Coordination Chemistry Reviews, 49 (1983) 383—443
Elsevier Scientific Publishing Company, Amsterdam — Printed in The Netherlands

Chapter 6

ELEMENTS OF GROUP 6

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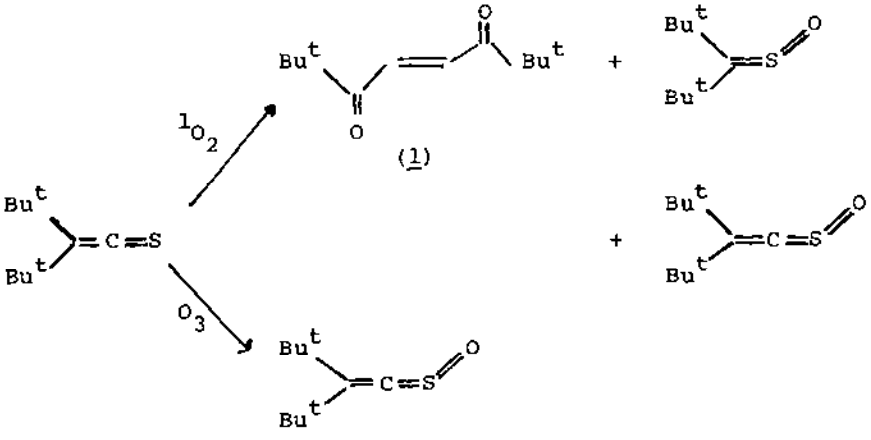
0010-8545/83/$18.30

6.1 OXYGEN

The solid state chemistry, crystal structures and energetics of ternary oxides have been reviewed. Several previously unpublished compounds are included in the review.[1]

The oxidation of thioketens by singlet oxygen and ozone has been shown to give unexpected products compared with other heterocumulenes particularly in the reaction with singlet oxygen. For example, di-t-butylthioketen readily reacts with singlet oxygen to give (1) and reacts with ozone in a quantitative manner to form the corresponding sulphoxide (2).[2]



(1)

(2)

The interaction of iron atoms with oxygen molecules and atoms in an argon matrix from 15 to 40K has been shown to give the following iron-oxygen species which were identified by oxygen-18 isotope shifts in the i.r. spectra: FeO$_2$ (side bonded), O-Fe-O (linear), O-Fe-O (metastable bent structure) and FeO.[3]

A study of the oxidation and dismutation of superoxide ion solutions gave results in agreement with theoretical predictions in that processes involving adiabatic electron transfer or a triplet state (e.g. the Fe^{III}(ClO$_4$)$_3$-O$_2^{-}\cdot$ and the HClO$_4$-O$_2^{-}\cdot$ systems) favour the formation of $^3\Sigma_g^-$ state O$_2$ and those that involve a singlet transition state (the ferrocinium ion-O$_2^{-}\cdot$ system) favour the formation of $^1\Delta_t$ state O$_2$.[4] It has been shown, somewhat unexpectedly, that 1,10-phenanthroline Cu(I)Cl reacts with dioxygen to give only one oxygenated complex, the stoichiometry of which is $(phenCuCl)_2O$. The quantitative transfer of the oxygen atom from the complex to triphylphosphine was also observed.[5] The solid state formula of the dioxygen adduct of manganese 4,4',4",4'"-tetrasulphonated phthalocyanine is thought to be best represented as $Mn(III)TsPcO_2^-$. An e.s.r. study shows that in solution an intramolecular electron transfer takes place between $Mn(II)TsPcO_2$ and $Mn(III)TsPcO_2^-$ which is pH dependent with the superoxide only being stable between a pH of about 11.5 and 13.5.[6]

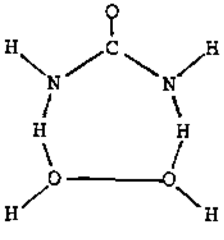
The photolysis of Cl_2-O_3-Ar mixtures gives a sequence of products which are a function of photolysis time. ClClO was observed after lhr of photolysis, the ClO dimer after 2hr and the ClOO molecule after 5 hours. The ClOCl molecule was not observed. The photolysis of Cl_2-O_2-Ar mixtures for 5hrs produced no chlorine oxides and thus the formation of ClOO by the direct reaction of chlorine and oxygen was conclusively ruled out.[7] The analytical solution of vibrational relaxation in a low-pressure gas has been applied to the thermal dissociation of O_3 in helium and of SO_2 in argon. Calculated weak-collision rate constants were in very good agreement with experiment in the case of SO_2 but agreement was only fair for ozone.[8]

The core binding energies of ozone and OF_2 have been calculated as the difference between the total Hartree-Fock energies of the hole states and neutral ground states. Agreement with experiment is very good except for the central atom of ozone.[9] The room-temperature, gas-phase reactions of OH^- with a variety of oxygen containing hydrocarbons, allene, propyne and toluene show proton transfer and solvation of the OH^-. Hydration with one molecule of H_2O was observed to reduce the rate slightly and lead to hydrated products or to stop the reaction completely.[10] The yields and decay rates of localised excess electrons absorbing in both the visible and in the infrared have been measured in water glasses and ice.[11]

The kinetics of oxidation by hydrogen peroxide has been the subject of several publications. Studies using compounds containing chlorine in its +1 formal oxidation state confirm a previous reaction mechanism which identified hydroperoxide ion and hypochlorous acid as the reactants in the corresponding singlet oxygen generating reaction between these compounds.[12] The oxidation of DMSO by H_2O_2 in the presence of a catalytic amount of Na_2WO_4 has been shown to be first-order with respect to the substrate and catalyst but independent of the concentration of H_2O_2 which is present in excess of the catalyst. In solution two main types of peroxytungstic acids (H_2WO_5 and H_2WO_8) were thought to be formed.[13] The kinetic study of the oxidation of H_2O_2 by $[Ag(bipy)_2]^{2+}$ in aqueous nitric acid has shown that the principal reactive species of Ag(II) is $[Ag(bipy)]^{2+}$ which exists in equilibrium with $[Ag(bipy)_2]^{2+}$. No evidence was found for the existence of intermediate complexes such as $Ag(II)(bipy)(H_2O_2)$.[14]

The photo-oxidation of formic, acetic and propionic acids with aqueous H_2O_2 is thought to proceed via a mechanism involving an initial H-atom abstraction followed by HO• formed by photodissociation of H_2O_2.[15] Studies of the smooth catalytic decomposition of hydrogen peroxide (mainly at 50°C) in the presence of iodine and iodate ions have shown that the overall rate need not be first order with respect to the peroxide concentration even though each peroxide step in the mechanism has that distinction. Although free radicals are undoubtably present in the reaction they are not necessarily involved in the smooth catalysis.[16] The rate of hydrogen peroxide photolysis has been shown to be markedly enhanced by the presence of Cu(II) even at concentrations as low as 9×10^{-8}M. Photolysis, is however, completely suppressed on the addition of metal complexing agents such as EDTA. This observation has therefore led the authors to conclude that no hydrogen peroxide photolysis would occur in the complete absence of transition metals in solution.[17] The reaction of hydrogen peroxide (30%) with molybdenum powder or MoO_3 has been shown to give two new molybdenum oxides.[18]

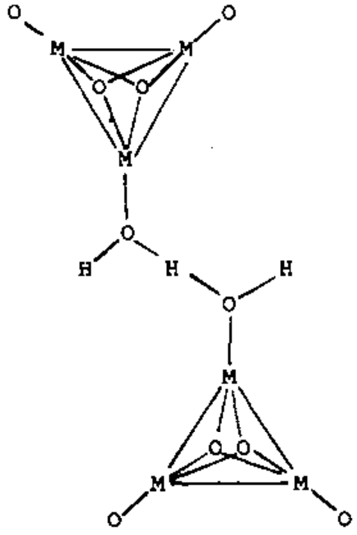
The structure of the urea-, hydrogen peroxide complex, $(H_2N)_2CO.H_2O_2$, (3), has been determined by neutron diffraction.



(3)

The O-O bond length in the hydrogen peroxide is 1.0005Å, the OOH angle is 102.53° and the H-OOH dihedral angle is 98.98°. Combining the O-O bond length with published moments of inertia enabled the following gas phase conformation parameters of H_2O_2 to be derived: OH bond length 0.958Å, OOH angle 98.7° and HOOH angle 118.9°.[19]

The preparation and structure of the first transition metal complex containing the $H_3O_2^-$ ion as a bridging ligand between two metal atoms has been reported. The compounds described have the general formula $[M_3O_2(O_2CC_2H_5)_6(H_2O)_2\text{-}H_3O_2\text{-}M_3O_2(O_2CC_2H_5)_6(H_2O)_2]Br.6H_2O$, where M = Mo or W. The structure is shown in (4). The short O-O distance (2.44-2.52Å) in the bridging group, and the presence of one hydroxide anion in the stoichiometry of the complex support the assignment of $H_3O_2^-$ to this group. As expected the O-O distances in the coordinated $H_3O_2^-$ ion are longer by about 0.15 to 0.23Å than in the free ion.[20]



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6.2 SULPHUR

6.2.1 The Element

Literature on the molecular composition of liquid sulphur has been comprehensively reviewed and some earlier work has been corrected and reinterpreted. At the melting point and after equilibration the liquid contains S_8 together with 5% π sulphur, while polymeric μ sulphur increases from 1% at 135°C to a maximum of 56% at 250 to 300°C. The heat of formation of S_π is 22 kJ/mol and the formation of S_μ is also endothermic. The author concludes that the exact molecular nature of both π and μ sulphur is not known and that both substances may well be mixtures. Doubt is also cast on the existing theories of polymerisation of S_8.[21] The same author has also published his own findings on the molecular composition of molten sulphur. Raman spectra of sulphur melts (115-300°C) of quenched melts and CS_2 extracts show the presence of S_8, S_6 and S_7 units, the formation of S_7 from S_8 being slow, taking more than 8h at 120°C. Pure crystalline S_7, S_{12}, αS_{18} and S_{20} were prepared and a mixture of larger rings isolated.[22]

Quantitative analysis of equilibrium melts showed that at the freezing point (115°C) the melt comprises 0.60% S_6, 2.8% S_7, 1.5% $S_x (x>8)$ and 95.1% S_8. The solubilities of S_7 and S_8 in CS_2 were found to be considerably enhanced by the presence of S_x.[23] Reverse phase HPLC has been used to isolate 13 new sulphur rings without decomposition. Melts of S_8 were found to contain all S_n rings with n from 6 to 26 whilst the mixtures obtained on reaction of SCl_2 or S_2Cl_2 with KI were found to consist of rings with n from 6 to 21 or of even numbered rings with up to 22 units.[24]

The oxidation of elemental sulphur in the presence of water under an oxygen pressure has been studied at temperatures between 125 and 230°C. Below 160°C, the S_λ and S_μ forms were found to have different chemical behaviours.[25] The crystal structures of S_{12} and the adduct $S_{12}.CS_2$ have been determined. S_{12} crystallises in the space group Pnnm and the molecules occupy sites of C_{2h} symmetry with mean S-S distances of 205.2pm, bond angles of 106.6° and torsion angles of 88°. The S_{12} unit of the adduct occupies sites of D_{3d} symmetry with bond lengths of 205.4pm, bond angles of 105.80, and 106.65° and torsion angles of 87.20°. The CS_2 molecule interacts only weakly with the S_{12} units.[26] Single crystal Raman spectra of the addition compounds $RI_3.3S_8$ (R = Sb, CH, As) have been reported. Since all three adducts have similar spectra it was concluded that $AsI_3.3S_8$ has the same structure as the other two adducts.[27]

6.2.2 Bonds to Halogens

The synthesis of ^{35}S labelled sulphur tetrafluoride from ^{35}S labelled elemental sulphur by the reaction

$$5S + 4IF_5 \rightarrow 5SF_4 + 2I_2 \qquad \ldots(1)$$

has been reported. The product was purified by reaction with BF_3 at 195K to give the adduct $^{35}SF_3^+BF_4^-$ from which unreacted material could be removed by pumping before the adduct was decomposed by adding dry diethyl ether.[28] Ab initio molecular orbital calculations have been carried out for SF_4 in both C_{2v} and C_{4v} symetries, SOF_2 and SO_2F_2. The predicted geometries agreed well with experiment, although S=O bonds were consistently predicted too long by about 0.03Å, and the variation in S-F bond lengths among different environments was underestimated. Replacement of F by OH was predicted to be more exothermic in SO_2F_2 than in SOF_2.[29] The kinetics of the thermal reaction between SF_4 and F_2 have been investigated at temperatures between -2.4°C and +24°C, SF_6 and very small amounts of S_2F_{10} were the only products observed. The reaction, which is a chain reaction of medium length, can be represented by the following mechanism:

$$SF_4 + F_2 \rightarrow SF_5 + F \qquad \ldots(2)$$

$$F + SF_4 \rightarrow SF_5 \qquad \ldots(3)$$

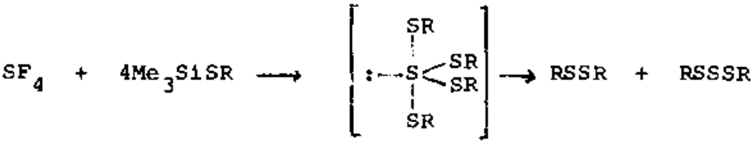
$$SF_5 + F_2 \rightarrow SF_6 + F \qquad \ldots(4)$$

$$SF_5 + F \rightarrow SF_6 \qquad \ldots(5)$$

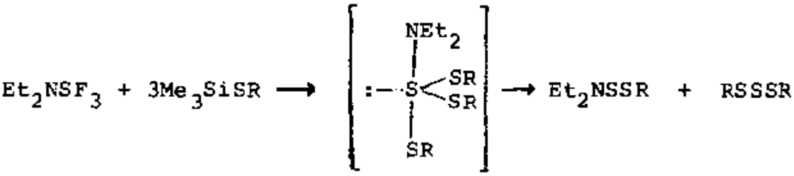
$$SF_5 + SF_5 \rightarrow S_2F_{10} \qquad \ldots(6)$$

Oxygen inhibits the reaction eliminating the SF_5 radicals, the final products being under these conditions $SF_5O_3SF_5$ and SF_6.[30]

A moderately stable hexacoordinated sulphur(VI) compound with four different kinds of ligand, $CF_3SF_2(CN)_2Cl$, has been prepared by the reaction of CF_3SF_4Cl with Me_3SiCN. The latter compound also reacts with SF_4 and $(CF_3)_2SF_2$ to give $F_2S(CN)_2$ and $(CF_3)_2S(CN)_2$. These four coordinate sulphur(IV) compounds decompose rapidly at 25°C but are stable at lower temperatures. With $OSCl_2$ and SCl_2, the white solids $OS(CN)_2$ and $S(CN)_2$ are formed thus providing a new, convenient route to the latter compound.[31] Attempts to prepare S(IV) derivatives by reaction of $Me_3SiSCMe_3$ with SF_4 or Et_2NSF_3 were unsuccessful with reduction taking place as shown by equations (7) and (8).[32]



$$SF_4 + 4Me_3SiSR \longrightarrow \left[:\!\!-\!S(SR)_4 \right] \longrightarrow RSSR + RSSSR \qquad ...(7)$$



$$Et_2NSF_3 + 3Me_3SiSR \longrightarrow \left[:\!\!-\!S(NEt_2)(SR)_3 \right] \longrightarrow Et_2NSSR + RSSSR \qquad ...(8)$$

$R = CMe_3$

Treatment of dimethyl(+) -L tartrate with SF_4 has been shown to result in the intermediate formation of 2-fluoro-1,2-bis(methoxycarbonyl)ethyl fluorosulphite which under the action of HF present in the reaction mixture, is converted into dimethyl-2-fluoro-3-hydroxy succinate.[33]

The reaction between CS_2 and SF_6, which is excited by CW CO_2 laser radiation, has been followed over a range of pressures and reactant ratios. The reaction gives SF_4, S, C, thiocarbonyl fluoride, tetrafluoromethane and hexafluoroethane, the ratio of the latter products being dependent on the partial pressure of the SF_6 in the reactants. The reaction mechanism is thought to include both the SF_6 sensitised decomposition of CS_2 and reaction between CS_2 and SF_6.[34] The quantitative fluorination of CO_2 to CF_2O has been achieved by the laser-induced breakdown of SF_6-CO_2 mixtures, equation (9).[35]

$$SF_6 + 2CO_2 \rightarrow 2CF_2O + SO_2F_2 \qquad ...(9)$$

Both methyl- and ethyl sulphur pentafluoride have been shown to react readily at low temperatures with AsF_5 or SbF_5 to form colourless solids that decompose irreversibly at room temperature (equation 10).

$$RSF_5 \; + \; EF_5 \xrightarrow{-70^\circ C} RSF_4{}^+EF_6{}^- \xrightarrow{20^\circ C} SF_3{}^+EF_6{}^- \; + \; RF \quad \ldots(10)$$

R = Et,Me; E = As, Sb.

These results indicate that the substitution of a single F atom in SF_6 by the Me or Et groups induces such a drastic change in the electronic properties of the molecule that the basicity of the remaining fluorine atoms is significantly increased or that the reactivity of SF_6 towards very strong Lewis acids has not been sufficiently well studied.[36]

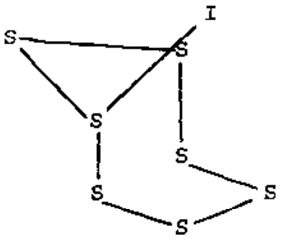
The radical SCl has been formed by photolysis of SCl_2 in a neon matrix. Use of three different isotopically enriched SCl_2 species enabled the characterisation of the radical to be unambiguous.[37] Photoionisation mass spectra of SCl_2, S_2Cl_2 and S_2Br_2 have been measured and heats of formation, bond energies, and ionisation potentials of fragments calculated from appearance potentials.[38]

Two compounds containing the S_7I^+ ion have been synthesised and their structures determined. Attempts to prepare S_8I^+ salts were unsuccessful. S_7IAsF_6 and S_7ISbF_6 were prepared by reactions (11) and (12) respectively in liquid SO_2 or AsF_3.

$$\frac{14}{8} S_8 \; + \; I_2 \; + \; 3AsF_5 \rightarrow 2S_7IAsF_6 \; + \; AsF_3 \quad \ldots(11)$$

$$\frac{42}{8} S_8 \; + \; 3I_2 \; + \; 10SbF_5 \rightarrow 6S_7ISbF_6 \; + \; (SbF_3)_3SbF_5 \quad \ldots(12)$$

The S_7I^+ cations were essentially identical in both salts having the conformation shown in (5).



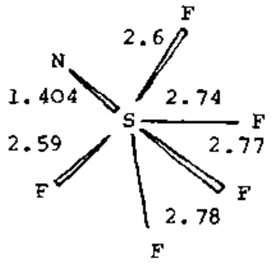
(5)

The sulphur-iodine bond length is 2.342Å corresponding to a bond order of 1. The sulphur-sulphur distances within the slightly twisted chair conformation ring vary from 1.905 to 2.389Å and there is one short intracationic iodine-sulphur contact of 3.39Å.[39] Sulphur has been shown to react with chlorine and arsenic trifluoride under pressure to give $[SCl_3]^+AsF_6^-$.[40]

6.2.3 Bonds to Nitrogen

Linear Compounds - The ability of polymeric sulphur nitride $(SN)_x$ to interact with metal cations and to bind them to the $(SN)_x$ surface has been used to construct an electrode for the photoinduced splitting of water. A polysulphur nitride single crystal electrode pretreated with a ruthenium catalyst has been shown to generate hydrogen gas for a sustained period of time in an aqueous supporting electrolyte surface on irradiation of the electrode surface with visible light.[41]

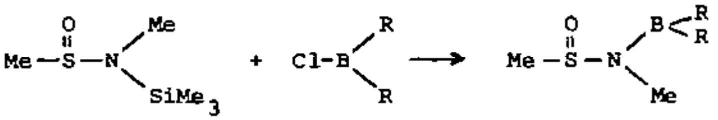
Crystal structure determinations on $NS^+SbF_5^-$ and $NS^+Sb_2F_{11}^-$ at 293K and on the latter compound at 121.5K have been carried out. All the structures may be described as ionic with each sulphur atom surrounded by five F atoms at distances between 2.6 and 2,8Å. The environment of the NS^+ ion in $NS^+Sb_2F_{11}^-$ at 121.5K is shown in (6).



(6)

The bond length of NS^+ was found to be very temperature dependent being 1.361 and 1.354 from the determination carried out at 293K but 1.404 at 121.5K. A vibrational analysis of the three structures was carried out and gave the corrected value as 1.42Å.[42]

Sulphinamidoboranes have been prepared by the cleavage of the Si-N bond of N methyl-N trimethylsilyl-methyl-sulphinamide with haloborane derivatives, equation (13).



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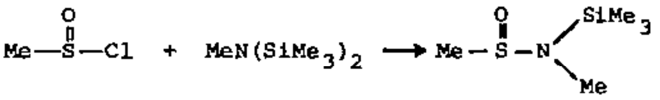
The same compounds could also be obtained from the reaction of $Me_3Si-N(R)-B(R_2)$ with $Me-S(O)-Cl$. N-Methyl N-trimethylsilyl-methylsulphinamide was prepared from heptamethyldisilazane and methylsulphinyl chloride, equation (14).[43]



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The first preparation of $\overline{CF_2CF_2CF_2CF_2S}=NLi$ has been described. The compound is a moderately stable precursor to several new (F-tetramethylene)sulphimides.[44] The preparation of (F-tetramethylene)sulphoxyimide may be carried out in high yield by the oxidation of the corresponding imide $\overline{CF_2CF_2CF_2CF_2S}=NH$ with m-chloroperbenzoic acid.[45] $CF_2CF_2CF_2CF_2S(O)=NH$ may then be used to prepare a large number of new N-substituted (F-tetramethylene)-sulphoxyimides.[46] Electron diffraction studies on the gas phase structures of $(CF_3)_2S=O$, $(CF_3)_2S=NCl$ and $(CF_3)_2SF_2$ have revealed some interesting effects when compared with the totally fluorinated analogues (Table 1).

Table 1. Bond lengths (Å) and angles (°) in $X_2S=O$.and $X_2S=NCl$ compounds.

Molecule	Parameter	X=F	$X=CF_3$
$X_2S=O$	S=O	1.415	1.469
	$X-\hat{S}-X$	92.7	94.2
$X_2S=NCl$	$X-\hat{S}-X$	89.3	99.4
	S=N	1.477	1.434
	N-Cl	1.723	1.676
	$S=\hat{N}-Cl$	138.2	121.0

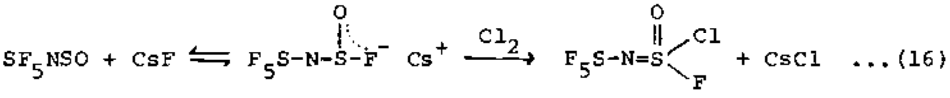
The study confirmed the axial position of the S-F bonds in the gas phase but the observed decrease in the equatorial bond angle from 101.5° in SF_4 to 97.3° in $(CF_3)_2SF_2$ is incompatible with the VSEPR model.[47]

The difluorooxosulphurimidato metallates, $Ag(NSOF_2)_2^-$ and $M(NSOF_2)_4^{2-}$ (M = Cu, Zn, Mn) have been prepared by the reaction of $AgNSOF_2$ with $Ph_4AsNSOF_2$ and $(Ph_4P)_2MBr_4$ respectively.[48] The reaction of N-perfluoroalkylsulphinylimide and Cl_2 in the presence of CsF at room temperature has been shown to give the sulphur oxide chloride fluoride imides RNSOFCl R = CF_3, C_2F_5, i-C_3F_7, C_6F_5. At prolonged reaction times or higher temperatures the difluorides $RNSOF_2$ were isolated in high yields. $(CF_3)_2CFNS(O)ClCF_3$, $(CF_3)_2CClNS(O)ClCF_3$ and $(CF_3)_2CFNS(O)FCF_3$ were also prepared by similar reactions. The latter compound may also be obtained by the addition of F_2 to $CF_3C{=}N{-}S(O)CF_3$ via XeF_2 in the presence of BF_3 but C-S bond cleavage also takes place.[49]

The reaction of $SF_5N{=}SF_2$ with sodium alkoxides and aryloxides have given both the mono- and disubstituted derivatives $SF_5N{=}S(F)OR$ and $SF_5N{=}S(OR)_2$. The reaction of $SF_5N{=}SCl_2$ with AgNCO produced $SF_5N{=}S(NCO)_2$ which could also be prepared from the reaction of $SF_5N{=}SCl_2$ with KOCN in liquid SO_2. The intermediate thought to be formed in the hydrolysis of $SF_5{=}N{=}SF_2$, $SF_5N{=}S{=}O$, was prepared from the low temperature reaction of $SF_5N{=}SCl_2$ and Ag_2O in $PhNO_2$.[50] The latter compound has also been prepared by other workers using the same reagents in nitromethane. The compound was thought to decompose to give $SF_5N{=}S{=}NSF_3$ by the reaction

$$2SF_5NSO \rightarrow \tfrac{1}{2}SF_5N{=}S{=}NSF_3 + \tfrac{1}{2}SO_2 + NSF_3 + OSF_2 \qquad \ldots(15)$$

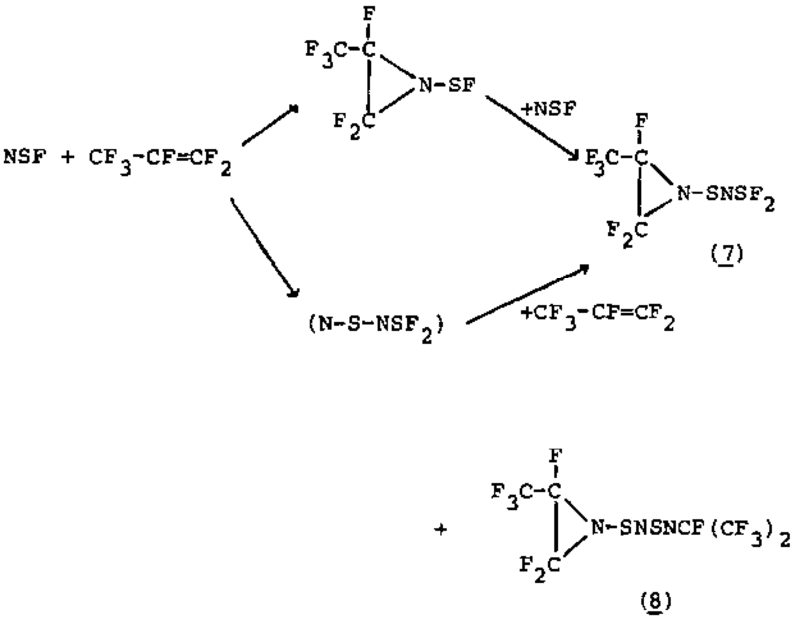
In the presence of CsF the compound reacts with chlorine to give $SF_5NSOClF$.[51]



$$SF_5NSO + CsF \rightleftharpoons F_5S{-}N{-}\overset{O}{\overset{|}{S}}{-}F^-\ Cs^+ \xrightarrow{Cl_2} F_5S{-}N{=}\overset{O}{\overset{\|}{S}}\begin{smallmatrix}Cl\\F\end{smallmatrix} + CsCl \qquad \ldots(16)$$

I.r. studies have shown the series of complexes $[M(NSF_3)_4(AsF_6)_2]$ where M = Mn, Fe, Co, Ni or Cu, to be isostructural with trans AsF_6 groups coordinated to the metal atom and N-S bonds appreciably longer than in free NSF_3. A crystal structure determination carried out on $[Mn(NSF_3)_4(AsF_6)_2]$ confirmed this observation and gave a mean N-S bond length of 1.365Å.[52]

Irradiation of thiazyl fluoride and hexa fluoro propene has been shown to give the sulphenylaziridenes (7) and (8) in yields of 28 and 12% respectively.[53]



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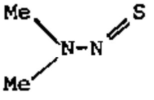
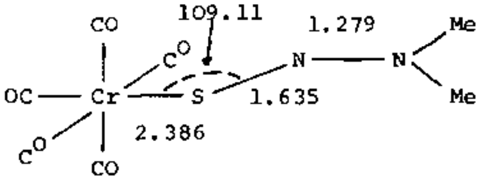
The missing compounds in the series of sulphur diimines R^1-N=S=N-R^2 with R = Ph, C_6H_5PhS, C_6F_5S, have now been prepared and all ten compounds investigated.[54] The sulphurdiimides R-N=S=N-R (R = tBu or Me_3Si) have been shown to react with KNH_2 to form the potassium salts $(R\text{-}N{=}S{=}N)^-K^+$ which can undergo metathetical reactions with Me_3SnCl or Me_2SnCl_2 to form the sulphurdiimides R-N=S=N-SMe_3 and $(R\text{-}N{=}S{=}N)_2SnMe_2$ respectively.[55] The unstable dimethyl(thionitroso)amine (9) reacts with $(CO)_5$Cr.THF to form a 1:1 complex (10) in the form of ruby-red crystals.



(9)

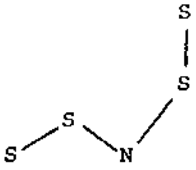
$$+ \ (CO)_5Cr.THF \longrightarrow \underset{(10)}{Me_2N_2S\text{-}Cr(CO)_5} + THF \qquad ...(18)$$

A structure determination showed that the dimethyl(thionitroso)-amine is coordinated to the chromium atom via the sulphur atom rather than the nitrogen atom which is how all previous N-S ligands have been coordinated.[56]



(10)

Calculations using the MNDO method have been made to determine the energy differences between the different isomers of S_4N^-, $S_3N_2O_2$ and $S_4N_3^-$. It was found that the *cis*-*trans* isomer (11) is more stable than either the *trans*-*trans* isomer (12) or the *cis*-*cis* isomer (13) by 20-30 kJ/mol due to stabilisation of the HOMO and to a coulomb attraction.



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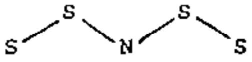

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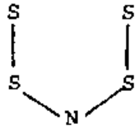
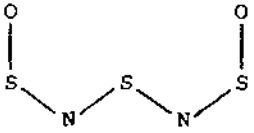


(13)

For $S_3N_2O_2$ calculations favoured isomers (14) and (15) with two sickle-like arrangement whilst for $S_4N_3^-$ only one isomer (16) is favoured.[57]



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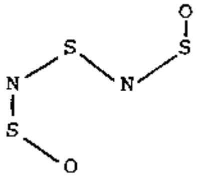

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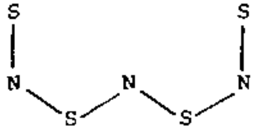
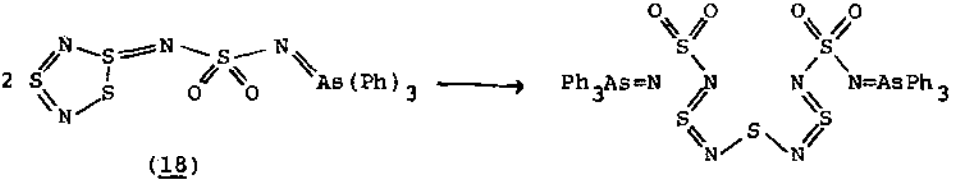


(16)

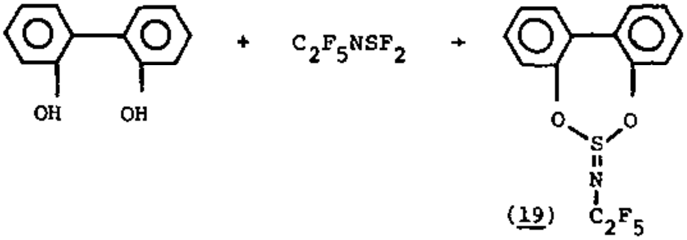
The crystal structure of $S_3N_2O_2$ has been redetermined and the earlier findings by Weiss for the overall geometry were confirmed. The NSO groups are *cis* with respect to the central sulphur atom, with central S-N distances and angles of 1.647Å and 97.3°, and adjacent N-S distances and angles at 1.535Å and 124.3°, and terminal S-O distances and angles of 1.446Å and 118.0°.[58] The synthesis and structure of a non-polymeric molecule containing eleven alternating sulphur and nitrogen molecules has been reported. The compound (17) is formed when (18) slowly loses S_4N_4 and sulphur in acetone solution probably via the formation of an intermediate dimer of (18) which contains a central ten-membered ring system S_6N_4. S-N bond lengths were found between 1.644 and 1.684Å.[59]



(18)

(17) ...(19)

Five membered heterocycles are formed when F-ethylimino sulphur difluoride is reacted with catechol or 2,3-dihydroxynaphthalene. With o,o'-biphenol, the 7-membered ring (19) is obtained.[60]



(19) ...(20)

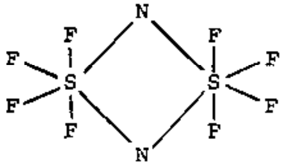
The S_4N^- anion has an approximately planar cis-trans chain with nitrogen as the central atom. Previous theoretical studies had postulated the existence of different geometries for the anion and this has now been confirmed by structural studies carried out on the Ph_4As^+ and PPN^+ salts of the ion.[61]

Ring Compounds - Using the framework of a molecular orbital model it has been possible to classify the apparently endless structural variety of sulphur nitrogen rings. The simple Hückel rule can be applied to the system and the structures of S_4N_4, $S_4N_4^{2+}$, $S_4N_5^+$, $S_4N_5^-$ and S_5N_6 were explained on the basis of an eight membered ring with 12 π electrons.[62] A separate theoretical exercise takes Lewis-Langmuir octet structures and then delocalizes some of the non-bonding electrons into bonding S-N orbitals. The resulting increased valence structures have one-electron bonds and fractional electron-pair bonds as well as normal electron-pair bonds. The hypothesis that fractional electron-pair bonds are shorter than one-electron bonds leads to deductions concerning the relative lengths of S-N bonds that are in general agreement with experimental values.[63]

In addition to the previously described product, $Cl_2N\text{-}SF_5$, the reaction of NSF with ClF also gives the novel four-membered heterocycle (<u>20</u>).

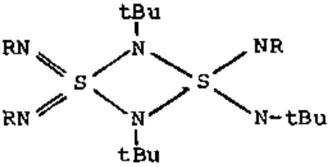
$$N{\equiv}SF_3 \;+\; ClF \longrightarrow (ClN{=}SF_4) \xrightarrow{+ClF} Cl_2N\text{-}SF_5 \qquad \ldots(21)$$

½



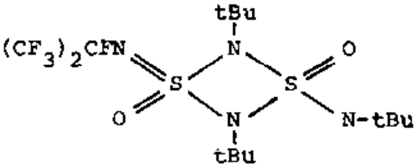
(<u>20</u>)

The compound, which is a colourless liquid at room temperature, is the first cyclodiazaλ⁶ thiane with hexacoordinated sulphur.[64] The reactions of sulphurtriimines and N-perfluoroalkylisocyanates or sulphinyl-amines has led to the preparation of compounds (<u>21</u>) to (<u>24</u>).[65]

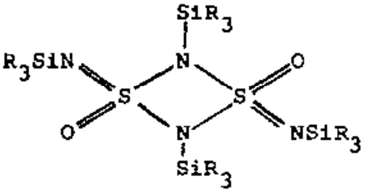


R = CF_3, C_2F_5, n-C_3F_7

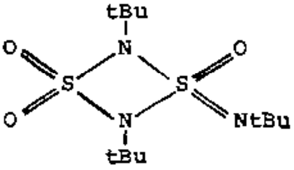
(<u>21</u>)



(<u>22</u>)

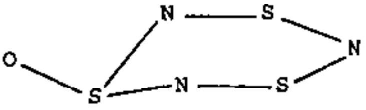


(23)



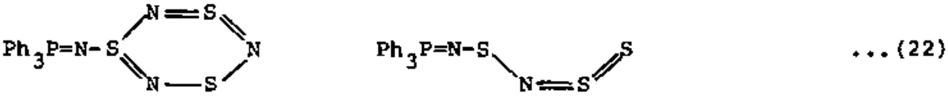
(24)

The oxidation of $S_3N_3^-$ with molecular oxygen has been shown to yield the new oxyanion $S_3N_3O^-$. The structure of (25) $(Ph_3P)_2N^+$ salt (25) shows S-N bond lengths to be between 1.554 and 1.648Å with ring bond angles between 105.4 (at the S atom bonded to oxygen) and 124.2°.



(25)

The N-S-N-S-N part of the ring is planar with the oxidised sulphur atom displaced so that there is a dihedral angle of 43°. The S-N bonds to the oxidised S atom are longer (mean 1.64Å) than those found in $S_3N_3^-$ (1.68Å).[66] The thermolysis of $Ph_3P{=}NS_3N_3$ (26) has been shown to produce the open-chain derivative $Ph_3P{=}NSN{=}S{=}S$ (27).

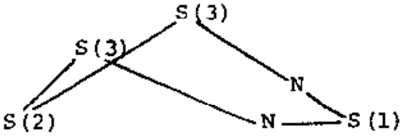


(26) (27)

The structure of (27) shows the sulphur and nitrogen atoms to be in an almost planar cis-trans arrangement. The short terminal S-S bond of 1.908Å suggests a bond order significantly greater than one and the two S-N bonds of the terminal S_3N group are almost equal (1.592 and 1.587Å). The thermolysis of $Ph_3As{=}NS_3N_3$ in acetonitrile leads to the elimination of S_2N_2 which rapidly dimerises to S_4N_4, but in the solid state thermolysis at 130°C and 10^{-3} torr the S_2N_2 can be isolated and converted to the $(SN)_x$

polymer.[67]

A low temperature (-100°C) crystal structure determination has shown S_4N_2 to consist of a six-membered ring in a "half-chair" conformation (28) with nitrogen atoms in the 1,3 positions. Bond distances were found to be S(1)-N = 1.561, N-S(3) 1.676, S(3)-S(2) 2.061Å and angles at S(1) = 122.9, N = 126.7, S(2) = 102.9 and S(3) = 103.4°.[68]

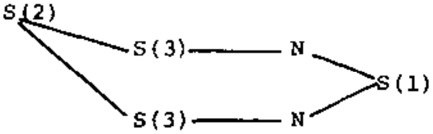


(28)

Two methods for the preparation of S_4N_2 have been described the latter of which gave crystals suitable for structure determination. The reaction between S_4N_3Cl and zinc sulphide induced by zinc is a convenient small scale method of preparing S_4N_2 and can best be expressed by equation (23)

$$8S_4N_3Cl + 2ZnS \rightarrow 2[S_4N_3]_2[ZnCl_4] + 3S_4N_2 + {}^3/_2S_4N_4 \qquad \ldots(23)$$

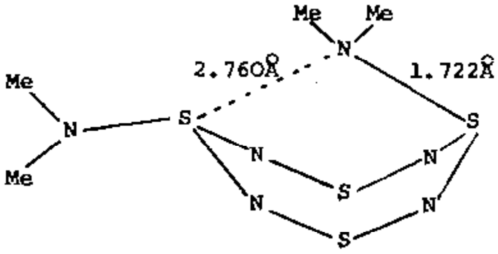
In the second method S_4N_3Cl vapour thermolysed at 130°C was passed over silver selenide at 180°C. S_4N_2 molecules are non-planar (29) with distances S(2)-S(3), 2.055, S(1)-N 1.561 and S3-N 1.661Å. The bond angles of S_4N_2 are under compression and this together with the significant intermolecular attractions (S---N = 3.015Å) and the space group symmetry facilitate its slow decomposition and polymerisation at 263K to $(SN)_x$.[69]



(29)

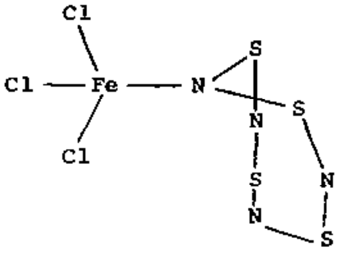
Sulphur K_α and K_β fluorescence spectra have been used to determine the charge distribution amongst the atoms of S_4N_4 and the distribution of the 3p-electrons of sulphur amongst its valence molecular orbitals. It was concluded that the HOMO is localised predominantly on the nitrogen atoms thereby explaining some of the chemical behaviour of S_4N_4.[70]

A simple synthesis for ^{15}N-enriched S_4N_4 from $^{15}NH_4Cl$ has been described. The method involves two steps, the preparation of S_4N_3Cl and its reduction with iodide ion in acetonitrile. A large number of S-N compounds were prepared from the enriched S_4N_4 and their ^{15}N n.m.r. spectra recorded.[71] The reaction of $S_4N_4Cl_2$ with Me_3SiNMe_2 has been shown to give S_4N_4 with two differently orientated dimethylamino groups (30). This is the first derivative of S_4N_4 with amino groups and one of the ligands forms a non-symmetrical bridge between positions 1 and 5 of the S-N ring.[72,73]



(30)

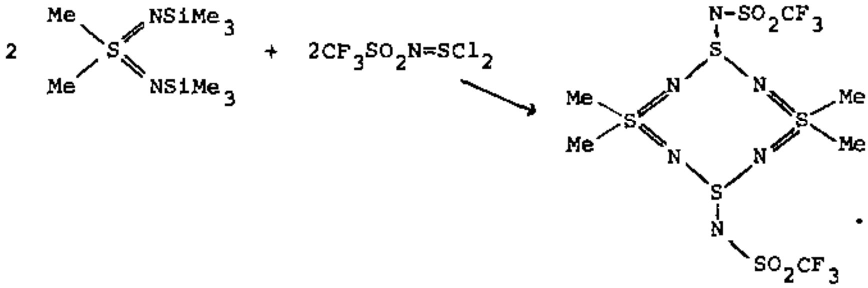
The reaction of S_4N_4 with $FeCl_3$ in CCl_3 has been shown to yield, among other products, two modifications of $FeCl_3.S_4N_4$. X-ray structure analysis of the β modification shows the S_4N_4 ligand is bound via one of its nitrogen atoms and completes the coordination tetrahedron around the iron atom (31).[74]



(31)

The reaction of $FeCl_3$ with S_4N_4 in CH_2Cl_2 at room temperature yields $S_6N_4^{2+}(FeCl_4^-)_2$. Structure analysis shows good agreement for the dimensions and conformation of the $S_6N_4^{2+}$ cation in this compound compared with its other salts. There exists one close S---Cl contact between each of the S atoms of the central S_4 ring and the neighbouring $FeCl_4^-$ anions.[75]

Reaction of $CF_3SO_2N{=}SCl_2$ with $XS[NSiMe_3]_2$ X = Me_2, C_4H_8, or C_5H_{10} yields the eight membered S_4N_4 derivatives, $S_4N_4(NSO_2CF_3)_2Me_4$, $S_4N_4(NSO_2CF_3)_2(C_4H_8)_2$ and $S_4N_4(NSO_2CF_3)_2(C_5H_{10})_2$.

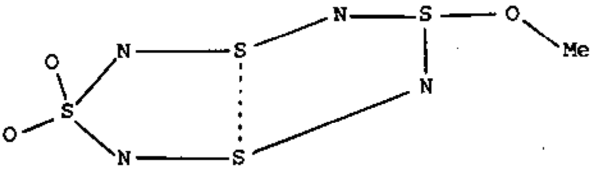

...(24)

X-ray structure analysis of $S_4N_4(NSO_2CF_3)_2(C_4H_8)_2$ showed the ring to have a chair conformation with an average S-N distance of 1.597Å at four-fold coordinated sulphur atoms and 1.650Å at three-fold coordinated sulphur atoms.[76]

The reactions of S_4N_5 with a series of Lewis acids has shown that PF_5 and PCl_5 are not strong enough oxidants to produce any S-N cationic species but give a simple adduct, and a mixture of chlorosulphanes and chlorophosphazenes respectively. $SbCl_5$, AsF_5 and SbF_5 however give compounds of the cation $S_4N_4^{2+}$. The compound $(S_4N_4)(AlCl_4)_2$ has also been prepared by oxidation of the $S_4N_4 \cdot AlCl_3$ adduct with Cl_2 in the place of a stoichiometric amount of $AlCl_3$ and the $(S_4N_4)(SO_3F)_2$ salt was prepared from the reaction of S_4N_4 with fluorosulphuric acid. Structure analysis shows the $S_4N_4^{2+}$ cation to have a boat shaped ring in the $SbCl_6$ salt but to be planar in the other salts, with equal bond lengths.[77]

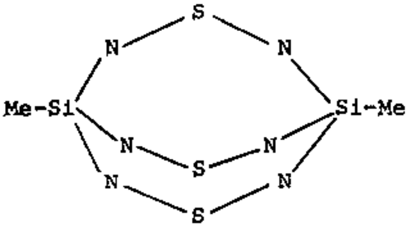
The reaction of triphenylphosphine with S_4N_4 results in the formation of $(Ph_3P{=}N)_2S_4N_4$ and small amounts of $(Ph_3P{=}N)_3S^+S_4N_5^-$. The structure of $(Ph_3P{=}N)_2S_4N_4$ consists of a 1,5 disubstituted S_4N_4 cage, the two exocyclic ligands being orientated in equatorial and axial directions. The asymmetry of the ligands distorts the S_4N_4 unit from the ideal C_4v symmetry and the otherwise symmetry related S-N bonds fall into two classes with bond lengths between 1.630 and 1.675 and between 1.583 and 1.613Å. The substituted sulphur atoms are separated by 3.727Å but the two unsubstituted sulphur atoms remain only 2.452Å apart suggesting significant σ bonding between these two atoms.[78]

S_4N_4 has been shown to undergo quantitative oxidation at room temperature by $S_2O_6F_2$ to give $S_4N_4(SO_4F)_2$. Conductance measurements in HSO_3F showed the compound to dissociate into ions and vibrational spectra showed the cation to be consistent with a flexible planar structure of D_{4h} symmetry and the anion to be SO_3F^-.[79] The reaction of $S_4N_4O_2$ with some nucleophiles (alcoholates, alcohols, azides and isocyanates) in alcoholic solution has led to the formation of a series of salts containing the $[S_4N_4O_2OR]^-$ ion. Structural analysis of $[S_4N_4O_2OMe]^-[PPh_4]^+$ shows the ring to have a transannular S-S bond 2.482Å with the conformation (32).



(32)

Structural analysis of $MeSi(NSN)_3SiMe$ (33) however showed no S-S bonds across the ring.[80]

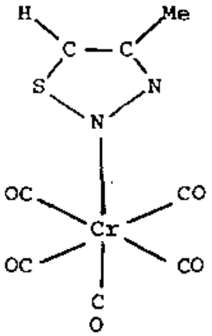


(33)

The MNDO method has been used to calculate the heats of formation, bond lengths and bond angles of four isomers of $S_5N_5^+$. The heart-shaped, and azulene structures were found to be the most stable isomers having almost equal energies.[81] The preparation, properties and reactions of a new thiazyl chloride, $S_5N_5^+Cl^-$ have been reported. The compound, which was prepared by the reaction of S_4N_4 and $(NSCl)_3$, enabled further new compounds (S_5N_5Br, $S_5N_5Br_3$, $S_5N_5I_2Cl$, and $S_5N_5SbCl_4$) to be prepared.[82]

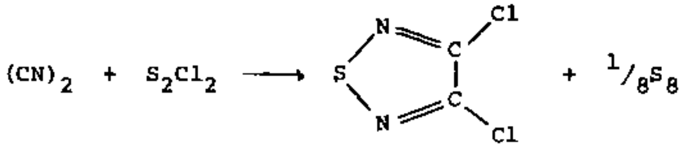
Two new compounds $(S_6N_4^{2+})(S_2O_2F^-)_2$ and $S_6N_4^{2+}(SO_3F^-)_2$, prepared by reaction of S_4N_4 and fluorosulphuric acid and a reliable synthesis of $(S_6N_4^{2+})(AsF_6^-)_2$ by the novel oxidation of S_4N_4 with S_8^{2+} has been reported. The compound previously thought to be contain the monomeric $S_3N_2^+$ cation was shown to be the dimer $(S_6N_4^{2+})(AsF_6^-)_2$ but the monomeric form was obtained from the reaction of $Te_6(AsF_6)_4$ and S_4N_4. The structure of $S_6N_4^{2+}$ may be simply described as being two S_3N_2 rings joined by two long S-S bonds without a significant change in the geometry of either S_3N_2 ring. A striking feature of all the $S_3N_2^+$ structures is that there is a considerable number of anion-cation contacts, in both the monomer and the dimer; the S(1)-S(2) bond is bridged by an oxygen, fluorine or disordered oxygen/fluorine atom in the anion.[83]

A series of substituted thiadiazol complexes has been prepared from reactions of THF.M(CO)$_5$ anf the substituted thiadiazol and selenadiazols. X-ray structure investigations showed the coordination of the ligand to the pentacarbonyl fragment (<u>34</u>) to be via the nitrogen atom in position 2.[84]



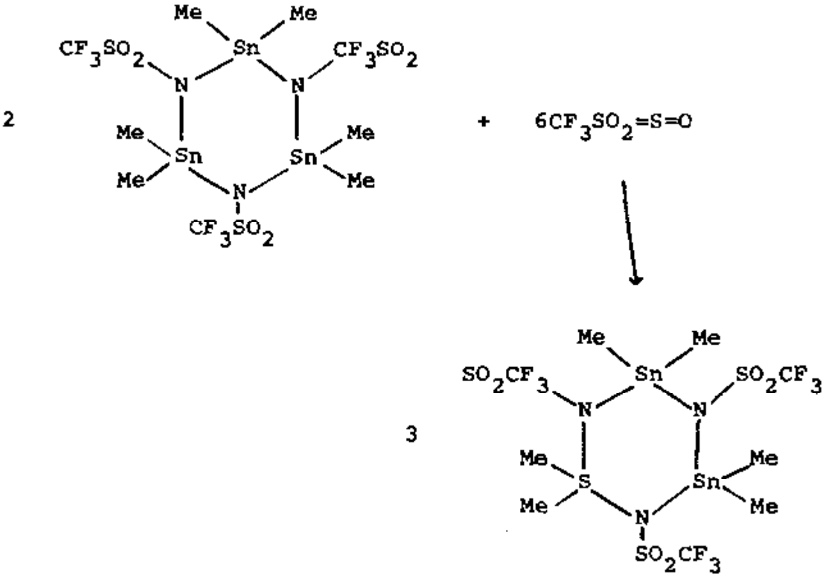
(<u>34</u>)

$SN_2C_2Cl_2$, prepared from $(CN)_2$ and S_2Cl_2 has been shown to react with BCl_3, $SbCl_5$ and SO_3 to yield 1:1 adducts. $TiCl_4$ was found to form a 1:2 adduct.[85]



...(25)

A new inorganic six-membered ring (35) containing the elements S, N and Sn was prepared by the reaction of $CF_3SO_2N{=}S{=}O$ and $(CF_3SO_2NSnMe_2)_3$.[86]



...(26)

6.2.4 Bonds to Oxygen

The Raman spectra for the fundamental modes of $S^{16}O_2$ and $S^{18}O_2$ have been measured. Values obtained were: $\nu_1 = 1151.3$, $\nu_2 = 518.2$, $\nu_3 = 1361.5$ for $S^{16}O_2$ and $\nu_1 = 1100.8$, $\nu_2 = 497.0$, $\nu_3 = 1318.0$ for $S^{18}O_2$. Band shapes were essentially identical and conformed to those expected for a nearly prolate symmetrically topped molecule.[87] The reaction products obtained by heating mixtures of ZnO and carbon in a stream of SO_2 at various temperatures have been characterised. The reaction between carbon and SO_2 takes place initially to form sulphur, above 600°C the ZnO reacts with SO_2 to form ZnS, and some of the ZnO is reduced by the carbon to zinc which then reacts with the sulphur to form ZnS.[88]

Doubt has been cast on the mechanism proposed in 1978 by Thom et al. to account for the production of elemental sulphur in the reaction of FeS with aqueous solutions of SO_2.[89] The reaction between $(Me_3Si)_2NH$ and SO_2 has been shown to result in the formation of an ionic solid with the empirical formula $NH_4Me_3SiOSO_2$. I.r., n.m.r. and XPS data have shown that the presence of RNH_3^+ and HSO_3^- ions is not possible and it is thought that the product is, in fact, ammonium(trimethylsilyl)sulphite with the silicon bonded to oxygen rather than sulphur.[90] A ^1H d.n.m.r. study has been carried out on a series of addition compounds formed from the gaseous reactions of di- and tri-methylamine and triethylamine with sulphur dioxide in the presence of small amounts of water in a liquid SO_2 solvent. The dynamic system involves an equilibrium of the general form $H^+ \rightleftharpoons$ amine.SO_2.[91]

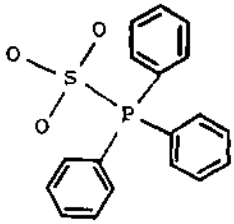
A crystal structure determination has shown that a new bridging geometry for SO_2 exists in the complex $[Mo(CO)_2(PPh_3)(pyridine)-(\mu SO_2)]_2.2CH_2Cl_2$. The molybdenum atoms are bridged by two SO_2 ligands that are coordinated to one metal through the S atom and one O atom and to the second metal by the remaining oxygen atom.[92]

Both strontium and barium sulphites have been prepared by different methods in the temperature range 0 - 100°C. Five different crystalline phases were identified for each salt, several of which were hydrated. The products obtained by passing SO_2 through aqueous suspensions of $SrCO_3$ or $BaCO_3$ were found to be sulphite-carbonate solid solutions.[93] Several hydrated sulphites have been characterised in the $FeSO_3$-H_2O and $NiSO_3$-H_2O systems by the use of a variety of techniques including single crystal data.[94] Single crystal structural studies have also been carried out on $MnSO_3$[95] and $Na_6[Pd(SO_3)_4]2H_2O$.[96] Calorimetric measurements of the enthalpy of protonation of sulphite ion and the enthalpy of proton transfer from bisulphite ion to carbonate ion have led to two independent values for the standard enthalpy of the acid dissociation reaction.

$$HSO_3^-(aq) \longrightarrow H^+(aq) + SO_3^{2-}(aq) \qquad ...(27)$$

Further measurements of ΔH^o, ΔCp^o and ΔV^o have enabled the temperature and pressure dependence of the equilibrium constant for the acid dissociation of $HSO_3^-(aq)$ to be calculated.[97]

The structure of the triphenylphosphine-SO_3 complex (<u>36</u>) has been determined. The complex contains a P-S bond and the S atom is shielded by the 3 aromatic rings.[98]



(36)

Solubilities and enthalpies of solution have been reported for trimethylaminesulphur trioxide, Me_3NSO_3 dissolving in water and in aqueous KBr and tetra-n-butylammonium bromide solution.[99] The compound $(Me_2N)_3P\text{-}Cl\ {}^{+}OS(O)Cl^{-}$ which may easily be prepared from $(Me_2N)_3P{=}O$ and $SOCl_2$ with dimethylformamide as a catalyst, has been successfully used as a mild condensation reagent for the synthesis of peptides.[100]

Raman spectra of the first stage intercalation compound of graphite with H_2SO_4 have shown it to contain the ion $S_2O_7^{2-}$. The interaction of the graphite planes and this molecule was found to be weaker than in material obtained by the action of HSO_3F on graphite.[101] A study of the Raman spectra of 26 H_2SO_4-H_2O mixtures covering the whole of the composition range has shown that SO_4^{2-} ions and "free" HSO_4^- ions do not co-exist with undissociated H_2SO_4 molecules in solution, and that two water molecules are required for the first ionization of H_2SO_4. A species with the composition $H_2SO_4.2H_2O$, assigned a hydrated ion-pair structure, reaches maximum concentration at the same composition at which SO_4^{2-}, free HSO_4^- and H_2SO_4 are at concentration minima. In the concentrated solution the only species observed were the ion pair and undissociated H_2SO_4.[102]

Acidity function measurements have been made in the H_2O-CH_3SO_3H system in the region of the composition 100% CH_3SO_3H.[103]

A dynamic n.m.r. study has been carried out of the acidity of super acid media (mixtures of HSO_3F and SbF_5 from 0 to 90 mol% SbF_5).[104] Phase equilibria in the systems Sb_2O_3-SO_3-H_2O and

Bi_2O_3-SO_3-H_2O within the concentration range 1 to 98.5% H_2SO_4 at 100°C have been studied.[105]

The crystal structure of $(ND_4)_3D.(SO_4)_2$ has been shown to be the same in outline as that of $(NH_4)_3H(SO_4)_2$ but the hydrogen bond O-H---O which links the two symmetrically related SO_4^{2-} ions is markedly affected by the deuteration.[106] The phase transition of $LiNH_4SO_4$ have been studied by i.r. spectra. For transition from phase I to II, the involvement of the NH_4^+ ion seems more important than that of the Li-O-S skeleton; but the latter is responsible for transitions II to II and III to IV.[107] The crystal structure of $LiNH_4SO_4$ at room temperature has been determined.[108]

A combination of DSC and Raman spectroscopic techniques has been used to study the polymorphism of anhydrous Na_2SO_4 between room temperature and 300°C.[108] The modification of Na_2SO_4 stable between 200 and 228°C, has been grown in the form of single crystals by the rapid evaporation of aqueous solutions of $Na_2SO_4\overline{\underline{V}}$ at temperatures of 50 or 60°C and its structure determined.[110]

Neutron diffraction data have been used to determine the D atom position in the compound $Na_2SO_4.2D_2O_2.NaCl$. The arrangement and molecular parameters of the ordered peroxide molecule have now been well established and the arrangement of hydrogen bonds within the tunnels found in this structure were also defined.[111] Osmotic and activity coefficients of sodium sulphate in water from 50 to 150°C have been measured.[112]

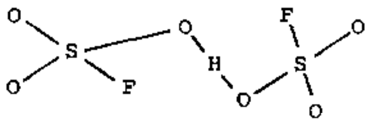
The crystal structure of K_2SO_4 in the region of its phase transformation at 853K has been determined by neutron diffraction. The β-structure was studied at 832K and the α phase structure at 847 and 913K. The α phase can be described by two models, the apex model in which one apex of the SO_4 tetrahedron is orientated statistically up and down or the edge model in which one edge of the tetrahedron is parallel to the 001 plane and three SO_4 groups are statistically superimposed.[113] The structure of $CsHSO_4$ has been shown to consist of hydrogen bonded sulphate groups running along the b-axis one dimensionally.[114]

$MgSO_4.{}^1/3Mg(OH)_2{}^1/3H_2O$ is composed of Mg^{2+} ions octahedrally coordinated by O atoms of four different SO_4^{2-} groups and two OH^- or H_2O groups. The structure is built up of straight chains of face sharing octahedra ${}^2/3$ of which have Mg^{2+} at their centres.[115] The kinetics of crystallisation of $CaSO_4.2H_2O$ has been studied in ammonia solution at 65°C as a function of supersaturation, ionic strength, and added electrolytes.[116] The potential constants of some tetrahedral SO_4^{2-} ions in 5 sulphate apatites of the type $A_3^IM_2^{II}(SO_4)_3X$ have been evaluated[117] and the crystal structures of the apatite phases with the composition $Ca_{10-x}Na_x(PO_4)_{6-x}(SO_4)_xF_2$ determined.[118]

The i.r. spectrum of Al_2O_3 doped with hydrated aluminium sulphate has been shown to be highly dependent on the extent of hydration of the surface in the range 1500 to 1000 cm^{-1}. On heating at 723K under vacuum a strong band appears at 1390 cm^{-1} which shows a linear dependence on SO_4^{2-} content and can be used for non destructive analysis of SO_4^{2-} in Al_2O_3.[119] The α form of $2PbO.PbSO_4$ which is stable at room temperature has been shown to consist of infinite double chains of edge connected OPb_4 tetrahedra with sulphate groups between the double chains connecting the tetrahedra.[120]

The effect of γ irradiation on $FeSO_4.7H_2O$ has been shown to result in the formation of $FeSO_4OH.2H_2O$.[121] The compound $2VOSO_4.H_2SO_4$ has been shown to consist of octahedral VO_6 units linked by monodentate sulphate tetrahedra to form polymeric $[VOSO_4]_\infty$ layers which are joined together by H_2SO_4 molecules.[122] The sulphate group in $Pr_2(SO_4)_38H_2O$ has however been shown to behave as a bidentate bridging group connecting two Pr atoms and as a 3 fold bridging ligand between three neighbouring Pr atoms.[123]

The crystal structure of $Cs^+[O_2FSO.H.OSFO_2]^-$ has provided the first evidence for the existence of the homoconjugated ion $O_2FSO.H.OSFO_2^-$ (37) which contain a very short and symmetrical hydrogen bond with O---O = 2.41Å.[124]



(37)

Indium(III) chloride has been shown to react with HSO_3F only under reflux to form $In(SO_3F)_3$. TlCl however react at room temperature to form $TlSO_3F$ which on reacting with $S_2O_6F_2$, also at room temperature, gives $Tl(SO_3F)_3$. Thermal decomposition temperatures and i.r. spectra of the compounds were determined.[125]

The reduction of ternary fluorosulphato complexes of Pb(IV) by bromine in liquid SO_2 at room temperature results in the formation of the tetrakis(fluorosulphato)palladate(II) ion in which the Pd^{2+} ion has a square planar environment.[126] The weak base dimethyl-N-chloroamine Me_2NCl has been shown to react with trifluoromethane sulphonic acid at -40 to -30°C to give $Me_2NClH^+CF_3SO_3^-$. The extremely hygroscopic salt decomposes on melting at 107 to 108°C and is thus slightly more stable than the hydrogen sulphate.[127]

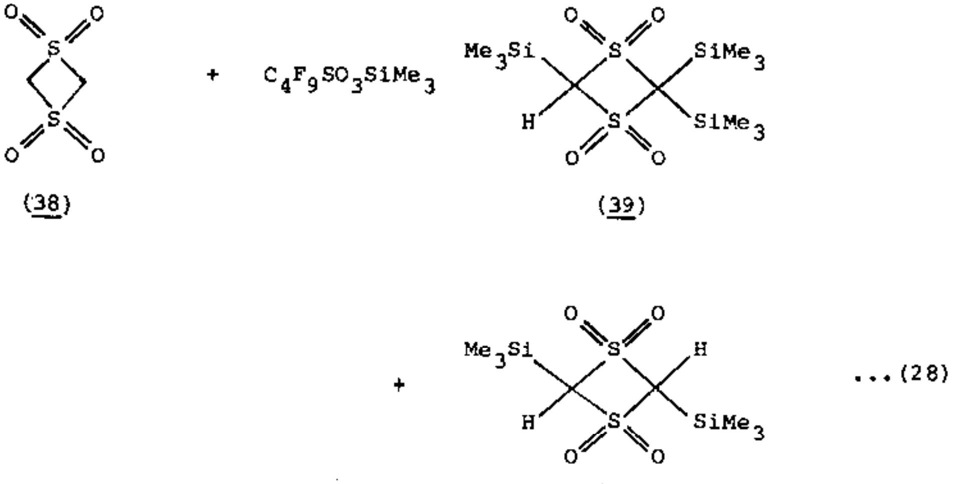
Sodium nitrite and sodium thiosulphate interact in acidic aqueous solution to form a yellow species which has now been identified as the S nitrosated ion $[O_3SSNO]^-$.[128] Sodium and potassium pyrosulphates have been prepared by the reaction of SO_3 with the corresponding anhydrous sulphates at 450°C.[129] The three binary systems, $Li_2S_2O_7$-$Na_2S_2O_7$; $Li_2S_2O_7$-$K_2S_2O_7$ and $Na_2S_2O_7$-$K_2S_2O_7$ have been studied.[130]

Aqueous HSO_5^- is catalytically decomposed to O_2 and HSO_4^- by the catalysts Ag^+ and $S_2O_8^{2-}$. Both oxygen atoms in the O_2 produced are derived from the terminal peroxide oxygen in HSO_5^-. A chain mechanism has been proposed in which a HSO_5 intermediate is formed by the reaction of Ag^{2+} and HSO_5^- with the latter rapidly decomposing in parallel bimolecular paths to produce $O_2 + 2SO_4^-$ and $O_2 + S_2O_8^{2-}$. The slow step is the well known reaction between Ag^+ and $S_2O_8^{2-}$.[131] The kinetics and mechanism of the oxidation of diaqua(nitrilotriacetato)cobaltate(II) by peroxodisulphate ion in aqueous acidic solutions have also been reported.[132] The enthalpies of reaction of $CsSO_4F$ and $Cs_2S_2O_8$ with aqueous HI have been measured by solution calorimetry and standard enthalpies of formation derived.[133]

Thionyl fluoride has been shown to undergo oxidation with chloramine-T, and reduction with $LiAlH_4$ and $NaBH_4$. At higher temperatures (>150°C) it reacts with metals such as Cu, Ag, Zn and Pb to form the corresponding metal sulphides, fluorides and SO_2.[134] The electrochemical fluorination of $MeCHClSO_2Cl$ has been shown to give the sulphonyl fluorides $C_2F_5SO_2F$ and $CF_3CFClSO_2F$ along with CH_4, SO_2F_2, SF_6 and ethane derivatives.[135] The iron(II) sulphonates, $Fe(CF_3SO_3)_2$ and $Fe(p\text{-}CH_3C_6H_4SO_3)_2$ have been prepared and on the basis of spectroscopic evidence have been assigned a layer lattice structure involving hexacoordinated Fe(II) and terdentate bridging anions.[136]

The series of papers by Gattow on the chalcogenolates has now passed 100 as this year saw the publication of parts 98 to 105. Topics covered in the series were, the crystal structure of $W[S_2C\text{-}SEt]$,[137] the synthesis and properties of alkali metal monothiocarbamates, $M[SOC\text{-}NH_2]$,[138] the preparation of the methyl esters of monothiocarbamic acid,[139] alkyl oxoxanthates of alkali metals,[140] the crystal structure of rubidium methyl oxoxanthate,[141] and potassium methyl oxoxanthate,[142] the reaction of guanidine with CS_2[143] and the synthesis and properties of guanidinodithioformic acid.[144]

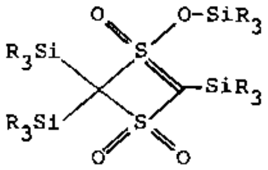
The silylation of (38) has been achieved by reaction with $C_4F_9SO_3SiMe_3$ in the presence of triethylamine to give (39) and (40)



(38) (39) (40)

...(28)

The first enol ether of a sulphone (41) was also prepared.[145]

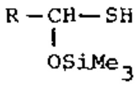


(41)

6.2.5 Sulphides

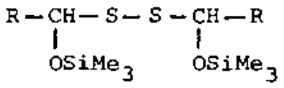
Sulphide, thiosulphate and polysulphide ions may be determined potentiometrically with a $AgNO_3$ standard solution from only two titrations. One aliquot is titrated, after making the titrand acidic with an acetate buffer, to get the end points of the sulphide and thiosulphate ions in the presence of free sulphur. The other is titrated, after sulphitolysis of the sample solution to show the end points of the sulphide and thiosulphate (the original thiosulphate plus that formed from polysulphide) ions in the presence of excess sulphite.[146]

Pulse radiolysis of an aqueous H_2S solution has been shown to lead to the formation of the radical cation $[H_2SSH_2]^+$ which has a three electron S-S bond in which two electrons form a σ bond and the third resides in an antibonding σ* orbital.[147] The reactions of H_2S, aldehydes and Me_3SiCl in pyridine has been used for the synthesis of of the α trimethylsiloxythiols (42). The disulphides (42) were also obtained from the oxidation of (41) with MnO_2.[148]



$R-\underset{|\atop \mathrm{OSiMe_3}}{CH}-SH$

(42)



$R-\underset{|\atop \mathrm{OSiMe_3}}{CH}-S-S-\underset{|\atop \mathrm{OSiMe_3}}{CH}-R$

(43)

Tetragonal Al_2S_3 has been prepared at ambient pressure, the compound crystallises with the spinel defect structure of the β In_2S_3 type.[149] Single crystals of α $ZnAl_2S_4$ with the spinel structure have been obtained by a chemical transport reaction at 740°C. Heating the compound to 800-900°C led to decomposition and the formation of a ZnS deficient phase with a defect spinel structure and a ZnS rich phase with a defect Wurtzite structure.[150]

Sodium thiophenoxide has been shown to react with dibromodifluoromethane to give bromodifluoromethylphenylsulphide. Peracid oxidation of the sulphide gave the corresponding sulphoxide and sulphone.[151] The chemical transport of SnS_2 by I_2 in a temperature gradient has been investigated, below 900K SnS_2 is transported into the high temperature region but at higher temperatures it is transported to the low temperature region.[152] The preparation of a number of organotin(IV) compounds containing Sn-S bonds has been described; n.m.r.; i.r., and Mössbauer data were also reported.[153] The reactions of $(Me_2N)_xCl_{3-x}P{=}S$ ($x = 1$, 2 and 3) with a wide variety of metal halides have been investigated. Spectral characterisation of the S-bonded adducts isolated allowed a qualitative evaluation of the soft character and relative strengths of the metal-sulphur bonds involved.[154]

Polycrystalline samples of the spinel system $AgCrSn(S_{1-x}Se_x)_4$ have been prepared over the whole range of x.[155] Non-stoichiometric titanium sulphide $Ti_{1+x}S_2$ where x varies from 0.11 to 0.33 has been prepared by reducing TiS_2 in an H_2S-H_2 atmosphere at 410°C.[156] Amorphous or poorly crystalline samples of RuS_2 and CoS_2 have been prepared by sulphurising $(NH_4)_2RuCl_6$ and $[Co(NH_3)_6]Cl_2$ at low temperatures with H_2S.[157] The same method has also been used to prepare OsS_2, PtS_2 and PdS_2.[158] The reaction of the sulphides (and selenides) of di, tri and tetra-tertiary arsanes with the salts $CoCl_2.6H_2O$ and $Ni(ClO_4)_2$ has been shown to result in the formation of chelate complexes in which the metal ions are tetrahedrally surrounded by ligands.[159]

The reaction products obtained on heating a mixture of MoO_3 and carbon in a sulphur dioxide stream at various temperatures have been examined. Up to 400°C, MoO_2 was formed, between 500 and 550° a small amount of Mo_4O_{11} was detected, above 700° the formation of MoS_2 in addition to MoO_2 was observed and at 1,000°C the only product was MoS_2.[160] The only ternary phase found in the Pb-Mo-S system $Pb_xMo_6S_y$ may be transported by a chemical transport reaction using $PbBr_2$ if an equilibrium mixture of the phase and Mo is present at the starting side.[161] The double sulphides of zirconium and hafnium with europium have been synthesised under combustion conditions and their compositions established as $EuZrS_3$ and $EuHfS_3$.[162] Starting from two basic structural units, the unit cells of both known and as yet unknown lanthanide polychalcogenides have been derived.[163]

The reaction of Na_2S or NaOH with t-Bu_2SbCl has been shown to yield new anhydrides or thioanhydrides of t-butyl stibinous acids which have structures with bridging oxygen or sulphur atoms.[164]

The rearrangement of terminal allylic hexafluoroisopropyl sulphides to the internal olefinic sulphide has been shown to take place under either photochemical or thermal conditions.[165] The chemical dissolution of PbS and Ag_2S by acid-base effects with HCl or by oxidation with $FeCl_3$ and $CuCl_2$ and their electrochemical dissolution have been studied in DMSO. The dissolution yields could reach 100% and solutions up to $0.5M\ell^{-1}$ could be obtained.[166,167]

The compounds $PMe_2P(X)-C_6H_4-P(X)Me_2$ with X = O, S, Se have been shown to undergo one-electron reduction at a Hg cathode or on reaction with solvated electrons in a K/18-crown-6/THF mixture.[168] The thermal decomposition of $(NH_4)_2\ Mo_3S(S_2)_6\ .nH_2O$ has been studied and it was found that the Mo(IV) triangle system was retained up to the formation of hexagonal MoS_2.[169]

The blackening of powdered red mercury(II) sulphide suspended in aqueous KI upon illumination has been shown to be due to the formation of metacinnabar.[170] Microelectrodes constructed from CdS with RuO_2 and Pt have been shown to be a surprisingly active catalyst for the cleavage of H_2O and H_2S.[171,172] Metal dithiolates and other sulphur containing complexes have also been shown to catalyse the photoproduction of hydrogen from water in the presence of tetrahydro- or dihydrofurans.[173]

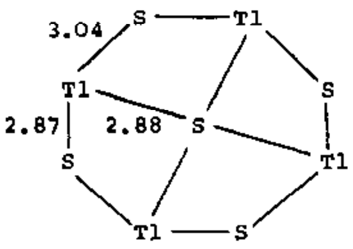
The mass spectra for 13 symmetrical and 35 unsymmetrical dialkyldisulphides have been determined and carbon-sulphur bond cleavage to give hydrocarbon ions as well as the formation of RS^+ ions was observed.[174] The one electron oxidation of $Me_2N-S-S-N-Me_2$ results in a change in structure from one in which the N and S lone pairs are perpendicular to each other to a planarized $N-\dot{S}-\overset{+}{S}-N$ skeleton of the radical cation.[175]

The vibrational spectra of the solid and liquid cage molecules βP_4S_5 and P_4S_7 have been recorded and it has been shown that on melting βP_4S_5 decomposes to P_4S_3, αP_4S_7 and βP_4S_6. Molten αP_4S_7 was also shown to undergo a limited dissociation to βP_4S_6 and sulphur.[176] The i.r. and Raman spectra of $K_4P_4S_8.2H_2O$ and $(NH_4)_4P_4S_8.2H_2O$ have been recorded and the vibrations of the anion assigned on the basis of D_{4h} symmetry.[177]

A series of transition metal sulphide and sulphates have been studied by e.s.c.a., for both metal ionising potentials as well as sulphide. The study demonstrated the usefulness of e.s.c.a. for the identification of phase transitions and oxidation state changes but could not safely distinguish between marcasite and pyrite types of FeS_2.[178] An i.r. and Mössbauer study of the spinels $FeCr_2(S_{1-x}Se_x)_4$ has indicated that the Fe_T^{2+} doublet observed in the Mössbauer spectra are due to the coordinated polyhedrons S_4, S_3Se, and S_2Se.[179]

A study of the transport properties, electrical conductivity, Hall effect and magneto-resistance of MoS_2 has shown that the compound undergoes an interaction with oxygen and water vapour in the atmosphere.[180] Solid solutions of the type $(Mn,Fe)S_2$ have been prepared by hydrothermal methods and studied by Mössbauer spectroscopy. The sulphur in the iron-rich material was found to have a tendency to oxidise to sulphate ion on standing in air for several days.[181] The electrical conductivity of the new ionic superconductor (LaO)AgS has been determined and was shown to be purely ionic. A crystal structure determination showed the structure to comprise of alternating LaO and AgS sheets from which the removal of Ag atoms was thought to be easy due to the large Ag-S and S-S bond lengths in the regular AgS_4 tetrahedra (2.67 and 4.05Å).[182]

Structural studies. The relationship between structure and magnetic properties in a large number of established ternary metal sulphides has been discussed in a recent review.[183] The new compound $Tl_2Sn_2S_5$, prepared by fusion of stoichiometric mixtures of the elements followed by prolonged heating at 300°C contains tin atoms coordinated by five sulphur atoms forming a considerably distorted trigonal bipyramid with a mean Sn-S distance of 2.497Å. The bipyramids are joined by common edges into chains which are cross-linked by sharing the remaining equatorial vertices. The thallium atoms are located in channels and are surrounded by nine sulphur atoms with Tl-S distances between 3.073 and 3.897Å.[184] The structure of Tl_4SnS_3 has been shown to be composed of sheets made up from Tl_4S_3 ring arrangements (44). Each Tl atom has three strong bonds within the ring and one longer bond in a pyramidal coordination (45). Each Sn atom has a distorted octahedral arrangement (46), with weaker Sn-S bonds linking the rings.[185]



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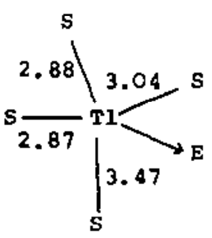

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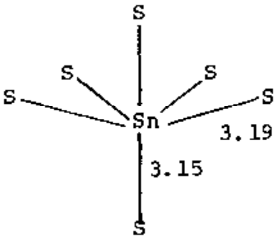
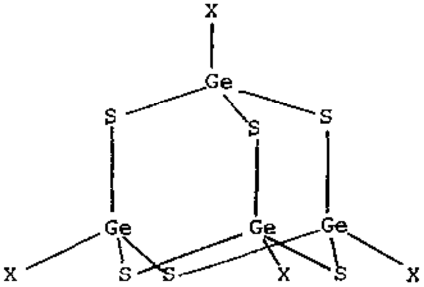


(46)

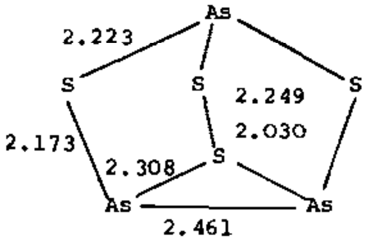
The reaction of GeX_4 (X = Br, I) and H_2S in CS_2 has been shown to give $Ge_4S_6Br_4$ and $Ge_4S_6I_4$. Crystal structure determinations show both compounds to consist of isolated adamantane-like molecules (47).[186]



(47)

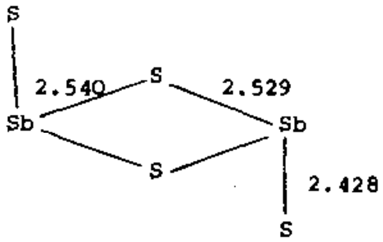
Pure thiohydroxogermanates have been prepared from aqueous solutions by reaction of either Na_2S and GeO_2 or NaOH and GeS_2. The structure of $Na_2GeS_2(OH)_2.5H_2O$ has been shown to contain novel monomeric $GeS_2(OH)_2^{2-}$ anions with Ge-S distances of 2.150 and 2.145Å, and with Ge-O lengths of 1.809 and 1.815Å. An extensive S---HO and O---HO hydrogen bond system connects the anions with the octahedrally coordinated Na^+ ions.[187] SnS has been shown to have a layer structure with each tin atom surrounded by 6 sulphur atoms forming a distorted octahedron with 3Sn-S bonds of 2.622Å, 2Sn-S bonds of 3.287Å and one Sn-S bond of 3.385Å. The layers are linked with weak Sn-S---Sn and Sn---Sn interactions.[188]

It has been shown that the reactions of As_4S_4 and a 1:1 As-Se melt with the Lewis acids AsF_5 and SbF_5 in a 1:3 molar ratio in SO_2 give the AsF_6^- and SbF_6^- salts of the novel arsenic chalcogen cation $As_3S_4^+$ and $As_3Se_4^+$. The two cations are isostructural having a cage structure derived by bridging three edges of a tetrahedron or three arsenic and one sulphur or selenium atoms by the remaining chalcogen atoms (48).[189]



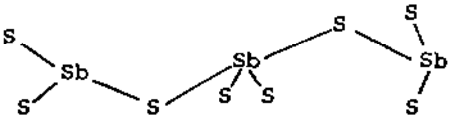
(48)

The compound $Ca_2Sb_2S_5$ has been shown to be comprised of isolated SbS_3 ψ tetrahedra and Sb_2S_4 four membered rings (49) with terminal sulphur atoms on the antimony atoms having a trans configuration.[190]



(49)

The ternary sulphide $Ba_8Sb_6S_{17}$ also contains isolated SbS_3 trigonal pyramids (ψ-tetrahedra) and the hitherto unknown $Sb_3S_8^{7-}$ unit which consists of a central SbS_4 ψ-trigonal bipyramid connected by the common axial sulphur atoms with two further SbS_3^{3-} groups (50).[191]



(50)

The complex $[Mo_2S_{10}]^{2-}$ has been isolated as one product of the reaction between $[NH_4]_2[Mo_2S_{12}]$ and PhSNa in $MeOH/S_2SO$. The anion has a terminal sulphido group bonded to each of the Mo atoms (Mo-S = 2.110Å) which are bridged by two μ sulphido groups (Mo-S 2.289 - 2.351Å). One of the molybdenum atoms is also bonded to a persulphido group (Mo-S = 2.395, S-S = 2.071Å) whereas the other is bonded to a tetrasulphido group (Mo-S = 2.406Å).[192] The structures and phase transitions of β and γ Ag_3IS have been studied. Two models for the structure of the room temperature β phase, which is a fast ion conductor were derived.[193]

Crystal structures have also been reported for the compounds collected in Table 2.

Table 2. Crystal Structure Determination

Compound	Ref.	Compound	Ref.
Cu_8SiS_6	194	Cr_3S_4	200
Tl_3PS_4	195	$BaHgS_2$	201
$C_{18}H_{15}AsS$	196	Ba_2HgS_3	202
$La_4O_3(AsS_3)_2$	197	ThGeS	203
$Li_{3x}Sb_{6-x}S_9$ $x = 0.33$	198	$Eu_3Sb_4S_9$	204
$BaVS_3$	199		

The following phase systems involving sulphides have been reported: Tl_2S-TlX (X = Cl,Br,I),[205] P_4S_3-Ag_4S_3,[206] CdS-SnS (and CdSe-SnSe),[207] Ga_2S_3-PbS,[208] GeS-SnS (and GeSe-SnSe),[209] CdS-Na_2S,[210] Fe-Nb-S[211] and Bi_2S_3-GaSe.[212]

6.2.6 Other Sulphur containing compounds

Cyclopolythianes $(H_2CS)_n$ (n = 3,4,5) show characteristic low-energy ionisation patterns in their photoelectron spectra which have been assigned to radical cation states with predominant sulphur-lone pair contributions.[213] The unstable Cl and Br thiocyanate molecules have been generated in the gas phase by the reaction of AgSCN solid or $(SCN)_2$ gas with molecular Cl_2 or Br_2 respectively. ISCN does not appear to be formed by this route.

The structure of the molecules was established as the non-linear X-S-C≡N molecules and the observed photoelectron spectra were assigned on this basis.[214]

The reaction of $MoCl_5$ with $(SCN)_2$, $(SeCN)_2$ and ICN in CCl_4 or H_2CCl_2 gave $MoCl_5(NCS)_2$, $MoCl_5(NCSe)_2$ and $MoCl_5NCl$ respectively. The compounds were found to be very sensitive towards hydrolysis and decomposed on heating.[215] Although $H_2NCS_2NH_4$ decomposes readily, a stable salt has been prepared as the Hg(II) complex. The structure of the complex consists of layers of two dimensional polymeric networks with dimeric subunits in the layer containing two each of mutually connected Hg atoms and dithiocarbamates which are further linked by other bridging dithiocarbamates to form a sheet like structure. Each Hg atom bonds to four S atoms from four separate dithiocarbamates with Hg-S distances of 2.499, 2.508, 2.533 and 2.629Å.[216]

The thio- and selenocyanato complexes, $(Ph_3P)_2CO(Cl)(H)IrX$ (X = SCN and SeCN) have been prepared from the corresponding tetrafluoroborato and trifluoromethanesulphonato compounds. The SCN ligand is sulphur bonded and the selenocyanato complex was obtained as a mixture of linkage isomers.[217] The magnetic susceptibilities of a series of Cu(II) dialkyldithiocarbamates have been measured between 4 and 290K and the crystal structures of two phases of the di-n-butyl derivatives, one of which showed on an antiferromagnetic coupling, determined. The copper environment is the usual pseudo square planar array of four S atoms from two bidentate ligands (Cu-S = 2.31Å) but there is a fifth long interaction (Cu-S = 2.899Å) leading to pseudo dimer formation in the antiferromagnetic phase.[218]

The salt $[N(PPh_3)_2][I(SCN)_2]$ has been prepared by the addition of thiocyanogen to $[N(PPh_3)_2]I$. I.r. and Raman spectra indicate a structure in which the sulphur atoms of the SCN groups are bound to the iodine atom to give a linear or near linear S-I-S unit. The salt $[N(PPh_3)_2][I_2(SCN)]$ could only be obtained in a mixture with I_3^- and $I(SCN)_2^-$ salts and it is thought that this ion has an unsymmetrical structure with I-I-S units.[219]

N-Silylated derivatives of thiourea which in addition carry three organic substituents on both nitrogen atoms have been shown to react with diethyl aluminium chloride and diisobutyl aluminium chloride to give monomeric thioureidoalanes.[220]

Complexes of the Li^+, Na^+, Co^+, Tl^+, and Ag^+ ion with the macrocyclic ligands dithia-18-crown-6 and trithia-12-crown-4 have been studied by multinuclear n.m.r. in several non aqueous solvents and their stabilities compared with the complexes formed by analogous polyethers. In all cases the substitution of the sulphur atoms for the oxygens results in a substantial decrease in the stability of the complexes.[221]

The crystal structure of diphenyldithiophosphinic acid $Ph_2P(S)SH$ has been determined. The individual molecules are linked together by almost linear S-H---S hydrogen bonds so that endless helical chains are formed.[222] Reaction of CF_3SSCF_3 with $(CH_3O)_2PR$ has been shown to give $CF_3SP(O)(OCH_3)R$, (R = CH_3O, $(CH_3)_2N$), whilst reaction of CF_3SSCF_3 with $(EtO)_2P(O)H$ gives good yields of $CF_3SP(O)(OEt)_2$ which on heating decomposes to $FP(O)(OEt)_2$.[223] The photolytic oxidation of methyl mercaptan, dimethylsulphide, and dimethyldisulphide has been studied and quantum yields obtained.[224]

The first accurate d.n.m.r. studies on complexes of the type $M(CO)_5L$ where M = Cr or W and L is an organosulphur six membered ring of the general formula $\overline{\text{SCHRSCHRECHR}}$ (E = S or CH_2; R = H or Me) have been reported. Six membered ring reversal, sulphur inversion and 1,3 metal shifts were observed.[225] The peribridged naphthalenes $C_{10}H_6XY$ with XY = SS, SSe, STe, SeSe, SeTe, TeTe, may be oxidised using $AlCl_3/H_2CCl_2$. The radical cations XY are all stable at room temperature.[226] The following transition metal complexes with sulphur containing ligands have been synthesised. $C_5H_5(PMe_3)Co(SR)_2$,[227] $[R_4X]_2WS_4$,[228] $[(CO)_5M(SH)(MCO)_5]^-$,[229] $[n\text{-}C_4H_9)_4N]_2[Ni(SSeC{=}C(CN)_2)_2]$.[230] $[Co(MoO_2S)_2]^{2-}$,[231] $[Cp_2Fe_2(S_2)(SR)_2]$, $[Cp_4Fe_4S_5]$ and $[Cp_4Fe_4S_6]$.[232]

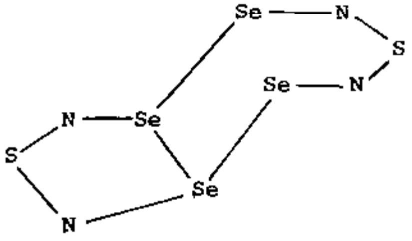
6.3 SELENIUM

6.3.1 The Element

Solutions containing the units Se_6, Se_7 and Se_8 in equilibrium have been shown to result from the dissolution of Se_8, or extraction of glassy or red amorphous selenium prepared from SeO_2, or by reduction with organic solvents. The existence of this equilibrium explains the concentration dependence of the molar absorption of such solutions observed earlier. Since the Raman spectra of red amorphous selenium does not show any lines due to Se_8 S_7 or Se_6, a rapid conversion of Se molecules in solution at 20°C is postulated.[233]

The reaction of S_4N_4 with $Se_4(AsF_6)_2$, $Se_4(Sb_2F_{11})_2$ and

$Se_8(AsF_6)_2$ in SO_2 have been found to give the first well characterised examples of S-Se-N cationic rings in the compound $(Se_4S_2N_4)(AsF_6)_2$ and $Se_4S_2N_2(SbF_6)_2$. In both salts the $Se_4S_2N_4^{2+}$ ion (51) is very similar to the bis(thiodithiazyl) cation in that it consists of two thiodiselenazyl rings linked by long Se---Se interactions of 3.12 - 3.18Å, between the diselenide bonds in each ring.[234]



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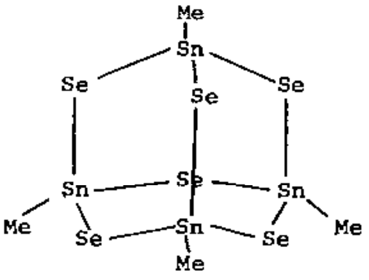
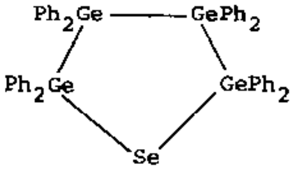


(52)

$(MeSn)_4Se_6$ has been synthesised by reaction of $MeSnBr_3$ and NaHSe in aqueous solution. The compound is composed of adamantane-like molecules (52) with Sn-Se = 2.53Å and Sn-C = 2.15Å.[235] The crystal structure of $(Ph_2Ge)_4Se$ shows a five-membered Ge_4Se ring (53) with Ge-Se = 2.373Å and the Ge-Se-Ge angle is 106.3°.[236]

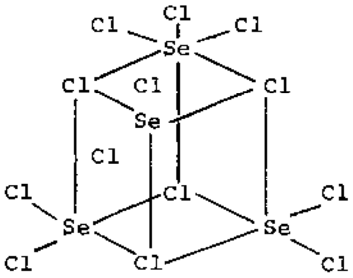


(53)

The kinetics of oxidation of Se(IV) by Ce(IV) has been studied spectrophotometrically at 50°C in aqueous perchloric acid. Ce(III) retards the reaction considerably and the reaction was observed to proceed through the formation of a 1:1 complex between Ce(IV) and Se(IV).[237] A systematic study of the cleavage of element-element bonds in compounds of the type RE-ER where R = $MeCF_3$ and E = Se, Te, P. As, by the Group IVA element hydrides Me_3MH, M = Si; Ge and Sn, has been carried out.[238,239]

6.3.2 Bonds to Halogens

The formation of SeF_2 (and SF_2) in an Ar matrix by the u.v. photolysis of CF_3SeF_3 (and CF_3SF_3) has been reported. A bond length of 1.725Å was derived for SeF_2 and the previously unknown deformation mode ν_2 of SeF_2 was measured.[240] The Se-$SeCl_4$ system has been shown to contain the intermediate phase SeCl which melts incongruently at -48°C. The tetrachloride is dimorphous with a stable α and a metastable β modification. The crystal structure of the β form was shown to contain tetrameric cubane-like molecules Se_4Cl_{16} (54) and to be an isotype of $TeCl_4$.[241]



(54)

The crystal structure of the solid α-form of $SeCl_4$ also contains the tetrameric cubane species Se_4Cl_{16} but with a different point symmetry and in positions which correspond to those of the atoms of the β-tungsten structure type.[242] The phase systems In_2X_3-InY_3 (X = Se, Te; Y = Cl, Br, I) are quasibinary and contain the intermediate ternary compounds InXY with incongruent melting behaviour. InSeCl and InSeBr show a significant phase width towards the respective trihalides.[243] Structural investigations on α-AsSeI (and α-AsTeI) have been carried out. AsSeI was shown to have an AsSe spiral with terminal iodine atoms whereas the tellurium compound has a double chain structure similar to that observed in SbSI.[244]

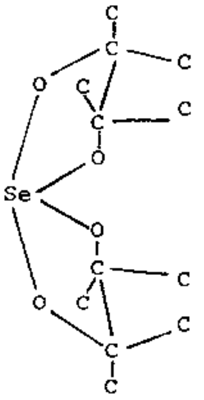
In the presence of $SbCl_5$ or BCl_3, the compound CF_3SeCl has been shown to react with $MeOPCl_2$ to form $CF_3SeP(O)Cl_2$.[245] The ^{77}Se chemical shifts of compounds of the type CF_3SeX have been shown to exhibit an extraordinary good, linear correlation with Huggins' electronegativities of X.[246]

6.3.3 Bonds to Oxygen

The crystal structure of $NaHSeO_3$ has been shown to contain Na^+ ions and two independent hydrogen bonded centrosymmetric $[HSeO_3]_2^{2-}$ dimers which are linked to form a three dimensional network by Na-O bonds.[247] The compound $Au_2(SeO_3)_2(Se_2O_5)$ has been prepared from gold metal and selenic acid at 553K. Structure determinations have shown the gold atom to be in square planar coordination with Au-O = 1.969 to 2.013Å and the extended structure to consist of three cross-linked systems of the form [···Au-(selenite or diselenite)-Au···].[248] $Cu(NH_4)_2(SeO_4)_2 6H_2O$ has been found to be isomorphous with $CuK_2(SeO_4)_2 6H_2O$ and the corresponding sulphate. The copper atom is located at a centre of symmetry and has typical 4+2 distorted coordination.[249]

An X-ray powder diffraction study of normal zirconium and hafnium selenites has shown them to be isostructural.[250] $CdSeO_4.H_2O$ has cadmium atoms coordinated to four SeO_4 groups and two water molecules with Cd-O distances of 2.25 and 2.42Å. The water molecules link the octahedra to form chains which are further connected by SeO_4 groups and hydrogen bonds.[251]

The reactions of $F_3CSe(O)OAg$ with $F_nCl_{3-n}CSCl$ ($n = 3,2,1$) have been shown to give the compounds $F_3CSeS(O_2)CF_nCl_{3-n}$ which decompose in the temperature range $-20^\circ C$ to $+39^\circ C$ to $F_3CSeCF_nCl_{3-n}$ and SO_2.[252] Matrix i.r., and Raman spectra of solid films of $SeOF_4$ have shown the molecule to have C_{2v} symmetry. The Se-O bond can be considered as a double bond with a force constant of $8.2 \times 10^2 N/m$. This value is smaller than that found in $SeOF_2$ whilst the reverse is found for the analogous sulphur compounds.[253] The compounds $MeOSeF_5$, $CH_2(OSeF_5)_2$, $CH(OSeF_5)_3$, $C(OSeF_5)_4$ and $Cl-CO-OSeF_5$ have been described.[254] The crystal structures of the tetraoxy spirocyclic selenurane $(C_6H_{12}O_2)_2Se$ (<u>55</u>) and the corresponding tellurane have been described. Both exist in a trigonal bipyramidal structure distorted by the equatorial lone-pair. In the tellurane, intermolecular Te-O contacts indicate a degree of polymerisation, making the tellurium atoms pseudo six coordinate but no such contact was observed in the selenurane.[255] The phase systems $Pb-SeO_2-H_2O$ and $Pb-SeO_3-H_2O$ have been studied.[256]



(55)

6.3.4 Selenides

High temperature flow pyrolysis reactions in the gas phase have led to the detection of B=Se, the first seleni boron species to be identified. Microwave spectroscopy indicated that r(B=Se) = 1.751Å.[257] Compounds with the composition $In_2S_xSe_y$ and $In_2Se_xTe_y$ where x+y = 3 have been synthesised by heating the elements in evacuated quartz ampoules. X-ray diffraction methods showed that In_2S_3 has a defect spinel lattice and can take up Se in a continuous substitutional solid solution.[258]

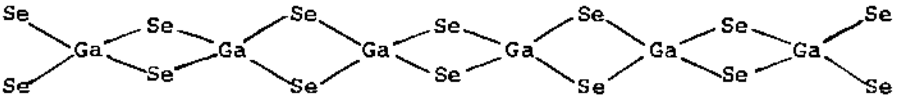
HgSe has been shown to react with H_2SiI_2 in benzene at 120°C to yield a polymer which on heating in benzene depolymerises to form cyclotri(silaselane),$(H_2SiSe)_3$.[259] Heat capacity measurements on an $Sn_{0.5}Se_{0.5}$ alloy corresponding to the previously described congruent stoichiometric compound SnSe have been made by drop calorimetry. Results were interpreted in terms of a polymorphic temperature transition taking place between 762 and 839K having a ΔH^o of 1600 J mol^{-1}.[260]

The chemical transport of V_xSe_2 has been carried out using I_2 as the transporting agent. The vapour pressure of Se was uniform throughout the tube and was the same as the equilibrium pressure of the starting material. The chemical transport reaction was shown to be as in equation (29).[261]

$$VSe_2(s) \;+\; 2I_2(g) \rightleftharpoons VI_4(g) \;+\; Se_2(g) \qquad \ldots(29)$$

Three new compounds, $Br_{0.25}NbSe_4$, $Br_{0.33}NbSe_4$, and $Br_{0.25}TaSe_4$ have been prepared by reaction of mixtures of the elements with different Br_2 pressures at temperatures between 500 and 600°C.[262] Polycrystalline $Hf(Se_xTe_{1-x})_2$ has been prepared by iodine mineralisation from the elements at 800°C. Homogeneous solid solutions result over the range $x = 0$ to 1 which show non Vegard behaviour.[263]

The crystal structures of several selenides have been published. $BaSe_2$ and $BaSe_3$ are both isotypic with the corresponding sulphides having Ba-Se distances in the ranges 3.28 - 3.36 and 3.36 - 3.45 respectively.[264] The first ternary compound in the Cs-Ga-Se system whose structure has been investigated is a solid of composition $Cs_{10}Ga_6Se_{14}$. The $Ga_6Se_{14}{}^{10-}$ anion is composed of six linearly edge-linked $GaSe_4$ tetrahedra (56).[265]



(56)

Crystal data have been reported for $BaAl_2Se_4$, $BaGa_2Se_4$, $CaGa_2Se_4$ and $CaIn_2Te_4$. The structures were strongly related to the TlSe structure.[266] The structure of $EuGa_2Se_4$ has been shown to be orthorhombic with each Se atom coordinated to two gallium and two europium atoms in a deformed tetrahedral configuration.[267] The structures of GdAsSe and NdAsSe have been determined.[268]

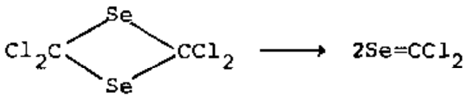
$Tl_4Ge_4Se_{10}$ has been synthesised by fusion of mixtures of Tl_2Se and $GeSe_2$. The crystal structure is characterised by adamantane-like anions $[Ge_4Se_{10}]^{4-}$ and Tl^+ cations.[269] Na_3FeSe_3 can be prepared by heating sodium carbonate with iron sponge at 1000K under a stream of H_2 saturated with selenium or by heating a mixture of NaOH and iron sponge with selenium in a glass ampoule with a temperature gradient from 700 to 800K. The compound was found to be isostructural with Na_3FeS_3 with the iron and selenium atoms forming isolated Fe_2Se_6 anions consisting of two edge-shared tetrahedra.[270] The crystal structure of $In_2Mo_{15}Se_{19}$ has been shown to contain the units Mo_6Se_8 and Mo_9Se_{11} which are stacked in the sequence Mo_6Se_8-In-Mo_9Se_{11}-In- along the trigonal c axis.[271]

The following phase systems of selenides have been studied CdSe-SnSe,[272] Tl-Sn-Se,[273] Cu-Tl-Se,[274] $HgCr_2Se_4$-$HgIn_2Se_4$,[275] CdSe-Cr_2Se_3-Se,[276] Cl-Cr-Se,[277] $GeSe_2$-Sn_2Se_3,[278] Eu_2Se_3-$GeSe_2$,[279]

Tl_2Se-YbSe,[280] TlSe(Tl_2Se)CdSe.[281]

6.3.5 Other Selenium containing compounds

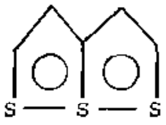
Selenophosgene, Se-CCl_2 has been prepared for the first time by vacuum pyrolysis of 2,2,4,4-tetrachloro-1,3-diselenetane. The dark-blue compound, which is stable only below -130°C, was characterised by mass, low temperature u.v., i.r. matrix, and Raman matrix spectroscopy.[282]



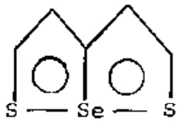
...(30)

A ^{13}C and ^{1}H n.m.r. study on thirty seven, 1,2,3-selenadiazoles has been performed. As well as a discussion of chemical shifts and coupling constants of ^{1}H and ^{13}C, selenium satellites were measured giving ^{1}H, ^{77}Se and ^{13}C ^{77}Se coupling constants.[283]

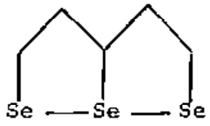
A solid state ESCA study of compounds (<u>57</u>) to (<u>59</u>) has obtained a S 2p spectrum comparable to that of trithia pentalene in the gas phase. The vibrational broadening of the S 2p and Se 3d lines from the terminal 1,6 atoms is related to the observed bond lengths within a simple model.[284]



(<u>57</u>)

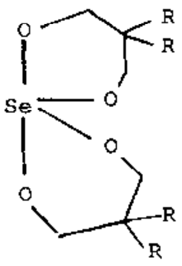


(<u>58</u>)



(<u>59</u>)

A series of tetraalkoxy selenuranes (<u>60</u>) has been prepared. Compounds with R = Me_2CH and Me_3CCH_2 were found to be sufficiently



(<u>60</u>)

stable to be obtained as crystalline solids. N.m.r. and X-ray studies showed the compounds to have a trigonal bipyramidal structure or nearly so and variable temperature n.m.r. showed them to undergo both inter- and intramolecular ligand reorganisation.[285]

^{77}Se and ^{13}C chemical shifts have been measured in compounds of the type Se=C=Se, Se=CF_2, Se=$C(NH_2)_2$, Se=C(tBu)$_2$ and 1,1,3,3-tetramethyl-2-indanselon. The shielding of both nuclei in the C=Se moiety was found to depend strongly on the lowest electron excitation energy. The ^{77}Se-^{13}C spin spin coupling constants for the C=S double bond are presented for the first time and were shown to have a strong dependence on the s-character of the carbon atom.[286]

The molecular geometry of $PF_2(NCSe)$ has been studied in the gas phase by electron diffraction. The overall symmetry was found to be C_s with the NCSe group lying <u>trans</u> to the F-P-F angle bisector.[287]

The complexes $Pt(PEt_3)_2(PF_2Y)X$ (X = Cl, Br or I, Y = S or Se), have been prepared by the reaction of trans $PtH(PEt_3)_2X$ with $PF_2H(Y)$.[288] $Pb[(EtOH)_2NiHg(SeCN)_4(SCN)_2]$ and $Pb[(EtOH)_2NiHg(SCN)_4(SeCN)_2]$ have been synthesised and characterised and have been used as Lewis acids.[289] $Co[Ag(SCN.SCN)]_2$ and its derivatives with a number of Lewis bases have been synthesised.[290]

The reaction of $NbBr_4(NCMe)_2$ with Sb_2Se_3 in MeCN solution has been shown to yield a tetranuclear adduct $Nb_4Br_{10}Se_3(NCMe)_4$ in which two of the metal atoms have a valence state of four, the remaining two being tervalent.[291] The structures of the first triply selenato bridged complex η^7-$C_7H_7Mo[\mu$-$Se(C_6H_5)].Mo(CO)_3$ and the isomorphous tellurium compound together with η^7-$C_7H_7Mo(CO)_2Se(C_6H_5)$ have been described.[292]

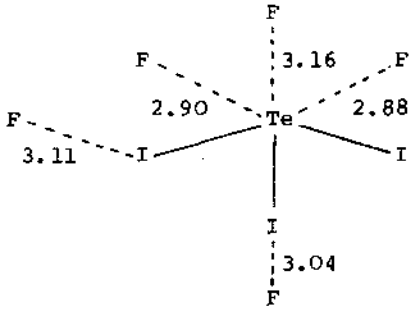
6.4 TELLURIUM

6.4.1 The Element

The isotopic composition of tellurium has been reported for two mineral fractions of the Allende meteorite which contain isotopically anomalous xenon.[293] Compounds containing tellurium metal clusters form part of a comprehensive review of the structures and reactivity of these compounds.[294]

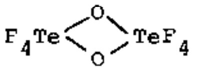
6.4.2 Bonds to Halogens

The ^{129}I Mössbauer spectra of PhTeI, pEtOPhTeI$_2^-$, pEtOPhTeI$_4^-$, Ph$_3$TeI, (Me$_2$TeI$_2$)$_2$Ph$_2$Hg and Na$_2$HgI have been measured and the data interpreted in terms of the bonding to tellurium in these compounds and ions. It was thought that PhTeI is polymeric but Ph$_3$TeI is best formulated as an ionic species.[295] The compound TeI$_3$AsF$_6$ has been prepared from the reaction of I$_2$, Te and AsF$_5$ in SO$_2$ solution. Crystal structure studies showed it to be composed of discrete TeI$_3^+$ cations and AsF$_6^-$ anions with some cation-anion interaction. The TeI$_3^+$ cation (61) has approximate C_{3v} symmetry with average Te-I distances of 2.667Å and an I-Te-I angle of 99.90°.[296]



(61)

Gem-bis(halooxy) compounds have been obtained by melting HOTeF$_5$ and Te(OH)$_6$ together. Isomers were separated using the trimethylesters and it was found that cis(Me$_3$SiO)$_2$TeF$_4$ is liquid but the trans derivative is solid and a structure determination was carried out.[297] Interaction of BCl$_3$ with HOTeF$_5$ has been shown to give B(OTeF$_5$)$_3$ in quantitative yield. Thermolysis of the compound above 130°C leads to TeOF$_4$ which could not be isolated but dimerises to

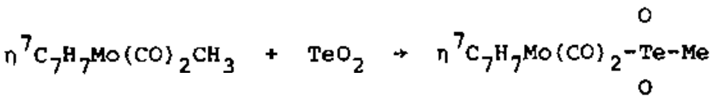

$F_4Te(\mu\text{-}O)_2TeF_4$

and polymerises to F$_5$Te[OTeF$_4$]$_n$OTeF$_5$. The compound reacts with CsOTeF$_5$ to give Cs[B(OTeF$_5$)$_4$] and with acetonitrile to give a 1:1 adduct.[298] The interaction of B(OTeF$_5$)$_3$ with SbF$_5$ was shown to yield SbF$_4$OTeF$_5$ and SbF$_3$(OTeF$_5$)$_2$.[299] The ^{125}Te Mössbauer spectra of a number of hexahalotellurates have been measured and no significant effects of the size or symmetry of the cation on the Mössbauer parameters was observed.[300]

The reactions of $XeOTeF_5^+AsF_6^-$ with BrF_5 have been studied in solution and shown to yield the new fluorine-bridged cations $FXeFXeOTeF_5^+$ and $XeF_2.BbOF_2$. The previously reported $XeOTeF_5^+$ cation was more fully characterised by Raman spectroscopy of the AsF_6^- and $Sb_2F_{11}^-$ salts and by multinuclear n.m.r. spectroscopy and its solution structure unambiguously established.[301] $Xe(OTeF_5)_4$, $Xe(OTeF_5)_6$ $O = Xe(OTeF_5)_4$ as well as mixed substituted derivatives have been described and discussed in context with the known compounds $Xe(OTeF_5)_2$ and $Xe(OSeF_5)_2$ whereas the structures of $Xe(OTeF_5)_4$ and $O = Xe(OTeF_5)_4$ are analogous to XeF_4 and $XeOF_4$, $Xe(OTeF_5)_6$ was found to be structurally comparable to monomeric gaseous XeF_6.[302] It has been shown that in MoF_6 fluorine can be replaced by F_5TeO groups by means of $B(OTeF_5)_3$.[303] The same reagent has been applied to the replacement of fluorine in WF_6.[304]

6.4.3 Bonds to Oxygen

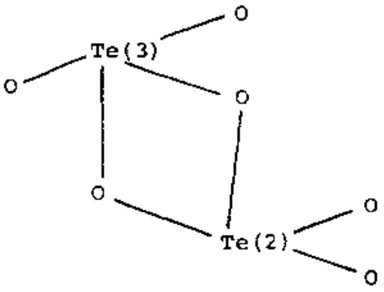
The thermal stability of the oxides TeO_3, Te_2O_5 and Te_4O_9 has been investigated by a variety of techniques. The oxide previously considered to be α-TeO_3 is now thought to have the composition $TeO_3.xH_2O$ where $x = 0.01$ to 0.15 and it is suggested that Te_4O_9 may also be a hydrate. Methods for the preparation of β-TeO_3 and Te_2O_5 were developed.[305] The isolation of "insertable" TeO_2 from the crystal has been achieved using a metal evaporator. Reaction of (62) with TeO_2 after condensation at $-196^{\circ}C$ in an ether matrix gave the insertion product (63) after 8 weeks at $-78^{\circ}C$.[306]



$$\eta^7C_7H_7Mo(CO)_2CH_3 + TeO_2 \rightarrow \eta^7C_7H_7Mo(CO)_2-\overset{O}{\underset{O}{Te}}-Me \qquad ...(31)$$

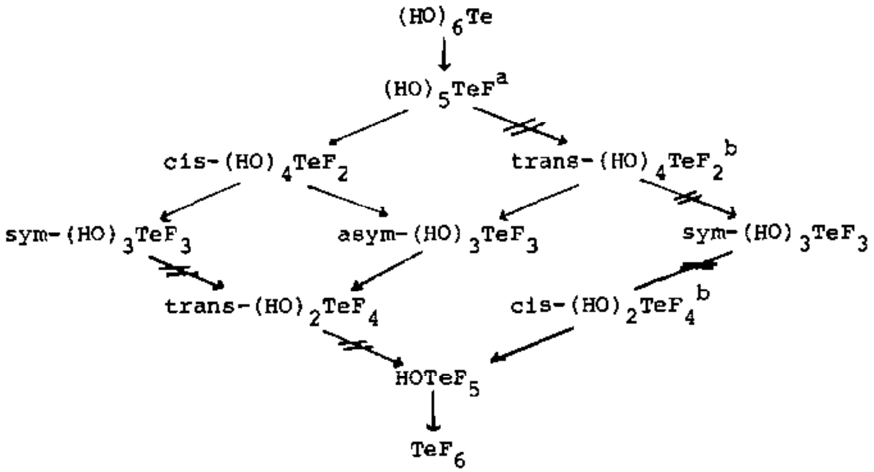
(62) (63)

The crystal structure of $Te_6O_{11}Cl_2$ has been shown to contain infinite cationic $(Te_{12}O_{22})_{\infty}^{4+}$ chains with three different sites for tellurium. There are three oxygen atoms in a ψ tetrahedral arrangement around Te(1) and four oxygen atoms in a ψ trigonal bipyramidal coordination around Te(2) and Te(3) (64).[307]



(64)

An X-ray diffraction study of a 1.5M aqueous solution of $Te(OH)_6$ at 25°C has given the Te-OH bond distance of 1.935Å. The experimental data was explained satisfactorily by a model in which twelve water molecules are hydrogen bonded to each $Te(OH)_6$ octahedron.[308] ^{125}Te n.m.r. has been used to follow the stereochemistry of the solvolysis of orthotelluric acid in HF. Reactions take place along the arrows as indicated in the reaction scheme below by dissolving the starting material in aqueous or anhydrous HF and warming the solution to about 60°C for approximately two hours.[309]



a) not observed in 48% HF

b) Hydrolysis products of TeF_6

In the crystal structure of $(NH_4)_2Te_4O_9$, which is built up from infinite sheets of $(Te_4O_9)_n^{2n-}$ linked through NH_4^+ cation interactions, the coordination around two independent tellurium atoms is a good example of the Te(IV) four-fold coordination (trigonal bipyramidal with the lone electron pair occupying the third equatorial position). The third tellurium atom has elements of 3-fold coordination with 3 shorter Te-O bonds from 1.844 to 1.913Å and a fourth bond considerably longer at 2.617Å. The fourth Te atom has pyramidal IV+1 coordination with one Te-O = 2.712 being a weaker bond and giving the fifth interaction.[310] $Na_2Te_2O_5$ is composed of $(Te_2O_5)_n$ chains linked by sodium atoms in distorted 5 and 6 coordination. The two independent Te atoms are linked by a single Te-O-Te bridge of 137°.[311] Ca_3TeO_6 has been shown to be isostructural with α-Na_3AlF_6 with regular TeO_6 octahedra.[312] The crystal structure of $Te(OH)_6.2Na_3P_3O_9.6H_2O$[313] and $Te(OH)_6K_3P_3O_9.2H_2O$[314] have been determined. Both compounds are examples of phosphate-tellurates in which the phosphate is condensed into the ring anion P_3O_9 with the TeO_6 octahedra being independent.[315] The structure of $Te(OH)_6(NH_4)_2SO_4$ is composed of TeO_6 octahedra alternating with planes of pure SO_4 tetrahedra. The TeO_6 octahedra are distorted in this compound with angles of 165 and 76.4°.[316] Single PO_4 tetrahedra and TeO_6 octahedra have been shown to be present in $Te(OH)_6 2Ag_2HPO_4$.[317] $Te(S_2O_7)_2$ has been shown to contain two bidentate pyrosulphate groups bonded to each tellurium atom. The Te cation is in a ψ trigonal bipyramidal configuration with a lone pair in the 1st equatorial position. Bond lengths were reported as $Te\text{-}O_{axial} = 2.06$, 2.07Å, $Te\text{-}O_{equatorial} = 1.96$ and 1.96Å.[318]

Several papers concerning the Te-Mo-O system have been published. The phase diagram for the TeO_2-MoO_3 system shows a new congruently melting phase Te_2MoO_7 to be formed which has a tendency to glass formation.[319] The glasses formed from TeO_2 to Te_2MoO_7 are thought to contain TeO_4 and MoO_5 groups as their basic structural units with the latter connected to form Mo_2O_8 complexes.[320] I.r. and Raman spectra of α-Te_2MoO_7 have been recorded and discussed.[321] Glass formation in the TeO_2-MoO_3-V_2O_5 system has been studied.[322] $NiTe_2O_5$ has been prepared from NiO. TeO_2 melts in sealed silicon glass ampoules at about 1100K. In its structure there are pyramidal TeO_3 groups and Te_3O_7 chains in which TeO_3 and TeO_5 pyramids are connected via common corners. The TeO_5 group is a distorted pyramid with one short apical Te-O bond of 1.886Å and two pairs of basal *trans* bonds each with bond lengths of 1.996 and 2.246Å.[323] The i.r. spectra of phases of the type Te_3MO_8 (M = Ti,Zr,Hf,Sn) have been studied. The spectra were complex and could not be assigned to definite vibrations of the M-O polyhedra present in the lattices.[324] The preparations of some new mixed oxides of the type $Sr_3M_2TeO_9$ (M = Al,Ga,In) and $Ca_3M_2TeO_9$ (M = Al,Ga,In,Co,Fe,Cr) have been described. Unit cell parameters were determined and vibrational spectra assigned.[325] Phase equilibria in the Ce-Te-O system have been studied. Several compounds were characterised and the TeO_2-CeO_2 phase diagram established.[326] Hydrothermal synthesis from a mixture of PbO, $UO_2(CH_3COO)2H_2O$ and TeO_2 at 230°C has given the compound $Pb_2[UO_2(TeO_3)_3]$.[327]

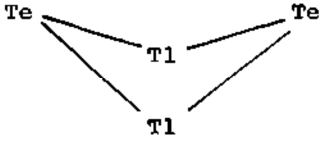
The interaction of Me_3SiCl with cis and trans $(HO)_2TeF_4$ and cis and trans $HOTeF_4OMe$ has been shown to give cis and trans $(Me_3SiO)_2TeF_4$ and cis and trans $Me_3SiOTeF_4OMe$ respectively.[328] The reaction of the deprotonated glycol dianion $(OCH_2CH_2O)^{2-}$ has been shown to react with $TeCl_4$ to give the anion $TeCl_3(O_2C_2H_4)^-$. Crystal structure determinations show Te in a tetragonal pyramidal coordination.[329] The oxygen-antimony-tellurium system has been investigated.[330]

6.4.4 Tellurides

The new compound $Na_6Si_2Te_6$ has been shown to be isotypic with $K_6Sn_2Te_6$ and to have a structure containing $[Si_2Te_6]^{6-}$ anions.[331] The i.r. and Raman spectra of Me_3PTe and the deuterated analogue have been recorded in the solid state.[332] The enthalpy of mixing of the ternary system In-Sb-Te has been determined using heat flow calorimetry at 918K.[333] Phase studies have been conducted on the following systems, Cd-Sn-Te,[334] Ag_2Te-GeTe,[335] CdTe-Sb_2Te_3 and Bi_2Te_3-CdTe,[336] and $RbSbTe_2$-Sb_2Te_3.[337]

6.4.5 Other Compounds containing Tellurium

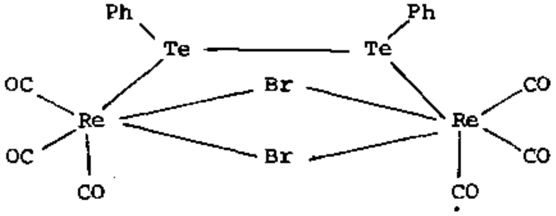
The crystal structure of $Te(HOCH_2CH_2(CH_3)NCS_2)_3SCN$ has been determined and shown to posses pentagonal bipyramidal molecules with near C_s symmetry in which the Te atom is coordinated to seven sulphur atoms.[338] The preparation and crystal structure of $(222\text{-crypt.}K^+)_2HgTe_2^{2-}$en. has been described. The compound possesses a linear $HgTe_2^{2-}$ anion - the first species of this type to be isolated for mercury.[339] The reaction of an alloy of composition KTlTe with 2,2,2,crypt in ethylenediamine has produced the compound (222 crypt $K^+)_2Tl_2Te_2^{2-}$en. The $Tl_2Te_2^{2-}$ ring has a butterfly shape (<u>65</u>) with Tl-Te distances between 2.929 and 2.984Å and a dihedral angle of 49.9°.[340]



(<u>65</u>)

Red orange solutions of $SnTe_4^{4-}$ have been obtained by treatment of Na-Sn-Te alloys with ethylenediamine. The anion does not appear to be a polyhedral cluster anion but rather a classical tin centred, tetrahedral tellurostannate ion.[341]

^{125}Te n.m.r. shifts and coupling constants of various types of Te-P compounds have been measured. The observed singlets from $R_3P{=}Te/PR_3$ mixtures corroborates the rapid Te migration between tertiary phosphanes.[342] The crystal structure of GaTeCl contains layers of $GaTe_3Cl$ tetrahedra which share common Te vertices with six neighbouring equivalent tetrahedra.[343] The crystal structure of $Re_2Br_2(CO)_6(Te_2Ph_2)$ consists of two pseudo octahedral Re centres joined by both bromide and Te_2Ph_2 bridges (<u>66</u>). The average bond distances are Re-Re 2.64Å, Te---Br 3.674Å, Re---Re 3.945Å and Te-Te 2.794Å.[344]



(<u>66</u>)

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