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Chapter 6

ELEMENTS OF GROUP 6

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6.1 OXYGEN

Well resolved solid-state oxygen-17 n.m.r. spectra of a wide variety of oxides and oxyanions have been observed by means of high-field (11.7T) magic angle and variable angle sample spinning. A very wide range of ^{17}O quadrupole constants (~0 to >5MHz), chemical shift anisotropies (~0 to >300ppm) and line widths (~0.3 to >40ppm), in addition to the expected overall 1200ppm isotropic chemical shift range are to be expected in solid state ^{17}O n.m.r. which will give a rich variety of spectral information. As an aid for the prediction of the types of results to be obtained in future studies the authors presented empirical relationships between quadrupole coupling constants and an average percent ionic character for several oxides and oxyanions. This paper represents an initial effort in delineating the types of systems amenable to investigation by ^{17}O n.m.r.[1] ^{17}Oxygen n.m.r. measurements have also been made on the carbonyl groups of six organometallic carbonyl complexes. Values of the ^{17}O electric quadrupole-coupling constants showed structural variation and so should be useful in the assignment of ^{17}O resonances.[2]

Aqueous dispersions of CdS loaded with noble metal oxides have been shown to evolve oxygen under illumination with visible light in the presence of $PtCl_6^{2-}$ as a scavenger for conduction band electrons. The catalytic activity of Rh_2O_3 was found to be superior to that of RuO_2 in promoting water oxidation under alkaline conditions. The presence of the redox catalyst was essential for oxygen generation.[3]

Reactions of glowing filaments of platinum and iridium with oxygen have confirmed the usefulness of this method for the determination of the formulae of the volatile compounds PtO_2 and IrO_3 under equilibrium conditions.[4]

Interest in the reactions of coordination compounds with oxygen continues, particularly with respect to complexes of manganese with the composition $MnLX_2$ where L = tertiary phosphine and X is an anion. The complexes $MnBr_2PMe_3$, $MnBr_2PEt_3$ and $MnBr_2PPhMe_2$ (prepared under anhydrous conditions with the elimination of all free phosphine) when exposed to dioxygenation/evacuation cycles in a specially designed infrared cell have been shown to interact with O_2. However, the extent of the reversibility of the interaction with dioxygen is markedly dependent upon the nature of the tertiary phosphine ligand employed. All of the solid state complexes also showed an irreversible decay in the presence of oxygen to a phosphine oxide complex at ambient temperature.[5] The complex $(C_6H_5CH_2)_2Mn.C_4H_8O_2$ has been shown to react with oxygen to form an unstable deep violet compound which changes to a stable insoluble yellow peroxide with the formula $C_6H_5CH_2MnO\text{-}OMnCH_2C_6H_5$. With excess oxygen a polynuclear complex of Mn(III) is formed with the composition $Mn_4O_4(OH)_4(OCHC_6H_5)_2$.[6]

Poly(2-methyl-1-vinylimidazole), molecular weight $>10^4$, forms a stable five coordinate complex with heme in aqueous ethylene glycol solution. This complex has been shown to give an oxygen adduct at -30°C whereas an irreversible oxidation was observed for low molecular weight-heme complexes with 2-methyl imidazoles. Oxygenation was also observed for heme complexes with copolymers of 2-methyl-1-vinylimidazole but not for those with ionic copolymers.[7] Calorimetric measurements have been carried out on the heat evolved when oxygen is bubbled into KNO_3 aqueous solutions of $Co(NO_3)_2$, tetraethylenepenta-amine (tetren) and HCl or when a $Co(NO_3)_2$ solution is added to a KNO_3 aqueous solution of tetren and HCl under anaerobic or aerobic conditions. The thermodynamic data for the binding of oxygen to complexes of Co(II) with tetren and other linear polyamines were compared and discussed.[8] The reaction of oxygen with the three coordinated copper(I) complex $Cu(Bpy2)^+$ has been shown to yield a binuclear oxocopper(II) species having a parallel-planar dihydroxo bridged dimeric structure.[9]

Emissions from excited SO_2 in its singlet and triplet states have been observed in gas-phase chemiluminescent reactions of ozone with a number of sulphur compounds. Disulphides were found to be more chemiluminescent than monosulphides and the absence of chemiluminescence from HCHO* in the reactions of O_3 with allylsulphide and disulphide was taken as evidence that the attack of O_3 is on the C-S bond in organic sulphides.[10]

The reaction chemistry for the combination of superoxide ion with carbon dioxide in aprotic media has been studied. The overall stoichiometry observed was one $O_2^{-}\cdot$ per CO_2 to give $C_2O_6^{2-}$ and O_2.

$$CO_2 + O_2^{-}\cdot \rightarrow \tfrac{1}{2}C_2O_6^{2-} + \tfrac{1}{2}O_2 \qquad \ldots(1)$$

The primary step appears to be a nucleophilic addition of $O_2^{-}\cdot$ to CO_2 to form the anion radical $CO_4^{-}\cdot$. The apparent configuration of the $C_2O_6^{2-}$ group is $OC(O)OC(O)OO^{2-}$ on the basis of the vibrational spectroscopy and the hydrolysis products of the isolated reaction product $(Me_4N)_2C_2O_6$.[11] Rate constants for the reaction of superoxide and dithionite ions with a number of oxidants have been reported.[12] The kinetics and mechanism of the reactions of aqueous superoxide ion and several Co(III) amine complexes and ferrocenium ion have been studied. The initial and rate-limiting step (and the only step for the ferrocenium ion reaction) is outer-sphere electron transfer from the superoxide ion to the metal complex. Dioxygen has a marked effect upon the Co(III) reactions, resulting in second order rate constants that are greater by a factor of 2 under anaerobic conditions than under aerobic. This effect was explained by the competing reactions of the Co(II) amine complexes produced in the electron transfer step with O_2 or O_2^{-}.[13]

Use of a Fourier transform ion cyclotron resonance spectrometer has enabled the generation of the long-lived $H_2O^{-}\cdot$ ion from the reaction of $O^{-}\cdot$ with any of the aliphatic amines, methylamine, ethylamine or dimethylamine to be observed. The generation of $HDO^{\overline{\cdot}}$ by the reaction of $O^{\overline{\cdot}}$ with CD_3NH_2 showed that one of the hydrogen atoms in $H_2O^{\overline{\cdot}}$ originate from the methyl group and the other from the amino group and that both types of hydrogen atoms in the substrate are essential for the formation of $H_2O^{\overline{\cdot}}$. Reaction of $H_2O^{\overline{\cdot}}$ with formaldehyde gave only OH^{-} as an observed reaction product and this reaction (equation 2) suggests that

$$H_2O^{\overline{\cdot}} \ + \ CH_2O \rightarrow OH^{-} \ + \ \cdot CH_2OH \qquad \ldots(2)$$

the $H_2O^{\overline{\cdot}}$ ion can best be described as a hydroxide ion to which a hydrogen atom is attached.[14]

A study of the infrared spectra of Nafion membranes in twenty different cationic forms has been carried out in order to characterise the water-anion-cation interactions at low water contents. Nafion consists of a perfluorinated polyethylene backbone with pendant ether linked side chains terminating with a sulphonate group, $-O-CF_2-CF_2-SO_3^{-}M^{+}$. Spectra in the OH stretching and H-O-H bending regions showed the distinction between hydrogen bonded and non-hydrogen bonded water molecules and yielded information on the mode of attachment of water molecules to the anion-cation pairs. When there is a good match between the Lewis acid strength of the cation and the Lewis base strength of the anion, the ion pairs are relatively stable and water molecules tend to attach on the outside where the respective acid and base strengths are mismatched, as is the case for small cations of high charge or for large cations of low charge; water molecules tend to be inserted between the ion pairs even at the lowest water contents.[15]

The trinuclear cluster ion $[M_3O_2(pr)_6(H_2O)_3]^{2+}$ where M = Mo or W and pr = $O_2CC_2H_5$) has been shown to undergo extensive hydrolysis in aqueous solution to produce oxo species. Dimerisation and polymerisation of these clusters proceeds via formation of the hydrogen oxide bridging ligand μ-$H_3O_2^-$ which is formed by a strong hydrogen bond between the hydroxo ligand of one cluster and an aquo ligand of another.[16]

O_2F_2 has been shown to be a potent fluorinating agent being capable of fluorinating plutonium oxides, oxyfluorides and PuF_4 to PuF_6 at room temperature.[17] Its reactions with a series of adamantane derivatives to give fluoroadamantanes have also been reported.[18]

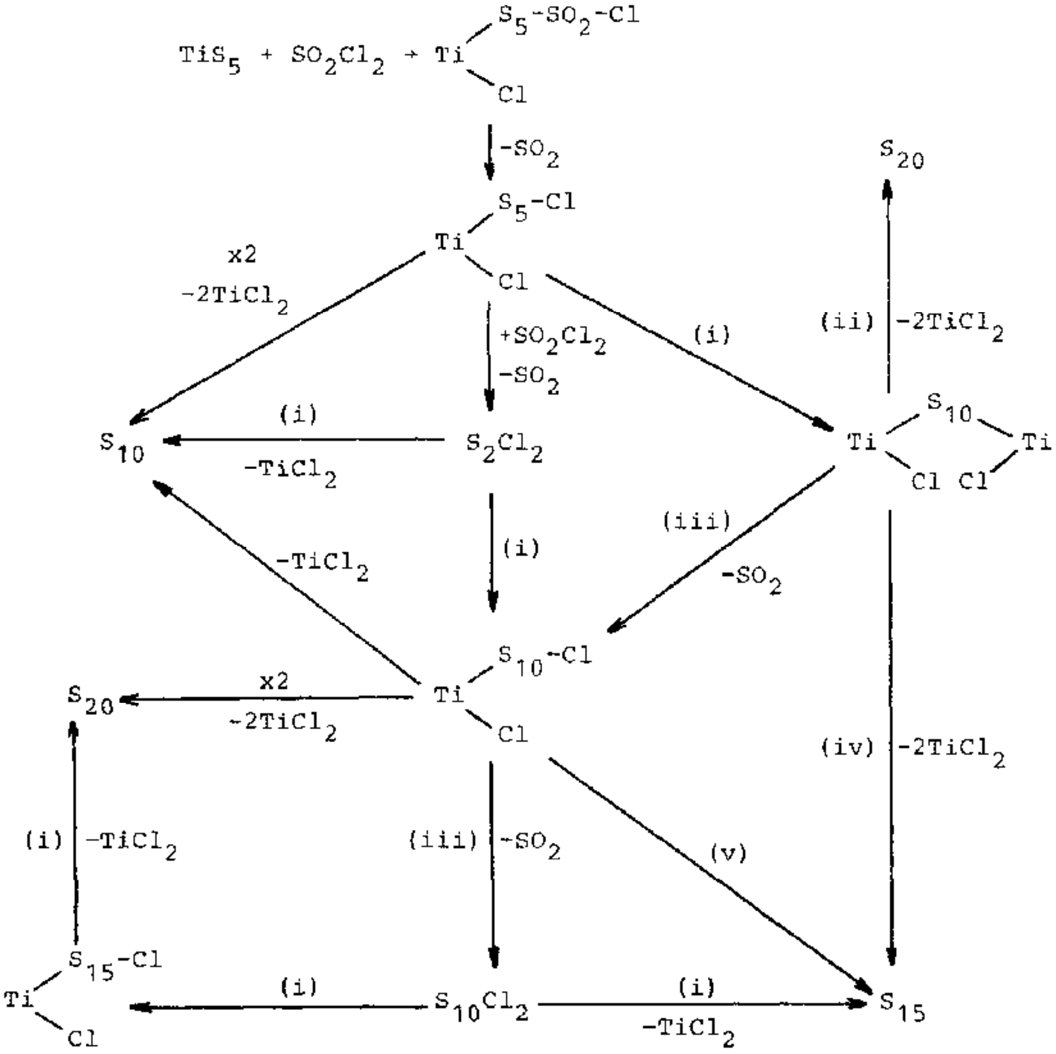
6.2 SULPHUR

6.2.1 The Element

Homocyclic S_{20}, the largest sulphur ring with a known structure, has now been synthesised in gramme quantities by the reaction of $[Ti(Cp)_2S_5]$ and SO_2Cl_2 in CS_2 solution.

$$[Ti(Cp)_2S_5] + SO_2Cl_2 \rightarrow \frac{1}{n}S_{5n} + [Ti(Cp)_2Cl_2] \qquad \ldots(3)$$

High pressure liquid chromatographic analysis of the reaction products showed the presence of S_{10}, S_{15}, S_{20} and S_{25} in order of decreasing concentration. The preferred formation of sulphur rings S_{5n} with n = 2 to 6 in the reaction can be understood by the series of reactions shown in Scheme 1 (Cp ligands omitted for clarity). The compound S_5 was not observed as a reaction product and hence S_{10} is not formed by the dimerisation of S_5 nor was S_{12} formation enhanced when the very reactive S_7 was added to the reaction mixture.[19] The thermal decomposition of a number of sulphur allotropes (S_6, S_7, S_8, S_{10}, S_{12}, S_{13}, S_{20} and polymeric



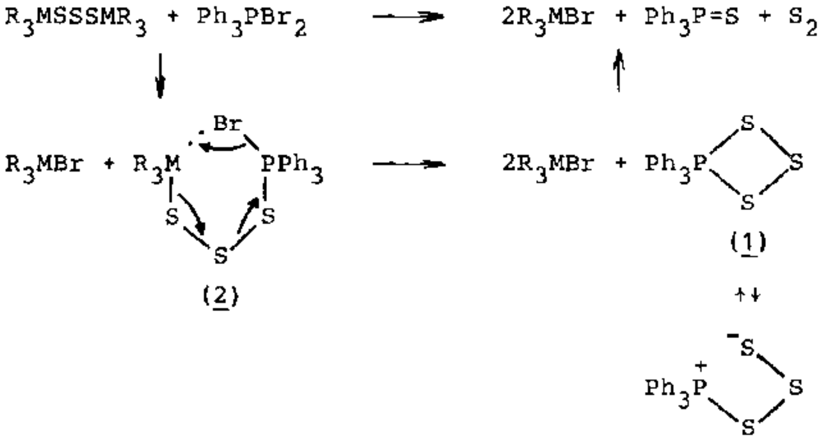
Scheme 1. Cp ligands are omitted. (i) $+[Ti(Cp)_2S_5]$; (ii) $+S_{10}Cl_2$; (iii) $+SO_2Cl_2$; (iv) $+S_5Cl_2$; (v) $+[Ti(Cp)_2Cl(S_5Cl)]$

sulphur) has been investigated both theoretically and experimentally by DSC and HPLC in the temperature range 30-250°C. The polymerisation of S_8 was endothermic and endentropic, that of S_7 exothermic and endentropic and S_6 exothermic and exentropic. Thus a floor temperature exists for the polymerisation of S_8 and a hypothetical very high ceiling temperature for S_6 whilst S_7 is unstable with respect to polymerisation over the whole temperature range. With the exception of S_8, all the allotropes investigated, yielded polymeric sulphur on heating to 60-150°C followed by depolymerisation to the equilibrium sulphur melt consisting mainly of S_8, some S_7 and traces of S_6, S_9, S_{12} and other rings. Polymeric sulphur slowly dissolves in CS_2 at 20°C to give S_8, S_7 and traces of other rings such as S_6, S_9 and S_{12}. On heating sealed ampoules of the $S\mu/CS_2$ mixture to 80-100°C complete dissolution took place within several hours with the formation of S_8 and S_7 as the main products.[20]

An attempt has been made to generate singlet S_2 by a reaction analagous to that used to prepare singlet oxygen ($R_3P + O_3 \rightarrow R_3P{=}O + {}^1O_2$) in which a series of silyl and germanium protected trisulphides served as latent stable masked sources for the S_3 unit.

$$R_3MSSSMR + Ph_3PBr_3 \xrightarrow[250°C]{CH_2Cl_2} 2R_3MBr + Ph_3P{=}S + \tfrac{1}{4}S_8 \qquad \ldots(4)$$

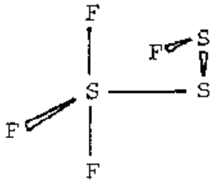
When the reaction was carried out in the presence of a conjugated diene, the formation of elemental sulphur was efficiently suppressed with the concomitant formation of the corresponding Diels-Alder adduct (eg. using  led to ). It was assumed that phosphine sulphide (1) or its probable precursor (2) was the responsible agent from which S_2 was liberated as shown in Scheme 2, but attempts to isolate or characterise these intermediates or ${}^1S_2$ itself have not been fruitful.[21]



Scheme 2

6.2.2 Bonds to Halogens

Cocondensation of SF_2 and SSF_2 gave the new compound 1,3-difluorotrisulphane-1,1-difluoride (3) which was formed in low yield and isolated by means of low temperature fractionation.

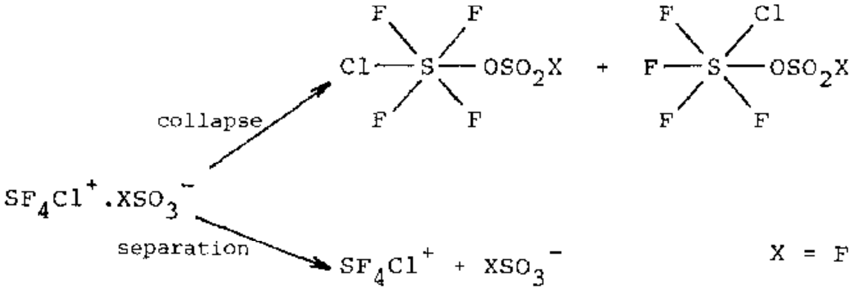


(3)

The unstable compound is a colourless, viscous liquid with an extrapolated boiling point of 94°C and a melting point of -62°C. It decomposes to SF_4 and SSF_2 in the gas phase.[22] The crystal structure determination of a disordered solid phase of SF_4 has shown it to have face centred cubic space group with a = 676pm and z = 4. During part of this study an unintentional hydrolysis in a glass capillary of the SF_4 took place to give SiF_4 and SOF_2. The products could however be separated and grown as crystals in the glass capillary tube and structural analysis carried out. SOF_2 was found to crystallise in the monoclinic space group $P2_1/c$ and to have isolated molecules of pyramidal geometry arranged in strongly folded layers with intermolecular S...O contacts.[23]

The reaction of $ClOSO_2F$, $BrOSO_2F$ and $ClOSO_2CF_3$ with SF_4 have been studied. It was found that the reactions proceed to form either trifluorosulphonium salts or covalent adducts. In the cases where the hypochlorites were used the unusual cation SF_4Cl^+ can be postulated as a reactive intermediate (Scheme 3).

$$SF_4 + ClOSO_2X \rightarrow SF_4Cl^+.XSO_3^-$$



X = F or CF_3

$$SF_4Cl^+ + SF_4 \rightarrow SF_5Cl + SF_3^+$$

Scheme 3

Characterisations of the new compounds $SF_3{}^+FSO_3{}^-$, $SF_3{}^+CF_3SO_3{}^-$, cis- and trans-$SF_4(Cl)OSO_2F$ and trans-$SF_4(Cl)OSO_2CF_3$ were reported. The $SF_3{}^+$ salts are thermally unstable decomposing to SF_4, SOF_2 and $(XSO_2)_2O$ (X = F or CF_3) by the routes postulated in Scheme 4.[24]

$$SF_3{}^+XSO_3{}^- \rightleftharpoons XSO_2OSF_3$$

$$XSO_2OSF_3 \rightleftharpoons XSO_2OSF_2{}^+ + F^-$$

$$F^- + SF_3{}^+ \rightarrow SF_4$$

$$XSO_2OSF_2{}^+ + XSO_3{}^- \rightleftharpoons (XSO_2O)_2SF_2$$

$$(XSO_2O)_2SF_2 \rightarrow (XSO_2)_2O + SOF_2$$

$$2SF_3{}^+XSO_3{}^- \rightarrow SF_4 + (XSO_2)_2O + SOF_2$$

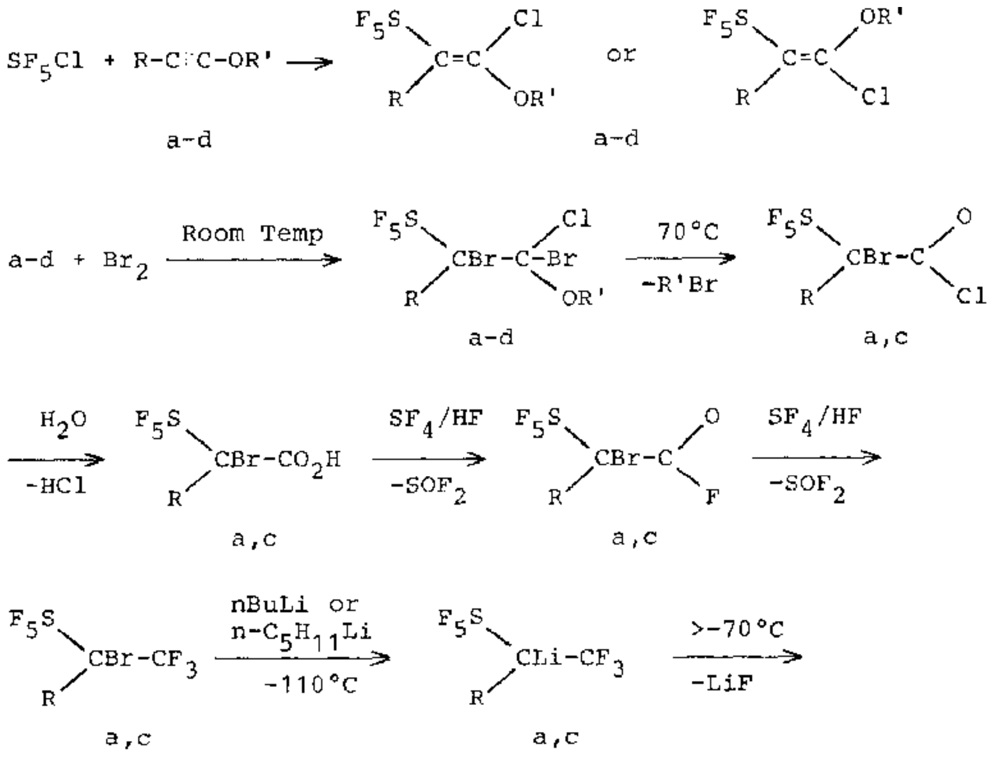
$$X = F \text{ or } CF_3$$

Scheme 4

The interaction of UF_5 with SF_4, SF_4O and some Lewis-acid pentafluorides of various strengths has been studied. In anhydrous HF solutions, SF_4 was shown to yield an adduct of composition $3UF_5.SF_4$ in which both ionic and fluorine bridged species are present. The pentafluorides of As, Ta and Nb combine with UF_5 to give adducts of composition $1.5UF_5.AsF_5$, $UF_5.2TaF_5$ and $UF_5.2NbF_5$ respectively.[25]

Pyrolysis reactions of various sulphur fluorides (F_2S_2, SF_4 and SF_6) over boron have been shown to yield the unstable species FBS, $(FBS)_2$ and $(FBS)_3$ in high yield. FBS and $(FBS)_2$ can be produced in a direct flow system and $(FBS)_3$ by revaporising a trapped monomer-dimer mixture.[26]

The new alkylidenesulphur tetrafluorides $CF_3CH{=}SF_4$ and $CF_3C(CH_3){=}SF_4$ have been prepared. The former is prepared from $HC{\equiv}C\text{-}OR$ and SF_5Cl in a multistep preparation shown in Scheme 5. $CF_3C(CH_3)SF_4$ and $F_2C{=}C(CH_3)\text{-}SF_5$ are also formed in several steps from $CH_3C{\equiv}C\text{-}OR$ and SF_5Cl. The compounds are especially stable and have structures analogous to those of $H_2C{=}SF_4$ and $CH_3CH{=}SF_4$.[27]



$F_3C-CR=SF_4 + F_2C=CR-SF_5$

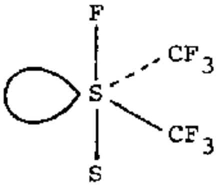
a,c a,c

	R	R'
a	H	CH_3
b	H	C_2H_5
c	CH_3	CH_3
d	CH_3	C_2H_5

Scheme 5

The compounds $CF_3-CFCl-SF_3$, $(CF_3-CFCl)_2SF_2$ and $CF_3-CFCl-SOF$ have been prepared and the ^{19}F n.m.r. spectra fully analysed. In $CF_3-CFCl-SF_3$ the chiral carbon atom leads to a splitting of the axial fluorine atoms on sulphur. $(CF_3-CFCl)_2SF_2$ exists in a dl form with equivalent (sulphur)-F atoms whilst $CF_3-CFCl-SPF$ exists in two diastereoisomeric forms.[28]

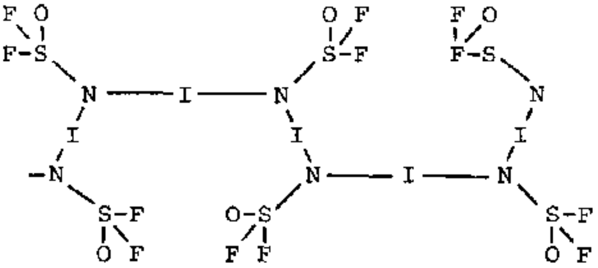
The geometric structure of $(CF_3)_2S(O)F_2$ (4) has been studied by gas electron diffraction. Its structure obeys the VSEPR model in that the most electronegative substituents occupy the axial positions in the trigonal bipyramidal molecule. The following geometrical parameters were determined C-F = 1.314, S=O = 1.422, S-F = 1.641, S-C = 1.891Å and the angles CSC = 97.8, FSF = 173.1



(4)

FCF = 109.4°. Comparison was made with the structures of SF_4, OSF_4 and $(CF_3)_2SF_2$ and an attempt made to explain the variations in the bond angles in terms of non-bonded fluorine-fluorine interactions.[29]

A crystal structure determination has shown that in $INSOF_2$ (5) the molecules are connected by intermolecular N-I bonds forming chains in which the N-I-N groups are almost linear but not symmetric.[30]



(5)

The new compound SFCl has been obtained by u.v. photolysis of FC(O)SCl in rare gas matrix and by u.v. photolysis of Cl_2/SF_3SF in the gas phase. The molecular identity of the compound was confirmed by isotope substitution experiments and force constants were determined.[31]

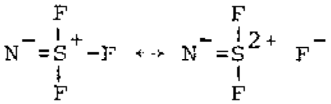
New thermal analysis and powder diffraction data in the binary system sulphur-chlorine have been used to construct a new phase diagram for the region 50-100 atom % Cl. Sulphur chlorides with elemental ratios of 1:1, 1:2, 1:3 and 1:4 were observed with the mp's -80, -125, -75 and -34°C, respectively. The 1:1 compound was confirmed as S_2Cl_2 by comparison with the crystal structural data published in 1983, whilst new data was obtained for SCl_2 by growing a single crystal by zone melting in a capillary tube, which showed the crystal structure to be comprised of angular SCl_2 molecules (S-Cl bond length between 200.58 and 201.83pm) arranged in bimolecular layers. SCl_3 is a new compound in the system and has an unknown structure, and SCl_4 is probably isotypic with α-$SeCl_4$ according to powder diffraction data.[32]

6.2.3 Bonds to Nitrogen

Linear Compounds - Theoretical vibrational spectra have been calculated for NSF and SNF by the use of the 6-31G* basis and have been shown to be sufficiently different to be useful in the identification of the yet unknown SNF. The activation energy for the conversion of SNF to NSF was predicted to be high enough to allow isolation of SNF at room temperature.[33] The gas-phase core binding energies of NSF, NSF_3 and several compounds of the types NSF_2R and F_2SNR have been determined. Qualitative interpretation of the data shows that $N(p\pi)\rightarrow S(d\pi)$ bonding is probably important in the NSF_2R compounds and in NSF_3, that the bonding of the sulphur atom in NSF is similar to that in SO_2, and that the nitrogen atom of NSF_3 is more negatively charged than that of NSF in spite of the stronger N-S bond in NSF_3. Quantitative interpretation shows the HOMO of NSF and NSF_3 to have principally nitrogen 2p character and is stabilised by interaction with a higher lying sulphur 3d orbital. Whilst there is no simple way to indicate the relative importance of these bonding contributions in a structural formula, and even the concept of bond order is difficult in this instance to define meaningfully the authors suggest that NSF and NSF_3 can be approximately represented as the resonance hybrids (6) and (7) respectively.[34]

$$N{\equiv}S{-}F \leftrightarrow N{\equiv}\overset{+}{S}\ F^{-}$$

(6)

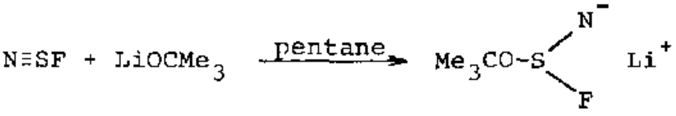


$$N^{-}{=}\overset{F}{\underset{F}{S}}{}^{+}{-}F \leftrightarrow N^{-}{=}\overset{F}{\underset{F}{S}}{}^{2+}\ F^{-}$$

(7)

Electronic structure calculations (SCF and CEPA) have been reported for SN^+, NSF, NSF_3, $[HNSF]^+$, $[HNSF_3]^+$ and $[CH_3NSF]^+$. The equilibrium distance obtained for SN^+ (1.44±0.01Å) is expected to be definitive. A marked stabilisation of SN and SF bonds arises if electrons are removed from the thiazyl group eg.

in going from NSF to NSF_3 or by complexing NSF or NSF_3 with electron acceptors. This effect appears to be correlated with the increased positive net charge on sulphur with bonding to the acceptors being most likely at the nitrogen with NSF_3 being a better donor than NSF.[35] Nucleophilic substitution at thiazyl fluoride has been proposed as a means of giving access to thiazyl derivatives R-S≡N but members of this class of compounds are only rarely stable since complex secondary reactions frequently take place. The addition of $LiOCMe_3$ to NSF is expected to be the initial step in a substitution of this type but the reaction product (8) may be converted into the more stable mixed salt (9). In the formation of (9) three moieties of (8) combine with four additional Li^+ ions to give two $Li_4(N/F)_4$ eight membered rings linked by four Me_3CO-S bridges.[36]



$$N{\equiv}SF + LiOCMe_3 \xrightarrow{\text{pentane}} Me_3CO{-}S\begin{smallmatrix} N^- \\ F \end{smallmatrix}\ Li^+$$

(8)

$Li_8[Me_3COS(N)F]_4F_2[Li_4(OCMe_3)_5]_2 \cdot 4C_5H_{12}$

(9)

The (E,Z) and (E,E) forms of dimethylsulphurdiimine have been fully optimized by ab initio STO-3G* calculations. The (E,Z) form was predicted to be more stable than the (E,E) form by about 41 kJ/mole, in agreement with experimental data.[37]

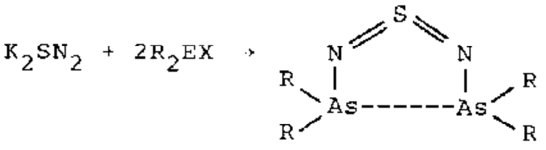
(Fluoroimido)tetrafluorosulphur has been shown to undergo a number of reactions with strong electrophiles, involving addition to the sulphur-nitrogen double bond and to react readily with fluoride ion to give the reactive nucleophile SF_5NF^-. Chlorine(I)-, and bromine(I)fluorosulphate and peroxydisulphuryldifluoride add to F_4S=NF to form the respective cis adducts. The ion SF_5NF^-, generated in situ from F_4S=NF and KF, reacts readily with Br_2 forming SF_5NBrF and with acyl fluorides to give $RCONFSF_5$; it also reacts with F_2C=NF to form $(SF_5NF)FC$=NF which is isomerised to the unusual azo compound F_5SN=NCF_3 in the presence of COF. Self reaction of F_4S=NF in the presence of KF does not produce the expected dimer $(SF_5NF)F_3S$=NF; instead, extensive decomposition takes place and a low yield of the unusual amine

$(SF_5)_2NF$ is obtained.[38]

The preparations of pentafluorosulphanylisocyanate and isothiocyanate have been described and the reactions of the former with alcohols, thiols, amines, aldehydes, formamides and sulphoxides and compounds containing reactive CH groups studied. Several new synthetic routes to the isothiocyanate were described and its first derivatives prepared. The isothiocyanate (<u>10</u>) can easily be prepared by the reaction of dichloro(pentafluorosulphanylimino)-methane with phosphorus pentasulphide in boiling toluene (equation 5).[39]

$$3SF_5{=}NCCl_2 + P_2S_5 \rightarrow \underset{(\underline{10})}{3SF_5N{=}C{=}S} + 2PSCl_3 \qquad ...(5)$$

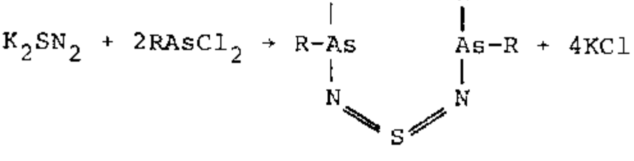
A suspension of the salt K_2SN_2 in acetonitrile has been shown to react with diorgano-element halides R_2EX (E = P,As,Sb,Bi; X = Cl or Br) at -40°C to give the new sulphur diimides (<u>11</u>).



...(6)

(<u>11</u>)

The arsino derivative is the most stable member of the series of tert-butyl compounds with the bismuth derivative decomposing under ambient conditions. Methyl, cyclohexyl and phenyl derivatives were also prepared with E = As.[40] Reaction of K_2SN_2 with organo arsenic chlorides ($RAsCl_2$) leads to sulphur diimides containing organoarsino substituents at both ends (<u>12</u>).



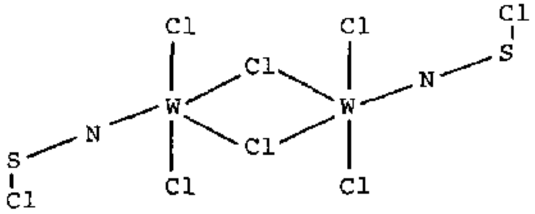
...(7)

(<u>12</u>)

X-ray structural data was obtained for the t-butyl derivative of (12) and also for the phenyl derivative of (11). In both compounds the sulphur diimide groups are coplanar with their directly bonded arsenic atoms which in the case of (12) leads to a boat configuration for the eight membered ring. In the case of the open chain compounds (11) a cis-cis configuration was found at the S=N double bonds which indicate an As---As interaction, indeed the As-As distance of 3.379Å is shorter than that found in (12) (3.683Å) the sulphur nitrogen distances are normal for sulphur diimides without significant π interaction with the substituents.[41]

The reaction of $S_3N_2Cl_2$ with $ReCl_5$ gives the chlorothionitrene complex $[ReCl_3(NSCl)_2]_2$ which has a dimeric structure with a chlorine bridge. Reaction of two moles of $ReCl_5$ and S_3N_2Cl gives $[N(SCl)_2]^+[Re_2Cl_9]^-$ in which the NS bond lengths of 162pm and the bond angles SNS (133.6°) and NSCl (117.6°) deviate considerably from the values of known $[N(SCl)_2]^+$ structures.[42]

WCl_6 reacts with trithiazyl chloride to give the chlorothionitrene complex $[WCl_4(NSCl)]_2$ in which the W atoms are linked via two chloro bridge (13).



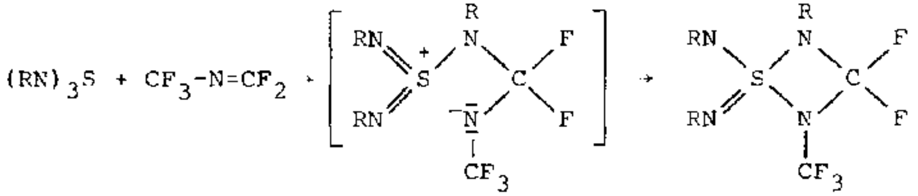
(13)

The NSCl groups are in a trans position to the longer of the terminal W-Cl bonds.[43]

Although the triatomic compound HNS is not known in the free state it has been observed as a six electron ligand in the binuclear iron complex $Fe_2(CO)_6(HNS)$.[44]

Trithiazyltrichloride reacts with $OsCl_3$ to give a product of composition $Os(NS)Cl_3$ which may be converted to $[PPh_4][(H_2O)Os(NS)Cl_4]$ in which the Os atom is octahedrally coordinated with H_2O trans to the NS group.[45]

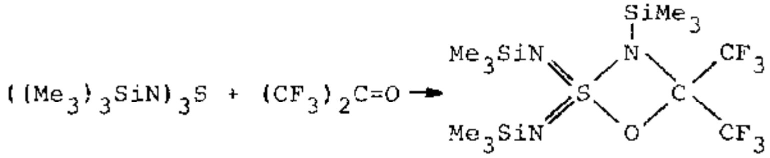
Cyclic Compounds - The reaction of the sulphur triimides $(RN=)_3S$ with R = Me_3C or Me_3Si with pent-fluoroazapropene gives the appropriate $1\lambda^6$,2,4-thiadiazetidines (14).



...(8)

(14)

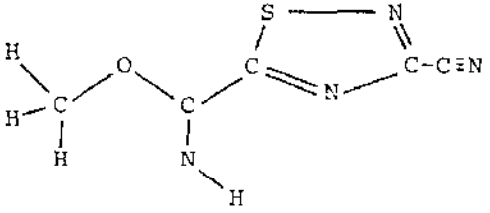
Reaction of $((Me_3)_3CN)_3S$ with $ClSO_2N{=}CCl_4$ gives the linear compound $Me_3C{-}N{=}C{=}N{-}SO_2Cl$, but $((Me_3)_3SiN)_3S$ with hexafluoroacetone gave the rather unstable $1,2\lambda^6,3$-oxathiazetidine (15).[46]



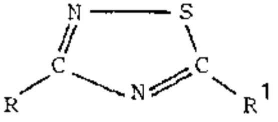
...(9)

(15)

Using the different reactivity of both nitrile groups of 1,2,4-thiadiazole-3,5-dicarbonitrile (16) against nucleophilic reagents; the imidic esters with R = CN, R^1 = C(=NH)OMe or R = R^1 = C(=NH)OMe, the thioamides with R = CN, R^1 = $CSNH_2$ or R = R^1 = $CSNH_2$ and the dicarboxamide with R = R^1 = $CONH_2$ have been prepared. X-ray analysis of (17) with R = CN, R^1 = C(=NH)OMe shows that the first attack occurs at the nitrile group adjacent to sulphur.[47]

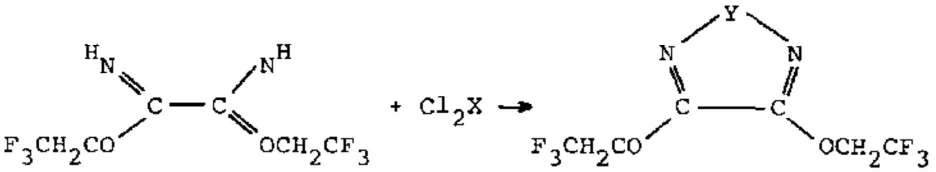


(17)



(16)

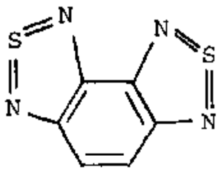
The reaction of cyanogen with CF_3CH_2OH in the presence of a base catalyst yields (18) which may be easily cyclised with halides such as S_2Cl_2, $SOCl_2$ or $SeOCl_2$ in Et_3N to yield five membered ring compounds (19) with Y = S or Se.[48]



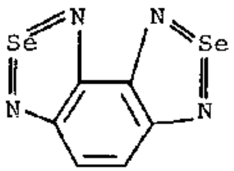
...(10)

(18) (19)

X-ray structure determinations have shown that the cyclic compounds (20) and (21) have a quasi aromatic π system in the 1,2,5-thiadiazole rings, with the aromatic character of the central benzene ring being strongly disturbed. The substitution of one sulphur by a selenium atom induces significant changes of comparable bond lengths. Quasi polymers in the form of ribbon-like structures are observed in (20) by short S---N contacts and in (21) by short Se---N contacts. In (21) $(SeN_2)_x$ chains are also formed.[49]

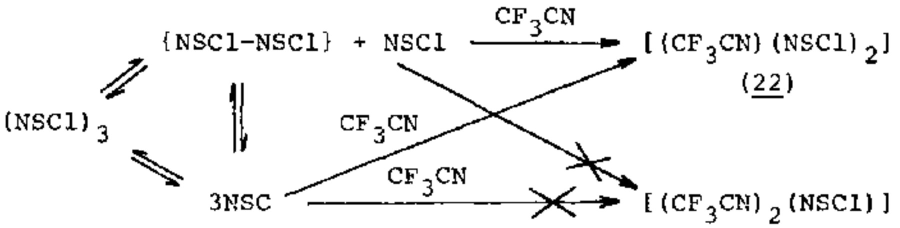


(20)



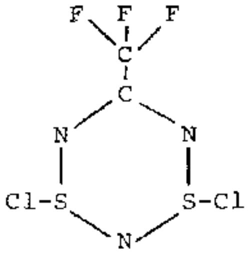
(21)

The preparation of cyclo$(CF_3CN)(NSCl)_2$ (22) from CF_3CN and $(NSCl)_3$ has been reported (equation 11). The structure of (22)



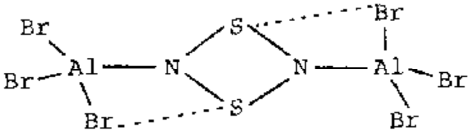
...(11)

was determined by X-ray diffraction and (22) may be dechlorinated by Zn in liquid SO_2 to give either $CF_3CN_3S_2$ or $CF_3CN_2S_2$ depending on the reaction conditions.[50]



(22)

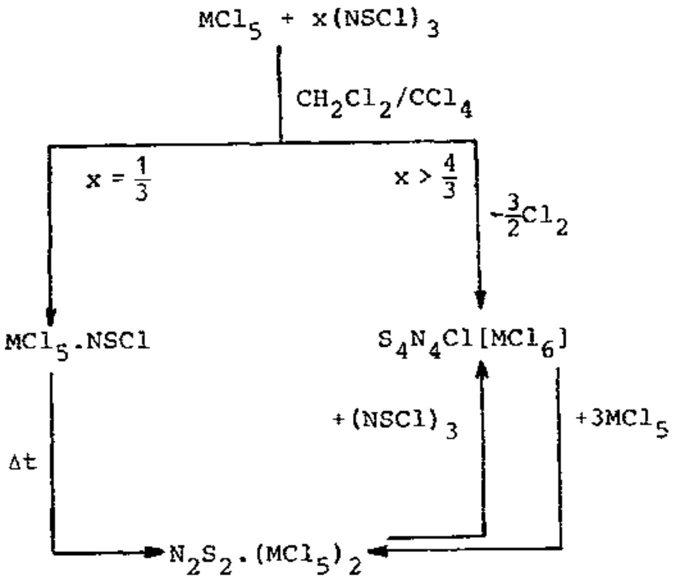
The compound $S_2N_2.2AlBr_3$ (23) has been prepared by the reaction of S_4N_4 with $AlBr_3$ in 1,2-dibromoethane at room temperature. The S_2N_2 has S-N bond lengths of 1.629 and 1.651Å with S-N-S and N-S-N bond angles of 95.8 and 84.2° respectively. Thus although the bond lengths agree closely with those of free S_2N_2 the angle at nitrogen is increased by 5° and the angle at S decreased by 5°. The sulphur atoms form two close S---Br contacts (3.149 intramolecular and 3.193Å intermolecular) such that the complexes are joined by the intermolecular attractive S---Br interactions to form infinite chains.[51]



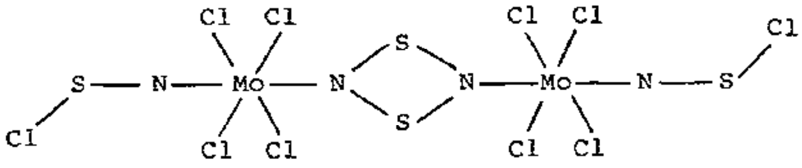
(23)

The pentachlorides of niobium and tantalum react with trithiazyl chloride in CCl_4 suspension to form the donor-acceptor complexes $MCl_5.NSCl$ and $(MCl_5)_2N_2S_2$. With excess $(NCl)_3$ the ionic compounds $S_4N_4Cl(MCl_6)$ are obtained, and another ionic species, $N(SCl)_2(MCl_6)$ was obtained from the reaction of the complexes $MCl_5.NSCl$ with SCl_2. Further reactions in this system are shown in Scheme 6.[52] Molybdenum pentachloride also reacts with $(NSCl)_3$ in CH_2Cl_2 suspension to give a mixture from which the complex μ-$(S_2N_2)[MoCl_4(NSCl)]_2$ (24) was extracted. The corresponding tungsten compound was obtained by extraction of SCl_2 and chlorine from $N(SCl)_2[WCl_5(NSCl)]$ which was prepared from WCl_6 and $N_2S_3Cl_2$.[53]

The ionic compound $[PPh_3Cl][ReCl_4(N_2S_2)]$ (25) has been prepared by the reaction of $[ReCl_3(NSCl)_2(POCl_3)]$ with triphenylphosphane.

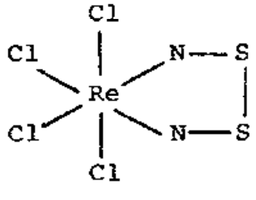


Scheme 6



(24)

The structure comprises PPh_3Cl cations and $ReCl_4(N_2S_2)$ anions in which the rhenium atom is six coordinated by four chlorine atoms and the nitrogen atoms of a ReN_2S_2 five membered ring in cis position. The Re-N bond lengths (181pm) and the NS bond lengths (152pm) are in the range of double bonds whilst the S-S distance is very long (253pm).[54]

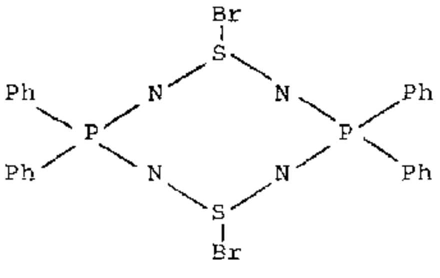


(25)

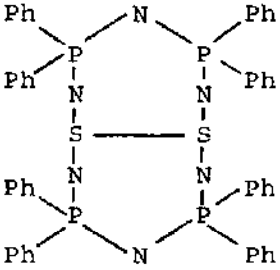
An ab initio valence bond calculation for S_2N_2 with the sulphur 3d orbitals omitted supports a conclusion obtained from a previous INDO study that the primary Lewis valence bond structure is a spin-paired diradical or long-bond structure. "Increased-valence" structures were used to provide qualitative valence bond mechanisms for the thermal polymerisation of S_2N_2 to $(SN)_x$ and electron conduction in $(SN)_x$.[55]

The geometric structure of $(ClNSF_4)_2$ has been studied by gas electron diffraction. The four membered SNSN ring is planar with the S-N bonds lengthened (1.734Å) due to angle strain (SNS = 99.3°). The out of plane chlorine atoms are in a trans position and the extremely short N-Cl bond lengths (1.638Å) are rationalised by the large SNCl bond angles (122.1°). Substitution effects on trans and cis S-F bond lengths of the SF_4 groups were also discussed.[56]

The eight membered ring 1,5-$(Ph_2PN)_2(SN)_2$ undergoes an oxidative-addition reaction with Br_2 or SO_2Cl_2 to give 1,5-$(Ph_2PN)_2(NSX)_2$ where X = Br or Cl. The crystal structure of the bromine compound (<u>26</u>) shows the ring to have the chair conformation with exocyclic bromine substituents in a trans configuration with sulphur-bromine distances of 2.454 and 2.440Å. This represents the first structural characterisation of a thiazylbromide and indicates appreciable ionic character in the S-Br bond. The average S-N and P-N bond lengths are 1.53 and 1.62Å respectively. In contrast the reaction of 1,3-$(Ph_2PN)_4(SN)_2$ with SO_2Cl_2 results in ring contraction to give $(Ph_2PN)_2(NSCl)$ whilst the reaction with Br_2 produces $[(Ph_2PN)_4(SN)_2]^{2+}[Br_3^-]_2$ (<u>27</u>). The reactions of 1,3,7,9-$(Ph_2PN)_4(SN)_2$ with iodine or excess Br_2 produced the six membered rings $(Ph_2PN)_2(NSI)$ and $(Ph_2PN)_2(SN)^+Br_3^-$, respectively.

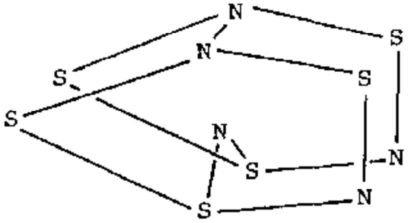


(<u>26</u>)



(27)

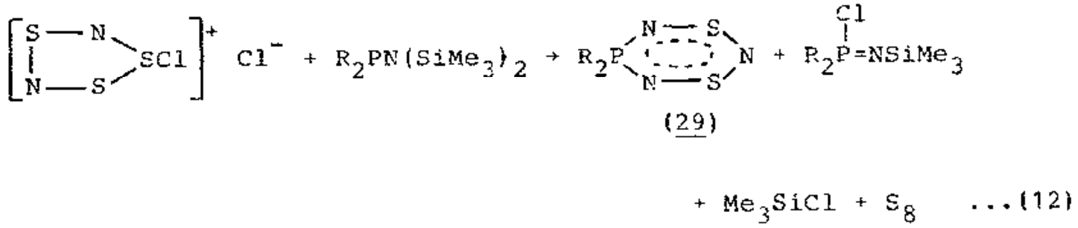
The e.p.r. spectrum of a persistent sulphur nitride radical cation, common to the oxidation of many sulphur-nitrogen compounds, has been obtained from solutions of S_4N_4/S_4N_2 mixtures highly enriched in both ^{15}N and ^{33}S. Analyses of solution and frozen spectra showed that the cation is planar $S_3N_2^+$ and that its ground state is $^2A_2$ in C_{2v} symmetry.[58] Crystalline $(S_3N_2)_2NAsF_6$ has been prepared from a 1:1 mixture of S_4N_4 and S_2NAsF_6 in liquid SO_2 at 0°C. The compound is essentially ionic with sulphur-fluorine cation-anion contacts. The $(S_3N_2)_2N^+$ cation is the first example of a mono-bridged bicyclic S-N cation and consists of two S_3N_2 groups connected together by a bridging nitrogen atom attached to a sulphur atom of each S_3N_2 ring. The S_3N_2 rings are cis with respect to the bridging nitrogen atom and are essentially eclipsed with respect to the SNS bridge (28).



(28)

The compound reacts with CsN_3 in liquid SO_2 solution to give impure poly(sulphur nitride) and $CsAsF_6$ and solutions of (28) in liquid SO_2 slowly disproportionate to $S_4N_3AsF_6$ and S_4N_4.[59]

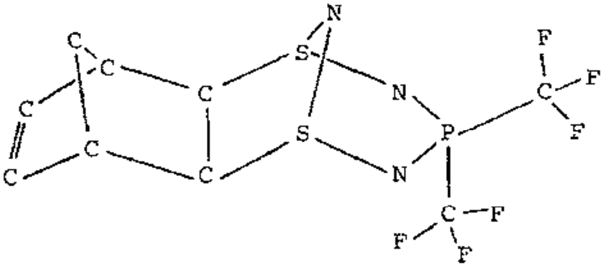
The reaction of $S_3N_2Cl_2$ with the (disilylamino)phosphanes $R_2P\text{-}N(SiMe_3)_2$ ($R = CF_3, C_2F_5$) leads to the formation of new cyclophosphadithiatriazenes of composition $R_2PN_3S_2$ (equation 12). The reaction of (29) with norbornadiene yields the 1:1 adduct (30)



(29)

+ Me_3SiCl + S_8 ...(12)

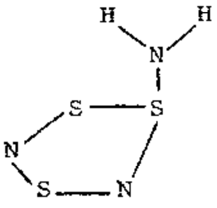
for which a crystal structure is reported. When (29) is allowed to stand for several days a crystalline compound of composition



(30)

$((CF_3)_2PN_2S)_2$ was formed which according to the X-ray structural data contains an eight membered ring with 1,3-$P(CF_3)_2$ groups.[60]

Protonation of the trisulphur trinitride ion $S_3N_3^-$ with HBF_4 has been shown to yield the ring contracted S-amino thiodithiazyl salt $S_3N_2NH_2^+BF_4^-$ for which an X-ray crystal structure was determined (31). The reasons for the instability of six membered rings of

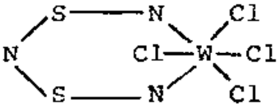


(31)

the type S_3N_3R were discussed in the light of MNDO calculations based on an S_3N_3H model.[61]

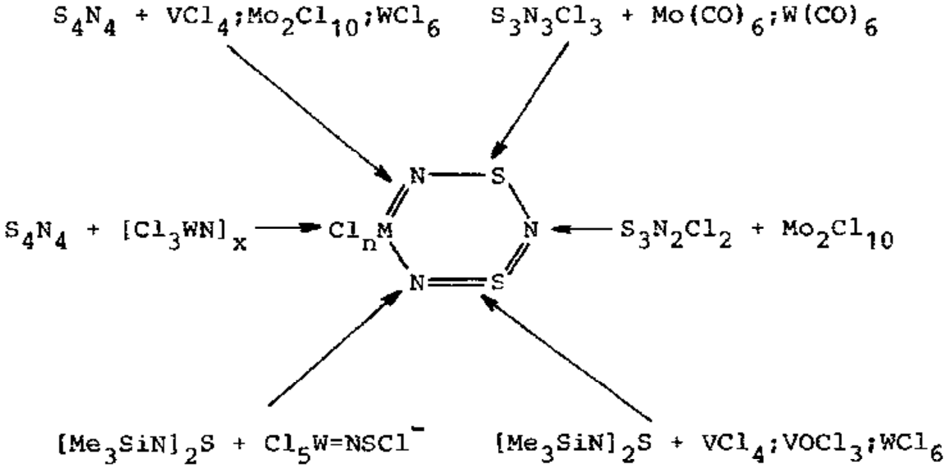
Two independent publication have described the preparation of the metallocycles $[MCl_3(S_2N_3)]_2$ where M = Mo,W. The first publication describes the preparation of the compound from quantitative reaction of $MoNCl_3$ with $(NSCl)_3$ and $WOCl_4$ or $WSCl_4$

with excess $(NSCl)_3$. The compounds are diamagnetic, thermally stable up to 200°C and only slightly sensitive to moist air, but react explosively with aqueous bases. I.r. spectra suggest the Mo compound to be dimerised via chloro bridges but the W compound is associated via the γ nitrogen atoms of the cyclothiazeno ligand. Reaction with $AsPh_4Cl$ gives the compounds $AsPh_4(MCl_4(N_3S_2))$ and a crystal structure determination of the tungsten compound shows it to be built up from $WCl_4(N_3S_2)$ anions in which the W atoms are coordinated in a distorted octahedral manner by 4 Cl atoms and 2 N atoms of the N_3S_2 ligand (32). The WN_3S_2 ring is planar and has SN bond lengths between 154 and 161pm.[62]



(32)

In the second publication the compounds were obtained by reaction of S_4N_4 with Mo_2Cl_{10} and WCl_6 and from $S_3N_3Cl_3$ with the metal carbonyls $M(CO)_6$. Several methods of preparation are shown in Scheme 7:



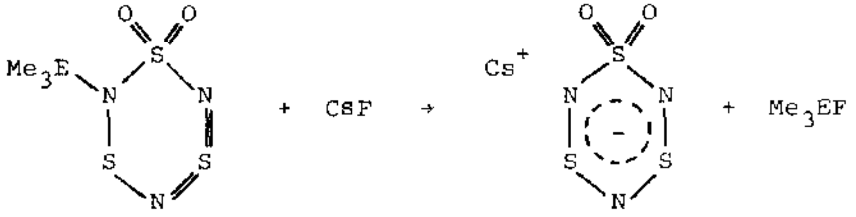
Scheme 7

The reaction of VCl_4 and $VOCl_3$ with $(Me_3SiN)_2S$ gave a compound of composition $(Cl_2VS_2N_3)_x$.[63]

Two papers have described the chemistry of the dark blue-violet cyclotrithiazene dioxide anion $S_3N_3O_2^-$. The synthesis and reactions of the ion were the subject of the first publication which described the following methods of synthesis 1) the reaction of $S_4N_4O_2$ with alkali azides:

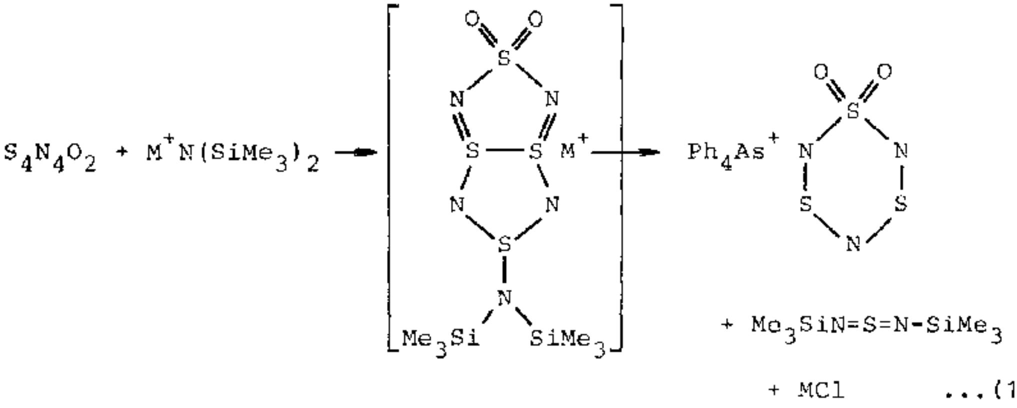
$$S_4N_4O_2 + M^+N_3^- \rightarrow M^+S_3N_3O_2^- + 2N_2 + \frac{1}{8}S_8 \qquad \ldots(13)$$

2) Metathesis of $Me_3ES_3N_3O_2$ (E = Si,Sn) with CsF:



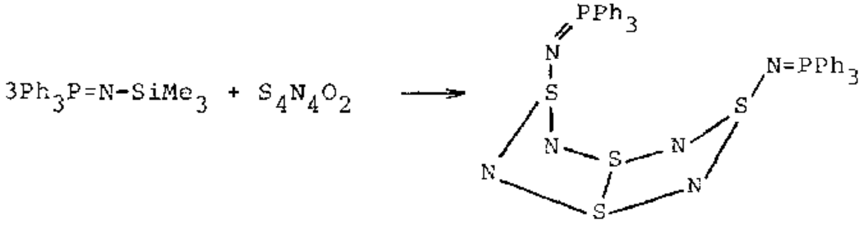
...(14)

3) The addition or $S_4N_4O_2$ and alkali bis(trimethylsilyl)amides followed by cation exchange with Ph_4AsCl:



...(15)

4) Reaction of $S_4N_4O_2$ with $Ph_3P{=}N{-}SiMe_3$ in a 1:1 molar ratio. Excess iminophosphorane leads to the formation of a covalent 1,5-di-substituted S_4N_4 derivative (<u>33</u>).[64]

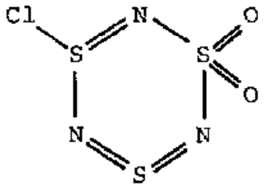


...(16)

(<u>33</u>)

The second publication describes the electrochemical reduction of the anions $S_3N_3O_2^-$, $S_3N_3O^-$ and $S_4N_5O^-$ together with the neutral molecules $S_4N_4O_2$, S_3N_2O, $Ph_2CNCNCO$ and $S(NSO)_2$. The polarographic reduction of the oxygenated derivatives $S_3N_3O^-$, $S_3N_3O_2^-$, $S_4N_5O^-$ and $S_4N_4O_2$ occurred at significantly less negative potentials than the corresponding binary species, with the coulometric reduction of $S_4N_4O_2$ giving a 70% yield of $S_3N_3O_2^-$. The controlled potential electrolysis of $S_3N_3O_2^-$ or $S_4N_5O^-$ resulted in the breakdown of the ring or cage. The reduction of $Ph_2CNSNSO$ led to the quantitative formation of $Ph_2CNSSNCPh_2$ and NSO^-, the latter anion reacts with S_4N_4 to give $S_3N_3O^-$ and with sulphur to give a red species tentatively identified as S_xNSO^- (x = 1 or 2).[65]

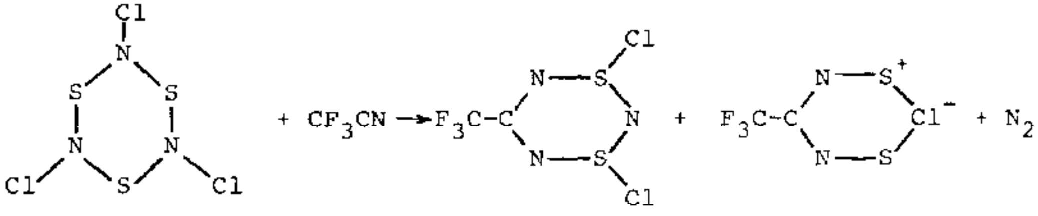
$S_3N_3O_2Cl$ has been isolated as a decomposition product of $S_3N_3O_2Cl_2$ in methylene chloride and its structure shown to contain a S_3N_3 ring with three differently coordinated sulphur atoms (<u>34</u>).[66]



(<u>34</u>)

The supporting electrolyte has been shown to have a marked effect on the electrochemical reduction of the $S_3N_3^-$ ion, which in the presence of R_4N^+ accepts two electrons to give the unstable $S_3N_3^{3-}$ anion. The reduction of $S_4N_5^-$ in the presence of R_4N^+ occurs in two steps each involving two electrons forming $S_3N_3^-$ probably via the unstable $S_4N_5^{3-}$ anion and then the $S_3N_3^-$ ion is reduced. The exhaustive electrolysis of S_4N_4 at -2.8V results in the uptake of eight electrons and the formation of the SN_2^{2-} ion.[67] Electrochemical reduction of S_4N^- has been shown to produce S_3N^- which may be further reduced to a new binary S-N anion tentatively assigned as the S_2N^- ion. Electrochemical reduction of S_7NH on a mercury pool resulted in the formation of S_4N^-, S_3N^- and HgS while at a platinum electrode the products were S_2N^-, $S_3^-\cdot$, S_4N^- and S_3N^-.[68]

The reaction of 1,3,5-trichloro-1,3,5,2,4,6-trithiatriazine with CF_3CN have been shown to depend on reaction conditions, solvent and even the material of the reaction vessel. In the absence of a solvent the products are as shown in equation (17) but if SO_2 is used as a solvent the reaction follows equation (18):



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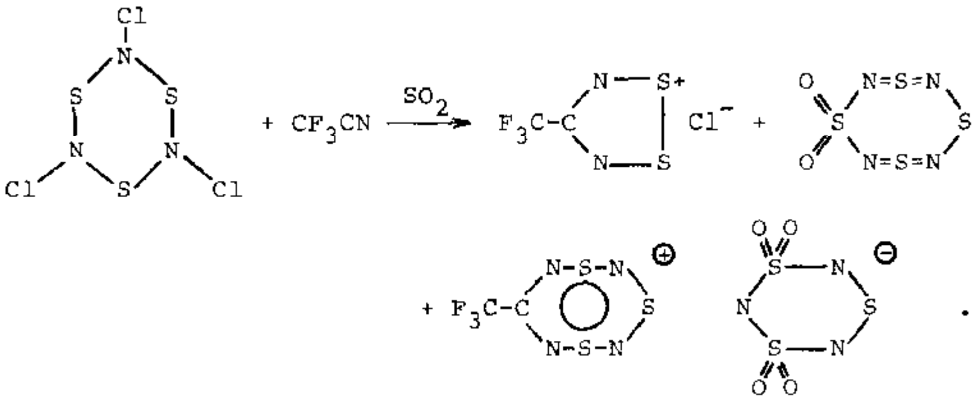
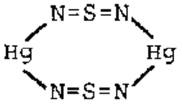


...(18)

(35)

The cation in (35) is the missing members of the series of isoelectronic heterocycles $S_4N_4^{2+}$ $RCS_3N_4^{+}$ and 3,7-$(RC)_2S_2N_4$. Crystal structure analysis of (35) showed there to be no transannular S-S interactions and the S-N distances (mean value 154.9pm) to be almost identical alternating only slightly more than in the $S_4N_4^{2+}$ ion.[69] The Hartree-Fock-Slater method has been used to elucidate the nature of the electronic spectrum of the planar $S_4N_3^{+}$ cation.[70] The crystal and molecular structures of the known compounds $HgN_2S.NH_3$ and of the new inclusion compound $2Hg(NH_3)_2I_2.S_4N_4$ have been reported. $Hg.N_2S.NH_3$ is dimeric with two Hg atoms bridged to form eight membered rings (36) with each Hg atom also coordinated by a NH_3 molecule and by a nitrogen atom of an adjacent ring. $2Hg(NH_3)_2I_2.S_4N_4$ is an inclusion compound



(36)

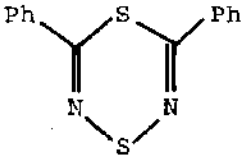
with S_4N_4 molecules in the holes of the lattice of the large $Hg(NH_3)_2I_2$ tetrahedra.[71]

The cathodic reduction of $S_3N_3Cl_3$ has been shown to yield S_4N_4 at room temperature and $(S_5N_5)Cl$ at -20°C with current efficiencies of 90% and 49% respectively.[72]

Two studies of the reactions of iron trichloride with trithiazyl chloride have been reported. The reaction yields $S_4N_4[FeCl_4]_2$, $S_3N_3Cl_2[FeCl_4]$ or $S_4N_4Cl[FeCl_4]$ depending on the reaction conditions. I.r. spectra confirmed the presence of $FeCl_4^-$ in all three compounds. A structure determination on $S_4N_4Cl[FeCl_4]$ showed it to contain the previously unknown cation $S_4N_4Cl^+$ which consists of a S_4N_4 ring built up of two nearly planar S_2N_2 fragments having a dihedral angle of 136°. The average SN bond length is 157pm and the SCl bond length is 214pm.[73]

In the second paper the same authors report that on separation the products formed in the reaction of $FeCl_3$ with $(NSCl)_3$ they obtained brown, moisture sensitive crystals of $S_4N_4FeCl_4$ which according to X-ray structure analysis contained the hitherto unknown radical cation $S_4N_4^+$. The ion has a puckered eight membered ring in which the sulphur atoms form an almost ideal square with nitrogen atoms located alternately 34, -59, 45 and -38pm above and below this square. The SN bonds are almost equal in length (average 154pm) and the NSN and SNS angles have mean values of 116.0 and 138.9°. The SN bond lengths are thus much shorter than those in S_4N_4 (162pm) but almost the same in length as those in the $S_4N_4^{2+}$ cation. The presence of $S_4N_4^{2+}FeCl_4^{2-}$ was ruled out on the basis of the Fe-Cl bond lengths and i.r. spectra.[74]

The reaction of S_4N_4 with diphenyl acetylene and phenyl acetylene has been shown to give two new, thermally stable heterocyclic systems, the 1,4,2,6-dithiadiazine (37) and the 1,3,2-dithiazolylimine (38) as minor products. The structures of the compounds were determined by X-ray diffraction and correct earlier assignments.[75]



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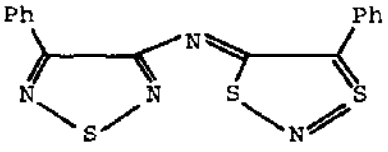
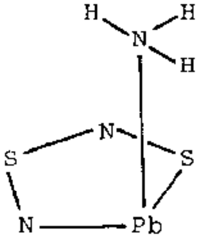


(38)

The structures of $PbN_2S.NH_3$, PbN_2S_2 and $SnCl_4.2S_4N_4$ which are the products of reactions of lead- and tin salts with S_4N_4 have been described. The first two compounds contain the same planar five membered PbN_2S_2 rings with no significant differences: in the first compound the NH_3 molecule is bound to Pb perpendicularly to the plane of the ring (39). In $SnCl_4.2S_4N_4$ the Sn atom is in six fold coordination with the two S_4N_4 rings attached trans to each other via a nitrogen atom (40).[76]



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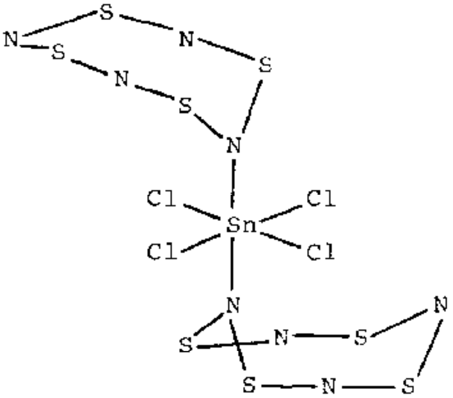
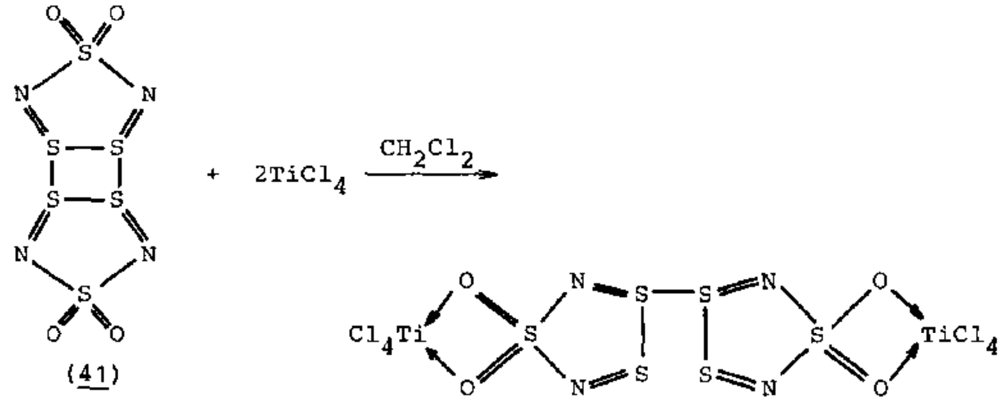


(40)

The reaction of $(NSCl)_3$ with $TiCl_4$ leads to chlorine abstraction and the formation of the adduct $TiCl_4(N_2S_2)$. I.r. spectroscopic data suggests that the N_2S_2 ring is bonded to the titanium via the nitrogen atoms to form a polymer. A by-product of the reaction is $(S_4N_5)_2(Ti_2Cl_{10})$ which consists of $S_4N_5^+$ cations which are nearly the same as those found in $(S_4N_5)Cl$ and $Ti_2Cl_{10}^{2-}$ anions as observed in $(PCl_4)_2(Ti_2Cl_{10})$.[77]

$S_6N_4O_4$ (41) has been prepared in high yield from $(Me_3Si)_2N\text{-}SO_2\text{-}N(SiMe_3)_2$ and SCl_2 in the molar ratio of 1:2. Several reactions of (41) were investigated and are given in equations (19-21). (41) is the first compound to contain an uncharged four membered sulphur ring.[78]

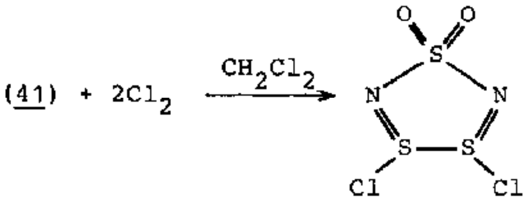
Crystals of $S_4N_4Cl_2$ (commonly called thiodithiazyl chloride) have been grown by three different methods based on 1) a reversible temperature dependent ring expansion-contraction $(S_6N_4Cl_2 \leftrightarrow S_4N_3Cl)$ equilibrium in $SO_2\text{-}SOCl_2$ mixtures, 2) a complex chemical transport reaction in a sealed tube containing $S_3N_2Cl_2$ and liquid SO_2 and 3) a controlled slow reaction of $S_3N_2Cl_2$ with liquid SO_2. A crystal structure determination showed the dimeric cation



(41)

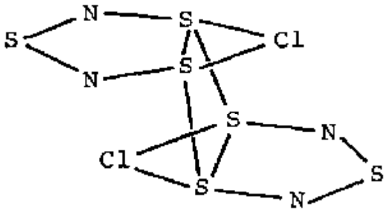
...(19)

$(\underline{41}) + AgAsF_6 \xrightarrow{SO_2} Ag(S_6N_4O_4)AsF_6$ ...(20)



...(21)

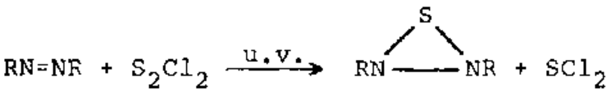
(42) to contain two centrosymmetric planar S_3N_2 rings in a chair (trans) conformation.



(42)

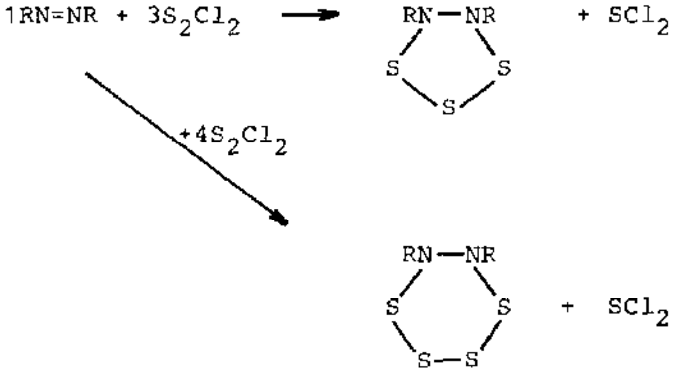
The dihedral angle between the S_3N_2 ring plane and the central S_4 ring is 110.4°. Strong, temperature independent ESR signals were obtained from solid $S_6N_4Cl_2$ suggesting the presence of some monomer.[79]

The structural dichotomy exhibited by cyclic thiazenes of the type $E(NSN)_2E$ where E = CR or SR has been analysed in the light of MNDO molecular orbital calculations on a variety of model structures. For $RS(NSN)_2SR$ molecules the activation energies for inversion at sulphur have been estimated and the formation of exo-endo and exo-exo isomers discussed in terms of the frontier orbitals involved in the free radical and electrophilic oxidation of transannular S-S bonds.[80] A new class of S-N heterocyclic compounds with the general formula $\overline{RN-S_x-NR}$ where R = CF_2Cl or C_2F_5 and x = 1,3 or 4 have been shown to result from the photolysis of RN=NR and S_2Cl_2 (equation 22):



...(22)

It is believed that these are the first examples of such compounds with divalent sulphur and when the reaction stoichiometries are changed, five and six membered heterocycles with vicinal nitrogen atoms are obtained in low yield. All of the new heterocycles

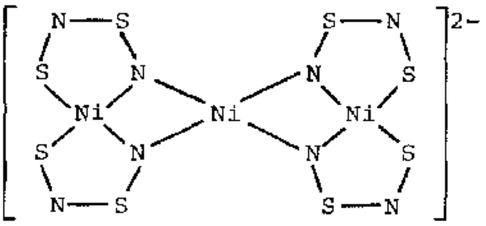


...(23)

...(24)

decompose on long standing at 25°C in Pyrex glass to bis(F-alkyl)-sulphane and -disulphane and nitrogen.[81]

A crystal structure determination has shown that the complex $(Ph_4P)_2(Ni_3N_8S_8)$ comprises two moieties of $[Ni(N_2S_2)_2]^{2-}$ linked to each other via a further nickel atom (43).[82]

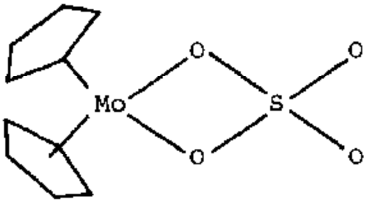


(43)

6.2.4 Bonds to Oxygen

The sulphur-33 chemical shift and ^{33}S and ^{17}O n.m.r. relaxation data have been reported for liquid sulphur dioxide. The ^{33}S nucleus in SO_2 is highly deshielded, 375±2ppm to high frequency of the sulphate ion and the temperature dependence of the ^{33}S and ^{17}O n.m.r. relaxation data can be described by an average activation energy of 6.3 kJ mole^{-1}.[83] Solubility and n.m.r. data have been presented for the SO_2-pyridine system and have been analysed to determine partial vapour pressures, activity coefficients and thermodynamic functions. The results indicate that a 1:1 complex is formed in these solutions.[84] X-ray and neutron scattering measurements on liquid SO_2 have been performed at 258 and 293K respectively. The intramolecular distances within SO_2 molecules in the liquid state were found to be S-O = 1.42Å, O-O = 2.47Å which do not differ significantly from those found in the liquid and gaseous states. Experimental intensities could be satisfactorily explained by a body centred cubic cluster model in which there were fifteen SO_2 molecules with a first neighbour distance of 4.25Å.[85] The density, conductivity and electrolysis of liquid phases in the two nonaqueous systems $LiCl\text{-}AlCl_3\text{-}SO_2$ and $NaCl\text{-}AlCl_3\text{-}SO_2$ have been determined.[86]

The reaction of Cp_2MH_2 (M = Mo,W) solutions with SO_2 has been found to rapidly and quantitatively give $Cp_2M(S_2O_3)$ and water. X-ray studies of the Mo product at -95°C showed bidentate coordination of thiosulphate to molybdenum (<u>44</u>) with Mo-O distances of 2.134 and Mo-S = 2.45Å with a dihedral angle between the Cp planes of 46.8° and a planar $MoOS_2$ ring.[87]



(<u>44</u>)

The reaction of Tl_2O with SO_2 under matrix isolation conditions gives rise to two distinct sets of product bands which were assigned to the primary reaction product being SO_3^{2-} in the $Tl_2^+SO_3^{2-}$ triple ion and the second set being assigned to the $S_2O_5^{2-}$ anion in a symmetrical oxygen-bridged form in contrast to the asymmetric S-S linked form observed at room temperature.[88] A study of the reaction of Mn(III) with S(IV) has shown that one Mn^{3+} is consumed for each SO_2 consumed and that dithionate is produced.[89]

F.T. i.r. spectroscopy has been used to study the gas phase reaction between NO_2 and $SOCl_2$. The initial products are NOCl, NO_2Cl and SO_2 but on standing a white solid which is a mixture of at least three different compounds is formed. Kinetic data show the initial reaction to be first order in $SOCl_2$ and second in NO_2. The chemistry of the reactions was partially explored and the results are shown in equations (25) to (31).[90]

$$NO_2 + SO_2 \rightleftarrows SO_3 + NO \qquad \ldots(25)$$

$$2SO_3 + NO_2Cl \rightarrow NO_2{}^+S_2O_6Cl^-(s) \qquad \ldots(26)$$

$$NOCl + SO_3 \rightarrow NO^+SO_3Cl^-(s) \qquad \ldots(27)$$

$$NO^+SO_3Cl^- + SO_3 \rightarrow NO^+S_2O_6Cl^-(s) \qquad \ldots(28)$$

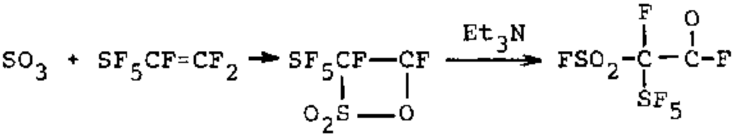
$$2NO_2 + SO_3 + SO_2 \rightarrow (NO^+)_2S_2O_7{}^{2-}(s) \qquad \ldots(29)$$

$$NO^+S_2O_6Cl^- + N_2O_4 \rightarrow NO_2Cl + (NO^+)_2S_2O_7{}^{2-}(s) \qquad \ldots(30)$$

$$NO_2{}^+S_2O_6Cl^- + N_2O_4 \rightarrow NOCl + (NO_2{}^+)_2S_2O_7{}^{2-}(s) \qquad \ldots(31)$$

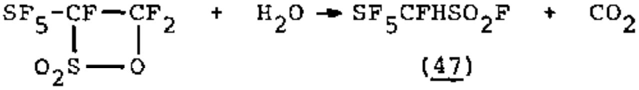
In agreement with recent experimental work a molecular orbital study of the formation of Na_2SO_4 and HCl from the reaction of SO_3, H_2O and NaCl shows no activation barrier. The reaction takes place by gas phase water reacting with SO_3 involving a linear O--H--O transition state giving closely associated hydroxyl and bisulphite which rearrange to become a hydrogen sulphate molecule. The latter then transfers a hydrogen atom to a surface chloride in solid NaCl and an electron and a sodium cation transfer to give sodium bisulphate and gaseous HCl.[91] Solubility[92] and compound formation[93] have been studied in the ZrO_2-SO_3-HCl-H_2O system. The diffusion of sulphuric acid in aqueous solution has been measured by a conductimetric technique at 25°C over a range of concentrations. At low concentrations dissociation to bisulphate and hydrogen ions produces a sharp increase in the rate of diffusion of the sulphuric acid component.[94] The excess acidity method has been used to investigate the thermodynamics of protonation of weak bases in H_2SO_4-H_2O media[95] and the hydration parameters in H_2SO_4-H_2O and $HClO_4$-H_2O media.[96] The interaction of 2,2',2"-nitrilotrisethanol with sulphuric acid has also been studied.[97]

The novel pentafluorosulphur-β-sultone, (45), has been prepared by reacting $SF_5CF{=}CF_2$ with distilled SO_3 in a modified Carius tube under pressure and mild heating (up to 100°C). Treatment of (45)



(45) (46) ...(32)

with a catalytic amount of Et_3N brought about a quantitative rearrangement to (46). An attempt to prepare the corresponding fluoroacetic acid derivative $FSO_2CF(SF_5)COOH$ by reacting the β-sultone with water failed, instead reaction occurred producing (47).[98]



(47) ...(33)

The structure of $MgSO_3.6H_2O$ has been refined from neutron diffraction data. The refined dimensions of the SO_3^{2-} ion are S-O = 1.528Å and O-S-O = 104.3°; the O-H distances in the water molecules are in the range 0.957 to 0.980Å.[99] The structure of $KHSO_5.H_2O$ has been determined: sulphur has tetrahedral coordination with the average sulphate-type S-O distance of 1.445Å, the peroxo S-O distance of 1.634Å, the peroxo O-O distance of 1.403Å and the S-O-O-H torsion angle of 87°.[100] Well formed crystals of $ZnSO_4$ and $Zn_3O(SO_4)_2$ have been prepared by chemical transport vapour phase deposition. Cl_2, $HgCl_2$, HCl, NH_4Cl and $PbCl_2$ were all found to be suitable transport agents, the halides being oxidised by SO_3 to the halogen which is the true transporting agent.[101] The addition of Na_2SiO_3 to mixtures of Na_2SO_4, Na_2S or $Na_2S_2O_3$ with sodium aluminate has been used to prepare sodium aluminosilicates with the cancrinite structure.[102] The thermal behaviour of

$3Mg(OH)_2.MgSO_4.8H_2O$ and $5Mg(OH)_2.MgSO_4.3H_2O$,[103] $K_6R_4(SO_4)_9$ and $K_7R_3(SO_4)_8$ (R = Lanthanide element),[104] and of $Al_2(SO_4)_3$ and $Ga_2(SO_4)_3$[105] have been studied. The available data for the solubility of calcium sulphate in water has been used to calculate the standard thermodynamic properties of the solution process.[106] The introduction of $SO_4{}^{2-}$ ion onto Fe_2O_3 gives a catalyst which exhibits pronounced catalytic activity for acid catalysed reactions. An i.r. study of the catalyst showed the formation of $>SO_2$ species after the oxidation.[107] Structural studies have been carried out on $Cu_4[(OH)_6SO_4].2H_2O$[108] and $LiKSO_4$.[109]

Several papers have described studies on phase systems involving the sulphate ion and these are collected together in Table 1.

Table 1. Phase systems involving the sulphate ion.

System	Ref	System	Ref
$Hf(SO_4)_2-H_2O$	110	$Al_2(SO_4)_3-In_2(SO_4)_3-H_2O$	116
$UO_2{}^{2+},Ti^{4+},NO_3^-,SO_4^{2-},H_2O$	111	$K_2SO_4,MgSO_4,ZnSO_4,H_2O$	117
K^+,Cs^+,SO_4^{2-},H_2O	112	$K_2S_2O_7-V_2O_3(SO_4)_2$	118
$RbVO_2SO_4-Rb_2SO_4-H_2SO_4-H_2O$	113	$K_2SO_4,MgSO_4,CuSO_4,H_2O$	119
$Li^+,Rb^+/F^-,SO_4{}^{2-}$	114	$K_2SO_4,MgSO_4,CoSO_4,H_2O$	120
$K,Rb/F^-,SO_4{}^{2-}$	114	K_2CO_3,Rb_2SO_4,H_2O	121
$(NH_4)_2HPO_4-K_2S_2O_3-H_2O$	115	$(NH_4)_2PO_4,(NH_4),H_2PO_4,K_2SO_4,H_2O$	122
$(NH_4)_2H_2PO_4-K_2S_2O_3-H_2O$	115	$(NH_4)_2HPO_4,(NH_4)H_2PO_4,K_2S_2O_3$	123
		$Li,Na,K/CO_3,SO_4,OH$	124

Metal oxidation in a $HSO_3F/S_2O_6F_2$ mixture has been used to prepare the fluorosulphate derivatives of germanium, $GeF_2(SO_3F)_2$, $(ClO_2)_2Ge(SO_3F)_6$ and $Cs_2[Ge(SO_3F)_6]$ and in the tin system a new fluorosulphate $M[Sn(SO_3F)_5]$ where M = K^+ or Co^+.[125] The same oxidising mixture has also been used to prepare fluorosulphates of Zn, Cd and Hg of the type $M(SO_3F)_2$.[126]

A simple synthetic route to pure $Pt(SO_3F)_4$ has been described: the compound is an excellent fluorosulphate ion acceptor forming either $[Pt(SO_3F)_6]^-$ or $[Pt(SO_3F)_5]^-$. In a solution of HSO_3F the novel dibasic acid, $H_2Pt(SO_3F)_6$ is formed.[127]

Bis[(trifluoromethyl)sulphonyl]imide, $(CF_3SO_2)_2NH$ has been prepared in 48% yield by the sequence of reactions shown in Scheme 8:

$$CH_3SO_2Cl \xrightarrow{KF} CH_3SO_2F \xrightarrow[HF]{ECF} CF_3SO_2F$$

(ECF = electrochemical fluorination)

$$CF_3SO_2F + 3NH_3 \xrightarrow{NH_3} NH_4NHSO_2CF_3 \xrightarrow{HCl} CF_3SO_2NH_2 \xrightarrow{NaOCH_3}$$

$$CF_3SO_2NHNa \xrightarrow{[(CH_3)_3Si]_2NH} CF_3SO_2N(Na)Si(CH_3)_3 \xrightarrow{CF_3SO_2F}$$

$$(CF_3SO_2)_2NNa \xrightarrow{H_2SO_4} (CF_3SO_2)_2NH \ (48\%)$$

Scheme 8

The strong acidity of $(CF_3SO_2)_2NH$ allows the preparation of many derivatives to be carried out in a straightforward manner as shown in Scheme 9:[128]

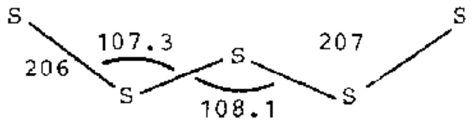
$$\begin{tikzcd}
CsN(SO_2CF_3)_2 + HF & \\
(CF_3SO_2)_2NH \arrow[u, "CsF"', "22^\circ C"] \arrow[r, "ClF", "-111 \text{ to } 0^\circ C"'] \arrow[d, "HSi(CH_3)_3"', "22^\circ C"] & (CF_3SO_2)_2NCl + HF \\
(CF_3SO_2)_2NSi(CH_3)_3 + H_2 &
\end{tikzcd}$$

Scheme 9

The indium thiosulphates, $In_2S_2O_3.2H_2O$, $In_2S_2O_3.InOH.2H_2O$ and $In_2S_2O_3.2InNO_3.2H_2O$ have been isolated as solid products from the reaction of Indium(I) with thiosulphate ion in aqueous solution.[129] The crystal structure of $Na_2S_2O_3$ has been determined at 120K, the average S-S and S-O bond distances were found to be 2.007 and 1.479Å, respectively.[130] A reinvestigation of the crystal structure of $K_2S_2O_5$ showed the compound to contain a plane of symmetry (S-S-O) and a long S-S bond (2.2194Å) between the thionite and thionate groups. The S-O distances are 1.4870Å in the thionite group and 1.453 and 1.4602Å in the thionate group.[131] The hydrolysis of the $N(SO_3)_2^{3-}$ ion has been studied. In a neutral environment the ion is stable even at 100°C, but in acid conditions the ion transforms itself into $NH(SO_3)_2^{2-}$ and then into NH_3SO_3 and finally into NH_4^+.[132] The electronic structure of the SF_5O^- anion has been calculated.[133]

6.2.5 Sulphides

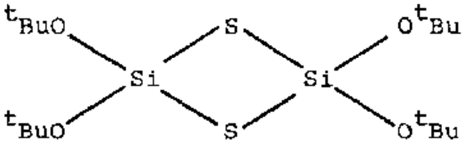
The crystal structure and Raman spectra of $Na_2S.5H_2O$ have been investigated with special attention being paid to the hydrogen bonds within the structure. Three different O-H---S bonds with O---S = 3.30, 3.32 and 3.45Å and with H---S = 2.35, 2.36 and 2.53Å were found.[134] Na_2S_5, formed by the reaction of β-Na_2S_2 and excess sulphur in a two stage reaction (at 200°C and 500°C), contains sulphur in the form of unbranched zig-zag chains of S_5^{2-} (48) in cis conformation.[135]



(48)

$Ag_6B_{10}S_{18}$ has been prepared as a novel thioborate from the reaction of Ag_2S, B and S at 700°C. According to the X-ray crystal structure analysis the anionic part of the compound contains $B_{10}S_{20}$ "supertetrahedra" consisting of ten parallel corner sharing BS_4 tetrahedra with a mean B-S bond length of 1.915Å.[136] A structural study has shown the ternary sulphide $KGaS_2$ to have a layer structure with each layer being made up of tetrahedral Ga_4S_{10} polyanions.[137] The new compound $Ba_5(GaS_4)_2$ contains isolated GaS_4^{5-} tetrahedra and is the first ortho-thiogallate(III) to be characterised.[138] A series of alkaline earth thioindates, MIn_2S_4 have been prepared by the reaction of alkaline earth metal oxoindates with H_2S. Thioindates of the type $M_3In_2S_6$ were also prepared.[139]

Two papers in a series of contributions to the chemistry of silicon-sulphur compounds have been published. The first deals with the ^{29}Si n.m.r. spectra of three series of compounds $(RO)_3SiSR'$, $(^iPrO)_{4-n}Si(SEt)_n$ and cyclic Si-S compounds.[140] The second describes the crystal structure of $[(^tBuO)_2SiS]_2$, prepared by the alcoholysis of SiS_2 by t-butanol. The molecule contains a planar Si_2S_2 ring (49) with Si-S bond distances of 214.2 and 213.1pm and bond angles S-Si-S = 97.8° and Si-S-Si = 82.2°.[141]



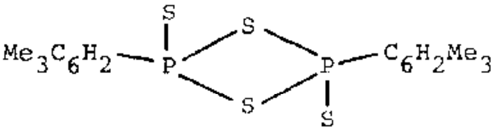
(49)

The preparation of the compounds $Na_8Si_4X_{10}$ and $Na_8Ge_4X_{10}$ where X = S or Se has been described.[142] The compounds Tl_4TiS_4, Tl_4SnS_4 and Tl_4TiSe_4 have been shown to be isostructural and to contain isolated tetrahedral thioanions which are connected to each other by Tl^+ ions. The mean bond lengths are Ti-S = 2.26, Sn-S = 2.40, Ti-Se = 2.38Å. Tl-S = 2.93 to 3.98Å and Tl-Se = 3.03 to 3.96Å.[143] The sulphide $In_5Sn_{0.5}S_7$ has been shown to have the same structure as In_6S_7 in which one indium 1+ ion is substituted by half a tin 2+ ion.[144]

An alternative explanation for the stability of PS_3As_3 relative to P_4S_3 and As_4S_3 has been proposed based on the concept of topological charge stabilisation.[145] P_4S_3 under glass-filtered u.v. irradiation is rapidly cleaved by alkyl and aryl disulphide to give tetrathiophosphate esters, $SP(SR)_3$ and trithiophosphite esters, $P(SR)_3$. In a competition reaction MeSSMe and PhSSPh reacted to a similar extent with P_4S_3 to give all eight possible products $S_xP(SPh)_n(SMe)_{3-n}$ where x = 0 or 1 and n = 0 to 3. P_4S_3 is similarly cleaved by sulphuryl chloride under thermal conditions to give $SPCl_3$ and PCl_3 with no evidence for intermediates being formed.[146] The reaction of P_4S_{10} with P_4O_{10} in different molar ratios has led to the identification of the following oxide sulphides; $P_4O_6S_4$, $P_4O_7S_3$, $P_4O_5S_5$, $P_4O_4S_6$, $P_4O_3S_7$, $P_4O_2S_8$ and P_4OS_9.[147]

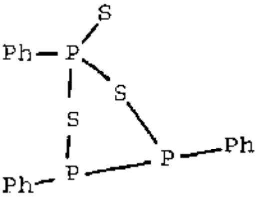
The 1:1 reaction between $PRCl_2$ (R = $C_6H_2Me_3$-2,4,6) and $(Me_3Si)S$ in toluene yield $(RPS)_4$ which slowly disproportionates to $(RPS)_2$

at temperatures between 35 and 40°C over 3 days. The eight membered $(PS)_4$ ring adopts the crown configuration but is disordered whilst $(RPS_2)_2$ (50) contains a four-membered ring with two trans exocyclic sulphur atoms.[148]



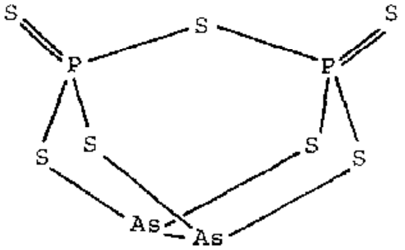
(50)

The 1:1 reaction between $PPhCl_2$ and $(SnMe_3)_2S$ in CS_2 provides a convenient direct route to $(PhP)_3S_3$ (51) which reacts with elemental sulphur to give $(PhP)_2S_4$. Compound (51) contains an unsymmetrical five-membered ring with one exocyclic sulphur atom and this structure does not agree with a previous proposal based on n.m.r. data. $(PhP)_2S_4$ contains a four membered ring with two trans exocyclic sulphur atoms.[149]



(51)

The crystal and molecular structure of $As_2P_2S_7$ (52) has been determined and has been shown to be isosteric with P_4S_7 with the mean bond lengths As-As = 250.9, As-S = 225.7, P-S = 208.3 and P=S = 193.2pm.[150]



(52)

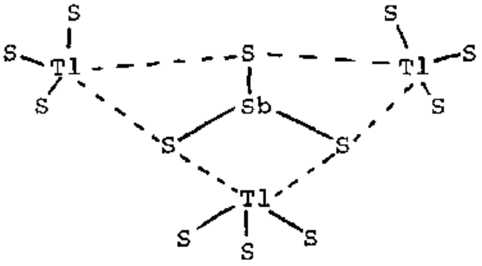
The vibrational spectrum of crystalline PAs_3S_3 and its Raman spectrum in the molten state have been measured. In the molten state a partial decomposition was observed according to equation (34).[151]

$$2PAs_3S_3 \rightleftarrows P_2As_2S_3 + As_4S_3 \qquad \ldots(34)$$

The crystal vibrational spectra of $P(CH_2CH_2CN)_3$ and its sulphide, oxide and selenide have been studied. The difference between $\nu(PS)$ in $P(CH_2CH_2CN)_3S$ and $\nu(PSe)$ in the selenide is much greater than the differences $\nu(PS)-\nu(PSe)$ usually observed in related PR_3S and PR_3Se molecules.[152]

A series of dicarboxymethylphosphane sulphides (and selenides) $MeP(S)[OC(O)R]_2$ have been prepared from $MeP(S)Cl_2$ and silver carboxylates and spectroscopically charaterised.[153] Ethylenediammoniumhexasulphide has been synthesised from ethylenediamine, sulphur and gaseous H_2S in aqueous solution. The sulphur atoms form unbranched zig-zag chains of S_6^{2-} in all-trans conformation.[154]

Crystal structures of four ternary antimony sulphides have been determined. Tl_3SbS_3 contains SbS_3 groups strongly bound to three Tl atoms through Sb-S-Tl bridges to give Tl_3SbS_{12} groups (53).[155]



(53)

$SrSb_4S_7.6H_2O$ contains anionic $(Sb_4S_7^{2-})_x$ strings which are arranged parallel in sheets separated by the hydrated Sr^{2+} ions.[156] $Sn_6Sb_{10}S_{21}$ was previously reported as $SnSb_2S_4$ and consists of bands of edge sharing half octahedra with the repeat unit consisting of two bands of composition $(M_{10}S_{12})_n$ and three of composition $(M_4S_6)_n$.[157] The structure of $Sn_3Sb_2S_6$ has been determined by high resolution transmission electron microscopy.[158] The structure of $Cu_4Bi_4S_9$ has been redetermined and refined.[159]

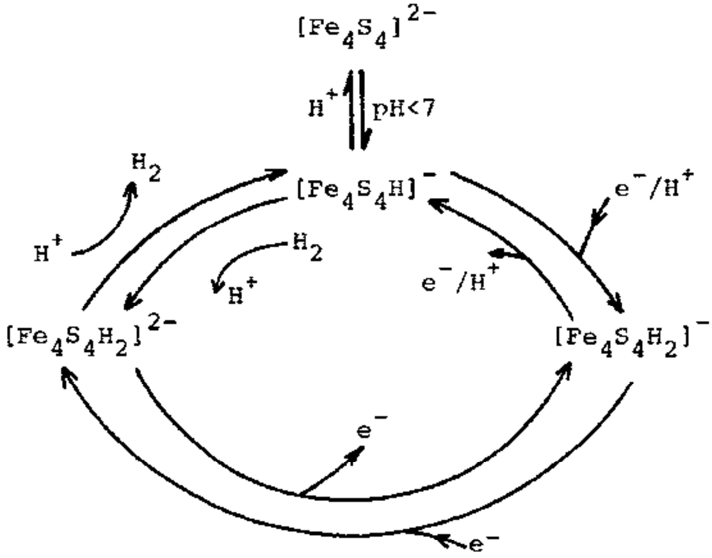
The electrochemical behaviour of sulphide ions in molten dimethylsulphone at 127°C has been carried out. The oxidation of the sulphide ion on a Pt electrode leads to sulphur through the formation of a blue polysulphide species but the oxidation of an amalgamated gold electrode in the presence of sulphide ions leads to the formation of mercury sulphide with an HgS_2^{2-} complex being formed.[160]

The photocatalytic decomposition of H_2S continues to be of interest. Three papers have given details on the improvements which can be made to the CdS catalysts. In the first paper a series of mixed semiconductor dispersions were compared with significant improvements being observed for a catalyst of composition CdS + TiO_2-RuO_2 (0.5wt%) in which electron transfer from the conduction band of CdS to that of TiO_2 takes place in alkaline suspensions containing SH^- ions.[161] In the second paper an improvement by a factor of 7 is claimed for a catalyst comprising CdS loaded with 0.5wt% RuS_2 compared with CdS loaded with 0.5wt% RuO_2.[162] The third paper describes a novel system comprising CdS crystallites embedded in a polymer (Nafion) matrix that also contains a hydrogen evolution catalyst (Pt).[163]

As in previous years a large number of publications have dealt with sulphides of transition metals either as binary or ternary compounds or as metal clusters. A selection of these publications are reviewed briefly in the following section.

Scanning electron microscopy has shown that the solid state reaction of polycrystalline CdS and Cr_2S_3 starts by covering the crystallites of the reactants with a layer of the reaction product $CdCr_2S_4$.[164] The interactions of the protein bovine insulin and bovine serum albumin with the water soluble cluster $Fe_4S_4(SCH_2CH_2CO_2)_4^{6-}$ have been described. Electrochemical studies indicate the direct involvement of protons as well as electrons in redox reactions and the mechanism shown in Scheme (10) was proposed for hydrogenase activity which was consistent with the present findings and with reports of the maximum rates of hydrogenase activity under acidic conditions.[165]

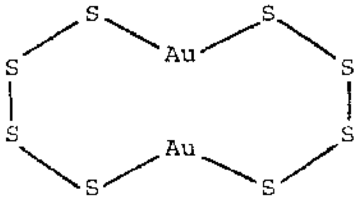
Resonance Raman spectra have been reported for the dimeric iron chalcogen complexes $[Fe_2X_2(Se)_4]^2$, $[Fe_2X_2(SePh)_4]^{2-}$, $[Fe_2X_2Cl_4]^{2-}$ and $[Fe_2S_2Br_4]^{2-}$ where X = S or Se.[166] Fe_7S_8, Co_9S_8 and Ni_3S_2 have been prepared as single phase polycrystalline materials by heating the appropriate metal sulphates in a controlled mixture of



Scheme 10

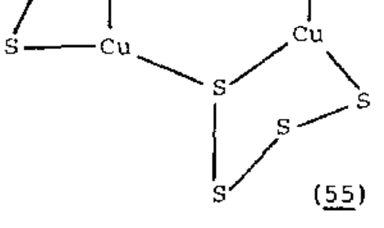
H_2 and H_2S at low temperature. The X-ray diffraction pattern and field-dependent magnetic susceptibility of Fe_7S_8 were found to be affected by the thermal history of the sample with the observed differences being related to the vacancy ordering associated with ferrimagnetic Fe_7S_8.[167] The synthesis and structures of three new iron-sulphur cluster compounds, $(Et_4N)_3(Fe_6S_6Cl_6)$,[168] $(Et_4N)_2(Fe_6S_6I_6)$[169] and $(Et_4N)_3Fe_8S_6I_8.2CH_2Cl_2$[170] have been announced. Examples of the homoleptic binuclear Fe(II) and Co(II) thiolates of the type $[M_2(SR)_6]^{2-}$ have also been synthesised and structurally characterised.[171]

Crystals of αNi_3S_2, NiS and NiS_2 together with solid solutions of $Fe_{1-y}Ni_yS_x$ have been grown by chemical transport reactions using halogens, hydrogen halides and GeI_2 as transport media.[172] The reaction of H_2S and PEt_3 with $Ni(C_2H_4)(PPh_3)_2$ has been used to prepare the mercaptodithiotrinickel complex $[Ni_3(\mu_3\text{-}S)_2(SH)(PEt_3)_5]BPh_4$ and a structure determination carried out.[173] Several publications have dealt with the chemistry of copper-sulphur cluster compounds. The addition of ethanolic polysulphide to a solution of $Cu(CH_3COO)_2.H_2O$ and PPh_4Br in CH_3CN gives the mixed crystal Cu(I) compound $(PPh_4)_2[Cu_4(S_4)(S_5)_2]_{0.4}$-$[Cu_4(S_5)_3]_{0.6}$. With a comparable preparative method different monocyclic polysulphide ring species of gold such as AuS_9^- and $Au_2S_8^{2-}$ could be obtained. The reaction of $HAuCl_4.4H_2O$ with ethanolic polysulphide enabled the remarkable highly symmetrical $Au_2S_8^{2-}$ ring (54) compound to be isolated as a diamagnetic PPh_4^+ salt.[174]



(54)

Two independent groups have described the preparation of the binary polynuclear copper complex $(Cu_6S_{17})^{2-}$ from either $Cu(acac)_2$ and ethanolic polysulphide solution[175,176] or by the reaction of methanolic Cu(I) thiolate solution with elemental sulphur.[177] A good agreement for the crystal structure of the anion was found, which had an unusual arrangement of the metal atoms and novel types of ligand coordination particularly of polysulphide S_4^{2-} and S_5^{2-} ions. The use of Li_2S in place of elemental sulphur yields the $Cu_{12}S_8^{4-}$ ion which has a closed metal-sulphur cluster in the shape of a cube with sulphur atoms at each corner and copper atoms at the midpoints of each side.[178] Two further copper-sulphur ring systems have been characterised; $(S_6)Cu(S_8)Cu(S_6)^{4-}$ which consists of two CuS_6 seven membered rings with different conformation (C_2 and C_3 symmetry) which are linked via an S_8^{2-} ligand: and $Cu_3(S_4)_3^{3-}$ (55) which consists of three CuS_4 five membered rings with half-chair conformation and a central Cu_3S_3 six membered ring with alternating long and short Cu-S bond lengths and chair conformation.[179]



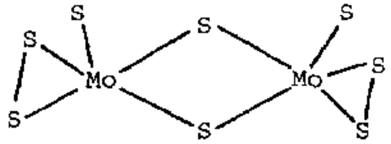
(55)

The synthesis and complete structural determination of the layered system $Mn_{0.87}Ci_{0.26}PS_3$ has been reported. The X-ray diffraction data showed the existence of disorder and led to Cu-S distances inconsistent with the data from EXAFS. This was accounted for by the fact that besides the classical S_3PPS_3 entities two distinct types of pseudooctahedra are randomly distributed between the layers - MnS_6 entities with the expected Mn-S distances of 2.61Å and $S_3Cu...CuS_3$ entities with centre to apex distances of 2.83Å.[180] Chemical transport methods have been used to grow single crystals of normal spinel phases in the pseudo binary system ABS_2-SnS_2 where A = Cu or Ag and B = Al, Cr.[181]

EXAFS studies have been carried out on the amorphous molybdenum and tungsten trisulphides and gave metal-metal distances between 2,74 and 2.79Å as well as normal, but disordered metal-chalcogen distances of Mo-S = 2.44, W-S = 2.41, Mo-Se = 2.53 and W-Se = 2.55Å. EXAFS of the triselenides gave Se-Se distances of 2.35 to 2.37Å. It is proposed that the important structural unit of these amorphous materials is a binuclear metal site with a triple bridge consisting of one chalcide ion and one dichalcide ion.[182] The tetrathiomolybdate ion MoS_4^{2-} can be readily oxidised by organic disulphides to the dinuclear complex $Mo_2S_8^{2-}$ which contains reduced pentavalent molybdenum (equation 35).

$$2MoS_4^{2-} + RSSR \rightarrow Mo_2S_8^{2-} + RS \qquad ...(35)$$

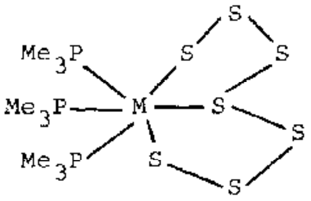
X-ray structural analysis confirmed the presence of the binuclear $Mo_2(S)_2(\mu S)_2(S_2)_2^{2-}$ ion (56) which is isostructural with the previously reported $Mo_2O_2(\mu S)(S_2)_2^{2-}$ ion.[183]



(56)

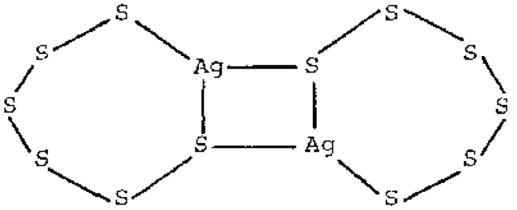
Passage of oxygen into an aqueous solution of $[(Mo^{III})_2(S)_2(CN)_8]^{6-}$ leads to the formation of a mixed-crystal which contains the isostructural ions $[Mo_2^{III/IV}(SO_2)(S_2)(CN)_8]^{5-}$ which is paramagnetic and $[(Mo^{IV})_2(SO_2)(S_2)(CN)_8]^{4-}$ which is diamagnetic.[184] Cyclic voltammetry has been used to characterise electrochemical reductions of the complexes cis-[$MoY(C_5H_{10}NO)_2$] Y = O_2, OS or S_2.[185]

Attempts to prepare single crystals of $(Me_3P)_3MS_6$ where M = Ru or Os by slow diffusion of hexane in solutions of the compounds in acetone led to the formation of (57) which is the first example of a polysulphide metal complex with a tridentate S_n^{2-} ligand.[186]



(57)

The novel inorganic condensed ring system $Ag_2(S_6)_2^{2-}$ (58) has been obtained as the PPh_4^+ salt from solutions of $AgNO_3$ and polysulphide in CH_3CN into which NH_3 and then H_2S were bubbled for a short time in the presence of PPh_4Br. The central four membered ring is exactly planar and the two seven membered rings have a distorted chair conformation.

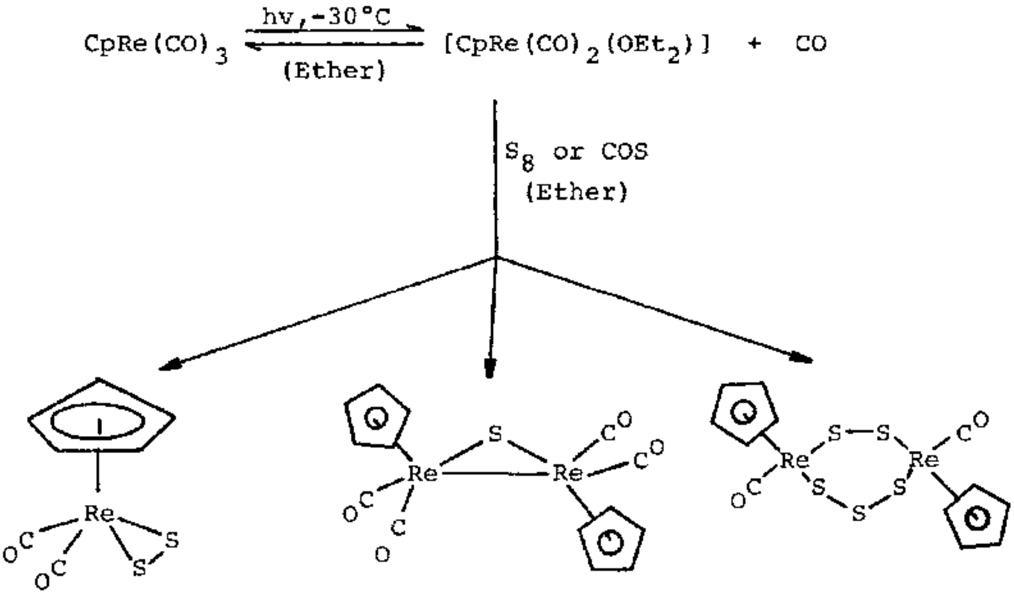


(58)

Also isolated were salts of AgS_9^- and the rather unstable heptasulphide $(PPh_4)(NH_4)S_7.CH_3CN$.[187]

The reaction of TaX_5 (X = Br or Cl) with Sb_2S_3 in molar ratio 3:1 leads to the formation of TaX_3S compounds which form complexes of the type $TaX_3S.2L$ (L = dimethyl sulphide, tetrahydrothiophene or MeCN) and $TaX_3S.L$ (L = 1,2(bis-phenylthioethane). Crystal structure determination of the chloride complex of the latter compound showed the metal to have a distorted octahedral coordination with a terminal Ta=S bond of distance 2.204Å, three metal-chlorine interactions and two bonds to the sulphur atoms of the ligand.[188]

The reactions of the coordinatively unsaturated fragment [$CpRe(CO)_2$], prepared by photolytic CO elimination from [$CpRe(CO)_3$], with either S_8 or COS are shown in Scheme (11).[189]



Scheme 11

The synthesis and crystal structure of $(Ph_4As)_4(Au_{12}S_8)$ has been described.[190] The compound has the same structure as reported for the $Cu_{12}S_8^{4-}$ ion mentioned earlier in this review (reference 178). The crystal structures of the mercury-sulphur compounds $[Hg(S_6)_2]^{2-}$,[191] and complexes with the general formula $(Me_4N)_4[E_4M_{10}(SPh)_{16}]$ where E = S, Se; M = Zn or Cd[192] have been reported.

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

6.2.6 Bonds to Carbon

The photoelectron spectrum of NCNCS, produced by thermal isomerisation of $S(CN)_2$ has been analysed by comparison with the spectra of related molecules and with the aid of MO calculations. The first ionisation potential was found to be 10.58eV and the observed separation of the first two photoelectron bands was consistent with a CNC bond angle of 155° reflecting the molecules

Table 2. Phase Systems

System	Ref.	System	Ref.
Tl_2S-GeS_2	193	SnS_2-HCl-$CaCl_2$-H_2O	198
Hg-Tl-S	194	As_2S_3-Yb_2S_3	199
Tl-Cd-S	195	Ga_2S_3-Ga_2O_3	200
Nd-S	196	$NbUS_3$-$TaUS_3$	201
Tl-Si-S	197	Fe_2As-Na_2S	202
		Cu_3As-ZnS	203

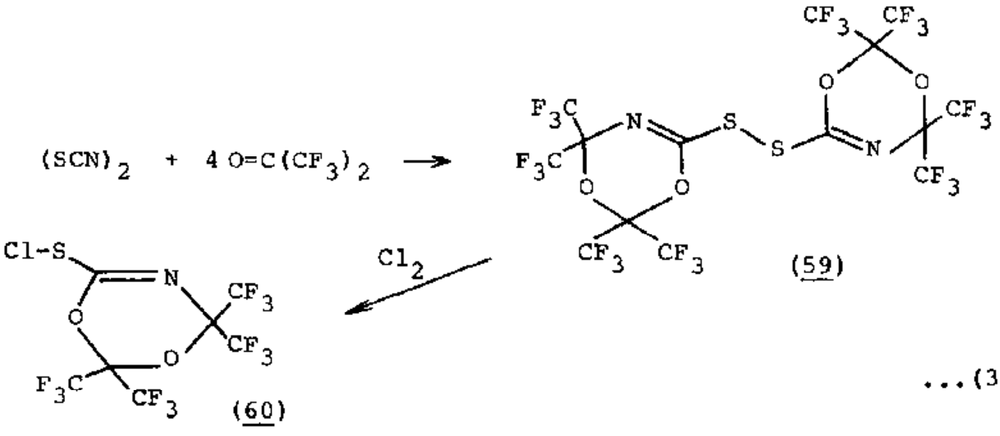
quasilinear character.[204] The radical cation $(CH_3)_2S^{+\cdot}$ has been found to be formed as an intermediate in the reaction of dimethyl sulphoxide with hydrogen atoms in aqueous solutions containing high concentrations of $HClO_4$. The radical cation absorbs at 285nm and is, in fact, assumed to exist as stoichiometrically defined three-electron-bonded complexes with $HClO_4$ or H_2O.[205] Sulphur atoms have been shown to react with CH_3SCH_3 to generate elemental sulphur and CH_3SSCH_3 as major products along with small amounts of C_2H_6; and with thietane to give $\overline{CH_2(CH_2)_2SS}$ and C_2H_4 in comparable yields. It is proposed that the primary adducts are vibrationally not thiosulphoxides which may then isomerise to the corresponding disulphide fragment via C-S cleavage. Bimolecular reactions between two thermalized ground state thiosulphoxide molecules and/or a thiosulphoxide molecule and an S_2-S_7 radical lead to regeneration of the substrate and to the formation of S_3-S_8 which ends up as elemental sulphur.[206] CH_3SH and $(CH_3S)_2$ as well as their mixtures have been photolysed in the presence of NO at 23°C. The identified reaction products were CH_3SNO, $(CH_3S)_2$, H_2 and N_2. Hydrogen atoms formed from the photolysis of CH_3SH reacted with both NO and CH_3SH.[207] Ab initio calculations of the geometries of H_2CS, HFCS and F_2CS as well as their protonated cations have shown that the H or F protonation leads to molecular complexes of the form $HX...YCS^+$ and for H_2CS and F_2CS the S-protonation site is favoured whereas for HFCS the linear complex $HF...HCS^+$ is the most stable form.[208] Calculations of the structures of $SH_3{\equiv}CH$, $SF_3{\equiv}CH$, $SF_3{\equiv}CF$ and the staggered and eclipsed forms of $SF_3{\equiv}C{-}CF_3$ have shown the SH_3 and SF_3 groups to have essentially octahedral configuration with XSF angles between 91 and 93° in every case. The remaining three sulphur orbitals make up the S≡C triple bond which has a length of 1.41-1.45Å compared with a S=C double bond length of 1.54Å in $SF_4{=}CH_2$.[209]

The compound $F_3C{-}C{\equiv}SF_3$ has been prepared by pumping $F_3C{-}CH{=}SF_4$ in the gaseous state at 50-60°C and 10^{-1}mbar through a 40cm long quartz tube packed with dried KOH (equation 36). The product is

$$F_3C{-}CH{=}SF_4 \rightarrow F_3C{-}C{\equiv}SF_3 + HF \qquad ...(36)$$

a colourless gas mp -122°C bp -15 to -10°C and is not as stable as $F_3C{-}CH{=}SF_4$ since it oligomerises to a product which is liquid at room temperature and crystalline at low temperature.[210]

Three publications have been concerned with reactions of $(SCN)_2$. The reaction of $(SCN)_2$ with SnI_4 has been shown to give a compound with the formula $ISn(NCS)_3.I_2$ in which I_2 molecules form charge-transfer complexes with the thiocyanate groups.[211] The oxidation of $[OsCl_5I]^{2-}$ with $(SCN)_2$ in CH_2Cl_2 yields the bond isomers $[OsCl_5(NCS)]^{2-}$ and $[OsCl_5(SCN)]^{2-}$ which have been isolated as pure compounds by ion exchange chromatography.[212] The cycloaddition of $(SCN)_2$ with hexafluoroacetone has been shown to give the 4H-dioxazine (59) in 82% yield. X-ray structure analysis of (59) showed the two 4-H dioxazine rings to be coupled via the disulphide bridge so that the molecule has an almost twofold symmetry axis perpendicular to the S-S bond which has a length of 202.0pm with a C-S-S-C torsion angle of -86.6° (59) can be cleaved at the S-S bond by chlorine to give the sulphenic acid chloride

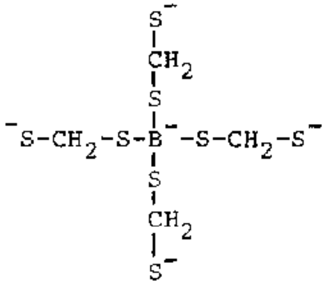


...(37)

(<u>60</u>) in 45% yield.[213]

Single crystals of the trithiocyanatoargentates $Rb_2Ag(SCN)_3$ and $CsAg(SCN)_3$ have been obtained by crystallisation from highly concentrated aqueous solutions. Tetrahedra of $Ag(SCN)_4$ are connected by common corners to give polymeric units in the Rb compounds but in the Cs compound dimeric $Ag_2(SCN)_6$ anions were found.[214]

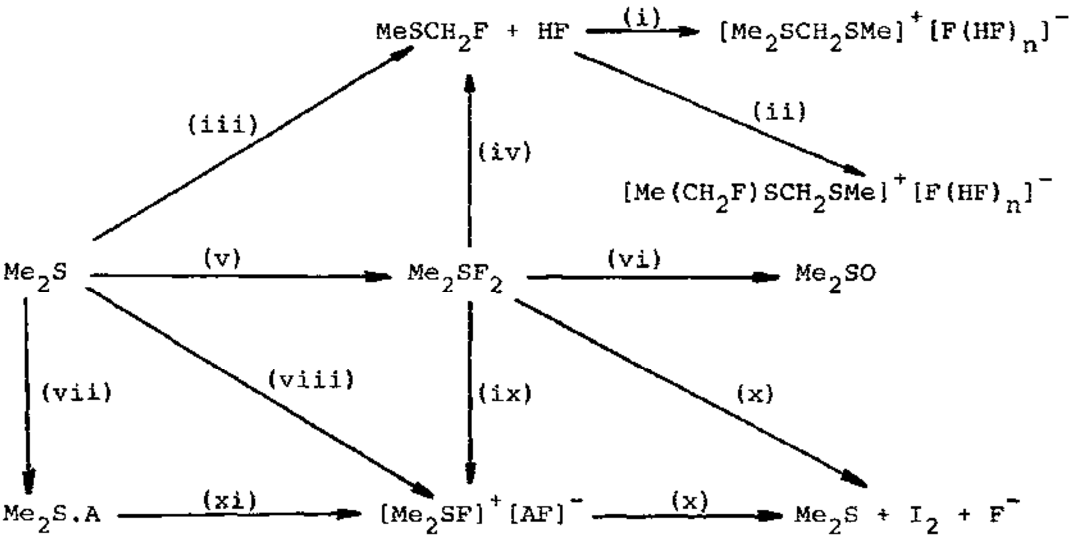
Carbon disulphide reacts with $NaBH_4$ in THF, acetonitrile or N,N-dimethylthioformamide to give pentasodium tetrakis(dithiomethylene)borate. The reaction mechanism for the formation of this new anion $[B^-(S-CH_2-S^-)_4]$ (<u>61</u>) can be described by step-wise CS_2 insertion into the B-H bonds of BH_4^- and H^- transfer from BH_4^- to the intermediates.[215]



(<u>61</u>)

The factors responsible for affecting the metal-promoted head-to-head dimerisation of CS_2 to C_2S_4 have been studied. Addition of CS_2 to a solution of $[RhCl(C_2H_4)_2]_2$ in THF and triphos in the presence of $NaBPh_4$ gives the diamagnetic complex [triphos-Rh(μC_2H_4)-Rh-triphos]$(BPh_4)_2$ whilst in the presence of $NaBPh_4$ the complex [triphos-RhCl($\eta^2 CS_2$)] is formed. The latter may be converted to the former complex by treatment with Lewis acids.[216]

The controlled reaction of dimethylsulphide with XeF_2 in a non-acidic media gives rise via CH_2FSMe to a product best formulated as $[Me_2SCH_2SMe]^+[F(HF)_n]^-$. In HF solution at -23°C the reaction gives the cation Me_2SF^+ solid derivatives of which may also be prepared by the reaction of XeF_2 with $Me_2S.A$ (A = BF_3 or AsF_5). The formation of dimethylsulphur difluoride are given in Scheme 13.[217]

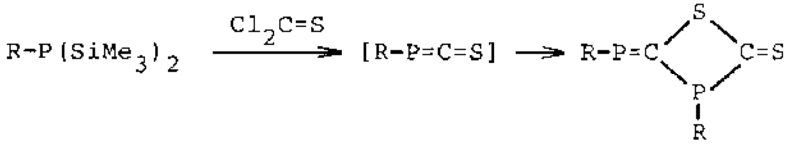


(i) Me_2S; (ii) HF; (iii) XeF_2-CD_3CN or XeF_2-$CFCl_3$ + CsF; (iv) heat; (v) AgF_2-$CDCl_3$; (vi) Pyrex; (vii) A = $(HF)_n$, BF_3, or AsF_5; (viii) XeF_2-HF; (ix) BF_3; (x) I^-(aq); (xi) XeF_2.

Scheme 13

The crystal structures of the lithium dithiocarbamates, $Li(C_5H_{10}NS_2].3H_2O$,[218] $Li[C_3H_6NS_2].4H_2O$[219] and $Li[C_7H_{14}NS_2].3H_2O$[220] have been described. In each structure pairs of distorted $Li(H_2O)_4^+$ tetrahedra are formed by edge-sharing with the pairs being linked to a three dimensional network by six O-H...S hydrogen bonds.

The reactions of dithiooxamide with chloromethylsilanes have been shown to give, N,N'-silylsubstituted dithiooxamides, cyclic dithiooxamides and a dithiooximide depending on the reaction conditions used.[221] Neutron diffraction data at 15K has been used to refine the crystal structure of thioacetamide. The structure contains two symmetric independent molecules; one rotamer has close to m symmetry with planar S=C-C-N and C-C-NH_2 moieties, in the other the methyl group is twisted by 15.6° and the S=C-C-N and C-C-NH_2 moieties are significantly non planar.[222] The first evidence for the existence of a phosphathioketene has been published. The reaction of R-P$(SiMe_3)_2$ with thiophosphagene in dioxane was assumed to give the [R-P=C=S] intermediate which on addition of acetonitrile underwent an unsymmetrical [2+2] cycloaddition to form (62).[223]



(62)

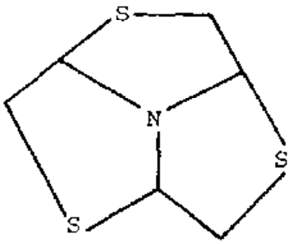
...(38)

Two papers on the chemistry of trimethylsilylxanthic acid have been published: the first describes the synthesis and properties of trimethylsilylxanthates $M[S_2C\text{-}OSiMe_3]$ with M = Li, Na, K, Rb and Cs,[224] and the second paper describes the preparation of the hitherto unknown S-alkyltrimethylxanthates $Me_3SiO\text{-}CS\text{-}SR$ where R = Me and Et.[225] Three different methods have been described for the preparation of the esters RO-CO-NCS (R = Me,Et), RS-CO-NCS and RS-CS-NCS with R = Et, nPr.[226] nPrS-CO-F, EtS-CS-F and ^{n}PrS-CS-F have been prepared by reaction of the corresponding chloro-compound with KF using phase transfer catalysts and the esters RS-CS-Br (R = Et, nPr) by reaction of RSH with $SCBr_2$ in the presence of pyridene.[227]

The reaction of $ClSCF_2CF_2SCl$ with aqueous H_2O_2 has been shown to result in the formation of $ClSO_2CF_2CF_2SSCF_2CF_2SO_2Cl$ which was characterised by ^{19}F n.m.r., mass, i.r., and Raman spectroscopy.[228]

As a contribution to the research on synthetic metals derived from (bis-ethylenedithio)tetrathiafulvalene, (ET) the synthesis and structure determination of $(ET)_2ReO_4$ and the new isostructural derivative $(ET)_2BrO_4$ have been carried out. Contrary to earlier work on $(ET)_2ReO_4$ neither of these $(ET)_2X$ derivatives possessed a structure similar to the known metallic conductor tetramethyltetraselenafulvalene.[229] Tetrathiafulvalene reacts with $SnCl_4$ or $SnBr_4$ to give the corresponding salts $(ttf)_2SnX_6$, and with $SnX_6{}^{2-}$ to give $(ttf)_3SnX_6$.[230]

The crystal structure of (63) reveals a general flattening of the molecule with the nitrogen atom being pulled slightly into the



(63)

plane defined by the three sulphur atoms. Ab initio calculations and the photoelectron spectrum of the compound were used to give some insight into the electronic nature of this rather unusual molecule.[231]

The kinetics and mechanism of the decomposition of thionitrites derived from thiourea have been determined by studying the decomposition of $(NMe_2)_2CSNO^+$ to $(NMe_2)_2CSSC(NMe_2)_2{}^{2+}$ + NO· spectrophotometrically.[232]

6.2.7 Other Compounds of Sulphur

The synthetic potential of the $MeOSO^+$ cation is convincingly demonstrated by its ability to alkylate even the monocation in (64) which leads to the salts (66) which contain the dication $[Me_2N)_2SF_2]^{2+}$. When $N{\equiv}SF_2\text{-}NMe_2$ and $MeOSO^+MF_6^-$ are allowed to react in 1:2 molar ratio in SO_2 (65) is formed in quantitative yield.[233]

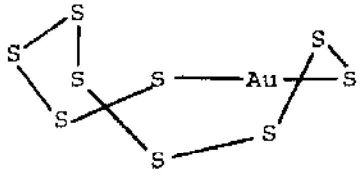
$$\begin{tikzcd} N{\equiv}SF_2NMe_2 + [MeOSO]^+MF_6^- \arrow[r] & {[MeNSF_2NMe_2]^+MF_6^-} \arrow[d, "+[MeOSO]^+SF_6^-"] \\ & {[Me_2NSF_2NMe_2]^{2+}(MF_6^-)_2} \end{tikzcd} \qquad ...(39)$$

(64) (65)

M = As or Sb.

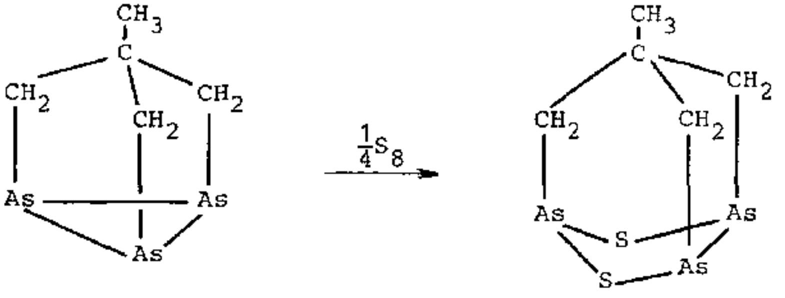
A novel type of S-H...S hydrogen bond has been observed in dithiotropolone in that intramolecular S-H...S bonds with very short S...S separations of 3.13Å and with S...H = 2.10Å and bond angle S-H...S = 136° are formed. The S-H stretching frequency is lowered by $120cm^{-1}$ from the value of the free SH group.[234]

A cyclic nonasulphidoaurate(I), $[Ph_4As][AuS_9]$ is formed as the main product of the reaction of $K[Au(SCN)_2]$ with tetraphenylarsonium polysulphide in absolute ethanol. X-ray structure analysis shows the anion to consist of a puckered AuS_9 ring (66) in which a chain of nine sulphur atoms is bound as a chelate ligand to the gold atom. The S-Au-S angle of 176° is consistent with linear coordination and the S-S bond lengths (average = 204.5), Au-S distance 227.1pm correspond to covalent single bonds.[235]



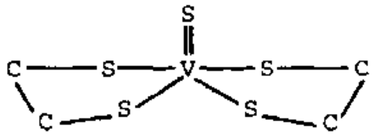
(66)

Ab initio and semi empirical CI calculations have been performed on 3,7-dihydro-1,5-dithia-2,4,6,8-tetrazocine and on the corresponding amino compound.[236] The novel 1,4-dithia-2,6-diaza-3,5-diborinane ring system results from the reaction of 3,5-dialkyl (or disec amino)substituted 1,2,4-trithia-3,5-diborolanes with 1,3-disubstituted sulphur diimide by replacement of the disulphane bridge.[237] The melting of $CH_3C(CH_2As)_3$ with elemental sulphur or selenium in the molar ratio of 1:2 results in the formation of the noradamantanes $CH_3C(CH_2As)_3E_2$ (67).[238]



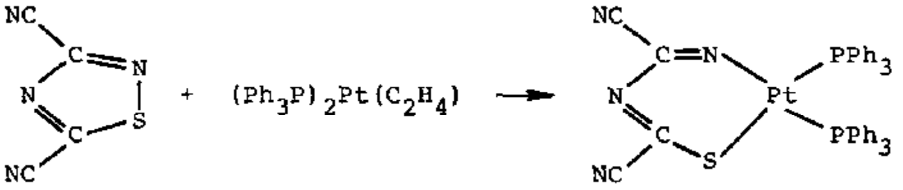
(67) ...(40)

A series of thio-chloro compounds of pentavalent niobium and tungsten have been prepared. $WSCl_3$ was obtained by the reaction of $(WSCl_4)_2$ with C_2Cl_4, with PPh_4Cl in CH_2Cl_2 it yields $(PPh_4)_2(WSCl_4)_2$ which has a dimeric structure with chloro bridges. The reaction of PPh_4Cl with $NbSCl_3$ gives $(PPh_4)(NbSCl_4)$ which contains the quadratic pyramidal $NbSCl_4^-$ ion with a Nb=S bond length of 209pm.[239] Two vanadium thiolate complexes have been prepared and their structures determined. The anion $VS(SC_2H_4S)_2]^{2-}$ (68) contains vanadium with a strongly distorted square pyramidal coordination with a V=S bond length of 2.098Å in the apical position and V-S bond lengths to the ligand are 2.348 to 2.386Å.[240]



(68)

The reaction of a Pt(O) complex with a 1,2,4-thiadiazole has been shown to give a six membered metallaheterocycle (69) in which the Pt atom has been inserted into the S-N bond of the thiadiazole.[241]



...(41)

(69)

The crystal structures of the following molybdenum complexes have been determined $(PPh_4)_2(Mo_2O_5(SC_6H_4O)_2)$,[242] $M\eta^{2}-(S_2CCH_2Bu^{+})(CO)_2(nC_5H_5)$ M = Mo and W,[243] and $MoBr_2(NO)_2(OSMe_2)_2$.[244]

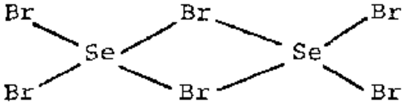
6.3 SELENIUM

6.3.1 Bonds to Halogens

The structures of crystalline SeF_4 and TeF_4 have been determined. In SeF_4 the selenium is bonded to four fluorine atoms so that including the lone pair of electrons a distorted pseudo trigonal bipyramid with longer axial S-F bonds results. In TeF_4 each tellurium atom is bonded to five fluorine atoms (distorted tetragonal pyramid) two of which (cis orientated) bridge a further neighbouring tellurium each.[245] The compounds $F_2Se(OSeF_5)_2$, $F_2Se(OTeF_5)_2$ and $F_2Te(OTeF_5)_2$ have been prepared and their structures investigated by n.m.r. spectroscopy. All three compounds have pseudo trigonal bipyramidal structures with axial $-OSeF_5$ $(-OTeF_5)$ ligands with the fluorine ligands in equatorial positions in accordance with electronegativity arguments. $F_2Te(OTeF_5)_2$ reacts further with $FOTeF_5$ to give mer-$F_3Te(OTeF_5)_3$ but no fac-$(F_3Te(OTeF_5)_3$.[246]

The novel anion $SeBr_4^{2-}$ has been prepared by dissociation of

$SeBr_2$ and subsequent reaction with bromide in acetonitrile solution. X-ray structure determination of the tetraphenyl phosphonium salt shows the salt to contain monomeric $SeBr_4^{2-}$ anions with square planar coordination of SeII and a mean bond length Se-Br of 2.598Å. $(PPh_4)_2Se_2Br_6$ was obtained from the reaction of $SeBr_4$ and Br^- in acetonitrile. The compound contains a novel type of centrosymmetric $Se_2Br_6^{2-}$ ions again with square planar coordination of the selenium (<u>70</u>). The mean terminal and bridging Se-Br bond lengths are 2.442 and 2.799Å respectively.[247]



(<u>70</u>)

6.3.2 Bonds to Oxygen

Single crystals of $SrSeO_4$ have been prepared by hydrothermal synthesis (equation 42).

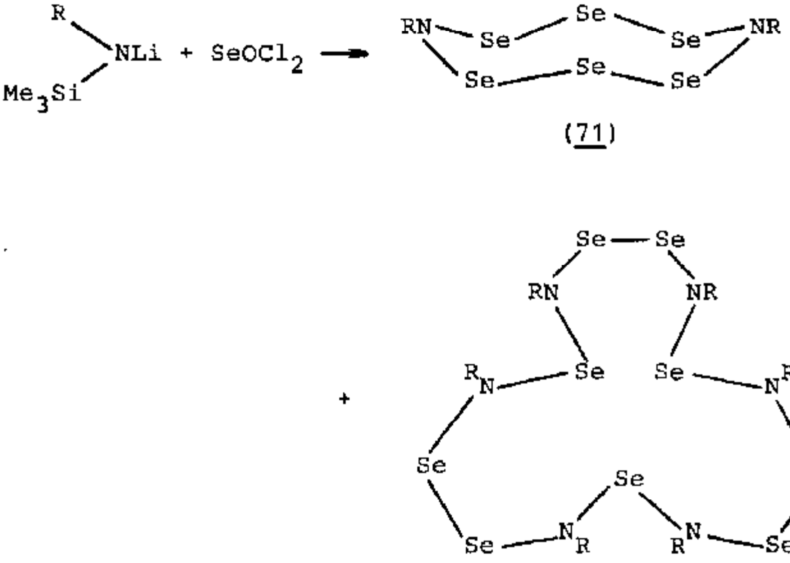
$$SrSeO_3 + NaNO_3 \rightarrow SrSeO_4 + NaNO_2 \qquad ...(42)$$

A crystal structure determination showed the compound to be ionic with SeO_4 tetrahedra with a mean Se-O distance of 1.647Å and nine coordinated Sr^{2+} ions.[248] Solubility isotherms in the $CuSeO_4$-H_2SeO_4-H_2O system have been studied at 25 and 100°C. The dehydration of $CuSeO_4.5H_2O$ and the thermal dissociation of $CuSeO_4.H_2O$ were described.[249] The following selenate phase systems have been studied; $ZnSeO_4$-H_2SeO_4-H_2O,[250] $MgSeO_4$-UO_2SeO_4-H_2O[251] and $Nd_2(SeO_4)_3$-$Sm_2(SeO_4)_3$-H_2O.[252] H_2SeO_4 or H_2TeO_4 have been used to enhance the activity of ZrO_2 catalysts. $Zr(OH)_4$ was exposed to 0.05M H_2SeO_4 or H_2TeO_4 followed by calcination in air at 600-800°C. The resulting dehydrogenation catalyst converted propan-2-ol into acetone with 100% selectivity.[253]

6.3.3 Bonds to Nitrogen

The previously unknown F_5Se-N=C=O has been prepared from $Xe(OSeF_5)_2$ and HCN. Compared with that of F_5S-N=C=O the isocyanate reactivity is reduced in F_5Te-N=C=O and even more in F_5Se-N=C=O.[254]

Diselenium dichloride and seleninyl chloride react with the lithium salt of silylated tert-butylamine with the elimination of LiCl and Me_3SiCl or LiCl, Me_3SiCl and $(Me_3Si)_2O$ respectively to form the cyclic compounds hexaselenadiazocin (71) and nonaselenahexaazacyclopentadecane (72).



(71)

(72)

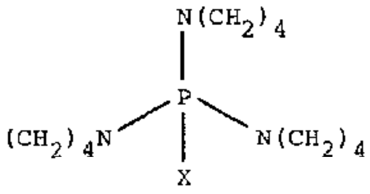
...(43)

The conformation of the N_2Se_6 ring in (71) is similar to that of the eight membered ring of the sulphur molecule and has the bond lengths S-N 183.0, Se-Se 233.5pm and angles N-Se-Se 110.0°, Se-N-Se 114.8° and Se-Se-Se 108.8°.[255]

6.3.4 Selenides

The crystal structure of $(LaO)GaSe_2$ has been shown to comprise alternating (LaO) and $(GaSe_2)$ layers thus resembling the structure of $(CaO)_4Ga_2S_5$ and being very different from $LaGaOS_2$.[256]

The thermal stabilities of the selenides of the elements of groups IV and V have been determined from a study of the curvature of the liquidus at the melting point.[257] The new compounds $K_6Ge_2Se_6$ and $K_6Ge_2S_6$ have been shown to crystallise in the monoclinic system and to be isotypic with the $K_6Si_2Te_6$ structure. $Na_6Ge_2Te_6$ however has the $K_6Sn_2Te_6$ structure.[258] The problems of the directed synthesis of solid solutions based on lead selenide and telluride which are promising opto-electronic materials have been considered by studying the P - T - x - y diagram of the Pb-Se-Te system. The conditions required for the growth of crystals from the vapour were determined and the composition of hetero structures based on lead and tin chalcogenides were studied by Auger-electron spectroscopy.[259] The structures of the compounds $[(CH_2)_4N]_3PSe$ and $[(CH_2)_4N]_3OTe$ have been determined. In both compounds (73) there is disorder in one or more of the five membered rings but this did not cause any ambiguity with regard to the torsion angles about the P-N bonds. The P-Se bond length was found to be 2.105 and 2.107Å for the two non equivalent molecules of the Se compound and 2.355Å for the Te compound.[260]



(73)

X = Se or Te.

The compounds $(Me_2N)_3PSe$, $(Me_2N)_3PTe$ and $(Me_2N)_3PBH_3$ have been studied by ^{11}B, ^{15}N, ^{31}P, ^{77}Se and ^{125}Te n.m.r. spectroscopy.[261] Room temperature single crystal structure determinations have been carried out on Tl_3PSe_4 and Tl_3AsS_4 by neutron Time of flight diffraction.[262]

Dimethyl(phenylchalcogeno)bismuthanes with the general formula Me_2BiEPh (E = S, Se and Te) have been synthesised by the reactions of tetramethyldibismuthane and diphenyldichalcogenides. These thermolabile compounds are the first molecules with a Bi-Se or Bi-Te bond and react with increasing rate in the series S-Se-Te to give MeBiEPh and $BiMe_3$.[263]

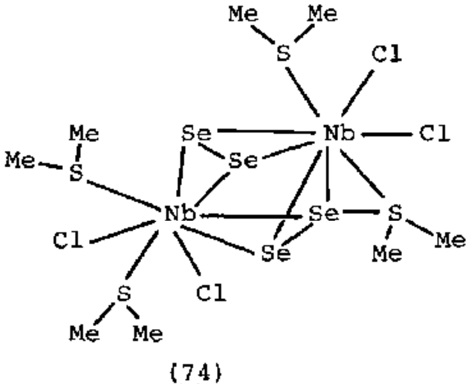
$$Me_2Bi\text{-}BiMe_2 + PhE\text{-}EPh \rightarrow 2Me_2Bi\text{-}EPh$$

$$2Me_2BiEPh \rightarrow Me_3Bi + MeBi(EPh)_2$$

A study of the $Zn_{1-x}Ga_{0.67x}Cr_2Se_4$ system has shown that spinel type solid solutions with x from 0 to 0.6 have a relatively large phase width with respect to the metal selenium ratio. Ternary $Ga_{0.67}Cr_2Se_4$ does not exist since it decomposes to Cr_2Se_3 and Ga_2Se_3.[264] Single crystals of the compounds $CuCrZrSe_4$ and

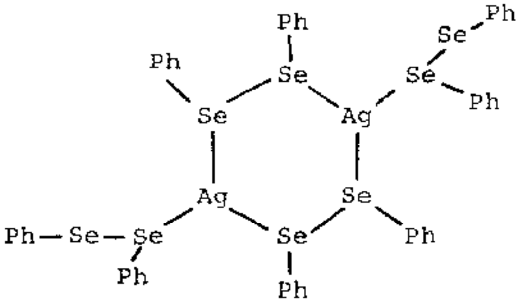
$CuCrSnSe_4$ have been grown by chemical transport using mixtures of $AlCl_3$ and I_2 as transporting agents. The compounds were both found to be normal spinels.[265]

On the basis of a crystal structure determination, the selenide V_2Se_9 can be described as a pseudo one-dimensional compound characterised by infinite $(V_2Se_9)_x$ chains. No bonding was thought to be possible between the atoms in different chains.[266] Tight binding calculations have been performed on various MSe_4 chains (as present in $(MSe_4)I$, M = Nb, Ta) to probe how one-dimensional phenomena such as Peierls distortion and charge density wave formation are affected by band filling. It is found that the d_z2 band of an MSe_4 chain is well separated from other bands and the effect of interchain Se---Se interactions upon the d_z2 band is only appreciable for certain wave vectors.[267] The reactions of $NbCl_3Se$ with some sulphur donor ligands and the reaction of $NbBr_3Se$ with tetrahydrothiophen under moisture- and oxygen-free conditions have been described. The crystal structure of the niobium compound $[(dms)_2Cl_2Nb(Se_2)_2NbCl_2(dms)_2]$ (dms = dimethyl sulphide) showed it to contain centrosymmetric dimers (74) in which each niobium atom is bonded to two chlorine atoms (Nb-Cl = 2.527, 2.510Å) four selenium atoms in two bridging Se_2^{2-} groups (Nb-Se = 2.638, 2.630, 2.640, 2.625Å) and two sulphur groups from the $(CH_3)_2S$ group (Nb-S = 2.739Å).[268]



(74)

The reaction of Ph_2Se_2 with $AgAsF_6$ in liquid SO_2 leads to the formation of $[Ag_2(Ph_2Se_2)_4][AsF_6]_2$ which is isostructural with the corresponding sulphur compound. The structure of the compound (75) shows a centrosymmetric six membered ring inwhich two silver atoms are connected by bridging Ph_2Se_2 ligands and further unidentate Se ligands complete the irregular three coordination at silver.[269]



(75)

Thin films of CdSe with a surface area of 1cm², electrodeposited from sulphate solutions onto titanium plates have been shown to give light power conversion efficiencies between 5 and 5.5%.[270]

Various lanthanide selenide iodides of the type LnSeI have been synthesised and their lattice parameters determined.[271] Several selenide phase systems have been studied and are collected together in Table 3.

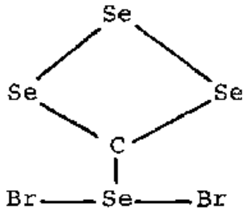
Table 3. Selenide Phase Systems.

System	Ref	System	Ref
$Eu_{1.2}Mo_6S_8$-$Eu_{1.2}Mo_6Se_8$	272	Yb-Sn-Se	277
$LaMo_6Se_8$-$EuMo_6Se_8$	272	CdSe-La_2Se_3	278
$Ag_2Se_{0.5}Te_{0.5}$-Ag_2S	273	As_2Se_3-CoSe, Sb_2Se_3-CoSe	279
$Ag_2S_{0.5}Te_{0.5}$-Ag_2Se	273	As_2Se_3-YbSe	280
Bi_2Se_3-FeSe	274	Cu_2Se-Pr_2Se_3	281
Cu_2GeSe_3-CdSe	275	$GeSe_2$-CoSe	282
SnSe-Fe(Co,Ni)Se	276	PbTe-TlSe	283
		PbTe-InSe	284

6.3.5 Bonds to Carbon

As a preliminary to the identification of the unknown molecule selenoformaldehyde $H_2C{=}Se$, its ionization pattern was calculated by ab initio methods. The experimental preparation of the compound utilised the pyrolysis of the precursors $H_3CSeSeCH_3$, H_3CSeCN, H_3CSeCl and $(H_2CSe)_3$ with analysis of the products with photoelectron spectroscopic real-time analysis. After a computerized spectral stripping procedure an ionization pattern was extracted which correlated satisfactorily with that predicted by the quantum mechanical calculations for $H_2C{=}Se$. To further support the assignment, $CH_3CH{=}Se$ and $F_2C{=}Se$ were prepared by the thermal monomerisation of $(MeHCSe)_3$ and $(F_2CSe)_2$ respectively.[285] Ab initio calculations have also been used to study the rotational barriers for the diselenide bridge Se-Se in dimethyl diselenide.[286]

The bromide ion catalysed reaction between CSe_2 and Se_2Br_2 gives CBr_2Se_4 which a crystal structure determination shows to be planar with an overall symmetry near to C_{2v}. In CBr_2Se_4, (76), three different environments are observed for the selenium atom. The three C-Se bond lengths are similar with an average value of 1.847Å; the two Se-Se bonds are similar to the bonds in elemental selenium, the Br-Se-Br fragment is linear and the structure of CBr_2Se_4 appears to be strongly stabilised by short intermolecular interactions between Se and Br.



(76)

The kinetics of the formation of CBr_2Se_4 indicate that Se_2Br_2 is converted by bromide ion into a bromodiselenide ion which attacks CSe_2 in the rate determining step. The different surroundings for the two Br atoms and the preferred directions of crystal growth suggest that the crystal is formed from $CBrSe_4{}^+Br^-$ ion pairs.[287]

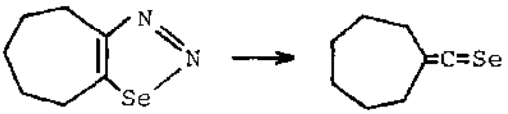
Fluorination of CF_3SeCl with AgF leads to $CF_3Se(O)OH$ and

$CF_3SeSeCF_3$ after reactions of the primary products with glass. Condensation of $(CF_3S)_2NH$ and $(Me_3Si)_2NH$ with CF_3SeCl gave $CF_3SeN(SCF_3)_2$ and $(Me_3Si)_2NSeCF_3$, $(CF_3Se)_2NSiMe_3$, $CF_3SeN(H)SiMe_3$ respectively. The reaction of FC(O)SCl with $Hg(SeCF_3)_2$ gave beside $FC(O)SSeCF_3$ also $CF_3SeSSeCF_3$. When a mixture of $(CF_3Se)_2NH$ with $Cl_3S_3N_3$ is heated to 500°C $CF_3SeN{=}S{=}NSeCF_3$ is formed.[288]

Three papers have been published describing the preparation of dialkyl esters of chalcogenocarbonic acids. The first describes the preparation of O,Se-dialkyl mono-selenocarbonates, RSe-CO-OR';[289] the second the preparation of O,Se- and S,Se-dialkyl mono-thio-mono-selenocarbonates,[290] and the third paper the preparation of S,Se-dialkyldithio-monoselenocarbonates and evidence for the existence of alkylselenoxanthates $[S_2C\text{-}SeR]^-$.[291] The same group have also described the synthesis and properties of Se-alkyl esters of chloromonothiomonoselenoformic acid, RSe-Cs-Cl.[292] The gas phase pyrolysis of cyclohexeno-1,2,3-selenadiazole and cycloocteno-1,2,3-selenadiazole has been investigated by variable temperature p.e.s. and matrix i.r. spectroscopy. The ring contracted, highly reactive products, cyclopentylidenselenoketene, (77), and cycloheptylidenselenoketene, (78), which had not been found in liquid phase thermolysis experiments have been detected.[293]

(77)

...(44)

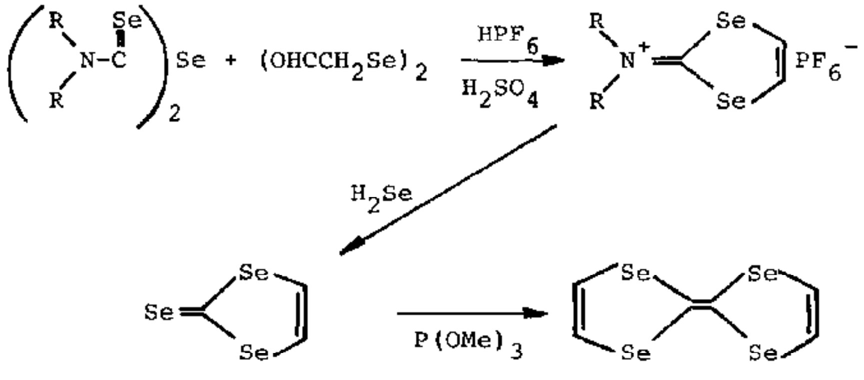


(78)

...(45)

The ^{77}Se chemical shifts and $^{1}H\text{-}^{77}Se$ and $^{77}Se\text{-}^{77}Se$ coupling constants have been measured for a series of substituted tetraselenafulvalenes. Cis/trans assignments could be made by measuring the homologous ^3J selenium 77 coupling constants, which is related to the dihedral bond angle such that large coupling constants (80-100Hz) are observed for cis orientation of the atoms while trans arrangements give rise to much smaller values (10–25Hz).[294]

A high yield synthesis of tetraselenafulvalene (79) involving a novel catalysed exchange reaction between diselenide and bis(N,N-dialkylselenocarbamoyl)selenides has been reported and is shown in Scheme 14.[295]



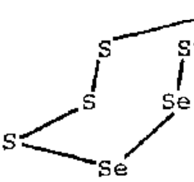
(79)

Scheme 14

The thermal reaction of some metal(II) thioselenocarbamate complexes to form mixed ligand chelates has been studied by e.p.r. and mass spectrometric methods.[296] Crystal structures have been published for the following compounds $C_5H_{11}NO_2Se$,[297] $C_{12}H_{10}Cl_2O_2Se$,[298] $C_{20}H_{24}Se_8{}^{+}ReO_4{}^{-}$ [299] and SrHg(SeCN)$_4$4 Pyridine.[300]

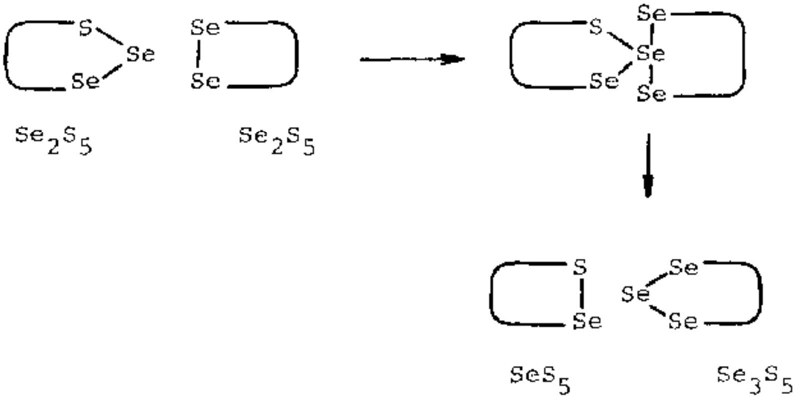
6.3.6 Other Compounds Containing Selenium

The range of cyclic selenium – sulphur rings has now been extended by the preparation of SeS_5 and Se_2S_5, previously only 8 or 12 membered rings were known. The reaction of titanocene pentasulphide with Se_2Cl_2 produces Se_2S_5 which decomposes in CS_2 solution at 25°C to give SeS_5 and Se_3S_5. The Se-Se bond in Se_2Cl_2 is retained in Se_2S_5 (80) according to its Raman spectrum which shows only one Se-Se and two Se-S stretching frequencies.



(80)

The formation of SeS_5 and 1,2,3-Se_3S_5 from 1,2-Se_2S_5 can be accounted for by the reaction mechanism shown in Scheme 15, in which a spirocyclic intermediate, structurally related to SeF_4 is postulated. This species forms by insertion of a Se atom into the reactive SeSe bond of a second molecule and subsequent decomposition to SeS_5 and Se_3S_5.[301]

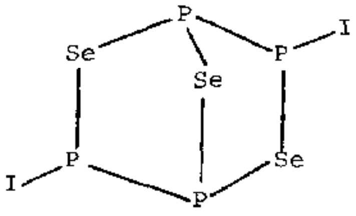


...(46)

Scheme 15

The molecular and crystal structures of the norheteroadamantanes $CH_3C(CH_2As)_3[C(COOCH_2CH_3)_2]_2$ and $CH_3C(CH_2As)_3Se_2$ have been determined, attempts to prepare $CH_3C(CH_2As)_3Te_2$ were not successful.[302]

The aluminium chalcogenide halides AlSeX and AlSX (X = Cl,Br,I) have been prepared and a tentative structural characterisation made on the basis of their vibrational spectra. Both compounds are thought to have a dimeric structure with planar four membered Al_2Se_2 or Al_2S_2 rings and short "terminal" Al-X bonds.[303] α^1-$P_4Se_3I_2$ and α^1-$P_4S_3I_2$ have been prepared by the reaction of P_4Se_3 (P_4S_3) with I_2 in the molten state. The structure of the α isomer (81) of $P_4Se_3I_2$ is compared with the previously known β isomer (82) below.[304]



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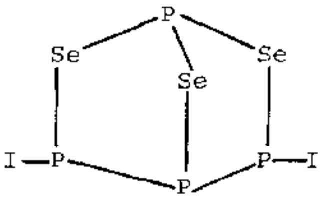


(82)

The crystal structures of bis(diethyldithiophosphato)-selenium(II)[305] and tris(m-trifluoromethylphenyl)phosphine selenide[306] have been determined.

The carbonylation of nitrobenzene in ethanol is catalysed by compounds of selenium. The activity of selenium compounds may be comparable with, or higher than elemental selenium particularly if they are treated with an activator prior to the reaction. The activators applied have the common feature of liberating elemental Se or COSe from the compounds used.[307]

6.4 TELLURIUM

6.4.1 The Element

Te_3 molecules have been made in a matrix reaction by condensing a mixture of 76% Te atoms and 24% Te_2 molecules in a nitrogen matrix at 15K followed by annealing at 25K. The Resonance Raman spectrum of Te_3 contained 8 overtones of the symmetrical stretching vibration and using a 1:1 mixture of ^{126}Te and ^{130}Te the bond shape of the envelopes of the superimposed spectra of all possible Te_3 species could only be explained by assuming a bent structure with an angle of 120°±10°. Force constant data was considered to reflect multiple bonding in the structure of the molecule.[308] A ^{125}Te and ^{77}Se n.m.r. study has been carried out on the $Te_2Se_6{}^{2+}$ cation. The solid state structure of $Te_2Se_6{}^{2+}$ has been determined from the compound $(Te_2Se_6)(Te_2Se_8)(AsF_6)_4(SO_2)_2$ and is derived from a cube with the two tellurium atoms at opposite corners. Thus both the tellurium atoms are equivalent as are the six selenium atoms. The n.m.r. spectra confirmed that the solid state structure is retained in solution.[309]

6.4.2 Bonds to Halogens

A new and improved synthesis of TeF_5OF by means of the reaction

$$B(OTeF_5)_3 + 3F_2 \rightarrow 3TeF_5OF + BF_3 \qquad ...(47)$$

gives an 80-95% yield at 100 to 115°C after 1-3 days. Since commercial F_2 is the fluorinating agent, the need for synthesising the hazardous $FOSO_2F$ (as required for the previous method of synthesis) is eliminated The authors believe this preparation of TeF_5OF is the first example of the formation of a hypofluorite involving the fluorinative scission of a boron-oxygen bond.[310]

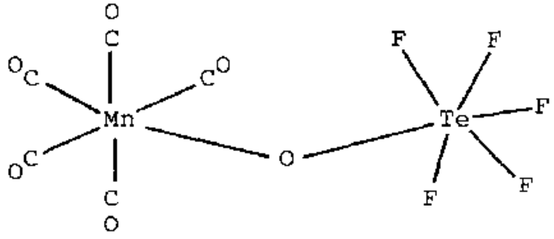
The reaction of $TeClF_5$ with MeOH and $MeOSiMe_3$ has been shown to lead to a mixture of cis and trans $(MeO)TeClF_4$ in a ratio of 1:6 as well as some unidentified Te(IV) product. The vibrational spectrum of the mixture of isomers was accounted for on the basis of the predominant pseudo C_{4v} trans isomers. $TeClF_5$ is unreactive towards anhydrous HF, SbF_5, $AlCl_3$, SO_2, F_2 and ClF at room temperature, but over the temperature range 70-250°C it decomposes to TeF_6, TeF_4 and Cl_2. It slowly reacts with CsF to form $CsTeF_5$, TeF_6, Cl_2 and small amounts of ClF and with $HNMe_2$ it is also reduced to form $TeF_4.HNMe_2$.[311]

A study of TeO_2 in solution of HCl by u.v.-visible and Raman spectroscopy has shown that three Te(IV) chloroanions are present; $TeCl_6^{2-}$, $Te(OH)Cl_4^-$ and a monochlorotellurate(IV) with the probable composition $TeCl(OH)_4^-$. The compound $Me_4N[Te(OH)Cl_4]$ was prepared and characterised.[312]

$As(OTeF_5)_3$ has been shown to behave chemically like AsF_3 in its ability to form adducts with simple Lewis bases, (σ-acidity) and to form complexes with low valent transition metals (π-acidity). This occurrence of both σ and π acidity in the same molecular species is rare.[313] The compound $Mn(CO)_5(OTeF_5)$ has been prepared by the reaction:

$$MeMn(CO)_5 + HOTeF_5 \rightarrow CH_4 + Mn(CO)_5(OTeF_5) \qquad \ldots(48)$$

The compound, which is the first example of a low valent transition metal with a high valent $OTeF_5$ moiety, is stable in the solid state under nitrogen but slowly decomposes in CH_2Cl_2. A crystal structure determination showed the molecule (83) to have a high degree of ionic character in the Mn-O bond, but despite this the $OTeF_5$ group is firmly bonded to manganese and is not replaced by CO.[314]



(83)

A series of mixed fluoro/penta fluoroorthotellurate, ($OTeF_5$) derivative of Xe(VI) oxyfluorides, $XeOF_4$ and XeO_2F_2 as well as those of XeF_4 have been prepared. The compound $O_2Xe(OTeF_5)_2$ was prepared for the first time along with the previously reported $Xe(OTeF_5)_4$ and $XeO(OTeF_5)_4$.[315]

6.4.3 Bonds to Oxygen

The solid state reaction between TeO_2 and SeO_2 in inert atmosphere has been shown to produce $\alpha TeSeO_4$ at 300°C. The compound is stable at room temperature under anhydrous conditions but decomposes above 320°C. In the system TeO_2-SeO_2-H_2O hydrated mixed oxides are formed with $3TeO_2.SeO_2.nH_2O$ being identified.[316] The crystal structures of $MgTeO_3.6H_2O$ and $MgSeO_3.6H_2O$ have been determined. Both are isomorphous with $MgSO_3.6H_2O$ and have the following bond lengths and angles; Te-O 1.859, Se-O 1.697Å; O-Te-O 98.6° and O-Se-O 101.4°.[317] The reactions of the components in the $NdCl_3$-TeO_2 and YCl_3-TeO_2 system have been studied. $TeNd_2O_2Cl$ which melts congruently at 720°C is formed in the $NdCl_3$-TeO_2 system.[318]

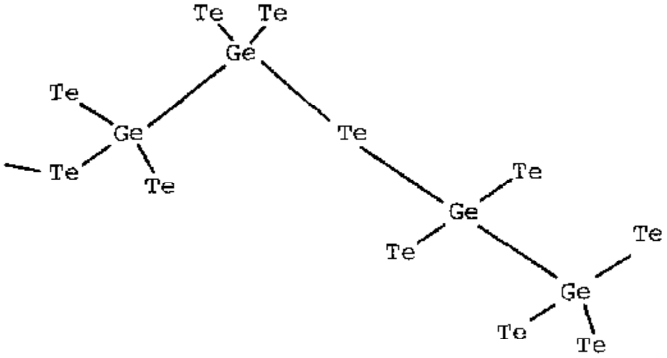
The oxygen exchange reaction between arsenate ions and water is catalysed by the addition of a small amount of tellurate ions. The catalytic process was interpreted in terms of the reversible condensation of arsenate ions with tellurate ions to form the arsenatotellurate ion.[319] In studying Li, Na and K orthotellurates with polyphosphates, the latter were found to decompose to the ortho, pyro- and tetraphosphates and the melt to contain tellurium(IV) and (VI) compounds.[320]

The structure of the adduct of orthotelluric acid and potassium iodate, $Te(OH)_6.KIO_3$, contains orthotelluric acid molecules and iodate anions connected by hydrogen bonds to form a three dimensional network. The orthotelluric acid is in a slightly distorted octahedral arrangement and the iodate ion is a trigonal pyramid.[321] Slightly distorted $Te(OH)_6$ octahedra, with the Te atom placed at the centre of symmetry are also observed in the structure of telluric acid-glycine monohydrate, $Te(OH)_6.2C_2H_5NO_2.H_2O$. The Te-OH distances range from 1.905 to 1.929Å and in addition each glycine group is linked through hydrogen bonds such as Te-OH..O-C to either one or two corners of the $Te(OH)_6$ octahedra.[322] The following phase systems have been studied: Li_2O-MoO_2-TeO_2,[323] $PbCl_2$-MoO_3-TeO_2[324] and Bi_2O_3-Bi_2I_3-

TeO_2.[325]

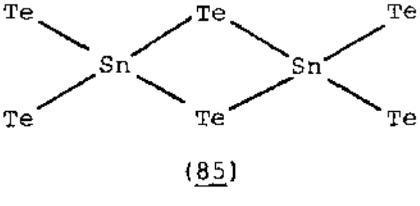
6.4.4 Tellurides

The first binary alkaline earth polytelluride, $BaTe_3$ which crystallises in the tetragonal system (space group $P\bar{4}2m$) is isotypic with BaS_3 and $BaSe_3$ and contains the bent Te_3 anion.[326] The new compound $Ba_2Ge_2Te_5$ contains distorted Ge_2Te_6 trigonal prisms connected by common corners to form infinite chains (84).



(84)

The Ge-Te-Ge bridging distances are 264.4 and 259.2 and 260.6pm.[327] The reaction of KSn with Te at high temperature gives the congruently melting K_4SnTe and Sn. Depending on the cation and solvent used, a variety of products can be isolated from solutions of $SnTe_4^{4-}$, including Te_4^{2-} and $Sn_2Te_6^{4-}$. The compound $(Me_4N)_4Sn_2Te_6$ was structurally characterised and was found to be isostructural with B_2H_6 and to posses the ditinhexatelluride ion (85) with terminal Sn-Te distances of 2.700 and 2.689Å and



(85)

bridging Sn-Te distances of 2.794 and 2.804Å.[328]

A new, potentially general method for the preparation of novel, amorphous materials based on the oxidation of main group polyanions by transition metal cations in solution, has been described. Using this method the compounds M_2SnTe_4 (M = Cr,Mn,Fe or Co) have been prepared from M^{2+} and $SnTe_4{}^{4-}$. When solutions of $FeBr_2$ and K_4SnTe_4 in methanol are mixed at -20°C a black precipitate of composition Fe_2SnTe_4 immediately forms. Fe_2SnTe_4 has a metallic appearance, with a low electrical resistivity and decomposes at 600°C according to equation (49).

$$Fe_2SnTe_4 \rightarrow FeTe_2 + FeTe + SnTe \qquad \ldots(49)$$

Raman spectra suggest that the $SnTe_4$ tetrahedral unit is structurally intact in amorphous Fe_2SnTe_4.[329] Transition metal tetratelluride chains MTe_4 (M = Nb,Ta) adopt a structure different from that of other tetrachalcogenide chains. Tight-binding calculations on $NbTe_4$ show that multidimensional character is substantially stronger in $NbTe_4$ than in $(MSe_4)_nI$. The band electronic structure of $NbTe_4$ is consistent with the view that in $NbTe_4$, each metal ion Nb^{4+} is surrounded by eight $Te_2{}^{2-}$ dimers.[330]

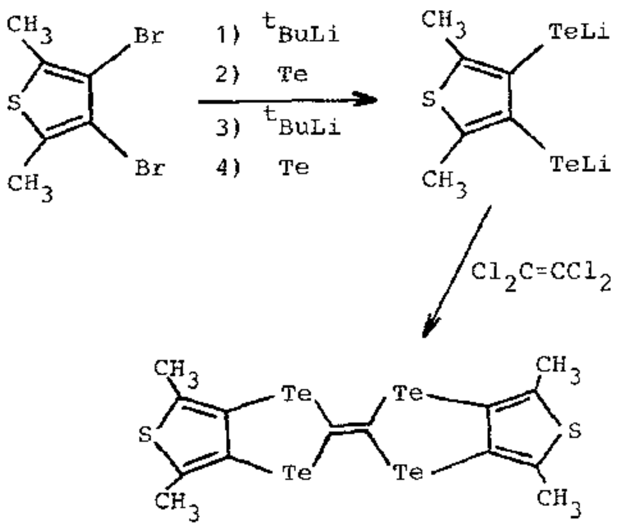
Several studies of telluride phase systems have been carried out and these are collected in Table 4.

Table 4. Telluride Phase Systems.

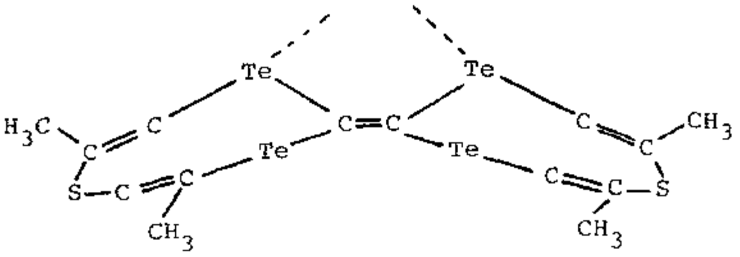
System	Ref	System	Ref
Dy-Bi-Te	331	Cd-Bi-Te	336
SnTe-FeSe	332	Ga-Fe-Te	337
Sb_2Te_3-GdTe and Sb_2Te_3-TbTe	333	$Hg_{1-x}Cd_xTe$-HgI_2-CdTe	338
Yb-Ga-Te	334	Cu-Cu_2Te-Ag_2Te-Ag	339
Zn-Bi-Te	335		

6.4.5 Bonds to Carbon

A convenient synthetic pathway (equation 50), the molecular structure (86) and physical properties of a novel electron donor, bis(dimethylthieno)tetratellurafulvalene have been described. The compound is non planar, exhibiting an unusual and very asymmetric boat conformation. Quantitatively the dihedral angles between the tetratelluraethylene core and the exterior dimethyl-



...(50)



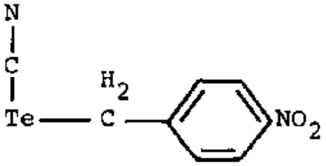
(86)

thienoditellural planes are dramatically different at 47.1 and 16.0°. Some of the deviations are thought to be due to the presence in the solid of dimers which are coupled together through short intermolecular Te...Te contacts at 3.666 and 3.758Å, the former of which is somewhat shorter than twice the van der Waals radius of Te.[340] The crystal structure of diethylammonium tetrachloro(p-phenoxyphenyl)tellurate has been determined. The primary geometry around tellurium is based on a square pyramid with a secondary interaction on the vacant side of the tellurium coordination octahedra.[341]

The crystal structure of $[Te(Ph)_3{}^+]_2[Hg_2Cl_6{}^{2-}]$ contains trigonal pyramidal Ph_3Te^+ cations and chloro-bridged dimeric $Hg_2Cl_6{}^{2-}$

anions which consist of two distorted $HgCl_4$ tetrahedra sharing an edge; interionic Te...Cl interactions complete a distorted octahedral geometry at Te.[342] A structure determination of a new form of bis(p-chlorophenyl)ditelluride, $C_{12}H_8Cl_2Te_2$, shows the Te-Te bond length of 2.680 to be shorter than the values reported for diphenylditellurides in earlier investigations. The molecular geometries observed in diphenyl ditellurides appear to be dependent on the packing modes alone.[343]

The crystal structures of 4-nitrobenzyl tellurocyanate, selenocyanate and thiocyanate, and benzyl selenocyanate have been described. The tellurium atom in the tellurocyanate (87) forms two fairly strong intermolecular bonds to oxygen atoms from neighbouring nitro groups of 2.949 and 3.182Å and the compound may therefore be described as a distorted square planar tellurium(II) complex.[344]

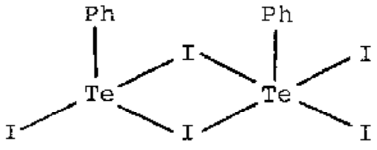


(87)

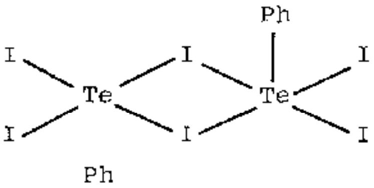
A range of organotellurium(II) compounds together with two selenium compounds have been used as donors to form donor-acceptor complexes with tcnq. Generally the stoichiometry is 1:1 but two ditellurides provide on exception in giving $R_2Te_2.2tcnq$ (R = Ph or C_6H_4OEt-p).[345] The structure of the 1:1 adduct of $C_{10}H_8I_2N_2Te$ with $C_{10}H_8I_2N_2$ consists of discrete molecules with a pair of each being linked into centrosymmetric dimers by weak Te...I linkage. The coordination about Te is a distorted octahedron with two Te-C bonds (2.14Å), two axial Te-I bonds (2.886,2.911Å) and two longer equatorial Te-I bonds trans to Te-C (3.761, 3.788Å), the longer contact being to an iodine of the organic diiodide.[346]

The oxidative addition of diaryl ditellurides to $IrCl(CO)(PPh_3)_2$ in toluene solution has been followed by visible spectrophotometry. An i.r. spectroscopic study of the reaction in CCl_4 shows the relatively rapid formation of an adduct before the final stages of the process occur. A mechanism is suggested which involves the initial addition of ditelluride to Ir(I), followed by homolytic cleavage of the Te-Te bond and formation of the final trans product.[347] A similar mechanism involving the homolytic cleavage of a Te-Te bond to produce RTe radicals and a subsequent chain reaction involving alcohol has been proposed to account for the observation that when toluene solutions containing alcohol and R_2Te_2 (R = p-ethoxyphenyl) are irradiated near the visible absorption maximum of the ditelluride, the colour of the solution gradually disappears.[348]

The crystal and molecular structures of cis and trans phenyltellurium(IV)triiodide and two polymorphs of diphenyltellurium(IV)-diiodide have been determined. Both triiodides form iodine bridged dimers with square-based pyramidal geometry at the tellurium (88 and 89).

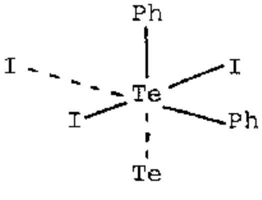


(88)



(89)

No Te...I secondary interactions were observed but I...I Interactions were present, Te-I distances are: 2.775-2.792Å (terminal) and 3.152-3.285Å (bridging). Both polymorphs of the diiodide have pseudo trigonal bipyramidal geometry with one vacant position and have either one or two Te...I secondary bonds occupying the fifth and sixth positions of distorted octahedra (90).[349]



(90)

The crystal structures of $(p\text{-}MeOC_6H_4)_2Te(O_2CMe)_2$, $[Ph_2Te(O_2CCF_3)]_2.H_2O$ and $PhI(O_2CCF_3)_2$ all have pseudo trigonal bipyramidal geometry and form secondary bonds to give pentagonal planar systems around Te and I.[350]

6.4.6 Other Compounds of Tellurium

Crystal structures have been published for the compounds bis(diethyldithiophosphato)tellurium(II) which contains a P-S-Te-S-P chain;[351] $(Ph_4P)_2Te_4.2MeOH$ which contains a tetratelluride 2-anion with MeOH molecules hydrogen bonded to each end;[352] $C_2H_2N_2Te$ which is a heterocycle containing N-Te-N bonds[353] and $C_{20}H_{40}N_4O_8S_8Te$ which has the central tellurium atom bonded to all eight sulphur atoms in a highly distorted dodecahedral configuration.[354]

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