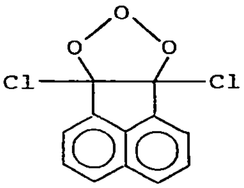
6.1 OXYGEN

The electrolysis of HF containing up to 20% H_2O in the presence of O_2 and O_3 has been shown to yield OF_2. The maximum yield of OF_2 is obtained with a water concentration of 2% at voltages between 5 and 9v, with a concentration of about 45% by volume of OF_2 in the anodic gas. The yield decreases with water concentrations above 2% and with increasing voltage and below 2% H_2O elementary fluorine is produced. The formation of OF_2 is thought to depend upon the formation of a black layer on the surface of the nickel anode during an induction period.[1]

An ^{17}O n.m.r. study has concluded that the hydronium ion H_3O^+ is practically planar[2] but this conclusion has been challenged and using the same data and other arguments it has been proposed that the ion has a pyramidal structure with a bond angle of about 111.3° for the mean HOH bond.[3] When hydroxy radicals, formed in ice or various aqueous systems by ionizing radiation, are cooled from ca. 30 to 4K they are extensively converted into O^- ions, as observed from e.s.r. spectra. The conversion, which is almost complete for $\cdot OD$ in D_2O, is thought to be formed by the equilibrium.[4]

$$\cdot OH + H_2O \rightleftharpoons O^- + H_3O^+ \qquad \ldots(1)$$

The kinetics of the reactions of hydrogen peroxide with some complexes of dioxovanadate(V) have been studied spectrophotometrically at an ionic strength of 1.0M($NaClO_4$) in the pH range 3 to 6 between 15 and 35°C. With a large excess of H_2O_2 over vanadium(V) complex concentration, a faster reaction followed by a slower one was observed. Rate expressions for the reactions were obtained and it was thought that an associative mechanism, through a seven-coordinate transition state, was operative.[5] The first primary ozonide which can be isolated as a result of its exceptional stability has been generated from 1,2-dichloroacanaphthalene and has been characterised as (1). The normal ozonide (2) formed by rearrangement of (1) appears as a side product.[6]



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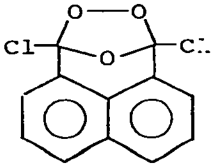


(2)

6.2 SULPHUR

6.2.1 The Element

X-ray structural analysis of two monoclinic allotropes of cycloheptasulphur carried out at $-110^{\circ}C$ has revealed almost identical chair-like molecular structures of approximately C_s symmetry. Bond distances between 199.5 and 218.2pm, bond angles between 101.5 and 107.5° and torsion angles between 0 and 109° were observed.[7]

Dichlorodisulphane (S_2Cl_2) dissolved in CS_2 has been shown to react with aqueous solutions of potassium iodide at $20^{\circ}C$ to form S_2I_2. The product decomposes spontaneously to a mixture of S_6, S_8, S_{12}, S_{18}, S_{20} and larger homocyclic sulphur molecules as well as I_2. Pure S_6 can be prepared using this method in 36% yield but the yields of S_{12} (1-2%), S_{18} (0.4%) and S_{20} (0.4%) are much lower.[8]

The use of resonance Raman techniques has shown that the radical species S_3^- is present, at least to some extent, in the blue solutions of sulphur in $CsCl-AlCl_3$ melts.[9] The observed chemical transport of Ta_2O_5 with sulphur at temperatures from 1273 to 1173K has been shown to correspond to the calculations based on the equilibrium.[10]

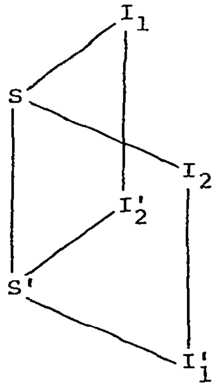
$$Ta_2O_{5(g)} + \frac{12.5}{2} S_{2(g)} \longrightarrow 2TaS_{5(g)} + 2.5SO_{2(g)} \qquad ...(2)$$

Several products have been reported for the reactions of elemental sulphur with AsF_5 in SO_2. $S_2I_4^{2+}(AsF_6^-)_2$ has been prepared by the reaction.

$$\tfrac{1}{4}S_8 + 2I_2 + 3AsF_5 \xrightarrow{SO_2} S_2I_4^{2+}(AsF_6^-)_2 + AsF_3 \qquad ...(3)$$

A crystal structure determination showed the $S_2I_4^{2+}$ cation (3) to have a distorted right-triangular prismatic structure with one S_2 and two I_2 units joined by weak S-I bonds. The S-S bond distance is the shortest reported in an isolated compound and is indicative of the presence of a $3p_\pi$-$3p_\pi$ bond and a bond order greater than two.[11]

The oxidising ability of AsF_5 is greatly enhanced by traces of Br_2, and in its presence, $S_4(AsF_6)_2.xSO_2$ ($x \leq 1$) may be prepared in quantitative yield from AsF_5 and S_8 in SO_2.



$S\text{-}S' = 182.8\text{pm}$
$S\text{-}I_1 = 285.8\text{pm}$
$S\text{-}I_2 = 319.5\text{pm}$
$I_1\text{-}I_2' = 259.7\text{pm}$
$S'\text{-}S\text{-}I_1 = 101.6^\circ$
$S'\text{-}S\text{-}I_2 = 92.9^\circ$
$I_1\text{-}S\text{-}I_2 = 89.5^\circ$
$S\text{-}I_1\text{-}I_2' = 87.0^\circ$
$I_1\text{-}I_2'\text{-}S_1' = 78.4^\circ$

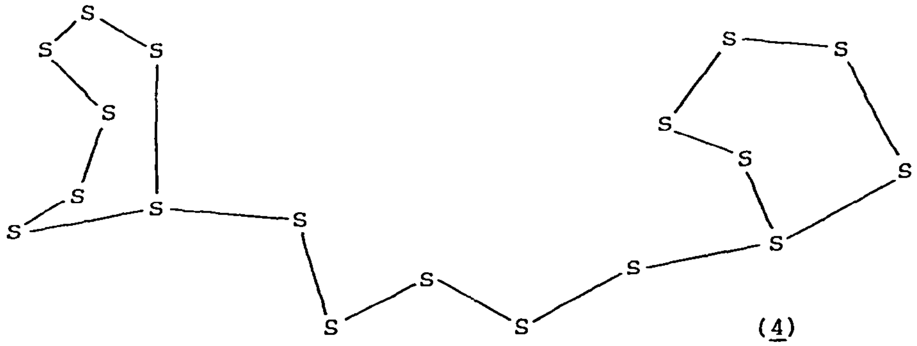
(3)

$$\tfrac{1}{2}S_8 \;+\; 3AsF_5 \xrightarrow[\text{trace } Br_2]{SO_2} S_4(AsF_6)_2.xSO_2 \;+\; AsF_3 \qquad ...(4)$$

An X-ray structural study of $S_4(AsF_6)_2.0{\cdot}6SO_2$ and of $(S_7I)_4S_4(AsF_6)_6$ prepared by the reaction

$$4S_8 \;+\; 2I_2 \;+\; pAsF_5 \xrightarrow{SO_2} (S_7I)_4S_4(AsF_6)_6 \;+\; 3AsF_3 \qquad ...(5)$$

confirmed the square planar geometry of the S_4^{2+} cation in both salts; the former having a S-S bond distance of 2.014Å and the latter 1.98Å.[12] The structure of the compound previously thought to be $S_{16}(AsF_6)_2$ has been determined and was shown to be $S_{19}(AsF_6)_2$. The structure contains discrete AsF_6^- anions and S_{19}^{2+} cations, the latter consisting of two seven-membered rings joined by a five-atom chain (4).

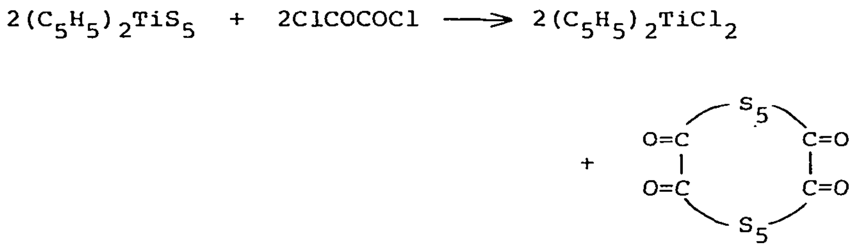


(4)

One of the rings has a boat conformation and the other ring is disordered, existing 80% in a chair conformation and 20% in a boat conformation, significant bond length alternations were observed in both rings. E.s.r. and absorption spectra of solutions obtained by the oxidation of sulphur with AsF_5 in SO_2 were investigated and the presence of S_{19}^{2+}, S_8^{2+}, S_5^{+} and two other radical species have been confirmed.[13]

The reaction of sulphur and tin tetraiodide in toluene at room temperature gives the compound $2S_8.SnI_4$. A crystal structure determination shows each SnI_4 unit to be surrounded by twelve S_8 molecules and conversely every S_8 ring is surrounded by six SnI_4 molecules. A mixed sulphur-selenium adduct was also prepared by the melting of sulphur and selenium in a molar ratio of 6:2, quenching, extracting the mixture in boiling toluene and addition of SnI_4. On cooling to -20°C crystals were obtained corresponding to the formulation $2S_nSe_{8-n}.SnI_4$.[14]

The first 14-membered sulphur ring compound, $S_{10}(CO)_4$ has been prepared by the condensation of Cp_2TiS_5 with oxalyl chloride in CS_2. The compound is stable at room temperature and forms yellow crystals.



$$2(C_5H_5)_2TiS_5 + 2ClCOCOCl \longrightarrow 2(C_5H_5)_2TiCl_2$$

...(6)

The conformation of the tetracyclic tetraone corresponded to expectations having a mean value of the S-S bond lengths of 205.1pm which is comparable with that of S_{12}(205.3pm). The S-S bonds adjacent to the long S-S bonds are shortened as in S_7O.[15]

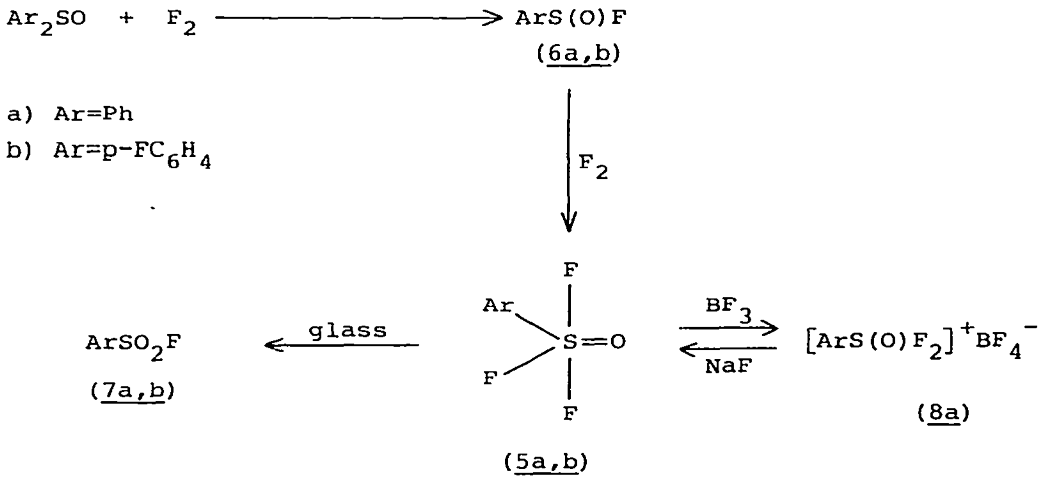
6.2.2 Bonds to Halogens

The reaction of both elemental sulphur and COS with elemental fluorine, in a metal high-vacuum apparatus, has been shown to give a mixture of SF_6, SF_4, $S{=}SF_2$ and S_2F_4. At -78°C, S_2F_4 can be freed from impurities and has been isolated in a pure state. Determinations of its molecular weight, density, melting point, vapour pressure, boiling point, i.r., u.v., ^{19}F n.m.r. and mass spectra were reported.[16]

A series of nucleophilic displacement reactions between F-ethyl- and F-n-propylsulphurimide dihalides with a large number of nucleophiles has been reported. Reaction of $C_2F_5N{=}SF_2$ and $LiOCH_2CF_3$, NaOMe, or Me_2NSiMe_3 gave $C_2F_5N{=}SX_2$ ($X{=}OCH_2CF_3$, OMe, NMe_2) and also in the latter case $C_2F_5N{=}(F)NMe_2$ which could be reacted further with NaOMe to give $C_2F_5N{=}S(OMe)NMe_2$. However, with $LiN{=}C(CF_3)_2$ an extensive rearrangement occurs to give $i\text{-}C_3F_7N{=}S{=}NC_3F_7\text{-}i$ and CF_3CN. With chlorinating agents such as $AlCl_3$ or PCl_5, $RN{=}SF_2$ ($R{=}C_2F_5$, $n\text{-}C_3F_7$) gives $RN{=}SCl_2$ which, in turn, when $R{=}C_2F_5$ with AgNCO, gives $C_2F_5N{=}S(NCO)_2$.[17]

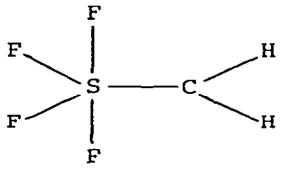
SF_2 and CF_3SF have been shown to form unusual chemical equilibria with their dimers F_3SSF and $CF_3SF_2SCF_3$ involving the two different bonds S-F and S-S. The equilibrium between F_3SSF and SF_2 is disturbed by a decomposition reaction of these compounds giving SF_4 and SSF_2 : both the equlibrium constants and dissociation enthalpies have been determined. In both systems kinetic hindrance was shown to delay the achievement of the equilibrium and the rates for dissociation and decomposition were shown to be surface dependent.[18]

Two new arylsulphur(VI)trifluoride oxides (5a,b) have been prepared by direct fluorine addition to the sulphinic fluorides (6a,b).



The fixed trigonal bipyramidal ligand arrangement was determined from ^{19}F and $^{13}C\{^1H\}$ n.m.r. data. In glass vessels (5) was shown to undergo decomposition which was catalysed by HF to give the corresponding sulphonic fluorides (7). Action of BF_3 on (5a) gave the difluorophenylsulphoxonium salt (8a) by fluoride abstraction whilst dry distillation of (8a) with NaF reformed (5a).[19]

Ab-initio calculations have been used to compute a general valence force-field for SF_4. This technique was used since it was found to be impossible to compute a unique and meaningful general force-field from experimental values.[20] Single crystals of methylenesulphurtetrafluoride, $H_2C{=}SF_4$, with a melting point ca. -135°C, have been grown using a miniaturized Bridgman technique. In the molecule (9) the sulphur atoms have approximately a trigonal bipyramidal environment with the CH_2 group occupying the position of the non-bonding electron pair in SF_4. The hydrogen atoms were found in the plane of the S, C and axial fluorine atoms. The bond lengths, S-F (159.2 to 156.1pm) S-C (155.4pm) were reported.[21]



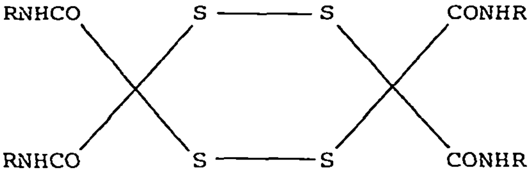
(9)

The i.r. and Raman spectra of S_2F_{10} vapour have been recorded and new assignments made for several of the fundamental modes. In particular the band pumped in laser dissociation experiments is an E_1 radical S-F stretch rather than a B_2 axial S-F stretch as earlier thought.[22] The preparation, structure and properties of new SF_5Br-fluoro olefin adducts have been reported. The extent and direction of SF_5Br addition to 7 fluoroolefins were studied and steric factors were found to be the most significant factor for this addition.[23]

The behaviour of SF_6 in the quartz and Al_2O_3 tubes of a flow-reactor, capacitatively coupled to a radio frequency generator has been investigated at a pressure of 20 torr and at various power levels and flow rates. A combination of spectroscopic techniques showed the presence of SO_2F_2, SOF_4, SOF_2, SiF_4, F_2O_2, together with unreacted SF_6 in the discharge products.[24] Studies of the chemiluminescent reactions of SF_6 and SF_4 with metastable calcium and strontium atoms under single-collision conditions have enabled the F_5S-F and F_3S-F bond dissociation energies to be determined.

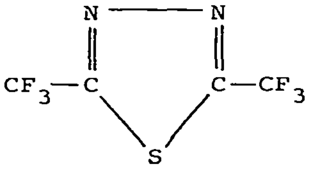
The results were combined with known heats of formation to deduce the complete series of step-wise bond dissociation energies.[25] The mobilities of positive and negative ions at 296K have been measured at pressures in the range 50 to 1200 torr for H_2S and SF_6.[23]

The unstable radicals SCl and SBr have been prepared by photolysis of S_2Cl_2, SCl_2 and S_2Br_2 respectively and by passing the stable molecules through a microwave discharge in the presence of argon in large excess. The radicals were trapped in an argon matrix at 9K.[27] The reactions of a series of N,N'-dialkyl and N,N'-diaryl malondiamides with disulphur dichloride have been reinvestigated. The claim, made almost 60 years ago, that the products of this reaction are dithioketones R_2CS_2 were shown to be unfounded in that the structures of the products were shown to be the unsymmetrically substituted 1,2,4,5-tetrathianes (10).[28]



(10)

Insertion reaction of fluorinated methylenes into the S(II)-Cl bond have been studied. $(CF_3)_2CN_2$ and CF_3CHN_2 react with $(CF_3)_2C{=}NSCl$ to give $(CF_3)_2CN{=}S{-}CCl(CF_3)_2$ and $(CF_3)_2C{=}N{-}SCHClCF_3$ respectively. The reaction of $CFCHN_2$ and $(NSCl)_3$ gives $CF_2CH{=}N{-}S{-}CHClCF_3$ and (11).[29]



(11)

Two crystalline modifications of $[SCl_3][ICl_4]$ have been characterised by elemental analysis, Raman and n.q.r. spectroscopy. Analysis of the spectra indicates that both the stable and the metastable forms involve distortion from the square planarity of the

ICl_4^- ion.[30] The i.r. (gas, Ne and Ar matrix) and Raman (liquid and solid) spectra of CF_3SCl have been investigated. All possible fundamentals were identified as well as several combination bands. The i.r. spectra of three different isotopically enriched SCl_2 species in Ne matrices were also recorded.[31] When SCl_2 or S_2Cl_2 vapours diluted with argon and mixed with Br_2 or I_2 are passed through a microwave discharge reaction takes place to give the previously unknown compounds SBr_2 and SI_2. The compounds were isolated in an argon matrix at 9K and were identified by their i.r. spectra.[32] The fragmentation of these sulphur halides and of the SCl_2/Br_2 and S_2Cl_2/Br_2 mixtures under electron impact conditions in the ion source of a mass spectrometer have also been studied. In the system SCl_2/Br_2 the main products are SBr^+ and SBr_2^+ and in the case of S_2Cl_2/Br_2 large amounts of S_2Br^+ and $S_2Br_2^+$ were observed.[33]

Four new addition compounds of SCl_4 all containing the SCl_3^+ ion have been prepared ($SCl_3^+.GaCl_4^-$; $SCl_3^+.InCl_4^-$; $SCl_3^+.TeCl_5^-$ and $2SCl_3^+.ZrCl_6^{2-}$) but attempts to form addition compounds between SCl_4 and $SeCl_4$ or $PbCl_4$ were unsuccessful.[34] The preparation of two further complexes of this type, $SBr_3^+.AlX_4^-$ (X=Cl,Br) have been described. Synthesis of pure compounds containing chlorobromo-sulphonius cations is apparently extremely difficult and a variety of reactions involving a sulphur halide (SCl_2, S_2Cl_2 or S_2Br_2), a halogen (Br_2 or Cl_2) and a Lewis acid $AlCl_3$, $AlBr_3$ or $SbCl_5$) gave only a mixture of products. An exception, however, was the product from S_2Br_2, $3Br_2$ and $2AlCl_3$ for which both the analytical data and Raman spectrum were consistent with the formulation $SBr_3^+AlCl_4^-$.[35]

6.2.3 Bonds to Nitrogen

A comprehensive review covering the past twenty-five years since the first sulphur-nitrogen-fluorine compounds were synthesised has been published. The review is based on the small molecules thiazyl fluoride (NSF) and thiazyl trifluoride (NSF_3) and deals initially with their preparations and their chemical and physical properties. These compounds are key substances in that nearly all sulphur-nitrogen-fluorine compounds may be derived from them and the review deals comprehensively with their synthetic application.[36] Ab-initio molecular orbital theory has been used to study sulphur-nitrogen and sulphur-carbon configuration in the compounds, $(SN)_2$, $(SN)_4$, SN oligomers, the $(SCH)_2$ isomers, and their fluoro- and cyano-substituted counterparts. In quantitative energy comparisons between valent and hypervalent sulphur-containing molecules the inclusion of sulphur d-orbitals was found to be mandatory. The sulphur d-orbitals decrease the ionic character of the S-N bond, increase the overlap populations and may contribute to extravalent intermolecular interactions, but their role in sulphur-carbon compounds is less as a result of the decreased ionicity of this linkage with respect to the sulphur-nitrogen bond.[37]

The first direct chemical synthesis of polymeric sulphur nitride $(SN)_x$ from solution has been reported. Trichlorocyclotrithiazane, $(NSCl)_3$ and trimethylsilylazide or sodium azide react together in acetonitrile at -15°C to give the polymeric $(SN)_x$ in good yield.[38]

$$2Me_3SiN_3 + (NSCl)_3 \longrightarrow \frac{3}{x}(SN)_x + 3Me_3SiCl + \frac{9}{2}N_2 \qquad ...(7)$$

The preparation of the first conducting iodinated polymeric sulphur nitride has been described. Tetrathiatriazenium chloride (S_4N_3Cl), vaporized at 130°C, when treated with sodium iodide supported on glass wool at 250°C, followed by cooling of the exit gas to 10°C, gives a black product with the formulation $(S_aN_bI_c)_x$ with the approximate values of a=3.0, b=2.1, c=0.5. A lower condensation temperature was found to give a product contaminated with iodine. The conducting polymeric product is moisture sensitive and decomposes above 40°C in vacuo (ca. 10^{-6} torr) to sulphur, tetrasulphur tetranitride and iodine.[39]

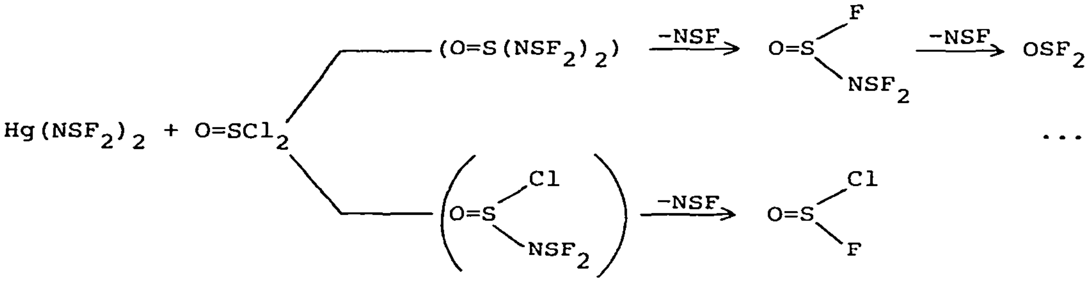
Linear sulphur-nitrogen compounds

The reactions of perfluoroisobutene with thiazylfluoride and thiazyltrifluoride have been described. Thiazylfluoride and $(CF_3)_3C{=}CF_2$ react together in the presence of CsF at 130°C to yield $(CF_3)_3C{-}N{=}S{=}N{-}S{-}C(CF)_3$. With NSF_3 the reaction gives $NSF_2C(CF_3)_3$ which isomerizes above 100°C to $(CF_3)_3CNSF_2$. The compound $NSF_2C(CF_3)_3$ also reacts with fluoro Lewis acids to give the 1:1 adducts $(CF_3)_3CSF_2N.MF_5$ (M=As,Sb), whilst $(CF_3)_3CNSF_2$ in 50% aqueous KOH undergoes hydrolysis to give the amine $(CF_3)_3CNH_2$.[40] The formation of some sulphur-sulphurdifluoride imides in reactions involving $Hg(NSF_2)_2$ have been described. $Hg(NSF_2)_2$ reacts with S_2Cl_2 to give $(SNSF_2)_2$ by the mechanism :

$$\begin{tikzcd}
\tfrac{1}{2}Hg(NSF_2)_2 + S_2Cl_2 \arrow[r] & ClSSNSF_2 + \tfrac{1}{2}HgCl_2 \arrow[d, "+\tfrac{1}{2}Hg(NSF_2)_2"] \\
 & F_2S{=}N{-}S{-}S{-}N{=}SF_2 + \tfrac{1}{2}HgCl_2
\end{tikzcd}$$

...(8)

The reactions of $OSCl_2$ or SF_5NSCl_2 and $Hg(NSF_2)_2$ give the compounds $OSF{-}NSF_2$ and $F_5S{-}NSF{-}NSF_2$ according to the schemes[41]



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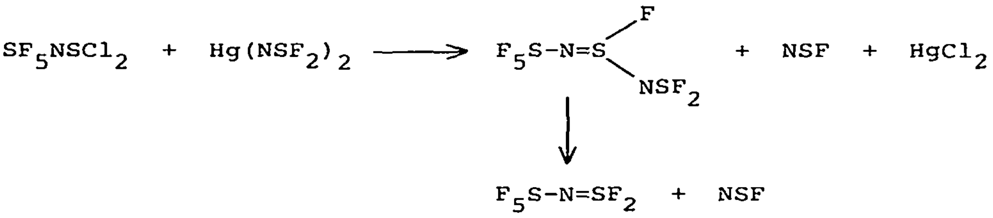
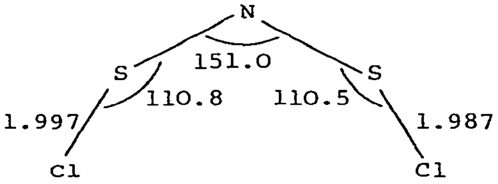


...(10)

The reaction of the diimidosulphur compounds $S(NR)_2$ ($R{=}Bu^t$, Ph, $4{-}MeC_6H_4$ or $4{-}O_2NC_6H_4$) in 1,2-dimethoxyethane solution with a potassium mirror in vacuo has been shown to give fairly stable solutions of the corresponding anion radicals $[S(NR_2)_2]^-$ which have been studied by e.s.r. spectroscopy. The frozen-solution e.s.r. spectrum of $K[S(NBu^t]_2$ was also recorded. The experimental evidence indicates the two nitrogen atoms to be magnetically equivalent and alkali metal coupling constants for the species $M[S(NBu^t)_2]_2$ ($M{=}{}^7Li$, ${}^{23}Na$ or ${}^{39}K$) indicate that the metal-anion interaction increases in the order $K<Na<Li$. Potassium metal reduction of $M(CO)_4(S(NBu^t)_2)$ where M=Cr, Mo or W, was shown to produce the corresponding anions with well defined isotropic e.s.r. spectra. The results indicate that the unpaired electron is located mainly on the $S(NBu^t)_2$ ligand.[42] The i.r. and Raman

spectra of some $N(SCl)_2^+$ salts have been reported and two possible assignments of the normal modes were discussed. It was shown that the usual correlation between force constants and bond lengths are not valid for N-S cations.[43]

The synthesis of some complexes containing the bis(chlorosulphur)-nitrogen cation $N(SCl)_2^+$ has been described. The crystal structures of $N(SCl_2)_2AsF_6$, $N(SCl)_2BCl_4$ and $N(SCl)_2AlCl_4$ were all found to be different. A full structure determination on the aluminium compound showed the $N(SCl)_2^+$ cation to have the structure (12).[44]



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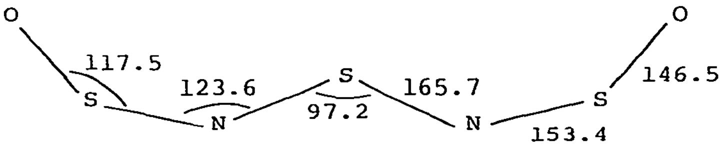
A determination of the crystal and molecular structure of $S(NSO)_2$ has shown the chain-like molecule to have the parameters (13).

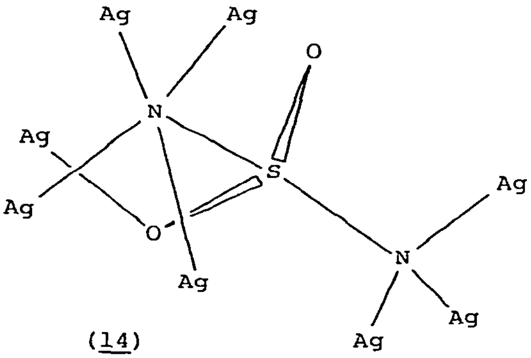


(13)

The molecular geometry was shown to be C_s and i.r. and Raman spectra were reported and assigned. No evidence was found for conformational changes when crystalline $S(NSO)_2$ was taken into solution.[45]

The thermal decomposition of $PPN^+S_4N_5^-$ ($PPN^+ = (Ph_3P)_2N^+$) in acetonitrile at 78°C has been shown to lead sequentially to the corresponding salts of the $S_3N_3^-$ and S_4N^- anions. The crystal and molecular structure of the dark blue salt, $PPN^+S_4N^-$ has been determined and shows the S_4N^- anion to have an essentially planar, cis-trans chain with nitrogen as the central atom. The terminal S-S bond distances are remarkably short, 1.879 and 1.943Å, and the S-N bond lengths show a pronounced inequality, 1.667 and

1.521Å. The bond angles at the internal sulphur atoms are ca. 110.5 and the angle at the nitrogen is 120.8°. I.r. and Raman spectra of the compound show that the vibrational frequencies at 592 and 565cm^{-1} may be assigned to the stretching modes of the unequal S-S bonds. Theoretical calculations were also carried out so that the bonding in the S_4N^- ion may be determined[46]. The crystal and molecular structure of tetrasilver(I) sulphamide has been determined. The structure (14) consists of a network of sulphamide groups linked by covalently bonded Ag atoms. With the exception of one Ag-O bond, all Ag atoms are coordinated to the nitrogen atoms of the sulphamide group. One of the nitrogen atoms shows an unusual five coordination.[47]



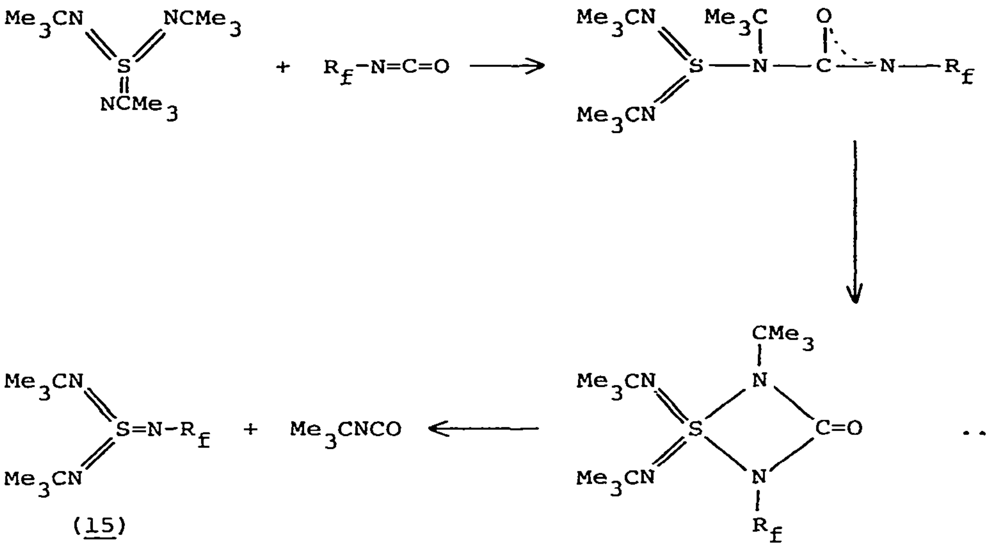
(14)

Diffuse reflectance spectra of the diamagnetic compounds $O_2S(NHAg)_2$ and $O_2S(NAg_2)_2$ have been measured in the region from 700nm to 200nm at 300K and 77K respectively. A shift, observed for the SO stretching modes together with the thermal and mechanical instability of the compounds is thought to be due to the transfer of charge from the S=O bond region via the nitrogen atoms to the silver atoms.[48]

Tri-tert-butylsulphur triimide has been shown to react with a variety of isocyanates to give the corresponding di-tert-sulphur triimides (15) in high yield.

Using the same method, the bis(trimethylsilyl) derivative $(Me_3SiN)_2S(N\text{-}CF(CF_3)_2)$ was also prepared.[49]

The simplest fluorinated sulphur(VI)imide F-N=SF_4 has been prepared by the series of reactions (12) - (14). The i.r. spectrum of $FNSF_4$ is very similar to that of SOF_4 with an additional N-F stretching frequency. The N=S valence vibration



(15) ...(11)

$R_f = CF_3$, C_2F_5, n-C_3F_7, i-C_3F_7, SO_2Cl, SO_2F, SF_5, $C(CF_3)=N-SO_2F$.

$Cl_2N-SF_5 + F_2 \longrightarrow FClN-SF_5 + ClF$ ...(12)

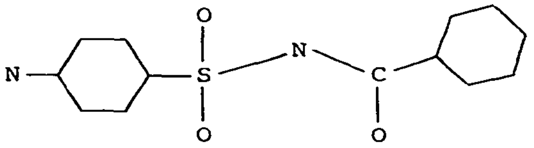
$FClN-SF_5 + Hg + CF_3COOH \longrightarrow FHN-SF_5$ ...(13)

$FHN-SF_5 + KF \longrightarrow FN=SF_4 + HF$ ...(14)

was observed at about 100cn^{-1} lower than expected which was considered to be surprising in view of the observed rigidity of the molecule. A highly complicated ^{19}F n.m.r. spectrum was observed which was interpreted on the basis of an A_2BCD spin system and which showed the sulphur to have a trigonal bipyramidal environment with one equivalent pair and one non-equivalent pair of fluorine atoms. The N-F group was thought to occupy an equatorial position with the N-fluorine atom orientated in the axial plane. The absence of dimerization to form a dimer with an $(NS)_2$ four membered ring as is observed in $(Cl-NSF_4)_2$ is, as yet, unexplained. $F-N=SF_4$ forms only a weak adduct with AsF_5 and with SbF_5 an explosive interaction was observed at -10°C.[50]

The aminolysis of $(NPCl_2)_2NSOPh$ by methyl and ethyl amine in diethylether has been shown to proceed mainly by a non-geminal substitution pattern. In acetonitrile both geminal and non geminal substitution was observed.[51]

The crystal structure of a form of sulphabenzamide (16), obtained by recrystallization from water has been determined. The form, which is characterized by a transition at 172°C has two independent molecules in the unit cell with the bond lengths, S-N=1.656, 1.680Å; S-O=1.439, 1.417 and 1.417, 1.421; C-S=1.738, 1.735Å.[52]



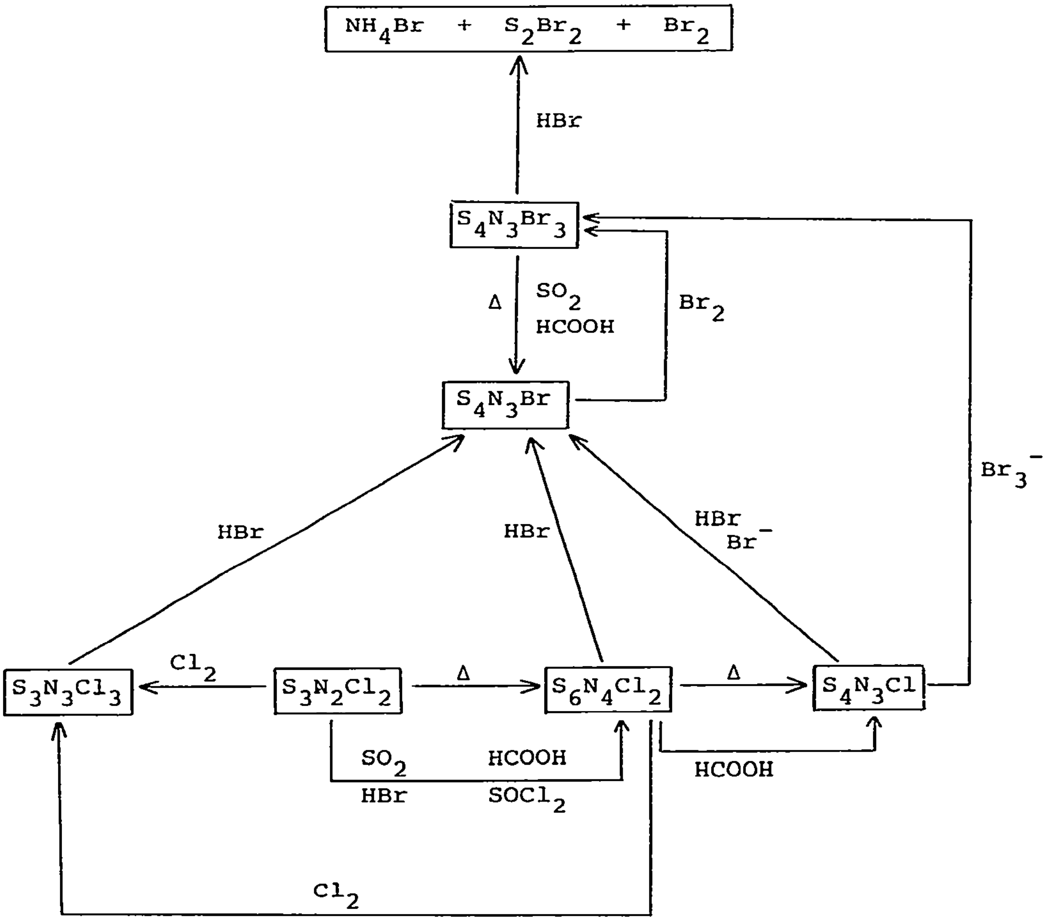
(16)

The reaction of S_4N^- with triphenylphosphine in acetonitrile has been shown to produce S_3N^- which reacts with $NiCl_2$ to give the compound $Ni(S_3N)_2$, vibrational spectra of $S_3\overset{*}{N}^-$ ($^*N$=30% ^{15}N) suggest an $^-S{-}N{=}S{=}S$ arrangement of atoms in the anion.[53]

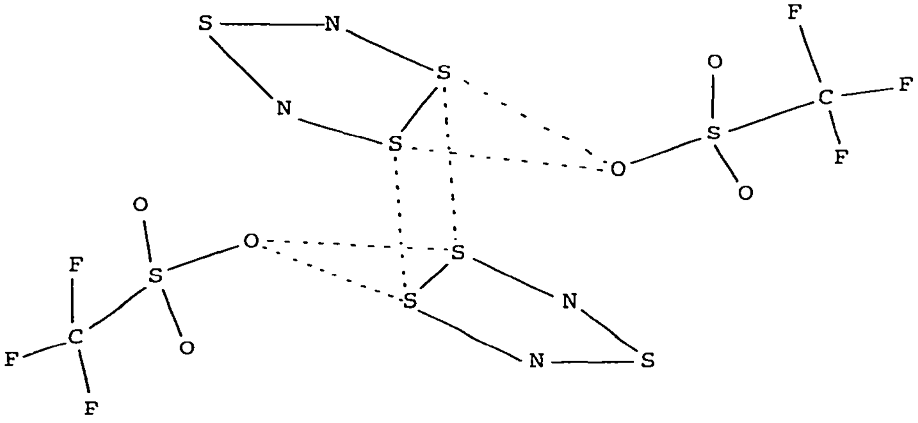
Cyclic sulphur-nitrogen compounds

The gas phase u.v.-photoelectron spectra of SN, S_2N_2, S_4N_4 and a number of open-shell cationic states have been investigated and assigned on the basis of ab initio molecular orbital calculations. The electronic structures of S_2N_2 and S_4N_4 were investigated by transformation of the wave-functions to a localised bond basis. A significant amount of S-S bonding was calculated for S_4N_4 but no N-N bonding and across-ring bonding was absent from S_2N_2.[54] A second study of the X-ray photoelectron spectrum of S_2N_2 gas has concluded that $N_{p\pi}-S_{d\pi}$ back bonding is not necessary for a clear understanding of the bonding and charge distribution in S_2N_2 or S_4N_4, and that S→N charge transfer is greater in S_4N_4 than in S_2N_2.[55] A vibrational spectroscopy study of the compound $Pb(S_2N_2)$ and its ammoniate $Pb(S_2N_2).NH_3$ has been carried out using normal coordinate analysis.[56]

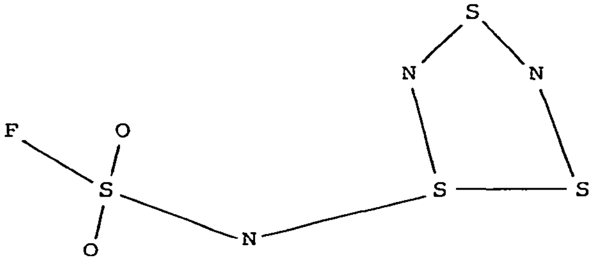
The stability of different thiazyl halogenides in the presence of reducing agents, polar solvents and HBr has been studied. The solubilities of $S_3N_2Cl_2$ and $S_6N_4Cl_2$ are low and the best solvents are $SOCl_2$, liquid SO_2 and HCOOH, but an interaction is always observed between the solvent and the thiazyl chloride. The principal reaction observed is the destruction of the cyclic compound and formation of the $S_6N_4^{2+}$ or $S_4N_3^{+}$ cyclic ions. The reaction of HBr with $S_3N_3Cl_3$, $S_3N_2Cl_2$ and $S_6N_4Cl_2$ was shown to give substitution products with the elimination of HCl. S_4N_3Br may be obtained from S_4N_3Cl at -80°C but at higher temperatures the reaction is more complex and an impure product was obtained. With the other thiazyl chlorides the reaction was violent at all temperatures, the thiazyl cycle was destroyed and S_4N_3Br or $S_4N_3Br_3$ were formed. The reactions studied are shown in the scheme below.[57]



The molecular and crystal structures of $S_3N_2^{+}SO_3CF_3^{-}.\frac{1}{2}CH_3CN$ (17) and $S_3N_2NSO_2F$ (18) have been determined.



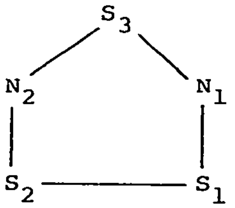
(17)



(18)

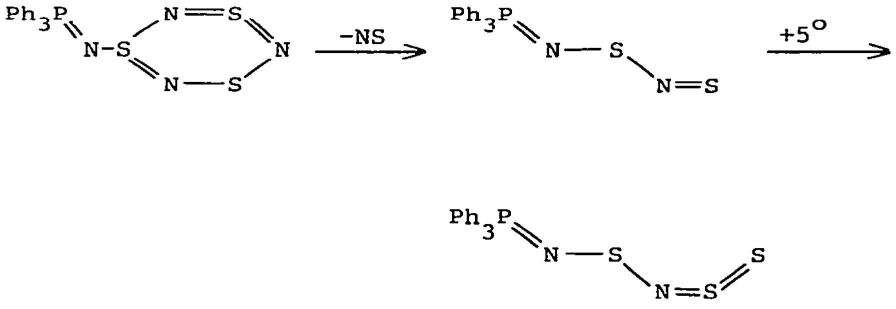
The $S_3N_2^+$ radical cation in (17) is planar and two cations are connected via weak S-S bonding interactions to form dimers with a chair configuration. The S_3N_2 ring of (18) in which the NSO_2F group is covalently bonded to one of the sulphur atoms of the S-S group is not planar and the S-S bond is weaker than that of (17). The observed bond lengths and angles measured for the $S_3N_2^+$ groups in the two compounds are shown below.[58]

	(17)	(18)
S_2-S_1	213.8	220.0
S_1-N_1	161.2	163.5
N_1-S_3	157.5	156.5
S_3-N_2	156.2	157.8
N_2-S_2	161.7	164.4
S_2-N-SO_2F	-	160.3



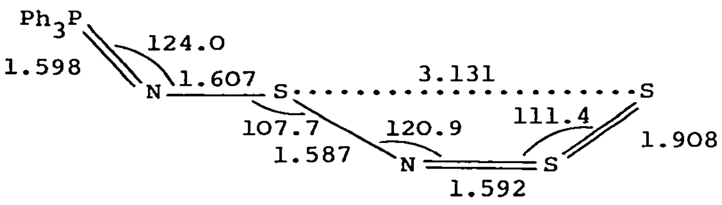
	(17)	(18)
$N_1-S_1-S_2$	97.0	97.9
$N_2-S_2-S_1$	97.1	94.0
$N_1-S_3-N_2$	107.8	109.4
$S_1-N_1-S_3$	119.0	117.2
$S_2-N_2-S_3$	119.0	119.1

The thermal decomposition of $Ph_2P=N-S_3N_3$ has been shown to lead to the open chain derivative $Ph_3P=NSNSS$.



...(15)

X-ray studies have shown that the five atom chain exists in a nearly planar cis-trans configuration (19) with a very short (1.905Å) terminal S=S bond.[59] A low temperature (90K) X-ray diffraction study has been used to determine the electron density



distribution in thiotrithiazyl nitrate, $S_4N_3NO_3$. The electron density maps were in reasonable agreement with an earlier theoretical study except in the lone-pair regions of the chemically equivalent N(2) and N(3) atoms where experiments showed little density, while for the N(1) atom opposite the disulphide group, both theory and experiment indicate a clear lone-pair peak.[60]

Some reactions of cyclotetrathiatriazenium chloride S_4N_3Cl vapour with hot metal surfaces have been described. Reaction with iron wire at 300°C gave S_3N_2Cl, S_4N_4 and $(NSCl)_3$ as principal products and the main reaction was thought to be:

$$2S_4N_3Cl \xrightarrow{\Delta} S_4N_4 + 2NSCl + 2S \xrightarrow[300^oC]{Fe/FeS} 2S_3N_2Cl + N_2 + \tfrac{1}{4}S_8 \qquad \ldots(16)$$

With titanium sponge complete breakdown of S_4N_3Cl took place according to equation (17):

$$Ti + 4S_4N_3Cl \longrightarrow TiCl_4 + 2S_8 + 6N_2 \qquad \ldots(17)$$

and with silver wool it was considered that the initial pyrolysis of S_4N_3Cl (equation 18), was followed by the splitting of S_4N_4 into

$$2S_4N_3Cl \longrightarrow S_4N_4 + 2NSCl + 2S \qquad \ldots(18)$$

S_2N_2 and the dehalogenation of NSCl by silver or Ag_2S as shown in equations (19) and (20).[61]

$$2NSCl_{(g)} + 2Ag_{(s)} \longrightarrow S_2N_{2(g)} + 2AgCl_{(s)} \qquad \ldots(19)$$

$$2NSCl_{(g)} + Ag_2S_{(s)} \longrightarrow S_2N_{2(g)} + \tfrac{1}{2}S_{2(g)} + 2AgCl \qquad \ldots(20)$$

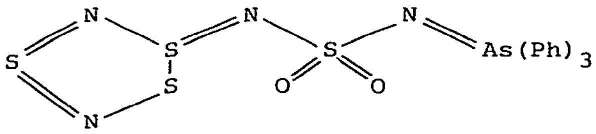
New methods for the synthesis of S_4N_4 have been described. The first study involves the reduction of $S_3N_3Cl_3$ by various metals (Hg, Cu, Sn), and reaction is carried out in either an inert solvent such as CCl_4 or directly in the gas phase. Reaction was found to be complete and was thought to proceed according to equations (21) and (22).[62]

$$S_3N_3Cl_3 \longrightarrow 3NSCl_{(g)} \qquad \ldots(21)$$

$$NSCl + Cu \longrightarrow CuCl + \tfrac{1}{4}S_4N_4 \qquad \ldots(22)$$

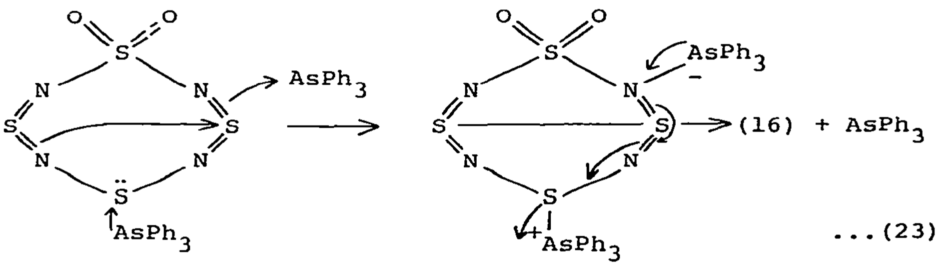
A second study describes the preparation of S_4N_4 by the reduction of S_4N_3Cl, $(NSCl)_3$, $S_3N_2Cl_2$, or S_3N_2Cl using a variety of reducing agents. New routes to bis(tetrasulphur tetranitride)tin(IV) chloride, tetrathiotetraimide and cyclopentathiapentazenium tetrachloroferrate(III) are also discussed.[63] An ab initio molecular orbital study of S_4N_4 has also been described.[64]

A predictable degradation reaction of the S_4N_4 derivative $S_4N_4O_2$ has been found in that reaction with $AsPh_3$ leads to the symmetrically substituted sulphamide (20) in high yield.



(20)

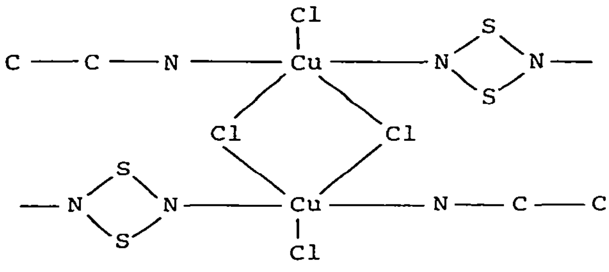
X-ray diffraction studies showed the five membered ring in (20) to be comparable with rings in $S_3N_2{=}N{-}SO_2F$ and $S_3N_2{=}N{-}P_3N_3F_5$. The degradation of $S_4N_4O_2$ was thought to take place via a transition state involving two molecules of triphenylarsane as shown in equation (23).[65]



...(23)

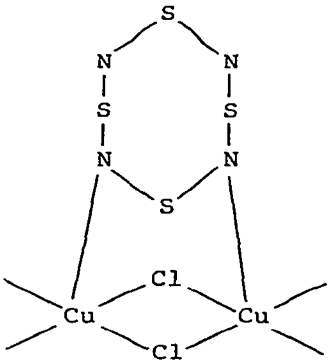
The crystal and molecular structure of bis(tetrasulphurtetraimide)-silver(I) perchlorate sesquihydrate has been shown to consist of $[Ag(S_4N_4H_4)_2]^+$ cations, ClO_4^- anions and water molecules all interconnected by an extensive hydrogen bonded network. The cation has a sandwich structure with the S_4N_4 crowns arranged so that the sulphur atoms are nearest to the cation and there are no Ag-N bonds. The silver is displaced sideways from a central position and the $S_4N_4H_4$ ligands are tilted to an angle of 20.4° between the two S_4 mean planes and the ligands also adopt a staggered configuration with respect to the two S_4 groups. As a result the two sulphur atoms from each ligand are closer (2.696-2.792Å) to the metal than the other two pairs (3.141-3.226Å) and are so arranged that a distorted tetrahedral metal coordination is produced. The bonds between the four nearest sulphur atoms and the metal ion are thus considered to possess a significant degree of covalent character. The authors consider this to be the first example of a complex of a sulphur imide and the first proven example of donor sulphur rather than donor nitrogen in any sulphur nitride or imide complex.[66]

S_4N_4 has been shown to react with $CuCl_2.2H_2O$ in acetonitrile to give, amongst other products, the polymeric copper(II) complex $(Cu(CH_3CN)Cl_2)_2S_2N_2$ (21). An X-ray structure analysis shows the



(21)

crystal to contain parallel chains with copper atoms bridged by Cl and S_2N_2 bridges. The coordination of the copper atom is square pyramidal and the S_2N_2 ring (S-N bond distances 1.633 and 1.641Å) is planar.[67] A second product of the same reaction has been shown to be the polymeric complex $CuCl_2.S_4N_4$ (22). This compound also contains parallel chains with the copper atoms bridged by Cl and S_4N_4 bridges. The coordination of the copper atom is now that of a distorted octahedron with four equatorial Cl atoms and two axial nitrogen atoms. The S_4N_4 ring is connected to the Cu atoms by two neighbouring N atoms and in its conformation and dimensions it is very similar to the uncomplexed S_4N_4 molecule.[68]

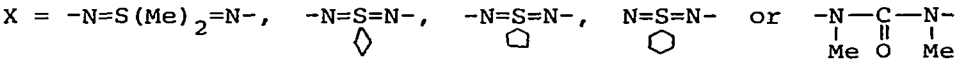


(22)

The reaction of S_4N_4 with $FeCl_3$ in CCl_4 gives the monomeric adduct α-$FeCl_3.S_4N_4$. In the complex the S_4N_4 ring is bonded via one of its nitrogen atoms to the iron atom of the $FeCl_3$ group to give a tetrahedral coordination around the iron atom. The structure thus resembles that of $BF_3.S_4N_4$ which was previously known.[69]

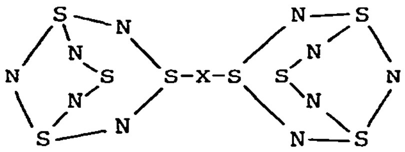
The reaction of S_4N_5Cl with silylated sulphodiimides or a substituted urea in a molar ratio of 1:1 has been shown to lead to the covalent derivatives (23).

$$S_4N_5Cl + Me_3Si{-}X{-}SiMe_3 \longrightarrow \underset{(23)}{S_4N_5{-}X{-}SiMe_3} + Me_3SiCl \qquad ...(24)$$



$$X = {-}N{=}S(Me)_2{=}N{-},\quad {-}N{=}S{=}N{-},\quad {-}N{=}S{=}N{-},\quad N{=}S{=}N{-}\quad \text{or}\quad {-}\underset{Me}{N}{-}\underset{O}{\overset{}{C}}{-}\underset{Me}{N}{-}$$

The reactions of $S_4N_5{-}N{-}S(Me)_2{=}N{-}SiMe_3$ have been studied under a variety of conditions. The reaction of S_4N_5Cl with $Me_3Si{-}X{-}SiMe_3$ in a molar ratio of 2:1 was shown to yield (24) which contain two S_4N_5 cages bridged by a sulphodiimide group and were extremely explosive compounds.[70]

$2S_4N_5Cl + Me_3Si{-}X{-}SiMe_3 \longrightarrow$  $+ 2Me_3SiCl$

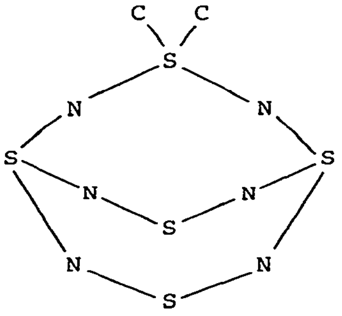
(<u>24</u>)

...(25)

$X = {-}N{=}S(Me_2){=}N$ or ${-}N{=}\underset{\diamond}{S}{=}N{-}$

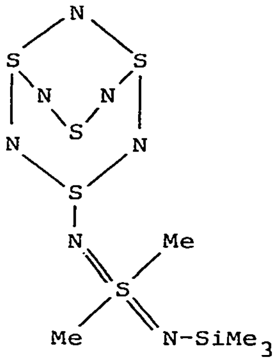
Qualitative arguments from molecular orbital theory have been used to rationalize the essential features of the structures of $S_4N_5^-$, $S_4N_5^+$ and S_5N_6. Possible degenerate rearrangements of all three species were discussed and an extension of the proposed model also allowed an understanding of the structures of As_4S_5 and β-P_4S_5 to be gained.[71]

Pentasulphur hexanitride, S_5N_6 and dimethylpentasulphur hexanitride $S_5N_6(CH_3)_2$ (<u>21</u>) have been prepared in high yield by the reaction of S_4N_4Cl with $Me_3SiN{=}S{=}NSiMe_3$ and $Me_3SiN{=}S(Me_2){=}NSiMe_3$ respectively. A crystal structure analysis of (<u>25</u>) showed a basket structure in which an $-N{=}S(CH_3)_2{=}N-$ unit bridges two sulphur atoms of an S_4N_4 cradle.



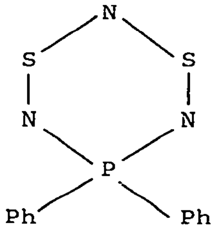
(<u>25</u>)

Whereas the bonding in the S_4N_4 cradle is similar to that in S_5N_6, with transannular S...S distances of 2.433 and 3.908Å, the S-N bonds of the handle are much shorter than those in S_5N_6. A crystal structure determination of $S_5N_7SiMe_5$ (<u>26</u>) prepared from the reaction of $S_3N_3Cl_3$ with $Me_3SiN{=}S(Me_2){=}NSiMe_3$, showed the neutral S_4N_5 unit to contain an S_3N_3 ring having three sulphur atoms of coordination number 3 in which there is a high degree of π delocalisation. This ring is bridged by an -N=S=N- unit with N-S bonds of predominantly single and double bond character. Five S...S interactions were observed in the range 2.736-2.846Å with a sixth of 3.814Å.[72]



(26)

The reaction of S_4N_4 with tetraphenyldiphosphine in toluene has been shown to give the six membered heterocycle $Ph_2PS_2N_3$ (27) the structure of which has been determined by X-ray crystallography.

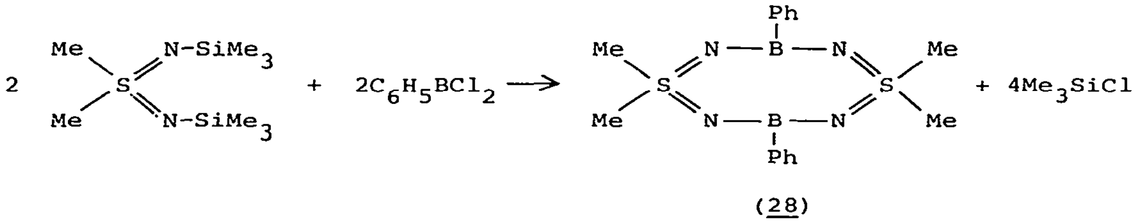


(27)

The five atoms N-S-N-S-N were coplanar to within 0.05Å but the phosphorus atom was found to be 0.28Å out of plane. S-N bond lengths were between 1.560 and 1.583Å.[73]

Chlorine-35 n.q.r. spectra for the six membered ring systems, α-$(NSClO)_3$, cis$(NSClO)_2(NPCl_2)$ and $(NSClO)(NPCl_2)_2$ have been recorded in the temperature range 77 to 300K and at 293K and pressures in the range 1-700 kgcm^{-1}.[74] An eight membered S-N-B ring compound (28) has been synthesized by the reaction of dichlorophenylborane with S,S-dimethyl-N,N'-bis(trimethylsilyl)-

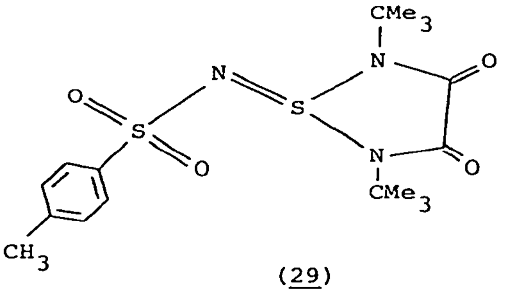
sulphodiimide.


(28)

...(26)

An X-ray structure determination showed the ring to exhibit significant deviations from planarity.[75]

An X-ray structural analysis of the compounds (29) and (30) has been described. Two types of S-N bonding are found in the pyramidal $S^{IV}N_3$ moieties in both compounds with the exocyclic bond being significantly shorter than the two endocyclic bonds. The S=N bond in these compounds is more similar to those in sulphur diimides containing a twofold coordinated S^{IV} than to those in N-sulphonylsulphilimides or the SN_3 moiety in the tris(tosyl)-sulphurtriimide dianion, which contain a three-fold coordinated S^{IV}. This analysis shows that the length of the formal S^{IV}=N double bond does not in general depend on the coordination number of the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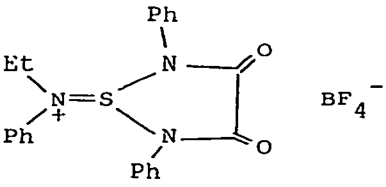
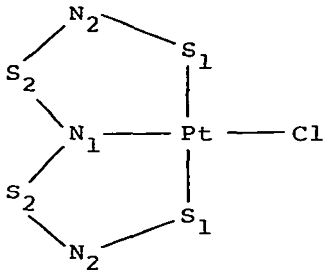

(30)

sulphur.[76]

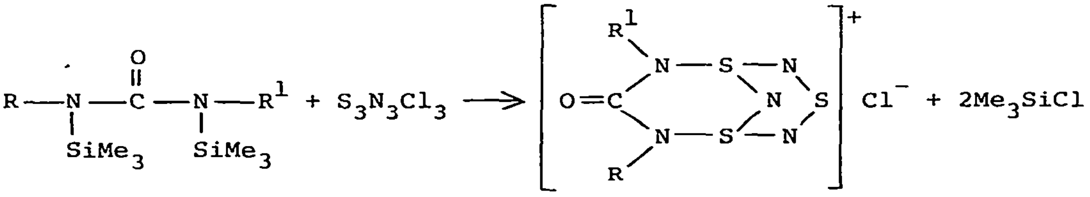
The reaction of S_4N_4 with cis-$PtCl_2(NCPh)_2$ has been shown to yield the novel complex (31) in which a formally singly negatively charged S_3N_3 group is coordinated as a planar tridentate ligand to the Pt^{II}.



(31)

All S-N bond lengths have values between those for a single bond and a double bond, the shorter distances of 1.59Å (S_1-N_2, S_2-N_2) correspond to those found in S_4N_4 (1.60-1.63Å), and the longer distances of 1.68Å (S_2-N_1) to those found in $S_4N_4H_4$ (1.663-1.669Å. A geometrically very similar S_4N_3 skeleton has been found in 1,7-bis(p-tolyl)tetrasulphur trinitrogen chloride. The compound has a melting point above 250°C and is soluble in toluene and acetone to give red solutions.[77]

Some cyclic sulphur-nitrogen compounds containing one carbon atom in the ring have been prepared. The reaction of trimethylsilyl substituted ureas with $S_3N_3Cl_3$ gives the compound (32).



(32)

...(27)

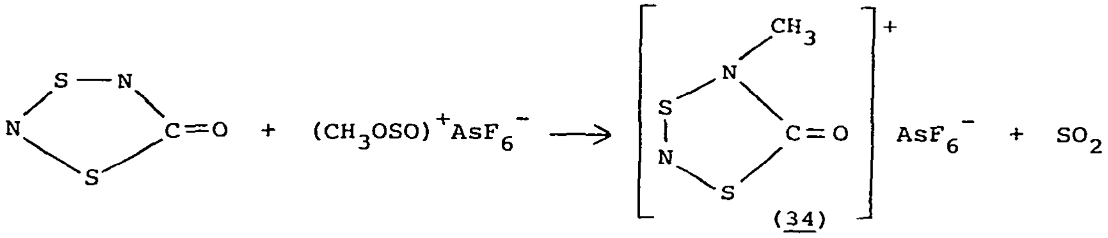
$R = R^1 = Me$ or $R = Me$, $R^1 = Ph$.

The chloride ion in (32) can be replaced by the anions $SbCl_6^-$, $SnCl_5^-$, $TiCl_5^-$ and AsF_6^- and the reaction of (32) when $R=R^1=Me$, has been shown to give the substitution product (33) which contains an exocyclic S-N bond.

$$(32) + Me_3SiNR_2 \longrightarrow (S_3N_5(Me)_2CO)NR_2 + Me_3SiCl \qquad ...(28)$$

R=Me, Et. (33)

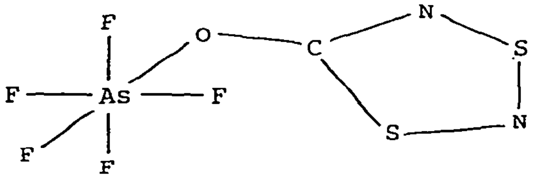
The methylation of a nitrogen atom in S_2N_2CO has been shown to be possible by reaction with $(CH_3OSO)^+AsF_6^-$ to yield (34), the structure of which was discussed on the basis of mass- and i.r. spectroscopic investigations.[78]



(34)

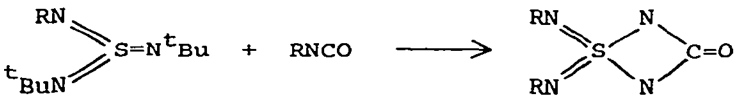
...(29)

The synthesis and X-ray structure of a 1:1 adduct of S_2N_2CO and the Lewis acid AsF_5 has been described. The adduct (35) comprises a five membered ring bonded by the exocyclic oxygen of the C=O group to an octahedrally coordinated As atom.[79]



(35)

A series of λ^6-thiadiazetidinones (36) have been prepared from the reaction of sulphur triimides and an excess of RNCO. Reaction



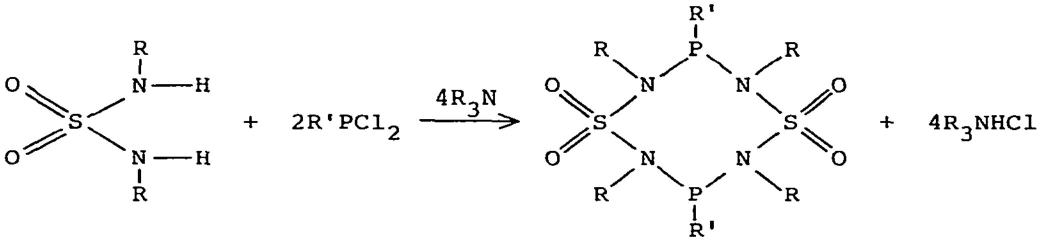
(36)

...(30)

mechanisms for the formation of (36) and the properties of this class of compounds were discussed.[80]

The reduction of 4-phenyl-1,2-dithia-3,5-diazolium chloride with thiocyanate ions has been shown to give the black, air sensitive compound $(PhCN_2S_2)_2$. A crystal structure determination has shown that within each dimer the bridging mean S...S distance is 310.9pm, and that the two half molecules within each dimer are slightly twisted with respect to each other. The short mean CN_2S_2 ring distances (C-N 133, S-N 162 and S-S 209pm) and the $PhCN_2S_2$ coplanarity suggest that the rings are aromatic with one electron pair delocalised at the four disulphide sulphur atoms.[81]

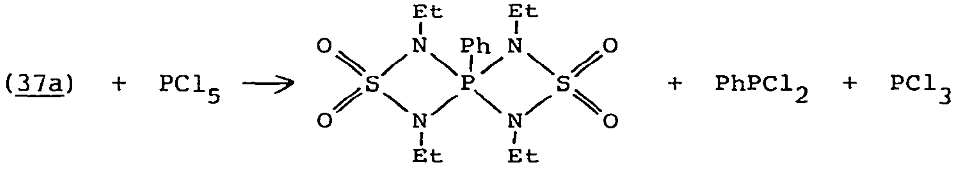
The eight membered ring compound (37) $[SO_2(NR)_2PR']_2$ with R=Me, Et, R'=Me, Ph has been prepared from substituted sulphamides and dichlorophosphanes in the presence of a tertiary amine. Reaction of (37a) with PCl_5 yields the spirocyclic derivative (38), whilst reaction with methyl iodide results in the opening of the 8 membered ring and the formation of phosphonium salts (39).[82]



(37)

...(31)

	R	R'
37a	Ph	Et
b	Me	Et
c	Ph	Me
d	Me	Me



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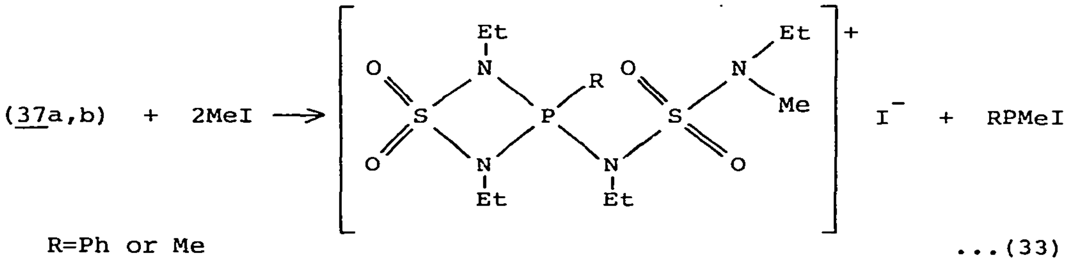
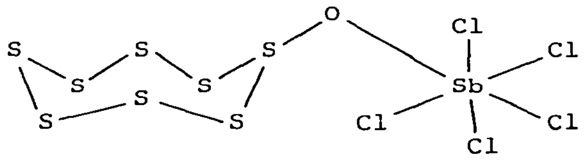


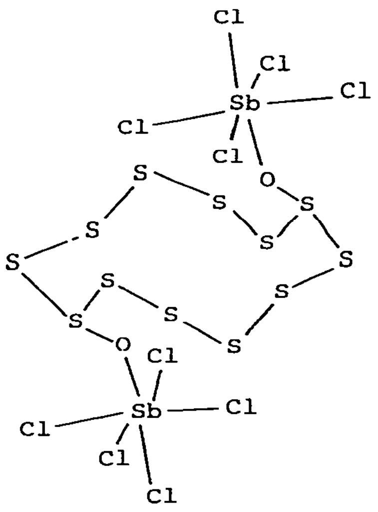
6.2.4 Bonds to oxygen

The reaction of S_8O and $SbCl_5$ in CS_2 has been shown to yield the adduct $S_8O.SbCl_5$ (40) in 71% yield. X-ray structural analysis showed that the compound contained S_8O in an isomeric conformation compared with pure S_8O. The latter may be recovered from the adduct in its usual conformation by recrystallisation from acetone or CS_2. The S_8O unit differs from molecular S_8O by an equatorially bonded oxygen atom as well as by significantly different S-O and S-S bond lengths. The S-O bond length increases from 148.3 in S_8O to 155pm and the adjacent S-S bond lengths have decreased from 220.0 to 211.1pm. At 25°C decomposition of the adduct to $SOCl_2$, $SbCl_3$ and S_8 was observed to be complete within five minutes.[83]



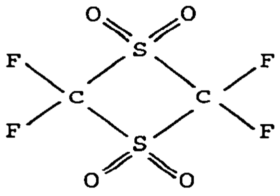
(40)

The first complex of a homocyclic sulphur oxide, (41) formed from S_6O is in an otherwise unprecedented dimerization has been described. The reaction of S_6O, $SbCl_5$ and solvent CS_2 at -50°C has been shown to yield the adduct $S_{12}O_2.2SbCl_5.3CS_2$. In the crystal the $SbCl_5$ groups together with bridging oxygen atoms have approximate O_h geometry. The conformation of the S_{12} ring differs completely from that observed in cyclo-S_{12}.[84]



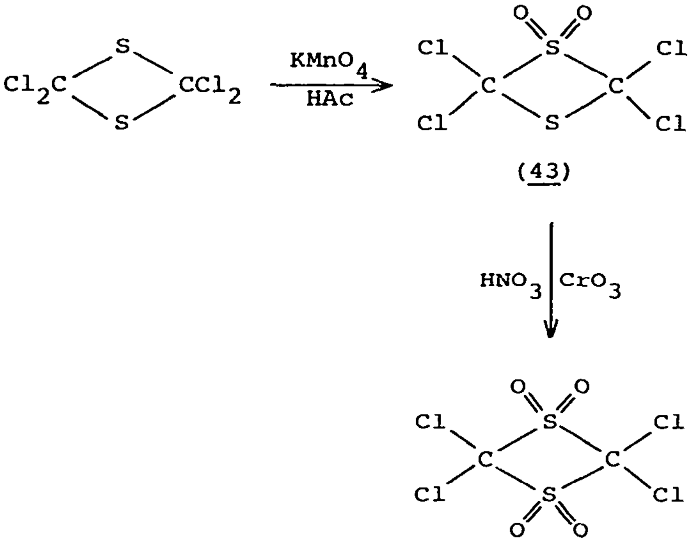
(41)

The smallest perfluorinated cyclic disulphone (42) has now been obtained by the oxidation of the corresponding cyclic disulphide with CrO_3/HNO_3 mixture. The white crystalline product, isolable



(42)

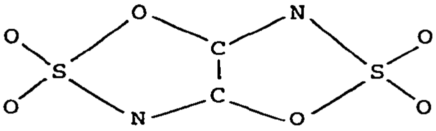
by sublimation, possesses an unusually high symmetry, having a planar ring with F and O atoms each in a plane vertical to each other and to the ring plane. The analogous reaction of tetrachloro-1,3 dithietane by the same method was found to fail due to rapid hydrolysis, but the reaction with $KMnO_4$ in glacial acetic acid gave the product (43) which is likewise sublimable and was recrystallised from petroleum ether.[85]



...(34)

Electronegativities for some RSO_2 groups have been estimated from the S-Cl bond lengths of sulphonic acid chlorides by the use of the Schomaker-Stevenson equation.[86]

An X-ray structural study has been carried out on the 2:1 addition product of SO_3 to dicyane. The compound (44) proved to be a formal "criss-cross" cycloaddition product in which two molecules of SO_3 are added to dicyane to form a heteropentalene system, in which the bicyclic ring system is planar.[87]

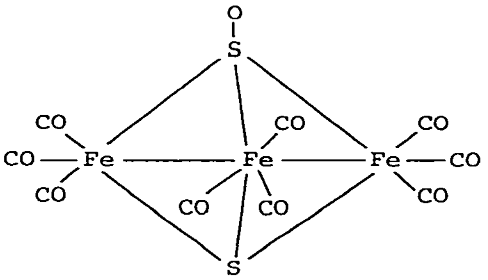


(44)

A new, and more direct method for the preparation of 1,1,1-trimethyl-N-sulphinylsilanamine, $Me_3Si{-}N{=}S{=}O$ has been described. A measured amount of SO_2 was added to hexamethyldisilazane (1:1 or 1:3 HMDS:SO_2) cooled to liquid nitrogen temperature. On warming to room temperature reaction proceeds as soon as the mixture becomes molten. The detailed stoichiometry of the reaction has not been determined with certainty but the amount of $Me_3Si{-}N{=}S{=}O$ produced represents some 22% of the total mass of reactants used.[88] A crystal structure study has shown the adduct $LiAlCl_4.3SO_2$ to be comprised of parallel strings of composition $Li(SO_2)_{6/2}$. The spaces between the strings being occupied by nearly ideal tetrahedral $AlCl_4$ ions.[89]

The complexes $Rh(NH_3)_5OH^{2+}$ and $Cr(NH_3)_5OH^{2+}$ have been shown to react very rapidly with dissolved SO_2 to form the oxygen-bonded sulphito species $Rh(NH_3)_5OSO_2^{+}$ and $Cr(NH_3)_5OSO_2^{+}$ respectively. The unstable $Mn(NH_3)_5OSO_2^{+}$ species lose SO_2 on acidification to regenerate $Mn(NH_3)_5OH^{2+}$ or undergo subsequent isomerization and/or substitution reaction. The kinetics of the SO_2 uptake were studied over wide pH and total sulphur ranges.[90]

The first compound to contain the SO ligand, (45) may be regarded as an intermediate in the reduction of sulphite to sulphide by iron carbonyl hydrides.



(45)

The Fe_3SO group is of interest as a model for the chemisorption of SO_2 onto metals. The S-O bond length of 147pm corresponds to that in free SO (148pm) and many other S=O double bonds.[91] I.r. and Raman spectra for $Fe_3(CO)_8SO_2$ in the solid state at 300 and 100K have been reported.[92]

The crystal structure of $FeSO_3 2\frac{1}{2}H_2O$ has been reported. The S-O distances in the sulphite ion are 1.527, 1.540 and 1.534Å and the Fe-O distances are in the range 2.037 to 2.284Å.[93] An X-ray study of the anhydrous sulphite $FeSO_3$ shows the iron atom to possess a distorted octahedral coordination involving oxygen atoms from six different SO_3 groups. The SO_3 groups have the point group symmetry C_1 with average dimensions of S-O 1.543Å, O-O 2.415Å and an O-S-O bond angle of 103.04°.[94] Thermal analysis, X-ray, i.r. and Raman data have been reported for a series of hydrates of manganese and zinc sulphites. Under an SO_2 atmosphere the sulphite hydrates could be dehydrated without the simultaneous dissociation to the oxide and sulphur dioxide taking place.[95]

The structure of the HSO_3^- ion has been determined for the first time in a study of the crystal structure of $CsHSO_3$. The sulphur atom shows tetrahedral coordination with three pyramidal S-O bonds and a S-H bond in the other direction. Bond distances (S-O 1.454Å) were found to be similar to those observed in the SO_4^{2-} ion and differed markedly from those observed in the SO_3^{2-} ion.[96] The kinetic behaviour for the decomposition of $M_2S_2O_6$ to M_2SO_4 in the solid state has been studied by following the ν_s mode of S_2O_6. The sodium salt was found to follow first order kinetics but the behaviour of the potassium salt could not be accounted for.[97] The same vibrational mode has also been used to study the kinetic behaviour of $M_2S_2O_8 \rightarrow M_2S_2O_7$ using Raman spectroscopy.[98]

A survey has been conducted of the triboluminescence of 45 common inorganic sulphates.[99] The mixed crystals $KNaSO_4$ and $K_3Na(SO_4)_2$ have been prepared by heating mixtures of K_2SO_4 and Na_2SO_4 in Pt crucibles at 1273K for 2h. Both compounds possess structures built up of tetrahedral SO_4 groups with different types of M-O polyhedra.[100] The crystal structure of the high temperature form of K_2SO_4 has been redetermined. The net entropy change (5.02 J $mol^{-1}K^{-1}$) at the phase transition point (860K) was successfully explained by the configurational change of the SO_4^{2-} groups in the low and high temperature forms.[101] The phase system $NH_4^+||SO_4^{2-}, SO_3NH_2^-, -H_2O$ has been studied and the 40, 60 and 80°C isotherms obtained.[102] An X-ray and neutron diffraction study of $HgSO_4.H_2O$ has shown the mercury atom to be coordinated to one oxygen atom of the SO_4 group and one water molecule forming discrete $HgSO_4.H_2O$ groups. The three dimensional structure is made up by hydrogen bonding and four more distant oxygen atoms from different sulphate groups complete the irregular octahedral coordination of the Hg atom.[103] The formation of anhydrous double sulphates of the type $NaR(SO_4)_2$ has been established for the entire series of rare earth elements. Five different structural types were observed and unit cell parameters were determined.[104] The preparation, i.r. and visible spectra of some new hydrated sulphate complexes of uranium(IV) have been reported. The use of i.r. spectra enabled neutral and basic sulphates to be distinguished.[105]

Changes in the thermodynamic functions ΔG^o, ΔH^o and ΔS^o for the formation of Ag(I) complexes with the general formula $Ag(S_2O_3)_n(SCN_2H_4)_m(SCN)_p^{1-2n-p}$ and the diagrams defining the range of existence of the following complexes : $Ag(S_2O_3)_n(SCN)_p^{1-2n-p}$ and $Ag(SCN_2H_4)_m(SCN)_p^{1-p}$ in an aqueous medium have been reported.[106] The thermal decomposition of $Na_2S_2O_3$ and $K_2S_2O_3$ have been studied using T.G.A. and by recording the i.r. and Raman spectra of products formed when the two salts are heated to various temperatures in air and in N_2. The polysulphides, Na_2S_2 and γ-Na_2S_5 were formed from $Na_2S_2O_3$ and K_2S_3, K_2S_4 and K_2S_5 in the case of $K_2S_2O_3$. In air subsequent oxidation gave the sulphate as the final product. Studies on the decomposition of solid mixtures of $Na_2S_2O_3$ and Na_2SO_3 supported the hypothesis that sulphite is an intermediate in the decomposition.[107] A crystallographic study of $Na_2S_2O_6.2H_2O$ and $Na_2S_2O_6.2D_2O$ has been carried out and the electron distribution in the $S_2O_6^{2-}$ anion determined on the basis of four models.[108] The thermal decomposition of compounds of the type $M_2S_2O_8$ where M=Na, K, Rb or Cs, has been studied. In addition to the detection of isotherms representing the decomposition of peroxydisulphate to pyrosulphate, and the endotherm associated with the fusion of pyrosulphate, the previously unreported phase changes of $Cs_2S_2O_8$ and $K_2S_2O_7$ were observed.[109] The kinetics of the Ag(I)-catalysed decomposition of the peroxydisulphate ion in aqueous solution have been investigated. The reaction rate is not influenced by the addition of Ce^{3+} ions, but is greatly accelerated by acrylamide and/or Cu^{2+} ions, and retarded by acrylonitrile. The formation of oxygen due to the reaction was observed to be completely retarded by the addition of Ce^{3+} ions.[110]

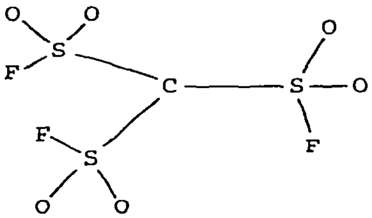
Standard heats of formation of SO_2ClF and PbClF have been determined from heats of hydrolysis and precipitation respectively. The enthalpy of PbClF was found to be more negative than the mean of the corresponding difluoride and dichloride but the opposite was true for SO_2ClF. These result appear to controvert the claim that reaction of PbF_2 with SO_2Cl_2 produces SO_2ClF exclusively.[111] Detailed energy balance studies of the single-collision chemiluminescent reaction of metastable Sr atoms with SOF_2 and SO_2F_2 have provided the following bond dissociation energies (in kJ/mol) FSO-F = 362, SO-F = 337, FSO_2-F = 379 and SO_2-F = 229.[112]

Tris(fluorosulphonyl)methane, $HC(SO_2F)_3$ has been prepared by the following sequence of reactions.

$$H_3C\text{-}CO\text{-}NHPh \xrightarrow[K_2CO_3]{oleum} HC(SO_3{}^-K^+)_3 \xrightarrow{Ba^{2+}} HC(SO_3{}^-B^+_{0.5})_3$$

$$\xrightarrow{H_2SO_4} HC(SO_3H)_3 \xrightarrow{SF_4} HC(SO_2F)_3 \qquad ...(35)$$

Salts with K^+, Rb^+ and Cs^+ as counterions crystallise from water in order of decreasing solubility and crystal structure analysis shows the CS_3 skeleton to be planar (46). The halogen derivatives $XC(SO_2F)_3$ were also synthesised.[113]



(46)

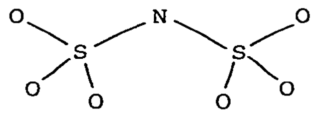
In the reaction of $MeSO_2F$ with hydroxylamine, the products $MeSO_2N(H)OH$, $H_3NOH^+MeSO_3{}^-$ and $H_5N_2{}^+MeSO_3{}^-$ have been observed. $H_2NO\text{-}SiMe_3$ reacts with $MeSO_2F$ to give mainly $H_5N_2{}^+MeSO_3{}^-$ and these results were explained on the basis of consecutive reaction of the intermediate $MeSO_2ONH_2$.[114] The novel salt $NF_4{}^+SO_3F^-$ has been prepared by the reaction of NF_4SbF_6 and $CsSO_3F$ in anhydrous HF solution at -78°C. In HF solution the compound is stable at room temperature but on removal of the solvent the solid slowly decomposes at temperatures above 10°C to produce $FOSO_2F$ and NF_3. The ionic nature of the compound both in the solid state and in HF solution was established by Raman and ^{19}F n.m.r. spectroscopy. Cs_2SO_4 was found to react with anhydrous HF to give $CsSO_3F$ as the major product.[115] $Au(SO_3F)_3$ has been shown to be an excellent fluorosulphate ion acceptor giving the ion $[Au(SO_3F)_4]^-$ and a number of complexes of the ion with $Br_3{}^+$, $Br_5{}^+$, $Br(SO_3F)_2{}^+$ and $I(SO_3F)_2{}^+$ have been prepared.[116]

The synthesis and characterisation of the new hypohalites CF_3SO_3Cl and CF_3SO_3Br by the reaction of CF_3SO_3H with ClF and CF_3SO_3Cl with Br_2 have been described. The assignments of the Raman spectra were aided by the analysis of the spectra of CF_3SO_2F and CF_3SO_2OH which are reported for the first time.[117] Aqueous SO_4F^- has been shown to decompose to form O_2, H_2O_2 and $HSO_5{}^-$. The

H_2O_2 and O_2 products both contain one oxygen atom from solvent and one from the fluoroxysulphate. The HSO_5^- product also contains one oxygen from the solvent in its terminal peroxide position.[118]

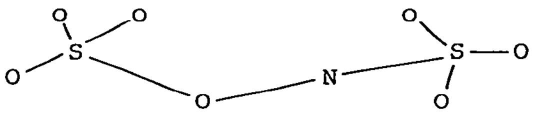
A high pressure mass spectrometric technique has been employed to determine the heats of formation of SO_2Cl^- and $(SO_2)_2Cl^-$. Values obtained were $\Delta H^o{}_f(M) = -151.5$ (SO_2Cl^-) and -234.8 $(SO_2)_2Cl^-$ k cal/mol.[119] The electrochemical fluorination of $ClCH_2SO_2Cl$ has been shown to give CF_4, CF_3Cl, SO_2F_2, SF_6, CF_3SO_2F and $ClCF_2SO_2F$ as the main products.[120] A study of the methane sulphuric acid solvent system shows it to be a weaker acid than H_2SO_4. Acid-base titrations in the acid with strong acids indicate that the bulk of the current is carried by $CH_3SO_3H_2^+$ and $CH_3SO_3^-$ ions.[121].

The crystal structure of $K_3[CH(SO_3)_3].H_2O$ has been determined. The S-C-S angles (ca. 113°) indicate an expansion from tetrahedral stereochemistry and the S-C bond lengths (ca. 1.81Å) are appreciably longer than those found in di- and mono-sulphonate salts.[122] A crystal structure study of $K_3[N(SO_3)_2].H_2O$ has shown the nitridosulphonate ion to have the structure (47) and to possess an N-S bond length (1.609Å) markedly shorter than those observed for $K(NH_2SO_3)$ (1.666Å), $K_2[NH(SO_3)_2]$ (1.674Å), $K_3(N(SO_3)_2).2H_2O$ (1.71Å) and $NH_3^+SO_3^-$ (1.76Å).[123]



(47)

The molecular conformation (48) has been found in the compound $K_2(O_3SONHSO_3)$. In this ion the N-S bond length (1.704Å) is longer than that found in $K_2(NH(SO_3)_2)$ in which both sulphonate groups are bound directly to nitrogen.[124]



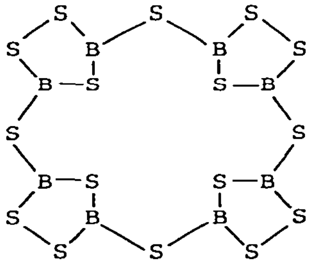
(48)

Electrical conductivity measurements have been reported for solvent ions in trifluoromethanesulphonic acid of a number of simple and complex bases, including univalent and divalent metal trifluoromethanesulphonates.[125] The synthesis of the first trifluoromethanesulphonate esters of the type $CF_3SO_3(CH_2)_nO_3SCF_3$ (n=1,2,3) has been reported. The new compounds are prepared from $Cl(CH_2)_nCl$ by substitutive, electrophilic dehalogenation reaction with CF_3SO_2OX (X=Cl,Br). The extension of this reaction to $HCCl_3$ results in the formation of $HC(O_3SCF_3)_3$ but at 22°C the compound is unstable.[126] The preparation of trifluoromethyl trifluoromethane sulphonate $CF_3OSO_2CF_3$ has been reinvestigated and the results did not agree with earlier work and a revised reaction mechanism was proposed.[127] An e.s.r. study of the generation and structure of aminosulphuryl (sulphamoyl) radicals $R_2NSO_2\cdot$ has been carried out.[128] Extensive ab initio molecular orbital calculations on six sulphonyl radicals XSO_2 (X=H, Me, NH_2, OH, F and Cl), the simplest sulphinic acid HSO_2H and its isomeric sulphone H_2SO_2, the HSO_2^- anion of sulphinic acid, the isomeric anion SO_2H^- and the SO_2H radical have been described.[129] The reactions of hexafluoroacetone with some simple alkyl sulphides as a route for the formation of cyclic sulphuranes has been studied.[130]

6.2.5 Sulphides

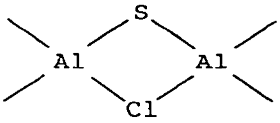
The reaction of sodium and sulphur in liquid ammonia under pressure has been used to prepare Na_2S_3 whose existence has previously been in dispute. For reaction temperatures of 300 to 320K and a pressure of 2000 bar a compound $Na_2S_3.NH_3$ was isolated. Crystal structure studies showed it to contain bent S_3^{2-} polyanions as a characteristic feature. The compound decomposes at 510K.[131]

The extremely hydrolysis sensitive compound $(BS_2)_8$, obtained by fusion of a mixture of B_2S_3 and S_8 in vacuo at 100-300°C has been found to have a planar structure (49) analogous to porphine.[132]



(49)

Raman spectroscopic measurements on a series of LiCl-CsCl and CsCl-$AlCl_3$ melts have shown that dissolved tetrachloroaluminate and sulphide ions at temperatures around 400°C react in a ratio close to 1:1 to form clear solutions sometimes with gel precipitates. A glassy compound $(CsAlSCl_2)_\infty$ was prepared indicating the possible existence of a homologous series of chain-like ions $(Al_nS_{n-1}Cl_{2n+2})^{n-}$ with n≥3 and polymeric $(AlSCl_2)_n^{n-}$ for large values of n. These ions are characterized by a strong polarized Raman band near 325 cm^{-1} which was assigned to $AlCl_2$-S-$AlCl_2$ units. In neutral and acidic chloroaluminate melts the ions dissociate, forming solid AlSCl and dissolved species such as $(Al_nS_{n-1}Cl_{2n+2-m})^{(n-m)-}$. The solutions gave a Raman signal assignable to the doubly bridged units (50) within the ions.[133]



(50)

The crystal structure of the new compound In_5S_4 shows corner sharing In_2S_3 tetrahedra with one of the In atoms at the centre of the tetrahedron and the other In atom as the common corner of four tetrahedra.[134]

The new ternary compounds $Rb_6In_2S_6$ and $Rb_4In_2S_5$ have been prepared by a disproportionation reaction starting from elementary Rb and indium monosulphide. The basic unit of both compounds was the quasi-molecular $[In_2S_6]^{6-}$ group which is isoelectronic with the gas phase molecule In_2Cl_6. The group consists of two edge sharing InS_4 tetrahedra.[135]

An excitation spectrum of the triplet-singlet band system of CS_2 vapour has been measured in the range 365-378nm using a tunable laser source.[136] Carbon disulphide has been shown to react with trans-$[(PMe_3)_2Pd(CH_3)I]$ by insertion into the Pd-CH_3 bond to form the dithioacetate complex trans-$[(PMe_3)_2Pd(S_2CCH_3)I]$. In contrast, insertion of CS_2 into one of the Pd-PMe_3 bonds occurs in the reaction of CS_2 with trans-$[(PMe_3)_2Pd(COCH_3)I]$ and $[(PMe_3)_3PdR]BPh_4$ (R=CH_3, $COCH_3$, C_6H_5) to give the complexes $[(PMe_3)(S_2CPMe_3)Pd(COCH_3)I]$ and $[(PMe_3)_2Pd(S_2CPMe_3)R]BPh_4$, being the first chelate complexes containing the zwitter-ion moiety $^-S_2CP^+Me_3$.[137] $C_5H_5(PMe_3)Co-(h^2-CS_2)$

has been shown to react with $C_5H_5(PMe_3)Co(\mu\text{-}CO)_2Mn(CO)C_5H_4Me$, not to form the expected $[C_5H_5(PMe_3)Co]_2CS_2$ but to give the trinuclear complex $(C_5H_5Co)_3(S)(CS)$. X-ray structure analysis shows the presence of a novel triply bridging thiocarbonyl ligand, in which the C-S distance of about 170pm is near to that expected for a C-S single bond.[138]

Knudsen effusion studies of the decomposition of Sn_2S_3 have shown that the compound decomposes according to the reaction:

$$Sn_2S_3(s) \longrightarrow 2SnS(s) + \tfrac{1}{2}S_2(g) \qquad \ldots(36)$$

The standard heat of formation and absolute entropy of Sn_2S_3 were found to be -254.5 kJ/mol and 170.5 J/K.mol respectively.[139]

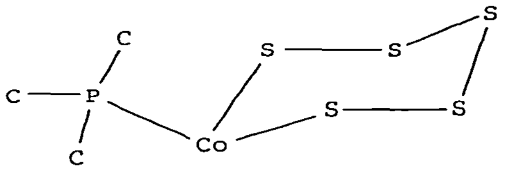
The vibrational spectra of the cage compounds P_4S_3, P_4Se_3 and As_4Se_3 have been studied in both the solid and molten states. The spectrum of crystalline As_4Se_3, which decomposes during melting was also investigated.[140] The gas phase i.r., and liquid phase Raman spectra of $(CF_3)_2EXCH_3$ (E=P, As; X=Se, S) have been investigated and the spectra assigned on the basis of C_s local symmetry.[141] Crystals of $Ta(PS_4|S_2)$ have been grown by vapour transport and a structure determination showed the presence of TaS_{12} units linked by tetrahedral PS_4 units to form endless chains.[142] A new method; the reaction of P_4S_3 with PI_3 in CS_2 solution, has been used to prepare $\beta\text{-}P_4S_3I_2$. Attempts to prepare $As_4S_3I_2$ by classical methods failed : the reaction of As_4S_3 with AsI_3 led to the formation of As_4S_4 whilst As_2S_3 and As_4S_4 reacted with AsI_3 to give AsSI.[143]

The reaction of SnS and SbI_3 mixtures has been used to prepare the new compound $Sn_2SbS_2I_3$; the structure of which is composed of parallel ribbons of $(Sn_2S_2I_2)_n$ linked together by coordination polyhedra of antimony.[144]

The existence of the thiovanadyl ion $V{=}S^{2+}$ has been established by reaction of V=O(salen) and V=O(acen) with B_2S_3. Spectra indicate that the V=S stretching vibration appears in the $550cm^{-1}$ region and its stretching force constant is substantially less than that of the vanadyl analogues.[145,146] Single crystals of several V_5S_8 and V_2S_3 compounds have been grown by chemical transport.

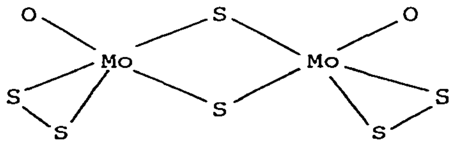
Electrical conductivity measurements showed metallic behaviour without any dependence on compositional variation.[147] The transition metal carbonyls $M(CO)_6$ M=Cr, Mo, W, and $M_3(CO)_{12}$ M=Ru, Os but not $Fe(CO)_5$ have been found to be active homogeneous catalysts for the water gas shift reaction in the presence of a large excess of sulphides generated by the dissociation of Na_2S in aqueous methanol.[148] The EXAFS technique has been used to study short range order in non-crystalline iron(III) sulphide. The average iron sulphur distance was 2.285Å and the presence of Fe-Fe interactions was inferred.[149] Magnetic properties of the solid solution series $CsGa_{1-x}Fe_xS_2$ have been measured.[150]

Two preparations of $C_5H_5(PMe_3)CoS_5$ have been described and its crystal structure determined. The chair form of the six membered CoS_5 ring (51) corresponds to that of the compounds $(C_5H_5)_2TiS_5$ and $(C_5H_5)_2VS_5$.[151]



(51)

The equilibrium vaporization behaviour of twelve compounds of the type MeX (Me=Zn, Cd, Hg and X=O, S, Se, Te have been studied by means of high temperature mass spectrometry.[152] The unexpected chemical transport of TaS_2 with sulphur, which proceeds to the high or low temperature zones depending on temperature and pressure has been observed. It was concluded that the transport reaction proceeds via the formation of the gaseous molecule TaS_5 which has only a small vapour pressure.[153] The crystal structure of $(NH_4)_2[(S_2)_2Mo(S_2)_2Mo(S_2)_2].2H_2O$ has been shown to contain two crystallographically independent $[Mo_2(S_2)_6]^{2-}$ ions.[154] The reactions of the two non-equivalent S_2^{2-} ligands of the previous compound have been shown to be significantly different; the final product of the reaction with OH^- in aqueous solution being $[Mo_2O_2S_2(S_2)_2]^{2-}$ (52), which could be isolated in high yield.[155]



(52)

The chemical transport method has been used to obtain layer monocrystals of MoS_2 using Br_2, $GeBr_2$ and $SnBr_2$ as transporting agents.[156] Lead-molybdenum chalcogenides of the type $PbMo_6(S_{1-x}Se_x)$ have been synthesized from the elements across the entire solid solution range from $PbMo_6S_8$ to $PbMo_6Se_8$. Superconductivity, magnetic susceptibility and crystal structure were studied.[157] CdS has been prepared by heating an aqueous solution of thiourea and cadmium chloride, a reaction which was thought to involve the intermediate $CdCl_2SC(NH_2)_2$.[158] The ternary sulphides $Na_2Re_3S_6$ and $K_2Re_3S_6$ have been synthesized by the reaction of alkali carbonates with Re at 800°C in a stream of H_2S. Structural studies showed the presence of the previously unknown Re_6S_8 clusters.[159] Structural studies have also been carried out on the following binary sulphides, Th_2S_5, U_2S_5, $ThSe_3$;[160] $MoS_{2-x}Se_x$,[161] NbS_2,[162] HfOS,[163] and Ni_3S_2.[164] Crystal structure data have also been published for a large number of ternary sulphides and these are collected in Table 1.

Table 1 Crystal Structure Determinations.

Compound	Reference	Compound	Reference
$A_xMo_4S_6$	165	$BaTiS_3$	172
$A_2Mo_{15}S_{20}$	165	$HgBi_2S_4$	173
$Cs_2Zn_3S_4$, $Rb_2Zn_3S_4$	166	$BaSn_2S_3$	174
KCu_4S_3	167	Tl_2PbGeS_4	175
NH_4CuS_4	168	$Ba_2ZnGe_2S_6O$	176
$M^ICu_4S_3$	169	$BaHgSnS_4$	177
$M^ICu_4Se_3$	169	$BaZnSnS_4$, $BaMnSnS_4$	178
$CsCu_4S_3$, $CsCu_3S_2$	170	$BaCdGeS_4$	179
$Tl_2Fe_3S_4$	171	$BaCdSnS_4$	180
		$Ti\text{-}P_2S_6$	181

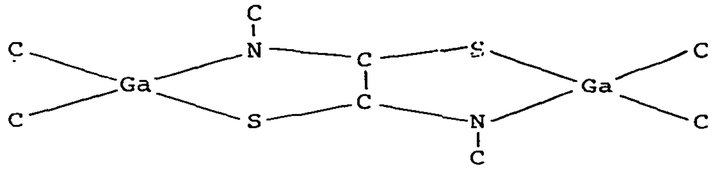
Several phase systems involving sulphides have been investigated and these are collected in Table 2.

Table 2. Phase Systems.

System	Reference	System	Reference
$Fe_{1-x}S$-PbS-ZnS	182	As-S,As-Se	187
$CuCrS_2$-MS_2	183	As_2S_3-InSe	188
Na_2S-P_4S_{10}-GeS_2	184	Ag_2S-Na_2S	189
Ag-Bi-S	185	CoS-In_2S_3	190
Ag-As-S	186	In_2S_3-NiS	190

6.2.6 Other sulphur containing compounds

Monomeric bis(dimethylgallium)N,N'-dimethyldithiooxamide has been prepared by the reaction of $GaMe_3$ and $[HN(Me)C(=S)-]_2$ in a 2:1 molar ratio. Two configurational isomers are formed both of which consist of two fused five-membered rings (53) with an almost planar structure.[191]



(53)

A series of papers have described studies carried out on trithioallophanic acid, H_2N-CS-NH-CS(SH) which may be prepared by reaction of a suspension of $K[S_2C$-NH-CS-$NH_2]$ in diethylether and a solution of HCl in Et_2O at -15°C.[192] The alkali-metal salts were prepared by reaction of H_2S with the corresponding dithiocarbimate.[193] Esters and metal (I,II) salts were also prepared.[194,195]

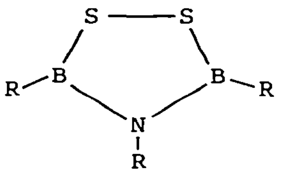
The oxidation of hexathioethanes to tetrathioethene radical cations using $AlCl_3/H_2CCl_2$, $NOBF_4$ or I_2 has been described.[196] The crystal structure of O-methyl-, S-methyl- and potassium thiocarbazate have been determined. They crystallize in the form of hydrogen-bridged dimers with the imino nitrogen as the donor atom, through NH...N, NH...O and NH...S respectively.[197]

The reaction of $(MePNMe_4)$ with sulphur has been shown to yield

$(MePNMe_4)S_3$. Its crystal structure shows a completely unsymmetrical molecule which does not undergo ring conversion in solution.[198] 2,5-Diaza-1,6-dioxa-6a-thiapentalene and its Se and Te analogues have been studied by ESCA in the gas phase.[199]

A new microwave spectrum has been detected during flow pyrolysis experiments involving sulphur dicyanide vapour. Analysis of the spectrum indicates that $S(CN)_2$ dimerises to NCNCS at 850°C.[200]

The crystal and molecular structures of (54), (55) and (56) have been determined. A planar ring structure was found for (54) and (55) and therefore these heterocycles may be described as five membered 6π-electron systems. In contrast (56) forms a tricyclic system and is present as a dimer.[201]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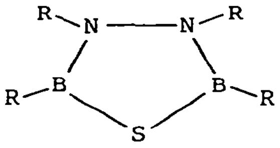
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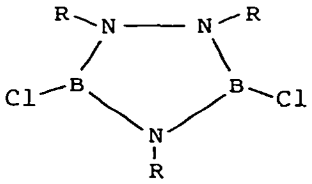

(56)

6.3 SELENIUM

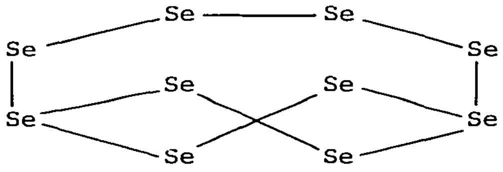
6.3.1 The Element

A review of liquid metals and liquid semiconductors has included the properties of covalent liquid selenium.[202] Elemental selenium has been found to catalyze reductions with the components of water gas (CO/H_2O). Nitroarenes are transformed in the presence of Se and triethylamine to arylamines and it was thought that H_2Se was the reaction species.[203]

The crystal structure of a new allotrope of cyclooctaselenium, γ-monoclinic selenium has been determined. The allotrope crystallizes from a solution of dipiperidinotetraselane in CS_2 and contains two crown shaped Se_8 rings in the asymmetric unit with bond lengths, bond angles and dihedral angles in the ranges 2.326-2.344Å, 103.3-109.1° and 96.5-107.2°. The average values were found to be the same as in α and β monoclinic selenium but there are more short contacts between the rings in the γ form.[204]

The reactions of black selenium powder with morpholine or piperidine in the presence of Pb_2O_4 have been studied. In the case of piperidine the tetraselane was obtained whereas with morpholine the di-, tri- and tetraselanes could be prepared. In the two tetraselanes the N-Se-Se-Se-Se-N chains occur in the trans-trans form,[205] which was also observed in the corresponding dimorpholinotetrasulphane.[206] In the triselane the N-Se-Se-Se-N chains occur in the trans form whilst in the diselane the N-Se-Se-N chain has a Se-Se bond of 2.346Å.[207]

Preparative routes for the compounds $Se_{10}AsF_6)_2$, $Se_{10}(AlCl_4)_2$ and $Se_{10}(SbF_6)_2$ have been described and the crystal structure of $Se_{10}(SbF_6)_2$ determined. The Se_{10}^{2+} cation (57) consists of a six-membered boat-shaped ring linked across the middle by a chain of four selenium atoms. The Se-Se bonds vary greatly in length



(57)

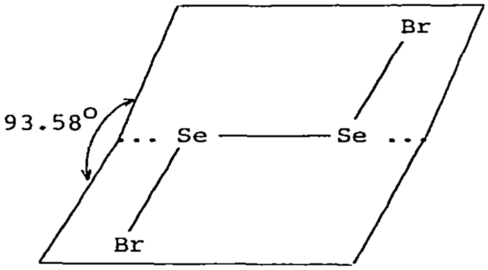
from 2.24 to 2.44Å.[208]

Aqueous polyselenide (or polytelluride) solutions have been found to react with $B_9H_{13}S(CH_3)_2$ to form the $B_9H_{12}X^-$ (X=Se or Te) anions which were isolated as the tetramethylammonium salts. Oxidation of these salts with iodine produced the $B_9H_{11}X$ molecules in benzene, and pyrolysis of $B_9H_{11}Se$ gave mixtures of B_9H_9Se and $B_{11}H_{11}Se$.[209]

6.3.2 Bonds to halogens

A recent study of the thermodynamic data of SeF_4, $SeOF_2$ and SeF_6 has been critically examined and recalculations have been made using more reliable information.[210]

The crystal structure of $SeOCl_2.C_4H_8O_2$ has been reported. The compound has primary pyramidal coordination with Se-O 1.572 and Se-Cl 2.235 and 2.203Å, and the packing of the compound involves infinite layers of $SeOCl_2$ bridged by dioxan molecules and further cross linked by Se-O...Se interactions.[211] The characterization of the compound CF_3SeX (X=H, Cl, Br, $CNCF_3$, $SeCF_3$) has been completed by the reporting of mpt, bpt, enthalpies of vaporization and entropies of vaporization.[212] The structure of CuHgSeCl has been shown to comprise a three dimensional network of Se-HglSe chains connected to Se_2Cl_2 distorted tetrahedra in which copper atoms occupy an off-centre position.[213] A single crystal of β-SeBr has been grown from the melt in a glass capillary in a temperature gradient of 25 to $-13^{o}C$ and its structure determined at $-80^{o}C$. The crystals contain Br-Se-Se-Br molecules (58) with a Se-Se distance of 2.241Å which is significantly shorter than that found in elemental Se (2.373 or 2.318Å).[214]



(58)

The crystal structure of $SeBr_3SbF_6$ shows the cation to have essentially C_{3v} symmetry with an average Se-Br distance of 2.269Å and an average bond angle Br-Se-Br of 100.9Å. The crystal structure of $TeBr_3AsF_6$ was also determined.[215] The ternary system Se-Te-I has been investigated.

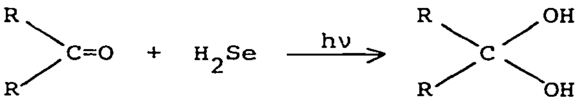
6.3.3 Bonds to Oxygen

The crystal structure of monoclinic Se_2O_5 has been determined. The structure consists of zig-zag chains $[-Se(O)-O-Se(O)_2-O-]_n$ with alternating Se(IV) and Se(VI) atoms. Each Se atom is coordinated tetrahedrally, Se(VI) by four O atoms, Se(IV) by three O atoms and a lone electron pair.[217]

Phase equilibria in the system Bi_2O_3-SeO_2-H_2O at $100^{o}C$ have been studied and the crystallization fields and conditions for formation of $Bi(SeO_3)_3$ and $Bi(SeO_3)_3H_2SeO_3$ determined.[218] The i.r. and Raman spectra of the salts $M^+CF_3SeO_2^-$ ($M=NH_4^+$, K^+, Rb^+) and a normal coordinate analysis of the $CF_3SeO_2^-$ anion has been reported.[219] A crystal structure study has shown that in the compound $(NH_4)_2Ni(SeO_4)_2.6H_2O$, the SeO_4^{2-} ion is regular as judged by the average bond angle of 109.5^{o} but the Se-O bond lengths show the same pattern as in the corresponding chromate in that one Se-O bond length is shorter (1.622Å) than the other three (1.642Å).[220] The preparation and structures of the following three types of double selenates, $M^{I}Tl^{III}(SeO_4)_2$, $M_3^{I}Tl^{III}(SeO_4)_3$ and $M_5^{I}Tl^{III}(SeO_4)_4$ have been described.[221]

6.3.4 Selenides

A new application of H_2Se in organic synthesis is envisaged in the photoreduction of carbonyl compounds. Unlike most other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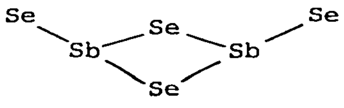
reducing agents, H_2Se does not lead to 1,2-diols, but instead to monoalcohols.[222]

A new modification of Cs_2Se has been synthesized from the elements in the mole ratio 2:1 in liquid NH_3 at 300°C and 2000bar. Structural studies showed the selenium lattice to be diamond-like with 4Cs tetrahedra (16 atoms) filling the remaining four tetrahedral holes of the unit cell.[223] Similar reaction conditions have been used to synthesize Cs_2Se_3, Cs_2S_3, Rb_2Se_3 and Rb_2S_3. These compounds all adopt the K_2S_3 type of structure and contain bent polyanions of the type X_3^{2-} (X=S, Se).[224] The action of Br_2 on the Ge-Ge bond in the ternary selenide $Na_6Ge_2Se_6$ in methanolic solution has been shown to lead to the formation of Na_3GeSe_3Br. An identical reaction was also observed for the analogous ternary sulphide.[225] A crystal structure determination of β' Ag_8GeSe_6 has shown the Ge atoms to be in tetrahedral coordination by selenium atoms. Two of the Ag atoms are tetrahedrally coordinated by Se whilst three other silver atoms are surrounded by three Se atoms in an almost planar triangular arrangement. The Se atoms are in 4, 5, 6 and 8-fold coordination.[226]

Selenium transfer between PR_3Se and PR_3 [R_3=$MePh_2$ or $Ph_2(CH_2PPh_2)$] in solution has been found to be rapid (on the n.m.r. time scale) and a bimolecular process is thought to take place.[227] $MPSe_3$ (M=Mn, Fe) has been shown to react with pyridine molecules to form intercalation complexes.[228] The oxidation of di- and tri-tertiary arsanes, $A[-R-AsMe_2]_2$ and $B[-R-AsMe_2]_3$ by elementary selenium or sulphur has been shown to result in the formation of the selenides and sulphides $A[-R-As(X)Me_2]_2$ and $B[-R-As(X)Me_2]_3$ (X=S, Se) respectively.[229]

Three different anionic SbSe groups (59)-(61), the first selenoantimonate(III) ions, have been shown to be present in $Ba_4Sb_4Se_{11}$.



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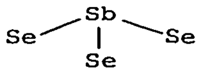

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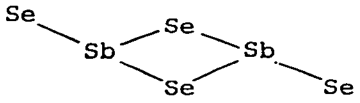


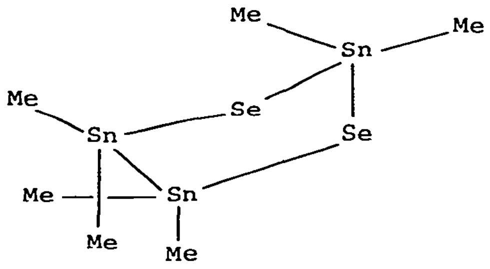
(61)

The formal linkage of pyramids (60) to give dinuclear entities (59) and (61) was not previously known.[230,231] Structural information has also been published on the following selenides $Tl_2Mo_6Se_6$,[232] $InMo_6Se_8$ and $In_2Mo_{15}Se_{19}$,[233] $BaBiSe_3$ and $BaSbTe_3$,[234] $InMo_3Se_3$, $InMo_3Te_3$, $TlMo_3Se_3$ and $TlMo_3Te_3$,[235] $Na_4SnSe_4.16H_2O$,[236] $Cu_3Nb(S_xSe_{1-x})_4$, $Cu_3Nb(Se_xTe_{1-x})_4$, $Cu_3Ta(S_xSe_{1-x})_4$ and $Cu_3Ta(Se_xTe_{1-x})_4$.[237]

The following phase systems have been studied HgSe-GeSe-$GeSe_2$,[238] HgSe-Cr_2Se_3,[239] $RbSbSe_2$-Sb_2Se_3,[240] Cr_sSe_3-Cu_2Se-Se[241] and $CuCr_2Se_4$-$ZnCr_2Se_4$.[242]

6.3.5 Other compounds containing selenides

The crystal structure of $Se_2Sn_3(CH_3)_6$ has been determined. The five membered ring (62) has envelope conformation with one axial, one equatorial and four isoclinic methyl substituents.[243]



(62)

E.s.r. spectra assigned to the σ^* selenuranyl radicals $R_2Se^{\bullet}$-X have been detected in solution during the photochemical generation of X$\cdot$ ($CF_3S\cdot$, R'C(O)S$\cdot$, $Me_3CO\cdot$ or $Me_3SiO\cdot$) in the presence of dialkyl or alkylarylselenides.[244] The sulphur selenium chains in the dianions, selenotetrathionate and diselenotetrathionate have been shown to be unbranched and non-planar in crystal structure determinations on the compounds $K_2SeS_3O_6.H_2O$;[245] and $[Co(en)_2Cl_2]_2Se_2S_2O_6.H_2O$[246] respectively. The crystal structure of $[Co(en)_2Cl_2]_2SeS_3O_6.H_2O$ was also determined.[245] The structure of the selenotrithionate dianion was determined from a study of $K_2SeS_2O_6$.[247]

The compound $SeCF_2$ has been produced by the reaction of AlI_3 with $Hg(SeCF_3)_2$ in octamethylcyclotetrasiloxane, and the Cs, Tl, Me_4N and Ag compounds prepared. In sunlight $SeCF_2$ dissolved in $CFCl_3$ undergoes dimerization to form the cyclic compound 2,2,4,4-tetrafluoro-1,3-diselenetane.[248] The reaction of 1,1,1-tris(diiadoarsinomethyl)ethane with NaSeH has been shown to give the new cage compound $CH_3C(CH_2As)_3Se_2$.[249] I.r. spectra have been reported for tetramethylselenoureadiiodide, the perdeuterated and the ^{15}N substituted compounds.[250] The mass spectra of benzene seleninic acid and of diphenyl diselenide have been examined and a full analysis reported.[251] Treatment of $B_9H_{12}S^-$ with potassium polyselenide has been shown to form B_9H_9SSe, and $B_9H_9S_2$ when the polyselenide was present in only small amounts.[252]

6.4 TELLURIUM

6.4.1 The Element

The reaction of elemental tellurium with C_2F_6 has been shown to give $(CF_3)_2Te$ which was also identified in small amounts from the reaction of C_2F_6 with $TeCl_4$ or $TeBr_4$.[253] The reaction of tellurium with various modifications of phosphorus have been studied by DTA, X-ray diffraction and microstructural methods.[254]

6.4.2 Bonds to Halogens

Preparative methods based on the fluorination of orthotelluric acid with HF and on the hydrolysis of pentafluorotellurates(VI) have led to the isolation of stereoisomers of the tetrafluorotellurates(VI), $(HO)_2TeF_4$, $HOTeF_4OMe$, and $(MeO)_2TeF_4$.[255] The compounds $I(OTeF_5)_5$ and $O{=}I(OTeF_5)_3$ have been characterized and the mixed substituted compounds $F_xI(OTeF_5)_{5-x}$ and $F_xI(OSeF_5)_{5-x}$

shown to exist.[256] $TiCl_4$ has been shown to react with $HOTeF_5$ to give $TiCl_3OTeF_5$ which decomposes via $TiCl_2(OTeF_5)_2$ and $TiCl(OTeF_5)_3$ to $Ti(OTeF_5)_4$.[257]

The reaction of TeO_2 with concentrated HCl gives a solution from which $(Ph_4As)_2TeCl_6$ may be precipitated. Mössbauer and TGA studies were reported for the compound.[258] Crystal structures have been reported for the compounds $C_{12}H_8OTeCl_2$,[259] $(C_6H_5)_3TeCl$,[260] $(4\text{-}EtOPh)TeCl_3$, $(4\text{-}EtOPh)TeBr_3$ and $(4\text{-}MeOPh)TeI_3$,[261] and $[(C_6H_5)_4P]_2Te_2Br_{10}$.[262]

Crystals of $H_2TeI_6.8H_2O$ have been obtained in incident light from solutions of tellurium iodides in concentrated hydriodic acid on cooling. Under normal conditions the phase is stable only in contact with its concentrated solution and decomposes to HI, H_2O and TeI_4 under vacuum. Structurally the compound may be described as $(H_7O_3^+)_2[TeI_6]^{2-}.2H_2O$.[263] The following phase systems have been studied, $K_2TeBr_6\text{-}Rb_2TeBr_6\text{-}HBr\text{-}H_2O$,[264] Te-O-I,[265] $TeCl_4\text{-}SbCl_5$[266] and $TeCl_4\text{-}PCl_5$.[267]

6.4.3 Bonds to Oxygen

An ESCA study of the mixed oxygen compounds Te_2O_5, Te_4O_9 and $H_2Te_2O_6$ has shown no evidence for two oxidation states since the splitting of the peaks associated with Te(IV) and Te(VI) is insufficient.[268] The conversion (in 27-40% yield) of some phenyl hydrazines to diaryltellurium dichlorides by TeO_2 in refluxing acetic acid containing LiCl has been studied.[269] The crystal structure of Tl_2TeO_3 has been determined and the influence of each cations lone-pair on the coordination of the Te(IV) and Tl(I) atoms described.[270] A crystal structure study of basic tellurium nitrate has led to the reformation of the compound as $(Te_2O_4H)^+NO_3^-$ with a basic structural element consisting of a charged two dimensional puckered $Te_2O_4H^+$ network with discrete NO_3^- anions.[271] Crystal structures have also been described for $NH_4TeO_3(OH)$,[272] $Te(OH)_6.Na_2SO_4$,[273] $Te(OH)_6.Na_2HPO_4.NaH_2PO_4$,[274] and $Te(OH)_6.K_2SO_4$.[275]

The hydrogen reduction of α and β Te_2MoO_7 has been studied.[276] The vibrational spectra of the spinel phases Co_5TeO_8, $Co_3Zn_2TeO_8$, $CoZn_4TeO_8$, $NiZn_4TeO_8$ and $N_2Zn_3TeO_8$ have been recorded and discussed. Full assignments of the TeO_6 internal vibrations in these lattices were proposed.[277] The crystal data of $CdTeMoO_6$ and the new phase $MgTeMoO_6$ have been determined from X-ray powder diffraction patterns.[278] The following phase systems have been studied, TeO_2-MoO_3-V_2O_5,[279] TeO_2-Cu_2O,[280] TeO_2-Nb_2O_5,[281] TeO_2-Ta_2O_5,[282] and TeO_2-M_2O_3 (M=Er or Y).[283]

6.4.4 Tellurides

Two reduction reactions of H_2Te with organic compounds have been described. The reduction of carbonyl compounds with H_2Te generated *in situ* leads conveniently and very mildly to alcohols.

$$3RR^1CO + Al_2Te_3 + 6H_2O \longrightarrow 3RR^1CHOH + 3Te + 2Al(OH)_3 \quad \text{...(38)}$$

This method offers particular advantages in the production of deuterated alcohols from Al_2Te_3 and D_2O.[284] Aromatic nitrogen compounds may also be reduced by the same type of reaction.[285]

$$\text{Aryl } NO_2 + Al_2Te_3 + 4H_2O \longrightarrow \text{Aryl } NH_2 + 3Te + 2Al(OH)_3 \quad \text{...(39)}$$

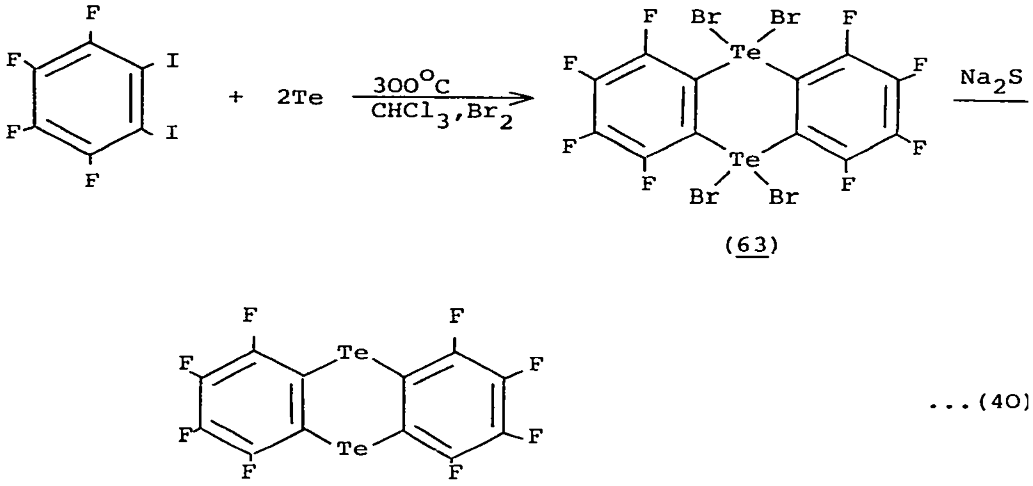
Reaction of tellurium with Cs or Rb in liquid ammonia under hypercritical conditions at 500K and 1000 bar has been shown to give the first polytellurides of Rb and Cs, Rb_2Te_3 and Cs_2Te_3. The former crystallizes with the K_2Te_3 type structure, the latter with the K_2S_3 type structure and both contain bent Te_3^{2-} polyanions.[286] Tellurium vapour pressures above Cr-Te alloys have been measured in the range of the NiAs-type structure between 800 and 1300K.[287] The oxidation of $MoTe_2$ in air at temperatures above 250°C has been studied. An earlier proposed novel composition $MoTe_{1.8}O_{4.9}$ was shown to be a mixture of Te_2MoO_7, $TeMo_5O_{16}$ and Te.[288] The ternary telluride Ag_8SnTe_6 has been synthesized by different methods and may show silver ion conductivity.[289] The phase systems, I-In-Te,[290] Cd-Pb-Te,[291] and Au-Ag-Te[292] have been investigated.

6.4.5 Other compounds containing Tellurium

The reaction of Na_2Te and ${}^tBu_2PCl$, together with the reaction shown below, have been shown to give the first tellurium compound to contain only R_2P substituents.[293]

$$2\,{}^tBu_2P\text{-}Te\text{-}SiMe_3 \longrightarrow (Me_3Si)_2Te + Te({}^tBu_2P)_2 \quad \text{...(40)}$$

The reaction of tetrafluoro-1,2-diidobenzene with Te has been shown to yield an oil which on treatment with bromine yields (63). The latter is reduced by Na_2S to perfluorotelluranthrene (64), the crystal structure of which was determined.[294]



(63)

(64)

...(40)

The crystal structure of $[O(CH_2CH_2)_2N]_3PTe$,[295] tris(ethylenethiourea-S)tellurium(II) perchlorate and of two modifications of tris(trimethylenethiourea-S)tellurium perchlorate[296] have been determined.

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